

Contamination characteristics and possible sources of PM₁₀ and PM_{2.5} in different functional areas of Shanghai, China

Jun Wang*, Zimei Hu, Yuanyuan Chen, Zhenlou Chen, Shiyuan Xu

Key Laboratory of Geographic Information Science of Ministry of Education, East China Normal University, Shanghai 200062, China

HIGHLIGHTS

- ▶ Analyzed the contents of PM_{2.5}, PM₁₀, metal elements at different functional areas.
- ▶ Compared the levels of PM₁₀, PM_{2.5}, heavy metals with cities in other countries.
- ▶ The total levels of PM and heavy metals were slightly higher than developed countries.
- ▶ Identify the possible sources of PM₁₀ and PM_{2.5} with SEM and PCA.
- ▶ Preliminary source apportionment results suggested that PM mainly from local sources.

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ABSTRACT

From July 2009 through September 2010, PM₁₀ and PM_{2.5} were collected at two different functional areas in Shanghai (Baoshan district, an industrial area, and Putuo district, a mixed-use area of residential, commercial, and educational compounds). In our analysis, 15 elements were determined using a 710-ES Inductively Coupled Plasma-Emission Spectrometer (ICP-AES). The contents of PM_{2.5}, PM₁₀, and metal elements at the two different sites were comparatively analyzed. The results show that the mean annual concentrations of PM₁₀ and PM_{2.5} (149.22 $\mu\text{g m}^{-3}$ and 103.07 $\mu\text{g m}^{-3}$, respectively) in Baoshan district were significantly higher than those in Putuo district (97.44 $\mu\text{g m}^{-3}$ and 62.25 $\mu\text{g m}^{-3}$ respectively). The concentrations of PM₁₀ and PM_{2.5} were both greatest in winter and lowest in summer, with the two different sites exhibiting the same seasonal variation. It was found that the proportions of 15 metal elements in PM₁₀ and PM_{2.5} in Baoshan district were 20.49% and 20.56%, respectively, while the proportions in Putuo district were higher (25.98% and 25.93%, respectively). In addition, the proportions of eight heavy metals in PM₁₀ and PM_{2.5} were 5.50% and 3.07%, respectively, for Baoshan district, while these proportions in Putuo district were 3.18% and 2.77%, respectively, indicating that heavy metal pollution is more pronounced in Baoshan district. Compared with cities in developed countries, the total levels of PM₁₀, PM_{2.5} and heavy metals in Shanghai were slightly higher. Scanning electron microscopy (SEM) and principal component analysis (PCA) suggested that the possible sources of PM₁₀ in Baoshan district were ground level fugitive dust, traffic sources, and industrial activities, whereas PM_{2.5} mainly originated from industrial activities, coal combustion, and traffic sources. The sources are same for PM₁₀ and PM_{2.5} in Putuo region, which originate from traffic sources and ground level fugitive dust.

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1. Introduction

In recent years, China's dramatic economic rise, rapid industrial development, population growth, construction and demolition projects, and the increase in traffic flow critically affected the atmospheric environment, especially with regards to contamination of atmospheric particulate matter. However, in particular, airborne PM₁₀ (atmospheric dynamics equivalent diameter $\leq 10 \mu\text{m}$) and PM_{2.5} (atmospheric dynamics equivalent diameter $\leq 2.5 \mu\text{m}$) particles are very harmful to the environment, climate, and human

* Corresponding author. Key Laboratory of Geographic Information Science of Ministry of Education, East China Normal University, No. 3663, Zhongshan North Road, Shanghai 200062, China. Tel.: +86 21 6223 2083; fax: +86 21 6223 2416.

E-mail addresses: jwang@geo.ecnu.edu.cn, wangjunjolly@gmail.com (J. Wang), zimeihu0@gmail.com (Z. Hu), chenmengmeng0701@163.com (Y. Chen), zlchen@geo.ecnu.edu.cn (Z. Chen), syxu@geo.ecnu.edu.cn (S. Xu).

health. Particulate sizes of less than 10 μm are able to absorb more toxic substances than coarse particles, and can enter the human body by deposition in the lungs through respiration, resulting in various respiratory and cardiovascular diseases (Makkonen et al., 2010). Some epidemiological studies have confirmed a significant correlation between fine particles (particle size $\leq 2.5 \mu\text{m}$) and mortality (Lim et al., 2010). Due to their relatively large size, coarse particles generally fall to the ground through wet deposition. Fine particles can remain in the atmosphere for several weeks and can be transported further by atmospheric circulation. Therefore, fine particles greatly impact the environment (Furuta et al., 2005). Furthermore, atmospheric particulate matter not only results in reduced visibility but also affects cloud formation and cessation, which affects heat transfer in the atmosphere, thereby contributing to climate change. In 1997, the United States (US) Environmental Protection Agency (EPA) set a maximum limit for PM_{2.5} (an annual average of $15 \mu\text{g m}^{-3}$, with a daily average of $65 \mu\text{g m}^{-3}$) (Hester et al., 1998), and then redefined the limits of PM_{2.5} (annual average $15 \mu\text{g m}^{-3}$, daily average $35 \mu\text{g m}^{-3}$) in 2006 to further reduce the hazards of fine particles on the environment, human health, and climate. Directive 1999/30/EC (EU Commission, 1999) asks member states of the European Union to perform and report PM_{2.5} measurements in addition to PM₁₀ measurements (Gehrig and Buchmann, 2003). China's Ambient Air Quality Standard, issued in 1996 (GB 3095-1996, 1996), specified the standard for PM₁₀ and put this index into use for Daily Air Quality detection. This standard has played an active role in strengthening the protection of public health and air pollution control. However, with China's rapid economic development, environmental air pollution has changed from coal-burning to more complex sources, and regional pollution due to atmospheric fine particulate matter has been increasing. Some cities often experience long periods of hazy days, which result in a serious threat to public health; at the same time, there are differences between the subjective feelings of people and the evaluation results released by local environmental protection agencies. In view of this, China's state environmental protection department revised the original ambient air quality standards on September 30th, 2011, revised standard II by tightening the limits of PM₁₀ concentration (annual average limit $70 \mu\text{g m}^{-3}$, daily average limit $150 \mu\text{g m}^{-3}$) and added limits to PM_{2.5} (annual average limit $35 \mu\text{g m}^{-3}$, daily average limit $75 \mu\text{g m}^{-3}$).

Currently, research on inhalable particulates focuses on physical characteristics, chemical composition, and source apportionment of inhalable particulates. Research on physical characteristics includes the analysis of particle size, color, shape, and optical properties performed using optical microscopes and scanning electron microscopes (SEM). The observation and analysis of particle structure and composition is done with an SEM or with a spectroscope and transmission electron microscope (Kang et al., 2012; Shao et al., 2009; Furuta et al., 2005). Chemical composition research consists of assessing the composition and contents of metal elements and organic pollutants in particulate matter (Lin et al., 2012; Dong et al., 2012; Callén et al., 2009). The most widely used methods in source apportionment research involve receptor models which are based on sources of pollution and contaminated areas. Receptor model methodology includes microscopy, as well as physical and chemical methods, such as chemical mass balance (CMB) and principal component analysis (PCA), the two most broadly used methods at present (Deshmukh et al., 2012; Lim et al., 2010; Sun et al., 2008; Almeida et al., 2005). In this study, pollution sources are determined using a combination of several methods.

The primary pollutants in the atmospheric environment of Shanghai are inhalable particulate matter (Wang et al., 2007). In

recent years, environmental pollution caused by PM₁₀ and PM_{2.5} in Shanghai has been aggravated, demonstrated by, for example, the increased number of hazy days (Wu et al., 2007). Some scholars have researched the contamination status of inhalable particulate matter in Shanghai. However, most of these studies focused on the pollution property and source apportionment of PM₁₀, and did not consider the pollution property of PM_{2.5}, nor did they conduct comparative studies of different functional areas. In this study, two typical and representative functional areas in Shanghai (industrial area: Yuepu Town in Baoshan district; mixed-use area: Changfeng Community in Putuo district) were chosen to study the content of PM₁₀, PM_{2.5}, metal elements, and heavy metals, as well as the possible sources of these pollutants. Specifically, this study includes the following four aspects: (1) a comparative analysis of the temporal variation of the PM₁₀ and PM_{2.5} content levels in different functional areas in Shanghai; (2) a comparative analysis of the content levels of 15 metal elements in PM₁₀ and PM_{2.5}, focusing on the pollution property of heavy metals; (3) the combination of SEM and PCA to identify the possible sources of PM₁₀ and PM_{2.5} in the two functional areas; (4) the content levels of heavy metals and inhalable particulates were then compared horizontally, to determine the pollution levels of PM₁₀ and PM_{2.5} in Shanghai. The results from this study will be useful for the Shanghai municipal government in terms of the scientific and rational measures that should be used to effectively alleviate environmental pollution from inhalable particulates.

2. Experimental methods

2.1. Sites characteristics

In this study, the sampling site in the industrial area was located 9 m above the ground on the roof of a building in Yuepu Town, Baoshan district. This site is close to the Baoshan Iron and Steel Group and the Shidongkou power plant. Here, Yunchuan Road is located to the east and the traffic flow is heavy. The sampling site reflects a mixture of characteristics from several different pollution sources. The mixed-use sampling site was located 9 m above the ground on the roof of an office building at East China Normal University (Changfeng Community in Putuo district). This district is mainly composed of residential areas, with no large industrial emission sources around the site. Instead, it is surrounded by many commercial malls and supermarkets, with the heavy traffic of Jinshajiang Road located to the east (Fig. 1). Thus, these sampling sites are a good representation of a wide variety of sources and areas.

2.2. Sampling and analysis

During the period of July 2009 through September 2010, PM₁₀ and PM_{2.5} samples were collected at the two sampling sites. We selected two precipitation-free sunny days every month and sampling occurred at least 48 h after precipitation.

All PM₁₀ and PM_{2.5} filter samples were collected simultaneously using low-volume samplers (Minnivol™ Tactical Air Sampler), at a rate of 8 L min^{-1} . Particles were collected on Air-metrics PK100 glass fiber filters with a diameter of 47 mm, for a duration of 48 h. A total of 93 PM₁₀ and PM_{2.5} valid samples were collected, as some of the samples were invalid or missing due to mechanical failures or bad weather. After the samples were weighed at a constant temperature, the filters were shredded with plastic scissors and transferred to a PTFE (polytetrafluoroethylene) tank. Then, 2 ml of HNO₃, 3 ml of HF, and 1 ml of HClO₄ were added to the tank, and the steel jar outside the tank

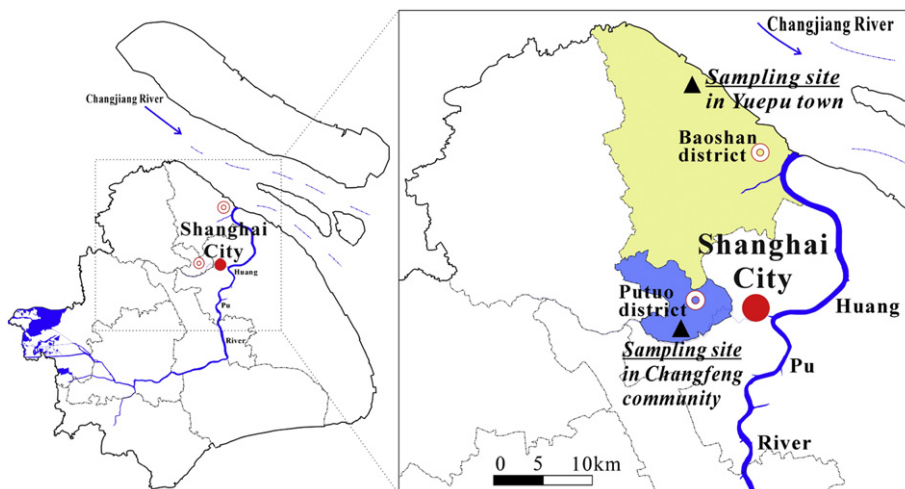


Fig. 1. Sampling sites.

was closed tightly to ensure no leakage of the acidic gas. The PTFE tank was baked in an oven at 180 °C for 5 h. After digestion and cooling, the tank was moved to an electro-thermal board at 130 °C in order to drain the remaining acid until white smoke appeared. The tank was cooled again, then calibrated at final volume of 25 ml with 2 ml of HNO₃. Next, the glass fiber filters were analyzed using a 710-ES Inductively Coupled Plasma-Emission Spectrometer (Agilent Varian) in order to determine the concentration of 15 elements (Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, and Zn). Finally, we calculated the volume concentration of each element in the atmosphere according to the sample size. The entire experimental process was conducted with strict quality control. Two blanks and two GSS-6 reference materials were included in each batch of sample digestion in order to determine the digestion of each blank and to provide reference material (GSS-6) recovery. The recovery value was between 80% and 110%, within the error range.

For SEM, the PM10 and PM2.5 glass fiber membrane samples from the two sites were cut to about 64 mm² using resin scissors and attached to a conductive metal gasket with double-sided adhesive. The samples were then gilded by a vacuum coating machine and put into the SEM sample compartment. The SEM (JSM-5610 LV) was used, with a working voltage of 30 kV for the electron microscope.

3. Results and discussion

3.1. PM10 and PM2.5 levels in different functional areas

The annual mean concentrations (in $\mu\text{g m}^{-3}$) of PM10 and PM2.5 in Baoshan District were 149.22 and 103.07, respectively. Of these, the PM10 level exceeded the recently released ambient air quality standard II (annual average limit $70 \mu\text{g m}^{-3}$), while the PM2.5 level was three-fold higher than the new standard II (annual average limit $35 \mu\text{g m}^{-3}$). The annual mean concentrations (in $\mu\text{g m}^{-3}$) of PM10 and PM2.5 in Putuo District were 97.44 and 62.25, respectively. The PM10 level was higher than the new standard II, while the PM2.5 level was nearly two-fold higher than the new standard II. Therefore, PM10 and PM2.5 concentration levels in Baoshan district were higher than those in Putuo district.

An obvious seasonal variation could be observed for PM10 and PM2.5 (Fig. 2). In Baoshan district, the maximum concentrations of

PM10 and PM2.5 appeared in winter ($207.48 \mu\text{g m}^{-3}$ and $168.45 \mu\text{g m}^{-3}$, respectively), with the minimum in summer ($105.81 \mu\text{g m}^{-3}$ and $51.53 \mu\text{g m}^{-3}$, respectively). The concentrations of PM10 and PM2.5 in Baoshan district were higher in autumn ($171.35 \mu\text{g m}^{-3}$ and $113.85 \mu\text{g m}^{-3}$, respectively) than in spring ($131.86 \mu\text{g m}^{-3}$ and $65.35 \mu\text{g m}^{-3}$, respectively). In Putuo district, the maximum concentrations of PM10 and PM2.5 also appeared in winter ($110.02 \mu\text{g m}^{-3}$ and $75.89 \mu\text{g m}^{-3}$, respectively) with the minimum in summer ($63.67 \mu\text{g m}^{-3}$ and $35.25 \mu\text{g m}^{-3}$, respectively). However, the concentrations of PM10 and PM2.5 in Putuo district were higher in spring ($108.53 \mu\text{g m}^{-3}$ and $67.28 \mu\text{g m}^{-3}$, respectively) than in autumn ($79.33 \mu\text{g m}^{-3}$ and $54.72 \mu\text{g m}^{-3}$, respectively), in contrast to Baoshan district. The similar seasonal variations, with the greatest concentrations in winter and the lowest in summer, were due to seasonal changes in atmospheric dynamics. In summer, Shanghai is influenced by the plum rain season (a special type of rain process, mainly occurring in southern China) and the typhoon period, which both bring precipitation at high frequency and volume. This increases the wet deposition of atmospheric particles in this season, thus providing effective self-purification of the air; good atmospheric diffusion conditions decrease the concentrations of the pollutants. On the other hand, in winter, the atmosphere is relatively stable, often associated with subsidence inversion,

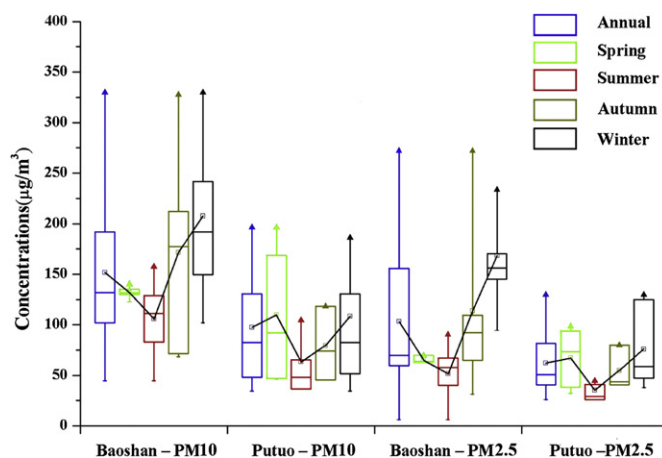


Fig. 2. Seasonal variation in PM10 and PM2.5 concentrations in Baoshan and Putuo districts.

resulting in atmospheric pollutants diffusion difficult; in addition, seasonal industrial and human activities (such as heating) lead to higher accumulated concentrations of particles. In Shanghai, windy weather and subsidence inversion happen frequently in spring, which result in increased amounts of fugitive dust and pollutants from external sources in the air. So, fugitive dust and external pollutants were found in higher concentrations in spring in Putuo district.

The ratio of PM_{2.5}/PM₁₀ was approximately 0.62 for Baoshan district and 0.68 for Putuo district. The squared correlation coefficients were 0.799 and 0.837 for Baoshan and Putuo districts, respectively, which show an obvious correlation between PM₁₀ and PM_{2.5} (Fig. 3). This result indicates that most of the PM₁₀ is composed of PM_{2.5}, and these particles may have similar sources. Thus, PM_{2.5} is the main reason for atmospheric particulate matter pollution.

3.2. Metallic element concentration levels in PM₁₀ and PM_{2.5} for the sampling sites

In total, 15 metallic elements accounted for 20.49% of PM₁₀ in Baoshan district, where 19.69% of PM₁₀ was made up of the metals Na, Fe, Ca, Al, Mg, and K (Table 1). These 15 elements made up 25.98% of PM₁₀ in Putuo district, in which the metals Na, Ca, Al, Mg, K, and Fe made up 25.29% of PM₁₀, both of which were much higher than in material from Baoshan district (Table 2). For PM_{2.5}, the proportions of the 15 elements and the main elements (Na, Ca, Al, Fe, Mg, and K) were 20.56% and 19.56%, respectively, in Baoshan district (Table 3), while in Putuo district (Table 4), the proportions were 25.93% and 24.96%, respectively, much higher than in Boshan district.

The metallic elements of K, Li, Mg, Na, Sr, Cd, Cr, Cu, Mn, Ni, Pb, and Zn in PM₁₀ and PM_{2.5} (and Ca for PM₁₀) in Baoshan district were greatest in concentration during winter. Most of these metals are heavy metals, such that seasonal industrial production, human activities (coal combustion), and a stable atmospheric environment (such as thermal inversion) in winter resulted in a high concentration; other elements had no obvious seasonal differences. Al, Ca, K, Li, Mg, Na, Cr, Cu, Fe, Mn, and Ni of PM₁₀ in Putuo district were greatest in concentration during spring. Al, Ca, K, Fe, Li, Mg and Na are crustal elements, and blustery weather often happens in spring, which leads to a large amount of fugitive dust in the air. Cr, Cu, Mn and Ni are trace metals, and as there is no industry in Putuo, wind-blown matter from external pollution sources could have been the

source. The elements in PM_{2.5} showed no obvious seasonal differences.

Eight heavy metals account for, respectively, 5.50% and 3.07% of PM₁₀ and PM_{2.5} in Baoshan district, and 3.18% and 2.77%, respectively, in Putuo district. Thus, the metallic element content in Baoshan district was significantly higher than in Putuo district.

3.3. Comparison of inhalable particulate pollution levels in Shanghai

In order to laterally compare the pollution levels of PM₁₀, PM_{2.5}, and heavy metals in Shanghai with other areas, we chose related data from the published literature for several cities in China (Hangzhou and Hong Kong) and foreign countries (India, Spain, Finland, and the US) (Table 5).

The content of PM₁₀ and PM_{2.5} in Shanghai is slightly higher than that in Hangzhou, and then the PM_{2.5} content level in Shanghai is significantly higher than that in Hong Kong. Compared with Agra, India, a country at the same development stage as China, the PM_{2.5} and PM₁₀ concentrations in Shanghai are lower. However, the content of PM₁₀ and PM_{2.5} in Shanghai are higher when compared to that of cities in developed countries.

In total, the heavy metal content of PM₁₀ and PM_{2.5} in Baoshan district are both higher than that in Hangzhou, except Zn and Cu; the heavy metal content of PM_{2.5} is higher in Shanghai than in Hong Kong. In contrast, the heavy metal levels of PM₁₀ and PM_{2.5} in Shanghai are both lower than those in Agra, India, but higher than those found in developed countries, which indicates that there is still a gap between Shanghai and developed cities in terms of urban air quality.

Furthermore, Cd, Pb, and Ni were found at similar concentrations in PM₁₀ and PM_{2.5} particles, both in Putuo and Baoshan areas, which confirmed that heavy metals accumulate in PM_{2.5} more easily than in PM₁₀; PM₁₀ and PM_{2.5} also had similar pollution sources.

3.4. Possible sources of PM₁₀ and PM_{2.5}

The microstructural characteristics of PM₁₀ and PM_{2.5} were observed by SEM (JSM-5610LV), and the principal components of PM₁₀ and PM_{2.5} were identified with PCA in order to determine the possible sources of particulate matter. According to the SEM images (Fig. 4, scale bar 1 μ m), the types of single inhalable particles

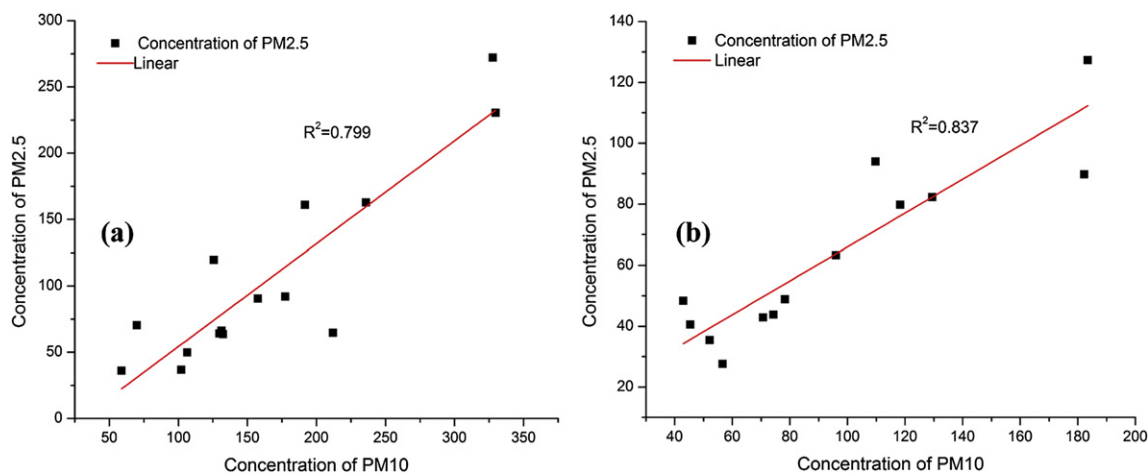


Fig. 3. Linear fitting of PM₁₀ and PM_{2.5} for Baoshan (a) and Putuo (b) districts.

Table 1
Metal element levels in PM10 in Baoshan district (ng m^{-3}).

Element	Mean \pm SD	Spring	Summer	Autumn	Winter	Max	Min	Mass fraction (%)
Al	3712 \pm 2.315	5846	2174	3605	4412	11,516	108	2.593
Ca	4641 \pm 2.018	5299	5091	2455	5616	7532	114	3.242
K	2583 \pm 1.210	2804	1780	2122	4219	5157	919	1.805
Li	6 \pm 0.003	5	4	6	9	11	0.2	0.004
Mg	3378 \pm 0.865	3732	3231	2957	3972	5024	1858	2.360
Na	7047 \pm 4.461	9016	6388	2585	11,872	18,034	839	4.923
Sr	95 \pm 0.070	61	69	57	169	260	4	0.066
Cd	3 \pm 0.003	2	2	2	8	14	0.2	0.002
Cr	56 \pm 0.044	32	41	51	115	134	0	0.039
Cu	41 \pm 0.024	25	32	33	59	94	7	0.029
Fe	6827 \pm 3.910	7807	7950	5487	5921	17,564	2177	4.769
Mn	189 \pm 0.140	323	150	144	197	823	23	0.132
Ni	32 \pm 0.029	25	26	21	61	131	2	0.022
Pb	137 \pm 0.117	77	84	112	286	510	16	0.096
Zn	590 \pm 0.415	318	455	601	985	2049	88	0.412

Table 2
Metal element levels in PM10 in Putuo district (ng m^{-3}).

Element	Mean \pm SD	Spring	Summer	Autumn	Winter	Max	Min	Mass fraction (%)
Al	3115 \pm 3.232	4458	2744	1607	2743	14,709	549	3.116
Ca	4137 \pm 2.007	5271	4590	165	4467	7226	19	4.138
K	2622 \pm 2.360	3832	1279	873	2511	11,790	336	2.663
Li	6 \pm 0.003	7	3	2	6	15	0	0.006
Mg	2985 \pm 1.263	3446	3029	2118	2910	4998	313	2.986
Na	9731 \pm 6.524	13,576	4516	1200	10,294	29,604	588	9.733
Sr	160 \pm 0.114	125	331	29	188	407	4	0.160
Cd	2 \pm 0.001	2	2	1	2	5	0.02	0.002
Cr	22 \pm 0.015	31	11	16	17	54	3	0.022
Cu	22 \pm 0.011	23	34	21	23	49	9	0.022
Fe	2660 \pm 3.49	4634	1238	1289	1683	12,910	370	2.661
Mn	92 \pm 0.058	111	69	51	100	218	24	0.092
Ni	11 \pm 0.012	19	15	9	6	43	0.5	0.011
Pb	71 \pm 0.069	70	55	52	92	203	0.5	0.071
Zn	303 \pm 0.177	321	382	218	323	590	76	0.303

from the different sampling sites mainly include the following. (1) Mineral particles, mostly from windblown sand as well as road and construction dust. These exist in both regular and irregular shapes, with the regular particles generally being gypsum and the irregular particles mainly consisting of crustal materials (Yang et al., 2007). (2) Soot aggregation, mostly from emissions of combustion sources, including coal, vehicle exhaust, and biomass burning. These particles appear as fluffy chain-like aggregations and fluffy round aggregations. (3) Coal fly ash, generally spherical, and derived from coal combustion. (4) Oil droplet residue particles, which are porous. (5) Biomass particles. These come from varied

sources, such as human hair and dander, as well as pollen and spores from natural sources (Shao et al., 2009).

In Baoshan district, the single particle types were mainly mineral particles, soot aggregation, and not fully burned oil droplet residue particles. In Putuo district, single particle types were mainly mineral particles, followed by soot aggregation, and a small amount of biomass particles.

The results of the principal components analysis of the 15 metal elements indirectly suggested the same pollution sources for PM10 and PM2.5. Among the 15 elements of PM10 in Baoshan district, the elements that made up the cumulative contribution

Table 3
Metal element levels in PM2.5 in Baoshan district (ng m^{-3}).

Element	Mean \pm SD	Spring	Summer	Autumn	Winter	Max	Min	Mass fraction (%)
Al	2905 \pm 3.313	3826	2253	2394	3217	15,376	261	2.789
Ca	3407 \pm 1.574	4507	3222	1774	4105	5031	0	3.271
K	2253 \pm 1.203	1643	1654	1626	3501	4683	645	2.163
Li	4 \pm 0.002	4	4	3	6	7	2	0.004
Mg	2323 \pm 1.312	3175	1674	1839	2963	4052	324	2.231
Na	7105 \pm 5.042	7577	5357	2516	12,163	18,576	810	6.822
Sr	212 \pm 0.195	142	142	81	398	767	11	0.204
Cd	3 \pm 0.003	1	1	2	6	10	0.2	0.003
Cr	31 \pm 0.024	36	16	28	49	69	0.2	0.030
Cu	29 \pm 0.016	19	21	22	43	64	5	0.028
Fe	2381 \pm 1.049	2013	2960	1617	2144	4639	918	2.286
Mn	132 \pm 0.141	81	144	127	134	750	41	0.127
Ni	27 \pm 0.028	41	14	16	39	123	0.4	0.026
Pb	133 \pm 0.117	46	58	95	263	411	13	0.128
Zn	465 \pm 0.328	229	299	406	775	1261	114	0.447

Table 4
Metal element levels in PM2.5 in Putuo district (ng m^{-3}).

Element	Mean \pm SD	Spring	Summer	Autumn	Winter	Max	Min	Mass fraction (%)
Al	1542 \pm 1.235	1254	2984	425	1485	4519	0	2.477
Ca	3008 \pm 1.392	3642	3279	19	3499	4940	0	4.832
K	1674 \pm 0.867	1922	1504	418	2060	3948	22	2.689
Li	4 \pm 0.002	5	5	1	4	8	0	0.006
Mg	1866 \pm 1.166	1709	1785	2496	1801	3825	83	2.997
Na	6120 \pm 4.400	9104	1484	727	8096	16,566	363	9.831
Sr	206 \pm 0.216	191	215	9	300	984	3	0.331
Cd	1 \pm 0.001	2	1	1	1	3	0.05	0.002
Cr	9 \pm 0.009	10	5	13	7	34	0	0.015
Cu	15 \pm 0.008	14	21	12	13	28	6	0.024
Fe	1328 \pm 1.084	1858	1209	356	1282	4182	87	2.133
Mn	66 \pm 0.032	66	82	51	62	135	18	0.106
Ni	9 \pm 0.009	8	19	7	6	36	1	0.015
Pb	59 \pm 0.057	69	37	52	64	187	6	0.095
Zn	236 \pm 0.118	250	258	172	235	414	45	0.379

rate over 85% were Al, Ca, Cd, Cr, and Cu (Fig. 5(a)). The contribution rate of Al, as the first component, was 47.15%; this mainly comes from crustal soil dust. The second component, Ca, with a contribution rate of 14.74%, mostly originates from dust associated with construction (Pey et al., 2010) and roads (Lim et al., 2010). In Baoshan district, as an industrial area, Cd, Cr, and Cu were the main pollutants, which are related to anthropogenic activities such as non-ferrous metal industries and chromium plating (Mohanraj et al., 2004; Chandra Mouli et al., 2006; Gioda et al., 2006). Therefore, PM10 in Baoshan district chiefly comes from non-ferrous metal melting, construction dust, and wind-blown sand from soil and road dust.

The principal components of PM2.5 in Baoshan district were Zn, Sr, Pb, Ni, and Mn (Fig. 5(b)), much different from the composition of PM10. The first component, Zn, with a contribution rate of 41.65%, is related to non-ferrous metal melt, gasoline use, and vehicle wear and tear in the transportation industry (Huang et al., 2011; Caggiano et al., 2010). The contribution rate of Sr was 20.11%, which is produced by the melting of non-ferrous metals and chemical production (Lim et al., 2010). In addition, Pb and Ni are related to coal combustion and motor vehicle exhaust. According to this analysis, PM2.5 in Baoshan district mainly consists of heavy metals, which originate from anthropogenic activities, including non-ferrous metal melt, coal combustion, and traffic sources (Huang et al., 2009; Caggiano et al., 2010).

As mentioned above, the squared correlation coefficient of PM10 and PM2.5 was 0.799, which is indicative of a notable correlation and similar sources. However, the results from the PCA indicate distinctly different principal components for PM10 and PM2.5. For PM2.5, heavy metal pollution was significant (Zn, Pb, Ni, and Mn); here, we infer that fine particles, compared with coarse particles, are prone to absorbing more heavy metal elements, which are closely related to anthropogenic sources (e.g., industrial activities, vehicle exhaust). This also reflects the serious industrial pollution in Baoshan district.

The principal components of PM10 and PM2.5 were very similar in Putuo district, and included Al, Ca, Cd, and Cr, as well as Cu for PM2.5 (Fig. 5(c), (d)). Construction and road dust are responsible for Al and Ca. Cd and Cr are typically associated with non-ferrous metal melting; however, since there are no big industries in Putuo district, the possible pollution source may be the small hardware factory near the sampling site. Cu, as one of the principal components of PM2.5, mainly originates from road dust due to traffic. In addition, the SEM images revealed the existence of coal combustion particles. Therefore, excluding interference from the sampling site, the pollution sources are same for PM10 and PM2.5 in Putuo district, which are mainly the road dust from traffic, construction dust, and coal combustion.

Integrating the results from our source apportionment analysis, the pollution sources can be generalized into four categories:

Table 5
Concentration of particulates and heavy metals (ng m^{-3}) in the ambient air of urban areas in different parts of the world.

	Baoshan (China)	Baoshan (China)	Putuo (China)	Putuo (China)	Hangzhou (China) ^a	Hangzhou (China) ^a	Hong Kong (China) ^b	Agra (India) ^c	Agra (India) ^c	Barcelona (Spain) ^d	Barcelona (Spain) ^d	Helsinki (Finland) ^e	Helsinki (Finland) ^e	Florida (USA) ^f
	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM2.5	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5	PM2.5
	143.1	–	100.0	–	111	–	–	154.2	–	49.8	–	12.8	–	–
	–	104.1	–	62.3	–	77.5	29	–	104.9	–	34.5	–	11.8	12.7
Cd	3	3	2	1	–	–	–	–	–	–	–	–	–	–
Cr	56	31	22	9	36	13	1	300	600	6	6	–	–	–
Cu	41	29	22	15	134	76	5	40	200	70	50	6	3	2
Fe	6827	2381	2660	1328	220	726	100	2900	1900	0.9	0.3	500	100	80
Mn	189	132	92	66	108	46	10	900	100	10	10	9	3	2
Ni	32	27	11	9	11	7	4	200	300	7	6	0.8	2	1
Pb	137	133	71	59	288	128	–	1100	1100	200	100	2	6	5
Zn	590	465	303	236	892	651	200	500	900	300	200	8	10	10

^a Bao et al. (2010).

^b Hagler et al. (2007).

^c Kulshrestha et al. (2009).

^d Querol et al. (2001).

^e Pakkanen et al. (2001).

^f Olson et al. (2008).

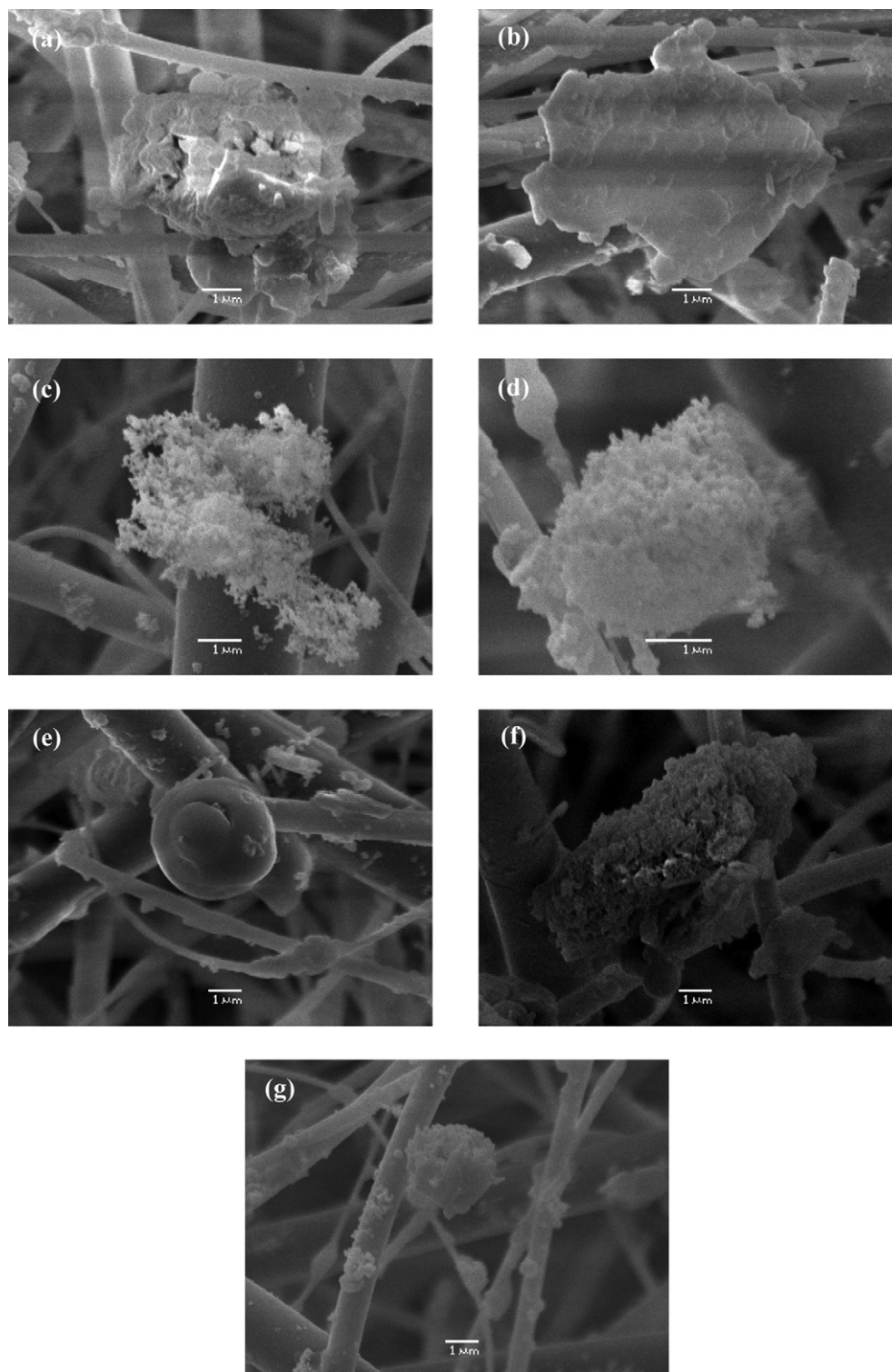


Fig. 4. Morphological types of PM₁₀ collected in Baoshan and Putuo districts (scale bar 1 μm) (a) Irregular mineral particle (Feng et al., 2009; Zhao et al., 2004), (b) regular mineral particle (Zhang et al., 2008), (c) fluffy chain-like soot aggregation (Shao et al., 2009), (d) fluffy round soot aggregation (Shao et al., 2009), (e) coal fly ash (Zhao et al., 2004; Norra et al., 2007), (f) oil droplet residue particle (Yang et al., 2007), and (g) biomass particle (Zhao et al., 2004; Shao et al., 2009).

industrial activities (non-ferrous metal melting and chromium plating), traffic sources (motor vehicle exhaust and road dust due to traffic), ground level fugitive dust (windblown soil dust and construction dust), and coal combustion. The major PM₁₀ contributors in Baoshan district included ground level fugitive dust, traffic sources, and industrial activities, while the major PM_{2.5}

contributors were industrial activities, coal combustion, and traffic sources. The pollution sources were the same for PM₁₀ and PM_{2.5} in Putuo district, its main contributors being traffic sources, ground level fugitive dust, and coal combustion. Our comprehensive analysis of the data shows that pollution in PM₁₀ and PM_{2.5} at two different sites arose from local sources.

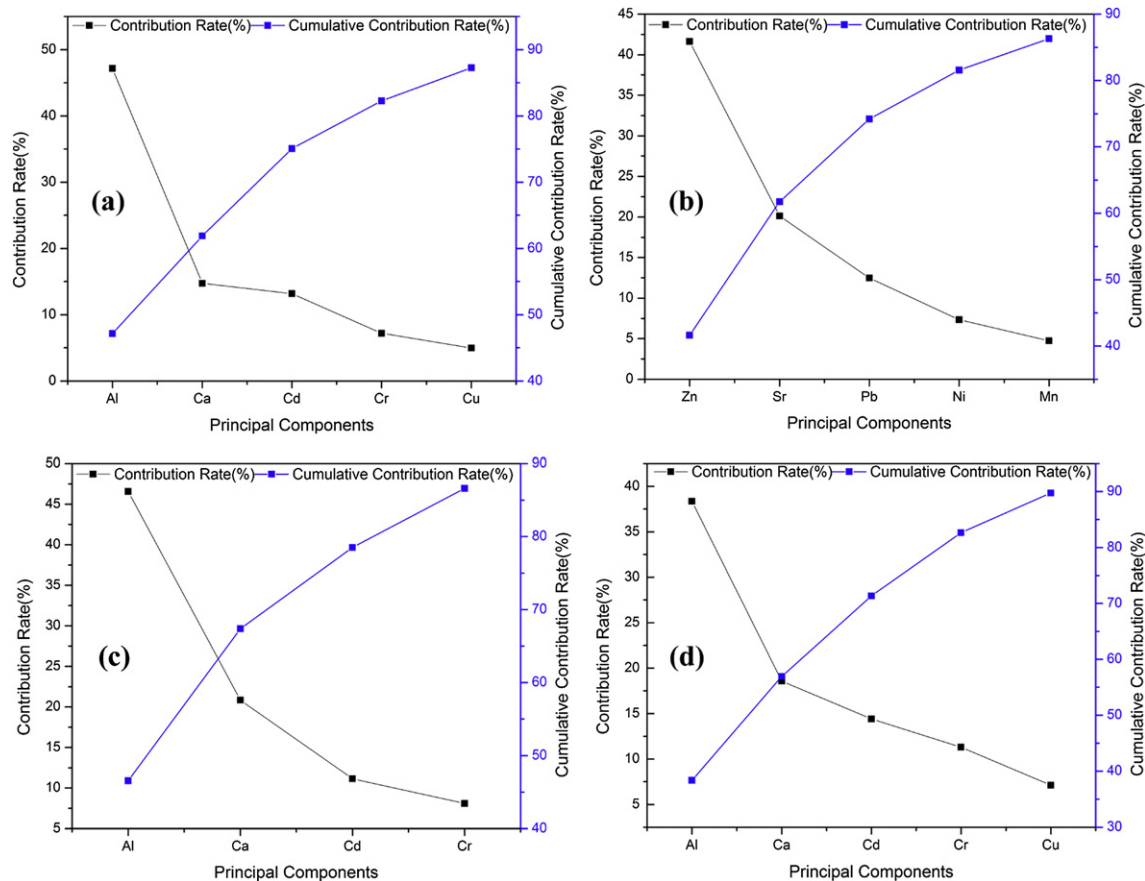


Fig. 5. Contribution rate of the principal components of (a) PM10, (b) PM2.5 in Baoshan District; (c) PM10 and (d) PM2.5 in Putuo district.

4. Conclusions

The two different sampling sites in Shanghai showed some pollution of PM10 and PM2.5, but there were obvious differences regarding the pollution properties. The concentrations of PM10 and PM2.5 in Baoshan district were $149.22 \mu\text{g m}^{-3}$ and $103.07 \mu\text{g m}^{-3}$, respectively and in Putuo district were $97.44 \mu\text{g m}^{-3}$ and $62.25 \mu\text{g m}^{-3}$, respectively; both sites exceeded the new standard II (the annual average and daily average limits of PM10 are $70 \mu\text{g m}^{-3}$ and $150 \mu\text{g m}^{-3}$, respectively; for PM2.5, they are $35 \mu\text{g m}^{-3}$ and $75 \mu\text{g m}^{-3}$, respectively) to different degrees. PM10 and PM2.5 simultaneously cause environmental pollution in Baoshan district, while PM2.5 is the primary source of environmental pollution in Putuo district. Seasonal variation shows that the highest concentrations of PM10 and PM2.5 at both sampling sites occurred in winter and the lowest concentrations occurred in summer.

The proportions of the 15 metal elements in PM10 and PM2.5 in Baoshan district were 20.49% and 20.56%, respectively; the same proportions in Putuo district were 25.98% and 25.93%, respectively, which are higher than those in Baoshan district. Atmospheric environmental pollution due to PM10 and PM2.5 is also higher in Shanghai compared to cities in developed countries. The contents of PM10, PM2.5 and heavy metals in Shanghai are greater than those in Spain, Finland, and the US, which indicate atmospheric pollution and a gap in urban air quality between Shanghai and other cities in developed foreign countries.

The sources of PM10 and PM2.5 at the two different sampling sites in Shanghai were significantly different, but both originated from local sources. The SEM images and PCA results indicated the possible sources of inhalable particles; the major PM10

contributors in Baoshan district included ground dust, traffic sources, and industrial activities, while the major PM2.5 contributors were industrial activities, coal combustion, and traffic sources. The pollution sources were the same for PM10 and PM2.5 in Putuo district, with the main contributors being traffic sources, ground dust, and coal combustion. According to a comprehensive analysis of the data, the inhalable particle pollution assessed at the two sampling sites originated from local sources.

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