Seasonal Variations, 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 variations, potential sources, and health risks of heavy metals 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 the PM_{2.5} were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). We used enrichment factors and principal component analysis/absolute principal component scores (PCA/APCS) to determine the sources of these heavy metals, and models from the United States Environmental Protection Agency (EPA) to assess both the carcinogenic and non-carcinogenic risks to adults and children. Results showed that the average annual mass concentration of the PM_{2.5} was 62.7 µg m⁻³, which exceeded the limit specified in the Chinese National Ambient Air Quality Standards (NAAQS). The average annual concentrations of the Pb, Cd, and As were 57.2 ng m⁻³, 1.5 ng m⁻³, and 4.7 ng m⁻³, respectively, which were below the NAAQS limits. The highest total concentrations for the heavy metals occurred in winter, whereas the lowest concentrations were observed in summer. Enrichment factor analysis indicated that the Sb, Cd, Pb, Se, As, and Tl were mainly from anthropogenic sources. Additionally, source apportionment by PCA/APCS identified four major sources for the studied metals: coal combustion and motor vehicles (46.3%), soil and construction dust (37.1%), steelworks (6.9%), and other smelting industries (6.8%). The carcinogenic risk of heavy metals in Ningbo fell within the safe level of exposure for both children and adults. However, the total non-carcinogenic risk exceeded the safe level (HI = 1.38), which warrants further research on sources of air pollution and measures for controlling pollutants in Ningbo, China.

Keywords: PM_{2.5}; Heavy metal; Enrichment factor; Principal component analysis/absolute principal component scores; Health risk assessment.

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 (Pope *et al.*, 2002; Hoek *et al.*, 2013; Li *et al.*, 2015; GBD 2015 Risk Factors Collaborators, 2016). 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

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emission sources, PM_{2.5} concentration showed significant regional and seasonal variation (Ming *et al.*, 2017; Gao *et al.*, 2018; Mukherjee and Agrawal, 2018).

While exposure to PM_{2.5} is known to cause disease, the constituents 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 *et al.* (2012) found that heavy metals were slow to biodegrade and enriched in PM_{2.5}. Exposure to these metals have been associated 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 (Song *et al.*, 2006; Chen *et al.*, 2015); however, limited studies have been conducted based on long-term air 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, the objectives of 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}.

MATERIALS AND METHODS

Study Area and Sampling Procedure

Ningbo is a sub-provincial city located in eastern China in 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's fourth largest port (Ningbo Port) is located east of Ningbo, about 60 km from the 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 of 17.8°C.

The measurement site was situated on the roof (~15 m above ground level) of the Ningbo Center of Disease Control and Prevention (CDC)'s 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 within 2 km were detected. It can represent the urban environment in Ningbo. PM_{2.5} samples were collected by medium-volume (2.3 m³ h⁻¹) samplers (MSV6; Sven Leckel, Germany). The samplers, which captured PM_{2.5} on 47-mm quartz filters (QM-A; Whatman), 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–May), summer (June–August), autumn (September–November) and winter (December–February).

Mass Concentration Analysis

All quartz filters were equilibrated in a desiccator under a constant temperature of 25 ± 1°C and humidity condition of 50 ± 5% for 48 hours. The filters were weighed with a microbalance (10-μg resolution, XS205DU; Mettler Toledo) 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.

Analysis of Elemental Content

After sampling, daily (23-h) 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 (Sb, As, Cd, Cr, Pb, Mn, Ni, Se, Tl, Al, Be and Hg) concentrations in the digestion solutions were measured by using inductively coupled plasma mass spectrometry (ICP-MS; Elan 9000; PerkinElmer SCIEX, USA). Certified reference sample (GSB 04 1767-2004, National Analysis and Testing Center for Nonferrous Metals and 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).

Data Analysis

Enrichment Factor

Enrichment factor (EF) analysis, 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:

$$(EF)_i = \frac{(X_i/X_R)_{sample}}{(X'_i/X'_R)_{soil\ background}} \quad (1)$$

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.

Fig. 1. PM_{2.5} sampling site (the red star) in Ningbo.

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).

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 (Thurston and Spengler, 1985; Kothai *et al.*, 2008). 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.

The 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 σ_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 metal 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:

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

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 (Thurston and Spengler, 1985; Guo *et al.*, 2004). In this study, we used the samples from a whole year to estimate source contributions.

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 U.S. EPA human health risk assessment models (U.S. EPA, 2009). 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 (U.S. EPA, 2009):

$$EC = CA \times ET \times EF \times ED/AT \quad (5)$$

where EC is exposure concentration, $\mu\text{g m}^{-3}$; CA is the 95% upper confidence limit (UCL) of the log-transformed data because most of the studied heavy metals approximated lognormal distributions, $\mu\text{g m}^{-3}$ (Li *et al.*, 2016); ET is exposure time, assumed to be 24 h day^{-1} ; EF is the exposure frequency, assumed to be 350 days year^{-1} ; 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 $ED \times 365 \text{ days year}^{-1} \times 24 \text{ h day}^{-1}$ for non-carcinogens and $70 \text{ years} \times 365 \text{ days year}^{-1} \times 24 \text{ h day}^{-1}$ 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)):

$$HQ = EC/(RfC \times 1000 \mu\text{g mg}^{-1}) \quad (6)$$

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

The hazard index (HI), which is the sum of the HQs for each metal, estimates the total non-carcinogenic risk of mixed heavy metal contaminants.

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

(3) Carcinogenic risk assessment

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

$$CR = IUR \times EC \quad (7)$$

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

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). Lead is considered a probable carcinogen (Group 2A). 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 U.S. EPA Regional Screening Levels (RSL). We did not discuss Sb and Tl because their RfC was unavailable.

RESULTS AND DISCUSSION

Concentration of $PM_{2.5}$

The average annual and seasonal concentrations of $PM_{2.5}$ during the sampling period are summarized in Table 1. The annual average mass concentration of $PM_{2.5}$ was $62.7 \pm 35.8 \mu\text{g m}^{-3}$ during the sampling period, which is much higher than the limit of annual concentration of $PM_{2.5}$ according to the Chinese NAAQS (GB3095-2012), which is $35 \mu\text{g m}^{-3}$ (MEP, 2012), and World Health Organization (WHO) air quality guidelines ($10 \mu\text{g m}^{-3}$). The levels of $PM_{2.5}$ in Ningbo were lower than those in Chinese cities like Shijiazhuang ($139 \mu\text{g m}^{-3}$) (Xie *et al.*, 2019), Xi'an ($108 \mu\text{g m}^{-3}$) (Dai *et al.*, 2018), Xinxiang ($94 \mu\text{g m}^{-3}$) (Yang *et al.*, 2019), and Beijing ($83 \mu\text{g m}^{-3}$) (Ji *et al.*, 2019), while it was higher than Fuzhou ($27 \mu\text{g m}^{-3}$), Xiamen ($28 \mu\text{g m}^{-3}$) (Fu *et al.*, 2018), Nanjing ($55 \mu\text{g m}^{-3}$) (Nie *et al.*, 2018), and Chengdu ($57 \mu\text{g m}^{-3}$) (Qiu *et al.*, 2019). The annual average concentration of $PM_{2.5}$ in this study was unexpectedly lower than the value of one rural site of Ningbo ($96.2 \mu\text{g m}^{-3}$) (Ming *et al.*, 2017). The reason may be due to regional pollution 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 $94.8 \mu\text{g m}^{-3}$ and $39.6 \mu\text{g m}^{-3}$, 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,

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

	Spring (Mar.–May) (n = 24)	Summer (Jun.–Aug.) (n = 24)	Autumn (Sep.–Nov.) (n = 24)	Winter (Dec.–Feb.) (n = 24)	Annual (n = 96)
PM _{2.5} (μg m ⁻³)	54.2 ± 21.5	39.6 ± 14.4	74.8 ± 29.3	94.8 ± 45.6	62.7 ± 35.8
Sb (ng m ⁻³)	3.8 ± 2.3	3.1 ± 1.5	4.5 ± 2.6	5.0 ± 4.0	4.1 ± 2.8
As (ng m ⁻³)	4.3 ± 1.9	3.2 ± 1.4	5.0 ± 2.6	7.0 ± 4.5	4.7 ± 3.1
Cd (ng m ⁻³)	1.2 ± 0.6	1.1 ± 0.5	1.7 ± 0.6	2.1 ± 1.5	1.5 ± 1.0
Cr (ng m ⁻³)	2.1 ± 1.2	5.0 ± 3.0	2.5 ± 1.7	3.3 ± 2.4	3.4 ± 2.5
Pb (ng m ⁻³)	51.6 ± 21	40.6 ± 19.9	74.9 ± 38.6	72.3 ± 40.5	57.2 ± 32.9
Mn (ng m ⁻³)	36.6 ± 11.1	37.4 ± 15.4	31.6 ± 9.3	34.8 ± 16.7	35.6 ± 13.9
Ni (ng m ⁻³)	4.0 ± 2.4	5.5 ± 3.2	3.3 ± 2.1	3.2 ± 1.8	4.2 ± 2.7
Se (ng m ⁻³)	3.0 ± 1.5	3.2 ± 1.8	4.7 ± 2.3	5.7 ± 3.4	4.0 ± 2.6
Tl (ng m ⁻³)	0.3 ± 0.1	0.3 ± 0.2	0.7 ± 0.3	0.8 ± 0.5	0.5 ± 0.4

Fig. 2. Monthly variation of PM_{2.5} concentrations in Ningbo.

and better deposition conditions can contribute to lower PM_{2.5} concentrations (Guinot *et al.*, 2006). Similar seasonal trends have also been shown in other cities like Beijing (Zhao *et al.*, 2009; Duan *et al.*, 2012), Chengdu (Li *et al.*, 2016), Shanghai, Nanjing and Hangzhou (Ming *et al.*, 2017).

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, and 4.7 ng m⁻³, respectively, which were below the limits of NAAQS (500 ng m⁻³, 5 ng m⁻³ and 6 ng m⁻³, respectively) (MEP, 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 standards 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 4.1 ng m⁻³ and 0.5 ng m⁻³, respectively,

Fig. 3. Seasonal concentration of elements found in PM_{2.5} in Ningbo.

which, to our knowledge, had been rarely assessed in mainland China. The concentration of Sb and Ti 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, Sb, As, Cd, and Se exhibited their highest average seasonal concentrations during the winter (Table 1 and Fig. 3). The highest average seasonal concentrations of 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 pollutant 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.

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 Ti during autumn and winter were much higher than 10, indicating these elements mainly originate from anthropogenic sources (Fig. 4). The EFs of Cr and Ni for all four seasons and EFs of As and Ti during spring and summer were between 1 and 10, indicating their mixed source.

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 (PCs) 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 (Ge *et al.*, 2004; Duzgoren-Aydin, 2007; 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 steelworks (Kuang *et al.*, 2004; Chen *et al.*, 2014; Chen *et al.*, 2016). PC 3 showed a high loading of Mn and explained 12.8% of the total variance. Mn concentration closely tracks dust (Trapp *et al.*, 2010) and indicates a soil and construction dust source (Duan *et al.*, 2012). 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 may have made the soil and dust be blown into the air by wind. The contribution from steelworks and other industry was 6.9% and 6.8%, respectively. The industries also contributed to the air pollution in Ningbo.

Risk Assessment of Heavy Metal 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 and research 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

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

Table 2. Principal component analysis (PCA) with varimax rotation for all PM_{2.5} data from Ningbo.

Element	Factor			
	1	2	3	4
Sb	0.4780	0.010	0.289	0.735
As	0.886	−0.066	0.008	0.290
Cd	0.845	0.022	0.279	0.281
Cr	−0.005	0.777	0.263	−0.358
Pb	0.855	−0.056	0.287	0.284
Mn	0.265	0.199	0.898	0.165
Ni	−0.098	0.907	0.005	0.223
Se	0.926	−0.028	0.112	−0.028
Tl	0.945	−0.071	0.148	0.095
% of variance	47.65	16.45	12.82	11.11
Cumulative %	47.65	64.09	76.92	88.02
Source	Coal combustion and motor vehicle exhaust	Steelworks	Soil and construction dust	Other smelting industries

carcinogenic risk followed by As, Cd, Ni and Pb. The carcinogenic risk of Cr(VI) and As were higher than 1×10^{-6} , but below the acceptable level (1×10^{-4}). The total carcinogenic risk reached 2.50×10^{-5} for adults and 6.24×10^{-6} for children, both being higher than 1×10^{-6} but within the acceptable level, indicating that the carcinogenic risk posed by the heavy metals to both children and adults were below EPA carcinogenic safe levels 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).

CONCLUSION

The average annual PM_{2.5} mass concentration in Ningbo exceeded the NAAQS limit, but the average annual

concentrations of Pb, Cd, and As, and Mn and Ni fell below the limits of the NAAQS and the WHO guidelines, respectively. The levels of PM_{2.5} and its heavy metal components displayed significant seasonality. Whereas the maximum and minimum concentrations for PM_{2.5} occurred during winter and summer, respectively, the maximum concentrations for As, Cd, and Se occurred during winter, and those for Sb and Pb occurred during autumn. Enrichment factor analysis indicated that anthropogenic sources were responsible for the levels of Sb, Cd, Pb, and Se year round and for those of As and Tl during autumn and winter. Furthermore, PCA/APCS revealed four major sources for the studied metals: coal combustion and motor vehicles (46.3%), soil and construction dust (37.1%), steelworks (6.9%), and other smelting industries (6.8%).

The total carcinogenic risk of the heavy metals in Ningbo was within the safe level of exposure, but the total non-carcinogenic risk was higher than the safe level. The

Fig. 5. Source contributions of heavy metals found in PM_{2.5} in Ningbo.

Table 3. Carcinogenic and non-carcinogenic risks from toxic elements in PM_{2.5}.

Element	RfC _i (mg m ⁻³)	IUR (μg m ⁻³) ⁻¹	Non-carcinogenic	Carcinogenic	
				Children	Adults
As	1.50E-05	4.30E-03	2.87E-01	1.59E-06	6.35E-06
Cd	1.00E-05	1.80E-03	1.34E-01	2.06E-07	8.26E-07
Cr(VI)	1.00E-04	8.40E-02	5.99E-03	4.31E-06	1.73E-05
Pb		1.20E-05		5.45E-08	2.18E-07
Mn	5.00E-05		6.87E-01		
Ni	1.40E-05	2.40E-04	2.67E-01	7.69E-08	3.08E-07
Se	2.00E-02		1.85E-04		
Total			1.38E+00	6.24E-06	2.50E-05

government should implement stricter and more effective measures for controlling air pollution in this region, such as replacing traditional energy sources with clean energy, improving the vehicular exhaust emission standards, and sprinkling water regularly on roads and construction sites. Additionally, more research is needed to assess the potential non-carcinogenic risks to the population.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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