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Physico-chemical characterization of $PM_{2.5}$ in the microenvironment of Shanghai subway

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ABSTRACT

The Shanghai subway metro system has brought great convenience to the city's travelling public, although passengers are exposed to airborne particles in this built micro-environment. However, investigations on the physicochemical characterization of $PM_{2.5}$ air pollution in the Shanghai subway system are to date very limited. Three subway stations along the No. 7 line were selected as subway $PM_{2.5}$ monitoring sites: Pan'guang, Shanghai University (SHU), and Jing'an, which are located in an outer suburban area, a suburban area and the urban area, respectively, airborne $PM_{2.5}$ on the subway station platforms and in the ambient atmosphere above-ground was synchronously collected from 19th March to 4th, May, 2012. Cutting-edge techniques, including scanning electronic microscopy coupled with energy dispersive X-ray (SEM/EDX), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray absorption near-edge structure (XANES) were employed to investigate microscopic characterization, chemical elements and speciation of the main heavy metals in subway $PM_{2.5}$. Our results demonstrated that mass levels of $PM_{2.5}$ in the subway stations were higher than that in ambient air. Mass levels of $PM_{2.5}$ in the subway stations and in ambient air ranged from 49.17 ± 19.7 μg/m^3 to 66.15 ± 25.20 μg/m^3, and 24.52 ± 3.3 μg/m^3 to 65.60 ± 5.6 μg/m^3, respectively. The microscopic characterization of $PM_{2.5}$ in ambient air and in subway stations showed marked differences. The $PM_{2.5}$ in the subway stations was mainly composed of iron-containing particles and mineral particles, while the $PM_{2.5}$ in ambient air largely consisted of mineral particles and soot aggregates. Fe was the most abundant element in subway $PM_{2.5}$, followed by: major elements (mass level > 100 ng/m^3) including Na, Mg, Al, K, Ca, Zn, Mn, Ba; sub-major elements (10 ng/m^3 < mass level < 100 ng/m^3) including Li, Cr, Ni,Cu, Ga, Sr, Pb; and minor elements (mass level < 10 ng/m^3), Be, V, As, Se, Rb, Ag, Cd, Tl, Bi. The mass levels of Ca, Al and Zn in ambient $PM_{2.5}$ were higher than those in subway $PM_{2.5}$, however those of the remaining 26 measured elements in subway $PM_{2.5}$ were higher than in ambient $PM_{2.5}$. The speciation of Fe in $PM_{2.5}$ was in the form of Fe^{2+}, while for Cu, that in the finer fractions (<0.25, 0.5 and 1.0 μm) was in the form Cu^{2+}, but in the $PM_{2.5}$ fraction itself, was as Cu^{1+}.

1. Introduction

Owing to their convenience, metro systems (underground or subway rail systems) are considered an important mode of urban transport, in order to improve the quality of transport, relieve congestion, and to fill gaps in insufficient alternative

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public transport and road surface capacity in many cities (Vasconcellos, 2001). Being the biggest city in China, Shanghai (with more than 22 million people) is situated on the east coast (longitude 120°51′–122°12′E ~ latitude 30°40′–31°53′N) (Fig. 1), and is considered one of the most prosperous and densely populated in the world (Feng et al., 2010; Shi et al., 2015). There are 12 subway lines and 266 subway stations in Shanghai at present. The total length of the 12 metro lines has reached 538 km, making it the longest in the world, and there are expected to be 20 subway lines in 2020. It is estimated that the Shanghai metro system carries more than 8 million persons per day (Shanghai Shentong Metro Group Co., Ltd, 2014). Since travelers generally spent from 0.3 h to 3 h in the subway system, they are exposed to particles from a different microenvironment, since the subway system is relatively closed and poorly ventilated, a situation where train and commuter traffic results in continuous recirculation and resuspension of both particulate matter (Mugica et al., 2012) and gaseous pollutants (Feng et al., 2010). Exposure to the microenvironment of the subway system has recently raised great concern (Seaton et al., 2005; Midander et al., 2012), and attention has been directed to establishing the physicochemical composition, and the potential health effects of airborne particles in the subway system (Adams et al., 2001; Chan et al., 2000; Chillrud et al., 2004; Nieuwenhuijsen et al., 2007; Kam et al., 2011). Previous studies have reported that the mass concentration of ambient particles in subway system was higher than in other outdoor and indoor environments. Some others have claimed that outdoor ambient particles could significantly influence underground air quality (Brains, 2006), and additionally that heavy metals, such as Fe, Mn, Ni, and Cr could be absorbed on fine particles (Mbengue et al., 2014), which hence could become more toxic than those in ambient airborne particles (Nieuwenhuijsen et al., 2007). However, there have been very few papers on $PM_{2.5}$ in the microenvironment of the Shanghai metro system.

Zhang et al. (2011) conducted research on the magnetic characterization and geochemistry of dust particles in the Shanghai metro system. Their results demonstrated that the magnetic properties of the dust particles were of scrap-iron and spherical magnetic particulates, and that there were higher levels of Fe and Mn, and lower levels of Al and Ti, in metro system dusts. Bao (2009) claimed that S could be found in the particles sampled in the subway atmosphere and the S in coarse particles was in the form of metal-sulfides, which originated from friction between rail and wheels. Wang (2012) reported that mass number of particles inside the carriage showed a correlation with the particle numbers in ambient air. In order to reveal differences between the physicochemical composition of particles in the Shanghai metro microenvironment and in ambient air, a sampling campaign for $PM_{2.5}$ was carried out at three subway stations in 2012: the Jing'an (urban area), Shanghai University (suburban) and Pan'guang (outer suburban) stations along line 7 of the subway system. Microscopic characteristics, chemical elements and chemical species of the main heavy metals were investigated by using scanning electronic microscopy coupled with energy dispersive X-ray (SEM/EDX), inductively coupled plasma mass spectrometry (ICP-MS) and synchrotron radiation methods (X-ray absorption near-edge structure, XANES). These results provide fundamental data that could be used in the development of health risk assessments with respect to exposures to airborne fine particulates in the Shanghai metro system.

2. Methods

2.1. Sampling protocol

Shanghai subway line No. 7 opened on the February of 2010; starting from the Meilan Lake in Baoshan District, it stretches 44.4 km southeast to the Huamu Road in Pudong New Area. It passes five districts (Baoshan, Putuo, Jing'an, Xuhui and Pudong) and there are 32 stations on the line. On this Line 7, three subway stations, Pan'guang, Shanghai University (SHU), and Jing'an, which are located in an outer suburban area, a suburban area and an urban area, respectively, were selected as monitoring sites (Fig. 1). Information on the sampling sites is given in Table 1.

Two portable $PM_{2.5}$ samplers and one portable sampler with a multi-sampling-head (size range: 2.5, 1.0. 0.5, 0.25 μm) with flow meter 10 L min^{-1} (Buck LP-20, A.P.BUCK Co., USA),

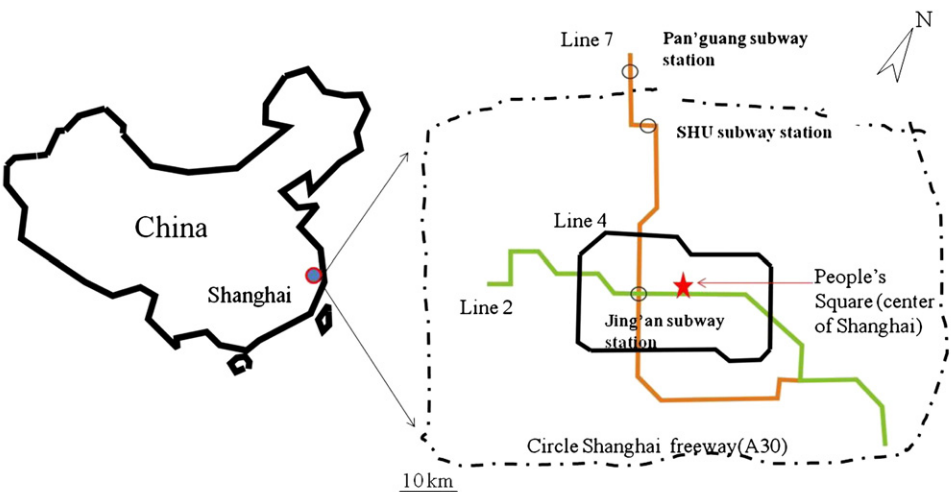

Fig. 1. Sketch map of sampling sites.

were employed to collect ambient particles in each subway station and in the above ground ambient air. The two $PM_{2.5}$ samplers, carried on our shoulders, were used to collect $PM_{2.5}$ in the air of the subway station (underground platform), and in the ambient atmosphere above-ground synchronously within the metro service time. A size-resolved particle sampler was used to collect subway $PM_{2.5}$, so as to identify the speciation of heavy metals. The sampling time for each sample was 6 h (from7:00 am to13:00 pm). The sampling campaign started from 19th March, and ended on 4th May, 2012. A total of 10 samples (5 samples at each subway platform, with another 5 samples outside the station) were collected at each monitoring site during the sampling period. Another 3 groups of size-resolved particles were collected at the SHU station and were used to identify speciation of the main heavy metals in subway $PM_{2.5}$, using XANES (X-ray Absorption Near-Edge Structure) instrumentation. The particles were collected on polycarbonate filters (Millipore, UK, pore size, 0.6 mm). The filters were weighted before and after collection with a 0.01 mg precision microbalance, after preconditioning for 48 h at constant humidity (40–42%) and temperature (20–22 °C); the mass concentration of the $PM_{2.5}$ was then calculated.

2.2. Microscopic characterization of individual particles

Microscopic characterization of X airborne particles can be used to identify their original sources, the method being described in detail by Lu et al. (2008) (see also Song et al., 2014). Briefly, approximately 1 cm^2 of each polycarbonate filter (randomly selected from each of the five samples at each sampling site) was cut and mounted onto a copper washer using epoxy resin to form a drum-like mounting. The samples were observed using environmental scanning electron microscopy (ESEM) JSM-6700F (JEOL, Japan), equipped with an energy dispersive X-ray system (EDX) which was used for the chemical elemental analysis. The EDX spectrometer used was a Link ISIS instrument with a Si(Li) detector, which allows X-ray detection from elements higher than carbon ($Z > 6$). The system was equipped with software that enables elemental weight percentages to be calculated using standard ZAF (atomic number, absorption, fluorescence) corrections. Operation conditions of the SEM were 20 kev accelerating voltage and 600 pA beam current with spectral acquisition times of 100 s. The diameter of spot of electron beam was 1 mm. The instrument allowed the observation of particles down to 0.5 mm.

2.3. Chemical elements analysis

Chemical elements in the particles were not only used to explore their source apportionment; but they also played a key role in the assessment of particle toxicological effects (Donaldson et al., 1997). The filters were immersed in 5 ml deionized water (resistivity > 18.3 MΩ) for 1 h, then were sonicated for 30 min in ultrasonic cleaner (Shanghai Zixin Co.). After sonication, the filters were moved out of the eppendorf tube and the solution was transferred to a Teflon (TFM) vessel (Matthews, USA), and was enriched in an ETHOS 1600 microwave labstation (Milestone, USA). After enrichment, the particles in the vessel were digested by concentrated HNO_3 (61%) for 1 h. After digestion, the sample in the vessel was enriched again, and the vessel was then washed three times with 2% HNO_3. This solution was filtered through a membrane filter (0.45 μm) (Whatman, UK) and 200 ppb Indium was added and made up to 25 ml for ICP-MS (Agilent Technologies, 7700 series) analysis. A filter with no particles was used as a control. Twenty nine elements were analyzed, namely: Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Cs, Ba, Tl, Pb, Bi, Th, U.

2.4. Speciation of typical heavy metals

The speciation of the heavy metals is essential to making an assessment of their possible toxicological effects; for example, Cr^{5+} is more toxic than Cr^{3+}. Therefore, speciation identification was conducted of the main heavy metal in the subway $PM_{2.5}$. Because different elements have different absorption edge energy, XANES has become a powerful technique to investigate chemical speciation in atmospheric particles (Wang et al., 2006; Lin et al., 2009). The speciation of the potentially toxic chemical elements iron and copper in the subway $PM_{2.5}$ (at SHU sampling site), was investigated using XANES. Fe and Cu L-edge XANES spectra were measured using Beamline 4B7B of the Beijing Synchrotron Radiation Facility (BSRF), Beijing, China. The electron energy in the storage ring is ~2.2 Gev with a current of about 100 mA. The L-edge absorption of copper and iron was measured with a Monk–Gillieson mono-chromator. The energy region of X-ray selected was from about 900 to 980 eV (the LIII absorption edge values of copper and iron are 932.7 eV and 720 eV, respectively). Within this energy region about 250 experimental points were set up. The measurement time for each point was from 2 to 3 s. The aerosol particles were exposed to the incident X-ray beam with an incident angle 45°. The beam path and the samples were placed in a vacuum to suppress X-ray scattering and absorption by air. The compounds Fe_2O_3, $FeSO_4$, CuO, Cu_2O, and $CuSO_4$ were selected as reference materials, and were employed to investigate the speciation of Fe and Cu by XANES. Background removal, normalization and deconvolution of XANES spectra were carried out using an IFEF FIT package (Newyille, 2001).

Table 1
Sampling site information.

Sampling sites	Sampling date	Sampling time	Open time	Sampling filter numbers	locations	Characterization of subway station and line	Passager numbers per day (thousands)
Pan'guang	2012/04/01–04/19	6 h	2010.12	5	31°21′46.43″ N, 121°21′26.64″E	Located 13 m underground with 3 exits	~5
SHU	2012/03/19–03/29	6 h	2009.12	5/3 groups of size-resolved particles	31°19′19.66″N 121°23′4.19″E	Located 14 m underground with 3 exits	~50
Jing'an	2012/04/24–05/04	6 h	1999.10	5	31°13′24.95″N 121°26′51.96″E	Located 17 m underground with 10 exits and there is one cross-point for line 2	~200

2.5. Statistical analysis

Data from the experiment were analyzed with GraphPad InStat software (Version 3, GraphPad Software, Inc., La Jolla, CA, USA). We determined statistical significance using one-way analysis of variance, with post-hoc Tukey's pair-wise comparisons for individual particle statistics.

3. Results

3.1. Mass concentration of $PM_{2.5}$

The mass concentrations of $PM_{2.5}$ collected at the three different sites showed some marked differences (Fig. 2). The mass levels of $PM_{2.5}$ recorded in both outer and inner suburbs (Panguang and SHU station), as might be expected, were higher in the subway stations than those in the ambient air above. However, the highest level of $PM_{2.5}$ was found in Pan'guang subway platform station (66.15 ± 25.20 μg/m^3), while the lowest recorded was at SHU station (49.17 ± 19.7). SHU station also recorded the lowest levels in the ambient air (24.52 ± 3.30 μg/m^3). In contrast, the mass levels of $PM_{2.5}$ in Jing'an subway station, in the city center, had virtually the same levels in the subway (64.15 ± 13.46 μg/m^3) as in the ambient air (65.66 ± 5.6 μg/m^3). All of the mass concentrations of Shanghai subway $PM_{2.5}$ collected at the platforms, were higher than National Air Quality standard (Grand I, 35 μg/m^3, Ministry of Environmental Protection, 2012).

3.2. Microscopic characterization of $PM_{2.5}$ in Shanghai subway system and individual particles statistics

$PM_{2.5}$ samples collected at each subway station and in ambient air were randomly selected for SEM observation. One hundred individual particles from each sample were selected to indentify chemical elements in the $PM_{2.5}$ by EDX. The SEM/EDX results showed that microscopic characterization of $PM_{2.5}$ in subway station (Fig. 3a) was different from that in ambient air (Fig. 3b). The $PM_{2.5}$ in the subway station was mainly composed of a mixture of iron-containing particles (Fig. 3c,d), mineral particles (Fig. 3e, f), soot aggregates (Fig. 3g, h). On the other hand, the $PM_{2.5}$ in ambient air largely consisted of mineral particles (Fig. 3a), although more soot particles were also found in the ambient $PM_{2.5}$ (Fig. 3a, b).

Individual particle statistics results showed that the weight percentages of five chemical elements ("Al + Si + Ca", S and Fe) in $PM_{2.5}$ were different at the different sampling locations (Tables 2 and 3). The number of Fe-containing particles in subway $PM_{2.5}$ was much higher than that in ambient $PM_{2.5}$. The mass level percentages of Fe-containing particles in the Pan'guang, SHU and Jing'an subway's $PM_{2.5}$ were 48.44%, 50.42% and 71.29%, respectively, while in contrast, the percentages in the ambient $PM_{2.5}$ was 16.15%, 18.47% and 28.88%, respectively. However, the mass percentages of "Al + Si + Ca" in subway $PM_{2.5}$ (33.47%, 44.56% and 23.92% in Pan'guang, SHU, and Jing'an, respectively) were lower than those found in ambient $PM_{2.5}$ (65.82%, 79.16% and 68.11% in Pan'guang, SHU, and Jing'an, respectively). Mass concentration of sulfur and iron in subway $PM_{2.5}$ had significant difference ($p < 0.01$, $n = 3$) (data not shown).

3.3. Chemical elements in $PM_{2.5}$

Twenty nine elements in the samples of $PM_{2.5}$ were analyzed by ICP-MS (Fig. 4). The results showed that the total mass of elements in subway $PM_{2.5}$ was higher than that in ambient $PM_{2.5}$. Mass levels of the elements in $PM_{2.5}$ collected in Pan'guang, SHU and Jing'an subway stations were 23,064.34, 6586.73 and 8986.36 ng/m^3, respectively, and 14,346.38, 4824.2, 2298.61 ng/m^3 were found in the ambient particles accordingly. Fe was the most abundant element in subway $PM_{2.5}$, its mass levels at Pan'guan, SHU, Jing'an platforms were 11,245.67, 3042.09 and 5403.22 ng/m^3, respectively, much higher than the mass concentrations of iron in ambient $PM_{2.5}$. The elements in subway $PM_{2.5}$ could be divided into three groups according to their mass levels: major elements (mass level > 100 ng/m^3), which included Na, Mg, Al, K, Ca, Zn, Mn, Ba; sub-major elements (10 ng/m^3 < mass level < 100 ng/m^3), including Li, Cr, Ni,Cu, Ga, Sr, Pb; and minor elements, which were Be, V, As, Se, Rb,Ag, Cd, Tl, Bi. It was noted that the mass levels of Ca, Al and Zn in ambient $PM_{2.5}$ were higher than those in subway $PM_{2.5}$, and that the mass concentration of the remaining 26 measured elements in subway $PM_{2.5}$ were higher than those in ambient PM2.5.

3.4. Speciation of major heavy metals in $PM_{2.5}$

The speciation of only two metals in the $PM_{2.5,}$ Fe and Cu, could be identified using XANES. The speciation of others metals

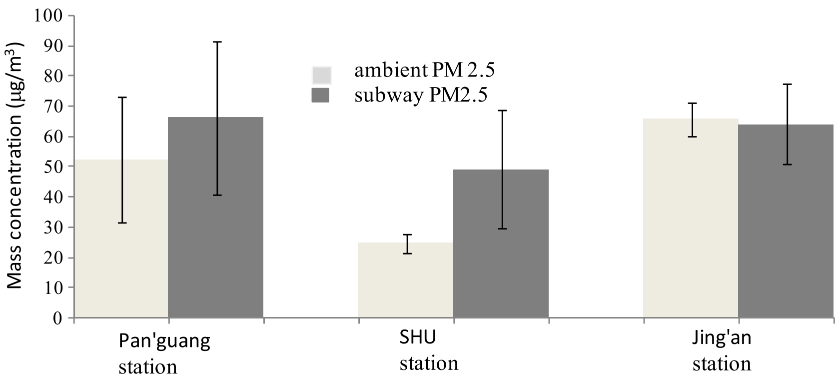

Fig. 2. Mass concentrations of $PM_{2.5}$ in Shanghai subway stations and in ambient air.

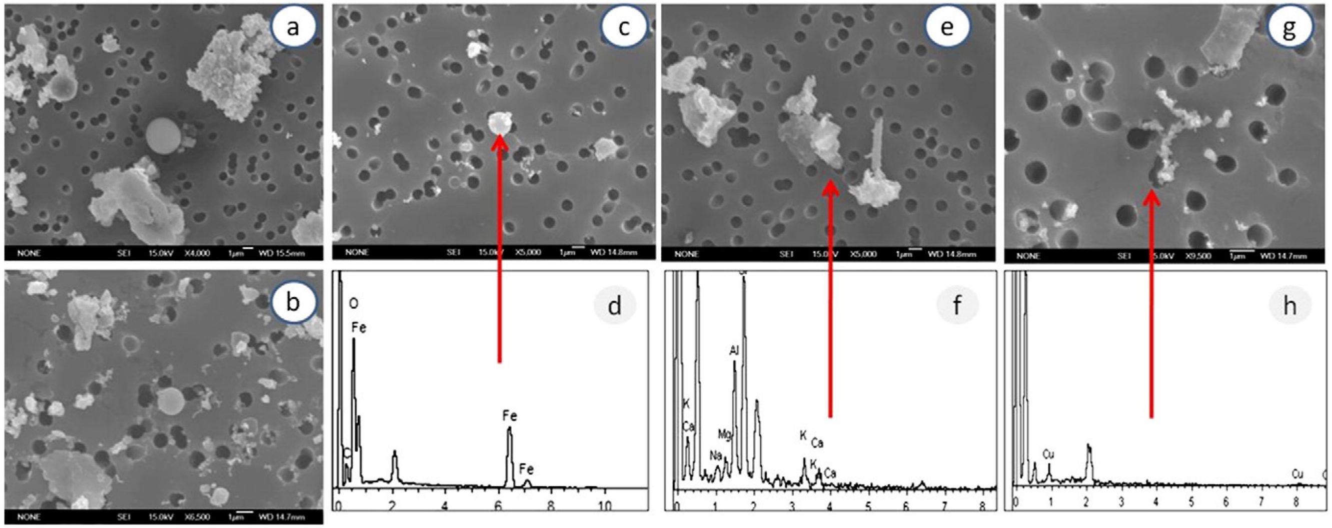

Fig. 3. Microscopic characterization of $PM_{2.5}$ in Shanghai subway stations; a — ambient $PM_{2.5}$; b — subway $PM_{2.5}$; c, d — Fe containing particles and their EDX spectrum; e, f — soot aggregates and their EDX spectrum; g — mineral particles and their EDX spectrum.

Table 2
Numbers of Fe-containing particles in $PM_{2.5}$ collected in subway stations and in ambient air.

	Pan'guan		SHU		Jing'an	
	Subway	Ambient	Subway	Ambient	Subway	Ambient
Iron particles	48	7	48	16	63	23
Measured total particles	96	100	103	109	99	106

could not be detected in this study, probably due to their lower mass levels. The XANES results showed that spectra of the reference materials of Fe^{3+} (Fe_2O_3, $Fe_2(SO_4)_3$) were different from the spectra of Fe^{2+} ($FeSO_4$). Compared with these spectra, the speciation of Fe in $PM_{2.5}$ was found to be in the form Fe^{2+}.

The speciation of Cu in different ambient size particles were shown to be different (Fig. 5). The XANES results showed that the spectra of reference materials Cu_2O [Cu^{1+}] and CuO [Cu^{2+}] were different. Fig. 6 shows that the spectrum of Cu^{1+} has a conspicuous pre-edge peak at approximately 930 eV, while Cu^{2+} exhibits a very weak pre-edge structure. Hence it was found that the speciation of Cu in the finer filtered fractions (PM < 0.25; 0.5 and 1.0 μm) was the same as that for Cu^{2+} in CuO and $CuSO_4$, while the speciation of Cu^{1+} in the larger particles ($PM_{2.5}$) was the same as Cu in Cu_2O.

4. Discussion

4.1. Mass level of $PM_{2.5}$ in Shanghai subway stations and in ambient air

Mass levels of $PM_{2.5}$ in the subway stations were higher than that outside the stations, except for the Jing'an $PM_{2.5}$ mass level. The mass levels of $PM_{2.5}$ in subway stations ranged from 49.17 ± 19.7 μg/m^3–66.15 ± 25.20 μg/m^3, while the mass concentration of $PM_{2.5}$ in ambient air was between 24.52 ± 3.3 μg/m^3 and 65.60 ± 5.6 μg/m^3. Ripanucci et al. (2006) reported that PM level concentrations in Rome underground railway were from 3- to 7-fold higher than in their outside ambient air. Our results probably demonstrate that the clean system in Shanghai metro prevents dust and refuse accumulation around the subway platforms. Mugica et al. (2012), Johansson and Johansson (2003) also report that the metro cleaning system decreases mass levels of airborne particles in the Mexico city subway system and in Stockholm subway, respectively.

In this study it was estimated that there exists a close relationship between the mass level of $PM_{2.5}$ sampled in Shanghai subway stations and in ambient air ($R^2 = 0.87$), suggesting an important influence of airborne particles introduced through the ventilation grids and by commuters (Mugica et al., 2012). Considering mass level of ambient $PM_{2.5}$ in Shanghai air has gradually decreased (Feng et al., 2009), it can be anticipated that the influence of ambient air quality to the subway $PM_{2.5}$ will also weaken. However, compared with the Chinese National Air Quality Standard (annual average limit 35 μg/m^3), the average mass concentration of the Shanghai subway $PM_{2.5}$ was still high, implying that some health exposure risk might occur in the subway micro-environment.

4.2. Physicochemical characterization of $PM_{2.5}$ in Shanghai subway system

4.2.1. Individual particles in $PM_{2.5}$

Our SEM/EDX results demonstrated that the $PM_{2.5}$ sampled in the subway comprised a mixture of mineral particles, soot aggregates, and Fe-rich particles. The major difference between the microscopic characterization of $PM_{2.5}$ in Shanghai subway platforms and in ambient air was that percentage number (Table 2) and percentage mass (Table 3) of Fe-rich particles in the subway were higher than those in ambient air. These results are consistent with literature findings for subway aerosols elsewhere. Mugica et al.(2012) reported that Fe and Cu were abundant in $PM_{2.5}$ collected in the Mexico subway system. However, it was concluded by Jung et al. (2012) that Cu-rich particles could not have been detected in the Seoul metro system. This high percentage number of Fe-rich particles reported in subway systems probably originates from mechanical friction and wear processes. Soots found in the present study (Fig. 3g) in subway $PM_{2.5}$ were mainly composed of carbon, although since polycarbonate filters were used to sample particles, C in the EDX spectrum was deleted. Carbon-rich particles come mainly from combustion processes, such as from fossil fuel emissions (Lu et al., 2008; Calvo et al., 2013). This study found that the composition of minerals (Fig. 3e) in Shanghai $PM_{2.5}$ comprised a mixture of Al, Si, and Ca, and that the percentage mass of the "Al + Si + Ca" was higher in ambient air $PM_{2.5}$ at SHU station, compared with that at the other two sampling sites. The result may indicate that fugitive dusts are caused here by the large amount of passenger movement at this station. These minerals could originate from geological materials such as soil, road dust or gravel from around the rails. S-containing particles found in the subway $PM_{2.5}$ could be associated with friction between rails and brakes, because S is a component of railway steel in China (Li et al., 2006; Xia et al., 2008). Our results agree with those of Bao (2009), who reported that S could be found in Shanghai

Table 3
Mass percentage of chemical elements in $PM_{2.5}$ based on individual statistic results.

	Pan'guan		SHU		Jing'an	
	Subway	Ambient	Subway	Ambient	Subway	Ambient
(Al + Si + Ca)%	33.47	65.82	44.56	79.16	23.92	68.11
Fe%	48.44	16.15	50.42	18.47	71.29	28.88
S%	9.70	7.83	4.15	1.81	2.44	2.17

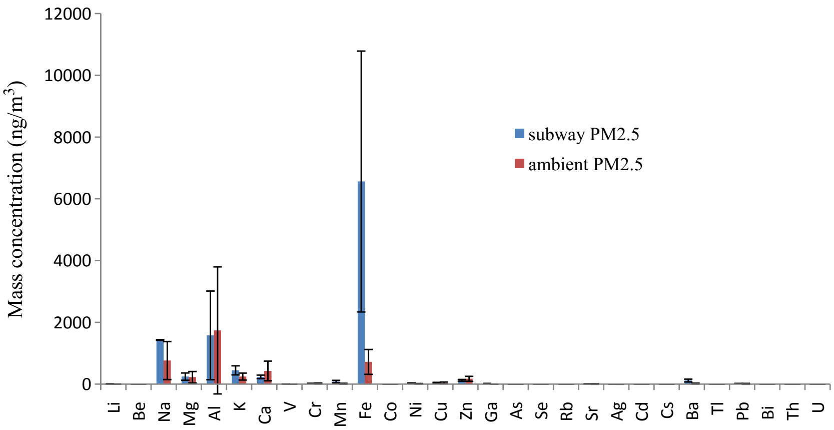

Fig. 4. Comparison of mass levels of chemical elements in subway $PM_{2.5}$ and ambient $PM_{2.5}$.

subway $PM_{2.5}$, and deduced that the sulfur was present as a sulfide, such as in FeS and MnS.

4.2.2. Chemical elements in $PM_{2.5}$

Fe was the most abundant element in the subway $PM_{2.5}$ (Table 4), its average mass level in Shanghai subway $PM_{2.5}$ being 6563.33 ± 4223.11 ng/m^3, i.e. nearly 10 times higher than that measured in ambient $PM_{2.5}$ (723.93 ± 402.61 ng/m^3). High mass concentrations of Fe have also been found in London (Seaton et al., 2005), Mexico city (Mugica et al., 2012) and Helsinki (Aarnio et al., 2005) subway $PM_{2.5}$. This phenomenon implies that the Fe-containing particles are most likely derived from mechanical friction and wear processes between rails, wheels and brakes (Kam et al., 2013). The other 3 main elements, Ba, Mn, and Ga, in Shanghai subway $PM_{2.5}$ were also in far higher concentrations than those found in ambient $PM_{2.5}$. The higher mass level of Mn in subway $PM_{2.5}$ has been reported in Helsinki and in Mexico city subway stations (Salma et al., 2007; Mugica et al., 2012).

The Mn is also likely to be produced from processes at rail-wheel–brake interfaces, because Mn is another component of Chinese rail steel (Li et al., 2006; Xia et al., 2008). Ba and Ga levels were highly correlated with those of Fe in Shanghai subway $PM_{2.5}$ (R^2 = 0.97 and R^2 = 0.99 respectively). Furuya et al. (2001) reported that the major constituent causing wear on brakes in Tokyo subway stations was barium sulphate and barite. Therefore, the Ba found here in subway $PM_{2.5}$ probably originated from mechanic processes between rails and wheels. Ga is constantly used also in electronics, so apportionment of Ga in the subway $PM_{2.5}$ needs further study.

Cu and Zn were reported by Gustafsson et al. (2012) as originating from the vehicle brake system in the Stockholm ground-level subway system. However, the mass levels of these two heavy metals in $PM_{2.5}$ collected in Jing'an ambient air was higher than that in the subway system (Table 4), suggesting that, in this case, the Cu and Zn came not only from the brake system, but also from other sources. The mass concentrations of the other chemical elements in the Shanghai subway $PM_{2.5}$ and in ambient $PM_{2.5}$ were at about the same level, implying they could have the same sources.

4.2.3. Speciation of main heavy metals in Shanghai subway $PM_{2.5}$

The XANES spectrum of the subway $PM_{2.5}$ was similar to that of Fe_2O_3, rather than $FeSO_4$, therefore, Fe in subway $PM_{2.5}$ was present as Fe_2O_3. Speciation of iron in the different sized particles showed no differences, indicating that the speciation

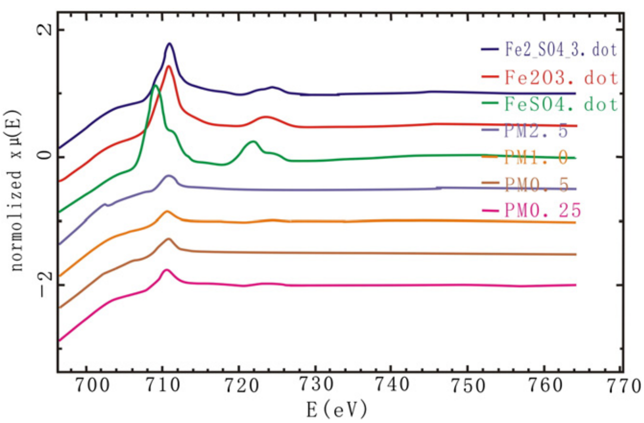

Fig. 5. Speciation of iron in $PM_{2.5}$ sampled in subway stations.

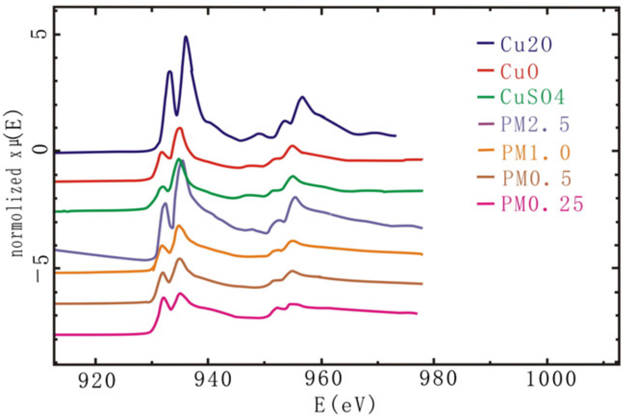

Fig. 6. Speciation of copper in $PM_{2.5}$ sampled in subway stations.

of iron in the subway $PM_{2.5}$ was stable. Our results agree with the report by Wang et al. (2007). However, Oakes et al. (2012)) argued that iron in single particles (Atlanta, USA) was present as a mixture of Fe(II) and Fe(III); it was concluded that differences in iron redox state may indicate iron originating from different regions.

The Cu L-edge absorption spectrum in the finer fractions of subway particles (PM < 0.25; 0.5 and 1.0 μm) were different from that with the largest particles ($PM_{2.5}$). A significant amount of Cu was present as Cu (I) in the finer fractions of the sampled subway particles. Osan et al. (2010) also reported that the Cu speciation differed among size-fractionated ambient particles. However, Wang et al. (2007) reported that the oxidation state of Cu was divalent in Shanghai ambient particles, and that the XANES spectra of $PM_{2.5}$ and PM_{10} in their sampling sites in the Shanghai area showed no obvious difference, suggesting that samples with different particle sizes had similar speciation. The speciation of Cr, Mn, and Zn in Shanghai subway $PM_{2.5}$ could not have been measured by this XANES in this study, and the reason needed further study.

Table 4
Average mass concentrations of chemical elements in Shanghai subway $PM_{2.5}$ and comparison with those in other metro systems.

	Shanghai subway		Ambient air				3		4		5		
	PM2.5	Stdv	PM2.5	Stdv	1	2	a	b	a	b	a	b	c
Li	11.35	10.01	3.84	3.41									
Be	0.37	0.32	0.01	0.02									
Na	1431.35	10.85	766.41	617.00									
Mg	246.36	118.50	227.72	184.53		47.15	350	130.00	296	130			
Al	1581.88	1435.62	1741.26	2056.60	15,790	106.25			531	93	55	273	276
K	450.09	146.75	247.60	113.24		59.85			318	127	108	226	149
Ca	237.50	56.89	429.27	318.36	16,410	131.85	2470	930	2.57	413	55	327	144
V	4.63	2.49	1.82	2.04	30		25.46	160			14	5	8
Cr	25.83	5.62	22.88	15.33	30	12.6	20.25	16.52	35	15	1	42	59
Mn	83.89	40.26	15.20	14.50	1670	45.35	38.3	25.74	310	148	9	234	311
Fe	6563.66	4223.11	723.97	402.61	87,090	5544.85	5570	2590	33.5	15.5	713	20,703	28,643
Co	1.34	0.81	0.61	0.32		0.67	2.29	1.63					
Ni	34.15	9.08	15.66	9.07	70	6.65	7.58	6.17	29	8	7	23	34
Cu	48.08	12.17	40.94	29.80	520	51.15	950	220	496	190	13	173	117
Zn	126.87	26.76	174.84	80.59	280	26.8	234.11	131.16	118	50	30	124	34
Ga	19.51	8.15	3.05	2.60									
As	1.98	0.87	1.00	0.88									
Se	1.40	0.44	0.88	0.56	170								
Rb	1.28	0.47	0.98	0.86									
Sr	10.34	4.61	9.89	10.83									
Ag	0.16	0.18	0.44	0.71									
Cd	0.43	0.06	0.24	0.29		0.56							
Cs	0.17	0.04	0.11	0.07									
Ba	119.06	45.46	18.64	14.78		117	90	30.00	145	ND			
Tl	0.12	0.02	0.03	0.05									
Pb	21.04	5.16	12.47	12.70	300		76.99	59.73	47	21	7	10	13
Bi	0.87	0.91	0.19	0.18									
Th	0.52	0.39	0.36	0.46									
U	0.04	0.06	0.03	0.04									

Note: 1 — London; 2 — Los Angeles; 3 — Mexico city subway (a — PM_{10}; b — $PM_{2.5}$);4 — Budapest (a — PM_{10}-2; b — PM_2); 5 — Helsinki $PM_{2.5}$ (a — ground level; b— Rautatientori underground; c — Sornainen underground).

4.2.4. Implications for health risk might caused by ambient subway particles

A previous study found that subway particles were more toxic than ambient airborne particulates, and comparable to the toxicity of welding dusts (Seaton et al., 2005). The higher toxicity may be due to a higher iron content, and additionally, the speciation of iron in the subway PM can play a key role in its toxicological effect (Karlsson et al., 2005).

Our XANES results demonstrated that in subway $PM_{2.5}$ the speciation of iron was Fe^{2+}, while copper was in the form of both Cu^{1+} and Cu^{2+}. Zhang et al. (2011) concluded that Fe in Shanghai subway dusts was in the form of hematite (Fe_2O_3) and magnetite (Fe_3O_4). This may explain the oxidative capacity of the subway particles, since magnetite exhibits both Fe^{2+} and Fe^{3+} in a crystalline oxide structure. The mechanism behind the release of free radicals by particles most often discussed is the production of hydroxyl radicals in the presence of hydrogen peroxide and Fe^{2+} via the Haber–Weiss and Fenton reactions ($Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + OH\bullet$) (Fubini and Mollo, 1995; Donaldson et al., 1997). Cu also has the ability to generate free radicals in a similar reaction ($Cu^{1+} \rightarrow Cu^{2+}$). Therefore, the reactive oxygen species (ROS) formation by the iron-rich particles (or other trace metals, such as Cu) may also lead to increased particle uptake by cells due to lipid peroxidation of cell membranes, and so do harm to the human lung. Further work is therefore needed to determine the exact mechanisms of action of particulate matter from metro systems.

5. Conclusions

1. The average mass levels of $PM_{2.5}$ recorded in the Shanghai subway station platforms (49.17 ± 19.7–66.15 ± 25.20 μg/m^3) were higher than those in the ambient air (24.52 ± 3.3–65.60 ± 5.6 μg/m^3).
2. The microscopic characteristics of $PM_{2.5}$ in ambient air and in subway station were different. The $PM_{2.5}$ in the subway stations was mainly composed of iron containing particles and mineral particles, while the $PM_{2.5}$ in ambient air largely consisted of mineral particles and soot aggregates.
3. Fe was the most abundant element in subway $PM_{2.5}$, followed by a series of major chemical elements (mass level > 100 ng/m^3), including Na, Mg, Al, K, Ca, Zn, Mn, Ba; sub-major X elements (10 ng/m^3 < mass level < 100 ng/m^3), Li, Cr, Ni,Cu, Ga, Sr, Pb; and X minor elements (mass level < 10 ng/m^3), Be, V, As, Se, Rb,Ag, Cd, Tl, Bi. Mass levels of Ca, Al and Zn in ambient $PM_{2.5}$ were higher than those in subway $PM_{2.5}$, and the other left 26 measured chemical elements in subway $PM_{2.5}$ were also higher compared to those in ambient $PM_{2.5}$.
4. The speciation of Fe in $PM_{2.5}$ was in the form of Fe^{2+}. The speciation of Cu in the finer fractions (<0.25, 0.5 and 1.0 μm) was in the form of Cu^{2+}, while Cu in $PM_{2.5}$ was as Cu^{1+}. Potential free radical generation ability of these heavy metals might imply that health risks exist after exposure to the metal-containing ambient particles.

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