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

Yue Wu[a,†], Beibei Lu[b,†], Xinlei Zhu[c], Aihong Wang[b], Meng Yang[c], Shaohua Gu[b], Xiaoxia Wang[c], Pengbo Leng[b], Kristina M. Zierold[d], Xiaohai Li[b], Ke Kerri Tang[d], Lanyun Fang[b], Ruixue Huang[a], Guozhang Xu[b,*], Lv Chen[a,*]

[a] Department of Occupational and Environmental Health, Xiangya School of Public Health, Central South University, Changsha, China.

[b] Zhejiang Provincial Key Laboratory of Health Risk Appraisal for Trace Toxic Chemicals, Ningbo Municipal Center for Disease Control and Prevention, Ningbo, China.

c Xiangya Medical School, Central South University, Changsha, China.

[d] School of Public Health, University of Alabama at Birmingham, Birmingham, Alabama, United States of America.

* Co-Correspondence: chenlv@csu.edu.cn; xugz@nbcdc.org.cn

[†] These authors contributed equally to this work.

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 μg 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 Ningo, 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℃.

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℃ 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 HNO_3 and 3 ml $HClO_4$ 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:

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

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 ≥ 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

$$Z_{ik} = (C_{ik} - \overline{C_i})/\sigma_i \quad (2)$$

where C_{ik} is the concentration of heavy metal i in sample k; $\overline{C_i}$ 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

$$(Z_0)_i = (0 - \overline{C_i})/\sigma_i = -\overline{C_i}/\sigma_i \quad (3)$$

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

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

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):

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

where EC is exposure concentration, μg m^{-3}; CA is the 95% upper confidence limit (UCL) of the log-transformed data because most-studied heavy metals approximated lognormal distributions, μg 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 × 365 days/year × 24 hours/day for non-carcinogens and 70 years ×365 days/year × 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):

$$HQ = EC/(RfC \times 1000\,\mu g/mg) \quad (6)$$

where HQ is hazard quotient; EC is exposure concentration (μg 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 ≤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):

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

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 35μg 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) , while it was higher than 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 39.6μg 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

255 categorized into three types, as follows: (1) the upper continental crustal material with an EF
256 value <1, (2) anthropogenic elements with an EF value >10, and (3) mixed source elements with
257 an EF value between 1 and 10 (Chen et al., 2015). The EFs of Sb, Cd, Pb, and Se for the four
258 seasons and EFs of As and Tl during autumn and winter were much higher than 10, indicating
259 these elements mainly originate from anthropogenic sources. The EFs of Cr and Ni for all four
260 seasons and EFs of As and Tl during spring and summer were between 1 and 10, indicating their
261 mixed source.
262
263 **3.4. Principal component analysis/absolute principal component scores (PCA/APCS) in**
264 **source appointment**
265 To further explore $PM_{2.5}$ sources and quantify their contributions, the PCA/APCS model was
266 used. Four principal components (PC) were extracted by principle component analysis (PCA)
267 (Table 2), accounting for over 88% of the explained variance. Generally, the sources can be
268 identified by fingerprint elements of sources. The PCA results showed that PC 1 had high
269 loadings of Se, As, Cd and Pb with the maximum percentage of variance (47.65%). Pb and Cd
270 are fingerprint elements of automobile exhaust (Fang et al., 2010). The elements, As and Se are
271 often used as specific tracers of coal in China (Duzgoren-Aydin, 2007; Ge et al., 2004; Kang et
272 al., 2011). Consequently, PC 1 was a mixed source of coal combustion and motor vehicle
273 exhausts. PC 2 mainly consisted of Ni and Cr with 16.5% of the total variance, which were
274 recommended as fingerprints for metal processing industry, especially for steel works (Chen et
275 al., 2016; Chen et al., 2014; Kuang et al., 2004). PC 3 showed a high loading of Mn and
276 explained 12.8% of the total variance. Mn concentration closely tracks dust and indicates a soil
277 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 1×10^{-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 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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Table 1 Average concentration of $PM_{2.5}$ and heavy metals in Ningbo, March 2015 – February 2016.

	Spring (March to May) (n=24)	Summer (June to August) (n=24)	Autumn (September to November) (n=24)	Winter (December to next February) (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	5.1 ± 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

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	Steel works	soil and construction dust	Other smelting industries

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

Element	RfC_i	IUR	Non-carcinogenic	Carcinogenic	
	($mg\ m^{-3}$)	$(\mu g\ m^{-3})^{-1}$		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

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 to $PM_{2.5}$ in Ningbo.