



## Concentrations and source apportionment of particulate matter in different functional areas of Shanghai, China

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### ABSTRACT

Concentrations of atmospheric particulate matter with different sizes and 9 metallic elements (Al, Ca, Mg, Fe, Cu, Mn, Ni, Pb and Zn) were measured in two sampling sites of Baoshan District and Putuo District from July 2009 to September 2010, to investigate the size distribution and the possible sources of particulate matter. The results showed that in these two sampling sites, crustal elements mainly distributed in coarse mode and heavy metals all distributed in fine mode. Source apportionment results by enrichment factor and principal component analysis indicated that in Baoshan sampling site,  $PM_{0.43-2.1}$  was mainly from industrial metallurgical processes, while  $PM_{2.1-10}$  was mainly from re-suspended soil dust. Local road traffic source was the dominant contributor to  $PM_{0.43-2.1}$  and  $PM_{2.1-10}$  in Putuo sampling site.

**Keywords:** Particulate matter, size distribution, seasonal variation, source apportionment, different functional areas



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### 1. Introduction

Particulate matter (PM) in the atmosphere are complex mixtures of elemental and organic carbon, mineral dust, trace elements and water (Lim et al., 2010). They originate from both the natural (involving sea-salt particles, wind-blown sand, volcanic ash, etc.) and anthropogenic sources (industrial processes, traffic sources, fuel combustion, etc.) (Lim et al., 2010). Particulate matter has negative effects on human health, air quality, visibility as well as global climate change (WHO, 2006; IPCC, 2007; Colette et al., 2008; Chen et al., 2010). And the pollution caused by particulate matter is not only related to its concentrations, but also associated with particle sizes. In general, particulate matter with smaller sizes can adsorb more pollutants (toxic heavy metals, acidic oxides, organic pollutants, large amounts of bacteria and viruses, etc.) and deposits in the lungs and reaches the alveoli (Samet et al., 2000). In addition, fine particulate matter has a longer atmospheric residence time for several days or weeks and is transported through atmospheric circulation, affects the surrounding atmospheric environment more significantly (Harrison and Pio, 1983).

In recent years, in most cities of China, particulate matter has been the primary pollutant in the atmosphere, and there is no exception for Shanghai. From 2005 to 2010, the annual average concentration of  $PM_{2.5}$  (particle aerodynamic diameter less than or equals to 2.5  $\mu m$ ) in Shanghai is between 44  $\mu g m^{-3}$  and 53  $\mu g m^{-3}$ , which exceeds the new National Standard II of Air Quality (annual average of 35  $\mu g m^{-3}$ ). In 2010, the total deaths of circulatory system disease and cardiovascular disease caused by  $PM_{2.5}$  in

Shanghai were 2 980 and which also resulted in economic losses of about 390 million dollars (Pan et al., 2012).

Considering the adverse effects of particulate matter pollution in Shanghai, many related investigations have been carried out, mainly including chemical compositions (Shen et al., 2002), physical characteristics (Yang et al., 2007), variations of particulate matter concentrations (Lu et al., 2008) and source apportionment (Yao et al., 2010). However, the former studies focused on the pollution property and source apportionment of  $PM_{10}$  (particle aerodynamic diameter equals to or less than 10  $\mu m$ ) or  $PM_{2.5}$ , and did not consider the pollution properties of particulate matter in different sizes, nor did they conduct comparative studies of different functional areas. The aim of the present study is to (1) investigate the size distribution of particulate matter; (2) discuss the differences of particulate matter and 9 associated elements (Al, Ca, Mg, Fe, Cu, Mn, Ni, Pb and Zn) among four seasons; (3) identify the possible sources of particulate matter with different sizes in different functional areas.

### 2. Materials and Methods

#### 2.1. Sampling sites

Shanghai is located in 30°23'–31°27'N, 120°52'–121°45'E. It belongs to subtropical monsoon climate, prevails northwest wind in winter and southeast wind in summer. Its annual average temperature is about 16 °C, and the annual average rainfall is about 1 125 mm, while 60% of the total rainfall occurs in spring, summer and autumn.

The sampling site in the industrial area is located on the roof of a building in Yuepu Town, Baoshan District, which is 9 m above the ground. The site is close to Baoshan Iron and Steel Group and Shidongkou Power plant and both industrial sectors are coal-fired. The residential-commercial sampling site is located on the roof of an office building in Changfeng Community of Putuo District, which is also 9 m above the ground. This site is surrounded by many commercial malls and supermarkets, with heavy traffic of Jinshajiang Road (Figure 1).

## 2.2. Sampling and analysis

From July 2009 to September 2010, atmospheric particulate matter samples were collected using Ambient Eight Stage Non-Viable Cascade Impactor Sampler (TE-20-800, BGI/TISCH, America) at a rate of  $28.3 \text{ L m}^{-1}$ , with stages 0 to 7 representing the aerodynamic equivalent diameters of  $9.0\text{--}10 \mu\text{m}$ ,  $5.8\text{--}9.0 \mu\text{m}$ ,  $4.7\text{--}5.8 \mu\text{m}$ ,  $3.3\text{--}4.7 \mu\text{m}$ ,  $2.1\text{--}3.3 \mu\text{m}$ ,  $1.1\text{--}2.1 \mu\text{m}$ ,  $0.7\text{--}1.1 \mu\text{m}$  and  $0.43\text{--}0.7 \mu\text{m}$ , respectively. The sampling medium was 81 mm glass fiber filter (TE-20-301). Before and after sampling, the glass fiber filters were conditioned in an oven for 48 h ( $25 \text{ }^\circ\text{C}$ ,  $40\pm 5\%$  relative humidity), and then they were weighted. In Baoshan sampling site, 14 groups of samples were collected, and each group of 8 samples with a total 108 valid filter samples (excluding 4 missing samples). In Putuo sampling site, 12 groups of samples were collected, a total of 94 valid filter samples (excluding 2 missing samples).

The filters were shredded using plastic scissors and transferred to a PTFE (polytetrafluoroethylene) tank. 2 mL of  $\text{HNO}_3$ , 3 mL of HF, and 1 mL of  $\text{HClO}_4$  were added to the tank to digest the samples. Then they were heated in an oven at  $180 \text{ }^\circ\text{C}$  for 5 h. After digestion and cooling, the tank was moved to an electro-thermal board at  $130 \text{ }^\circ\text{C}$  in order to drain the remaining acid.

Sample was cooled again and the final volume was adjusted to 25 mL with 2 mL  $\text{HNO}_3$  (Wang et al., 2013). Subsequently, the concentrations of metallic elements (Al, Ca, Fe, Mg, Cu, Mn, Ni, Pb and Zn) were determined by a 710-ES Inductively Coupled Plasma-Emission Spectrometer. Two blanks and two reference materials (soil standards, GSS-6) were used for quality assurance and quality control. The recovery of the analyzed elements was between 80% and 110%.

## 3. Results and Discussion

### 3.1. Mass concentrations and size distribution of particulate matter and metallic elements

The aerodynamic equivalent diameter of  $2.5 \mu\text{m}$  is always regarded as the boundary of coarse particulate matter ( $\text{PM}_{2.5\text{--}10}$ ) and fine particulate matter ( $\text{PM}_{2.5}$ ) (Chaloulakou et al., 2003). Since the sampler does not have a cut-off head of  $2.5 \mu\text{m}$ ,  $2.1 \mu\text{m}$  was regarded as the boundary of coarse and fine particulate matter in this study. Particulate matter with diameter of less than  $2.1 \mu\text{m}$  was classified as fine particulate matter ( $\text{PM}_{0.43\text{--}2.1}$ ), particulate matter with diameter greater than  $2.1 \mu\text{m}$  and less than  $10 \mu\text{m}$  was classified as coarse particulate matter ( $\text{PM}_{2.1\text{--}10}$ ). The monthly average concentrations of particulate matter in different sizes were displayed in Table 1. In the two sampling sites, monthly average concentration of  $\text{PM}_{9.0\text{--}10}$  was the highest and the concentration of  $\text{PM}_{0.43\text{--}0.7}$  was the lowest. The monthly average concentrations of particulate matter with different sizes in Baoshan sampling site were all higher than those in Putuo sampling site, which suggesting that industrial processes were significantly associated with the high concentrations of particulate matter in the atmosphere.

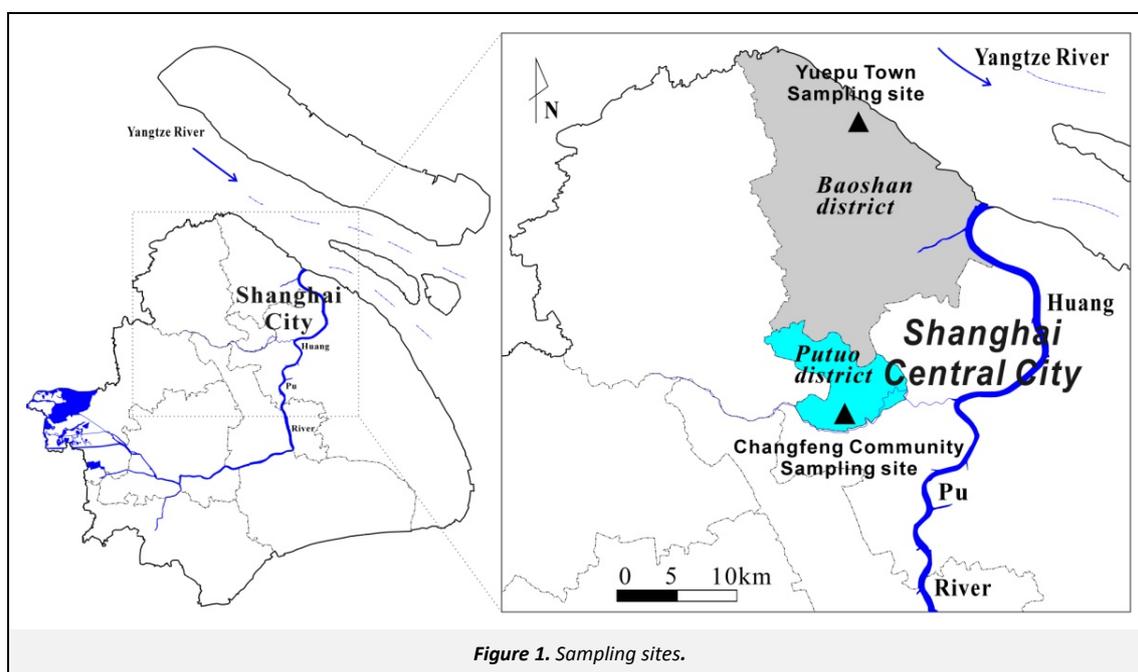


Figure 1. Sampling sites.

Table 1. Monthly average concentrations (mean $\pm$ SD) of particulate matter with different sizes in different sampling sites ( $\mu\text{g m}^{-3}$ )

Sampling sites	$\text{PM}_{0.43\text{--}0.7}$	$\text{PM}_{0.7\text{--}1.1}$	$\text{PM}_{1.1\text{--}2.1}$	$\text{PM}_{2.1\text{--}3.3}$	$\text{PM}_{3.3\text{--}4.7}$	$\text{PM}_{4.7\text{--}5.8}$	$\text{PM}_{5.8\text{--}9.0}$	$\text{PM}_{9.0\text{--}10}$
Baoshan	13.98 $\pm$ 11.91	25.77 $\pm$ 31.18	25.77 $\pm$ 27.11	14.25 $\pm$ 8.67	18.20 $\pm$ 10.90	25.29 $\pm$ 32.97	26.26 $\pm$ 16.99	47.98 $\pm$ 31.62
Number of samples	12	13	14	13	14	14	14	14
Putuo	8.14 $\pm$ 5.82	14.19 $\pm$ 11.12	15.87 $\pm$ 12.00	10.63 $\pm$ 7.02	14.43 $\pm$ 10.56	13.51 $\pm$ 7.25	23.40 $\pm$ 11.44	35.43 $\pm$ 16.25
Number of samples	11	12	12	12	12	11	12	12

The 9 metallic elements were classified into two categories: crustal elements (Al, Ca, Mg and Fe) and heavy metals (Cu, Mn, Ni, Pb and Zn). Compared to heavy metals, the concentrations of crustal elements were all significantly higher in both sampling sites. The concentrations of Fe and Zn in Baoshan sampling site were relatively higher than those in Putuo sampling site. This may be related to the industrial processes in Baoshan sampling site. The concentrations of heavy metals (Cu, Mn and Pb) in Putuo sampling site were higher than those in Baoshan sampling site, these metals were mainly associated with traffic related emissions (Allen et al., 2001; Rajsic et al., 2008), which suggested a heavy traffic in Putuo sampling site.

The size distributions of metallic elements are presented in Table 2. In Baoshan sampling site, the highest concentrations of crustal elements were found in the coarse mode (particle size greater than 2.1  $\mu\text{m}$ ), while the highest concentrations of heavy metals were in the fine mode (particle size less than 2.1  $\mu\text{m}$ ). In Putuo sampling site, the highest concentrations of Ca and Mg were in coarse mode (3.3–4.7  $\mu\text{m}$ ), while for Al and Fe, they were in fine modes (0.7–1.1  $\mu\text{m}$  and 0.43–0.7  $\mu\text{m}$ , respectively). Usually, crustal elements are found in the coarse modes, and are primarily of crustal origin. Fe was primarily from industrial metallurgical processes and road traffic, and former investigations have confirmed that Fe approximately equally distributed in both fine and coarse modes (Chan et al., 1997; Hueglin et al., 2005). Considering there's no metallurgical industry in Putuo, so we infer that Fe mainly came from road traffic. For Al, it distributed in the fine mode indicating road and pavement erosion due to traffic (Laden et al., 2000; Arditsoglou and Samara, 2005). This phenomenon illustrated that traffic-related emissions constituted the most significant source of Al and Fe in Putuo sampling site. For heavy metals, their highest concentrations all distributed in the fine mode (0.43–0.7  $\mu\text{m}$ ), which suggesting the dominance of anthropogenic contributions (Wang et al., 2006).

### 3.2. Seasonal variations of particulate matter and metallic elements

One-way analysis of variance (ANOVA) is used to study the effects of a factor on the test results and to compare whether there is a significant difference between two or more populations. We used this method to identify whether there is a significant seasonal difference of particulate matter in the two sampling sites.

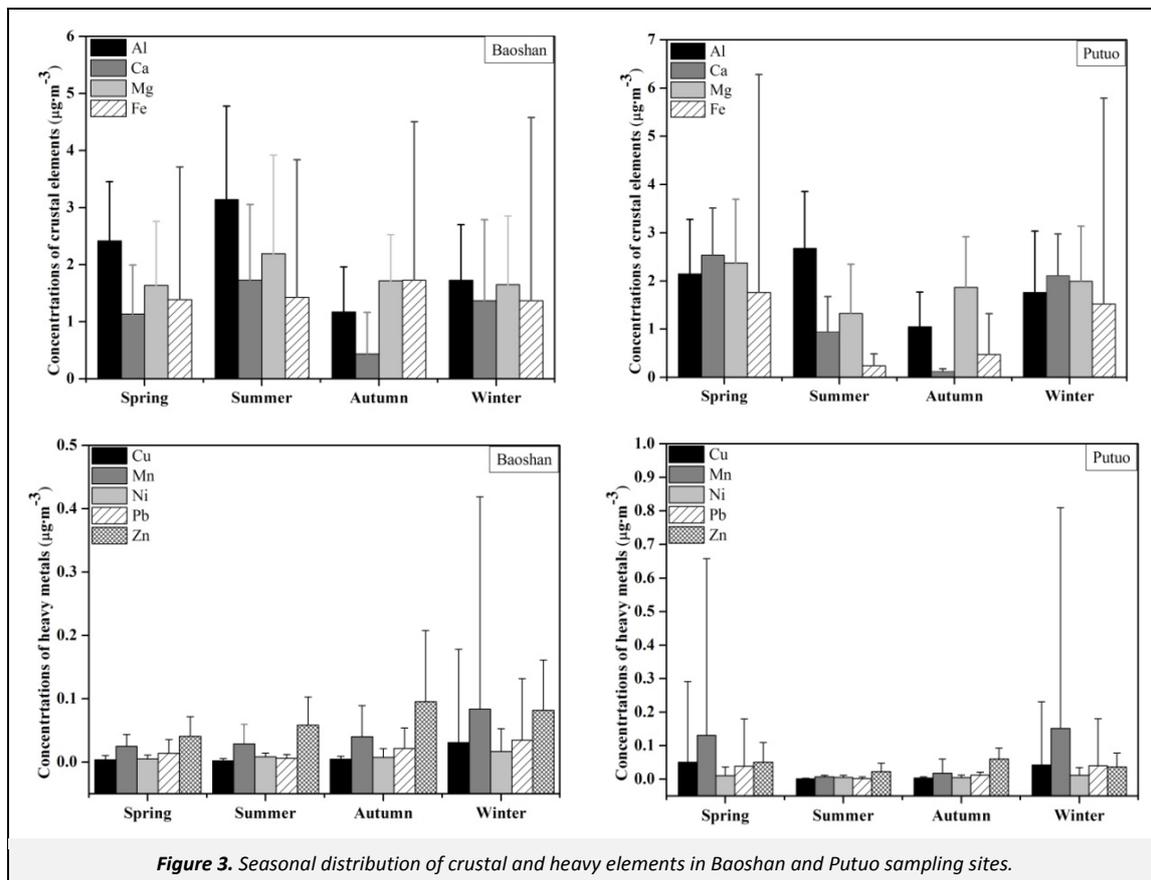
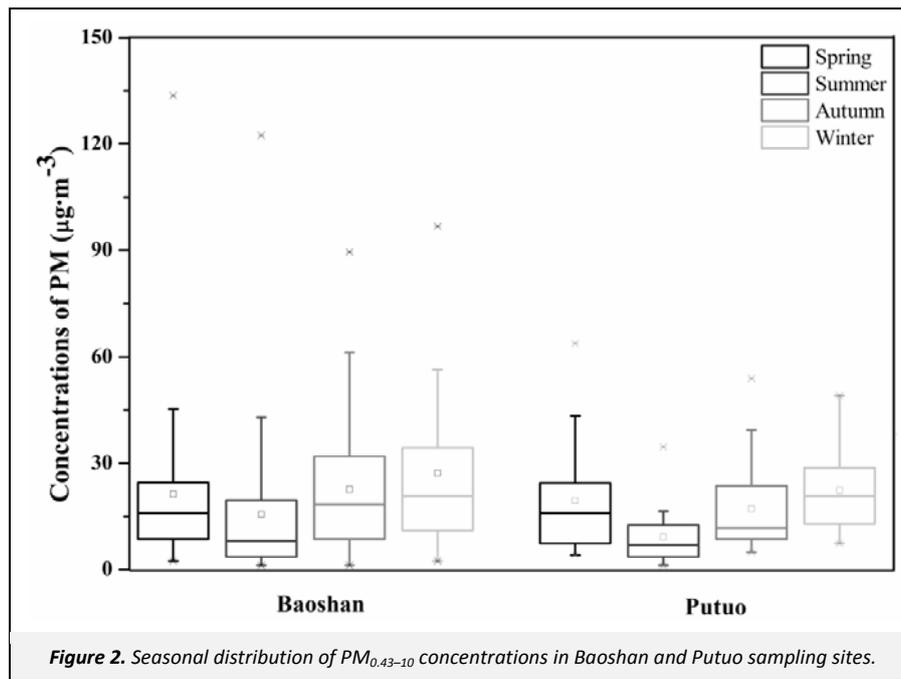
The results of one-way ANOVA illustrated that there were no significant differences of particulate matter concentrations ( $P>0.05$ ) among four seasons in Baoshan sampling site, while the seasonal differences of particulate matter concentrations were significant ( $P<0.05$ ) in Putuo sampling site. Particulate matter concentration was the highest in winter and the lowest in summer (Figure 2). In Baoshan sampling site, concentrations of crustal elements (distributed in coarse modes) were higher in summer than those in winter, while in Putuo sampling site, only the concentration of Al was higher in summer than that in winter, the concentrations of heavy metals (which distributed in fine modes) were higher in winter than in summer both in Baoshan and Putuo (Figure 3). This phenomenon explained that crustal elements had higher concentration in summer and heavy metals had higher concentration in winter. In addition to affected by emission sources, meteorological conditions might be a reasonable explanation (Yang et al., 2005). In summer, the frequent precipitation processes are effective for the removal of particulate matter from air. In addition, influenced by the high-pressure system and strong solar radiation, the higher wind speeds and temperatures favor the diffusion of particulate matter in summer, reducing its concentration. In winter, the atmospheric conditions are stable and prone to thermal inversion, breezes and calm winds inhibit the diffusion and dilution, resulting in an exponential increase of pollutants near the ground. In winter and early spring, the air is dry and strong north-west winds bring abundant dust to Shanghai, which increases the concentration of particulate matter in the atmosphere.

### 3.3. Source apportionment

**Enrichment factor analysis.** The enrichment factor (EF) proposed by Zoller et al. (1974) has been widely used as the first step in evaluating the enrichment degree and the potential strength of pollution-emitting sources. The choice of reference element is of great importance during enrichment factor analysis. Usually Al, Ti, Fe or Si is used as the reference element, as these elements have stable chemical properties and are influenced little by human activities (Hong et al., 2011), but there is no universally accepted rule for this choice. In this study, Al was used as the reference element, as it has low spatial variability and stable chemical properties. For these reasons it is frequently used. The abundance of elements in the earth's crust was taken from Taylor (1964). The enrichment factor of element  $C_n$  can be described as below:

**Table 2.** The size distribution of metallic elements (mean $\pm$ SD) in Baoshan and Putuo sampling sites ( $\mu\text{g m}^{-3}$ )

Baoshan	0.43–0.7 $\mu\text{m}$	0.7–1.1 $\mu\text{m}$	1.1–2.1 $\mu\text{m}$	2.1–3.3 $\mu\text{m}$	3.3–4.7 $\mu\text{m}$	4.7–5.8 $\mu\text{m}$	5.8–9.0 $\mu\text{m}$	9.0–10 $\mu\text{m}$	Sum
Al	1.690 $\pm$ 1.159	1.655 $\pm$ 1.391	2.213 $\pm$ 1.489	2.172 $\pm$ 1.369	2.467 $\pm$ 1.407	1.955 $\pm$ 1.568	1.524 $\pm$ 1.069	1.881 $\pm$ 1.328	15.557
Ca	1.142 $\pm$ 1.096	1.085 $\pm$ 1.051	1.417 $\pm$ 1.749	1.539 $\pm$ 1.477	1.192 $\pm$ 1.194	1.084 $\pm$ 1.229	0.505 $\pm$ 0.683	0.911 $\pm$ 1.049	8.875
Mg	1.609 $\pm$ 1.021	1.839 $\pm$ 1.385	2.170 $\pm$ 1.681	2.412 $\pm$ 1.299	1.897 $\pm$ 1.077	1.684 $\pm$ 1.134	0.944 $\pm$ 0.831	1.716 $\pm$ 0.939	14.271
Fe	1.560 $\pm$ 4.865	1.147 $\pm$ 0.115	0.860 $\pm$ 1.393	1.187 $\pm$ 2.652	0.909 $\pm$ 0.617	0.881 $\pm$ 0.652	1.808 $\pm$ 1.999	3.987 $\pm$ 3.787	12.339
Cu	0.068 $\pm$ 0.224	0.003 $\pm$ 0.003	0.004 $\pm$ 0.005	0.003 $\pm$ 0.003	0.002 $\pm$ 0.002	0.001 $\pm$ 0.001	0.005 $\pm$ 0.009	0.006 $\pm$ 0.006	0.092
Mn	0.173 $\pm$ 0.522	0.020 $\pm$ 0.017	0.038 $\pm$ 0.043	0.035 $\pm$ 0.050	0.018 $\pm$ 0.007	0.018 $\pm$ 0.006	0.043 $\pm$ 0.058	0.046 $\pm$ 0.026	0.391
Ni	0.014 $\pm$ 0.026	0.008 $\pm$ 0.008	0.019 $\pm$ 0.041	0.018 $\pm$ 0.034	0.007 $\pm$ 0.004	0.006 $\pm$ 0.006	0.004 $\pm$ 0.003	0.005 $\pm$ 0.006	0.081
Pb	0.064 $\pm$ 0.145	0.025 $\pm$ 0.029	0.030 $\pm$ 0.036	0.009 $\pm$ 0.010	0.006 $\pm$ 0.005	0.013 $\pm$ 0.022	0.005 $\pm$ 0.004	0.006 $\pm$ 0.005	0.158
Zn	0.048 $\pm$ 0.048	0.074 $\pm$ 0.070	0.167 $\pm$ 0.170	0.062 $\pm$ 0.070	0.062 $\pm$ 0.047	0.054 $\pm$ 0.037	0.045 $\pm$ 0.040	0.071 $\pm$ 0.060	0.583
Putuo	0.43–0.7 $\mu\text{m}$	0.7–1.1 $\mu\text{m}$	1.1–2.1 $\mu\text{m}$	2.1–3.3 $\mu\text{m}$	3.3–4.7 $\mu\text{m}$	4.7–5.8 $\mu\text{m}$	5.8–9.0 $\mu\text{m}$	9.0–10 $\mu\text{m}$	Sum
Al	1.717 $\pm$ 1.333	3.164 $\pm$ 2.588	1.898 $\pm$ 1.286	1.896 $\pm$ 1.290	2.098 $\pm$ 1.172	2.090 $\pm$ 1.565	1.598 $\pm$ 0.986	1.473 $\pm$ 1.025	15.934
Ca	1.377 $\pm$ 1.250	1.559 $\pm$ 1.311	1.289 $\pm$ 1.184	1.524 $\pm$ 1.351	1.722 $\pm$ 1.324	1.674 $\pm$ 1.297	1.357 $\pm$ 1.249	1.129 $\pm$ 1.342	11.631
Mg	1.745 $\pm$ 1.247	2.110 $\pm$ 1.722	1.867 $\pm$ 1.406	2.006 $\pm$ 1.390	2.157 $\pm$ 1.300	2.133 $\pm$ 1.482	1.752 $\pm$ 0.941	1.573 $\pm$ 1.374	15.343
Fe	3.927 $\pm$ 8.647	0.320 $\pm$ 0.698	0.167 $\pm$ 0.222	0.368 $\pm$ 0.630	0.475 $\pm$ 0.540	0.635 $\pm$ 1.127	1.168 $\pm$ 1.483	1.090 $\pm$ 1.084	8.150
Cu	0.191 $\pm$ 0.426	0.002 $\pm$ 0.002	0.002 $\pm$ 0.002	0.001 $\pm$ 0.001	0.003 $\pm$ 0.005	0.001 $\pm$ 0.001	0.004 $\pm$ 0.004	0.006 $\pm$ 0.005	0.210
Mn	0.582 $\pm$ 1.230	0.010 $\pm$ 0.008	0.015 $\pm$ 0.010	0.009 $\pm$ 0.009	0.012 $\pm$ 0.013	0.015 $\pm$ 0.020	0.021 $\pm$ 0.025	0.036 $\pm$ 0.056	0.700
Ni	0.027 $\pm$ 0.047	0.005 $\pm$ 0.004	0.007 $\pm$ 0.005	0.004 $\pm$ 0.004	0.004 $\pm$ 0.004	0.008 $\pm$ 0.008	0.006 $\pm$ 0.009	0.006 $\pm$ 0.009	0.067
Pb	0.130 $\pm$ 0.270	0.014 $\pm$ 0.011	0.025 $\pm$ 0.017	0.003 $\pm$ 0.003	0.003 $\pm$ 0.003	0.004 $\pm$ 0.005	0.004 $\pm$ 0.004	0.009 $\pm$ 0.013	0.192
Zn	0.051 $\pm$ 0.070	0.039 $\pm$ 0.024	0.089 $\pm$ 0.053	0.029 $\pm$ 0.021	0.029 $\pm$ 0.021	0.025 $\pm$ 0.014	0.022 $\pm$ 0.020	0.049 $\pm$ 0.053	0.333



$$EF = \frac{(C_n/C_{ref})}{(B_n/B_{ref})} \quad (1)$$

where,  $EF$  denotes the enrichment factor and  $C_{ref}$  is a reference element of crustal material.  $B_n$  and  $B_{ref}$  represent the abundance of elements in the particle sample and reference element of crustal material respectively in the reference system.  $C_n/C_{ref}$  is the ratio of concentration of  $C_n$  to  $C_{ref}$  in the particle sample.  $B_n/B_{ref}$  is the ratio of concentration of  $B_n$  to  $B_{ref}$  in the crustal reference system. If the value of  $EF$  approaches unity, crustal soils are most likely to be the

predominant source of element  $C_n$ , while if the value of  $EF$  is over 5, the element can be considered enriched and to have a significant contribution from non-crustal sources. The  $EF$  values of 8 elements in both the fine ( $PM_{0.43-2.1}$ ) and coarse ( $PM_{2.1-10}$ ) fractions are presented in Table 3.

In Baoshan sampling site,  $EF$  values greater than 5 were found for Cu, Ni, Pb and Zn in the fine particles fraction,  $PM_{0.43-2.1}$ , and for Pb and Zn in the coarse particles fraction,  $PM_{2.1-10}$ . This phenomenon revealed the dominance of non-crustal sources. It is

worth noting that the EF value of Pb reached 111.5 in the fraction of  $PM_{0.43-2.1}$ , which was significantly higher than that in the fraction of  $PM_{2.1-10}$  (EF=19.4), indicating a stronger contribution of fine particulate matter compared to coarse particulate matter and therefore greater risk for human health. Ca, Mg and Fe showed no enrichment either in the coarse or fine particle fractions, these elements were mainly of crustal origin (Wang et al., 2013).

In Putuo sampling site, the EF values of toxic heavy metals of Cu, Mn, Ni, Pb and Zn were greater than 5 in  $PM_{0.43-2.1}$ . In  $PM_{2.1-10}$ , the EF values of Pb and Zn were greater than 5. Thus, we believe that these elements were primarily from non-crustal sources (such as industrial activities, road traffic, home cooking). The crustal elements did not enrich, suggesting the dominance of natural origin (such as wind-blown sand, sea-salt particles).

**Results of principal component analysis.** Principal component analysis (PCA) is a numerical approach to account for statistical variance by deriving the least number of major factors. It is useful in reducing the dimensionality of the large data sets and in clarifying the relationship between the variables. To further identify pollution sources of  $PM_{0.43-2.1}$  and  $PM_{2.1-10}$  in the two different sampling sites, PCA was carried out with varimax rotation.

In Baoshan sampling site (Table 4), three factors of  $PM_{0.43-2.1}$  with eigenvalues greater than 1 were selected. The cumulative variance was 86.0%. In factor 1, elements with the high scores including Fe, Cu, Mn and Pb suggested that these elements were mainly associated with non-ferrous smelting, iron and steel smelting, traffic emissions (Hueglin et al., 2005; Contini et al., 2010). Thus, factor 1 represents industrial activities and road traffic. The high scores of Ca and Mg in factor 2 were attributed to re-suspension of soil dust and sea-salt particles (Hueglin et al., 2005). The score of Zn was over 0.6 in factor 3, which had complex sources, such as waste incineration, non-ferrous metal smelting, and vehicle exhaust emissions (Chan et al., 1997; Zhang et al., 2002; Arditoglou and Samara, 2005). Considering there were no industries located in Putuo sampling site, but a waste incineration plant located in the northwest and a heavy traffic flow, here, we infer that vehicle exhausts and waste incineration were the dominant emission sources for Zn.

Three factors of  $PM_{2.1-10}$  were also extracted with eigenvalues greater than 1. Factor 1, including Al and Mg, can be interpreted as

being re-suspension of soil dust and sea-salt particles (Arditsoglou and Samara, 2005; Rajsic et al., 2008). It explained that  $PM_{2.1-10}$  was mainly composed of crustal elements as well. The high score of Mn in factor 2 was associated with non-ferrous smelting (Arditsoglou and Samara, 2005). Pb with a score of over 0.6 was dominant in factor 3, that could be considered as traffic related contributions such as vehicular exhausts and abrasion (Allen et al., 2001; Rajsic et al., 2008).

The PCA analysis results were consistent with EF results. The enriched elements of Pb, Zn, Cu, Ni and Mn, were mostly from anthropogenic activities, while Al, Ca, Mg, Fe were not enriched and they were primarily associated with natural sources. In summary, the dominant pollution source of  $PM_{0.43-2.1}$  in Baoshan sampling site was primarily from industrial metallurgical processes (non-ferrous smelting, iron-steel smelting), followed by re-suspension of soil dust, sea-salt particles, and combustion sources (including vehicular exhausts and waste incineration). For  $PM_{2.1-10}$ , re-suspension of soil dust was the predominant pollution source, followed by industrial metallurgical processes and traffic related sources.

In Putuo (Table 5), there were two components extracted from  $PM_{0.43-2.1}$ . Factor 1, including Cu, Fe, Mn, Ni, Pb and Zn, was strongly influenced by traffic related sources (vehicular exhausts, tire and brake abrasion). The scores over 0.6 were found in factor 2, including the crustal elements of Ca and Mg, which generally from soil dust and sea-salt particles (Wang et al., 2006; Lim et al., 2010). Four components were extracted from  $PM_{2.1-10}$ . Factor 1 was composed of the crustal metals (Al and Mg), which was mainly associated with natural sources, such as ground dust, sea-salt particles and re-suspended soil dust (Contini et al., 2010). Pb in factor 2 might be from vehicular exhausts (Hueglin et al., 2005; Contini et al., 2010). The high score of Ca in factor 3 was attributed to construction dust (Caggiano et al., 2010). Higher score of Ni observed in factor 4 may be derived from industrial combustion (Almeida et al., 2005). The results of factor analysis revealed that the dominant pollution sources of  $PM_{0.43-2.1}$  in Putuo sampling site including local road traffic sources, re-suspended soil dust. Natural sources, including ground dust, re-suspended soil dust and construction dust were the main pollution sources contributing to  $PM_{2.1-10}$ . Vehicular exhaust was also an important source contributing to  $PM_{2.1-10}$ .

**Table 3.** Enrichment factor (EF) values of crustal and heavy metals in different sampling sites

		Crustal elements			Heavy metals				
		Ca	Mg	Fe	Cu	Mn	Ni	Pb	Zn
Baoshan	$PM_{0.43-2.1}$	1.26	3.61	0.67	18.71 <sup>a</sup>	3.57	7.89 <sup>a</sup>	111.5 <sup>a</sup>	86.89 <sup>a</sup>
	$PM_{2.1-10}$	1.06	3.11	1.33	2.28	1.39	4.52	19.14 <sup>a</sup>	33.37 <sup>a</sup>
Putuo	$PM_{0.43-2.1}$	1.19	2.91	0.88	37.56 <sup>a</sup>	6.55 <sup>a</sup>	6.05 <sup>a</sup>	111.93 <sup>a</sup>	28.53 <sup>a</sup>
	$PM_{2.1-10}$	1.6	3.71	0.6	2.26	0.9	3.41	13.36 <sup>a</sup>	19.97 <sup>a</sup>

<sup>a</sup> EF values > 5

**Table 4.** Varimax rotated factor loadings and contributions obtained in PCA applied to the  $PM_{0.43-2.1}$  and  $PM_{2.1-10}$  fractions in Baoshan sampling site

	Element	Al	Ca	Mg	Fe	Cu	Mn	Ni	Pb	Zn	Contribution (%)
$PM_{0.43-2.1}$	Factor 1	-0.535	-0.182	-0.552	0.923 <sup>a</sup>	0.939 <sup>a</sup>	0.955 <sup>a</sup>	0.387	0.876 <sup>a</sup>	-0.339	47.804
	Factor 2	0.53	0.845 <sup>a</sup>	0.713 <sup>a</sup>	0.301	0.253	0.232	0.549	0.101	0.607 <sup>a</sup>	26.578
	Factor 3	0.315	-0.394	-0.038	-0.008	0.082	0.11	-0.494	0.351	0.634 <sup>a</sup>	11.604
$PM_{2.1-10}$	Factor 1	0.725 <sup>a</sup>	0.493	0.817 <sup>a</sup>	0.412	0.236	0.532	0.588	0.337	0.593	30.634
	Factor 2	-0.364	-0.82	0.437	0.595	0.477	0.677 <sup>a</sup>	-0.253	0.4	0.541	28.352
	Factor 3	0.065	0.176	0.095	-0.641	0.529	-0.358	-0.523	0.643 <sup>a</sup>	0.353	18.609

<sup>a</sup> Scores > 0.6

**Table 5.** Varimax rotated factor loadings and contributions rate obtained in PCA applied to the PM<sub>0.43–2.1</sub> and PM<sub>2.1–10</sub> fractions in Putuo sampling site

	Element	Al	Ca	Mg	Fe	Cu	Mn	Ni	Pb	Zn	Contribution (%)
PM <sub>0.43–2.1</sub>	Factor 1	0.552	0.655 <sup>a</sup>	0.341	0.971 <sup>a</sup>	0.964 <sup>a</sup>	0.948 <sup>a</sup>	0.988 <sup>a</sup>	0.966 <sup>a</sup>	0.665 <sup>a</sup>	66.389
	Factor 2	0.517	0.663 <sup>a</sup>	0.848 <sup>a</sup>	–0.219	–0.236	–0.221	–0.104	–0.249	–0.024	18.343
	Factor 1	0.721 <sup>a</sup>	0.575	0.823 <sup>a</sup>	–0.539	–0.495	–0.683	0.519	–0.083	0.009	31.185
PM <sub>2.1–10</sub>	Factor 2	0.264	0.368	0.372	0.465	0.42	0.477	0.261	0.775 <sup>a</sup>	0.583	21.915
	Factor 3	0.224	0.613 <sup>a</sup>	–0.034	0.536	–0.546	0.391	–0.357	–0.06	–0.603	18.775
	Factor 4	0.387	–0.262	0.009	0.297	0.36	0.279	0.676 <sup>a</sup>	–0.529	–0.339	15.177

<sup>a</sup> Scores > 0.6

#### 4. Conclusions

In Baoshan and Putuo sampling sites, monthly average concentration of PM<sub>9.0–10</sub> was the highest and the concentration of PM<sub>0.43–0.7</sub> was the lowest. Affected by the industrial activities, concentrations of particulate matter in different sizes were higher in the atmosphere of Boshan sampling site.

Heavy metals both in the two sampling sites were found in the fine modes, mainly derived from anthropogenic activities. Crustal elements in Baoshan were in the coarse modes, while, in Putuo, Al and Fe were in the fine modes, which were influenced by road traffic.

There were no significant differences of particulate matter concentrations ( $P > 0.05$ ) among four seasons in Baoshan sampling site, while the seasonal differences of particulate matter concentrations were significant ( $P < 0.05$ ) in Putuo sampling site. Controlled by meteorological factors, particulate matter concentration was the highest in winter and the lowest in summer, and crustal elements had higher concentration in summer and heavy metals had higher concentration in winter.

Source apportionment by enrichment factor (EF) and principal component analysis (PCA) showed that the primary sources were mainly dominated by anthropogenic activities. In Baoshan sampling site, the dominant pollution source of PM<sub>0.43–2.1</sub> was industrial metallurgical process, while re-suspended soil dust and sea-salt particles were the predominant pollution sources of PM<sub>2.1–10</sub>. The primary pollution sources of PM<sub>0.43–2.1</sub> in Putuo sampling site including local road traffic sources, re-suspended soil dust, while the primary pollution sources of PM<sub>2.1–10</sub> mainly included ground dust, re-suspended soil dust and construction dust.

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