



Characterization and Source Apportionment of PM_{2.5} in an Urban Environment in Beijing

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ABSTRACT

Daily 24-hour PM_{2.5} samples were collected continuously from January 1 to December 31, 2010. Elemental concentrations from Al to Pb were obtained using particle induced X-ray emission (PIXE) method. This was the first full year continuous daily PM_{2.5} elemental composition dataset in Beijing. Source apportionment analysis was conducted on this dataset using the positive matrix factorization method. Seven sources and their contributions to the total PM_{2.5} mass were identified and quantified. These include secondary sulphur– 13.8 µg/m³, 26.5%; vehicle exhaust– 8.9 µg/m³, 17.1%; fossil fuel combustion– 8.3 µg/m³, 16%; road dust– 6.6 µg/m³, 12.7%; biomass burning– 5.8 µg/m³, 11.2%; soil dust– 5.4 µg/m³, 10.4%; and metal processing– 3.1 µg/m³, 6.0%. Fugitive dusts (including soil dust and road dust) showed the highest contribution of 20.7 µg/m³ in the spring, doubling those in other seasons. On the contrary, contributions of the combustion source types (including biomass burning and fossil fuel combustion) were significantly higher in the fall (14.2 µg/m³) and in the winter (24.5 µg/m³) compared to those in the spring and summer (9.6 and 8.0 µg/m³, respectively). Secondary sulphur contributed the most in the summer while vehicle exhaust and metal processing sources did not show any clear seasonal pattern. The different seasonal highs and lows from different sources compensated each other. This explains the very small seasonal variations (< 20%) in the total PM_{2.5}.

Keywords: Aerosol emission sources; Elemental composition; Particle induced X-ray emission; Positive matrix factorization.

INTRODUCTION

Atmospheric particulate matters (PM) can affect the visibility of the atmosphere and play important roles in the formation of acid rain, climate change, and human health (Wang *et al.*, 2001; Zhang *et al.*, 2003; Ianniello *et al.*, 2011). Particles smaller than 2.5 µm (PM_{2.5}) have been paid special attention due to their adverse effects on human health since they can readily penetrate into human lungs (Rupp, 2009). To design effective PM_{2.5} reduction strategies, major sources of PM_{2.5} and contributions from each source need to be understood thoroughly (Gu *et al.*, 2011). Source apportionment methods have thus been developed for this

purpose. These methods include positive matrix factorization (PMF) (Oh *et al.*, 2011; Gugamsetty *et al.*, 2012), principal component analysis (PCA) (Lee and Hieu, 2011), chemical mass balance (CMB) (Ni *et al.*, 2012), UNMIX (Murillo *et al.*, 2012), etc. Among these methods, PMF is a powerful and widely used multivariate method that can resolve the dominant positive factors without prior knowledge of sources (Cohen *et al.*, 2010; Mooibroek *et al.*, 2011). PMF can provide not only source profiles but also time series of source contributions.

PM pollution is a serious issue in Beijing, China. A recent study by the World Health Organization (WHO) investigating air pollutants in 1100 cities around the world showed that Beijing is one of the ten dirtiest capitals in the world (WHO, 2011). The current routine monitoring program in Beijing only measures PM₁₀. There was no systematic record of PM_{2.5} concentrations in Beijing, partly because air quality standard for PM_{2.5} has not been established in China. This situation will be changed since a new PM_{2.5} air

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quality standard will be implemented in 2016 (BJEPB, 2012). Thus, there is an urgent need in understanding the $PM_{2.5}$ sources and contributions from each source in Beijing in order to develop emission policy controls for reducing $PM_{2.5}$ levels.

Several studies have investigated $PM_{2.5}$ characterization and sources in Beijing in the past few years (Song *et al.*, 2007; Xu *et al.*, 2007; Zhang *et al.*, 2007; Wang *et al.*, 2008, 2009). These studies identified six to eight potential source profiles. However, the time series of source contributions was not identified in any of these studies due to the limited number of samples, short durations of sampling, or discontinuous sampling. The concentrations and chemical composition of $PM_{2.5}$ change rapidly on hourly and daily basis. A long period (e.g., full year) of daily $PM_{2.5}$ data is needed in order to obtain a precise source identification (Tamoaki *et al.*, 2004). The present study was designed to fill this gap.

Elemental composition and characterization in $PM_{2.5}$ can provide important information on the sources of $PM_{2.5}$, despite that these trace elements only constitute a small portion of the total PM mass. Because large amounts of carbon, ionic components, and major crustal elements are included in most of the common sources, the sources of $PM_{2.5}$ can be distinguished using specific trace elements (Lim *et al.*, 2010). This study reports for the first time a full year (2010) continuous daily $PM_{2.5}$ elemental composition measurements in Beijing. The PMF method is used to determine the source profiles and source contributions to the total $PM_{2.5}$ based on the knowledge of the variation of the elemental concentrations, their periodicity, correlation with other elements and meteorological parameters. The application of a full year continuous data could not only improve the efficiency of PMF analysis, but also help to assess the impudence of various sources by using time series analysis.

METHODS

Aerosol Sampling

The aerosol sampling took place on top of a 6-m height

building at Beijing Normal University (BNU). Beijing Normal University is located in the urban area of Beijing (Fig. 1), about 8 km north from the center of Beijing, and within 200 m from the third ring road highway. The site can be considered as a typical urban background site.

Daily 24-hour $PM_{2.5}$ samples were collected continuously from 12:00 am to 12:00 am the next day using Automated Cartridge Collection Unit (ACCU) of Rupprecht & Patashnick Co. with 47 mm diameter Teflon filters (0.2 μm of pore size, Whatman Co., UK). Flow rates were typically 16 L/min. A total of 361 daily $PM_{2.5}$ samples were collected continuously from 1 January to 31 December 2010 (four samples were missed due to the instrument breakdown). 24-hour $PM_{2.5}$ concentrations were monitored with a TEOM (tapered element oscillating microbalance, R & P 1400, Rupprecht and Patashnik, Co.) from 1 January to 31 December 2010. Local meteorological parameters were obtained from Institute of Atmospheric Physics located 2 km north of the site.

Chemical Analysis

The elemental composition of the samples was determined by particle induced X-ray emission (PIXE) analytical method in a 2×1.7 MV tandem electrostatic accelerator, which belonged to the College of Nuclear Science and technology of Beijing Normal University (Zhang *et al.*, 2010, 2011). The PIXE analysis was carried out using 2.5 MeV proton bombardments with a beam of 1–20 nA. The evaluation of X-ray spectra was done by GUPIXWIN program, a code developed by Guelph University in Canada. Concentrations of the following 21 elements were determined: Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Ba and Pb. The detection limit varied between 1 and 10 ng/m^3 depending on the element, while the uncertainty of the determination of concentration was between 2% and 10%.

PMF Analysis and Source Identification

Source apportionment analysis was carried out using the positive matrix factorization receptor model (version PMF 3.0) developed by US EPA. In PMF model, any data matrix X with dimension n rows by m columns, where n and m are the number of samples and the number of species, can

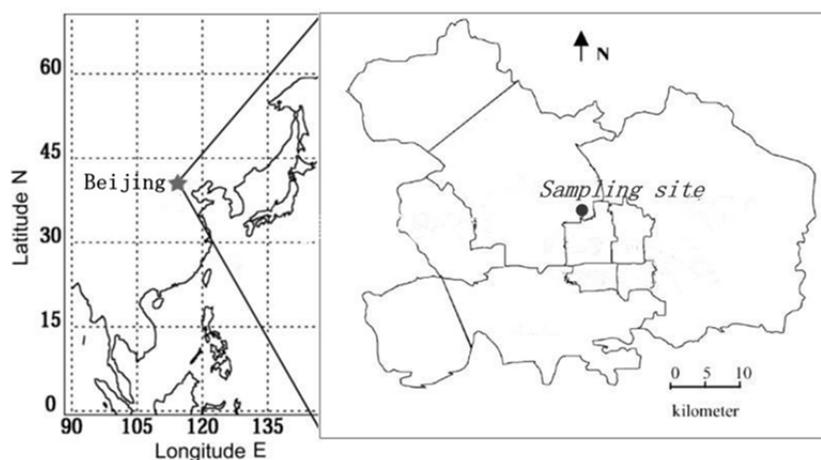


Fig. 1. Sampling site.

be factorized into two matrices, namely G ($n \times p$) and F ($p \times m$), and the residual matrix, E , where p is the number of factors or sources extracted.

$$X = GF + E \quad (1)$$

$$\text{or } x_{i,j} = \sum_{k=1}^p g_{i,k} f_{k,j} + e_{i,j} \quad (2)$$

$$Q = \sum_{i=1}^n \sum_{j=1}^m \frac{e_{i,j}^2}{s_{i,j}^2} \quad (3)$$

The product of G and F can explain the systematic variations in X . If a p -factor model is being considered, G is an $n \times p$ matrix of source contributions, describing the temporal variation of the source strengths. The matrix F is a $p \times m$ matrix of source chemical compositions, or source profiles. The main process of the PMF is minimizing the Q -value which is defined in the Eq. (3) as the sum of square of the residuals ($e_{i,j}$) weighted inversely with error estimates ($s_{i,j}$) of the data point.

It requires two inputs to run PMF, namely concentration and its uncertainty. In the present work, if the concentration is less than or equal to the method detection limit (MDL) provided, the uncertainty is calculated using the following equation (Polissar *et al.*, 1998; Reff *et al.*, 2007; Norris *et al.*, 2009)

$$\text{Unc} = \frac{5}{6} \times \text{MDL} \quad (4)$$

If the concentration is greater than the MDL provided, the uncertainty is then calculated according to

$$\text{Unc} = \sqrt{(\text{Error Fraction} \times \text{concentration})^2 + (\text{MDL})^2} \quad (5)$$

Missing data were substituted with the median value and their uncertainties were replaced by four times the median value. We included the $\text{PM}_{2.5}$ mass concentrations as a total variable (weak species) (Lee *et al.*, 2011), and all the species were categorized as ‘strong’ (signal-to-noise ratio ≥ 2), ‘weak’ ($0.2 \leq$ signal-to-noise ratio ≤ 2), or ‘bad’ (signal-to-noise ratio < 0.2) species. The ‘weak’ species were down-weighted by tripling the uncertainty. Since there was no species with signal-to-noise ratio < 0.2 in this study, no species was categorized as ‘bad’. An extra modeling uncertainty was set as 5% as suggested by Norris *et al.* (2009). Before applying the PMF model, the data screening was applied to remove extremely high values (Norris *et al.*, 2009). After the data screen, total 6 samples were excluded from the PMF analysis and a data matrix with a dimension of 355×22 (355 samples by 22 species) was prepared.

The optimal number of factors was identified after analyzing the goodness-of-fit Q -values for the entire run, the scaled residual matrices, G -space plots, and physical meaningfulness of the factor profiles and contributions (Lee *et al.*, 1999). The model was run 20 times with seven

factors and a seed of 25 (in order to replicate the results). All runs converged and a global minimum was found. The Q -robust of the present study was found to be equal to the Q -true, indicating no outliers impacting the Q value. After a reasonable solution was found, the uncertainties in the modeled solution were estimated using a bootstrapping technique. A total of 100 bootstrap runs were performed with a minimum r^2 -value of 0.6. Of the 100 runs, all the 7-factors were mapped to a base factor in every run indicating a stable result. Residuals were also found to be between 3 and -3 for all the species. An overall correlation between the reconstructed $\text{PM}_{2.5}$ mass from all the sources (Y) and the observed $\text{PM}_{2.5}$ mass concentrations (X) showed $Y = 0.92X$ ($R^2 = 0.78$). In general, the performance of PMF on the source apportionment of $\text{PM}_{2.5}$ at the study site was found to be satisfactory.

In this study, the identification of sources was conducted using major marker species that can be estimated according to a number of references. The sources are mainly confirmed based on the percentage of the species for the source. Moreover, analysis on source contributions in relation to seasonal or meteorological conditions helps to understand the source characteristics.

RESULTS AND DISCUSSION

Overview of $\text{PM}_{2.5}$ Concentrations

Statistics of annual and seasonal $\text{PM}_{2.5}$ generated from daily samples are shown in Table 1. In 2010, daily $\text{PM}_{2.5}$ concentration ranged from 9.8 to 219 $\mu\text{g}/\text{m}^3$ with an annual average (\pm standard deviation) of $55.4 \pm 40.2 \mu\text{g}/\text{m}^3$. The annual average in Beijing was comparable with that in Guangzhou (53.7 $\mu\text{g}/\text{m}^3$, Tao *et al.*, 2012), but substantially higher than those in Taipei (30 $\mu\text{g}/\text{m}^3$, Chang *et al.*, 2010) and Seoul (43.5 $\mu\text{g}/\text{m}^3$, Heo *et al.*, 2009). The annual average was almost four times higher than the US EPA annual $\text{PM}_{2.5}$ standard of 15 $\mu\text{g}/\text{m}^3$. In this particular year, 229 days had daily $\text{PM}_{2.5}$ exceeded the US EPA 24 h $\text{PM}_{2.5}$ standard of 35 $\mu\text{g}/\text{m}^3$.

Seasonal variations in $\text{PM}_{2.5}$ (the percentage difference of $\text{PM}_{2.5}$ mass loading in two seasons) were generally small (i.e., $< 20\%$). Seasonal average concentrations in the four seasons were all in the range of 50–60 $\mu\text{g}/\text{m}^3$. If excluding the springtime five Asian dust (AD) episodes (for a total of 14 days), spring and summer had lowest average concentrations during the year. This was likely caused by the stronger winds in spring (Fig. 2) and more precipitation in summer. For example, average $\text{PM}_{2.5}$ during the days with wind speed higher than 2 m/s (excluding the AD days) was lower by 13% than those during the days with weaker wind speed. Average $\text{PM}_{2.5}$ during the rainy days was lowered by 21% than those during days without rain. The highest seasonal average appeared in winter and was partly due to the low mixing layers. The increased emissions due to heating in cold weather might also be an important factor causing high $\text{PM}_{2.5}$ concentration in winter.

Asian dust events were quite common in Northern China in the spring. During 2010, five episodes (a total of 14 days) were detected and $\text{PM}_{2.5}$ levels during the AD period (105.1

Table 1. Brief summary of annual and seasonal PM_{2.5} concentrations (µg/m³).

	Mean	SD	Min	Max	Number
Winter ^a	57.5	45.6	11.6	219	92
Spring with AD	59.1	39.1	15.8	203.7	91
without AD	51.7	31.1	15.8	119.2	77
AD period	105.1	46.7	60.5	203.7	14
Summer	51.2	28.2	9.8	112.5	91
Fall	54.3	47.1	10.1	191.6	91
Annual 2010	55.5	40.2	9.8	219	365

^a (Spring: March–May; Summer: June–August; Fall: September–November; Winter: January, February and December).

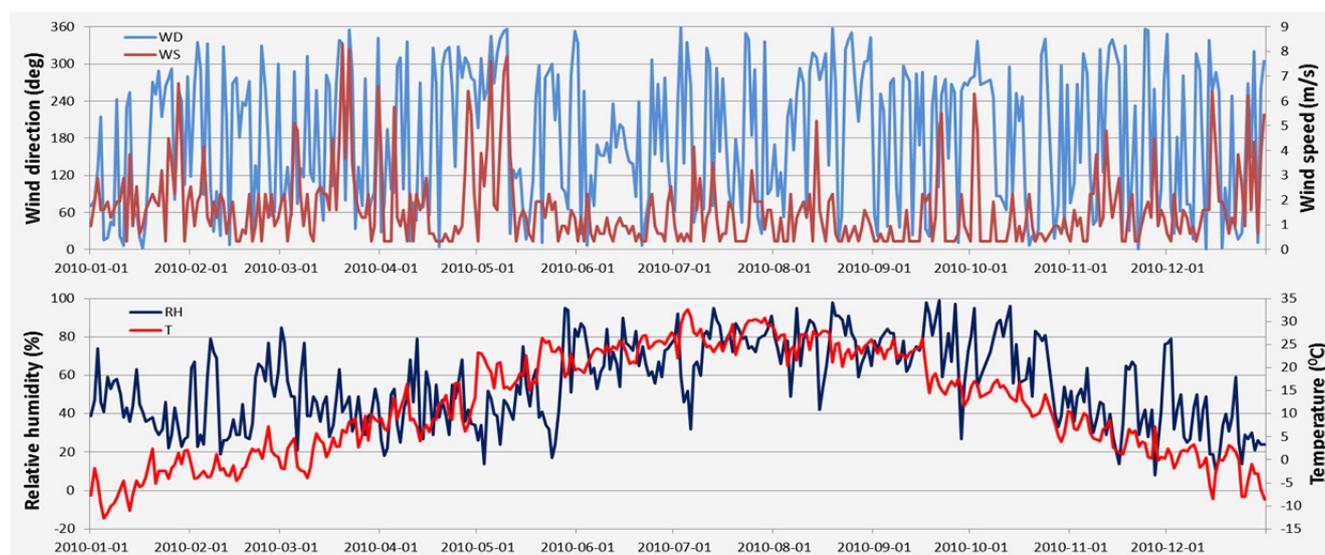


Fig. 2. Related meteorological variables during sampling time, including the wind direction (WD), wind speed (WS), relative humidity (RH) and temperature (T).

$\pm 46.7 \mu\text{g}/\text{m}^3$) doubled those during general days (Table 1). Thus, if including the AD period, spring average PM_{2.5} became the highest among the four seasons.

Overview of Selected Trace Elements

Fig. 3 shows the daily concentrations of selected elements which were present in appreciable amounts and/or served as markers for relevant sources analysis. The daily average Si concentration during the Asian Dust days was $3.8 \pm 3.2 \mu\text{g}/\text{m}^3$ ($n = 14$), much higher than that in the rest of the spring days ($1.4 \pm 1.2 \mu\text{g}/\text{m}^3$, $n = 78$). The maximum Si concentration appeared on March 19 ($5.5 \mu\text{g}/\text{m}^3$), on which day the largest dust storm since 2006 invaded Beijing (BPNEP, 2010). Al, Ca, Fe and Ti concentrations showed very similar trends. The behavior of these elemental concentrations was mainly caused by desert dust transport and this was supported by the fact that these elements were generally used as tracers for soil dust particles.

S showed the highest concentrations among all the elements analyzed. S is present in the aerosols in the form of sulphate and is mainly attributed to “secondary aerosol” source (Yao et al. 2003; Viana et al., 2008). Secondary aerosol is produced as a result of the reaction and transformation between the emitted pollutants in air. The concentrations of S were extremely high in summer (Table 2). Previous studies

(Ramadan et al., 2000; Song et al., 2001, 2002) also showed that sulfate aerosol had strong seasonal trends with high summer values when photochemical activities were highest.

Pb is the only metal listed in ambient air quality standards in China. The annual maximum acceptable limits for Pb in total suspended particles (TSP, PM with aerodynamic diameters $\leq 100 \mu\text{m}$) are $1.0 \mu\text{g}/\text{m}^3$ and $0.5 \mu\text{g}/\text{m}^3$ for China and Europe, respectively. The annual PM_{2.5} Pb concentration ($117 \pm 143 \text{ ng}/\text{m}^3$) in 2010 was well below China air quality standard for TSP Pb, and was decreased significantly compared to the values ($180 \pm 233 \text{ ng}/\text{m}^3$) in Beijing during 2001–2006 (Wang et al., 2008). However, this level was still considerably higher than those in western European cities: e.g., Rotterdam, Netherlands, $8.9 \pm 12 \text{ ng}/\text{m}^3$ (Mooibroek et al., 2011); Nice, France, $11.4 \pm 5.2 \text{ ng}/\text{m}^3$ (Fabretti et al., 2009). Regarding the daily Pb concentrations, no apparent seasonal variation was observed. This may imply dominance of local emissions such as vehicle exhaust.

Cl is often associated with sea salt in coastal cities (Mazzei et al., 2008; Moon et al., 2008). However, Beijing is an inland city. Both the chemical analysis of ambient PM_{2.5} samples (Duan et al., 2006) and source profiles measured in the laboratory (Zheng et al., 2005) have indicated that Cl can be considered as an elemental tracer for coal combustion in Beijing. This was confirmed by the seasonal variations of

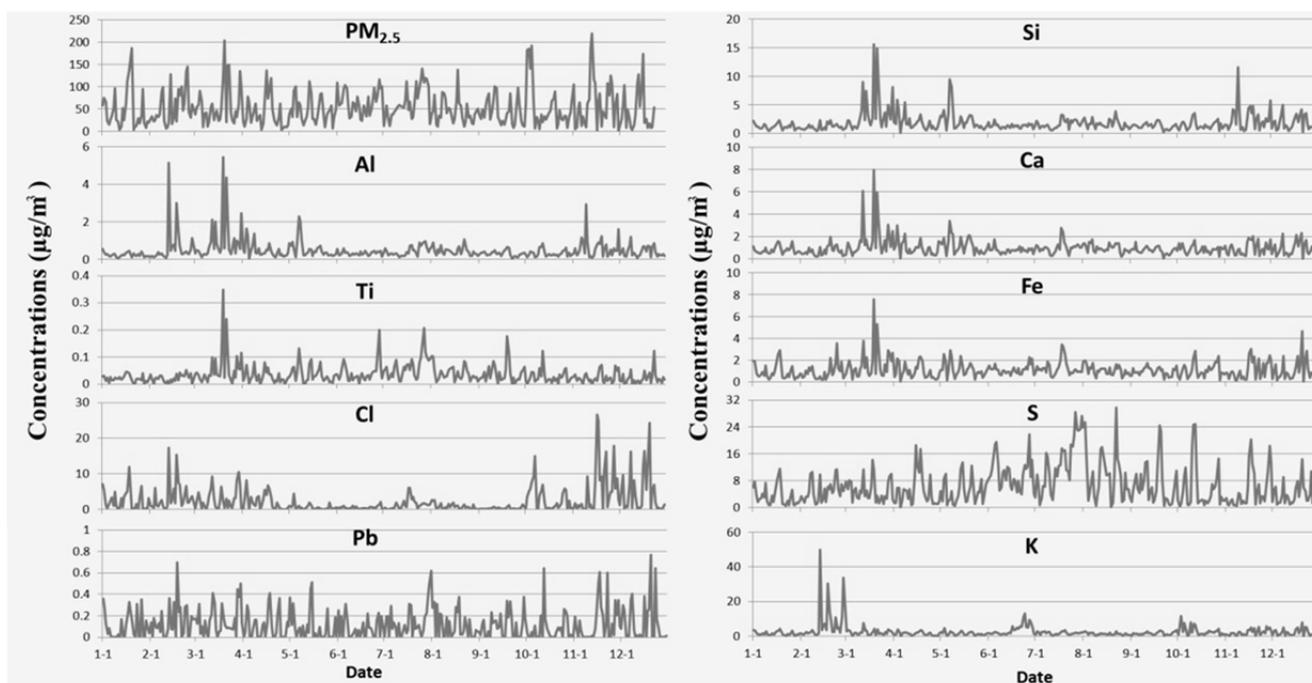


Fig. 3. Daily concentrations of selected elements.

Table 2. Seasonal average concentrations of elements in $PM_{2.5}$ in Beijing (unit: ng/m^3).

Elements	Spring	Summer	Fall	Winter	Average
Mg	105.6	89.6	72.0	96.0	90.8
Al	685.6	459.4	405.9	412.2	490.8
Si	2750.5	1569.4	1583.5	1649.0	1888.1
P	26.7	15.4	45.1	23.7	27.7
S	4559.3	7433.5	5318.1	3842.2	5288.2
Cl	2463.9	1617.2	1449.4	3286.6	2204.3
K	1881.6	2088.0	2142.1	2776.4	2222.0
Ca	1284.9	1114.4	1089.7	703.5	1048.1
Ti	21.4	42.6	49.3	31.4	36.2
V	15.5	14.3	12.9	18.6	15.3
Cr	23.6	22.1	18.0	25.8	22.4
Mn	67.6	56.1	49.8	74.6	62.0
Fe	1261.2	893.1	1149.7	1051.8	1089.0
Ni	24.4	23.8	35.3	28.9	28.1
Cu	41.6	31.9	35.3	38.3	36.8
Zn	256.0	306.8	357.1	332.2	313.0
As	32.1	33.1	45.1	41.1	37.9
Se	39.6	32.4	27.2	53.0	38.1
Br	53.0	65.9	53.1	68.6	60.2
Ba	98.3	89.6	76.8	88.1	88.2
Pb	126.4	118.8	111.4	112.7	117.3

Cl concentrations. Cl concentration in winter was $3286.6 ng/m^3$, which was markedly higher than the values in the other seasons: $2463.9 ng/m^3$ (spring), $1617.2 ng/m^3$ (summer) and $1449.4 ng/m^3$ (fall). This should be related to the rapidly increase in coal burning for heating in winter. K was used as an unambiguous tracer of biomass burning (Ryu *et al.*, 2007). Fireworks can also generate large amounts of K (Vecchi *et al.*, 2008). As shown in Fig. 3, fireworks were

responsible for the high concentrations of K during the spring festival periods (February 13–28, 2010).

Source Apportionment

The full year daily $PM_{2.5}$ elemental composition dataset obtained in Beijing is sufficient for us to apply PMF techniques to determine sources and their contributions to the total $PM_{2.5}$ mass. Seven factors were identified by PMF based on the dataset. Fig. 4 presents the identified source profiles, Fig. 5 shows time series of estimated daily contributions from each source to the $PM_{2.5}$ mass concentrations, and Fig. 6 shows the seasonal and annual average source contributions to $PM_{2.5}$ mass. Detailed discussions on each source factor and its relative contributions are presented in the following sections.

Factor 1 - Secondary Sulphur

The secondary sulphur factor was identified in most urban PMF work (Mazzei *et al.*, 2008; Cohen *et al.*, 2010; Lee *et al.*, 2011). In the present study, this factor was found to contribute most among all the identified factors to the total $PM_{2.5}$ mass concentrations, accounting for $13.8 \mu g/m^3$ (or 26.5%) of the total $PM_{2.5}$ on annual basis. The factor was dominated by a large fraction of S (71%). As expected, the seasonal variation of this factor resembles the long-term average of sulphur. This factor contributed $19.5 \mu g/m^3$ to the total $PM_{2.5}$ in summer, and $9.9 \mu g/m^3$ (winter) to $13.9 \mu g/m^3$ (fall) in other seasons.

Factor 2 - Vehicle Exhaust

The second factor identified from PMF analysis was a source related to vehicle exhausts. This factor consisted large fraction of Cu (46%), Zn (48%), Mn (32%), Br (60%), Pb (29%), and Ba (91%). Cu and Zn are major additives to

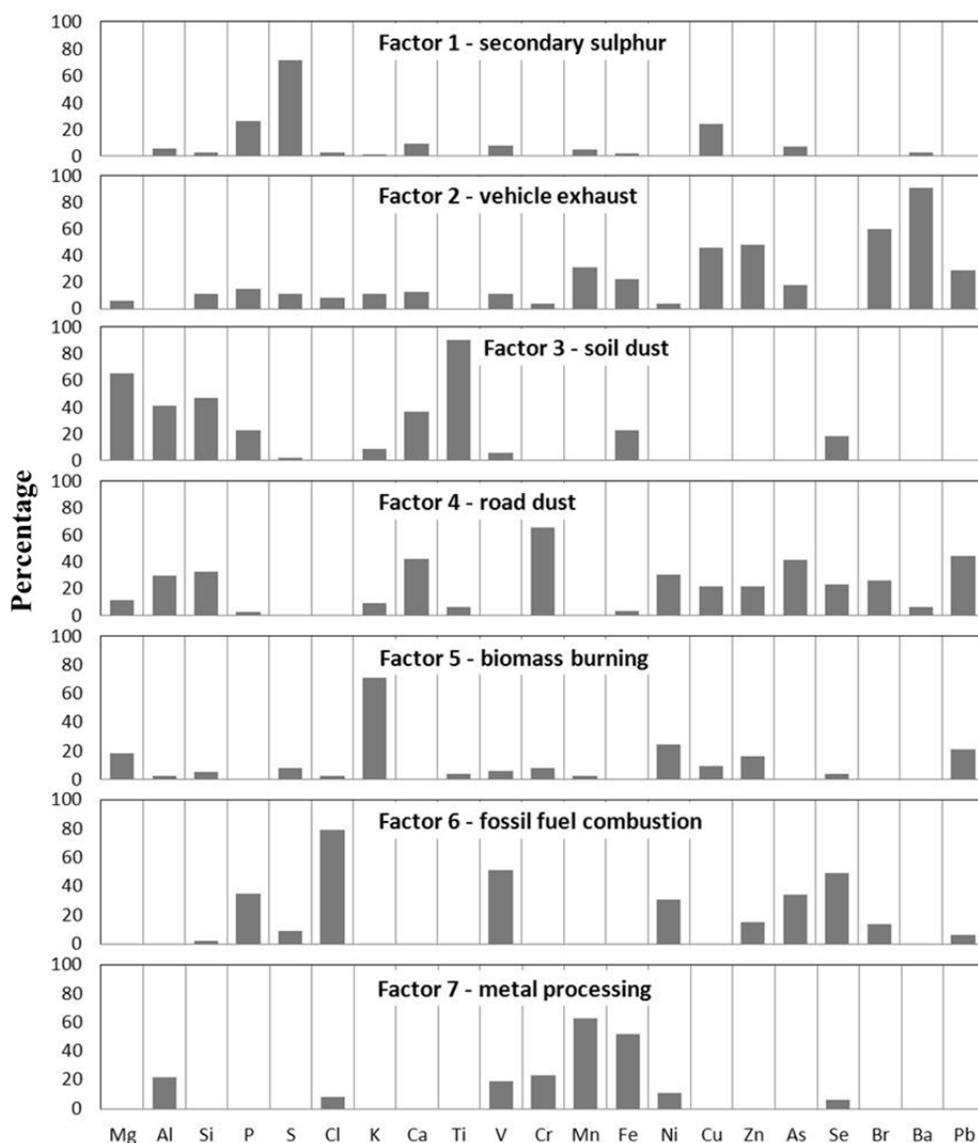


Fig. 4. PMF factor profiles.

lubricating oils. Zn, Mn and Ba emissions are also linked to other transportation activities such as brake and tire wear (Lough *et al.*, 2005; Mooibroek *et al.*, 2011). In Beijing the use of Pb additives in gasoline has been banned in 1997. As a result, there was a decreasing trend of Pb in $PM_{2.5}$ as discussed in previous section. Vehicular Pb emissions are now caused mainly from wear rather than fuel combustion (Smichowski *et al.*, 2008). The PMF results showed that there was a small drop in the factor contribution on weekends compared to weekdays (i.e., weekends $8.4 \mu\text{g}/\text{m}^3$ and weekdays $9.2 \mu\text{g}/\text{m}^3$), consistent with reduced traffic on weekends. This source constituted as high as 17.1% of the $PM_{2.5}$ on daily basis with an annual average of $8.9 \mu\text{g}/\text{m}^3$. There was no obvious seasonal variation based on the time series of the factor contributions.

Factor 3 - Soil Dust

The soil dust factor mainly represents wind-blown soils from Beijing periphery dust areas, not including the

resuspended road dust discussed in the next factor. This factor accounted for 65, 41, 47, 90, 36, and 22% of total Mg, Al, Si, Ti, Ca, and Fe, respectively. The contribution of this source to $PM_{2.5}$ was $5.4 \mu\text{g}/\text{m}^3$, or 10.4% on annual average. The factor showed the highest contribution in spring ($10.6 \mu\text{g}/\text{m}^3$) and lowest in summer ($3.0 \mu\text{g}/\text{m}^3$). As shown in the time-series plot (Fig. 5), its contribution increased noticeably when the intense AD events occurred in the spring of 2010.

Factor 4 - Road Dust

The fourth source type was responsible for not only crustal elements (Si, Fe, Al and Ca) but also Cr, Ni, Cu, Zn, As, Ba and Pb. Cu, Zn and Ba were associated with tailpipe emissions as well as brake and tire wear as mentioned above. It was also reported that particles emitted from the asphalt pavement were characterized mainly by high concentrations of Zn, Cu, Cr, Ni, As and Pb (Sorme *et al.*, 2001; Canepari *et al.*, 2008). Therefore this source was

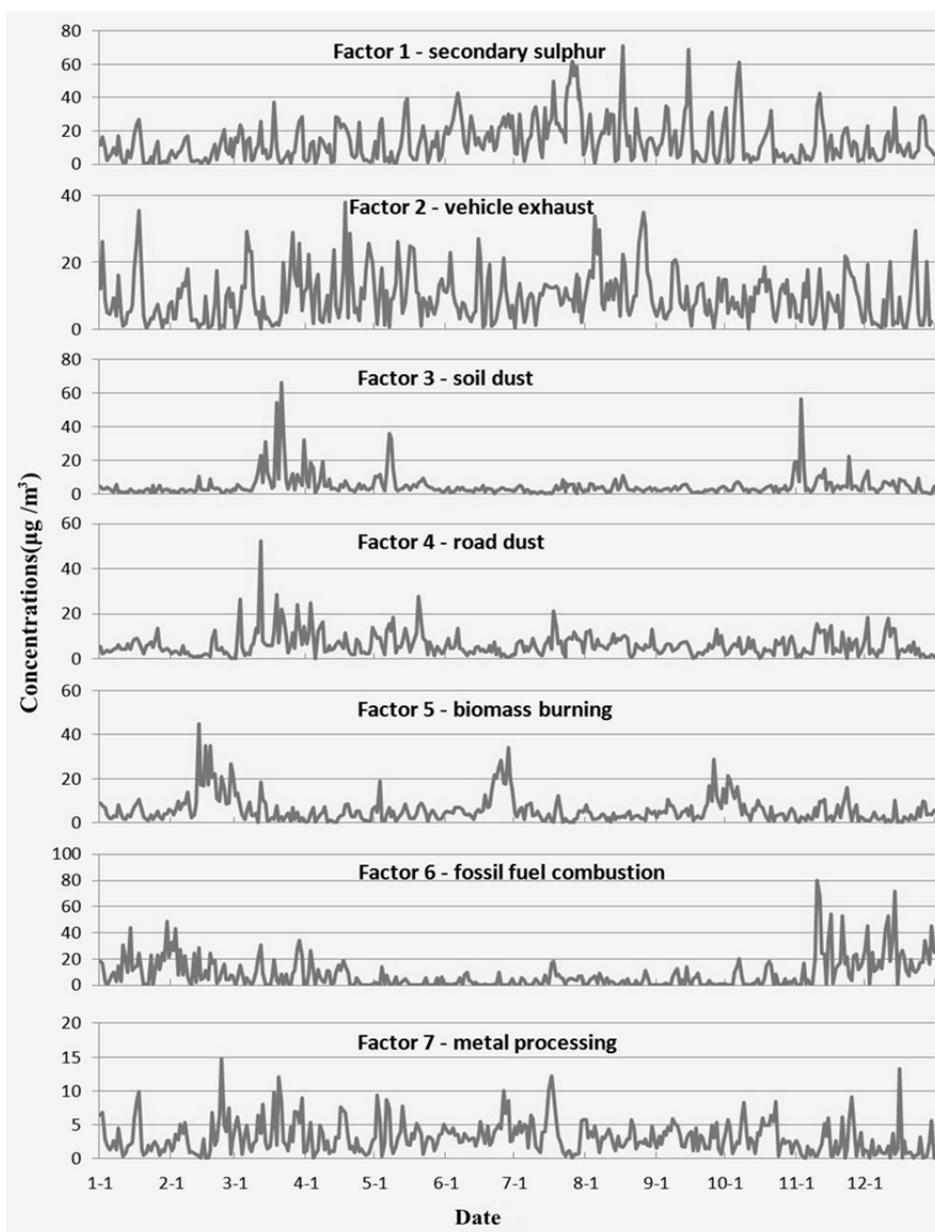


Fig. 5. PMF factor $PM_{2.5}$ contributions.

identified as road dust. Vehicles emissions, tire/brake wear debris, and road abrasion contaminate soils with metals, especially along roads with heavy traffic loads, such as the third ring road near the sampling site. The contaminated soils were commonly resuspended by mobile transportation or wind blowing. Road dust source constitutes $6.6 \mu\text{g}/\text{m}^3$, or 12.7%, of $PM_{2.5}$ on annual basis. The contribution from this source factor was the highest in the spring ($10.1 \mu\text{g}/\text{m}^3$) due to resuspension caused by rapidly increased wind speed and low humidity (Fig. 2). The factor contribution level is maintained relatively lower during the rest of the year, e.g., $6.2 \mu\text{g}/\text{m}^3$ in the summer, $5.4 \mu\text{g}/\text{m}^3$ in the fall, and $4.7 \mu\text{g}/\text{m}^3$ in the winter.

Factor 5 - Biomass Burning

The fifth factor was biomass burning, which was

characterized by high percentages of K (71%). The mass and percentage contributions were $5.8 \mu\text{g}/\text{m}^3$ and 11.2%, respectively. To understand more clearly the factor contributions during the whole year, several extremely high K concentration values during the period of spring festival were excluded when doing the PMF work. As shown in Fig. 5, besides the spring festival time, biomass burning also presented high contributions in June and October. In Beijing and surrounding areas, harvest takes place in June for wheat and in late September to early October for corn. This was clearly reflected in the factor contribution time series. The direct link between the harvest periods and biomass burning pollution events should be due to burning of wheat-stalk and cornstalk after harvest. Although the Ministry of Environmental Protection in China established rules to forbid the burning of agriculture residues in Beijing

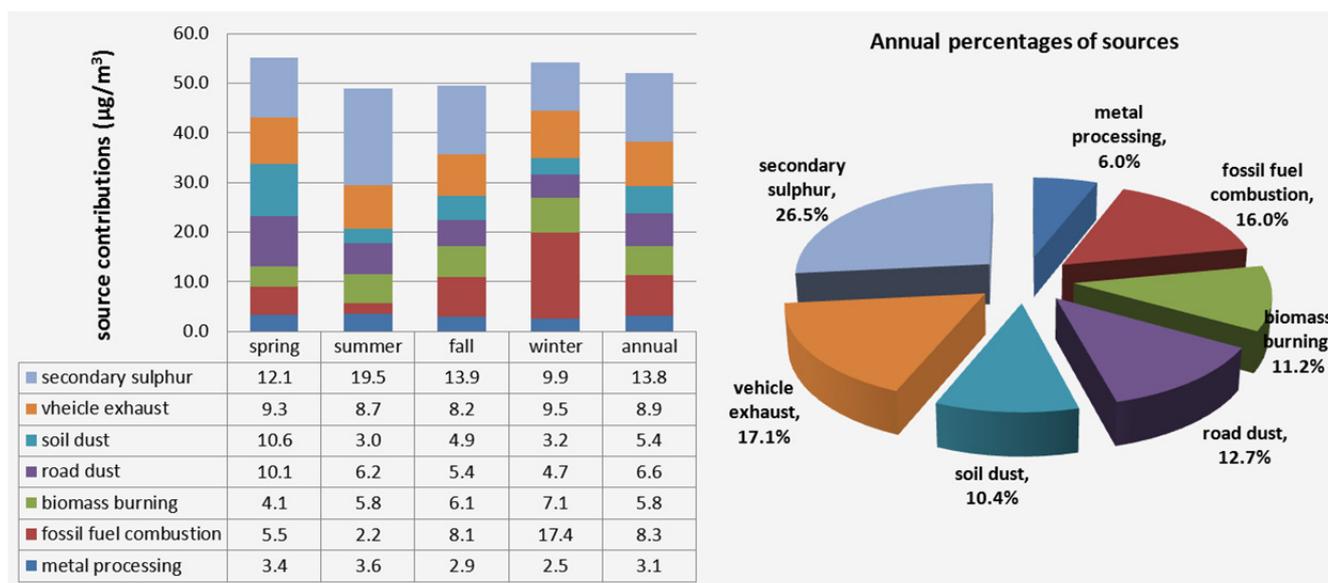


Fig. 6. Seasonal and annual average source contributions to PM_{2.5} mass.

suburban districts as well as in neighboring provinces in 1998, the rules might not be strictly enforced in 2010. Comparison of seasonal trends shows that winter had slightly higher value with 7.1 µg/m³, followed by 6.1 in the fall, 5.8 in the summer, and 4.1 µg/m³ in the spring.

Factor 6 - Fossil Fuel Combustion

The sixth source was assumed as fossil fuel combustion. The source profile was reflected by high percentages (%) of Cl (79), Se (49), V (51), Ni (31), As (34), and Pb (26). Ni and V are widely used as markers for oil combustion (Mazzei *et al.*, 2008; Kocak *et al.*, 2009; Lee *et al.*, 2011). Cl can be considered as an elemental tracer for coal combustion in Beijing as mentioned in previous sector. Jayasekher (2009) also found that there was a marked increase in the concentration of Ni, Pb, Se and As near a coal fired thermal power plant when compared to the background site. Therefore, this factor can be considered as an incontrovertible fossil fuel combustion source including the combustion of coal and oil. Coal was commonly used in coal-fired power plants and was still used in the suburban areas of Beijing for cooking and space heating. There were also many oil combustion sources in Beijing such as oil-fired power plants and homes and buildings using heating oil. The fossil fuel combustion represented 15.6% of the total PM_{2.5} mass, which is a significant fraction of the total mass. Regarding the seasonal trends of factor contributions, winter had observably high value with 17.4 µg/m³, followed by fall (8.1 µg/m³), spring (5.5 µg/m³), and summer (2.2 µg/m³). The enhanced level during winter should be attributed to coal and oil burning for heating which contributed substantially to the PM_{2.5} pollution.

Factor 7 - Metal Processing

This factor accounted for only 3.1 µg/m³ or 6% of total PM_{2.5} mass. When we reduced the number of factors in PMF work, this factor still existed. It was rich in Fe (52%)

and Mn (63%) and with moderate level of Al (19%), V (18%) and Cr (23%). These elements should mainly come from local metal processing. Wang *et al.* (2009) also reported a similar factor using PMF for the PM_{2.5} source apportionment in Beijing. They explained that the factor was due to many small courtyard and curbside metal workshops where metal processing was carried out in the open space in the juncture belt between urban and rural areas of Beijing. The emissions from these small factories might have transported to the urban areas. Furthermore, it was noteworthy that there were many construction plants in central area of Beijing, where metal cutting and welding were carried out throughout the year.

CONCLUSIONS

Daily PM_{2.5} samples were collected continuously during the whole year of 2010 at an urban environment in Beijing, the capital of China. The characterization of PM_{2.5} elemental composition was achieved using PIXE method and the sources contributing to PM_{2.5} were identified using PMF. Seven types of sources were identified, which include secondary sulphur (13.8 µg/m³, 26.5%), vehicle exhaust (8.9 µg/m³, 17.1%), fossil fuel combustion (8.3 µg/m³, 16%), road dust (6.6 µg/m³, 12.7%), soil dust (5.4 µg/m³, 10.4%), biomass burning (5.8 µg/m³, 11.2%), and metal processing (3.1 µg/m³, 6.0%).

Fugitive dusts (including soil dust and road dust) showed the highest contribution of 20.7 µg/m³ in the spring, doubling those in other seasons. On the contrary, contributions of the combustion source types (including biomass burning and fossil fuel combustion) were significantly higher in the fall (14.2 µg/m³) and in the winter (24.5 µg/m³) compared to those in the spring and summer (9.6 and 8.0 µg/m³, respectively). Secondary sulphur contributed the most in the summer while vehicle exhaust and metal processing sources did not show any clear seasonal pattern. The different seasonal highs and

lows from different sources compensated each other and resulted in a much smaller seasonal variation in the total PM_{2.5} mass concentrations.

The application of PMF to the one year continuous daily data provided a general understanding of the sources and their strengths to the formation of PM_{2.5} in an urban environment. It demonstrated the usefulness of certain elemental species as tracers for specific activities or source types. The sampling of PM_{2.5} is still ongoing aiming to provide a long-term continuous PM_{2.5} composition record, which will contribute to a better understanding of the characteristics and sources of urban PM_{2.5} in Beijing.

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