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CONTENTS

Size distribution of chemical elements and their source apportionment in ambient coarse, fine, and ultrafine particles in Shanghai urban summer atmosphere

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Abstract

Ambient coarse particles (diameter 1.8–10 μm), fine particles (diameter 0.1–1.8 μm), and ultrafine particles (diameter < 0.1 μm) in the atmosphere of the city of Shanghai were sampled during the summer of 2008 (from Aug 27 to Sep 08). Microscopic characterization of the particles was investigated by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX). Mass concentrations of Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, and Pb in the size-resolved particles were quantified by using synchrotron radiation X-ray fluorescence (SRXRF). Source apportionment of the chemical elements was analyzed by means of an enrichment factor method. Our results showed that the average mass concentrations of coarse particles, fine particles and ultrafine particles in the summer air were 9.38 ± 2.18, 8.82 ± 3.52, and 2.02 ± 0.41 μg/m^3, respectively. The mass percentage of the fine particles accounted for 51.47% in the total mass of PM$_{10}$, indicating that fine particles are the major component in the Shanghai ambient particles. SEM/EDX results showed that the coarse particles were dominated by minerals, fine particles by soot aggregates and fly ashes, and ultrafine particles by soot particles and unidentified particles. SRXRF results demonstrated that crustal elements were mainly distributed in the coarse particles, while heavy metals were in higher proportions in the fine particles. Source apportionment revealed that Si, K, Ca, Fe, Mn, Rb, and Sr were from crustal sources, and S, Cl, Cu, Zn, As, Se, Br, and Pb from anthropogenic sources. Levels of P, V, Cr, and Ni in particles might be contributed from multi-sources, and need further investigation.

Key words: airborne size-resolved particles; chemical elements distribution; source apportionment

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Introduction

Epidemiological studies have shown that increasing levels of airborne particulate matter are associated not only with exacerbations of respiratory diseases but also with increased morbidity and mortality from cardiovascular conditions (Dockery et al., 1993; Dockery and Pope, 1994; Hetland et al., 2004; Künzli et al., 2000; Samet et al., 2000; Stieb et al., 2002). According to their aerodynamic diameter (d), airborne particulates can be divided into three categories: (1) coarse particles ($2.5 \leqslant d \leqslant 10$ μm); (2) fine particles ($d < 2.5$ μm); and (3) ultrafine particles (UFPs) ($d < 0.1$ μm). A number of studies of Shanghai air quality have focused on the physicochemical characterization of coarse particles and fine particles (Lu et al., 2008; Fu et al., 2008; Wang et al., 2006), but until now, relatively few works have investigated the character of ultrafine particles (Lu et al., 2011). However, surface area-to-mass ratios and

deposition efficiency of UPFs in the alveoli are higher than those of either coarse particles or fine particles (Duffin et al., 2007), and the size and chemical composition of ambient particles are important determinants of their potential impacts on human health. These findings have motivated researchers to investigate the physicochemical characterization of ultrafine particles in the urban atmosphere. For example, Wu et al. (2008) conducted a two-year study of particle numbers and size distribution (3 nm–10 μm) of airborne particulates in Beijing, China. They reported annual average particle number concentrations in several ways: the nucleation mode (3–20 nm), the Aitken mode (20–100 nm), and the accumulation mode (0.1–1 μm), giving values of 9000, 15900, and 7800 cm^{-3}, respectively. Allen et al. (2001) measured the size distributions of Ba, Cd, Co, Cu, Hg, Mn, Ni, Pb, Sn, Se, Sr, Zn and Fe in atmospheric aerosols at three background sites in central England and southern Scotland. They concluded that the size distributions obtained in Scotland, which were typically trimodal, significantly differed from those

in central England, where modes were more variable. Lin et al. (2005) reported on the size distribution of chemical elements in size-resolved ambient particles near a highway in Taiwan. Their results showed that anthropogenic elements, such as Zn, Ni, and Pb, were mainly distributed in the size range of 1.0–0.56 μm. As the largest commercial city in China, ambient inhalable particles (PM_{10}, $PM_{2.5}$) in the Shanghai atmosphere have been investigated recently (Ye et al., 2000; Wang et al., 2006; Fu et al., 2008; Zhang et al., 2009). We have also reported the physicochemical character and potential toxicity of Shanghai ambient coarse/fine/ultrafine particles, and have concluded that fine particles have a higher toxicity than either coarse particles or UPFs, and in particular that the crustal element calcium can be enriched in the ultrafine particles (Lu et al., 2011). Nevertheless, relatively few studies have focused on the physicochemical characterization of differently sized airborne particles and their source apportionment. Hence this study has focused on the size distribution of individual elements in size-resolved airborne ambient particles in Shanghai, and interpretation of their source apportionment.

1 Experiments

1.1 Field sampling

The sampling site was located in Xujiahui (XJH), one of commercial centers of Shanghai (Fig. 1). A 13-stage MOUDI125 B (Micro-Orifice Uniform Deposit Impactor, MSP, Co., Minneapolis, USA) with the flow rate of 10 L/min was employed to collect the size-resolved ambient particles. The particles were collected on polycarbonate filters (Millipore, 47 mm diameter, 0.6 μm pore size). The MOUDI impactor effectively separated the particulate matter into 13 ranges (at 50% efficiency) with the following equivalent cutoff diameters (μm): 10–5.6, 5.6–3.2, 3.2–1.8, 1.8–1.0, 1.0–0.56, 0.56–0.32, 0.32–0.18, 0.18–0.1, 0.1–0.056, 0.056–0.032, 0.032–0.018, and 0.018–0.010

Fig. 1   Sketch map of sampling site.

μm. The sampler was mounted on the roof of a building at the Shanghai Environmental Monitoring Center (31°11′20.42″N; 121°26′09.99″S). The sampling site was about 15 m high above the ground. The sampling campaigns were performed from Aug 27 to Sep 10, 2008.

A total of five groups (65 samples) of size-segregated ambient particle samples were collected. The sampling period for each group was set at 48 hr. If it was rainy day during the sampling times, the sampling campaign would be stopped; therefore, the sampling dates were on Aug 27, Aug 30, Sep 02, Sep 04 and Sep 08. Meteorological data during the sampling times were also recorded (Table 1). The sampled filters were kept in desiccators (with room temperature and around 50% RH) until analysis. The filters were weighed before and after sampling, under the same conditions at constant temperature (20 ± 1)°C and humidity ($40\% \pm 5\%$) with a microbalance (Model CP225D, Sartorius, Germany), then, mass concentrations of the size-resolved ambient particles were obtained by the following equation:

$$C = \frac{(W_2 - W_1)}{L \times t} \qquad (1)$$

where, C (μg /m^3) is mass concentration; W_1 (μg) and W_2 (μg) are weight of the filters before and after sampling, respectively; L (m^3/min) is sampling flow of air; t (min) is sampling time.

Table 1   Meteorological data during sampling times

Dates	Aug 27	Aug 30	Sep 02	Sep 04	Sep 08
Temperature (°C) (ave.)	32	26	24	26	26
Humidity (%) (ave.)	67	80	62	60	71
Wind Speed (km/hr) (ave.)	5	12	6	7	8
Wind direction	ESE	ES	W	ES	EN

Ave. means average value of 48 hr.

1.2 Analysis methods

1.2.1 Scanning electronic microscopy

Sample preparation for SEM observation was as described by Lu et al. (2007). Briefly, for each sample, approximately 1.5×2 cm^2 of the polycarbonate filter was cut off using resin scissors and was attached to conductive metal pads using double-sided adhesive. The samples were examined using scanning electron microscopy (SEM) (JSM-6700F, JEOL, Japan), equipped with an energy dispersive X-ray system (EDX) which was used for the chemical elemental analysis. The EDX spectrometer was a Link ISIS spectrometer with a Si(Li) detector which allows X-ray detection from elements higher than carbon (atomic number, $Z > 6$). The system was equipped with software, and elemental weight percents were calculated using standard ZAF (atomic number, absorption, fluorescence) corrections. Operating conditions of the SEM were 10 KeV accelerating voltage and 10 μA beam current, with spectral acquisition times of 100 sec. The diameter of the spot of the electron beam was 1 μm. The instrument allowed observation of the diameter of particles down to 0.5 μm.

1.2.2 Synchrotron radiation X-ray fluorescence analysis

The synchrotron radiation technique has been used in other studies of the elemental composition and species of atmospheric particulate matter (Li et al., 2007, 2009; Lin et al., 2009; Wang et al., 2007). The chemical composition analysis of the size-segregated particles was carried out in Tsukuba, Japan, at the synchrotron radiation X-ray fluorescence analysis end station (BL-4A) of the Photon Factory's high energy accelerator research organization. The electron beam energy and ring current of the synchrotron radiation were 2.5 GeV and 300–450 mA, respectively, and the X-ray energy ranged from 1 to 20 keV. A double crystal monochromator was employed, and the monochromatic excitation energy was 19.5 keV. The electronic slot was adjusted to make the beam spot sizes 5 μm × 5 μm. Measurement time for each sample was set for 100 sec. The fluorescence signals were acquired by a Si(Li) semiconductor detector and sent into a 1024 channel pulse height analyzer to record the XRF spectrum. Recordings of the intensity of the fluorescent signal from each filter were repeated 3 times. The spectra were analyzed and processed by the software AXIL. The advantage of this method is that the analyzer recorded the intensity of fluorescence emitted by the measured particles, and the X-rays cannot do damage to the filter, therefore, the filter is kept in good condition during the experiment.

1.2.3 Source apportionment

Source apportionment of chemical elements in the size-resolved particles was studied by using an enrichment factor method. The enrichment factor (EF) is used to identify whether the measured chemical elements are emitted from natural sources (EF < 100), or from anthropogenic sources. The EF value is calculated by using the following equation:

$$EF_i = \frac{(M_i/M_r)_{aerosol}}{(M_i/M_r)_{crust}} \tag{2}$$

where, M_i is the concentration of the element in aerosol and M_r is the abundance of titanium in the crust. The titanium is selected as the reference element, which is relatively stable in the crust, and its distribution is not affected by human activities (Chen et al., 2008).

2 Results and discussion

2.1 Mass concentrations

Mass levels of the different size airborne particles are shown in Fig. 2. The total mass concentration of the ambient variously size-resolved particles was 74.63 μg/m³.

The average mass concentration of Shanghai coarse particles ($PM_{10-5.6}$, $PM_{5.6-3.2}$, $PM_{3.2-1.8}$) from Aug 27 to Sep 9, 2008 ranged from 7.3 to 12.47 μg/m³ with an average mean of 9.38 ± 2.18 μg/m³. The average mass level of the fine particles ($PM_{1.8-1.0}$, $PM_{1.0-0.56}$, $PM_{0.56-0.18}$, $PM_{0.18-0.1}$) ranged from 5.3 to 12.57 μg/m³ with an average mean of 8.82 ± 3.52 μg/m³, with higher
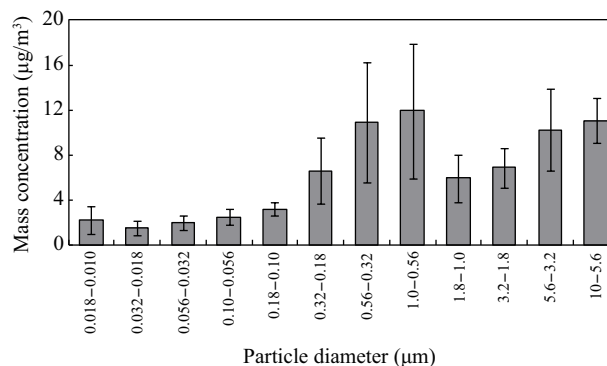
Fig. 2   Mass concentrations of size-segregated particles collected in the Shanghai atmosphere. Data are presented as means with standard deviations.

mass concentration of fine particles found on Aug 30 and Sep 2; relatively high humidity (80%) might contribute to the high mass levels. Mass concentrations of the ultrafine particles ($PM_{0.1-0.056}$, $PM_{0.056-0.032}$, $PM_{0.032-0.018}$, $PM_{0.018-0.01}$) ranged from 1.39 to 2.43 μg/m³ with an average mean of 2.02 ± 0.41 μg/m³. After the size-resolved particles were divided into coarse particles (size diameter, 1.8–10 μm), fine particles (size diameter, 0.1–1.8 μm) and ultrafine particles (size diameter < 0.1 μm), the mass percentage of the fine particles accounted for 51.47% in the total mass of PM_{10}, while the coarse particles and ultrafine particles accounted for 37.69% and 10.84%, respectively (Fig. 3).

The fine-to-coarse mass concentration ratios ranged from 54% to 68% with an average of 62%, indicating that Shanghai ambient particles were dominated by the fine particles. Zhao and Gao (2008) showed that $PM_{1.8}$ accounted for about 68% of the mass concentrations of PM_{10} in the New Jersey urban atmosphere from July to December 2006. Ntziachristos et al. (2007) demonstrated that mass levels of coarse, fine and ultrafine particles near the I-710 freeway in Los Angeles were 6.3 ± 0.88, 5.8 ± 0.95 and 1.7 ± 0.67 μg/m³, respectively. Additionally, we have previously reported average mass levels of coarse particles, fine particles, and UFPs, which were collected in winter at the same sampling site as used in this study, to be 6.2 ± 3.8, 12.9 ± 8.4, 2.7 ± 1.4 μg/m³, respectively
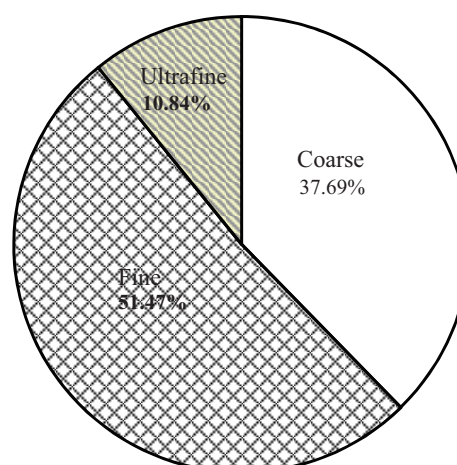
Fig. 3   Mass ratios of size-resolved particles in Shanghai summer atmosphere.

(Lu et al., 2011), Therefore, compared with the above mentioned results, particulate pollution in the center of Shanghai (XJH) is serious, and their mass levels show no significant variation from winter to summer.

2.2 Microscopic characterization of the size-resolved particles

The SEM results demonstrated that microscopic characterization of Shanghai particulates revealed that different size particles had visibly different attributes. Based on SEM morphological character (Fig. 4) and EDX spectrum (Fig. 5), individual particle types in the Shanghai atmosphere could be identified as irregular mineral particles (with main chemical elements, Si, Al, K, Na, Ca); regular mineral particles (S, O, Cl, Na); fly ash (Si, Al, O); soot particles (carbon); and unidentified particles. The coarse particles were mainly composed of mineral particles (Fig. 4a); fine particles were dominated by mineral particles, soot aggregates, fly ashes and unidentified particles (Fig. 4b); and ultrafine particles consisted of soot aggregates (Fig. 4c). The clustered soot aggregates (Fig. 4d), that had originated from combustion, were commonly found in all the size ranges.

Fly ash particles with a spherical shape (Fig. 4e) could be observed; they were largely derived from coal com-

bustion and metallurgical emissions (Lu et al., 2008). The cubic particles (Fig. 4f) were composed of sodium chloride, its chemical elements being identified as Na and Cl by EDX (Fig. 5a). Regular mineral particles with quadrate shape (Fig. 2g), of which the chemical elements were Ca, S, O (Fig. 5b), were mainly generated by atmospheric reactions, similar to particles identified in a case study in Phoenix, Arizona reported by Katrinak et al. (1995). It is noted that there were numerous particles which were dominated by sulfur; their micrographs are shown in Fig. 4h (with EDX spectrum, Fig. 5c) and Fig. 4i (with EDX spectrum, Fig. 5d). This phenomenon of S being deposited on particles could be used to demonstrate that S pollution exists in Shanghai air. Shi et al. (2003) and Li and Shao (2009) have also reported that sulfur could be readily observed in Beijing ambient particles.

2.3 Chemical elements analysis

The mass concentrations of a total of 20 elements in Shanghai size-segregated particles were investigated by SRXRF (Table 2). The chemical elemental analysis results showed that the value for the mass concentration of Si was the highest both in the coarse particles (1385.84 ± 143.87 ng/m^3) and in the ultrafine particles (111.75 ± 26.77 ng/m^3). Being the most abundant element in the
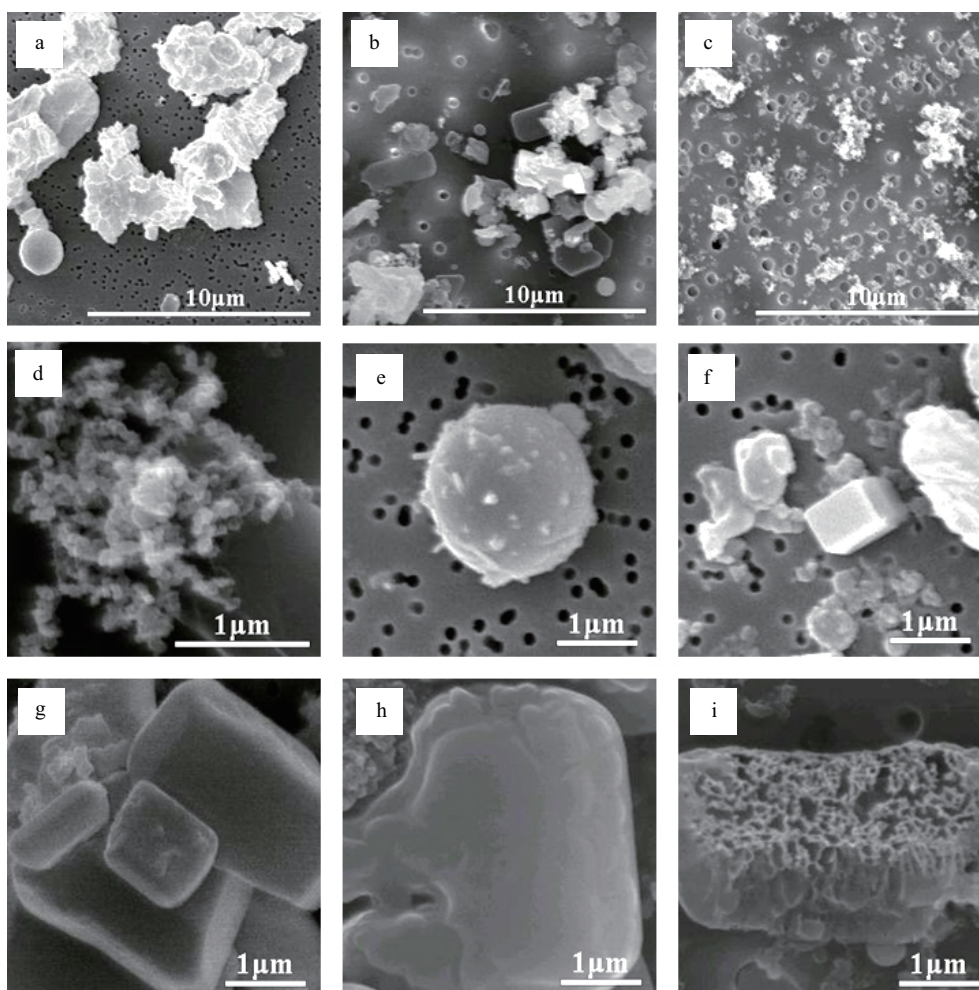

Fig. 4 SEM micrographs of size-segregated particles. (a) coarse particles; (b) fine particles; (c) ultrafine particles; (d) soot aggregates; (e) fly ash; (f), (g) mineral particles; (h), (i) irregular particles.

Table 2 Mass concentrations of 20 elements in coarse, fine, ultrafine particles (unit: ng/m^3)

Elements	Coarse particles	Fine particles	Ultrafine particles
Si	1385.84 ± 143.87	239.03 ± 45.24	111.75 ± 26.77
P	10.38 ± 2.51	18.86 ± 2.04	4.50 ± 0.59
S	88.74 ± 12.76	1124.29 ± 142.23	39.3 ± 3.09
Cl	148.57 ± 13.30	98.06 ± 10.03	18.23 ± 3.67
K	167.64 ± 23.40	139.5 ± 16.04	2.17 ± 0.77
Ca	488.13 ± 88.83	224.72 ± 41.04	6.23 ± 1.10
Ti	27.42 ± 3.37	4.23 ± 0.94	0.43 ± 0.08
V	3.87 ± 0.54	4.57 ± 0.83	4.00 ± 0.62
Cr	1.73 ± 0.29	2.49 ± 0.61	0.69 ± 0.15
Mn	6.92 ± 1.88	9.56 ± 1.23	0.48 ± 0.09
Fe	475.84 ± 63.92	447.69 ± 40.24	14.38 ± 2.39
Ni	0.84 ± 0.08	3.84 ± 0.84	0.61 ± 0.13
Cu	20.07 ± 1.73	36.31 ± 3.33	7.34 ± 1.09
Zn	33.64 ± 6.25	159.86 ± 20.83	2.06 ± 0.11
As	5.95 ± 1.30	2.59±0.48	2.16 ± 0.38
Se	0.17 ± 0.02	2.76 ± 0.50	0.08 ± 0.01
Br	3.27 ± 0.26	12.98 ± 1.40	1.34 ± 0.17
Rb	1.74 ± 0.23	1.19 ± 0.10	0.14 ± 0.02
Sr	2.22 ± 0.33	0.47 ± 0.03	0.03 ± 0.01
Pb	16.77 ± 1.67	103.24 ± 10.06	4.88 ± 0.41

crust, it is to be expected that high mass concentrations of Si could be found in ambient coarse particles (Lu et al., 2007). However, Lin et al. (2005) claimed that emissions from diesel engines could also contribute to concentrations of Si found in ambient nano particles. Therefore, the high concentrations of Si found here in the Shanghai ultrafine particles might be at least in part explained by the many vehicles (30,000 /day) driving around our sampling site.

Sulfur (1124.29 ± 142.23 ng/m^3) was the most abundant chemical element in Shanghai fine particles. Sulfur in ambient particles is a typical anthropogenic element, mainly contributed by coal combustion (Tang, 1990). The high mass level of sulfur in the Shanghai atmosphere suggested that coal combustion was one of the pollutant sources.

The mass concentrations of Ca in coarse, fine and

ultrafine particles were 488.13 ± 88.83, 224.72 ± 41.04, and 6.23 ± 1.10 ng/m^3, respectively. The corresponding mass level of Fe in coarse, fine, and ultrafine particles was 475.84 ± 63.92, 447.69 ± 40.24,and 14.38 ± 2.39 ng/m^3, while that for K was 167.64 ± 23.40, 139.5 ± 16.04, and 2.17 ± 0.77 ng/m^3. These three elements were mainly distributed in the coarse particles.

The mass levels of Zn and Pb in fine particles were 159.86 ± 20.83 and 103.24 ± 10.06 ng/m^3, respectively. Elevated mass concentrations of Zn in ambient particles have also been reported in the air of Cardiff (Moreno et al., 2004), Beijing (Lu et al., 2006) and Shanghai (Fu et al., 2008). We once reported that a high mass level of Pb (325 ng/m^3) could be found in Shanghai winter PM$_{2.5}$ (Lu et al, 2008); compared with our previous results, the mass level of Pb in fine particles reported here has decreased greatly. Because Pb in airborne particles is related with leaded gasoline combustion (Fu et al., 2008), leaded gasoline prohibition and air quality control measures might well have contributed to the Pb decrease.

The mass levels of other metal elements in the fine particles ranked in the following order: Cu (36.31 ± 3.33 ng/m^3) > Mn (9.56 ± 1.23 ng/m^3) > Ni (3.84 ± 0.84 ng/m^3) > Cr (2.49 ± 0.61 ng/m^3).

Figure 6 shows that all of the mass ratios of Si, Ca, Ti, Sr, Fe, K in the coarse particles were more than 50%, suggesting these abundant elements were mainly distributed in the coarse particles, while the mass ratios of S, Zn, Pb, Ni, Se in the fine particles were more than 50%, implying these elements were concentrated in the fine particles.

2.4 Size distribution of individual chemical elements

Figures 7 and 8 present the size distributions of the individual chemical elements in the Shanghai size-resolved
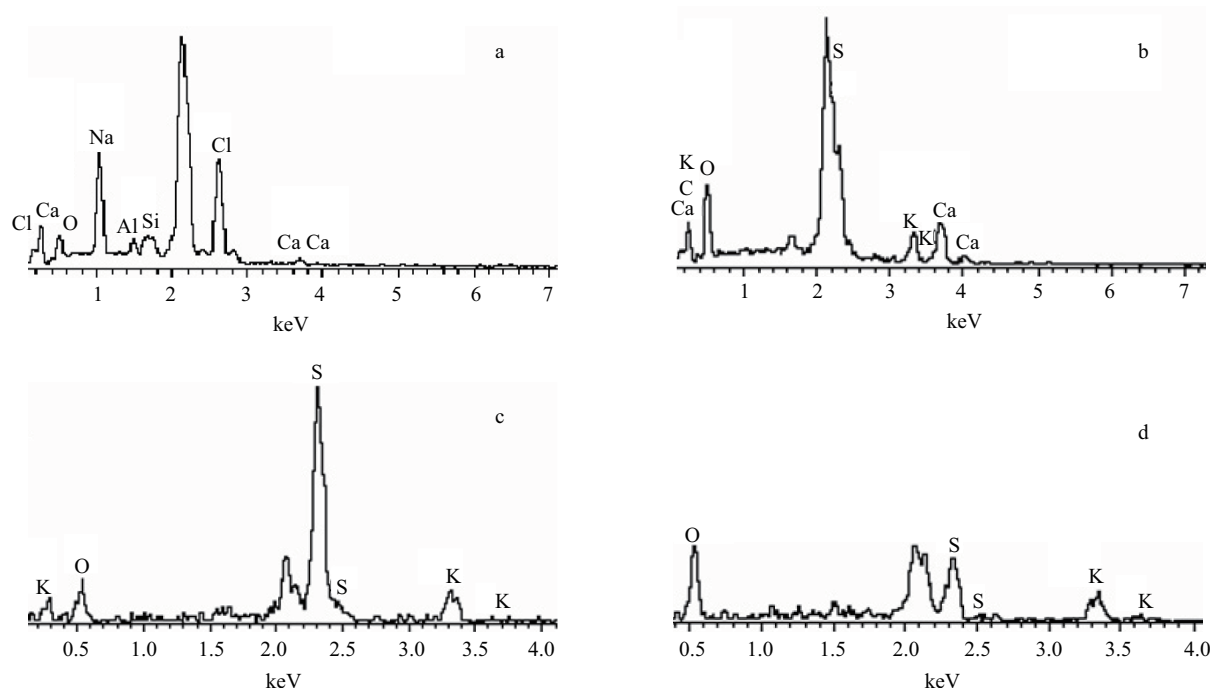

Fig. 5 EDX spectra of individual airborne particles in Shanghai atmosphere. (a) salt particles; (b), (c) sulfates; (d) particles containing S and K.
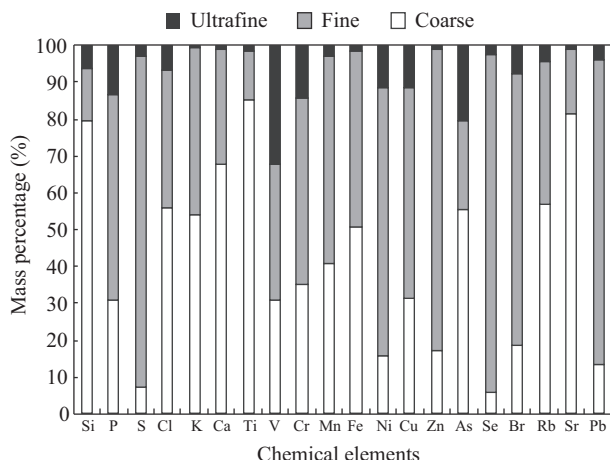
Fig. 6 Mass percentages of the 20 elements in coarse, fine and ultrafine particles in the Shanghai atmosphere.

particles.

Figure 7 shows the size distribution of the crustal elements Si, Fe, Ca, K (major chemical elements) in Shanghai airborne size-resolved particles. Si and Ca exhibited a single modal size distribution, and their highest mass peaks appeared in the 3.2–5.6 μm range. Fe and K exhibited approximately bimodal size distributions, with primary peaks in the 3.2–5.6 μm range and secondary peaks in the 0.56–1.0 μm range. However, Lin et al. (2005) reported that the four elements in particles which were sampled near a highway, showed different size distributions, with K exhibiting a trimodal size distribution, Ca and Si showing a bimodal size distribution, and Fe which was single modal. Therefore, it appears that the size distributions of chemical elements reflect their different emission sources.

Figure 8 shows that the size distributions of S, Pb, Sr and Se were single modal, their primary peak being at 0.56–1.0 μm. Although Zn, Cl, Ti, As, Sr also exhibited single modality, their peak values were different; the peak of Zn was in the range 0.56–1.8 μm, but the peak of Cl, Ti, As, and Sr was in the 3.2–5.6 μm fraction. The elements Pb, Cu, P, Mn and Rb exhibited bimodal size distributions. Pb, Cu, P, and Mn displayed the two peaks at 0.56–1.0 and 3.2–5.6 μm, but those of Rb were at 0.56–1.0 and 5.6–10 μm. The size distributions of V, Ni, and Cr were trimodal. The peaks of V were in the ranges 0.018–0.032, 0.18–0.32 and 1.8–3.2 μm; of Ni in 0.18–0.32, 1.0–1.8 and 3.2–5.6 μm ranges; and of Cr in 0.018–0.032, 0.18–0.32 and 3.2–5.6 μm ranges. The size distribution of trace elements in Shanghai urban ambient particles revealed that Zn, Pb, S, Cl, As, Sr, and Mn were mainly embodied in the fine particles, while V, Ni, Cr had a wide range of distribution. Therefore, it can be deduced that the complexity of size distribution of trace metals in Shanghai airborne particles brings challenges for the control of pollution caused by these elements.

2.5 Source apportionment

Table 3 shows that the enrichment factors of different chemical elements in coarse, fine, and ultrafine particles were different. The EFs of Si, K, Ca, Fe, Mn, Rb, and Sr in the coarse, fine and ultrafine particles were less than 10, implying these elements were emitted from natural sources. However, the EFs of S, Cl, Cu, Zn, As, Se, Br, and Pb in the three size ranges of particles were all much higher than 10, indicating these elements come from anthropogenic resources. It was noted that the EFs of P, V,
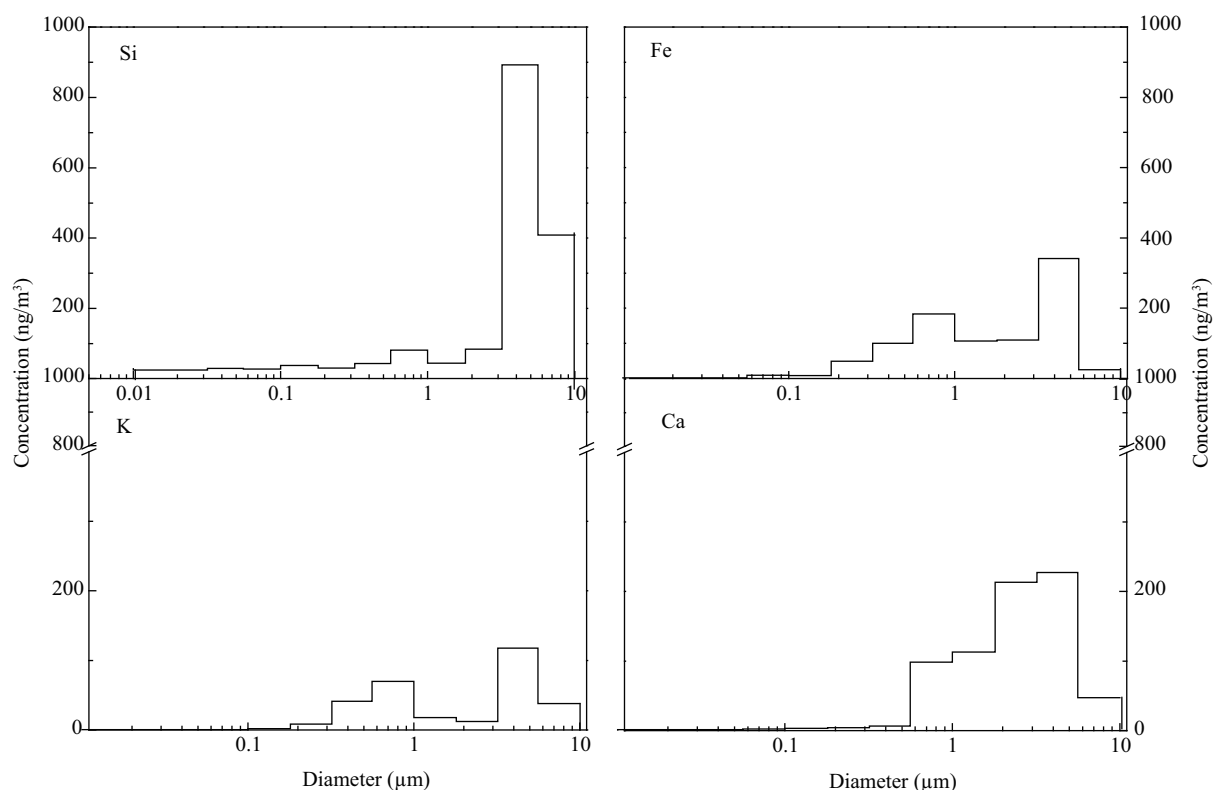

Fig. 7 Size distributions of crustal elements in size-resolved airborne particles in Shanghai.
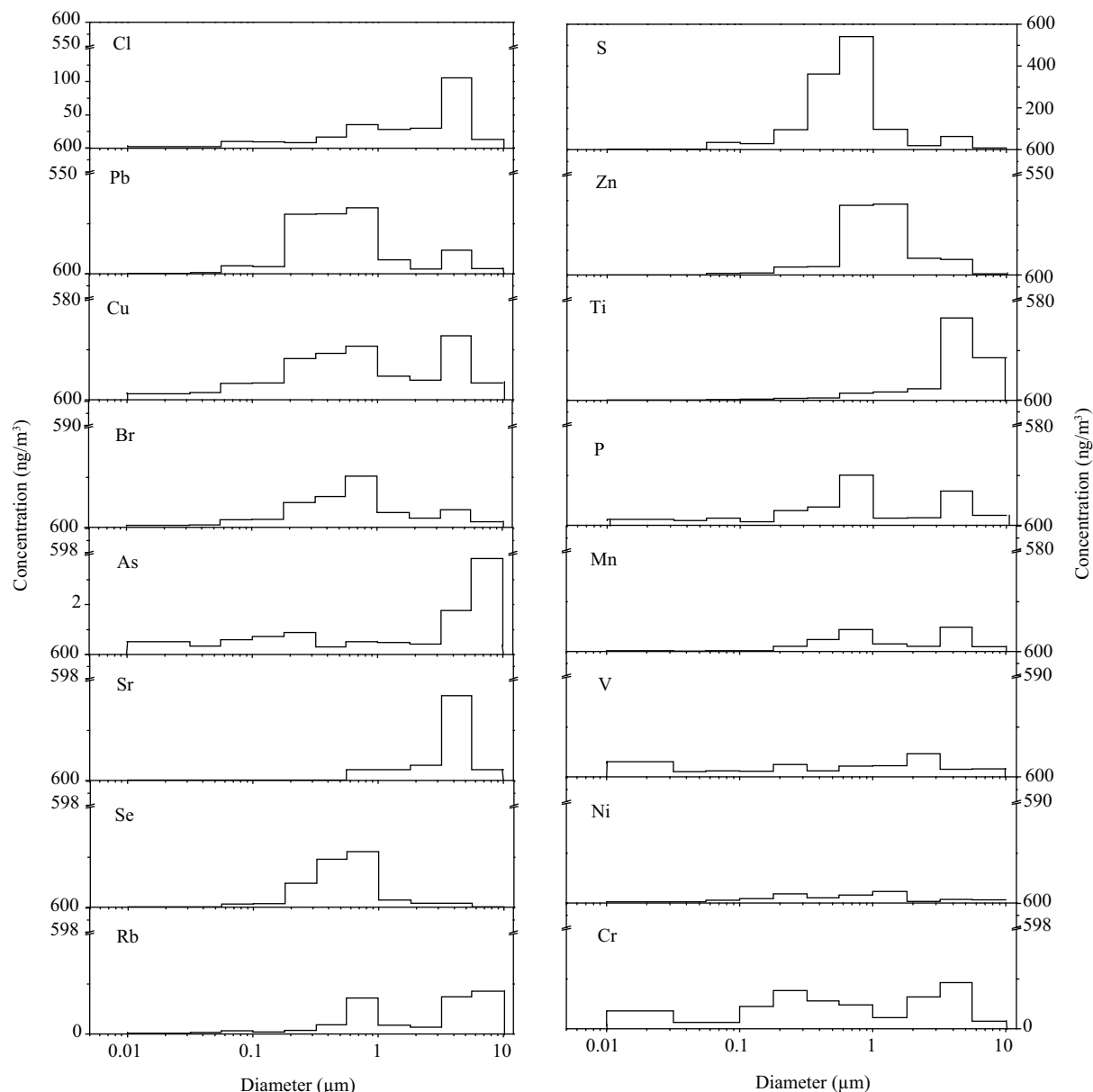
Fig. 8 Size distributions of trace elements in Shanghai size-resolved airborne particles.

Cr, Ni in coarse particles was less than 10, but their values in fine particles and in ultrafine particles were extremely high (> 10) implying that the four elements could be attracted to fine particles and ultrafine particles.

It can be seen (Fig. 9) that significant differences in the EFs of an individual element in different size categories reflect variations in their abundance in the different size particles. EF values of crustal elements (Si, K, Ca, Mn, Fe and Sr), and of anthropogenically-derived elements (S, Cl, Cu, Zn, As, Br, Pb), all had two peaks, with the primary peak in the 3.2–5.6 μm and secondary peak in the 0.56–1.0 μm range. However, the EF values of another anthropogenic element group (P, V, Cr, Ni) exhibited 3 peaks, in 3.2–5.6, 0.56–1.0 and 0.018–0.032 μm ranges respectively. It is noted that the pattern of abundance variation of the measured individual chemical elements was very similar to that of their size distribution, therefore the size distribution of chemical elements and their EFs could be used to evaluate particulate matter pollution in the urban atmosphere.

3 Conclusions

Size-resolved ambient particles were sampled in the center of Shanghai in the summer of 2008, and their physico-chemical characterization and source apportionment were investigated. The results from this work yield the following conclusions.

(1) The average mass concentrations of coarse particles, fine particles and ultrafine particles in summer in Shanghai atmosphere were 9.38 ± 2.18, 8.82 ± 3.52, and 2.02 ± 0.41 μg/m³ respectively. The mass percentage of the fine particles accounted for up to 51.47% of the total mass of PM_{10}, indicating that fine particles were the major component in Shanghai ambient particles; (2) Shanghai size-segregated particles can be divided into regular and irregular particles.

Table 3 Enrichment factors of coarse, fine, and ultrafine particles in the Shanghai atmosphere

	Coarse particles	Fine particles	Ultrafine particles
Si	0.80	0.90	4.13
P	1.59	18.70	43.85
S	54.76	4502.24	1546.69
Cl	183.36	785.37	1434.92
K	1.04	5.61	0.86
Ca	2.16	6.45	1.76
V	4.60	35.24	303.04
Cr	2.78	25.91	70.09
Mn	1.17	10.48	5.16
Fe	1.53	9.32	2.94
Ni	1.79	53.25	83.63
Cu	58.55	687.36	1365.58
Zn	77.10	2377.74	301.13
As	530.53	1499.87	12290.44
Se	548.72	57556.08	15348.84
Br	210.05	5404.52	5472.37
Rb	3.10	13.80	15.58
Sr	0.95	1.29	0.82
Pb	206.97	8268.52	3841.14
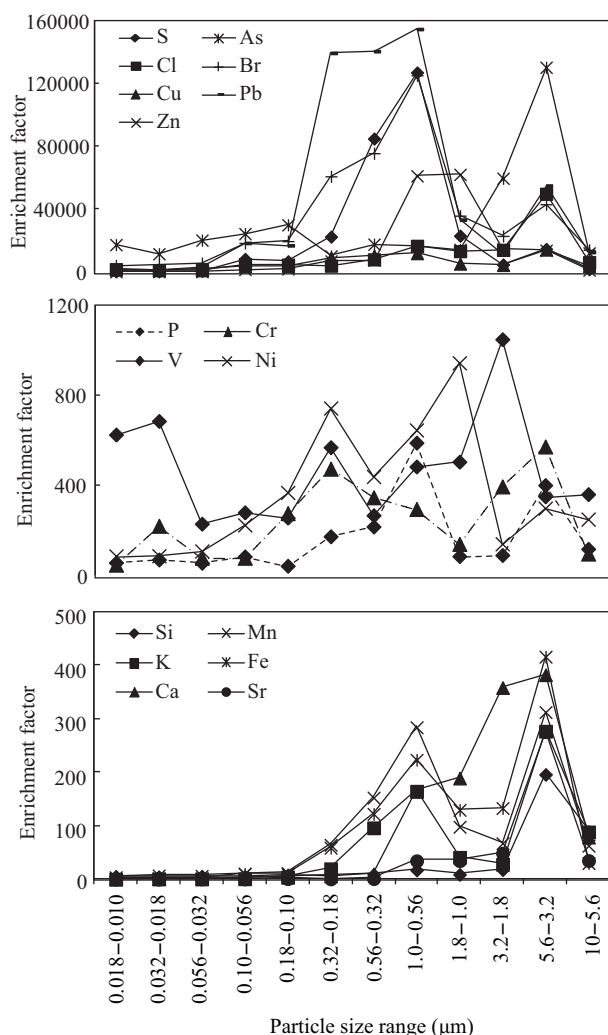
Fig. 9 Enrichment factor of individual chemical elements in Shanghai size-resolved particles.

from the point view of their microscopic character. The coarse particles were dominated by minerals, fine particles by soot aggregates and fly ashes, and ultrafine particles by soot particles and unidentified particles; (3) SRXRF results demonstrated that crustal elements such as Si, Ca and Fe were mainly distributed in coarse particles, and a higher mass level of S could be found in size-resolved particles. Heavy metals, including Cr, Mn, Ni, Cu, Zn, and Pb, were mainly distributed in the fine particle fraction; (4) source apportionment revealed that Si, K, Ca, Fe, Mn, Rb, and Sr were from crustal sources, and S, Cl, Cu, Zn, As, Se, Br, and Pb from anthropogenic sources. P, V, Cr, and Ni in particles might be contributed by multi-sources, and need further investigation.

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