Characteristics and Health Risks of PM$_{2.5}$-bound Metals in a Central City of Northern China: A One-year Observation Study

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ABSTRACT

Metals are important components of PM$_{2.5}$, with significant implications for the ecological environment and human health. This study comprehensively investigated the characteristics of 19 metals in PM$_{2.5}$ samples collected in Jinan from 16 December 2020 to 15 December 2021. The total concentration of the studied metals accounted for 5.3% of PM$_{2.5}$ (41.7 µg m$^{-3}$) in Jinan. The seasonal variation of PM$_{2.5}$-bound metals followed the order of spring (3.5 µg m$^{-3}$) > winter (2.2 µg m$^{-3}$) > summer (1.4 µg m$^{-3}$) > autumn (1.1 µg m$^{-3}$). Four sources could be extracted using the positive matrix factorization (PMF) model, namely resuspended dust (51.9%), oil combustion (19.9%), factories (16.5%), and traffic emissions (11.7%). According to the results of the enrichment factor (EF) and geo-accumulation (I$_{geo}$), Se, Sb, Tl, Ag, Cd, Zn, V, Pb, and Mo were mainly from anthropogenic sources, which was consistent with the PMF results. Applying the conditional bivariate probability function (CBPF), traffic emissions were found to be the main local contributor, with large contributions when the wind speed was lower than 2 m s$^{-1}$. The environmental influence of PM$_{2.5}$-bound metals was evaluated in terms of the ecological risk index, which was found to be higher than 600, indicating high ecological risk in Jinan. Regarding the human health risk, children were possibly more exposed to non-carcinogenic risks than adults, with hazard index (HI) values of 47.9 and 6.7, respectively. Moreover, the residents of Jinan were also exposed to moderate carcinogenic risk (children: $4.8 \times 10^{-5}$, adults: $4.9 \times 10^{-5}$), with Cr(VI), Pb, and Co as the dominant high-risk metals. Therefore, PM$_{2.5}$-bound metal pollution in Jinan cannot be overlooked, and appropriate measures should be implemented.

Keywords: Metal pollution, Ecological risk, Anthropogenic sources, Human health risk, Oral ingestion

1 INTRODUCTION

With their negative implications for public health and air quality, atmospheric particles have attracted the attention of numerous researchers (Peng et al., 2021; Zhang and Aikawa, 2023; Zhang et al., 2024). In particular, the dominant type of atmospheric particles during haze events is PM$_{2.5}$, which comprises particulate matters with aerodynamic diameters no larger than 2.5 µm (Guo et al., 2022). Possessing a considerable surface area, PM$_{2.5}$ can carry poisonous substances such as metals, viruses, and bacteria, aiding in the entry of these harmful substances into the...
circulatory system of the human body (Guo et al., 2021). Among particle-bound metals, Co, Pb, Cr(VI), and Cd are classified as carcinogens (IARC, 2016). Specifically, Cd may cause malformations in newborns and kidney damage to humans (Xie et al., 2020). High concentrations of Pb may lead to developmental disorders and intellectual impairment in children (Zhang et al., 2018). High levels of Ni in PM2.5 can lead to cardiovascular diseases, respiratory diseases, and even cancer in people over the age of 65 (Guo et al., 2021). In addition to these carcinogens, other typical metals (Se, Mo, Sb, V, Zn, Mn, Cu, etc.) are also of serious concern (Wang et al., 2018; Zhang et al., 2019; Liu et al., 2021; Zhang et al., 2021b).

To minimize the risks posed by PM2.5-bound metals, an important requisite is to identify their natural and anthropogenic sources. Zhang et al. (2023) conducted six-year PM2.5 field sampling at 100 survey sites in Japan, the results showed that ship emissions, industrial emissions, biomass burning, and coal combustion were the most important pollution sources, and the high risk metals included As, Sb, Pb, V, and Cr(VI). Hieu and Lee (2010) carried out particle sampling in Ulsan, Korea, and reported three primary sources of particle-bound metals, namely crustal dust (Fe, Al, Mg, K, and Na), automobile exhaust (Pb, Cr, Cd, Zn, and Ni), and industrial emissions (Pb, Fe, and Mn). Cheng et al. (2015) found that automobile exhaust was the largest contributor of particle-bound metals in Hong Kong, with Pb, Ni, and V serving as markers of combustion processes. Wang et al. (2018) confirmed that factories and coal combustion were the primary sources of particle-bound metals in Shandong province, especially in Jinan. Gu et al. (2014) performed positive matrix factorization (PMF) analysis for the sources of particle-bound metals in Jinan and indicated significant contributions of soil dust to Al, Ca, and Fe concentrations. Liu et al. (2020) reported soil dust as the largest contributor to particle mass, followed by industrial emissions, traffic emissions, and biomass burning.

Jinan, the capital city of Shandong province, is a historical and cultural center in the North China Plain (NCP), with industrial clusters located in the eastern regions and mountains in the south. Under the influence of the continental monsoon climate, Jinan experiences hot, humid summers and dry, chilly winters. According to the annual statistical report of 2021, the use of coal and gasoline was 2511.4 and 0.4 million tons, with a cumulative yearly increase of 2.0% and 4.3%, which may be one of the factors driving the occurrence of heavy pollution events (Jinan Statistical Yearbook, 2021). Although previous studies have investigated heavy metal pollution in this area, the focused only on typical pollutants, and the comprehensive risk of PM2.5-bound metals in Jinan remain unclear. In this study, 19 metals were investigated for an entire year, and the source contributions, ecological risks, and human health risks were comprehensively analyzed. The results will provide a scientific basis for the control of PM2.5-bound metals in Jinan and give lessons for other cities, which had similar conditions as Jinan, worldwide.

2 METHODS

2.1 Sampling

The sampling site of PM2.5 is located at the Keji (Sci-Tech) Building of Shandong Jianzhu University, as shown in Fig. 1. It is in the commercial and residential region of eastern Jinan, which has crowded trunk roads to the north and a refining and chemical company located 3 km northwest. The site has a complex surrounding environment, jointly affected by traffic emissions, and industrial and human activities. PM2.5 samples were captured using a mid-flow sampler (TH-16A, Wuhan Tianhong Instruments, China) with a flow rate of 100 L min⁻¹ from 16 December 2020 to 15 December 2021. Specifically, the samples were collected on quartz microfiber filters (diameter of 88 mm, Whatman). The sampling was set to begin at 8:30 am and end at 7:30 am the following day, reflecting a temporal resolution of 23 h. Field blanks were collected every 15 days. And the sampler was cleaned, and the flow rate of the sampler was calibrated prior to use.

The sampling seasons were divided according to the ambient temperature method (Ma et al., 2020). In this method, seasons are defined by the average temperature of each 5 consecutive days. Specifically, spring begins when the average temperature rises steadily from below 10°C to above 10°C. Summer begins when the average temperature steadily increases to above 22°C. Autumn begins when the average temperature drops steadily from above 22°C to below 22°C. And winter begins when the average temperature steadily decreases to below 10°C. For sampling
periods with unfavorable conditions, including rain and snow, power outages, and machine failures, a total of 264 samples had been covered for the entire study period (49 in spring, 81 in summer, 41 in autumn, and 93 in winter), and the samples were stored in freezers at –20°C for subsequent analysis. Meteorological parameters including the ambient temperature, wind speed, and wind direction were measured using an automatic meteorological station.

2.2 Chemical Analysis

In this study, 19 metals were investigated, namely Fe, Al, Se, V, Zn, Mn, Ti, Tl, Sb, Pb, Cr, Cu, Ba, Ni, Li, Cd, Mo, Co, and Ag. First, 1/8 of each sample was digested using a 10 mL acid mixture (55.5 mmol L⁻¹ HNO₃ and 167.5 mmol L⁻¹ HCl) in an ultrahigh throughput microwave digestion system (MARSXpress, CEM, Matthews, NC) at 200°C for approximately 45 min. Thereafter, the solution was cooled to indoor temperature (25°C) and then filtered. The mass concentrations of metals were finally measured by inductively coupled plasma mass spectrometry (Agilent 7800 ICP-MS, Agilent Technologies, USA). The ICP-MS instrument was calibrated using a multi-element standard under the guidance of the instrument manual. The Standard Reference Material 1648 ‘Urban Particulate Matter’ (Gaithersburg, MD, USA) was applied to validate the methods (Gao et al., 2014). The multi-element standard samples were diluted from the stock standards (Merck). Calibration curves were established by measuring the multi-element standard samples with the concentrations of 1, 2, 5, 10, 20, and 50 ng mL⁻¹, respectively. The correlation coefficient for each element was found to be larger than 0.999. To ensure data accuracy, one standard sample with a specific concentration was added every 50 samples during the measurement. The recovery of all studied metals was within the range of 79%–102%. The blank samples were subjected to the same procedure, and none of the studied metals were detected in the blank samples.

2.3 Data Analysis

2.3.1 Enrichment factor (EF) and geo-accumulation index (Igeo)

In this study, the enrichment factor (EF) method was applied to distinguish between metals from natural and anthropogenic sources (Luo et al., 2015). The calculation formula is as follows:
\[
EF = \frac{\left(\frac{C_{\text{sample}}^i}{C_{\text{ref}}^i}\right)}{\left(\frac{C_{\text{crust}}^i}{C_{\text{crust}}^{ref}}\right)}
\]

where \(\left(\frac{C_{\text{sample}}^i}{C_{\text{ref}}^i}\right)\) indicates the concentration ratio of the \(i\)th metal to the reference metal in the PM\(_{2.5}\) sample, and \(\left(\frac{C_{\text{crust}}^i}{C_{\text{crust}}^{ref}}\right)\) is the corresponding ratio in the earth crust. The reference metal was Ti (Zhang et al., 2019). Three clusters were identified: (1) \(EF < 10\) indicating natural sources; (2) \(EF > 100\) indicating anthropogenic sources; (3) \(10 < EF < 100\) indicating mixed sources (Cui et al., 2020; Juda-Rezler et al., 2020).

Geo-accumulation index (\(I_{\text{geo}}\)) was applied to analyse the pollution levels of metals by drawing a comparison between metal concentrations in PM\(_{2.5}\) and the background levels (Censi et al., 2017). \(I_{\text{geo}}\) is expressed as follows (Zhi et al., 2021):

\[
I_{\text{geo}} = \log_2 \left( \frac{C_{\text{sample}}^i}{1.5 \times C_{\text{crust}}^i} \right)
\]

where \(C_{\text{sample}}^i\) and \(C_{\text{crust}}^i\) have the same meanings as in Eq. (1). The constant factor 1.5 is the matrix correction value for regional background difference (Gujre et al., 2021). The contamination degree of metals can be classified into three levels from uncontaminated to severely contaminated (< 0: uncontaminated; 0–5: moderately contaminated; > 5: severely contaminated) (Wei et al., 2015).

### 2.3.2 Positive matrix factorization analysis

The positive matrix factorization (PMF) model (version 5.0, EPA) was used to identify the source contributions of atmospheric particles (Song et al., 2006). The datasets were composed of 264 rows (samples dating from 16 December 2020 to 15 December 2021) and 19 columns (element concentrations). One hundred bootstrap runs were performed to test the stability and uncertainty of the base run solution. Four to seven factors were tested, and the optimal diagnosis result was reached with four factors. For the concentration of the metals, it was set to 0 if less than the method determination limit. Data uncertainty (Unc) can be calculated using the following equations.

\[
Unc = \frac{5}{MDL} (\text{Con.} \leq \text{MDL})
\]

\[
Unc = \sqrt{\text{Error Fraction} \times \text{Con.}}^2 + (\text{MDL})^2 (\text{Con.} > \text{MDL})
\]

where Con. is the concentration of the specific metal, and MDL is the method determination limit, which was 0.09 ng m\(^{-3}\) for each of the metals in this study. The error fraction was set to 0.1 (Gao et al., 2014).

### 2.3.3 Conditional bivariate probability function (CBPF)

Along with PMF, the conditional bivariate probability function (CBPF) was applied using the Openair package for R language in RStudio software (Carslaw and Ropkins, 2012) to further evaluate the pollution possibility from the target sources under different wind directions and wind speeds. CBPF analysis was conducted by combining meteorological data with PMF source apportionment results, for which the 75th percentile value was set as the threshold (Mijic et al., 2012; Hui et al., 2021). The possibility is defined as follows (Squizzato et al., 2017; Hui et al., 2021):

\[
\text{CBPF}_{\Delta \theta, \Delta u} = \frac{m_{\Delta \theta, \Delta u}}{n_{\Delta \theta, \Delta u}}
\]
where $\Delta \theta$, $\Delta u$ describes the wind speed and wind direction intervals, $n_{\Delta \theta, \Delta u}$ represents the number of samples exceeding the threshold value in the wind direction intervals $\Delta \theta$ and $\Delta u$; $n_{\Delta \theta, \Delta u}$ represents the total number of samples for the same wind direction and speed interval.

### 2.3.4 Ecological risk

The ecological risk index (RI), which is based on the abundance and release capacity of metals, was applied to assess the influence of metals on the environment (Gujre et al., 2021). The value of RI was calculated using the following equations (Hakanson, 1980):

$$RI = \sum_{i=1}^{m} E_i^i \quad (6)$$

$$E_i^i = T_i^i \times \frac{C_{sample}^i}{C_{crust}^i} \quad (7)$$

where $E_i^i$ and $T_i^i$ are the potential ecological risk coefficient and toxic response factor of the $i$th metal. Detailed information is provided in Tables S1 and S2 (Chen et al., 2020; Gujre et al., 2021).

### 2.3.5 Human health risk assessment

Residents are vulnerable to risks associated with long-term exposure to PM$_{2.5}$-bound metals. According to Table S3, children have been exposed for 6 years and adults for 24 years (U.S. EPA, 2011a; Duan et al., 2021). The exposure poses risks to human health, including both non-carcinogenic risk and carcinogenic risk. The exposure primarily occurs through three pathways: deposited on ingestible substances for oral ingestion, direct inhalation, and adhesion and then absorption by the skin (Liu et al., 2019; Zhang et al., 2021b). Considering the different sensitivities of adults and children, the population was further divided into two groups in the analysis.

The population exposure dose was first calculated by applying the Human Health Assessment Model and Assessment Guidelines of the United States Environmental Protection Agency (USEPA 2011a). The exposure doses through oral ingestion (CDI$_{ing}$, mg kg$^{-1}$ day$^{-1}$), inhalation (EC$_{inh}$, $\mu$g m$^{-3}$), and dermal contact (DAD$_{der}$, mg kg$^{-1}$ day$^{-1}$) were calculated using the following equations (U.S. EPA, 2011a; Liu et al., 2019; Zhang et al., 2021b):

$$CDI_{ing} = C_{95\%} \times \frac{ING \times EF \times ED \times CF}{BW \times AT} \quad (8)$$

$$EC_{inh} = C_{95\%} \times \frac{ET \times EF \times ED}{AT_6} \quad (9)$$

$$DAD_{der} = C_{95\%} \times \frac{SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (10)$$

$$C_{95\%} = \exp \left( \ln X + 0.5 \times S_{\ln X} \times \frac{S_{\ln X} \times H_{95}}{\sqrt{n-1}} \right) \quad (11)$$

where $C_{95\%}$ represents the 95% upper confidence limit of metals in Jinan (the units of $C_{95\%}$ in Eqs. (8), (9), and (10) are mg kg$^{-1}$, $\mu$g m$^{-3}$, and mg kg$^{-1}$, respectively). Given PM$_{2.5}$ was able to enter the human body by being inhaled directly or deposited on the surface of the object through oral or dermal contact, the $C_{95\%}$ became different in the three routes. For oral ingestion and dermal contact, $C_{95\%}$ corresponds to the proportion of the metal concentrations to the mass concentration of PM$_{2.5}$, meanwhile for inhalation, $C_{95\%}$ corresponds to the PM$_{2.5}$-bound metal concentrations. In Eq. (11), $\ln X$ and $S_{\ln X}$ are the arithmetic mean and standard deviation of the
log-transformed concentration data, respectively; \( n \) is the number of samples; and \( H_{0.95} \) values depend on \( S_{lnX} \), \( n \) and the chosen confidence level (0.05) (Zhang et al., 2021b), which were referred from Gilbert (1987). The meaning of the parameters and the reference values in Eqs. (8)–(11) are described in Table S3 (U.S. EPA, 2011a).

The corresponding hazard quotient (HQ, for non-carcinogenic risk) and carcinogenic risk (CR) of PM_{2.5}-bound metals were evaluated using the following equations (U.S. EPA, 2011b; Zhang et al., 2018; Zhang et al., 2021b):

\[
HQ_{\text{ing}} = \frac{CDI_{\text{ing}}}{RfD_o}
\]

(12)

\[
HQ_{\text{inh}} = \frac{EC_{\text{inh}}}{RfC_i \times 1000}
\]

(13)

\[
HQ_{\text{der}} = \frac{DAD_{\text{der}}}{RfD_d \times GIABS}
\]

(14)

where \( HQ_{\text{ing}} \) is the hazard quotient through the pathway of oral ingestion for the non-carcinogenic risk, \( RfD_o \) (mg (kg day)^{-1}) is oral reference doses; \( HQ_{\text{inh}} \) represents the hazard quotient through the inhalation for the non-carcinogenic risk, \( RfC_i \) (mg m^{-3}) is inhalation reference concentration; \( HQ_{\text{der}} \) is the hazard quotient through the pathway of dermal contact for the non-carcinogenic risk, \( GIABS \) is gastrointestinal absorption factor.

\[
CR_{\text{ing}} = CDI_{\text{ing}} \times SF_O
\]

(15)

\[
CR_{\text{inh}} = EC_{\text{inh}} \times IUR
\]

(16)

\[
CR_{\text{der}} = DAD_{\text{der}} \times SF_O \times GIABS
\]

(17)

where \( CR_{\text{ing}} \), \( CR_{\text{inh}} \), and \( CR_{\text{der}} \) represent the carcinogenic risk through the three pathways, \( SF_O \) (mg (kg day)^{-1}) is oral slope factor and \( IUR \) (\( \mu g \) m^{-3}) is inhalation unit risk. The description and specific values of the parameters and the reference values in Eqs. (12)–(17) are described in Table S2 (U.S. EPA, 2011b).

The hazard index (HI), which is the sum of HQ, was used to estimate the non-carcinogenic risk. \( HQ > 1 \) or \( HI > 1 \) indicate significant risks (U.S. EPA, 2011a). The CR value reflects the possibility of humans suffering from cancer during their lifetime exposure to carcinogenic trace metals. CR values of < 10^{-6}, 10^{-6}–10^{-4}, 10^{-4}–10^{-2}, 10^{-2}–10^{-1}, and \( \geq 10^{-1} \) indicate very low, low, moderate, high, and very high risks, respectively (Hu et al., 2012; Zhang et al., 2021b).

3 RESULTS AND DISCUSSION

3.1 Annual and Seasonal Concentrations of PM_{2.5} and Metals

The annual concentration of PM_{2.5} was 41.7 \( \mu g \) m^{-3}, exceeding China’s National Ambient Air Quality Standards (NAAQS) of 35 \( \mu g \) m^{-3}. The PM_{2.5} concentration in Jinan was higher than that in Nanjing (41.1 \( \mu g \) m^{-3}), less than that in Hangzhou (46 \( \mu g \) m^{-3}), and much less than that in the Jing–Jin–Ji region, including Beijing, Tianjin, and Hebei (111.3, 230.7, and 149.9 \( \mu g \) m^{-3}) (Chen et al., 2017; Gao et al., 2018; Wu et al., 2019; Liu et al., 2020; Zhang et al., 2021a; Guo et al., 2022).

Seasonally, the highest and lowest concentrations of PM_{2.5} in Jinan were observed in winter and summer (54.4 and 28.7 \( \mu g \) m^{-3}), respectively, and intermediate levels were observed in spring and autumn (42.9 and 37.4 \( \mu g \) m^{-3}). The PM_{2.5} concentration being the highest in winter could be
explained by the low mixing layer height and poor atmospheric dispersion relative to other seasons (Hsu et al., 2016).

The annual concentration of all studied metals was 2.2 µg m⁻³, which accounted for 5.3% of PM2.5 (Table 1). Fe and Al were the dominant crustal metals, accounting for 51.9% and 18.2% of the total metals, respectively. Se, V, and Zn were also major metals, with concentrations of 177.4, 158.2 and 145.4 ng m⁻³, respectively. The concentrations of the other 14 metals were low, collectively accounting for only 9% of the total metals, and the concentration of 9 of these 14 metals, including Ba, Ni, Li, Cd, Mo, Co, and Ag, was no 10 ng m⁻³ each. As shown in Table 54, the concentrations of most major metals, including Fe, Al, V, and Zn, were much higher in Jinan than in the southern cities in China, including Shanghai, Nanjing, and Hangzhou (Chang et al., 2018; Wu et al., 2019; Guo et al., 2022), no matter the annual or winter average. The concentrations of Fe and Al showed much higher or similar results compared with other previous studies in the NCP, involving the results in summer in Beijing and Tianjin, the results in winter in Beijing, and the annual results in Baoding (Chen et al., 2017; Liu et al., 2020; Zhang et al., 2021a). But in these previous studies, the corresponding PM2.5 concentrations were at least twice higher than that in this study. Although the PM2.5 concentration level in Jinan was low, the relatively higher proportion of PM2.5-bound metals was the greatest concentration (3.5 µg m⁻³), and autumn (1.1 µg m⁻³). Fe and Al showed much higher or similar results compared with other cities showed that Jinan has a low PM 2.5 level, but equal or higher concentrations of PM2.5-bound metals. The comparisons indicated the relatively heavier contamination from their related emission sources remained quite stable throughout the year.

<table>
<thead>
<tr>
<th>Species</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
<th>Annual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1952.7 ± 1591.4</td>
<td>608.7 ± 271.4</td>
<td>565.8 ± 306.4</td>
<td>1457.1 ± 1146.9</td>
<td>1150.2 ± 1179.1</td>
</tr>
<tr>
<td>Al</td>
<td>747.5 ± 1171.1</td>
<td>223.4 ± 220.9</td>
<td>217.3 ± 64.1</td>
<td>461.9 ± 798.8</td>
<td>403.7 ± 726.3</td>
</tr>
<tr>
<td>Se</td>
<td>189.0 ± 18.1</td>
<td>163.3 ± 31.4</td>
<td>156.0 ± 7.9</td>
<td>193.2 ± 32.1</td>
<td>177.4 ± 31.2</td>
</tr>
<tr>
<td>V</td>
<td>167.1 ± 44.9</td>
<td>169.9 ± 42.2</td>
<td>141.5 ± 4.2</td>
<td>151.1 ± 26.4</td>
<td>158.2 ± 35.6</td>
</tr>
<tr>
<td>Zn</td>
<td>156.3 ± 89.1</td>
<td>94.0 ± 38.2</td>
<td>119.8 ± 46.3</td>
<td>209.1 ± 176.4</td>
<td>145.4 ± 117.7</td>
</tr>
<tr>
<td>Mn</td>
<td>83.7 ± 52.3</td>
<td>28.2 ± 25.8</td>
<td>26.4 ± 11.4</td>
<td>68.5 ± 44.3</td>
<td>52.4 ± 44.3</td>
</tr>
<tr>
<td>Ti</td>
<td>87.0 ± 70.6</td>
<td>19.8 ± 27.4</td>
<td>12.4 ± 6.9</td>
<td>60.4 ± 55.8</td>
<td>45.4 ± 54.8</td>
</tr>
<tr>
<td>Tl</td>
<td>34.9 ± 17.0</td>
<td>10.5 ± 12.0</td>
<td>0.1 ± 0.0</td>
<td>35.9 ± 30.8</td>
<td>21.3 ± 24.7</td>
</tr>
<tr>
<td>Sb</td>
<td>47.7 ± 45.6</td>
<td>9.0 ± 11.0</td>
<td>2.2 ± 1.1</td>
<td>25.4 ± 31.3</td>
<td>20.8 ± 31.6</td>
</tr>
<tr>
<td>Pb</td>
<td>1.3 ± 0.8</td>
<td>13.5 ± 14.5</td>
<td>22.8 ± 11.5</td>
<td>17.3 ± 23.9</td>
<td>14.1 ± 18.1</td>
</tr>
<tr>
<td>Cr</td>
<td>14.7 ± 6.6</td>
<td>11.5 ± 6.8</td>
<td>7.9 ± 4.4</td>
<td>13.6 ± 6.7</td>
<td>12.3 ± 6.7</td>
</tr>
<tr>
<td>Cu</td>
<td>10.7 ± 7.8</td>
<td>6.3 ± 4.0</td>
<td>8.4 ± 2.2</td>
<td>13.4 ± 11.3</td>
<td>10.0 ± 8.4</td>
</tr>
<tr>
<td>Ba</td>
<td>0.3 ± 0.2</td>
<td>6.1 ± 7.0</td>
<td>15.7 ± 5.8</td>
<td>6.5 ± 11.8</td>
<td>6.7 ± 9.2</td>
</tr>
<tr>
<td>Ni</td>
<td>9.0 ± 13.1</td>
<td>3.9 ± 3.6</td>
<td>2.9 ± 3.3</td>
<td>5.3 ± 4.1</td>
<td>5.2 ± 6.9</td>
</tr>
<tr>
<td>Li</td>
<td>3.4 ± 4.2</td>
<td>0.9 ± 0.9</td>
<td>0.7 ± 0.3</td>
<td>2.2 ± 2.7</td>
<td>1.8 ± 2.6</td>
</tr>
<tr>
<td>Cd</td>
<td>1.8 ± 1.2</td>
<td>0.8 ± 0.4</td>
<td>0.7 ± 0.3</td>
<td>1.8 ± 1.8</td>
<td>1.3 ± 1.3</td>
</tr>
<tr>
<td>Mo</td>
<td>1.5 ± 0.7</td>
<td>0.9 ± 0.4</td>
<td>0.7 ± 0.4</td>
<td>1.4 ± 1.0</td>
<td>1.1 ± 0.8</td>
</tr>
<tr>
<td>Co</td>
<td>1.7 ± 2.3</td>
<td>0.4 ± 0.5</td>
<td>0.3 ± 0.2</td>
<td>1.0 ± 1.6</td>
<td>0.8 ± 1.5</td>
</tr>
<tr>
<td>Ag</td>
<td>1.1 ± 1.3</td>
<td>0.4 ± 0.2</td>
<td>0.1 ± 0.0</td>
<td>1.0 ± 0.8</td>
<td>0.6 ± 0.8</td>
</tr>
<tr>
<td>PM2.5</td>
<td>3510.9 ± 2855.1</td>
<td>1380.5 ± 1012.5</td>
<td>1147.2 ± 293.8</td>
<td>2223.5 ± 1967.4</td>
<td>2215.1 ± 2008.5</td>
</tr>
</tbody>
</table>

Table 1. Seasonal and annual concentration of metals (ng m⁻³) and PM2.5 (µg m⁻³) (mean ± standard deviation).
3.2 Source Analysis

In this study, EF and Igeo were calculated to distinguish between anthropogenic and natural sources, as shown in Fig. 2. Ni, Mn, Co, Ba, Ti, and Al showed annual EF values < 10 and Igeo values ≤ 0, suggesting no pollution of these six metals in PM$_{2.5}$ in Jinan, which was consistent with the findings of previous studies (Liang et al., 2019; Huang et al., 2020; Duan et al., 2021). In contrast, Se, Sb, Tl, Ag, Cd, Zn, V, Pb, and Mo had EF values > 100 and Igeo values > 0, suggesting possible pollution of these metals via anthropogenic sources. In addition, the EF and Igeo values of Se ($4.4 \times 10^6$ and 15.8) and Sb ($1.3 \times 10^5$ and 10.7) were extremely high. Considering their extreme enrichment in the study area, the potential emission sources of these metals should be further controlled. The EF values of Cu, Cr, and Li were between 10 and 100, indicating mixed sources (Cui et al., 2020). Overall, the results suggest that the pollution of metals from anthropogenic sources in Jinan demands serious attention. Seasonally, most metals showed the highest EF values in autumn and the lowest in spring. A similar observation was made in a previous study, which suggested that the increase in industrial production activities and energy consumption in autumn were responsible for the high EF value compared to springs (Duan et al., 2021).

Further, by applying the PMF method, four sources of PM$_{2.5}$-bound metals in Jinan were extracted, as shown in Fig. 3. Specifically, the first source exhibited high contents of Li (60.6%), Al (65.6%), Ti (75.3%), Mn (50.9%), Fe (67.0%), and Co (60.0%), accounting for 51.9% of the total sources. Considering that Ti, Fe, and Al are the dominant crustal metals of airborne dust (Hieu and Lee, 2010; Jiang et al., 2018; Guo et al., 2021), the first source was explained as resuspended dust. Seasonally, resuspended dust exhibited the largest loading in spring (1601.4 ng m$^{-3}$), followed in winter (978.7 ng m$^{-3}$), autumn (477.7 ng m$^{-3}$), and summer (410.1 ng m$^{-3}$). The relatively dry and windy conditions in spring resulted in a greater possibility of resuspended dust in Jinan. The second source occupied 19.9% and was classified as oil combustion with high loadings of V (64.6%), Se (61.5%), Cr (51.4%), and Ni (27.3%) (Guo et al., 2021; Guo et al., 2022). In particular, V and Ni are markers of oil combustion (Taiwo et al., 2014). Further, oil combustion may be associated with petroleum industries and ship emissions. The third source exhibited high contents of Zn (63.6%), Mo (51.6%), Ag (76.9%), Cd (65.9%), Sb (83.1%), and Ti (94.9%). Previous studies implied that Ti is a marker of non-ferrous metal smelting (Li et al., 2015; Duan et al., 2021), and the major source of Cd is high-temperature industrial processes (Juda-Rezler et al., 2020). Thus, the third source was explained as factories, which accounted for 16.5% of the total sources. Factories presented much higher contributions in spring (1101.5 ng m$^{-3}$), and the lowest in summer (181.6 ng m$^{-3}$). According to the results of seasonal CBPF in Fig. S1, the source of factories in spring was mainly under low wind speeds compared to other seasons. This result indicated local factory emissions are responsible for the high contribution of factories in spring. In particular, the specific factory was probably the refining and chemical company located 3 km northwest of the study site. The last source exhibited strong correlation with Ba (88.6%), Pb (84.8%), and Cu (36.8%), with an annual contribution of 11.7%. Almost all motor vehicle brake friction linings feature high Ba and Cu loadings (Alves et al., 2020).
Although the usage of leaded gasoline has been forbidden in China since 2000, the wear of engine, brakes, and brake pads still generate Pb particles (Cui et al., 2020; Niu et al., 2021). Hence, the fourth source was explained as traffic emissions. Overall, the four sources analyzed by PMF were generally consistent with the characteristics of the metals determined according to EF and Igeo. Based on EF and Igeo, metals occupying large proportions in resuspended dust were identified as metals originating from natural sources, meanwhile metals occupying large proportions in oil combustion, factories, and traffic emissions were identified as metals originating from anthropogenic sources.

To determine possible source locations, CBPF analysis was conducted by combining meteorological data and the PMF source apportionment results, with the 75th percentile value as the threshold (Mijic et al., 2012; Hui et al., 2021). As shown in Fig. 4, resuspended dust most probably originated from the southwest direction of the sampling site, with wind speeds ranging from 3 to 3.5 m s⁻¹. Along this direction, subway stations were under construction, which could have increased dust generation. Oil combustion most probably originated from the northeast direction, with a wind speed of 3.5–4 m s⁻¹. This might come from industrial power plants using oil. This source showed a much higher contribution in winter than summer, corresponding to the increased energy consumption on cold days. The factories source showed strong distribution along the northeast to southeast directions (3–3.5 m s⁻¹), which was consistent with the location of factories related to metal welding, electromechanics, packaging materials, and machinery components in the eastern
regions around the sampling site. Traffic emissions were mainly controlled by stable atmospheric conditions at wind speeds lower than 2 m s⁻¹. In this study, traffic emissions showed strong correlation with the driving schools, auto repair shops, and many main roads in this direction. It is worth noting that all the high contributions of four sources occurred at wind speed no greater than 5 m s⁻¹, suggesting that long-range transportation had a limited influence on the pollution of PM₂.₅-bound metals in Jinan. Therefore, the control of local anthropogenic sources needs to be placed as the first priority, especially traffic emission.

3.3 Risk Assessment

3.3.1 Ecological risk

Due to the lack of toxic response factor for several metals, only 14 metals were taken into consideration in the potential ecological risk assessment. As shown in Fig. 5, Se, Sb, and Tl pose the highest risk with mean $E'_i$ values larger than $10^5$, reflecting extremely high ecological risk. Cd and Mo pollution also deserve further attention, and their $E'_i$ values were 6285.9 and 470.9, respectively, indicating still extremely high ecological risk. Pb posed considerable ecological risk, while V and Zn posed moderate ecological risk. Natural metals, including Cu, Ni, Cr, Co, Mn, and Ba, showed low ecological risks. Seasonally, the ecological risks associated with PM₂.₅-bound metals were found to be comparable across the four seasons; the risk posed by each metal remained consistently within the same category. In terms of the RI value (annual: $1.5 \times 10^5$, spring: $1.9 \times 10^5$, summer: $1.5 \times 10^5$, autumn: $9.2 \times 10^4$ and winter: $1.2 \times 10^5$), the total anthropogenic metals evidently present higher values by several orders of magnitude (> 600), indicating serious metal pollution in Jinan.

3.3.2 Human health risk

The exposure risk of PM₂.₅-bound metals for the residents in Jinan was investigated. Regarding non-carcinogenic risk, the HI values of the metals were 47.9 and 6.7 for children and adults, respectively, which were both above the safe level (Tables 2 and S5). For children, the dominant
pathway exposure was oral ingestion, with HQ values of 34.9, followed by dermal contact (11.9) and inhalation (1.1). For the oral ingestion, Sb, Se, and V contributed 37.1%, 24.5%, and 22.5% of the total HQ, respectively. For dermal contact pathway, V and Sb contributed 71.4% and 20.4% of the total HQ, respectively. For adults, oral ingestion presented a higher HQ value (3.7) compared to dermal contact (1.8) and inhalation (1.1). Sb, Se, and V almost entirely contributed to the HQ value of oral ingestion. Meanwhile, V was the major contributor for inhalation and dermal contact. Thus, regarding non-carcinogenic risk, oral ingestion risk should be controlled for adults, and both oral ingestion risk and dermal contact risk are of concern for children. On the whole, the results

Table 2. Health risks of studied metals through different exposure pathways.

<table>
<thead>
<tr>
<th>Metal</th>
<th>C95% Exposure dose</th>
<th>Exposure dose</th>
<th>HQ</th>
<th>CR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mg kg⁻¹) (μg m⁻³)</td>
<td>(Non-carcinogenic risk)</td>
<td>(Carcinogenic risk)</td>
<td>Children</td>
</tr>
<tr>
<td>V</td>
<td>5974.9 161.8</td>
<td>Ingestion 3.9 × 10⁻² 4.2 × 10⁻³</td>
<td>3.4 × 10⁻³ 1.4 × 10⁻³</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inhalation 8.0 × 10⁻² 8.0 × 10⁻²</td>
<td>6.8 × 10⁻³ 2.7 × 10⁻²</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dermal 1.1 × 10⁻⁵ 1.7 × 10⁻⁴</td>
<td>9.4 × 10⁻⁵ 5.8 × 10⁻⁵</td>
<td>8.5</td>
</tr>
<tr>
<td>Sb</td>
<td>789.1 29.1</td>
<td>Ingestion 5.2 × 10⁻³ 5.6 × 10⁻⁴</td>
<td>4.4 × 10⁻⁴ 1.9 × 10⁻⁴</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inhalation 1.4 × 10⁻⁵ 1.4 × 10⁻⁴</td>
<td>1.2 × 10⁻³ 4.9 × 10⁻³</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dermal 1.5 × 10⁻⁵ 2.2 × 10⁻⁵</td>
<td>1.2 × 10⁻⁵ 7.6 × 10⁻⁵</td>
<td>2.4</td>
</tr>
<tr>
<td>Se</td>
<td>6511.2 180.7</td>
<td>Ingestion 4.3 × 10⁻² 4.6 × 10⁻³</td>
<td>3.7 × 10⁻³ 1.6 × 10⁻³</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inhalation 8.9 × 10⁻² 8.9 × 10⁻²</td>
<td>7.6 × 10⁻³ 3.1 × 10⁻²</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dermal 1.2 × 10⁻⁵ 1.8 × 10⁻⁴</td>
<td>1.0 × 10⁻⁴ 6.3 × 10⁻⁵</td>
<td>0.2</td>
</tr>
<tr>
<td>Pb</td>
<td>855.6 28.5</td>
<td>Ingestion 5.6 × 10⁻³ 6.0 × 10⁻⁴</td>
<td>4.8 × 10⁻⁴ 2.1 × 10⁻⁴</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inhalation 1.4 × 10⁻⁵ 1.4 × 10⁻²</td>
<td>1.2 × 10⁻³ 4.8 × 10⁻³</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dermal 1.6 × 10⁻⁴ 2.4 × 10⁻⁵</td>
<td>1.4 × 10⁻⁴ 8.3 × 10⁻⁵</td>
<td>0.5</td>
</tr>
<tr>
<td>Co</td>
<td>25.2 0.8</td>
<td>Ingestion 1.7 × 10⁻⁷ 1.8 × 10⁻⁵</td>
<td>3.5 × 10⁻⁵ 1.4 × 10⁻⁴</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inhalation 4.1 × 10⁻⁴ 4.1 × 10⁻⁴</td>
<td>4.0 × 10⁻⁷ 2.4 × 10⁻⁷</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dermal 4.6 × 10⁻⁶ 7.1 × 10⁻⁷</td>
<td>2.1 × 10⁻⁵ 8.9 × 10⁻⁶</td>
<td>0.0</td>
</tr>
<tr>
<td>Cd</td>
<td>36.6 1.5</td>
<td>Ingestion 2.4 × 10⁻⁵ 2.6 × 10⁻⁵</td>
<td>2.1 × 10⁻⁵ 8.9 × 10⁻⁶</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inhalation 7.5 × 10⁻⁴ 7.5 × 10⁻⁴</td>
<td>6.4 × 10⁻⁵ 2.6 × 10⁻⁴</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dermal 6.7 × 10⁻⁶ 1.0 × 10⁻⁶</td>
<td>5.8 × 10⁻⁸ 3.5 × 10⁻⁷</td>
<td>0.3</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>413.4 12.9</td>
<td>Ingestion 3.9 × 10⁻⁵ 4.2 × 10⁻⁵</td>
<td>3.3 × 10⁻⁵ 1.4 × 10⁻⁵</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inhalation 9.1 × 10⁻⁴ 9.1 × 10⁻⁴</td>
<td>7.8 × 10⁻⁵ 3.1 × 10⁻⁴</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dermal 1.1 × 10⁻⁴ 1.7 × 10⁻⁶</td>
<td>9.3 × 10⁻⁷ 5.7 × 10⁻⁷</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Note: The Cr(VI) concentration was calculated as one seventh of the total Cr (Zhang et al., 2023).

Fig. 5. Potential ecological risk ($E_i$) of each metal during different sampling periods (annual, spring, summer, autumn, and winter from left to right).
showed that children were more vulnerable to toxic metals, consistent with the findings of previous studies (Liang et al., 2019; Zhang et al., 2021b).

The CR values of Pb, Cr(VI), Co, and Cd were calculated and are shown in Table 2. The CR value was $4.8 \times 10^{-5}$ for children and $4.9 \times 10^{-5}$ for adults. Undoubtedly, Cr(VI) posed the greatest carcinogenic risk for adults, with risks through inhalation reaching 53.5%, followed by dermal contact (23.3%), and oral ingestion (14.6%). Furthermore, attention should also be paid to the CR of Pb through oral ingestion ($4.1 \times 10^{-6}$ and $1.8 \times 10^{-6}$ for children and adults) and of Co through inhalation ($1.3 \times 10^{-6}$ for adults).

**4 CONCLUSIONS**

This study conducted PM$_{2.5}$ sampling in Jinan for a year and investigated the characteristics of 19 metals. The total concentration of PM$_{2.5}$-bound metals was 2.2 $\mu$g m$^{-3}$, among which Fe and Al had the largest contributions, accounting for approximately 51.9% and 18.2%, respectively. In terms of seasonal variation, the metals showed the highest concentration in spring, followed by winter, summer, and autumn. Resuspended dust, oil combustion, factories, and traffic emissions were identified as the major pollution sources, with contributions of 51.9%, 19.9%, 16.5%, and 11.7% to the total metals, respectively. In particular, traffic emissions were the main local contributor, and thus require serious attention. PM$_{2.5}$-bound metals were found to pose severe potential ecological risks in Jinan, and the corresponding ecological risk index was several orders of magnitude higher than the safe level. The non-carcinogenic risks were 47.9 and 6.7 for children and adults, respectively, which had relatively large contributions from Sb, Se, V, and Cr. Meanwhile, carcinogenic risks also exceeded the safe level, and Cr(VI) was identified as a high-risk metal. Therefore, the reduction of high-risk metals in Jinan is urgently required.

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**SUPPLEMENTARY MATERIAL**

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.230165

**REFERENCES**


real-time measurement of trace elements in China’s urban atmosphere: temporal variability, source apportionment and precipitation effect. Atmos. Chem. Phys. 18, 11793–11812. https://doi.org/10.5194/acp-18-11793-2018


bioavailability and potential ecological risk of copper and zinc in river sediment are affected by seasonal variation and spatial distribution. Aquat. Toxicol. 227, 105604. https://doi.org/10.1016/j.aquatox.2020.105604


