Seasonal variation, source apportionment and health risk assessment of heavy metals in PM$_{2.5}$ in Ningbo, China

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Abstract

In order to assess the seasonal variation, potential sources, and health risk of heavy metals found in fine particulate matter (PM$_{2.5}$), PM$_{2.5}$ samples (n = 96) were collected between March 2015 and February 2016 in Ningbo, China. Twelve heavy metals (Sb, As, Cd, Cr, Pb, Mn, Ni, Se, Tl, Al, Be and Hg) found in PM$_{2.5}$ were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). We used enrichment factor and principal component analysis/absolute principal component scores (PCA/APCS) to determine the sources of these heavy metals. We used models from the United States Environmental Protection Agency (EPA) to assess both carcinogenic and non-carcinogenic risk of heavy metals to adults and children. Results showed that the annual average mass concentration for PM$_{2.5}$ was 62.7 $\mu$g m$^{-3}$, which is higher than the Chinese National Ambient Air Quality Standards (NAAQS). The annual average concentrations of Pb,
Cd, and As were 57.2 ng m$^{-3}$, 1.5 ng m$^{-3}$, 4.7 ng m$^{-3}$, respectively, which were below the limits of the NAAQS. The highest concentrations of the total heavy metals occurred in winter, and the lowest concentrations were observed in summer. Enrichment factor analysis indicated that Sb, Cd, Pb, Se, As and Tl were mainly from anthropogenic sources. Source apportionment by PCA/APCS indicated four major sources: coal combustion and motor vehicles (46.3%), soil and construction dust (37.1%), steel works (6.9%) and other smelting industries (6.8%). The carcinogenic risk of heavy metals in Ningbo was lower than the safe level for both children and adults. However, the total non-carcinogenic risk was higher than the safe level (HI=1.38). This warrants further research to explore air pollution sources and implement effective measures to control air pollution in Ningbo, China.

**Keywords:** PM$_{2.5}$; Heavy metal; Enrichment factor; Principal component analysis/absolute principal component scores; Health risk assessment

1. Introduction

With the rapid economic growth, air pollution is worsening in China. In early 2013, severe heavy smog episodes occurred across most areas in China, which aroused widespread concern about fine particulate matter (with aerodynamic diameters not larger than 2.5 µm, or PM$_{2.5}$) due to the adverse effects on human health and reduced visibility (Chen et al., 2013). Studies have shown increases in lung cancer and cardiopulmonary mortality after long-term exposure to fine particulate air pollution (GBD Collaborators, 2016; Hoek et al., 2013; Li et al., 2015; Pope et al., 2002). Several recent studies have investigated the characteristics of PM$_{2.5}$ in metropolitan China (Chen et al., 2015; Li et al., 2016; Song et al., 2006). Due to different industrial structures, topography, climate and surrounding emission sources, PM$_{2.5}$ concentration showed significant
regional and seasonal variation (Gao et al., 2018; Ming et al., 2017; Mukherjee and Agrawal, 2018).

While exposure to PM$_{2.5}$ is known to cause disease, the components of PM$_{2.5}$ are also of concern. Heavy metals including arsenic, chromium and manganese are often found in PM$_{2.5}$ (Lu et al., 2012). Duan and colleagues found that heavy metals were low biodegradable and enriched in PM$_{2.5}$ (Duan et al., 2012). Exposure to these metals may link with cardiovascular diseases (Huang and Ghio, 2006), cancer (Nawrot et al., 2006; Wild et al., 2009) and many other adverse health effects (Kampa and Castanas, 2008).

Some studies on heavy metal components of PM$_{2.5}$ and their sources have been conducted in China and abroad (Chen et al., 2015; Song et al., 2006); however, limited studies have been conducted based on long-term monitoring. Understanding the heavy metals that are commonly found in PM$_{2.5}$ is necessary to design air quality improvement strategies and inform regulations. Therefore, it is essential to know the seasonal variations of heavy metals in PM$_{2.5}$, especially in polluted urban environments with dense populations.

While PM$_{2.5}$ has been studied throughout other areas in China, the pollution properties and seasonal variation of PM$_{2.5}$ have not been well studied in the urban area of Ningbo. Ningbo is one of the most industrialized and economically developed cities in the Yangtze River Delta region, having a population of more than 8 million people. To better understand the air pollution due to PM$_{2.5}$ and potential health risks in Ningbo, China, this study are to: (1) analyze the seasonal variations of PM$_{2.5}$ and heavy metal concentrations in PM$_{2.5}$, (2) investigate the source apportionment of heavy metals bound to PM$_{2.5}$, and (3) determine the health risks of heavy metals in PM$_{2.5}$. 
2. Materials and methods

2.1. Study area and sampling procedure

Ningbo is a sub-provincial city located in eastern China at the Yangtze River Delta (YRD) region, which is considered one of the most rapidly developing and polluted regions of China (Ming et al., 2017). The world fourth largest port (Ningbo Port) located in east of Ningbo, about 60 km from urban area. Over the past three decades, Ningbo has undergone rapid economic development and urban construction and there are over 8 million people in the city. The climate is temperate with an average temperature 17.8°C.

The measurement site was situated on the roof of the Ningbo Center of Disease Control and Prevention’s (CDC) (~ 20m above ground level) office building, located in a mixed educational, commercial, and residential area (Fig. 1). Xinma road is present at a distance of about 400 m in the north of sampling site. No major industrial air pollution sources around 2 km were detected. It can represent the urban environment in Ningbo. PM$_{2.5}$ samples were collected by medium-volume (2.3 m$^3$ h$^{-1}$) samplers (LECKEL MSV6, German). The samplers, which captured PM$_{2.5}$ on 47 mm quartz filters (Whatman QM-A) ran for 23 hours. Sampling was done on a daily basis in the middle of each month between March 2015 and February 2016. We collected 8 samples in every month; overall, 96 samples were collected. We defined four seasons based on local climate characteristics: spring (March to May), summer (June to August), autumn (September to November) and winter (December to next February).

2.2. Mass concentration analysis

All quartz filters were equilibrated in a desiccator under a constant temperature of 25 ± 1
and humidity condition of 50 ± 5% for 48 hours. The filters were weighed with a Mettler-Toledo XS205DU microbalance (10 μg resolution) before and after aerosol sampling to determine the mass concentration. After sampling, the filters were subsequently sealed in a filter holder and stored at -20°C until analysis. The field blank filters were set at the same time.

2.3. Analysis of elemental contents

After sampling, daily (23-hour) sample filters were cut into four equal fractions. For extracting the heavy metals, one quarter of the filter was cut into pieces and dissolved in the mixtures of 7 ml HNO₃ and 3 ml HClO₄ in Teflon vessels and heated in a microwave system. Heavy metal concentrations (Sb, As, Cd, Cr, Pb, Mn, Ni, Se, Tl, Al, Be and Hg) in the digestion solutions were measured by using inductively coupled plasma mass spectrometry (ICP-MS Elan 9000, Perkin-Elmer SCIEX, USA). Certified reference sample (GSB 04 1767-2004, National Analysis & Testing Center for Nonferrous Metals & Electronic Materials, China) was used to ensure accuracy and precision. The recovery values for all heavy metals were between 91.3% and 108.5%. Blanks (including filters) and duplicate samples were analyzed for approximately 10% of the samples. Relative standard deviations (RSDs) of replicate samples were less than 10%. The detection limits were 1.04, 3.58, 0.12, 1.25, 1.25, 0.12, 1.29, 1.58, 0.12, 0.96, 0.12 and 0.12 ng m⁻³ for Sb, As, Cd, Cr, Pb, Mn, Ni, Se, Tl, Al, Be and Hg, respectively. Since quartz filtration was not appropriate for Al analysis, Al was not included in the data analysis (Tan et al., 2014).

2.4. Data analysis

2.4.1. Enrichment Factor
Enrichment factor analysis (EF), which was proposed by Zoller and colleagues in the 1970s, has been widely used to differentiate elements originating from anthropogenic pollution and natural sources (Yang et al., 2015). The formula for calculation is:

\[(EF)_i = \frac{\left( \frac{X_i}{X_R} \right)_{\text{sample}}}{\left( \frac{X_i}{X_R} \right)_{\text{soil background}}} \tag{1}\]

where \(i\) is the heavy metal to be measured and \(R\) is the soil background element selected in this study. \(X_i\) and \(X_R\) are the concentrations of the corresponding elements in samples while \(X_i'\) and \(X_R'\) are the soil background values. The soil background value of each heavy metal element is taken as the arithmetic mean of the soil background value of upper crust in Ningbo (Station, 1990). Al, Mn and Si are mostly used as the background elements. Since quartz filters are not appropriate for Al, Mn was used as the reference element (Tan et al., 2014).

**2.4.2. Principal component analysis/absolute principal component scores (PCA/APCS)**

**receptor model**

The PCA/APCS model was applied to quantitatively analyze the sources of heavy metals in PM\(_{2.5}\) for this study. Detailed descriptions of the receptor model have been presented in other studies (Kothai et al., 2008; Thurston and Spengler, 1985). In brief, PCA was based on the dimension reduction algorithm for a smaller set of factors that retain most of the information in the original data set. Each factor explains the maximum total variance of the data set and this set is completely uncorrelated with the rest of the data. In this study, those main components with a cumulative contribution rate \(\geq 85\%\) were selected. Factor loadings determined the more representative heavy metals in each factor, and the elements with factor loadings \(>0.5\) were interpreted as fingerprints of emission source.
Absolute principal component scores (APCS) technique combined with multiple linear regression models were used to estimate source contributions of each pollutant (Guo et al., 2004; Kothai et al., 2008). The first step in APCS is the normalization of all species concentrations as

\[ Z_{ik} = (C_{ik} - \bar{C}_i) / \sigma_i \quad (2) \]

where \( C_{ik} \) is the concentration of heavy metal \( i \) in sample \( k \); \( \bar{C}_i \) is the arithmetic mean concentration of heavy metal \( i \); and \( \sigma_i \) is the standard deviation of heavy metal \( i \) for all samples included in the analysis.

The APCS was evaluated by adding an artificial sample with all the elemental concentrations equal to zero. Because the factor scores obtained from PCA are based on standardized data, with a mean of zero and standard deviation equal to unity the true zero for each factor score should be calculated as

\[ (Z_0)_i = (0 - \bar{C}_i) / \sigma_i = -\bar{C}_i / \sigma_i \quad (3) \]

The factor scores of the heavy metals are obtained from PCA by analysis of normalized heavy metals concentrations. The APCS for each component is then estimated by subtracting the factor scores for this artificial sample from the factor scores of each true sample.

Finally regression was used to derive the source contributions, expressed as

\[ M_i = (b_0)_i + \sum APCS_p \times b_{pi}, \quad p = 1, 2, ..., n. \quad (4) \]

where \( M_i \) is the sum of the mass concentrations of heavy metals in sample \( i \) (Song et al., 2006), \( (b_0)_i \) is contribution made by sources unaccounted for in the PCA, \( b_{pi} \) is the coefficient of multiple regression of the source \( p \) for heavy metal \( i \), and \( APCS_p \) is the rotated absolute component score for source \( p \) in sample \( i \). \( APCS_p \times b_{pi} \) is the mass contribution in sample \( i \) made by source \( p \). The mean of \( APCS_p \times b_{pi} \) of all samples represents the average contribution of the sources.
To achieve stable PCA results, the sample number must greatly exceed the number of selected species (Guo et al., 2004; Thurston and Spengler, 1985). In this study, we used the samples from a whole year to estimate source contributions.

2.4.3. Health risk assessment

The carcinogenic and non-carcinogenic health risks via the inhalation exposure of heavy metals attached to PM$_{2.5}$ were calculated according to US EPA human health risk assessment models (EPA, 2009a). The process for estimating health risk involves the following three steps:

(1) Estimating Exposure Concentrations

The exposure concentration (EC) via inhalation is calculated by the following equation (EPA, 2009b):

$$ EC = \frac{(CA \times ET \times EF \times ED)}{AT} $$  \hspace{1cm} (5)

where EC is exposure concentration, $\mu$g m$^{-3}$; CA is the 95% upper confidence limit (UCL) of the log-transformed data because most-studied heavy metals approximated lognormal distributions, $\mu$g m$^{-3}$ (Li et al., 2016); ET is exposure time, assumed to be 24 hours/day; EF is the exposure frequency, assumed to be 350 days/year; ED is the exposure duration, assumed to be 6 years for children and 24 years for adults; AT is the averaging time, assumed to be ED $\times$ 365 days/year $\times$ 24 hours/day for non-carcinogens and 70 years $\times$ 365 days/year $\times$ 24 hours/day for carcinogens.

(2) Non-carcinogenic risk assessment

After the EC values were calculated, the non-carcinogenic risk was determined for each metal by calculating the hazard quotient (HQ) (Eq. 6):

$$ HQ = \frac{EC}{(RfC \times 1000 \mu g/mg)} $$  \hspace{1cm} (6)

where HQ is hazard quotient; EC is exposure concentration ($\mu$g m$^{-3}$); RfC is the inhalation
reference concentration (mg m$^{-3}$),

The Hazard Index (HI), which is the sum of the Hazard Quotients for each metal, estimates the total non-carcinogenic risk of mixed heavy metal contaminates.

An HQ and/or HI value $\leq$1 indicates unlikely non-carcinogenic effects. Conversely, values $>$1 indicate that there is a greater chance of non-carcinogenic effects (EPA, 2009b; Li et al., 2013).

(3) Carcinogenic risk assessment

The carcinogenic risk (CR) exposed via the inhalation pathway can be estimated with the following equation (EPA, 2009b):

$$ CR = IUR \times EC $$  \hspace{1cm} (7)

where IUR is inhalation unit risk ($\mu$g m$^{-3}$)$^{-1}$.

The tolerable risk for regulatory purposes ranges from $10^{-6}$ (1 in 1,000,000) to $10^{-4}$ (1 in 10,000) (Ferreira-Baptista and De Miguel, 2005).

The International Agency for Research on Cancer (IARC) classifies As, Cd, Cr(VI) and Ni as well-known human carcinogens (Group 1) via the inhalation route of exposure (Tian et al., 2010). In this study, we assumed that 20% of the measured Cr was in the toxic hexavalent form (Tian et al., 2010). The exposure factors for these models and the RfC and IUR were from the integrated risk information system (IRIS) and the US EPA Regional Screening Levels (RSL). We did not discuss Sb and Tl because their RfC was unavailable.

3. Results and discussion

3.1. Concentration of PM$_{2.5}$
The average annual and seasonal concentrations of PM$_{2.5}$ during the sampling period were summarized in Table 1. The annual average mass concentration of PM$_{2.5}$ was 62.7 ± 35.8 µg m$^{-3}$ during the sampling period, much higher than the limit of annual concentration of PM$_{2.5}$ according to the Chinese NAAQS (GB3095-2012), which is 35 µg m$^{-3}$ annually (Ministry of Environmental Protection, China, 2012) and World Health Organization (WHO) air quality guidelines (10 µg m$^{-3}$). The levels of PM$_{2.5}$ in Ningbo were lower than those in China cities like Shijiazhuang (139 µg m$^{-3}$) (Xie et al., 2019), Xi’an (108 µg m$^{-3}$) (Dai et al., 2018), Xinxiang (94 µg m$^{-3}$) (Yang et al., 2019), Beijing (83 µg m$^{-3}$) (Ji et al., 2019), Fuzhou (27 µg m$^{-3}$), Xiamen (28 µg m$^{-3}$) (Fu et al., 2018), Nanjing (55 µg m$^{-3}$) (Nie et al., 2018) and Chengdu (57 µg m$^{-3}$) (Qiu et al., 2019. The annual average concentration of PM$_{2.5}$ in this study was unexpectedly lower than the value (96.2 µg m$^{-3}$) of one rural site of Ningbo (Ming et al., 2017). The reason may attribute to regional pollution events that overwrote the local background with no known emission sources surrounding the area.

The variation in the seasonal concentration of PM$_{2.5}$ is displayed in Table 1 and the variation of the monthly concentration is shown in Fig. 2. The concentrations of PM$_{2.5}$ were highest in winter and lowest in summer with average concentrations of 94.8 and 39.6 µg m$^{-3}$, respectively. High coal consumption and low boundary layer height (BLH) may contribute to the high PM$_{2.5}$ concentrations in winter (Zhao et al., 2009). In the summer, less coal and biomass burning, more particle dispersion, and better deposition conditions can contribute to lower PM$_{2.5}$ concentrations (Guinot et al., 2006). Similar seasonal trends have also shown in other cities like Beijing (Duan et al., 2012; Zhao et al., 2009), Chengdu (Li et al., 2016), Shanghai, Nanjing and Hangzhou (Ming et al., 2017).
3.2. Concentrations and seasonal variation of heavy metal components in PM$_{2.5}$

The concentrations of 9 heavy metals found in PM$_{2.5}$ are shown in Table 1 and Fig. 3. The annual average concentrations of Be (0.01 ng/m$^3$) and Hg (0.02 ng/m$^3$) were very small and were not included in Table 1 and the following analysis. The annual average concentrations of Pb, Cd and As were 57.2 ng m$^{-3}$, 1.5 ng m$^{-3}$, 4.7 ng m$^{-3}$, respectively, which were below the limits of NAAQS (500, 5 and 6 ng m$^{-3}$, respectively) (China, 2012). The average concentrations of Mn and Ni were 35.6 ng m$^{-3}$ and 4.2 ng m$^{-3}$, respectively, but as of today, there are no national standard for atmospheric Mn and Ni in China. However, the concentration of Mn and Ni were lower than the WHO guideline limits (150 ng m$^{-3}$ and 25 ng m$^{-3}$) (WHO, 2000). The annual average concentrations of Sb and Tl were 4.1ng m$^{-3}$ and 0.5ng m$^{-3}$, respectively, which, to our knowledge, had been rarely assessed in mainland China. The concentration of Sb and Tl in Ningbo were close to that in Mexico (4.6 ng m$^{-3}$ and 0.6 ng m$^{-3}$, respectively) (Saldarriaga-Norena et al., 2009).

As for seasonal variation, As, Cd, and Se exhibited highest concentrations during the winter. The highest concentrations of Sb and Pb were observed during autumn. These may relate to increased manmade emissions sources like biomass burning, coal combustion for heating demand in winter and autumn. Furthermore, unfavorable meteorological conditions (i.e. temperature inversions and low wind speed) also inhibit pollutants dispersion in these two seasons. The highest concentration of Cr and Ni were observed in summer, suggesting their sources were different from other elements. No clear seasonal trend was observed for Mn.

3.3. Analysis on enrichment factors

The calculated EF results for heavy metals are displayed in Fig. 4. These EFs can be
categorized into three types, as follows: (1) the upper continental crustal material with an EF value < 1, (2) anthropogenic elements with an EF value > 10, and (3) mixed source elements with an EF value between 1 and 10 (Chen et al., 2015). The EFs of Sb, Cd, Pb, and Se for the four seasons and EFs of As and Tl during autumn and winter were much higher than 10, indicating these elements mainly originate from anthropogenic sources. The EFs of Cr and Ni for all four seasons and EFs of As and Tl during spring and summer were between 1 and 10, indicating their mixed source.

3.4. Principal component analysis/absolute principal component scores (PCA/APCS) in source appointment

To further explore PM$_{2.5}$ sources and quantify their contributions, the PCA/APCS model was used. Four principal components (PC) were extracted by principle component analysis (PCA) (Table 2), accounting for over 88% of the explained variance. Generally, the sources can be identified by fingerprint elements of sources. The PCA results showed that PC 1 had high loadings of Se, As, Cd and Pb with the maximum percentage of variance (47.65%). Pb and Cd are fingerprint elements of automobile exhaust (Fang et al., 2010). The elements, As and Se are often used as specific tracers of coal in China (Duzgoren-Aydin, 2007; Ge et al., 2004; Kang et al., 2011). Consequently, PC 1 was a mixed source of coal combustion and motor vehicle exhausts. PC 2 mainly consisted of Ni and Cr with 16.5% of the total variance, which were recommended as fingerprints for metal processing industry, especially for steel works (Chen et al., 2016; Chen et al., 2014; Kuang et al., 2004). PC 3 showed a high loading of Mn and explained 12.8% of the total variance. Mn concentration closely tracks dust and indicates a soil and construction dust source (Duan et al., 2012; M. et al., 2010). PC 4 showed high loading of Sb
with 11.1% of the total variance that was commonly attributed to industrial effects (Hashimoto et al., 1994).

Multiple linear regression (MLR) of APCS showed the contributions of each source for the total heavy metals in PM$_{2.5}$ (Fig. 5). The maximum contribution of 46.3% was from a mixed source of coal combustion and motor vehicle exhaust. The urban area of Ningbo is characterized by high vehicular traffic daily. Coal is still the major energy source in Ningbo. The soil and construction dust contributed 37.1%. Tremendous construction activities including subway building made the uncovered soil may be blown into the air by wind. The contribution from steel works and other industry was 6.9% and 6.8%, respectively. The industries also contributed to the air pollution in Ningbo.

3.5. Risk assessment of heavy metals exposure to human health

PM$_{2.5}$-bound heavy metals can enter into the human body via inhalation and pose a threat to human health. As indicated in Table 3, the non-carcinogenic risks occurred from highest to lowest in the following order: Mn > As > Ni > Cd > Cr(VI) > Se. HQ values of every single toxic metal were lower than the safe level (HQ=1). However, the HI value (1.38) was higher than the safe level, indicating more attention should be paid to the accumulative non-carcinogenic risks to local residents. The HI value was lower than that in Chengdu (HI=7.96) (Li et al., 2016) and Nanjing (HI=1.86) (Sun et al., 2014)

After non-carcinogenic risks were assessed, carcinogenic risks were evaluated. Cr (VI) imposed the highest carcinogenic risk followed by As, Cd, Ni and Pb. The carcinogenic risk of Cr (VI) and As were higher than $1 \times 10^{-6}$, but below the acceptable level ($1 \times 10^{-4}$). The total carcinogenic risk reached $2.50 \times 10^{-5}$ for adults and $6.24 \times 10^{-6}$ for children, both being higher
than $1 \times 10^{-6}$ but within the acceptable level, indicating that the carcinogenic risk posed by the heavy metals to both children and adults was acceptable in Ningbo. In addition, carcinogenic substances posed greater cancer risk for adults than children. Compared to results in other cities in China, the carcinogenic values were lower than Nanjing (Sun et al., 2014) and Chengdu (Li et al., 2016), but higher than Tianjin (Chen et al., 2015).

4. Conclusion

The annual average mass concentration for PM$_{2.5}$ was higher than the annual limit in the NAAQS. The annual average concentrations of Pb, Cd and As were below the annual limits of the NAAQS and the concentrations of Mn and Ni were lower than the WHO guidelines. The concentrations of PM$_{2.5}$ and the studied heavy metals displayed significant seasonality. The concentrations of PM$_{2.5}$ were the highest in winter and the lowest in summer. As, Cd, and Se exhibited highest concentrations during winter while the highest concentrations of Sb and Pb were observed during autumn. The enrichment factor values for heavy metals indicated that Sb, Cd, Pb, and Se in all four seasons and As and Tl in autumn and winter originated from anthropogenic sources. Source apportionment by PCA/APCS indicated four major sources: coal combustion and motor vehicle (46.3%), soil and construction dust (37.1%), steel works (6.9%), and other smelting industries (6.8%).

The total carcinogenic risk of heavy metals in Ningbo was lower than safe level while the total non-carcinogenic risk was higher than the safe level. Government departments should implement more strict and effective measures to control air pollution in Ningbo, such as changing traditional energy use to clean energy, improving the vehicle exhaust limits, sprinkling
water regularly on roads and construction sites. Additionally, more research is needed to understand the non-carcinogenic risks that the population exposed to PM$_{2.5}$ may experience.

**Conflict of interest statement:** The authors declare no conflict of interest.

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**References**


Supplemental Guidance for Inhalation Risk Assessme).


Table 1 Average concentration of PM$_{2.5}$ and heavy metals in Ningbo, March 2015 – February 2016.

<table>
<thead>
<tr>
<th></th>
<th>Spring ( March to May ) (n=24)</th>
<th>Summer ( June to August ) (n=24)</th>
<th>Autumn ( September to November ) (n=24)</th>
<th>Winter ( December to next February ) (n=24)</th>
<th>Annual (n=96)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$ (µg m$^{-3}$)</td>
<td>54.2 ± 21.5</td>
<td>39.6 ± 14.4</td>
<td>74.8 ± 29.3</td>
<td>94.8 ± 45.6</td>
<td>62.7 ± 35.8</td>
</tr>
<tr>
<td>Sb (ng m$^{-3}$)</td>
<td>3.8 ± 2.3</td>
<td>3.1 ± 1.5</td>
<td>5.1 ± 2.6</td>
<td>5.0 ± 4.0</td>
<td>4.1 ± 2.8</td>
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<tr>
<td>As (ng m$^{-3}$)</td>
<td>4.3 ± 1.9</td>
<td>3.2 ± 1.4</td>
<td>5.0 ± 2.6</td>
<td>7.0 ± 4.5</td>
<td>4.7 ± 3.1</td>
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<tr>
<td>Cd (ng m$^{-3}$)</td>
<td>1.2 ± 0.6</td>
<td>1.1 ± 0.5</td>
<td>1.7 ± 0.6</td>
<td>2.1 ± 1.5</td>
<td>1.5 ± 1.0</td>
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<tr>
<td>Cr (ng m$^{-3}$)</td>
<td>2.1 ± 1.2</td>
<td>5.0 ± 3.0</td>
<td>2.5 ± 1.7</td>
<td>3.3 ± 2.4</td>
<td>3.4 ± 2.5</td>
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<tr>
<td>Pb (ng m$^{-3}$)</td>
<td>51.6 ± 21</td>
<td>40.6 ± 19.9</td>
<td>74.9 ± 38.6</td>
<td>72.3 ± 40.5</td>
<td>57.2 ± 32.9</td>
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<tr>
<td>Mn (ng m$^{-3}$)</td>
<td>36.6 ± 11.1</td>
<td>37.4 ± 15.4</td>
<td>31.6 ± 9.3</td>
<td>34.8 ± 16.7</td>
<td>35.6 ± 13.9</td>
</tr>
<tr>
<td>Ni (ng m$^{-3}$)</td>
<td>4.0 ± 2.4</td>
<td>5.5 ± 3.2</td>
<td>3.3 ± 2.1</td>
<td>3.2 ± 1.8</td>
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<tr>
<td>Se (ng m$^{-3}$)</td>
<td>3.0 ± 1.5</td>
<td>3.2 ± 1.8</td>
<td>4.7 ± 2.3</td>
<td>5.7 ± 3.4</td>
<td>4.0 ± 2.6</td>
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<tr>
<td>Tl (ng m$^{-3}$)</td>
<td>0.3 ± 0.1</td>
<td>0.3 ± 0.2</td>
<td>0.7 ± 0.3</td>
<td>0.8 ± 0.5</td>
<td>0.5 ± 0.4</td>
</tr>
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Table 2 Principal Component Analysis (PCA) with varimax rotation for all PM$_{2.5}$ data from Ningbo.

<table>
<thead>
<tr>
<th>Element</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
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</thead>
<tbody>
<tr>
<td>Sb</td>
<td>0.4780</td>
<td>0.010</td>
<td>0.289</td>
<td>0.735</td>
</tr>
<tr>
<td>As</td>
<td>0.886</td>
<td>-0.066</td>
<td>0.008</td>
<td>0.290</td>
</tr>
<tr>
<td>Cd</td>
<td>0.845</td>
<td>0.022</td>
<td>0.279</td>
<td>0.281</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.005</td>
<td>0.777</td>
<td>0.263</td>
<td>-0.358</td>
</tr>
<tr>
<td>Pb</td>
<td>0.855</td>
<td>-0.056</td>
<td>0.287</td>
<td>0.284</td>
</tr>
<tr>
<td>Mn</td>
<td>0.265</td>
<td>0.199</td>
<td>0.898</td>
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<td>0.907</td>
<td>0.005</td>
<td>0.223</td>
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<td>Se</td>
<td>0.926</td>
<td>-0.028</td>
<td>0.112</td>
<td>-0.028</td>
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<td>Tl</td>
<td>0.945</td>
<td>-0.071</td>
<td>0.148</td>
<td>0.095</td>
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<td>% of Variance</td>
<td>47.65</td>
<td>16.45</td>
<td>12.82</td>
<td>11.11</td>
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<tr>
<td>Cumulative %</td>
<td>47.65</td>
<td>64.09</td>
<td>76.92</td>
<td>88.02</td>
</tr>
<tr>
<td>Source</td>
<td>Coal combustion and motor vehicle exhaust</td>
<td>Steel works</td>
<td>soil and construction dust</td>
<td>Other smelting industries</td>
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Table 3 Carcinogenic and non-carcinogenic risks from toxic elements in PM$_{2.5}$

<table>
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<tr>
<th>Element</th>
<th>RfC$_i$ (mg m$^{-3}$)</th>
<th>IUR ($\mu$g m$^{-3}$)$^{-1}$</th>
<th>Non-carcinogenic Children</th>
<th>Non-carcinogenic Adults</th>
<th>Carcinogenic Children</th>
<th>Carcinogenic Adults</th>
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<td>As</td>
<td>1.50E-05</td>
<td>4.30E-03</td>
<td>2.87E-01</td>
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<td>6.35E-06</td>
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<td>Cd</td>
<td>1.00E-05</td>
<td>1.80E-03</td>
<td>1.34E-01</td>
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<td>2.06E-07</td>
<td>8.26E-07</td>
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<tr>
<td>Cr (VI)</td>
<td>1.00E-04</td>
<td>8.40E-02</td>
<td>5.99E-03</td>
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<td>4.31E-06</td>
<td>1.73E-05</td>
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<td>Mn</td>
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<td>5.45E-08</td>
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<td>2.67E-01</td>
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<td>7.69E-08</td>
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<td>6.24E-06</td>
<td>2.50E-05</td>
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</tbody>
</table>
**Figure captions**

Fig.1. PM$_{2.5}$ sampling site (the red star) in Ningbo

Fig.2. Monthly variation of PM$_{2.5}$ concentrations in Ningbo

Fig.3. Seasonal concentration of elements found in PM$_{2.5}$ in Ningbo

Fig.4. Seasonal variation of enrichment factors for elements in Ningbo.

Fig.5. Source contributions of heavy metals found in PM$_{2.5}$ in Ningbo.