



Size Distribution and Source Apportionment of Airborne Metallic Elements in Nanjing, China

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ABSTRACT

In order to investigate the temporal and spatial variations and the size distribution of atmospheric particulate matter and associated airborne elements, atmospheric particulate matter (TSP, PM_{2.5} and size-segregated aerosol particles) were collected monthly for one year from the traditional central district and suburbs of Nanjing, China. Source identification of airborne elements in PM_{2.5} was carried out using multivariate statistical analysis. The annual mass concentrations ranged from 49.4 µg/m³ to 391 µg/m³, with a mean of 135 µg/m³ for TSP and from 20.4 µg/m³ to 200 µg/m³ with a mean of 80.5 µg/m³ for PM_{2.5}. The distribution of annual size-segregated aerosol particles showed a bimodal pattern of coarse and fine particle fractions. Spatial and seasonal variations of elemental composition in atmospheric particulates were observed. The major elements (Al, Ca, Fe, Mg, Na and Mn) were mainly distributed in coarse fractions, while toxic elements, such as As, Cd, Pb and Zn, were significantly enriched in the fine fractions. The enrichment factor indicated anthropogenic inputs of As, Cu, Ni, Pb and Zn in the TSP and PM_{2.5} examined in this work. Four potential sources for PM_{2.5} were identified by principal component analysis. The source contributions calculated using absolute principal component scores were 37.5% for the first component, 34.1% for the second, 9.0% for the third and 19.8% for the fourth. The Na/Cr/Cu component identified by principal component analysis was divided into Na/Cr and Cu groups using R-mode cluster analysis of PM_{2.5}, and the Ti in the fourth component was assigned to Cluster 2, indicating a statistical difference in airborne metallic elements. The results of the investigation of element composition, size distribution, and source apportionment carried out in this work can help to better understand and manage the effects of these aerosols on health and air quality.

Keywords: Atmospheric particles; Chemical composition; Seasonal variation; Enrichment factor; Multivariate statistical analysis.

INTRODUCTION

The recent rapid economic development in China has led to deterioration of the local environment. For example, atmospheric particulate matters are reported to be the major air pollutant for most Chinese cities (Chan and Yao, 2008; Hu *et al.*, 2010). Atmospheric particulate matters result from various sources or are formed as secondary pollutants from primary emissions through chemical reactions. Therefore, these particulates may include a wide variety of chemical species ranging from elemental to organic and inorganic

compounds (Tsai and Cheng, 2004). Inorganic elements and metallic compounds are emitted by various natural and anthropogenic sources, such as crustal materials, construction activities, motor vehicle emissions, coal and oil combustion, incineration, and other industrial emissions (Wu *et al.*, 2007; Fang *et al.*, 2010). Re-suspension of surface soil or dust may also contribute to atmospheric particulates (Laidlaw and Filippelli, 2008; Laidlaw *et al.*, 2012). It has been reported that atmospheric particulates of Asia and China are enriched with abundant metallic elements (Wu *et al.*, 2007; Charlesworth *et al.*, 2011; Okuda *et al.*, 2008). Therefore, atmospheric particulate matters and associated trace metals are linked with both short- and long-term adverse health effects to human beings (Prieditis and Adamson, 2002; Kampa and Castanas, 2008; Wild *et al.*, 2009). Accordingly, multi-elemental surveys and source identification of atmospheric particulates have been widely applied to

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provide insight into the characteristics of aerosol pollution, health risk assessment and source control (Viana *et al.*, 2008; Fang *et al.*, 2010; Charlesworth *et al.*, 2011).

The size distribution of atmospheric particulates, together with their chemical composition and sources, plays an important role in understanding and managing aerosol effects on health, visibility, and climate (Mauderly and Chow, 2008; Wang *et al.*, 2012). For example, atmospheric coarse particles can be trapped in the nose, throat and upper respiratory tract, while fine particles (e.g., PM_{2.5}) can penetrate deep into the respiratory system, after which they are retained and absorbed by the body. In addition, fine particles have the longer atmospheric residence time than coarse particles and the ability of long-range transport. In the recent past, researches have been carried out on the seasonal variations and the size distribution of atmospheric particulates and associated elements and their source apportionment in various parts of world (Olmez *et al.*, 2004; Song *et al.*, 2006; Srivastava *et al.*, 2008; Wang *et al.*, 2010; Lee and Hieu, 2011; Gugamsetty *et al.*, 2012; Hu *et al.*, 2012a). Knowledge about the temporal and spatial variations and the size distribution of atmospheric particulates (TSP, PM_{2.5} and size-segregated aerosol particles) and associated metallic metals is still scarce, further study should be therefore carried out.

Nanjing (118°22' and 119°14'E, 31°14' and 32°37'N), located in the lower reaches of the Yangtze River, is the capital city of Jiangsu Province in China. Nanjing is one of the most important cities in the Yangtze River Delta, which is one of the fastest growing areas in China. The pillar industries in Nanjing are electronics, petrochemical, automobile and steel smelting. Accordingly, the release of heavy metals from various sources exerts great stress on urban environmental quality (Zhang *et al.*, 1999; Lu *et al.*, 2003; Zhang, 2009; Hu *et al.*, 2011; Hua *et al.*, 2011; Ma *et al.*, 2011). Furthermore, airborne metallic elements in Nanjing may pose potential health risks to humans via ingestion, dermal contact and inhalation pathways (Hu *et al.*, 2012b). In the present study, atmospheric particulates (TSP, PM_{2.5} and size-segregated aerosol particles) were collected monthly for one year from two sampling sites in the Nanjing metropolitan area; one in the traditional center district (Gulou) and the other in the suburbs (Pukou). The main objectives of this study were: 1) to assess the temporal and spatial variations of atmospheric particulates and associated metallic metals; 2) to analyze the size distribution of atmospheric particulates and associated metallic metals; 3) to identify potential pollution sources of PM_{2.5} based on principal component analysis/absolute principal component scores (PCA/APCS) and cluster analysis (CA). It will help understanding and managing aerosol effects on health and air quality.

METHODS

Sample Collection

Atmospheric particulates (TSP, PM_{2.5} and size-segregated aerosol particles) were collected from two sampling sites in Nanjing; one in the traditional center district (Gulou, the campus of Nanjing University) and the other in the suburbs

(Pukou, the campus of Nanjing University of Information Science & Technology). Samples of TSP and PM_{2.5} were collected monthly on PTFE filter membranes (20 × 25 cm²) using a large-volume air sampler (HY-1000, Qingdao Henyuan Instruments Co. Ltd., Qingdao, China) with a flow rate of 1.05 m³/min. The sampling time was set at 8 h for TSP samples and 16 h for PM_{2.5} samples. Four TSP samples and three PM_{2.5} samples were collected per month from June 2010 to May 2011 at each sampling site. Size-segregated aerosol particle samples were collected using an ambient eight-stage Andersen non-viable cascade impactor (TE-20-800, Tisch, NY, USA). PTFE filter membranes (Whatman 47 mm, 0.2 mm pore size) were placed on each stage to collect the particles. At a flow rate of 28 L/min, the nominal cutoff particle diameters for the stages are 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7 and 0.4 μm. A final stage retains particles smaller than the lowest cutoff diameter. The sampling time was set at 96 h and three sets of size-segregated aerosol particles were collected per month from May 2010 to April 2011 (one set of size-segregated aerosol particles was collected unsuccessfully in June, 2010 for Gulou and July, 2010 for Pukou) at each sampling site. Overall, 48 TSP samples, 36 PM_{2.5} samples, and 35 sets of size-segregated aerosol samples were obtained from each sampling site. All PTFE filter membranes were equilibrated in a desiccator for 48 h and then weighed before and after aerosol sampling to determine the aerosol mass. The PTFE filter membranes were subsequently placed into a clean glass vial with a Teflon-lined cap and stored at –20°C until analysis.

Sample Treatment and Analysis

A Milestone ETHOS 1 microwave sample preparation system (Milestone, Italy) with temperature control was used to digest the samples for measurement of the total metals. Briefly, 1/16 of a PTFE filter for TSP and PM_{2.5} and 1/2 of a PTFE filter for size-segregated aerosol particles were cut into fragments and then digested in 6 ml of 65% HNO₃ and 2 mL of 30% H₂O₂ using the following two-stage digestion program: Stage-1, heating to 200°C over 10 min; Stage-2, incubation at 200°C for 15 min. After cooling, the digested sample solutions were evaporated to near dryness, dissolved in 0.5 mL of 65% HNO₃ and then diluted to 10 mL with Milli Q (MQ) water in a 10 mL flask. The solutions were subsequently stored in 25 mL high density polyethylene vials at 4°C until instrumental analysis. Precision and accuracy were verified using standard reference materials available at the National Research Center for Geoanalysis, P. R. China (GBW07405, Soil). Blanks for digestion and samples were prepared in duplicate. MQ water was used for dilution and dissolution.

Element concentrations were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 5300, Perkin-Elmer SCIEX, USA) and an inductively coupled plasma mass spectrometer (ICP-MS, Elan 9000, Perkin-Elmer SCIEX, USA) under the conditions listed in Tables S1 and S2 of the supplementary materials.

Enrichment Factor (EF)

EF was used to differentiate anthropogenic sources from natural sources of elements within atmospheric particulate matters. EF values for elements in atmospheric particulate matters were calculated using the following equation (Zheng *et al.*, 2004; Chen *et al.*, 2008a):

$$EF_{\text{crust}} = (C_i/C_{\text{Fe}})_{\text{sample}} / (C_i/C_{\text{Fe}})_{\text{crust}} \quad (1)$$

where C_i is the concentration of the element considered in the studied samples or the continental crust and C_{Fe} is the concentration of the reference element (Fe) in the studied samples or the continental crust. The background values of soil elements in Jiangsu Province were used as the continental crustal elements in this study and there were 6.24, 1.82, 3.02, 1.81, 0.84, 1.17 and 0.41% for Al, Ca, Fe, K, Mg, Na and Ti, respectively and 10.0, 0.126, 77.8, 22.3, 585, 26.7, 26.2 and 62.6 mg/kg for As, Cd, Cr, Cu, Mn, Ni, Pb and Zn, respectively (CNEMC, 1990).

Statistical Analyses

Descriptive statistical analyses of the elemental data were carried out using SPSS 13 for Windows (SPSS Inc., Chicago, IL, USA). An independent samples t-test was used to determine the difference in concentrations of elements in TSP and PM_{2.5} between Gulou and Pukou. A $p < 0.05$ was taken to indicate statistical significance. Although various methods for source apportionment studies have been validated, PCA/APCS and CA are used most frequently in environmental studies without source profiles (Viana *et al.*, 2008). Accordingly, PCA and CA of the elemental data for PM_{2.5} in this study were carried out using SPSS 13 for Windows. In multivariate statistics, a normal distribution for the variables investigated is desirable, and serious violations of normality, such as too much skewness, can impair the reliability of statistical results (Zhang and McGrath, 2004; Chen *et al.*, 2008b). To avoid distortion of the results and low levels of significance, all measured values must be transformed. Logarithmic transformation is an important transformation method that has been widely applied (Webster and Oliver, 2001). In this study, logarithmic transformation of the measured data of PM_{2.5} was conducted, after which a one-sample Kolmogorov-Smirnov test showed that they were normally distributed. The transformed data were then analyzed using CA and PCA/APCAS. Varimax with Kaiser Normalization Rotation was applied to maximize the variances of the factor loadings across variances for each factor. APCS was carried out using Microsoft Excel.

RESULTS AND DISCUSSION

Mass Concentrations of Atmospheric Particulates

Mass concentrations of TSP and PM_{2.5} varied greatly over sampling time at both Gulou and Pukou (Fig. 1). The mass concentrations of TSP ranged from 54.1 $\mu\text{g}/\text{m}^3$ to 232 $\mu\text{g}/\text{m}^3$ with a mean value of 118 $\mu\text{g}/\text{m}^3$ for Gulou and from 49.4 $\mu\text{g}/\text{m}^3$ to 391 $\mu\text{g}/\text{m}^3$ with a mean value of 151 $\mu\text{g}/\text{m}^3$ for Pukou. The mass concentrations of PM_{2.5} ranged from 35.1 to 200 $\mu\text{g}/\text{m}^3$ with a mean value of 76.4 $\mu\text{g}/\text{m}^3$ for Gulou and from 20.4 to 193 $\mu\text{g}/\text{m}^3$ with a mean value

of 84.7 $\mu\text{g}/\text{m}^3$ for Pukou. The mass concentrations of PM_{2.5} showed a similar trend at both Gulou and Paoki (Fig. 1). The mass concentrations of PM_{2.5} in the present study were above the annual and daily threshold value (0.015 $\mu\text{g}/\text{m}^3$ and 0.065 $\mu\text{g}/\text{m}^3$, respectively) of the US-EPA Ambient Air Quality Standard, indicating that the air pollution levels in Nanjing were severe. Particulate pollution is also the major air pollution problem in other Chinese megacities such as Beijing, Shanghai, Guangzhou, Shenzhen, Xi'an, Shenyang, Chongqing, Wuhan, and Tianjin (Chan and Yao, 2008; Hu *et al.*, 2010). For example, the annual average PM₁₀ concentration generally ranged from 0.2 to 0.1 mg/m^3 from 2002 to 2006 in Beijing, Shenyang, Lanzhou, Chongqing, Shanghai, Wuhan, and Guangzhou (Hu *et al.*, 2010). The annual average concentrations of PM_{2.5} samples at four sites in Shanghai were 84 ± 30 , 65 ± 20 , 55 ± 18 , and 41 ± 10 $\mu\text{g}/\text{m}^3$ (Chen *et al.*, 2008a). Eastern China has a very high level of PM_{2.5} pollution, with an estimated annual average of more than 80 $\mu\text{g}/\text{m}^3$ (van Donkelaar *et al.*, 2010). The monthly mass concentration ratios of PM_{2.5} to TSP ranged from 0.46 to 0.78 (mean: 0.66) and from 0.25 to 0.83 (mean: 0.58) for Gulou and Pukou, respectively, suggesting that the variation of TSP and PM_{2.5} in Pukou was greater than in Gulou. Variations of TSP and PM_{2.5} were lowest in summer and highest in winter (Fig. 1). In Northern China, the urban central heating from November to March of the following year exacerbates air quality during winter. Coal burning for urban central heating releases particulates to the atmosphere. Nanjing is outside of the Chinese cities subject to urban central heating, but the long-range transport of air contaminants from Northern China due to the northeastern wind in winter might increase the concentrations of atmospheric particulates in Nanjing. The size distribution of mass concentration for all size-segregated samples showed a bimodal pattern (coarse and fine particle fraction) (Fig. 2), suggesting different origins of atmospheric particulates. Mass concentrations of all size fractions of particulates in summer were obviously lower than those in winter (Fig. S1, of the supplementary materials), suggesting the seasonal variations of the size-segregated aerosol samples.

Elemental Composition and Enrichment in TSP and PM_{2.5}

The concentrations of elements (Al, Ca, Fe, K, Mg, Na, As, Cd, Cr, Cu, Mn, Ni, Pb, Ti and Zn) in TSP and PM_{2.5} were analyzed (Table 1). The concentrations of Al, Ca, Fe, K, Mg and Na were much higher than those of the other elements in TSP and PM_{2.5} (Table 1), suggesting that they were the major elements of these fractions. Concentration of Al, Ca, Fe, K, Mg, Na, As, Cr, Mn, Ni, and Ti in TSP were significantly higher than those in PM_{2.5} at $p < 0.05$, but Cu in TSP was significantly less than that in PM_{2.5} at $p < 0.05$. There were no significant differences on concentrations of Cd, Pb and Zn between TSP and PM_{2.5} at $p < 0.05$. These findings were consistent with those of previous investigations of the chemical compositions of particles in Beijing, Shenyang, Lanzhou, Chongqing, Shanghai, Wuhan, and Guangzhou (Hu *et al.*, 2010). There were significant differences in the concentrations of Al, Fe and Mn in PM_{2.5}

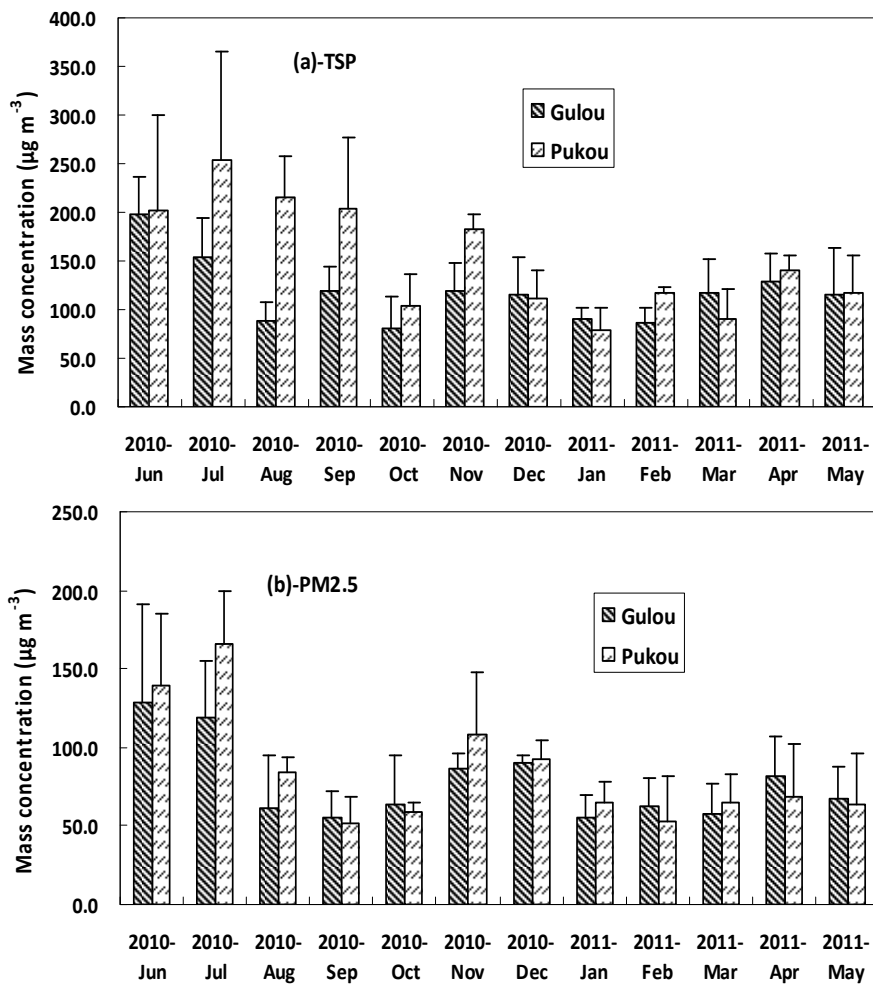


Fig. 1. Seasonal variation of mass concentrations of TSP and PM_{2.5}.

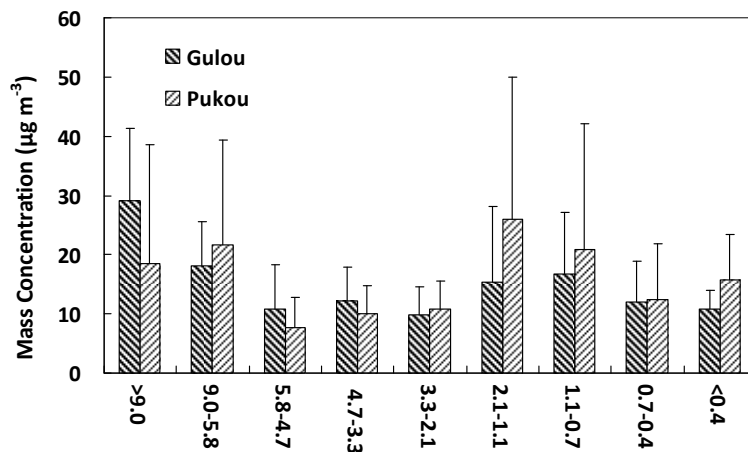


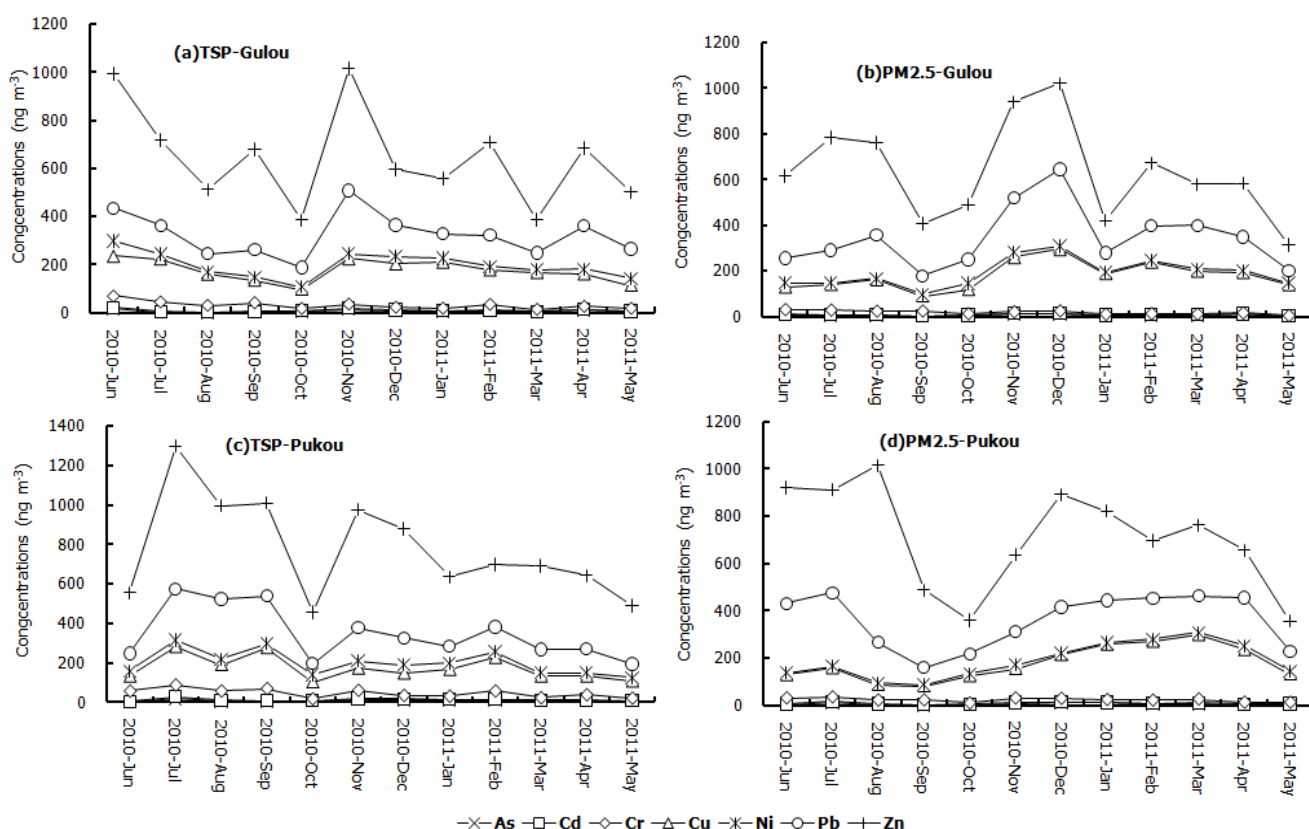
Fig. 2. Average mass concentrations of size-segregated aerosol samples.

and Fe, K, Cr, Mn, and Zn in TSP between Gulou and Pukou, suggesting spatial variation in the elemental composition of TSP and PM_{2.5}. The annual variation of toxic metals in TSP and PM_{2.5} is summarized in Fig. 3. A decrease in toxic metal concentrations in TSP and PM_{2.5} during the sampling year was observed, similar to the mass

concentrations of TSP and PM_{2.5} mentioned above. Toxic elements in the PM_{2.5} and TSP also showed seasonal variation (Fig. 3). Such variations in atmospheric pollutants have been reported in previous studies (Hao *et al.*, 2007; Kulshrestha *et al.*, 2009; Lee *et al.*, 2009). For example, elements in the aerosols of Qingdao displayed strong

Table 1. Average concentration of elements in TSP (n = 48) and PM_{2.5} (n = 36).

	TSP-Gulou		PM _{2.5} -Gulou		TSP-Pukou		PM _{2.5} -Pukou	
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
Unit: µg/m ³								
Al	0.68–9.76	2.20 ± 1.58	0.33–2.02	0.86 ± 0.39	0.44–4.30	2.40 ± 1.02	0.28–3.29	1.13 ± 0.72
Ca	1.27–18.2	7.23 ± 3.57	0.41–6.97	2.67 ± 1.33	0.55–18.1	7.38 ± 4.42	0.21–5.92	2.24 ± 1.53
Fe	1.04–5.56	2.58 ± 0.95	0.43–2.54	1.22 ± 0.51	1.67–12.1	4.76 ± 2.41	1.06–3.39	1.90 ± 0.71
K	0.32–2.65	1.11 ± 0.48	0.25–2.08	0.87 ± 0.43	0.47–3.97	1.47 ± 0.69	0.38–2.03	0.95 ± 0.42
Mg	0.21–5.97	0.79 ± 0.83	0.07–0.76	0.30 ± 0.17	0.13–1.88	0.94 ± 0.41	0.03–1.38	0.39 ± 0.28
Na	0.21–9.28	1.73 ± 1.92	0.16–3.57	0.89 ± 0.90	0.28–6.37	1.52 ± 1.48	0.23–2.52	0.85 ± 0.60
Unit: ng/m ³								
As	0.55–19.41	7.22 ± 4.96	0.86–15.6	5.38 ± 3.99	0.63–37.3	9.26 ± 7.17	0.95–15.5	6.79 ± 4.14
Cd	0.29–12.9	2.59 ± 2.31	0.20–8.35	2.49 ± 2.17	0.29–14.7	3.40 ± 2.89	0.29–6.01	2.62 ± 1.56
Cr	3.63–66.8	21.6 ± 15.6	3.03–29.2	11.3 ± 7.61	4.31–98.8	33.9 ± 23.5	3.52–32.2	13.7 ± 7.3
Cu	48.5–244	144 ± 51	34.7–282	160 ± 64	40.5–316	125 ± 62	45.6–293	155 ± 75
Mn	19.8–191	89.3 ± 36.7	13.0–126	58.5 ± 28.0	45.8–472	173 ± 110	28.0–186	90.4 ± 47.4
Ni	3.59–126	21.8 ± 20.2	2.95–48.6	11.2 ± 9.5	11.0–79.9	29.2 ± 16.0	3.78–27.3	10.1 ± 5.0
Pb	21.3–387	127 ± 70	36.2–542	153 ± 114	27.0–654	148 ± 125	44.1–461	169 ± 105
Ti	42.7–374	119 ± 74	20.6–105	53.0 ± 23.6	35.1–289	134 ± 63	15.4–169	66.1 ± 37.6
Zn	68.4–05	320 ± 162	59.9–790	289 ± 163	49.6–954	429 ± 217	116–875	343 ± 207

**Fig. 3.** Seasonal variation of toxic element concentrations in TSP and PM_{2.5}.

seasonal variation, with the concentrations of Fe, Ti, Mn, V, Ni, Cu, Pb, Zn and Cd being lowest in summer and highest in winter (Hao *et al.*, 2007). Coal burning for urban central heating in Northern China releases a great amount of toxic contaminants. Accordingly, the long-range transport of air contaminants from Northern China might increase the toxic metal concentrations in Nanjing.

The average concentrations of metallic elements in PM_{2.5} during 1995–2005 were in the order of Fe > Mg > Zn > Pb > Cu > Mn > Cr > Cd (Wu *et al.*, 2007). These findings are similar to those of the metallic element concentrations, which occurred in the order of Fe > Mg > Zn > Pb ≈ Cu > Mn > Cr > As > Cd. The average concentrations of As and Cd in PM_{2.5} in Shanghai were higher than those in the

present study, while the Cu in our study was higher than that in Shanghai (Chen *et al.*, 2008a). The concentrations of toxic elements in the present study were similar to or slightly lower than those in TSP collected in Beijing, China, from March 2001 to March 2006 (Okuda *et al.*, 2008). Concentrations of Pb, Cu, Zn, Cr, and Ni in TSP and PM_{2.5} in the present study were all in the median range of their concentration values in TSP and PM_{2.5} for Asian countries during 2000–2007 (Fang *et al.*, 2010).

To distinguish the anthropogenic inputs to atmospheric metals, the aerosol-crust enrichment factors were calculated (Fig. 4). According to conventional classification criteria, an EF value lower than 10 is taken as an indication that an element in an aerosol has a significant crustal source, while an EF value greater than 10 indicates an anthropogenic origin of an element that comprises a significant proportion of the total elements (Chen *et al.*, 2008a). The average EF values were below 10 for Al, Ca, Fe, K, Mg, Na, Ti, Cd, Cr and Mn, suggesting that they were mainly from natural sources. The average EF values for As, Cu, Ni, Pb and Zn were above 10, suggesting that they were from anthropogenic sources. The EFs of Cu, Zn, As, Cd and Pb in TSP collected in Beijing from March 2001 to March 2006 were greater than 10, suggesting that they were of anthropogenic origin (Okuda *et al.*, 2008). Moreover, high enrichment of Cu, Zn, As, Cd and Pb in PM_{2.5} in Shanghai was observed (Chen *et al.*, 2008a). Taken together, these findings indicate that Cu, Zn, As, Ni and Pb were the main anthropogenic toxic elements in atmospheric particulates in Nanjing.

Size Distribution of Element Concentrations in Atmospheric Particulates

Particles within the flow of an ambient eight-stage Andersen non-viable cascade impactor are aerodynamically segregated onto the different stages according to their sizes. In this study, elements in each stage were analyzed to investigate their size distribution. The size distribution varied greatly among elements (Fig. 5, supplementary materials - Table S3). The annual average concentrations of elements (Al, Ca, Fe, Mg, Na and Ti) decreased with the cutoff

particle diameters from 9.0 μm to 0.4 μm , suggesting that those elements were mainly distributed in coarse fractions. Al, Ca, Fe, Mg, Na and Ti are generally considered to be crustal elements; therefore, coarse fractions might have higher natural loads. The average annual concentrations of K increased slightly as the size decreased. K and Zn were generally relevant to the incineration of wastes and plants (Viana *et al.*, 2008). No significant differences in Cr, Mn and Cu were observed among different size fractions ($> 9.0 \mu\text{m}$, 9.0–5.8 μm , 5.8–4.7 μm , 4.7–3.3 μm , 3.3–2.1 μm , 2.1–1.1 μm , 1.1–0.7 μm , 0.7–0.4 μm , and $< 0.4 \mu\text{m}$). As, Cd, Pb and Zn were significantly enriched in the fine fractions (2.1–1.1 μm , 1.1–0.7 μm , 0.7–0.4 μm , and $< 0.4 \mu\text{m}$), suggesting more anthropogenic loads. Size distribution of elements in atmospheric particulates has been reported in previous studies (Yadav and Rajamani, 2006; Karanasiou *et al.*, 2007). Cd, Sn, Pb and Se in atmospheric aerosol particles at three background sites in central England and southern Scotland were found primarily within the accumulation mode, while Ni, Zn, Cu, Co, Mn and Hg were distributed between the fine, intermediate and coarse modes and Fe, Sr and Ba were mainly found within coarse particles (Allen *et al.*, 2001). The seasonal variation of studied elements in size fractions differed greatly (supplementary materials - Table S4). Some elements such as Al, Ca, Fe, K, Mg, Na, Mn, Pb, and Zn showed great seasonal variation in all size fractions, while others such as Ti and Cd had very weak seasonal variation in part of size fractions (e.g., Cd in coarse size fractions). In the present study, the element concentrations in different size fractions between Gulou and Pukou were compared (supplementary materials - Table S5 and S6). The concentrations of Al, Ca, Fe, K, Mg, Na and Mn in the $> 9.0 \mu\text{m}$ fraction at Gulou were significantly higher than those at Pukou at $p < 0.05$. The Zn in different fractions of samples other than the $> 9.0 \mu\text{m}$ fraction and the 4.7–3.3 μm fraction was significantly lower at Gulou than at Pukou. The size distributions of elements in atmospheric aerosols may have resulted from a combination of processes including local anthropogenic and natural sources, long-range transport and re-suspension.

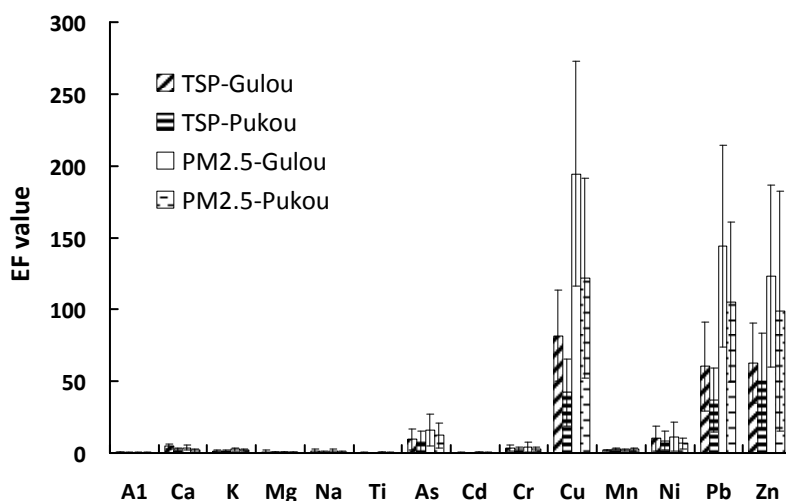


Fig. 4. Average EF values of elements in TSP and PM_{2.5}.

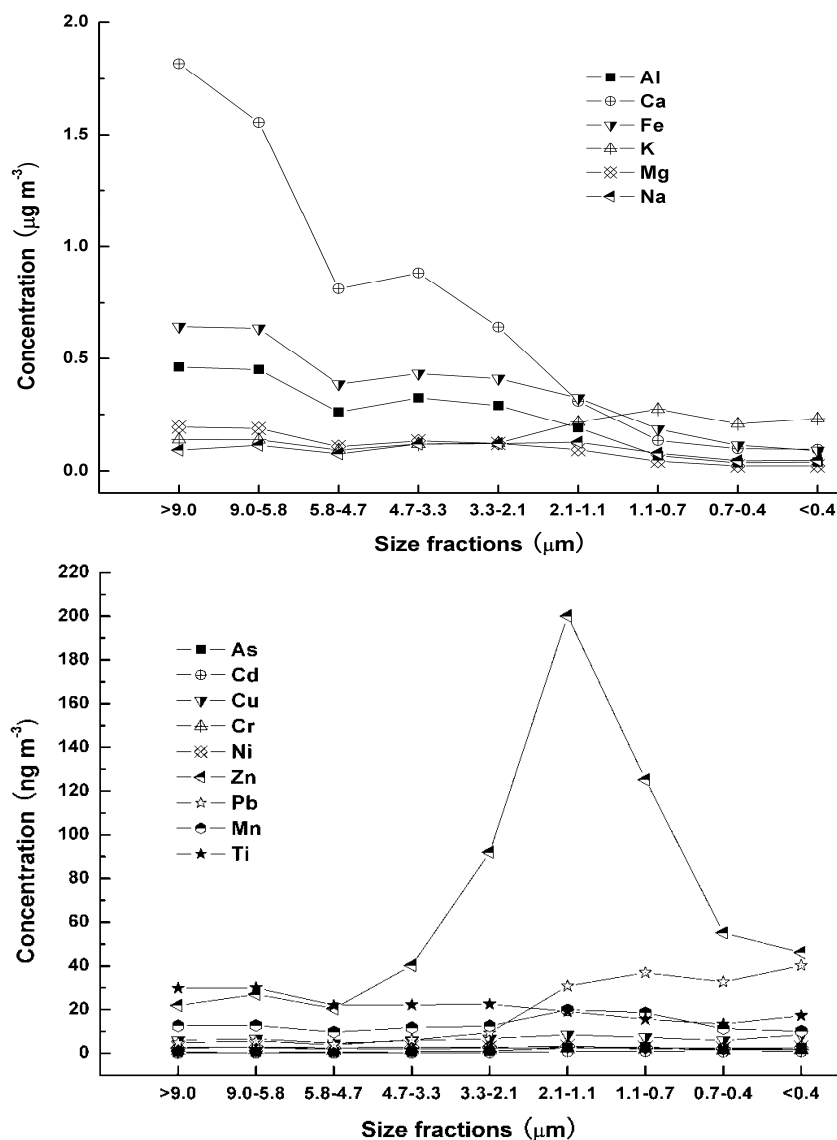


Fig. 5. Distribution of elements in different size fractions of size-segregated aerosol samples.

Source Identification of $\text{PM}_{2.5}$ by Principal Component Analysis/Absolute Principal Component Scores and Cluster Analysis

When compared with coarse particles (TSP), fine particles ($\text{PM}_{2.5}$) have a longer atmospheric residence time and can pose greater health risks to the residents via indirect inhalation exposure. Therefore, source identification of the elements in $\text{PM}_{2.5}$ was carried out.

Principal Component Analysis/Absolute Principal Component Scores

For PCA, the value of KMO (Kaiser-Meyer-Olkin's test) was 0.81, which meets the limit of 0.600 conventionally held as a critical value. Bartlett's test of sphericity showed that principal component analysis could be applied to the data at the $p < 0.01$ level. Four principal components were identified using Varimax with Kaiser Normalization for $\text{PM}_{2.5}$ (Table 2). The principal components accounted for 79.9% of the total variance in the dataset. The first

component (factor 1), which explained 26.3% of the total variance with an eigenvalue of 3.95, was most dependent on Cd, Pb, Zn, As and Mn. These elements are generally environmental contaminants that pose great concern and contributed from wide anthropogenic sources. EF values confirmed the enrichment of Cd, Pb, Zn and As in the present study (Fig. 4). Pb, Zn and Cd were representatives of automobile exhaust (Wu *et al.*, 2007; Fang *et al.*, 2010). The average As concentration in Chinese coal is 3.18 mg/kg, and As is one of the characteristic elements of coal combustion in China (Kang *et al.*, 2011). K was also present at high values in this component. K, Zn and Pb are considered to be trace elements of incinerators (Wu *et al.*, 2007; Fang *et al.*, 2010). Taken together, these findings indicate that this component may be attributed to anthropogenic sources mixed with industrial, coal combustion and traffic emission. The second component (factor 2), which explained 25.7% of the total variance with an eigenvalue of 3.86, appeared to represent natural sources since it was strongly correlated

Table 2. Rotated component matrix of elements in PM_{2.5} (n = 72)).

	Component			
	1	2	3	4
Al		0.82		
Ca		0.86		
Fe		0.70		
K	0.65	0.43		0.44
Mg		0.95		
Na			0.80	
As	0.68			0.41
Cd	0.91			
Cr	0.43		0.82	
Cu			-0.71	
Mn	0.55	0.68		
Ni				0.82
Pb	0.91			
Ti				0.74
Zn	0.78		0.44	
Eigenvalues	3.95	3.86	2.28	1.90
% Variance	26.3	25.7	15.2	12.6
Cumulative %	26.3	52.1	67.2	79.9

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

with Mg, Al, Ca, Fe and Mn (Fig. 4). Al, Ca, Fe, Mg and Mn are generally widely considered to be typical crustal elements. Ca, Al, and Mg are the tracer associated with soil, dust and their re-suspension sources (Wang *et al.*, 2006; Oura *et al.*, 2007; Srivastava *et al.*, 2008). These findings indicate that local, regionally transported, and re-suspended pre-existing elements may have contributed to this source. To investigate whether soil contributed mainly to the recovered metals, the Ca/Al, Ca/Ba, Ca/Fe, Ca/Mg and Ca/Mn ratios of PM_{2.5} were calculated for background soil in Jiangsu Province and this component (factor 2). The Ca/Al, Ca/Ba, Ca/Fe, Ca/Mg and Ca/Mn ratios were 2.64 ± 1.05 , 1.70 ± 0.96 , 7.78 ± 3.02 , and 37.4 ± 21.8 for factor 2, and 0.20, 0.43, 1.37, 23.0 for the local background soil (CNEMC, 1990), respectively, suggesting that local soil was not the exclusive contributor to this factor. Ca is considered to be indicative of cement and construction dust. Thus, this factor likely also reflected soil and dust from construction. The third component (factor 3) mainly consisted of Na, Cr, Cu and Zn, which explained 15.2% of the total variance with an eigenvalue of 2.28. This component appeared to be related to a mixture factor. Cu showed a high native relationship with Na and Cr, suggesting different origins (Table 2). For example, Na is regarded as a marker element of sea salt, sea-spray and marine sources (Viana *et al.*, 2008). Cu is a marker of automobile brake pads and worn tires (Garg *et al.*, 2000; Sternbeck *et al.*, 2002; Gietl *et al.*, 2010). The fourth component (factor 4) was mainly composed of Ni and Ti, and explained 12.6% of the total variance with an eigenvalue of 1.90. Ni is generally considered a fingerprint of oil combustion (Fang *et al.*, 2010), while coal combustion is the leading source of atmospheric nickel in Chinese cities (Tian *et al.*, 2012). It is difficult to explain the presence

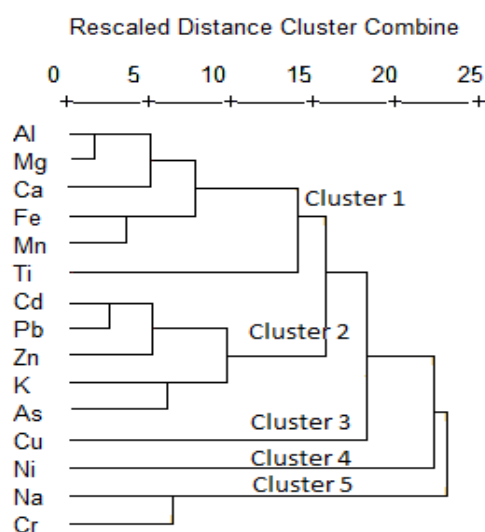
of Ti in this factor. Nevertheless, this factor likely reflects another anthropogenic source. Overall, principal component analysis of 23 TSP samples in Qingdao indicated the following three categories: Fe, Ti, Mn, V, and Ni represent the soil source factor; Cu represents mixed sources of soil and pollution; and Pb, Zn, Cd and S represents the pollution factor (Hao *et al.*, 2007). There are some conflicts among available studies of fingerprint elements of different sources. Indeed, the interpretation of factors based on elemental composition includes a great deal of subjective evaluation since there are no exclusive tracing elements for identified solutions. Therefore, the concurrent use of more methods may increase the rationalization of source identification.

To investigate the contributions of each of these sources, the absolute scores were calculated. A regression model was employed using the APCA Scores for the four sources and average mass concentrations (Tables S7 and S8). The contributions were 37.5% for the first component, 34.1% for the second component, 9.0% for the third component and 19.8% for the fourth component; therefore, the first and the second components were the dominant sources.

Cluster Analysis

Cluster analysis of all the examined elements (Al, Ca, Fe, K, Mg, Na, As, Cd, Cr, Cu, Mn, Ni, Pb, Ti and Zn) was conducted in R-mode, and five distinct groups or clusters were revealed. Cluster 1 contained Al, Ca, Fe, Mg, Mn and Ti, while Cluster 2 contained As, Cd, Pb, Zn and K, Cluster 3 contained Na and Cr, and Clusters 4 and 5 contained Cu and Ni, respectively (Fig. 6). These results indicated that elements belonging to the same group or cluster had strong correlations among themselves and may have originated from a common source.

The main difference between the results of the R-mode CA and those of the PCA was that the third component of PCA (Na, Cr and Cu) was divided into two clusters in the results of CA. In fact, Cu showed a high native relationship with Na and Cr (Table 2), suggesting different origins. Ti

**Fig. 6.** Dendrogram based on the average linkage of measured elements in PM_{2.5}.

in factor 4 was assigned to Cluster 2. This may have occurred because CA considers all variances while PCA uses most variance and produces cluster members that are distinct from members of other clusters. Overall, R-mode CA suggests that the analyzed elements could be classified into five groups with respect to source identification. Group 1, which consisted of As, Cd, Pb, Zn and K, may have resulted from anthropogenic activities (industrial and traffic emission sources). Group 2, Al, Ca, Fe, Mg, Mn and Ti, may have resulted from local soil/construction dusts (natural sources). Group 3, which was composed of Na and Cr, may have resulted from both anthropogenic and natural sources (sea salt and coal combustion). Group 4, which consisted of Cu, may be attributed to vehicle exhaust, while Group 5, composed of Ni, may have resulted from oil combustion.

CONCLUSIONS

In the present study, the annual mass concentrations for TSP and PM_{2.5} ranged from 49.4 µg/m³ to 391 µg/m³ (mean ± S.D.: 135 ± 61 µg/m³) and from 20.4 µg/m³ to 200 µg/m³ (mean ± S.D.: 80.5 ± 37.9 µg/m³), respectively. These findings indicated that the air pollution levels in Nanjing were severe. The monthly mass concentration ratios of PM_{2.5} to TSP ranged from 0.46 to 0.78 (mean: 0.66) and from 0.25 to 0.83 (mean: 0.58) for Gulou and Pukou, respectively. The mass concentrations of TSP and PM_{2.5} in winter were higher than those in summer during the sampling year. The size distribution of mass concentration for size-segregated samples showed a bimodal pattern (coarse and fine particle fraction). The differences in elemental concentrations in TSP and PM_{2.5} between Gulou and Pukou suggested spatial variation. Elemental concentrations in TSP and PM_{2.5} during winter were higher than those in summer, suggesting seasonal variations. The similar result was also observed on different size fractions of the size-segregated aerosol samples. The major elements (Al, Ca, Fe, Mg, Na and Mn) were primarily distributed in coarse fractions while toxic elements such as As, Cd, Pb and Zn were significantly enriched in the fine fractions. Enrichment factors indicated that the As, Cu, Pb and Zn in the studied TSP and PM_{2.5} were of anthropogenic loads. Source appointment for PM_{2.5} was conducted using PCA/APCS and CA. Four potential components were identified by PCA and their contributions calculated using absolute principal component scores were 37.5% for As/Cd/Pb/Zn/K, 34.1% for Al/Ca/Fe/Mg/Mn, 9.0% for Na/Cr/Cu, and 19.8% for Ni/Ti, respectively. Five potential groups were identified using R-mode cluster analysis of elemental data in PM_{2.5}. The Na/Cr/Cu identified by PCA was divided into a Na/Cr group and a Cu group and Ti in factor 4 was assigned to Cluster 2, indicating a statistical difference in airborne metallic elements. These findings indicate that the air pollution caused by atmospheric particles and associated toxic metals in Nanjing is severe. The compositive investigation on the temporal and spatial variations and the size distribution of atmospheric particulate matters and associated metallic metals and the source apportionment will help understanding and managing aerosol effects on health and air quality.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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