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Inter-annual variability of wintertime $PM_{2.5}$ chemical composition in Xi'an, China: Evidences of changing source emissions

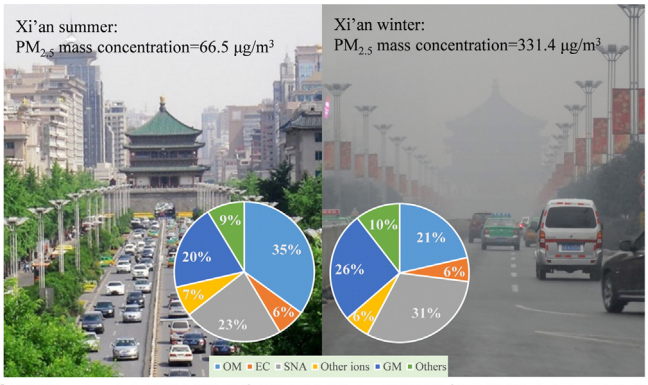
Hongmei Xu [a,b,*], Junji Cao [b,c,**], Judith C. Chow [b,d], R.-J. Huang [e], Zhenxing Shen [a], L.W. Antony Chen [d], Kin Fai Ho [f], John G. Watson [b,d]

[a] Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an, China
[b] Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China
[c] Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, China
[d] Desert Research Institute, Reno, USA
[e] Laboratory of Atmospheric Chemistry, Paul Scherrer Institute (PSI), Switzerland
[f] School of Public Health and Primary Care, The Chinese University of Hong Kong, Hong Kong, China

HIGHLIGHTS

- The contribution of coal combustion decreased from 31% in 2006 to 24% in 2010.
- The mobile source contributed stable with a slight increase from 19% to 21%.
- Increased contribution from fugitive dust was related to construction activities.

GRAPHICAL ABSTRACT



Note: OM (organic matter) =OC*1.4; SNA=SO_4^{2-}+NO_3^-+NH_4^+; Other ions=Na^++K^++Ca^{2+}+Cl^-; GM (Geological material) = Fe/3.5%
This picture is Xi'an landmark-Bell Tower.

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ABSTRACT

Chemical characteristics of $PM_{2.5}$ in Xi'an in wintertime of 2006, 2008, and 2010 were investigated. Markers of OC2, EC1, and NO_3^-/SO_4^{2-} ratio were calculated to investigate the changes in $PM_{2.5}$ emission sources over the 5-year period. Positive matrix factorization (PMF) model was used to identify and quantify the main sources of $PM_{2.5}$ and their contributions. The results showed that coal combustion, motor vehicular emissions, fugitive dust, and secondary inorganic aerosol accounted for more than 80% of $PM_{2.5}$ mass. The importance of these major sources to the $PM_{2.5}$ mass varied yearly: coal combustion was the largest contributor (31.2% ± 5.2%), followed by secondary inorganic aerosol (20.9% ± 5.2%) and motor vehicular emissions (19.3% ± 4.8%) in 2006; the order was still coal combustion emissions (27.6% ± 3.4%), secondary inorganic aerosol (23.2% ± 6.9%), and motor vehicular emissions (20.9% ± 4.6%) in 2008; while coal combustion emission further decreased (24.1% ± 3.1%) with fugitive dust (19.4% ± 5.5%) increasing in 2010. The changes in $PM_{2.5}$ chemical compositions and source contributions can be attributed to the social and economic developments in Xi'an, China, including

* Correspondence to: H. Xu, Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China.
** Correspondence to: J. Cao, Institute of Earth Environment, Chinese Academy of Sciences (CAS), No. 99 Yanxiang Road, Yanta Zone, Xi'an 710061, China.
E-mail addresses: xuhongmei@mail.xjtu.edu.cn (H. Xu), cao@loess.llqg.ac.cn (J. Cao).

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China aerosols
Fugitive dust

energy structure adjustment, energy consumption, the expansion of civil vehicles, and the increase of urban construction activities.

1. Introduction

Fine particulate matter ($PM_{2.5}$, particulate matter with aerodynamic diameters ≤ 2.5 μm) strongly affects air quality and human health, and is the most uncertain component in the radiative forcing of climate change (Dockery and Pope, 1996; Seinfeld and Pandis, 2006; Valsaraj and Kommalapati, 2009). Quantitative understanding of these effects requires a detailed knowledge of the particle sources, composition, and atmospheric transformation. However, such quantification has proven to be a challenging task, due in part to the complex chemical composition of $PM_{2.5}$, which can be directly emitted (primary aerosols) or formed by atmospheric reactions of gas-phase precursors (secondary aerosols). The sources of $PM_{2.5}$ include both anthropogenic and natural emissions, with the latter being dominant on a global scale. However, in the urban regions, aerosols stemmed from anthropogenic sources including fossil fuel combustion and biomass burning are often the major contributors to the $PM_{2.5}$ mass (Remer et al., 2009).

Compared to developed countries, the $PM_{2.5}$ sources in developing and emerging countries are much more complex. In China, the rapid economic development and high energy consumption have led to the large emissions of primary aerosols from a variety of sources, including coal combustion for residential heating and cooking as well as power plants, traffic engine exhausts, biomass burning, industrial activities, and fugitive dust from construction activities (Cao et al., 2005a; Zhang et al., 2013). The precursor gases emitted from these sources can form secondary aerosols via gas-to-particle conversion, including ammonium, sulfate, nitrate, and secondary organic aerosols (SOA) (Zhang et al., 2004; Chan and Yao, 2008). Quantitative understanding of the $PM_{2.5}$ sources is crucial for the mitigation of particle pollution. The multi-pollutant source identification is often realized by using receptor models (Chow and Watson, 2011), including chemical mass balance (CMB) and positive matrix factorization (PMF). The former depends strongly on the appropriate a priori selection of primary source profiles, while the output factors of PMF are driven by internal correlations between species used as model inputs. The PMF model has been widely used to investigate the aerosol sources in China in recent years due to the complexity of the sources and the incomplete knowledge of their source profiles (Wang et al., 2008a; Xie et al., 2008; Okuda et al., 2010; Xu et al., 2012; Zhu et al., 2012; Chen et al., 2014; Wang et al., 2015).

Xi'an (E 108.9°, N 34.3°), the capital of Shaanxi Province, is a megacity in northern China, located in the middle of the Yellow River valley and the center of the Central Shaanxi Plain. Xi'an's climate is dominated by the East Asian monsoon, with winds blowing from southern China during the warm period (May–October) and from north-western or western China (passing over the desert regions) during the cold period (November–April) (Zhang et al., 2002). Numerous studies have shown that airborne $PM_{2.5}$ levels in the Chinese urban regions are approximately 1–2 orders of magnitude higher than those observed in urban areas in the U.S. and European countries (Cao et al., 2005a, 2013a; Li and Feng, 2010). Previous studies (Cao et al., 2005a, 2007; Shen et al., 2008, 2009a) attributed elevated wintertime $PM_{2.5}$ concentration in Xi'an to a joint effect from stable atmospheric boundary layer, a shallow surface inversion, low temperatures, and increased emissions related to residential heating.

Coal burning produces more than 70% of China's electricity, and is still widely used for domestic heating and cooking (EOHB, 2008; Chan and Yao, 2008). The number of vehicles in Xi'an, like the rest of China, has dramatically increased over the past decade. Ambient $PM_{2.5}$ concentrations and chemical composition are expected to reflect the changes in emissions. In this study, we performed $PM_{2.5}$ measurements in Xi'an for 3 winter seasons over a 5-year period (2006–2010), providing a unique opportunity to evaluate the changes of $PM_{2.5}$ components and sources in the context of changing energy consumption and rapid urban development. Source contributions are quantified based on PMF receptor model simulation.

2. Material and methods

2.1. Sample collection and gravimetric analysis

Samples were collected on roof top of a two-storied building (~10 m above the ground) on the campus of the Institute of Earth Environment, Chinese Academy of Sciences (E 108.887°, N 34.229°), located ~10 km southwest of the city center in a commercial/light industrial/residential region. Daily 24-hour (10:00 am to 10:00 am next day, local standard time) integrated $PM_{2.5}$ samples were collected from 1st January to 28th February 2006, from 2nd January to 29th February 2008, and from 1st January to 28th February 2010 on pre-fired (780 °C, 3 h) 47 mm Whatman quartz microfiber filters (QM/A, Whatman Inc., U.K.) with the MiniVol Tactical Air Samplers (Airmetrics, Eugene, OR, USA) at a flow rate of 5 L/min.

Simultaneously, meteorological factors including temperature, relative humidity (RH), wind speed, precipitation, and visibility were obtained from Shaanxi Meteorological Bureau. The meteorological station is located in the northern part of Xi'an city, nearly 8.3 km away from our sampling site. Temperature and RH were measured with the use of a temperature/RH probe (Model QMH102, Vaisala, Helsinki, Finland); Wind speed was recorded by a wind monitor (Model QMW110A, Vaisala, Helsinki, Finland); Precipitation was measured by a rain gauge (Model RG13, Vaisala, Helsinki, Finland); Visibility was obtained from nephelometer (Model 3563, TSI, USA). In addition, boundary layer height data was recorded from the ECMWF (http://www.ecmwf.int/).

Samples were analyzed gravimetrically for mass concentrations with a Sartorius ME 5-F electronic microbalance (sensitivity: ±1 μg, Sartorius, Gottingen, Germany). Filters were weighed before and after sampling after equilibration at 20–23 °C and the RH of 35%–45% for 24 h. The absolute errors between replicate weights were less than 0.015 mg for blank filters and 0.020 mg for sampled filters. The exposed samples and field blanks were air-tightly sealed and stored in a refrigerator at <4 °C until chemical analysis.

2.2. Chemical analysis

Organic carbon (OC) and elemental carbon (EC) were measured on a 0.5 cm^2 filter punch using a Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) with IMPROVE_A (Interagency Monitoring of Protected Visual Environment) thermal/optical reflectance (TOR) protocol (Chow et al., 2005, 2007, 2011; Cao et al., 2013a). The method yielded four OC thermal fractions (OC1, OC2, OC3, and OC4 in a non-oxidizing helium (He) atmosphere at 140 °C, 280 °C, 480 °C, and 580 °C, respectively), one OP fraction (pyrolyzed carbon determined when the reflected laser light attained its original intensity after O_2 was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 in an oxidizing atmosphere of 2% oxygen (O_2) in a balance of 98% He at 580 °C, 780 °C, and 840 °C, respectively). The IMPROVE_A protocol defines total carbon (TC) as OC + EC, OC as OC1 + OC2 + OC3 + OC4 + OP, and EC as EC1 + EC2 + EC3 − OP.

Four anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in aqueous extracts of the filters were determined by an ion chromatograph (IC) analyzer (Dionex-600, Dionex, Sunnyvale, CA, USA) (Chow and Watson, 1999), which was equipped with an AS11-HC anion column and a CS12A cation column for separation. Details of the IC method are described in Shen et al. (2009a, 2009b) and Zhang et al. (2011).

The elemental concentrations of Ti, Cr, Mn, Fe, Ni, Zn, As, Br, Cd, and Pb in $PM_{2.5}$ collected on quartz-fiber filters were determined by Energy Dispersive X-ray Fluorescence (ED-XRF) spectrometry (the PANalytical Epsilon 5 ED-XRF analyzer, PANalytical, the Netherlands) (Watson et al., 1999; Steinhoff et al., 2000; Wasson and Guo, 2002; Xu et al., 2012; Cao et al., 2013a). Based on the 19 sets of collocated measurement using quartz-fiber and Teflon-membrane filters, experimental results showed high correlations ($R^2 = 0.72–0.94$, $P < 0.0001$) with slopes of 0.87–1.21 and low intercepts ($-0.10–0.09$ μg/m^3) for all the measured elements, suggesting that ED-XRF analysis of the quartz-fiber filters can meet the quality assurance objectives. Moreover, National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2783 was employed to validate the accuracy of the instrument. For example, the reference value for Pb in SRM 2783 is 317 ± 54 ng/filter by using the ED-XRF method, which was similar to the results analyzed by our ED-XRF (the eleven times average concentration of Pb was 319 ± 88 ng/filter). The relative errors for all measured elements were <6% between SRM 2783 and our ED-XRF results, which is well within the required range of error, demonstrating the accuracy of our ED-XRF. Replicate analysis of one quartz-fiber filter sample (five times) yielded an analytical precision between 3.9%–10.5%. Besides, 8 test samples were selected to compare our ED-XRF results with ICP-AES (inductively coupled plasma-atomic emission spectrometer) in Xi'an Jiaotong University lab to ensure the quality of the elements data in this study. Good correlations were observed between these two methods ($R^2 = 0.83–0.99$, $P < 0.0001$) with an averaged slope of 1.10 (95% confidence interval: 0.98, 1.20) for all the measured elements in this study. Details of the ED-XRF measurements are described in Xu et al. (2012) and Brouwer (2003).

2.3. Enrichment factors

Atmospheric concentrations of trace metals often vary by orders of magnitude. However, the values normalized to known or expected source concentrations. i.e., enrichment factors, (EFs) can provide insight into the potential sources of aerosols to certain extent (Chester et al., 1993). The calculated EFs relative to a reference for the Earth's upper continental crust have been used to evaluate crustal versus non-crustal contributions to elemental aerosol loadings (Taylor and McLennan, 1985; National Environmental Protection Agency, 1990). Using Fe as a reference element in this study, EF can be written as:

$$\mathrm{EF(Enrichment\ factor)} = [\mathrm{X/Fe}]_{\mathrm{sample}}/[\mathrm{X/Fe}]_{\mathrm{crust}} \quad (1)$$

where $[X/Fe]_{sample}$ represents the concentration ratio of an element of interest (X) to the reference element (Fe) in a filter sample, $[X/Fe]_{crust}$ represents the concentration ratio of an element of interest (X) to the reference element (Fe) in earth crust (Cao et al., 2005b; Xu et al., 2012).

2.4. Positive matrix factorization

Positive matrix factorization model (PMF3.0, USEPA) was applied to identify and quantify the major $PM_{2.5}$ sources. The PMF receptor modeling (Paatero and Tapper, 1993, 1994) has been widely used for $PM_{2.5}$ source apportionment in previous studies (Maykut et al., 2003; Kim et al., 2003a, 2003b; Wang et al., 2008a; Xie et al., 2008; Yatkin and Bayram, 2008; Chen et al., 2007, 2010). This model is a multivariate factor analysis technique and a descriptive model. PMF provides a solution that minimizes an objective function $Q(E)$ based on uncertainty for each observation (Paatero, 1997, 2000). In this study, the final PMF solution was determined by choosing the most stable results with respect to different input options and choosing the one with the most physically interpretable profiles and stable/minimal Q value.

3. Results and discussions

3.1. $PM_{2.5}$ mass concentrations

Summary of average $PM_{2.5}$ mass and concentrations of different particulate composition as well as meteorological characteristics during wintertime of 2006, 2008, and 2010 are shown in Table S1. The time series of $PM_{2.5}$ mass concentration observed during the entire study period are shown in Fig. 1. The $PM_{2.5}$ mass concentration exceeded the 75 μg/m^3, China's 24-hour Ambient Air Quality Standards (AAQS) (GB3095-2012, 2012; Cao et al., 2013b) on 56 (96.6%), 54 (93.1%), and 52 (92.9%) days for winter 2006, 2008, and 2010, respectively. Only 10 samples (5.8%) (Table S2) reached China's AAQS throughout the entire study period (172 days). All samples exceeded the 24-hour WHO $PM_{2.5}$ guideline of 25 μg/m^3.

Average $PM_{2.5}$ mass concentrations were at the similar level in winter 2006 and 2010, but decreased by ~16% in winter 2008. This could be attributed to the occurrence of a large-scale and persistent low-temperature, freezing rain and snow in a large area of China (including Xi'an) from 15th January to 10th February 2008 (Ding et al., 2008; Wang et al., 2008b; Min et al., 2009). The 2008 'frost and freezing rain' period was characterized with decreased temperature (~6 °C lower) and increased HR (20% more), precipitation (20 mm more) and boundary layer height (100 m more), compared to the rest of measurement period of 2008 (1st–14th January and 11th–29th February) (Table 1). Increased RH during the 'frost and freezing rain' period was due to increased precipitation which has effected in reducing the concentration of $PM_{2.5}$. Increased boundary layer height also played a role for diluting $PM_{2.5}$ mass. Therefore, $PM_{2.5}$ mass concentration reduced near 30% during the 'frost and freezing rain' period as a matter of $PM_{2.5}$ dilution from the favorable weather conditions.

3.2. $PM_{2.5}$ chemical composition

3.2.1. OC, EC fractions

Table S1 summarizes the average concentrations of different chemical compositions. TC accounted for 20.6% ± 4.2%, 20.1% ± 5.2%, and 22.4% ± 10.2% of $PM_{2.5}$ mass in 2006, 2008, and 2010, respectively. OC concentrations were in general 2–3 times higher than EC (Fig. 2). The lower OC and EC levels in 2008 agreed with the decrease of $PM_{2.5}$

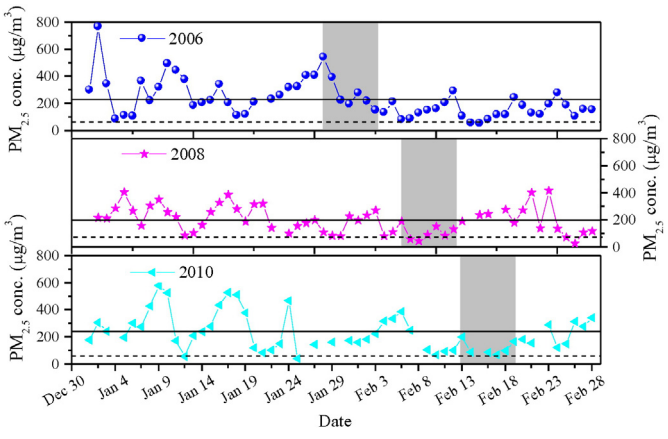

Fig. 1. 24-hour average $PM_{2.5}$ mass concentrations (unit: μg/m^3) in wintertime of 2006, 2008, and 2010 (solid line: average concentrations, dotted line: China's 24-hour $PM_{2.5}$ Ambient Air Quality Standard (75 μg/m^3), shadow zone: Chinese Spring Festival holiday season).

Table 1
Comparison of $PM_{2.5}$ mass and meteorological characteristics between 'frost and freezing rain' period and rest sampling period in 2008.

	'Frost and freezing rain' period (15th Jan.–10th Feb. 2008)	Rest sampling periods in 2008 (1st Jan.–14th Jan. and 11th Feb.–29th Feb.)
$PM_{2.5}$ mass (μg/m^3)	161.0 ± 80.8[a]	222.5 ± 101.9
Temperature (°C)	−3.1 ± 1.4	2.9 ± 2.9
Relative humidity (%)	82.6 ± 14.2	62.2 ± 13.2
Wind speed (km/h)	7.1 ± 3.4	8.4 ± 5.1
Precipitation (mm)	29.4 ± 2.0	7.7 ± 0.5
Boundary layer height (m)	815 ± 190	716 ± 284
Visibility (km)	3.1 ± 1.9	3.3 ± 1.6

[a] Arithmentic mean (± standard deviation).

mass. The OC and EC concentrations varied significantly, ranging from 7.9 to 116.2 μg/m^3 for OC and from 1.5 to 55.6 μg/m^3 for EC. The OC and EC concentrations were 30.8% and 54.7% lower during the Chinese New Year holiday seasons compared to the rest of measurement period (Fig. 2). The temporary closure of factories and reduction in vehicle/human outdoor activities during the holiday seasons could be the causes for the decrease in OC and EC emissions (Cao et al., 2003, 2005a; Wang et al., 2015).

Thermal carbon fractions of both OC and EC differ by sources (Watson et al., 1994; Chow et al., 2004; Niu et al., 2013), and have been used for the source apportionment of carbonaceous aerosol (Kim et al., 2003a, 2003b; Kim and Hopke, 2004; Cao et al., 2005a). Cao et al. (2005a) found different carbon fractions among coal combustion, biomass burning (maize residue), and motor vehicle exhaust samples (highway with heavy traffic). In the study of Cao et al. (2005a), OC2 accounted for 46.9% of TC in residential stove coal burning emissions, 30.5% in motor vehicle exhausts, and 29.2% in biomass burning emissions. EC1 constituted 15.4% of TC in motor vehicle exhausts, 5.6% in coal combustion emissions, and 0.4% in biomass burning emissions. Several previous studies have concluded that OC2 and EC1 are the markers of coal combustion emission and motor vehicle exhausts, respectively (Watson et al., 1994; Kim et al., 2003a, 2003b; Chow et al., 2004; Kim and Hopke, 2004; Cao et al., 2005a; Niu et al., 2013).

The concentrations of eight thermal carbon fractions and their relative contributions to TC during the three wintertime measurement periods are shown in Fig. 3. The relative contribution of each fraction (average of three winter periods) showed the following descending order: EC1 (31.3% ± 3.0%) > OC4 (19.1% ± 3.5%) > OC3 (17.2% ± 1.3%) > OC2 (13.5% ± 0.6%) > OP (9.5% ± 1.1%) > OC1 (7.9% ± 0.8%) > EC2 (1.0% ± 0.4%) > EC3 (0.5% ± 0.3%). Compared with the observations made at the same sampling site in winter 2003 (Cao et al., 2005a) which showed OC2 (26.6%) > OC4 (18.6%) > OP (18.3%) > OC3 (16.3%) > EC1 (15.1%) > OC1 (3.0%) > EC2 (2.0%) > EC3 (0.2%), our results showed that the OC2 fraction decreased from 26.6% to 13.5% between 2003 and 2010. This could be attributed to the widely use of clean fuels (e.g., natural gas) for domestic cooking and heating in the second half of the 2000s, which replace to some extent the consumption of coal for domestic usage. Although coal consumption in Xi'an has been increasing these years (with an exception in 2010, Xi'an Statistical Yearbook, 2004, 2007, 2008, 2009, 2010, 2011) (Fig. 4A), this increase is contributed by the large usage in power plants and industries. For example, in 2006, 59.7% of the coal was used for power plants and industries, but this proportion increased to 71.1% in 2009 (Shaanxi Statistical Yearbook, 2007, 2010). It should be noted that residential coal combustion has a much higher emission factor of OC (a factor of about 10^3) than that from industrial and power plant sectors (Zhang et al., 2008). The decrease of domestic coal consumption is offset by the increase in natural gas consumption for residential cooking and heating. For example, natural gas usage in Xi'an increased by 52.9% from 323 million m^3 in 2003 to 686 million m^3 in 2006, and increased by 58.9% from 686 million m^3 in 2006 to 1090 million m^3 in 2010 (Xi'an Statistical Yearbook, 2004, 2007, 2011) (Fig. 4B). On the other hand, the EC1 fraction measured between 2006 and 2010 was more than twice that in 2003, consistent with the increase of vehicle emissions. The number of civilian vehicles increased from 517,000 in 2003 to 608,200 in 2006, and to 1,253,500 in 2010 (Xi'an Statistical Yearbook, 2004, 2007, 2011) (Fig. 4C).

3.2.2. Water-soluble ions

Ions accounted for 42.0% ± 8.9%, 44.6% ± 12.4%, and 35.6% ± 10.2% of $PM_{2.5}$ mass in 2006, 2008, and 2010, respectively. Average ion concentrations ranged from 82.5 to 96.4 μg/m^3. SO_4^{2-}, NO_3^-, and NH_4^+ were the most abundant ions, accounting for >80% of total mass of measured ions and 33.5% ± 11.4% of $PM_{2.5}$ mass. In urban areas, SO_4^{2-} forms

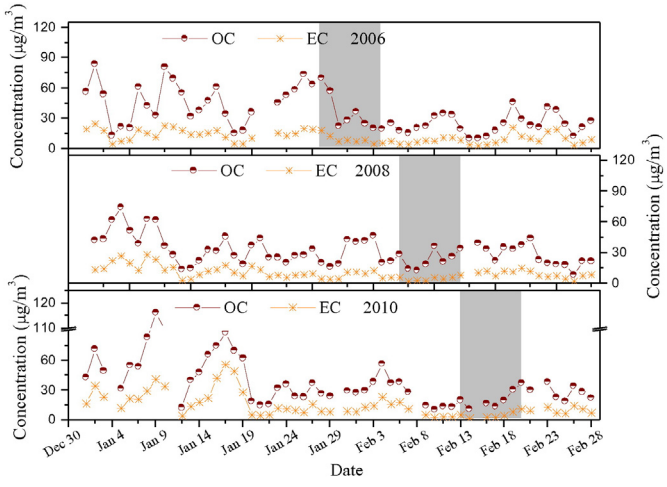

Fig. 2. The variations of OC and EC concentrations (unit: μg/m^3) in wintertime of 2006, 2008, and 2010 (shadow zone: Chinese Spring Festival holiday season).

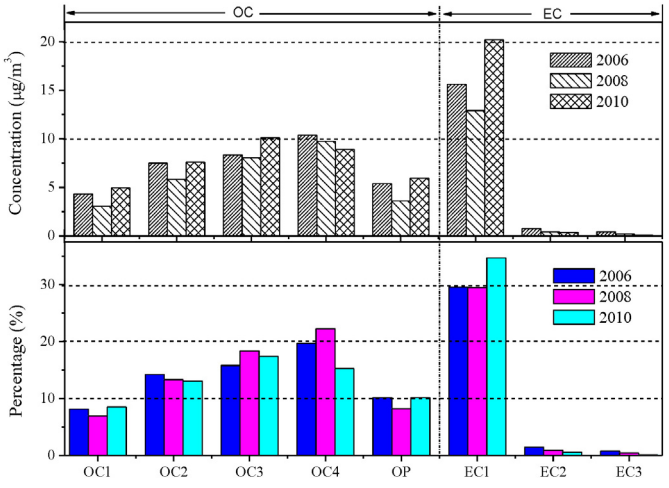

Fig. 3. The fractional concentrations of OC and EC (unit: μg/m^3) and percentages in TC (unit: %) in wintertime of 2006, 2008, and 2010.

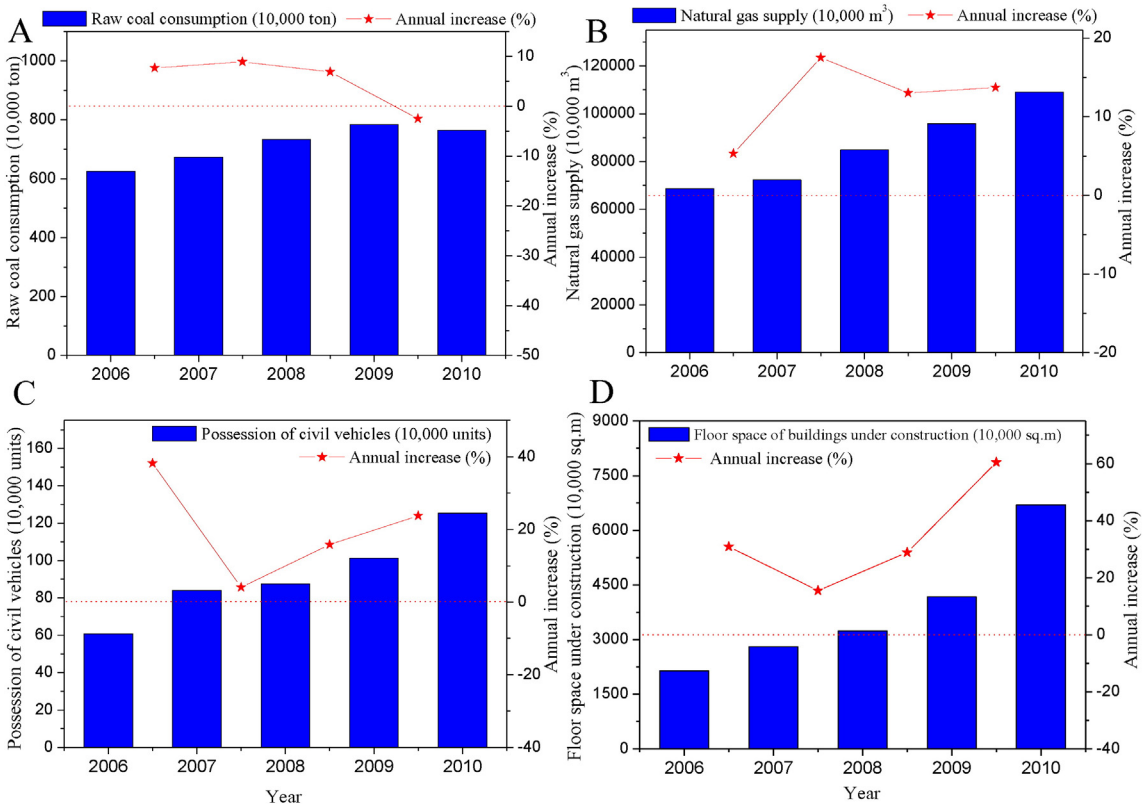

Fig. 4. Changes in energy consumption (A: raw coal; B: natural gas), (C) vehicle number, and (D) construction area from 2006 to 2010 in Xi'an (dotted line: annual increase rate = 0%).

primarily through atmospheric oxidation of SO_2 emitted mainly from coal combustion, while NO_3^- derives from NO_x emitted mainly from motor vehicle exhaust, industry, and power plants (Seinfeld and Pandis, 2006). SO_2 and NO_2 concentrations in Xi'an (January and February data involved only) were obtained from West of High-tech Zone Substation (E 108.886°, N 34.226°) in Xi'an where is the nearest substation (approximately 350 m) away from the $PM_{2.5}$ sampling sit in this study. Average SO_2 concentrations declined almost monotonously from 90.5 ± 18.3 μg/m^3 in 2006 to 63.9 ± 14.9 μg/m^3 in 2010, with the reduction rate of 29.4%. While NO_2 concentrations in Xi'an increased by 15.5% from 49.8 ± 16.7 μg/m^3 in 2006 to 57.5 ± 20.4 μg/m^3 in 2010 monotonously.

The SO_4^{2-} concentrations in urban Xi'an decreased from 2006 to 2010 by ~33%, consistent with the decrease of SO_2 since 2006, mainly due to the nationwide implementation of flue gas desulfurization (add SO_2 scrubbers) in coal-fired power plants (Wang et al., 2013). The measure to purify raw coal also led to lower sulfur emissions and therefore lower sulfate concentrations in the atmosphere. On the contrary, NO_3^- concentrations were slightly increased from 2006 to 2010, similar as the average NO_2 concentration variations. The upgrade of vehicle emission standard from National II (equal to Euro II) to National III (equal to Euro III) for light-duty gasoline and heavy-duty diesel vehicles in 2007 and for heavy-duty gasoline vehicles in 2010 in Xi'an (GB18352.3-2005, 2005; GB17691-2005, 2005) are somewhat offset by the increase of motor vehicle numbers and the enhanced idling times due to traffic jam.

NO_3^-/SO_4^{2-} ratios were used as a relative measure of the importance of mobile versus stationary pollution emission sources in many studies (Arimoto et al., 1996; Wang et al., 2005; Shen et al., 2008). Fig. 5 shows box plot of NO_3^-/SO_4^{2-} ratios calculated for the 2006, 2008, and 2010 measurement periods. The NO_3^-/SO_4^{2-} ratios in winter of 2006 (average: 0.44 ± 0.09, range: 0.24–0.65) and 2008 (average: 0.52 ± 0.15, range: 0.25–0.84) were much lower and less scattered than those in 2010 (average: 0.78 ± 0.22, range: 0.33–1.27). High NO_3^-/SO_4^{2-} values in 2010 implied stronger influences from motor vehicles, in the case of the decrease of SO_4^{2-} concentrations. The increased ratio of NO_3^-/SO_4^{2-} from 2006 to 2010 indicated that compared with the stationary source (coal-fired power plants), mobile source (vehicles) emissions increased slightly, consistent with the results obtained from OC/EC fraction analysis.

3.2.3. Elements and enrichment factors

Elements are important components in $PM_{2.5}$. The ten elements focused in this study (Ti, Cr, Mn, Fe, Ni, Zn, As, Br, Cd, and Pb) are common, abundant, and air pollution sources indicating ones. For example, Ti, Mn, and Fe may indicate the fugitive dust (Cao et al., 2008); As and Pb may indicate the coal combustion (Luo et al., 2004; Xu et al., 2012); Br and Pb may indicate the motor vehicle emissions (Bennet et al., 2005; Bukowiecki et al., 2005; Wang et al., 2006); Zn, Ni, and Cd may indicate

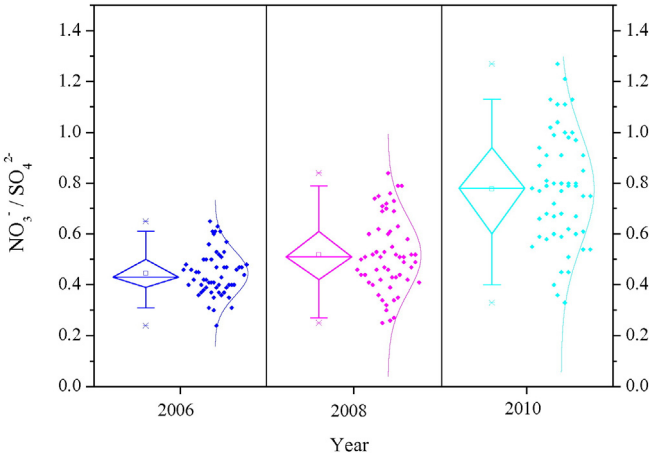

Fig. 5. The box plot of NO_3^-/SO_4^{2-} ratio in wintertime of 2006, 2008, and 2010.

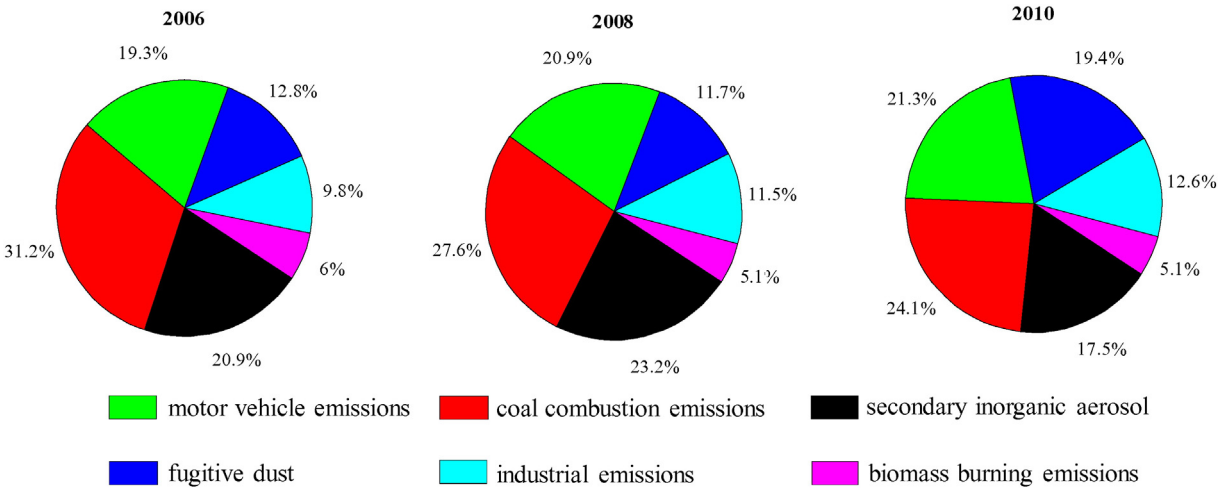

Fig. 6. Source apportionments by PMF model for $PM_{2.5}$ mass concentrations in wintertime of 2006, 2008, and 2010.

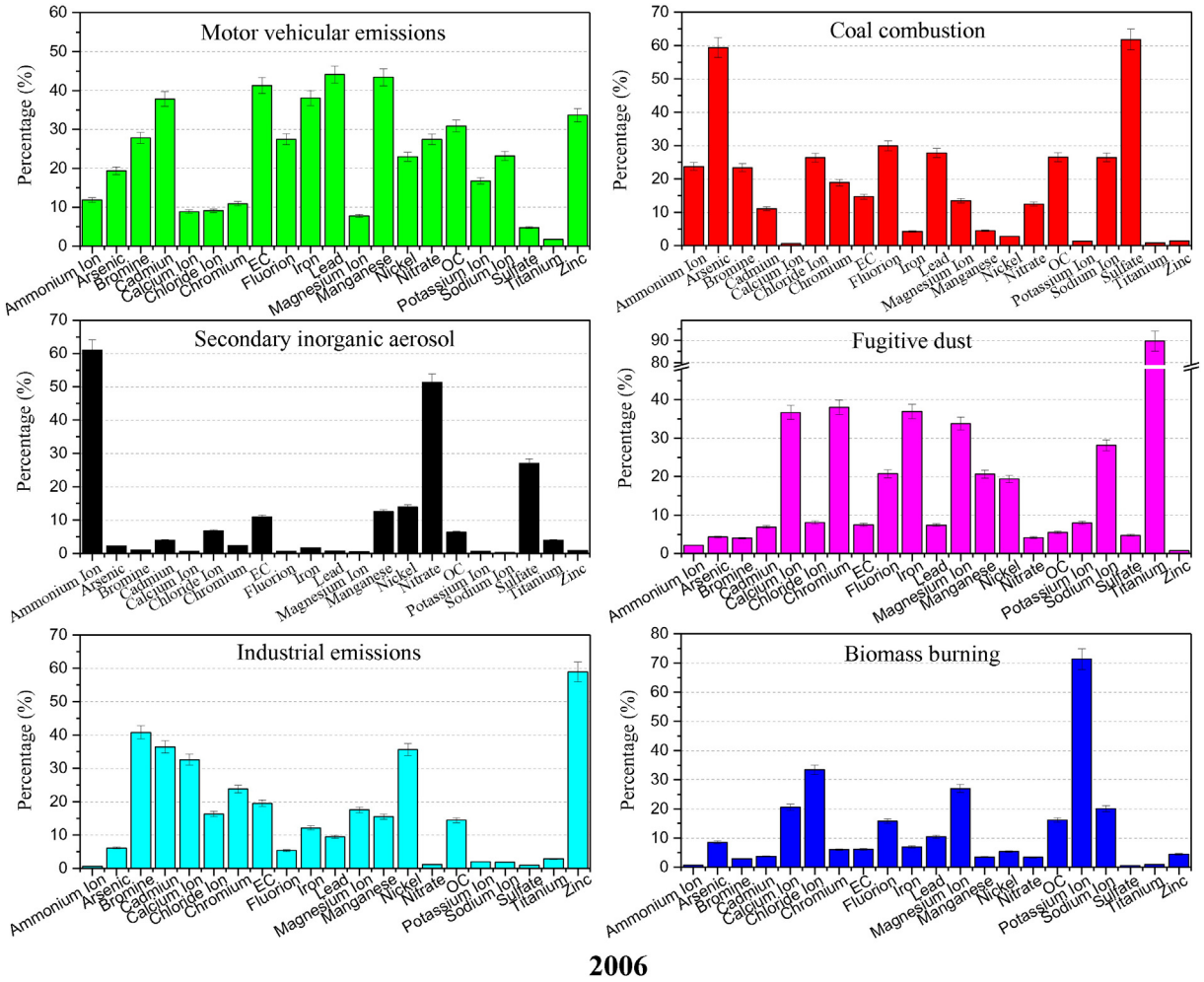

Fig. 7. Source profiles of each factor in the winter of 2006, 2008, and 2010 from PMF model.

the industrial emissions (Querol et al., 2004; Bennet et al., 2005; Lee et al., 2006; Fernández-Camacho et al., 2012). The total concentration of 10 elements measured in this study accounted for 1.5% ± 0.7%, 1.4% ± 0.9%, and 2.6% ± 1.9% of $PM_{2.5}$ mass for the 2006, 2008 and 2010 measurement periods, respectively. The element concentrations in 2010 were 1.8 and 2.2 times higher than those in 2006 and 2008. Fe

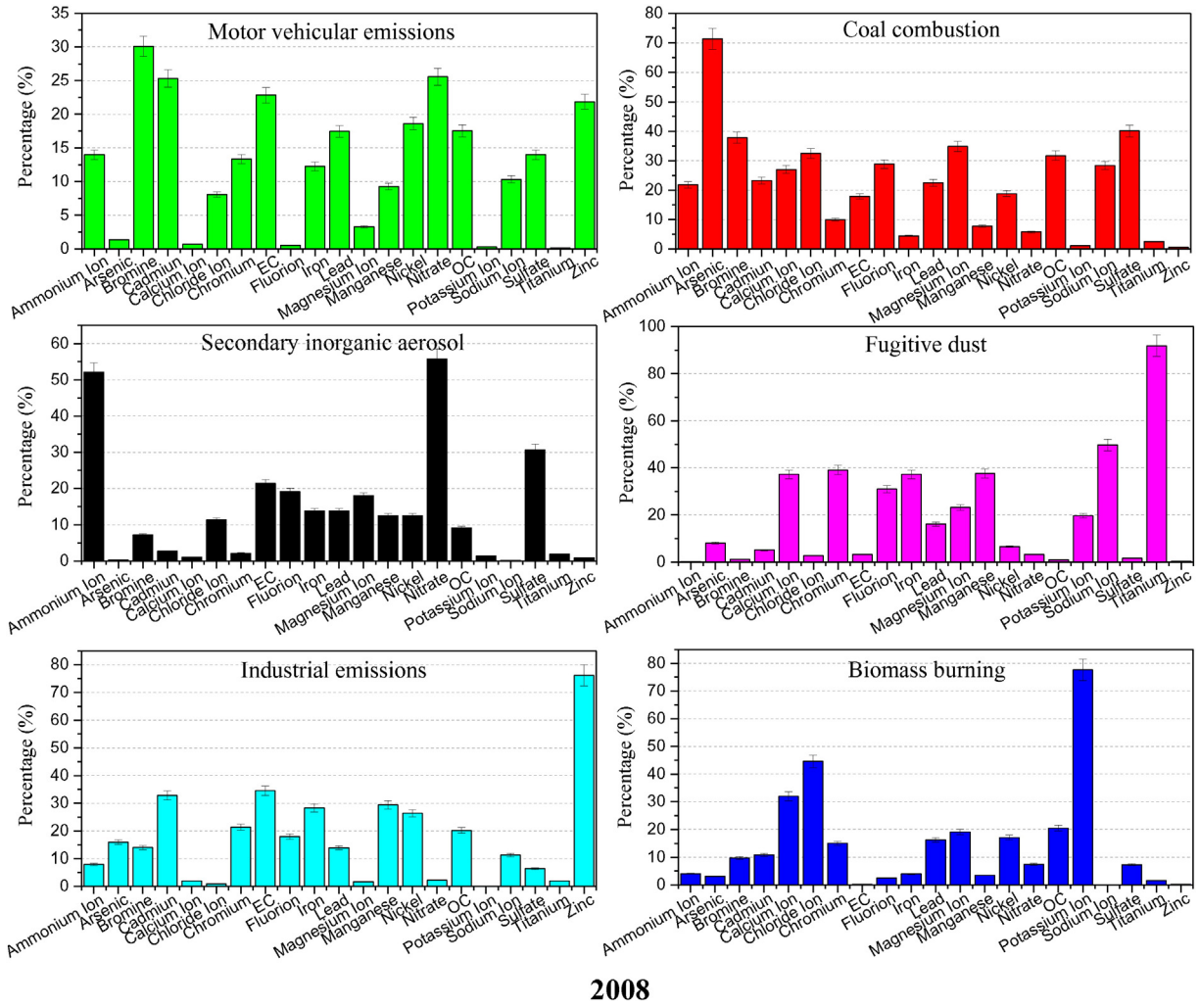

Fig. 7 (*continued*).

and Zn were found to be the dominant elements, accounting for ~75% of measured elemental concentrations.

Fe has been widely used to estimate the upper limit of geological material (Taylor and McLennan, 1985), which constitutes about 3.5% of the Earth's crust in loess plateau (Cao et al., 2005b). The amount of geological material was calculated by:

$$\text{Geological material} = (1/0.035) \times \text{Fe}. \quad (2)$$

Based on Eq. (2), it is found that geological material contributed to 24.3% ± 14.8% of $PM_{2.5}$ mass in 2010, which is approximately 60% and 80% higher than that in 2006 and 2008, respectively. Since there was no obvious dust storm occurred in the entire campaign periods, observations of enhanced geological material (fugitive dust) in 2010 sampling period could be a consequence of increasing local construction activities. The area of construction in Xi'an was only 21.4 million m^2 in 2006, but reached to 70.0 million m^2 in 2010, more than 3 times that in 2006 (Xi'an Statistical Yearbook, 2004, 2007, 2011) (Fig. 4D).

The EFs for Ti, Cr, and Mn were lower than 5, demonstrating that these elements are mainly from crustal sources. The EFs for Zn, As, Cd, and Pb, however, were much larger than 100, indicating their anthropogenic origins. As lead-containing gasoline has been phased out since 2000 in Xi'an, Pb in the air is mainly from coal combustion sources in Xi'an (Xu et al., 2012), especially in winter. EFs of Pb decreased with the values of 1015, 804, and 490 for 2006, 2008, and 2010, respectively. Moreover, EFs of As which is one of the typical coal combustion emissions marker (Luo et al., 2004) also displayed a declining trend, with the annual average of 963, 802, and 465 for 2006, 2008, and 2010, respectively. The EF values of Pb and As were consistent with the decreased coal burning emissions as discussed above. Zn variation in aerosols is mainly derived from the sources of galvanized industry (Fernández-Camacho et al., 2012), motor oil additive (Zhao and Hopke, 2006), and tire wear (Wang et al., 2008a). EFs for Zn were 471, 612, and 777 for 2006, 2008, and 2010, respectively, reflecting rapid increase of motor vehicles associated vehicle exhausts and the increase of galvanized industrial activities in Xi'an during the 5-year period to some extent.

3.3. $PM_{2.5}$ source apportionments by PMF model

A total of 21 species, including OC, EC, SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, K^+, Na^+, Ca^{2+}, Mg^{2+}, F^-, As, Br, Cd, Cr, Fe, Mn, Ni, Ti, Zn and Pb, as well as $PM_{2.5}$ mass from all the samples, were used as model input for the PMF source apportionment analysis. Based on the analysis of Q values as a function of factor numbers (Zhao and Hopke, 2004; Kim and Hopke, 2006), PMF was run several times with different FPEAK values to determine the range within which the objective function $Q(E)$ value remains relatively constant (Kim et al., 2003b). After that, 6-factor solution was selected as the optimal solution. We identified six main sources including motor vehicle emissions, coal combustion, secondary inorganic aerosol, fugitive dust, industrial emissions, and biomass burning.

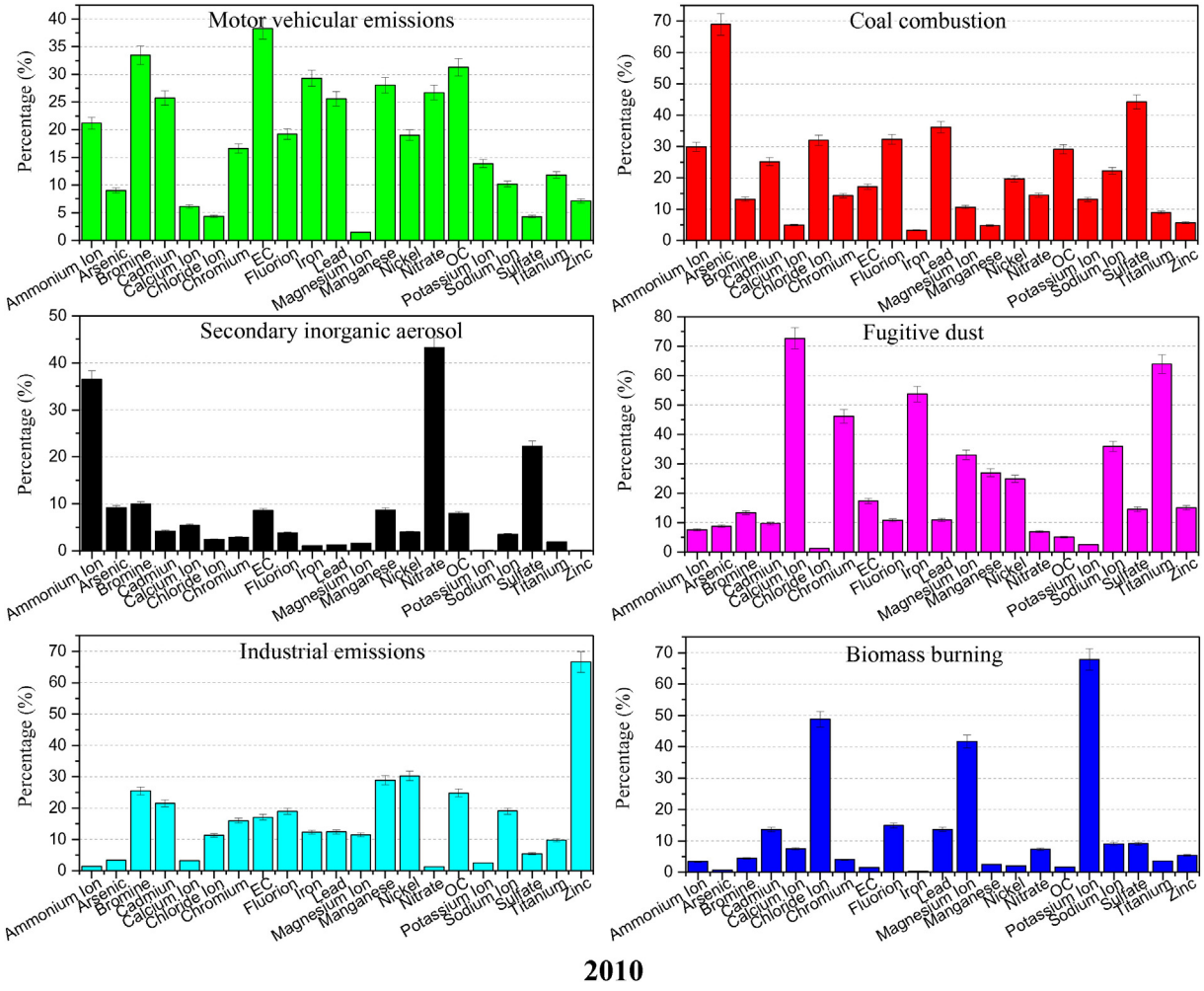

Fig. 7 (*continued*).

The contributions of quantified $PM_{2.5}$ sources and the source profiles are shown in Fig. 6 and Fig. 7.

The first factor is characterized with high loadings of OC, EC, NO_3^-, Zn, and Br, which is associated with motor vehicle emissions. Motor vehicular emissions have been shown to be an important source for OC and EC as well as NO_3^- in Xi'an (Cao et al., 2003). Zn is found in the exhaust from motor vehicles, and it is also found in tire wear particles (Wang et al., 2008a). Br is partly emitted from fuel combustion in internal combustion engines (Bennet et al., 2005; Bukowiecki et al., 2005). The PMF analysis suggested that motor vehicular emission was an important pollution source in Xi'an and contributed to 19.3% ± 4.8%, 20.9% ± 4.6%, and 21.3% ± 5.4% of $PM_{2.5}$ mass in winter 2006, 2008, and 2010, respectively. The second factor is loaded with SO_4^{2-}, OC, EC, and As, associated with coal combustion emissions (Yao et al., 2003; Luo et al., 2004). This factor constituted 31.2% ± 5.2%, 27.6% ± 3.4%, and 24.1% ± 3.1% of $PM_{2.5}$ mass concentrations in 2006, 2008, and 2010 winters, respectively. The decreased contribution of coal combustion emissions to $PM_{2.5}$ mass from 2006 to 2010 can be attributed to the stepwise replacement of coal usage by natural gas for domestic heating and cooking as discussed above. The third factor is characterized with high concentrations of SO_4^{2-}, NO_3^-, and NH_4^+, representing secondary inorganic aerosol. This factor accounted for 20.9% ± 5.2%, 23.2% ± 6.9%, and 17.5% ± 4.1% of $PM_{2.5}$ mass during winter of 2006, 2008, and 2010, respectively. The remarkable increase in 2008 may partly be related to the high relative humidity and low air temperature which caused by the 'frost and freezing rain' in 2008 (Table S1 and Table 1) (Wang et al., 2008b; Min et al., 2009). It is reported that high humidity promotes the formation of secondary sulfates (Dougle et al., 1996) and that the low temperature and high relative humidity favor the formation of NH_4NO_3 aerosol (Chow et al., 2002; Shen et al., 2008). The fourth factor is dominated by crustal elements (Fe and Ti) and crust-relevant ions (Ca^{2+} and Mg^{2+}). This factor represented fugitive dust derived mainly from unpaved road dust resuspension and construction activities (Cao et al., 2008). The significant increase of dust contribution from 2006 (12.8% ± 3.0%) to 2010 (19.4% ± 5.5%) was associated with the large increase of local construction activities in Xi'an as discussed above. The fifth factor is from industrial emissions, which is characterized with high contents of Zn, Cd, and Ni (Querol et al., 2004; Bennet et al., 2005; Lee et al., 2006; Fernández-Camacho et al., 2012). The industrial emissions accounted for 9.8% ± 3.1%, 11.5% ± 3.8%, and 12.6% ± 3.9% of $PM_{2.5}$ mass during the winter of 2006, 2008, and 2010, respectively. Querol et al. (2004) proved that Zn in industrial area in Spain is 3–5 times higher than that typically observed in other European cities. Fernández-Camacho et al. (2012) has shown that high concentrations of Zn and Cu have strong correlation with elements linked to the fresh industrial Cu-smelter emissions, and $PM_{2.5}$ showed high correlation with element linked to aged emissions from the oil refinery (e.g., Ni). Moreover, high concentrations of trace metals (e.g., Cd, Zn and Ni) are recorded during particle pollution events linked to industrial emissions (Fernández-Camacho et al., 2012). Non-ferrous metal plants and galvanizing plants are located in ~10–15 km northeast (upwind) of our sampling site. The sixth factor, biomass burning emissions, is characterized with high concentrations of K^+, Cl^-, Mg^{2+}, OC, and EC. Several studies (Kang et al., 2004; Xie et al., 2008; Zhang et al., 2014)

suggested K^+ to be a good marker for biomass burning. This factor had a stable fraction, 6.0% ± 2.3% for 2006, 5.1% ± 3.0% for 2008, and 5.1% ± 2.5% for 2010.

4. Conclusions

$PM_{2.5}$ samples collected during the wintertime of 2006, 2008, and 2010 were used to evaluate the changes in $PM_{2.5}$ chemical compositions and the major sources in response to the energy structure adjustment and urban development in Xi'an, China. The average 24-hour $PM_{2.5}$ mass concentrations in wintertime of 2006 (229.5 ± 134.7 μg/m^3) and 2010 (233.0 ± 137.8 μg/m^3) were slight higher than that during 2008 wintertime (199.4 ± 96.5 μg/m^3). Organic matter, sulfate, nitrate, and geological material were the most abundant constituents in $PM_{2.5}$ for all of three winters. The decreasing OC2 fraction and increasing NO_3^-/SO_4^{2-} ratio were notable from 2006 to 2010, consistent with the reduction of coal-related emissions due to the substantial substitution of coal by natural gas for residential usage and the great efforts in the fuel purification and the usage of SO_2 scrubbers in power plants. Contributions from mobile exhausts and fugitive dust to $PM_{2.5}$ showed increase from 2006 to 2010, supported by the increased EC1 and Fe fractions. In addition, source apportionment by PMF receptor model showed that motor vehicular emissions (tailpipe and non-tailpipe), coal combustion, secondary inorganic aerosol, and fugitive dust were the major sources, accounting for more than 80% of $PM_{2.5}$ mass. The contribution of coal combustion decreased from 31.2% ± 5.2% in 2006 to 24.1% ± 3.1% in 2010, while the mobile source contributed stable, only a slight increase from 19.3% ± 4.8% to 21.3% ± 5.4% over the 5-year measurement period, which were consistent with the estimates from markers (e.g., OC2 and EC1) and ratios of species. Increased contribution from fugitive dust (from 12.8% ± 3.0% in 2006 to 19.4% ± 5.5% in 2010) was most likely associated with increased construction activities in Xi'an. Our results therefore showed that the use of clean fuels could be an effective measure to reduce the particle pollution and that control of fugitive dust emissions from urban construction activities should be considered.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

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Appendix A. Supplemental data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.12.070.

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