Elemental Composition, Morphology and Sources of Fine Particulates (PM$_{2.5}$) in Hefei City, China

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ABSTRACT

Elemental composition and morphology were studied for atmospheric fine particles (PM$_{2.5}$) collected from a fast developing city, Hefei, with an aim of tracing the potential emission sources. The sampling was conducted every month at two urban sites between June 2014 and December 2015. We used X-ray fluorescence (XRF) to determine the elemental composition, and scanning electronic microscopy (SEM) and transmission electron microscope (TEM) to characterize the particles in morphology.

Our results showed that PM$_{2.5}$ contained large fractions of particles likely derived from fuel burning, construction and automobile emissions and was highly enriched in sulfur. Aggregations of particles suggested a strong secondary reaction under high SO$_2$ levels. Some discrepancies in elemental composition at the two sampling sites were observed, which were attributed to the difference in traffic density and construction fugitive dust emissions. A negative correlation existed between the polluted elements in PM$_{2.5}$ and the ambient temperature and a positive correlation existed with the pressure, likely caused by a reduction in the height of the terrestrial boundary layer and reaction rates of pollutants.

Keywords: PM$_{2.5}$; Elemental composition; Morphology; Sources identification.

INTRODUCTION

Large emissions of atmospheric particulates have attracted extensive attention worldwide, due to their potential risk to human health. The close associations between morbidity or mortality and particulate matter (PM) pollution have been demonstrated in various epidemiological studies, and this association appears to be especially prominent with PM$_{2.5}$ (particle size smaller than 2.5 µm) (Dockery et al., 1993; Schwartz, 1994; Xu et al., 1994; Kelsall et al., 1997; Pope et al., 2002; Levy et al., 2005; Ma et al., 2011).

Atmospheric particulate matter comprises a mix of mineral dust, elements, organic components, inorganic ions, and water. Studies on TSP (total suspended particulate), PM$_{2.5}$, and PM$_{10}$ about these variation, elements, soluble ions, and organic composition, are conducted across the world from time to time (Annegarn et al., 1992; Marcazzan et al., 2001; Shahid et al., 2016; Tung et al., 2018).

Aside from measuring the concentration and chemical composition of atmospheric particulates, it is the identification of pollution sources that is critical to contamination control and environmental administration. Several diverse source apportionment methods exist, which include chemical mass balance (CMB), positive matrix factorization (PMF), target transformation factor analysis (TTFA), and multiple linear regression (MLR), and these help evaluate the sources and their degree of contribution (Chen et al., 1999; Begum et al., 2007; Kothai et al., 2008; Shi et al., 2011). Prevailing source apportionment of airborne particulate matter is a huge amount of work, and demands considerable investments and long development periods. This paper researched a qualitative source identification via cluster analyses, elemental concentrations, enrichment factors and morphological characteristics.

The project involved PM$_{2.5}$ sampling of both industrial and residential townships, the older YaoHai and the nouveau-urban Shushan districts respectively, in Hefei (60 m above sea level, 31°N, 117°E), Anhui’s provincial capital, spread over 11,445.1 square kilometers, and with a 7.965 million populace (Hu et al., 2018). During the winters, coal-burning boilers supply their heating. Although reports on atmospheric particulate in recent years have...
focused on the main Chinese cities including Shanghai and Beijing (Wei et al., 1999; Ye et al., 2003; Sun et al., 2006), there is still a need for PM$_{2.5}$ systematic analyses in places like Hefei. The main aims of the research were to investigate levels, elemental compositions, morphological characteristics and possible sources of PM$_{2.5}$ in Hefei.

**SAMPLING AND MEASUREMENTS**

Provincial level monitoring stations are located at MingZhu square (Site A, 31°47′19″E, 117°12′26″N) and SanLi Street (Site B, 31°52′52″E, 117°19′72″N) in Hefei City, and those were same as the PM sampling sites (Fig. 1). Air sampling medium flow collective instruments (TH150D, produced by Wuhan Tianhong Ltd., China) were erected, as per PRC environmental protection standard (GB6921-86 and HJ 93-2013), in expansive areas, and over 3 meter heights. Polytetrafluoroethylene membrane filters, baked at 80°C for 2 hours, were then dried in the thermotank to remove any background variance matter. A 24-hour exposure at approximately 20°C, with 50% constant humidity, was conditioned. The particulate mass was evaluated for each PM$_{2.5}$ sample, collected almost 20 hours and subsequently weighed in a microbalance (Metler AE240, 0.0001g), prior to and following sampling. PM$_{2.5}$ samples were collected from June 2014 to December 2015, on days that were calm and without rain and snow. The 21 representative samples were thus chosen from hundreds of samples and then assessed (Table 1). Conventional parameters in meteorology (e.g., pressure, temperature, wind direction and velocity) were frequently obtained from the National Meteorological Information Center during the sampling.

X-ray fluorescence (Shimadzu Corporation, XRF-1800), with detection limit order a minimal µg cm$^{-2}$ of filter deposit, helped ascertain 23 element concentrations, as shown below: silicon (Si), calcium (Ca), aluminum (Al), iron (Fe),

![Fig. 1. Locations maps of sampling sites in Hefei City, Anhui, China.](image)

<table>
<thead>
<tr>
<th>start time</th>
<th>finish time</th>
<th>sampling site</th>
<th>Temperature (0.1°C)</th>
<th>Pressure (0.1 hpa)</th>
<th>wind velocity (0.1 m s$^{-1}$)</th>
<th>wind direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 3 2014</td>
<td>June 4 2014</td>
<td>Site A</td>
<td>221</td>
<td>10040</td>
<td>22</td>
<td>16</td>
</tr>
<tr>
<td>June 12 2014</td>
<td>June 13 2014</td>
<td>Site A and B</td>
<td>268</td>
<td>10036</td>
<td>22</td>
<td>3</td>
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<tr>
<td>July 8 2014</td>
<td>July 9 2014</td>
<td>Site A and B</td>
<td>272</td>
<td>9994</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>August 2 2014</td>
<td>August 3 2014</td>
<td>Site A and B</td>
<td>283</td>
<td>9987</td>
<td>16</td>
<td>16</td>
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<tr>
<td>October 8 2014</td>
<td>October 9 2014</td>
<td>Site A and B</td>
<td>185</td>
<td>10161</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
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<td>November 5 2014</td>
<td>Site A and B</td>
<td>118</td>
<td>10176</td>
<td>12</td>
<td>7</td>
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<td>December 6 2014</td>
<td>Site A and B</td>
<td>21</td>
<td>10266</td>
<td>10</td>
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<td>January 16 2015</td>
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<td>60</td>
<td>10253</td>
<td>11</td>
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<td>March 5 2015</td>
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<td>53</td>
<td>10238</td>
<td>31</td>
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<td>April 3 2015</td>
<td>Site A and B</td>
<td>145</td>
<td>9986</td>
<td>32</td>
<td>13</td>
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<tr>
<td>May 27 2015</td>
<td>May 28 2015</td>
<td>Site A and B</td>
<td>209</td>
<td>10021</td>
<td>18</td>
<td>4</td>
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sodium (Na), magnesium (Mg), titanium (Ti), phosphorus (P), potassium (K), chlorine (Cl), sulfur (S), zinc (Zn), vanadium (V), arsenic (As), nickel (Ni), chromium (Cr), selenium (Se), bromine (Br), strontium (Sr), zirconium (Zr), manganese (Mn), copper (Cu) and lead (Pb). Quality audits and laboratory intercomparisons were conducted. Unexposed filters were used to monitor the field blank background contamination; blank values were typically found to be lower than or closer to the detection limits. The element concentrations were established with reference to calibration standards, and applicable instrumental error adjustments. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to characterize the morphologies of the particles. The detailed description of experiment analysis was provided by He et al. (2001) and Wang et al. (2013). The SPSS software statistical techniques facilitated correlation, regression and cluster analyses.

RESULTS AND DISCUSSION

**PM$_{2.5}$ Concentrations and AQI**

The Hefei Environmental Protection Bureau’s online monitoring analysis platforms published the daily PM$_{2.5}$ concentrations data (hfeeb.hefei.gov.cn). Hefei’s 56 µg m⁻³ PM$_{2.5}$ sampling period average was higher than the China National Ambient Air Quality Standard (GB 3095-2012) second level value (35 µg m⁻³), and also the air quality guidelines standard (25 µg m⁻³) set by the World Health Organization (WHO, 2005).

A detailed description of AQI is given in Sharma et al. (2001). Two primary steps are involved in formulating an AQI: IAQI (Individual Air Quality Index) is calculated for each pollutant (PM$_{2.5}$, PM$_{10}$, CO, NO$_x$, SO$_2$ and O$_3$). After the different indexes (IAQI) have been determined for every pollutant, we selected the maximum index.

Based on the above methods, the main factor influencing AQI is the most seriously polluted chemical composition. Examining the relationships between PM$_{2.5}$ and AQI is of critical importance for gaining an insight into the particles source characterization. Strong positive correlations between PM$_{2.5}$ and AQI (Pearson coefficient R = 0.92, P < 0.01) based on the published data is shown in the Fig. 2, indicating that PM$_{2.5}$ have become the most prevalent pollutant. This result is consistent with previous studies in other cities in China (Han et al., 2014; Pui et al., 2014).

**Elemental Concentrations**

The following 13 elements shown in Table 2 were measured by XRF: Si, Ca, Al, Fe, Na, Mg, Ti, P, K, Zr, Cl, S and Zn. Lack of several elements such as Cu and Pb were results of the element concentration below the detectable limit.

The typical elements derived from the earth’s crust are Al, Si, P, K, Ca, Mn and Fe, whilst man-made pollution generates Ni, S, Cu and Pb, also called pollution elements. Earlier studies concluded that elemental compositions could help differentiate the sources of pollution. For instance, Al, Ca, Ti and Si originate in windblown re-suspended soil dust; Mn and Cu are industry emissions; S emanates from fossil fuel burning and rubber tyres wear and tear; Zn arises from soil dust, garbage waste and motor vehicle emissions; K is produced from biomass burning; and Pb that also emanates from industry, but is rare from motor vehicles, since leaded gasoline was phased-out in China after 2000 (Cohen et al., 1996; Vallius et al., 2003; Yue et al., 2006; Ling et al., 2015).

Some pollution elements from industrial productions such as Cu, Pb and Ni are to little to be detected in experiments, indicating that industrial emissions are not the contributory sources of PM$_{2.5}$ in Hefei. Elementary compositions of PM$_{2.5}$ at Site A and Site B are showed in Fig. 3. Carbon (C), oxygen (O) and so on are bated in pie charts because they are also involved in organic membrane.

![Fig. 2. The correlation between PM$_{2.5}$ and AQI.](image-url)
Table 2. PM$_{2.5}$ concentrations (µg m$^{-3}$) and elemental concentrations (ng m$^{-3}$) analyzed in samples collected by using filters. Estimates representing maximum, minimum, average values and standard deviation.

<table>
<thead>
<tr>
<th>Locations</th>
<th>PM$_{2.5}$</th>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Na</th>
<th>Fe</th>
<th>Mg</th>
<th>P</th>
<th>Ti</th>
<th>S</th>
<th>Zn</th>
<th>K</th>
<th>Zr</th>
<th>Cl</th>
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<tbody>
<tr>
<td></td>
<td>Average</td>
<td>54</td>
<td>348</td>
<td>91</td>
<td>83</td>
<td>187</td>
<td>55</td>
<td>26</td>
<td>15</td>
<td>293</td>
<td>1421</td>
<td>12</td>
<td>134</td>
<td>6</td>
</tr>
<tr>
<td>A</td>
<td>Maximum</td>
<td>90</td>
<td>551</td>
<td>110</td>
<td>116</td>
<td>254</td>
<td>85</td>
<td>39</td>
<td>27</td>
<td>413</td>
<td>2714</td>
<td>28</td>
<td>261</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>26</td>
<td>213</td>
<td>11</td>
<td>49</td>
<td>150</td>
<td>42</td>
<td>14</td>
<td>0</td>
<td>65</td>
<td>127</td>
<td>1</td>
<td>11</td>
<td>0</td>
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<tr>
<td></td>
<td>SD</td>
<td>22</td>
<td>114</td>
<td>28</td>
<td>21</td>
<td>35</td>
<td>12</td>
<td>7</td>
<td>8</td>
<td>86</td>
<td>881</td>
<td>7</td>
<td>83</td>
<td>7</td>
</tr>
<tr>
<td>B</td>
<td>Average</td>
<td>59</td>
<td>956</td>
<td>481</td>
<td>285</td>
<td>385</td>
<td>206</td>
<td>0</td>
<td>47</td>
<td>622</td>
<td>2257</td>
<td>30</td>
<td>220</td>
<td>6</td>
</tr>
<tr>
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<td>Maximum</td>
<td>96</td>
<td>1158</td>
<td>573</td>
<td>342</td>
<td>448</td>
<td>233</td>
<td>0</td>
<td>58</td>
<td>786</td>
<td>4643</td>
<td>44</td>
<td>378</td>
<td>12</td>
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<td>Minimum</td>
<td>30</td>
<td>779</td>
<td>298</td>
<td>199</td>
<td>274</td>
<td>167</td>
<td>0</td>
<td>35</td>
<td>368</td>
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<tr>
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<td>0</td>
<td>7</td>
<td>139</td>
<td>1573</td>
<td>11</td>
<td>75</td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 3. Elemental compositions of PM$_{2.5}$ in Hefei.

Based on elemental concentrations in PM$_{2.5}$, the dendrogram from cluster analysis is shown in Fig. 4. The first group and second group including Zn, Mg and K, Cl respectively are weakly associated with non-main sources of contamination such as traffic, biomass burning and waste incineration emission. The third group containing Si and Ca is typical terrestrial source with less anthropogenic source, while the fourth group S is originating from fuel combustion.

PM$_{2.5}$ in Site A shown in Table 2 were higher than that of Site B by more than two times for most elements, except a few elements such as Mg. There are probably several reasons: Firstly, Site A is located at Eastern 1st Ring Road (SanLi Street), one of the highest density traffic roads in Hefei; secondly, during the sampling, the adjacent roads (QuanJiao Road and LinQuan Road) were under construction, and the construction dust might impact ambient air severely; Thirdly, Site A in Yaohai District is located in an industry zone, and there are plenty of companies including power plants with coal as their main energy resource, while Site B is located in Shushan District where only a few industrial enterprises.

Enrichment Factors Analyses

Enrichment factors are extensively adopted to verify the enrichment degree, and thus trace the elemental source (natural or anthropogenic) in atmospheric particulates.

\[
Enrichment \ Factor = \frac{\left( C_i / C_n \right)_{\text{environment}}}{\left( C_i / C_n \right)_{\text{background}}} \tag{1}
\]

\(C_i\) represents the elements (S and Zn) evaluated, while \(C_n\) represents the reference elements (that exist in the earth's crust, and possess excellent chemical stability and low volatility). We calculated with the reference element Fe, applying the composition of continental crust, as Mason (1966) and Ardisoglou and Samara (2005) proposed. Elements are classified as non, medially and severely enriched as per corresponding values of EF < 10, 10 < EF < 100 and EF > 100 (Taner et al., 2013; Espitia-Pérez et al., 2018).

Table 3 shows partial elemental enrichment factors excluding terrestrial elements such as Na whose EF verge
on 1. The most enriched elements are S and Cl (EFs > 500), for which the significant anthropogenic origin namely fuel combustion can be suggested. The enrichment factors calculated for Zn are 2.50 in Site A and 3.00 in Site B, and for K are 4.69 in Site A and 2.06 in Site B ascertaining that Zn and K are in the degree of slightly polluted. The conclusion that Ca are mildly enriched is relatively infrequent in other people’s previous research, probably related with traffic and construction fugitive dust emissions.

Table 3. Enrichment factors in Site A and B.

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>Zn</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5374.80</td>
<td>2.50</td>
<td>557.44</td>
<td>4.69</td>
<td>2.27</td>
</tr>
<tr>
<td>B</td>
<td>2475.04</td>
<td>3.00</td>
<td>213.24</td>
<td>2.06</td>
<td>3.22</td>
</tr>
</tbody>
</table>

Correlation between Pollution Element Concentrations and Meteorological Factors

Meteorological factors are split into factors with direct effect such as velocity and direction of air flow and atmospheric precipitation and factors with indirect effect (temperature, air humidity and air pressure). The direct effect factors impacted by the indirect ones, and they have multiple effects on air quality. For instance, enhancing rainfall is beneficial for scavenging air and the high temperature increases the activity of particles (Kukkonen et al., 2005; Vardoulakis and Kassomenos, 2008).

It is found that the mean concentrations of main pollution elements S are significantly negatively correlated with the temperature, and significantly positively correlated with the pressure, with no obvious correlation with wind velocity and direction (Fig. 5). Because there is a negative correlation between air temperature and pressure. And this suggests that the higher the temperature is, the stronger the vertical convection, thus the more contributions it will make to transfer pollutants upward. Additionally, high temperature could also accelerate the thermal decomposition of pollutants (Lin et al., 2009; Zhao et al., 2012).

Morphology Characteristics

It is self-evident that a better understanding of particle morphology in PM can contribute significantly to contamination mitigation strategies. The observation of particle structure and composition by the SEM and TEM was put into use (Shao et al., 2009; Kang et al., 2012).

Some representative morphology properties identified by SEM are listed as follows (Fig. 6): 1. columnar particles; 2. similar-circular particles; 3. circular particles; 4. irregular particles; 5. the chain-like aggregates of columnar particles and circular particles; 6. flocculent aggregates; 7. foam-like residual. These granule shape features are anastomose with Buseck et al. (2000), Li and Shao (2009) and Satsangi and Yadav (2014).

Coal fly ashes are manifested by circular particles, with smoothing surface. Occasionally, particulate matters cohere together, possibly resulting from the secondary reaction after fly ashes releasing into the air. Regular-shaped particles in the research are primarily composed of coal fly ashes. Mineral grains exist in a visible form of similar-circular particles, and the constituent is aluminosilicate and quartz which are poorly polished and selected. Columnar
Fig. 5. The correlations between meteorological factors and S concentrations.

1. columnar particles; 2. similar-circular particles; 3. circular particles; 4. irregular particles;
5. the chain-like aggregates of columnar particles and circular particles; 6. flocculent aggregates; 7. foam-like residual.

Fig. 6. Morphology properties in SEM results.
particles are the actual particles from construction like cement particles, and the angular texture vary according to the situation that the sampling Site B is near the road construction sites. Flocculent aggregates are soot aggregation, resulting from fuel burning, biomass burning and motor vehicle exhausting (Wang et al., 2013). Different from the former researches, there are a lot of aggregations of columnar particles, suggesting the secondary reaction of construction particles. Meantime, foam-like residual is likely the decomposition products of sulphate derived from reaction products of SO$_2$ and other substances. The intensity of secondary reaction has also been confirmed by the above mentioned high concentrations of S in PM$_{2.5}$ and the high SO$_2$ concentrations from official monitoring. The elements composing the particulates are Si and S, agreeing with the data of elemental concentrations and compositions (Table 4). Furthermore, the result from TEM experiments reconfirmed these results (Fig. 7).

**CONCLUSION**

(a) 13 elements were detected, and thereinto pollution elements were S and Zn instead of some usual ones such as Cu, Pb, Ni illustrating that the major pollution sources were fuel burning, construction and automobile instead of heavy industries. (b) The major concentrations of Site A were higher than those of Site B more than twice, due to the traffic pollution and construction fugitive dust affecting in different degrees. (c) The concentrations of pollution elements were negatively correlated to the temperature and positively correlated to the temperature by an effect on the intensity of the vertical convection and decomposition reaction. (d) In the morphology, there were columnar particles, similar-circular particles, circular particles, irregular

<table>
<thead>
<tr>
<th>Species</th>
<th>Morphology</th>
<th>Elemental composition</th>
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<tbody>
<tr>
<td>fly ashes</td>
<td>circular</td>
<td>Ca, Si, Al, K, Fe</td>
</tr>
<tr>
<td>construction particles</td>
<td>columnar, irregular</td>
<td>Ca, Si, Al</td>
</tr>
<tr>
<td>soot dust aggregates</td>
<td>flocculent</td>
<td>C, O,S</td>
</tr>
<tr>
<td>resuspension dust</td>
<td>irregular</td>
<td>Si, Al, K, Ca, Fe</td>
</tr>
<tr>
<td>mineral grains</td>
<td>similar-circular</td>
<td>Al, Si</td>
</tr>
<tr>
<td>biomass particle</td>
<td>irregular</td>
<td>C, O, K, Pb</td>
</tr>
</tbody>
</table>

Table 4. The morphology, elemental composition and source of representative atmospheric particulates (Compiled from Pipal et al. (2014), Fromme et al. (2008) and Yue et al. (2006)).

![Fig. 7. Coal fly ashes, cement particles, mineral grains, and the aggregation of smoke dust in TEM experiments.](image)
particles, the aggregates of columnar particles and circular particles, flocculent aggregates, etc. The main components were circular particles and columnar particles, which declared the existence of air pollution and the sources of fuel burning, biomass burning and motor vehicle exhausting. The mass of aggregations demonstrated the strong secondary reaction of construction particles, especially the high SO₂ level, in accord with S concentrations.

Acknowledgement

The authors acknowledge the support from the National Natural Science Foundation of China (NO. 41173032) and the Anhui Environmental Protection Scientific Research Fund (2015004). We acknowledge editors and reviewers for polishing the language of the paper and for in-depth discussion.

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