Progress and prospects of atmospheric environmental sciences in China

Fahe Chai, Abdelwahid Mellouki, Yujing Mu, Jianmin Chen, Huiwang Gao, Hong Li
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Trace metals in atmospheric fine particles in one industrial urban city: Spatial variations, sources, and health implications

Shengzhen Zhou¹, Qi Yuan¹, Weijun Li¹,²,*, Yaling Lu¹, Yangmei Zhang³, Wenxing Wang¹

¹. Environment Research Institute, Shandong University, Shandong 250100, China. E-mail: zzjing@126.com
². State Key Laboratory of Coal Resources and Safe Mining, China University of Mining & Technology, Beijing 100083, China
³. Chinese Academy of Meteorological Sciences, China Meteorological Administration, Beijing 100081, China

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ABSTRACT

Trace metals in PM₃.₅ were measured at one industrial site and one urban site during September, 2010 in Jі’nan, eastern China. Individual aerosol particles and PM₃.₅ samples were collected concurrently at both sites. Mass concentrations of eleven trace metals (i.e., Al, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba, and Pb) and one metalloid (i.e., As) were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The result shows that mass concentrations of PM₃.₅ (130 µg/m³) and trace metals (4.03 µg/m³) at the industrial site were 1.3 times and 1.7 times higher than those at the urban site, respectively, indicating that industrial activities nearby the city can emit trace metals into the surrounding atmosphere. Fe concentrations were the highest among all the measured trace metals at both sites, with concentrations of 1.04 µg/m³ at the urban site and 2.41 µg/m³ at the industrial site, respectively. In addition, Pb showed the highest enrichment factors at both sites, suggesting that industrial activities existed around the city. Correlation coefficient analysis and principal component analysis revealed that Cu, Fe, Mn, Pb, and Zn were originated from vehicular traffic and industrial emissions at both sites; As, Cr, and part of Pb from coal-fired power plant; Ba and Ti from natural soil. Based on the transmission electron microscopy analysis, we found that most of the trace metals were internally mixed with secondary sulfate/organic particles. These internally mixed trace metals in the urban air may have different toxic abilities compared with externally mixed trace metals.

Introduction

Human health is highly impacted by the atmospheric aerosol pollution. A growing body of epidemic data suggest that increasing levels of fine particulate matter (PM) are associated with remarkable increase in human morbidity and mortality (Huang et al., 2012; Pope and Dockery, 2006). Although trace metals only account for a small proportion of PM mass concentration, it is known that they can exert toxic effects, posing human health risks and long-term burden on the biogeochemical cycling in the

ecosystem (Adriano, 2001; Hu et al., 2012). A number of studies have shown that Pb can cause severe health hazard in human blood through respiratory and digestive tract (He et al., 2009; Silbergeld, 1997). Zn as the major trace metal in urban air can make damage to plasmid DNA (Lü et al., 2006; Shao et al., 2006).

Atmospheric emissions of trace metals in urban cities are commonly from industrial activities, waste incinerating, and fossil fuel burning (Li and Shao, 2009; Zereini et al., 2005). Heavy industries are considered to be the major anthropogenic trace metal sources in industrial urban cities in China (Zheng et al., 2010). Tian et al. (2010) demonstrated that some trace metals emissions (e.g., Hg, As, and Se etc.) in Shandong Province are ranked on the
top of China in 2007 due to coal combustion. In this study, we investigated the metal compositions and sources of the metal aerosol particles in Ji’nan, an industrial city in eastern China and the capital of Shandong Province.

Bulk aerosol measurements are often used to evaluate concentrations and compositions of aerosol particles in the atmosphere in China, but they can only give averaged results. The mixing state of individual aerosol particles cannot be known. Recent studies found that most fine metal particles or soluble metals in the urban cities are associated with secondary particles (e.g., sulfate, nitrate and organics etc.), which may cause different health effects (Adachi and Buseck, 2010; Li et al., 2011). Therefore, we further determined the mixing state of the fine metal particles by using transmission electron microscope (TEM).

In this study, we determined the concentrations and spatial variations of the trace metals at two sites in Ji’nan, one urban and one industrial. Principal component analysis (PCA), correlation coefficient analysis and enrichment factor (EF) were applied to identify the possible sources of the eleven trace metals (i.e., Al, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba, and Pb) and one metalloid (i.e., As). In addition, mixing states of the metal particles were observed through a high-resolution TEM.

1 Experiments

1.1 Sampling sites and aerosol collections

Ji’nan is the capital of Shandong Province in eastern China. It has a population of over 6.5 million people and holds vehicle population over 2 million in 2010 (Ji’nan Statistical Yearbook, 2011). As an industrial city, there are three types of traditional pillar industries in this city, namely ferrous metal smelting, traffic equipment production, and petrol processing. Besides, there are several coal-fired power plants around the city.

One urban site and one industrial site were selected in Ji’nan (36°40′26″N, 117°0′0″E) (Fig. 1). The industrial site is located on the roof of a residential building surrounded by several plants of Ji’nan Iron and Steel Company, while the urban site is on the roof of a six-floor building on the campus of Shandong University, which is located in the commercial and residential areas of the city. The distance between the two sites is about 10 km. Ten PM$_{2.5}$ samples (including two blank samples) were collected at both sites from 17–28 September, 2010. Quartz filters with 47 mm diameter and 2 μm pore size (PALL Corporation, USA) were used for PM$_{2.5}$ sample collections. One Mini-Vol Sampler (Airmetric, USA) with a sampling flow rate of 5 L/min was used to collect PM$_{2.5}$ samples at the industrial site. An ambient air sampler (RAAS2.5-400, USA) with a flow rate of 16.7 L/min was used to collect PM$_{2.5}$ samples at the urban site. The two commercial samplers were calibrated and compared in a sampling site. The difference of the PM$_{2.5}$ mass concentrations between the Mini-Vol and RAAS2.5-400 samplers was less than 5%. The sampling flows were measured at the beginning and end of each sampling period at each site with a calibrated flowmeter (DryCal® DC-Lite, USA). The filter samples were weighed using a Sartorius ME-5F balance (readability: 1 μg) before and after sampling at a constant temperature (20 ± 0.5°C) and relative humidity (50% ± 2%) to determine their mass concentrations.

Individual aerosol particles were collected onto the copper TEM grids coated with carbon film (carbon type-B, 300-mesh copper, Tianld Co., China) by a single-stage cascade impactor with a 0.5 mm-diameter jet nozzle at a sampling flow rate of 5 L/min. Individual aerosol particles were collected onto the copper TEM grids coated with carbon film (carbon type-B, 300-mesh copper, Tianld Co., China) by a single-stage cascade impactor with a 0.5 mm-diameter jet nozzle at a flow rate of 1.0 L/min at both sites. The periods of the sampling time varied from 30 sec to 5 min, depending on the particles mass concentration. The detailed information has been described by Li and Shao (2010).

Hourly meteorological data during the sampling time were collected from the web site of Weather Underground (http://www.wunderground.com/).

1.2 Analysis methods

The PM$_{2.5}$ samples were dissolved at 170°C for 4 hr in 3 mL of concentrated nitric acid, 1 mL of concentrated
perchloric acid and 1 mL of concentrated hydrofluoric acid before they were cooled and oven-dried. Then each sample was digested with 1 mL of concentrated HNO\textsubscript{3} and was further diluted to 10 mL with de-ionized water. After treatments, trace metals were analyzed using ICP-AES (Model Ultima, JobinYvon Company, France). We measured eleven trace metals (Al, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba, and Pb) and one metalloid (As) which the standard solutions were available in the laboratory.

Individual aerosol samples were analyzed using a high resolution TEM (JEM-2100, JEOL, Japan) operated at 200 kV. The TEM can obtain the morphology, size, and mixing state of individual aerosol particles. Energy-dispersive X-ray spectrometer (EDS) can get the compositions of the targeted particles. Cu and C were excluded from the copper TEM grid with carbon film.

2 Results and discussion

2.1 Trace metal concentrations in PM\textsubscript{2.5}

Mean concentrations of eleven trace metals (i.e., Al, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba, and Pb) and one metalloid (i.e., As) in PM\textsubscript{2.5} at both sites are summarized in Table 1. The results show that mass concentrations of PM\textsubscript{2.5} (130 \mu g/m\textsuperscript{3}) and trace metals (4.03 \mu g/m\textsuperscript{3}) at the industrial site were 1.3 times and 1.7 times higher than those at the urban site (Table 1 and Fig. 2). The total concentrations of trace metals were 4.03 \mu g/m\textsuperscript{3} and 2.40 \mu g/m\textsuperscript{3} at the industrial site and the urban site, accounting for 3.1% and 2.4% of the total PM\textsubscript{2.5} concentration, respectively. This result indicates that industrial emissions have contributed anthropogenic metals into the atmosphere. Fe concentrations were the highest among the measured trace metals at both sites, with concentrations of 1.04 \mu g/m\textsuperscript{3} at the urban site and 2.41 \mu g/m\textsuperscript{3} at the industrial site. We also noted that Fe and Mn concentrations (Fe, 2.41 \mu g/m\textsuperscript{3} and Mn, 0.11 \mu g/m\textsuperscript{3}) at the industrial site were 2 times higher than those (Fe, 1.04 \mu g/m\textsuperscript{3} and Mn, 0.06 \mu g/m\textsuperscript{3}) at the urban site, which indicates an industrial source from steel smelting, the biggest heavy industry in this industrial area. In addition, Pb and Zn concentrations were 200 and 440 ng/m\textsuperscript{3} at the industrial site and 160 and 350 ng/m\textsuperscript{3} at the urban site, respectively. The differences of concentrations of Pb and Zn between the industrial site and the urban site were not as high as that of Fe, suggesting Pb and Zn may have other sources besides the industrial source. The sources of the trace metals will be discussed in Section 2.3.

Figure 3 shows the metal concentrations in Ji’nan and other cities in Asia. The result shows that trace metals con-

Table 1 Mean trace metal concentrations and enrichment factor (EF) in the PM\textsubscript{2.5} at the urban and industrial sites in September 2010 in Ji’nan

<table>
<thead>
<tr>
<th>Species</th>
<th>Urban site</th>
<th>Industrial site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean (\mu g/m\textsuperscript{3})</td>
<td>SD</td>
</tr>
<tr>
<td>PM\textsubscript{2.5}</td>
<td>101</td>
<td>42</td>
</tr>
<tr>
<td>Al</td>
<td>0.65</td>
<td>0.25</td>
</tr>
<tr>
<td>As</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Ba</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>1.04</td>
<td>0.57</td>
</tr>
<tr>
<td>Mn</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb</td>
<td>0.16</td>
<td>0.08</td>
</tr>
<tr>
<td>Sr</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Ti</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Zn</td>
<td>0.35</td>
<td>0.20</td>
</tr>
<tr>
<td>Total metals</td>
<td>2.4</td>
<td>4.03</td>
</tr>
<tr>
<td>(\Sigma\text{metals})/PM\textsubscript{2.5}</td>
<td>2.4%</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}: reference trace metal.
\textsuperscript{b}: the enrichment factor (EF) of trace metal Fe was not calculated.
centrations at industrial sites are much higher than those at urban sites, such as Beijing (Sun et al., 2004), Shanghai (Chen et al., 2008) and Ji’nan (this study), suggesting that industrial emissions are common sources of trace metals. It can also be seen that the concentrations of Fe, Zn, and Al are generally high in urban area. The Pb concentration in Ji’nan (200.7 ng/m$^3$) is close to that in other large-scale industrial cities in China, such as Anshan (246 ng/m$^3$) (Han et al., 2012), Nanjing (244.2 ng/m$^3$) (Yang et al., 2010), Shanghai (149 ng/m$^3$) and Beijing (200 ng/m$^3$), lower than that in Guangzhou in south China (304 ng/m$^3$) (Wang et al., 2006), Xi’an in northwest China (304 ng/m$^3$) (Xu et al., 2011), and Taichung in Taiwan (283 ng/m$^3$) (Fang et al., 2003), but much higher than those in other Asian cities such as Tokyo, Japan (39.2 ng/m$^3$) (Furuta et al., 2005), Singapore (74.3 ng/m$^3$) (Balasubramanian and Qian, 2004), Seoul (51 ng/m$^3$) (Heo et al., 2009) and Hong Kong (42.8 ng/m$^3$) (Ho et al., 2009). Therefore, the Chinese mainland is still facing serious Pb pollution compared to other developed countries and regions in Asia.

### 2.2 Enrichment factors and correlations among trace metals

The EFs were used to evaluate the contribution of anthropogenic metals: when EF$_i$ > 10, the metals are mostly contributed by anthropogenic sources (e.g., industries and vehicles); when EF$_i$ < 10, the metals are normally originated from natural source (e.g., dust/soil source) (Wei et al., 1999). However, if natural and anthropogenic sources contribute similar concentrations of metals, EFs cannot be used for differentiation (Xie et al., 2006). In this study, we did not calculate the EF of Fe due to the above mentioned reason. The EFs were calculated as the following equation:

$$\text{EF}_i = \frac{C_i}{C_{\text{ref}}_{\text{atmosphere}}} / \frac{C_i}{C_{\text{ref}}_{\text{crust}}}$$

where, examined trace metals ($C_i$) and reference trace metals ($C_{\text{ref}}$) in crust are based on the China background soil values from Wei (1990), ($C_i$)/$C_{\text{ref}}_{\text{atmosphere}}$ is the trace metals ($C_i$) and reference trace metals ($C_{\text{ref}}$) in aerosols. The common reference metals in previous studies were Al, Fe, Mn, Sc, and Ti (Han et al., 2006; Isakson et al., 1997; Xu et al., 2011). Given that the sampling area at the industrial site was exposed to the emissions of iron and steel smelting from surrounding plants, Fe and Mn were not chosen as the reference metals. In this study, Al was selected as the reference metal. Figure 2 shows that the EFs of Pb, As, Zn, Cu, Ni, Mn, and Cr were much higher at the industrial site than at the urban site, suggesting industrial activities have emitted trace metals into the atmosphere. The EFs order of the trace elements was: Pb > Zn > As > Cu > Ni > Mn > Cr > Sr > Ba > Ti, with the highest EF value exceeding 1000 for Pb at the industrial site. This result suggests that Pb was emitted from anthropogenic activities in this industrial area of the city. Given that leaded gasoline has been phased out in China since 1997, the accumulation of Pb in the atmosphere was probably affected by industrial activities and coal-fired power plants nearby. Similarly, As, Zn, and Cu showed high EFs (with EFs of As, Zn, and Cu of 330 and 635, 485 and 796, 141 and 280 in the urban and industrial sites, respectively), suggesting that they were emitted from anthropogenic sources (details in Section 2.3).

Pearson’s correlation coefficients of trace metals at both sites are listed in Table 2. As and Cr were highly correlated at the urban site, indicating their common source. Cu, Fe, Zn, Pb, and Mn were significantly correlated, and Ti, Al, and Ba were positively correlated at both sites. According to EFs of these metals (Table 1), the former metals (e.g., Cu, Zn, Pb, and Mn) with EFs larger than 10 are originated mainly from anthropogenic sources, and the later metals (e.g., Ti and Ba) less than 10 are originated mainly from the earth crustal source. Ni and Sr were positively correlated with Ba, Al, and Ti as well as Cu, Fe, Zn, Pb, and Mn, which implies that Ni and Sr may have mixed origins from both natural and anthropogenic sources. This result is consistent with the conclusion from Miguel et al. (1997).

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**Fig. 3** Comparison of PM$_{2.5}$ metal concentrations in major cities in China and Asia.
### Table 2  Pearson’s correlation matrix for the trace metal concentrations

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>As</th>
<th>Ba</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Sr</th>
<th>Ti</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.347</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.702</td>
<td>0.407</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.589</td>
<td>0.745</td>
<td>0.297</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.758</td>
<td>0.025</td>
<td>0.130</td>
<td>0.530</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.777</td>
<td>0.047</td>
<td>0.278</td>
<td>0.448</td>
<td>0.941</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.786</td>
<td>0.269</td>
<td>0.268</td>
<td>0.713</td>
<td>0.932</td>
<td>0.941</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ni</td>
<td>0.827</td>
<td>–0.007</td>
<td>0.498</td>
<td>0.243</td>
<td>0.819</td>
<td>0.901</td>
<td>0.756</td>
<td>1.000</td>
<td></td>
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<tr>
<td>Pb</td>
<td>0.692</td>
<td>–0.042</td>
<td>0.102</td>
<td>0.547</td>
<td>0.974</td>
<td>0.915</td>
<td>0.932</td>
<td>0.746</td>
<td>1.000</td>
<td></td>
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<tr>
<td>Sr</td>
<td>0.972</td>
<td>0.162</td>
<td>0.645</td>
<td>0.503</td>
<td>0.803</td>
<td>0.823</td>
<td>0.804</td>
<td>0.845</td>
<td>0.767</td>
<td>1.000</td>
<td></td>
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</tr>
<tr>
<td>Ti</td>
<td>0.938</td>
<td>0.346</td>
<td>0.737</td>
<td>0.404</td>
<td>0.600</td>
<td>0.624</td>
<td>0.579</td>
<td>0.782</td>
<td>0.480</td>
<td>0.890</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.741</td>
<td>0.252</td>
<td>0.117</td>
<td>0.731</td>
<td>0.949</td>
<td>0.882</td>
<td>0.966</td>
<td>0.667</td>
<td>0.936</td>
<td>0.762</td>
<td>0.553</td>
<td>1.000</td>
</tr>
<tr>
<td>Industrial</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.000</td>
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<td>0.077</td>
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<td>0.316</td>
<td>0.405</td>
<td>0.593</td>
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<td>0.592</td>
<td>0.572</td>
<td>0.571</td>
<td>0.236</td>
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2.3 Principal component analysis and source apportionment

The PCA has been widely used to identify the major sources of air pollutant emissions (Querol et al., 2008; Thurston and Spengler, 1985). The SPSS statistical software packages were carried out for the PCA statistical analysis (PASW Statistics18, USA). The PCA results show that three factors and two factors can explain 95.5% and 85.0% of the data variance of the urban site and industrial site samples, respectively (Table 3).

At the urban site: Urban Factor 1 (PC1) can explain 61.9% of the total variance of the data, with high loadings of Cu (0.974), Fe (0.920), Mn (0.916), Pb (0.982), and Zn (0.935). The analysis is consistent with the results from Pearson’s correlation (Section 2.2). Our data and analysis suggest that Pb was strongly emitted from anthropogenic sources. After the phase-out of leaded gasoline in China since 1997, vehicular emissions should no longer be one of the main sources. The Pb concentration was higher in the industrial site than in the urban site, suggesting that the smelting processes emitted certain amounts of Pb into the atmosphere. In addition, Zhang et al. (2009) reported that the major emission sources of Pb in airborne particulate matters in Shanghai were coal combustions. In this study, Fe, Zn, and Mn were likely originated from the smelting processes in the industrial area. Some studies showed that vehicles also emitted some Zn from physical processes (Thorpe and Harrison, 2008). Manoli et al. (2002) reported that diesel engines can emit Cu. Therefore, Urban Factor 1 has mixed sources from vehicles (such as diesel/gasoline combustion and wear products from brake linings and tyres), metal smelting processes and coal consumptions.

Urban Factor 2 (PC2) is dominated by Ba (0.933), Ti (0.838), and moderately associated with Ni (0.616) and Sr (0.677). According to the EF value of Ba at 3.27 and EF value of Ti at 1.17 in the section 2.2, Urban Factor 2 indicates that the natural soil and road fugitive dust are the main sources.

Urban Factor 3 (PC3) is dominated by As (0.939) and Cr (0.854), which has been reported mainly from the coal burning (Pacyna et al., 2007; Tian et al., 2010; Xie et al., 2006). One coal-fired power plant is located about 5 km northeast of the urban site and in the upwind of the main urban areas in September (Fig. 1). The coal-fired power plant should be responsible for this source.

At the industrial site: Industrial Factor 1 (PC1) has high loadings of Cu (0.877), Fe (0.952), Mn (0.874), Pb (0.927), and Zn (0.916) and with moderate loading of As (0.795) and Cr (0.647). This may be mainly from industrial sources, and coal combustion. Industrial Factor 2 (PC2) shows high loadings of Ba (0.894), Sr (0.915), Ti (0.833)
Table 3  Principal component analysis (PCA) of trace metals in the samples collected at the urban and industrial sites in September, 2010

<table>
<thead>
<tr>
<th>Metal (urban)</th>
<th>Principal components (cumulative 95.5%)</th>
<th>Metal (industrial)</th>
<th>Principal components (cumulative 85.0%)</th>
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<tr>
<td></td>
<td>PC1 (%)</td>
<td>PC2 (%)</td>
<td>PC3 (%)</td>
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<tr>
<td>As</td>
<td>−0.077</td>
<td>0.234</td>
<td>0.939</td>
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<tr>
<td>Ba</td>
<td>−0.032</td>
<td>0.933</td>
<td>0.239</td>
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<tr>
<td>Cr</td>
<td>0.482</td>
<td>0.083</td>
<td>0.854</td>
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<tr>
<td>Cu</td>
<td>0.974</td>
<td>0.184</td>
<td>0.054</td>
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<tr>
<td>Fe</td>
<td>0.920</td>
<td>0.322</td>
<td>0.007</td>
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<td>Mn</td>
<td>0.916</td>
<td>0.214</td>
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<td>Ni</td>
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<td>0.616</td>
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<td>Pb</td>
<td>0.982</td>
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<tr>
<td>Sr</td>
<td>0.693</td>
<td>0.677</td>
<td>0.106</td>
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<tr>
<td>Ti</td>
<td>0.419</td>
<td>0.838</td>
<td>0.175</td>
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<tr>
<td>Zn</td>
<td>0.935</td>
<td>0.094</td>
<td>0.324</td>
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<tr>
<td>%</td>
<td>65.9</td>
<td>16.6</td>
<td>13.0</td>
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and Ni (0.792). The result is consistent with the analysis in the urban site.

From the discussion above, PCA can roughly identify three sources, including a mixed source, a natural soil source and a source from coal-fired power plant. The mixed source from coal combustion, vehicles emissions, and industrial activities cannot be divided separately. The analysis is limited to separate the mixed sources in the industrial-urban area. In order to better identify the trace metals sources, we need to combine other source apportion methods. TEM can identify the sources from anthropogenic sources. Spheric particles are mostly from industrial sources with fossil fuel combustion at the high temperature condition (Li et al., 2013) (Fig. 4a). Irregular metal particles are likely from the physical processes such as vehicle brakes and tyre wear.

2.4 TEM analysis and potential implications

The fine particles can be efficiently deposited by diffusion mechanisms in all regions of the respiratory tract, especially the nano-sized particles (Oberdörster et al., 2005). Trace metals in the atmospheric aerosols (e.g., Fe and Zn) may involve in the free radicals release in lung fluid via Fenton reaction and are hypothesized to cause pulmonary inflammation (Birmili et al., 2006; Donaldson et al., 1997). In this study, mass concentrations of these metals were high in both sites (Table 1). Furthermore, Pb showed an average EF value exceeding 1000 at the industrial site, indicating a high accumulation of Pb from anthropogenic emissions. Pb toxicity in the atmosphere can cause some serious diseases for young children (He et al., 2009; Silbergeld, 1997). TEM observations show that these trace metals were mostly embedded within or attached to the hosted particles including sulfates, nitrates, and organic matters (Fig. 4). Similar results have been found in Mexico City (Adachi and Buseck, 2010) and Detroit (Utsunomiya et al., 2004). Li et al. (2011) suggested that large amounts of fine metal particles in the Ji’nan urban atmosphere can catalyze the transformation from S(IV) of SO2 into S(VI) of sulfate once trace metals were internally mixed within the sulfate particles. Adachi and Buseck (2010) proposed that the mixture of metal particles with sulfate and organic matters would lead to a larger size of trace metals and will deposit into shallow parts of the respiratory tract once inhaled. Moreover, the water-soluble materials will dissolve and leave the trace metals in different physiological areas and cause different effects on the body than free-floating trace metals (Adachi and Buseck, 2010). Although the mixing processes can shorten their life times in the atmosphere, these soluble coatings on the metal particles may further enhance their toxicity. In the industrial cities, the trace metals maintained a rather high concentration and further were internally mixed with soluble sulfate/organic particles. The result suggests that these metals in the industrial urban city could have different toxicities when internally mixed.

3 Conclusions

The mass concentrations of several trace metals were measured simultaneously at one urban site and one industrial site in Ji’nan. ICP-AES was used to determine the trace metals concentrations in PM2.5. Total trace metals concentration was 1.7 times higher at the industrial site than at the urban site. Trace metals in this study are higher than those of other cities in Asia. The enrichment factor results show that trace metals in the atmosphere of Ji’nan are heavily exposed to the anthropogenic emissions except Ba and Ti. Main trace metal sources were identified by combining the statistical techniques including correlation coefficient
analysis, principal component analysis and enrichment factor. The results show that: (1) Cu, Fe, Mn, Pb, and Zn are from emissions of vehicular traffic and smelting industry. (2) As, Pb, and Cr from coal-fired power plant. (3) Ba, Al, and Ti from natural soil and road fugitive dust. (4) Ni and Sr may have a mixed (both anthropogenic and natural) source. The high concentrations (e.g., Fe and Zn) and mixing states of the metal particles in this study strongly suggest that these trace metal particles may cause adverse effects on human health in Ji’nan city, particularly in the industrial area. Although the strategies to reduce emissions of SO₂ and NOₓ have already been adopted, ultra-fine (nano-sized particles) particles should also be removed during the industrial processes of large smelting industries and coal-fired power plants in the next stage. These primary metal particles can mix with water-soluble inorganic sulfate or organic matters after emitted into the atmosphere. The results indicate that the health implications of the trace metals are complex, and may lead to different toxic ability when internally mixed.

Acknowledgments

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