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Seasonal Levels, Sources, and Health Risks of Heavy Metals in Atmospheric $PM_{2.5}$ from Four Functional Areas of Nanjing City, Eastern China

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Abstract: Aerosol pollution is a serious environmental issue, especially in China where there has been rapid urbanization. To identify the intra-annual and regional distributions of health risks and potential sources of heavy metals in atmospheric particles with an aerodynamic diameter less than or equal to 2.5 μm ($PM_{2.5}$), this work collected monthly $PM_{2.5}$ samples from urban, industrial, suburban, and rural areas in Nanjing city during 2016 and analyzed the heavy metal compositions (Cu, Pb, Cd, Co, V, Sr, Mn, Ti, and Sb). Enrichment factors (EFs) and principal component analysis (PCA) were applied to investigate the sources. The atmospheric $PM_{2.5}$ pollution level was highest in the industrial area, followed by the urban and suburban areas, and was the lowest in the rural area. Seasonally, the concentrations of $PM_{2.5}$ and associated heavy metals in spring and winter were higher than those in summer and autumn. Besides natural sources, heavy metal pollution in $PM_{2.5}$ might come from metallurgical dust in the industrial area, while it mainly comes from automobile exhaust in urban and suburban areas. Health risk assessments revealed that noncancerous hazards of heavy metals in $PM_{2.5}$ were low, while the lifetime cancer risks obviously exceeded the threshold. The airborne metal pollution in various functional areas of the city impacted human health differently.

Keywords: atmospheric fine particulate matter; heavy metals; spatiotemporal distributions; source identification; human health risk assessments

1. Introduction

Atmospheric particulate matter (PM) contributes to air pollution continuously [1] and has critical influences on both the environment and human health. The World Health Organization (WHO) has reported that air pollution was responsible for 3.7 million deaths in 2012, including 29% of heart disease and stroke deaths, 16% of lung cancer deaths, 11% of chronic-obstructive-pulmonary-disease-related deaths, and approximately 13% of deaths that were due to respiratory infections [2]. Epidemiological studies have shown that PM is associated with increased disease morbidity and mortality, especially heart and lung diseases. PM has become the primary pollutant in the ambient air of China, typically as $PM_{2.5}$ [3]. $PM_{2.5}$ refers to atmospheric particles with an aerodynamic diameter less than or equal to 2.5 μm. The spatial distribution of $PM_{2.5}$ concentrations varies greatly in China, and $PM_{2.5}$ is generally higher in northern than in southern China [4]. Seasonal variation of $PM_{2.5}$ is obvious and the highest

concentration is during winter while the lowest is in summer [5]. $PM_{2.5}$ has a larger surface area than coarse PM; thus, it is more likely to adsorb toxic or harmful components such as heavy metals [6,7]. The chemical composition of PM can better identify pollution sources and explain the associated health effects [8]. Heavy metals are highly enriched in $PM_{2.5}$ and can be directly inhaled into the respiratory tract. Furthermore, they remain in the atmosphere for a long time and can be transported far away, thus making them a considerable cause for concern [9]. The As, Cd, Cr, Hg, Mn, Ni, Pb, and V in the environment can cause various diseases such as asthma, pneumonia, lung cancer, and cerebral hemorrhage [10]. Although heavy metals account for only a small part of the mass concentration of $PM_{2.5}$, they still pose threats to human health through respiration [11–13]. Spatial forecasting of urban air pollution might be beneficial for risk assessments, but it is necessary to know the actual distribution patterns [14–16].

Since previous research has already focused on the air pollution level of heavy metals [17], the objectives of this study were to investigate and compare the seasonal distribution characteristics, sources, and human health risks of $PM_{2.5}$-bound heavy metals in different functional areas of a typical megacity in eastern China.

2. Materials and Methods

2.1. Study Area

Located in the southwest of Jiangsu Province in eastern China, Nanjing (118°22′–119°14′ E, 31°14′–32°37′ N) is an important regional central city in the economic core of the Yangtze River Delta (YRD) region (Figure 1). Nanjing is a comprehensive transportation hub and industrial production base. The main sources of air pollution in Nanjing are motor vehicle exhaust, industrial emissions, coal combustion, construction dust, and mixed pollution caused by pollutant transport from other regions. The air sampling sites were located in four different functional areas in Nanjing [18]. Highways, light rail, and giant chemical and metallurgical industries are near the industrial site. For the downtown urban site, the nearby road network is complex, with heavy traffic and high building density. The suburban site is on a campus, and the rural site is located in a remote agricultural park.

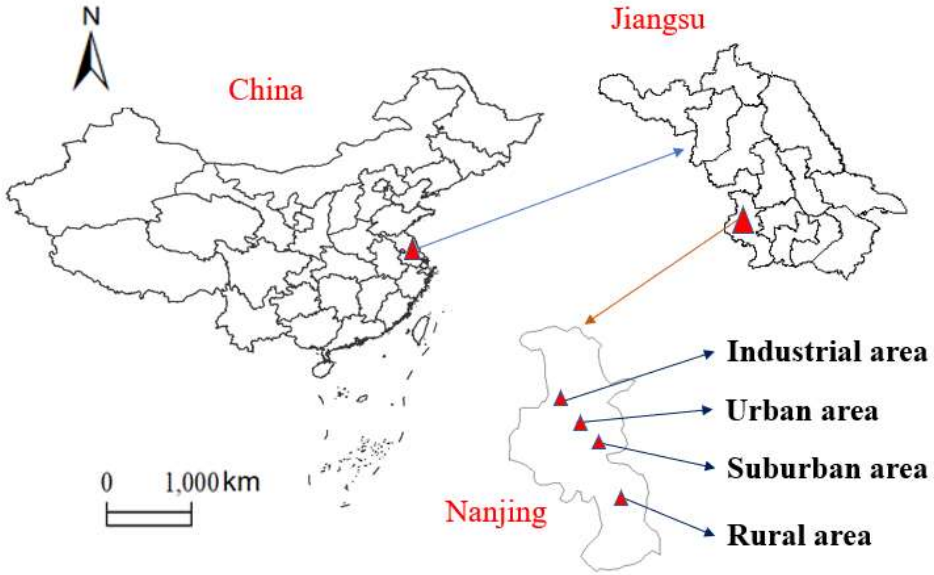

Figure 1. Locations of the four representative air sampling sites in Nanjing city, eastern China.

2.2. $PM_{2.5}$ Sampling

The daily 23 h $PM_{2.5}$ samples were collected on quartz microfiber filters (QMA, 203 × 254 mm, Whatman, UK) by high-volume air samplers (1000 L/min) synchronously from the four sites each

month. Filters were weighed before and after sampling, after equilibration in a constant temperature and humidity environment [19,20]. After sampling, the loaded filters were stored in a fridge before analysis. For this investigation conducted in 2016, 102 samples were obtained in both the industrial and urban areas from January to December, and 27 and 20 samples were collected in the suburban and remote rural areas from April to December, respectively.

2.3. Heavy Metal Analyses

Total concentrations of heavy metals accumulated in $PM_{2.5}$ samples were analyzed using filter subsamples with known particle masses, which were digested by concentrated HNO_3–$HClO_4$–HF acids and determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8000, PerkinElmer, Waltham, Massachusetts, USA) for Cu, Pb, Sr, Mn, Ti , Sb, and Al and by an ICP mass spectrometer (ICP-MS, NexION300X, PerkinElmer, Waltham, Massachusetts, USA) for lower levels of Cd, Co, and V [21,22]. Procedural blanks, sample replicates, and standard reference materials (NIST SRM 1648a, urban PM, San Francisco, California, USA) were randomly inserted for quality control. Then, the airborne metal concentrations (ng/m^3) were calculated based on the volume of sampled air.

2.4. Calculation of the Enrichment Factors (EFs) for Source Identification

EF is an analytical method for quantitatively evaluating the source of heavy metals in atmospheric particulates using the crust or soil as a reference medium calculated by the following equation [9]:

$$EF_i = \frac{(C_i/C_r)_P}{(C_i/C_r)_S} \quad (1)$$

where C_i is the concentration of the measured heavy metal i in the particulates or soil (mg/kg), C_r is the concentration of the reference element (Al), and $_P$ and $_S$ represent $PM_{2.5}$ and Jiangsu background soil, respectively [23,24]. There is no enrichment if the EF < 10 in $PM_{2.5}$ and the main source may be natural, such as rock weathering or soil, but the primary source is anthropogenic when EF > 10 [25].

2.5. Principal Component Analysis (PCA)

The metal concentration data of atmospheric particulates were analyzed by PCA. According to the correlation between different components, the principal component factors were summarized from multiple variables, and the load of each factor was calculated. Each common factor represents a different source [26].

2.6. Human Health Risk Assessments (HHRAs)

HHRAs can evaluate the adverse health effects (carcinogenic and noncarcinogenic) of environmental pollutant exposure [27]. The model recommended by the US Environmental Protection Agency (EPA) was applied [28]. The hazard quotient (HQ) indicates the noncarcinogenic risk of a single heavy metal through the respiratory pathway, which is small or negligible if HQ < 1. Increased lifetime cancer risk (ILCR) indicates the probability of cancer, which does not pose a cancer risk if ILCR < 1×10^{-6}. The current study focused on the risks of airborne metal inhalation calculated as follows:

$$HQ = \frac{ADD}{RfD} \quad (2)$$

$$ILCR = LADD \times SF \quad (3)$$

where ADD is the average daily dose of noncarcinogenic heavy metal (mg/kg/day); RfD is the reference dose, which means the maximum safe amount of heavy metal per unit body weight per day (mg/kg/day);

LADD is the lifetime average daily dose (mg/kg/day) of carcinogenic heavy metal; and SF is the slope factor ((kg × day)/mg) (Table 1). The exposure was evaluated by the following equations [29–31]:

$$\mathrm{ADD} = (\mathrm{C} \times \mathrm{InhR} \times \mathrm{EF} \times \mathrm{ED}) / (\mathrm{BW} \times \mathrm{AT}) \quad (4)$$

$$\mathrm{LADD} = \frac{\mathrm{C} \times \mathrm{EF}}{\mathrm{AT}} \left(\frac{\mathrm{InhR_{child}} \times \mathrm{ED_{child}}}{\mathrm{BWchild}} + \frac{\mathrm{InhRadult} \times \mathrm{EDadult}}{\mathrm{BWadult}} \right) \quad (5)$$

where C is the metal concentration (mg/m^3), InhR is the inhalation rate (m^3/day), EF is the exposure frequency (day/year), ED is the exposure period (year), BW is body weight (kg), and AT is average exposure time (day).

Table 1. Slope factor and the reference dose entering the human body through the respiratory route for human health risk assessments [26].

Metals	SF [1]	RfD [2]
Cd	6.3	1×10^{-3}
Co	9.8	5.7×10^{-6}
Pb	–	3.5×10^{-3}
Mn	–	1.4×10^{-5}
Cu	–	4×10^{-2}

[1] Slope factor, [2] Reference dose.

2.7. Statistics

The data were compiled using Microsoft Excel 2016 statistics (Microsoft: Redmond, Washington, USA) and plotted by Origin (2017), and the PCA was conducted by IBM SPSS statistics 24 (IBM: Armonk, NY, USA).

3. Results and Discussion

3.1. $PM_{2.5}$ Concentration Levels in Different Urban Functional Areas

From the perspective of the air concentration levels of $PM_{2.5}$ at four sampling sites in Nanjing during 2016, the annual average concentrations were 72.3 ± 32.7 μg/m^3 (industrial area), 69.9 ± 34.2 μg/m^3 (urban area), 62.8 ± 18.8 μg/m^3 (suburban area), and 41.1 ± 11.8 μg/m^3 (rural area) (Figure 2). China released an ambient air quality standard (Chinese NAAQS II) of 75 μg/m^3 $PM_{2.5}$ for 24 h [32], which is lower than the previous threshold value but still much higher than the values of the WHO AQG (25 μg/m^3) and US NAAQS-Primary (35 μg/m^3). The concentration of $PM_{2.5}$ in Nanjing was generally higher than the daily average concentration limit stipulated by the WHO and US air quality standards, indicating that the $PM_{2.5}$ pollution in Nanjing was serious. The annual concentrations of $PM_{2.5}$ in the YRD region were lower than those in northern China, such as Xingtai (109 μg/m^3), but higher than the annual concentrations in the Pearl River Delta region, such as Zhuhai (33.8 μg/m^3) and Shenzhen (32.0 μg/m^3) [12].

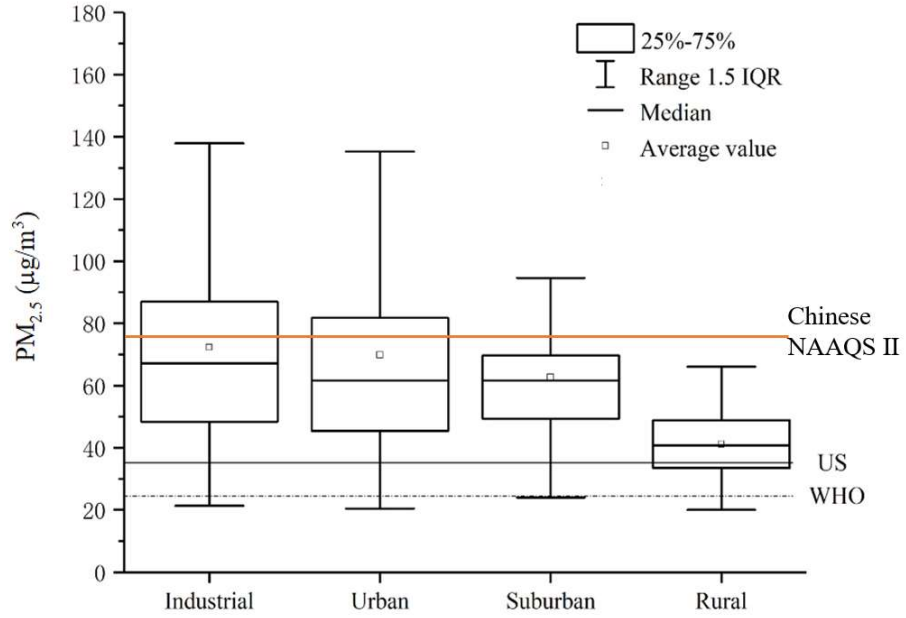

Figure 2. The concentrations of atmospheric particles with an aerodynamic diameter less than or equal to 2.5 μm ($PM_{2.5}$) in industrial, urban, suburban, and rural areas of Nanjing city during 2016 compared with typical international air quality guideline values (24 h).

Representatively, the seasonal distributions of $PM_{2.5}$ were compared between the industrial and urban areas, considering their intensive human activities and dense populations [18]. The seasonal concentrations of $PM_{2.5}$ in the two functional areas were winter > spring > autumn > summer, and in the industrial area, they were slightly higher than in the urban area (Figure 3). That may be due to the intensive pollutant sources from energy consumption. Also, the serious aerosol pollution in the cold season of Nanjing might be affected by meteorological conditions with less precipitation and lower atmospheric boundary layers [19].

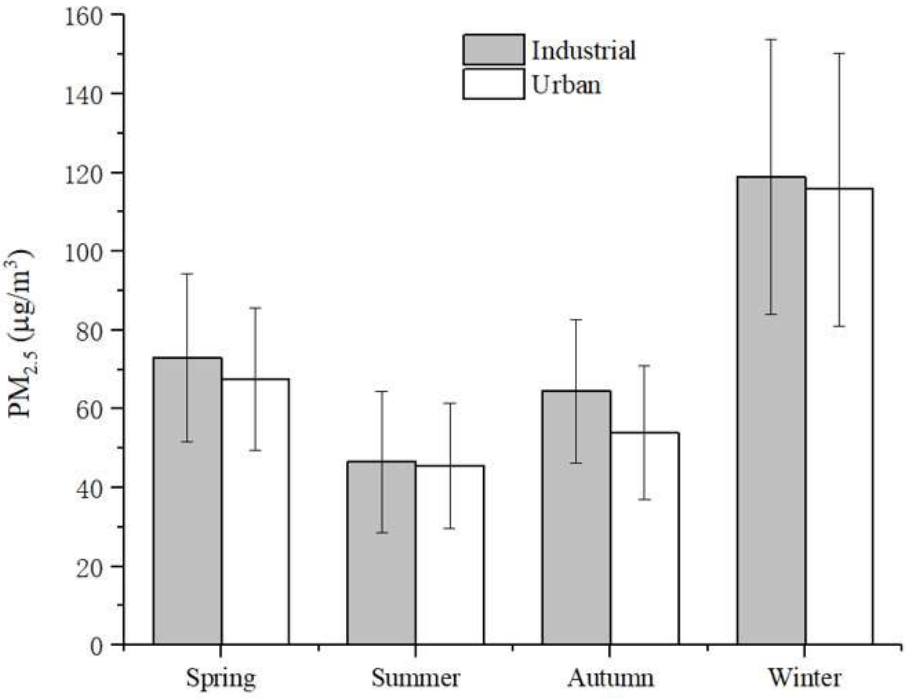

Figure 3. Seasonal average concentrations of $PM_{2.5}$ in industrial and urban areas of Nanjing city during 2016.

The average concentrations of $PM_{2.5}$ between the representative warm and cold seasons were compared among four different functional regions in Nanjing city during 2016 (Figure 4). The average concentrations of $PM_{2.5}$ in the four functional areas were cold season > warm season. However, the average concentration of $PM_{2.5}$ was highest in the suburban area in the warm season. That may be due to the fact that the impact of human activities is less than that of the other three areas.

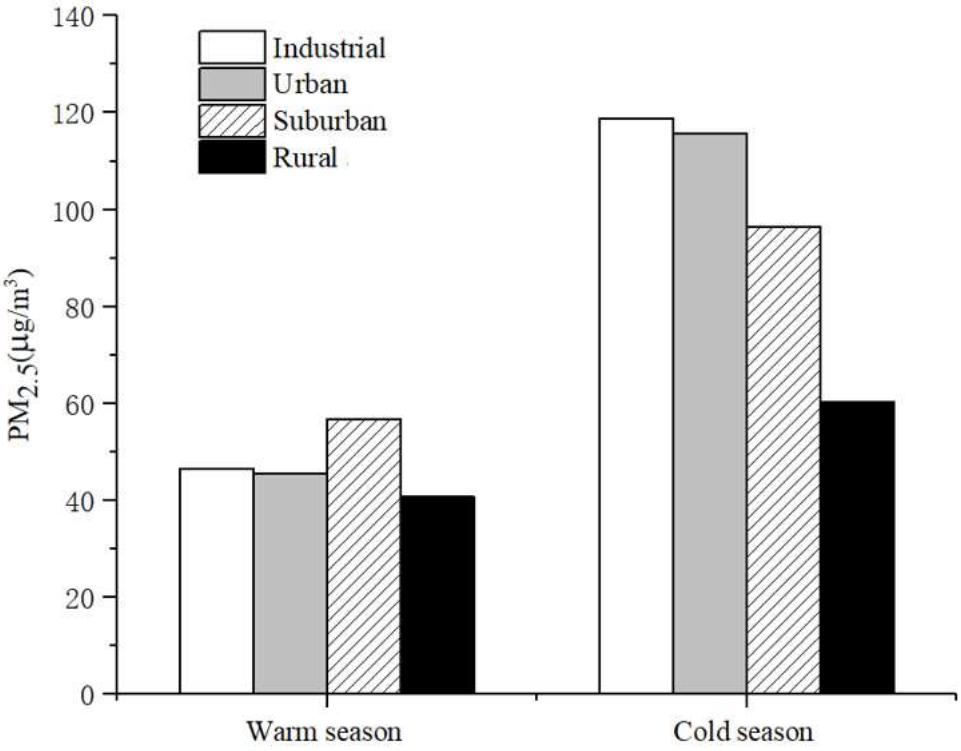

Figure 4. Comparison of average concentrations of $PM_{2.5}$ between the representative warm and cold seasons among four different functional regions in Nanjing city during 2016.

3.2. *Seasonal Distribution of $PM_{2.5}$-Bound Heavy Metal Concentrations in Different Urban Functional Areas*

The annual average concentrations of heavy metals in $PM_{2.5}$ in various areas of Nanjing are shown in Table 2 and Figure 5 and are compared with other domestic and international regions and international air quality guidelines [11,33,34]. The concentrations of atmospheric heavy metals in Nanjing were generally high, especially V and Ti.

Table 2. Atmospheric concentrations (ng/m^3) of heavy metals in $PM_{2.5}$ from industrial, urban, suburban, and rural areas of Nanjing, China compared with other regions.

Regions	Year	Sb	Pb	Co	Cd	Mn	V	Cu	Ti	Sr
WHO AQG					5	150				
Industrial area [a] (n = 102)	2016	5.63	69.5	1.02	2.34	45.9	8.43	55.3	55.6	10.6
Urban area [a] (n = 102)	2016	4.96	50.6	1.06	1.95	38.9	8.24	27.8	43.1	10.2
Suburban area [a] (n = 27)	2016	4.43	45.9	0.82	1.47	46.0	5.85	25.4	74.4	12.7
Rural area [a] (n = 20)	2016	3.34	30.1	1.02	1.01	22.0	4.65	20.2	35.4	7.12
Beijing (China) [b]	2013–2014		145		1.93	54.4	2.40	35.4	1.19	
Athens (Greece) [c]	2010		6.01	3.53		15.0				
Ahvaz (Iran) [d]	2016		4.4		0.004		6			

[a] This study, [b] [33], [c] [11], [d] [34].

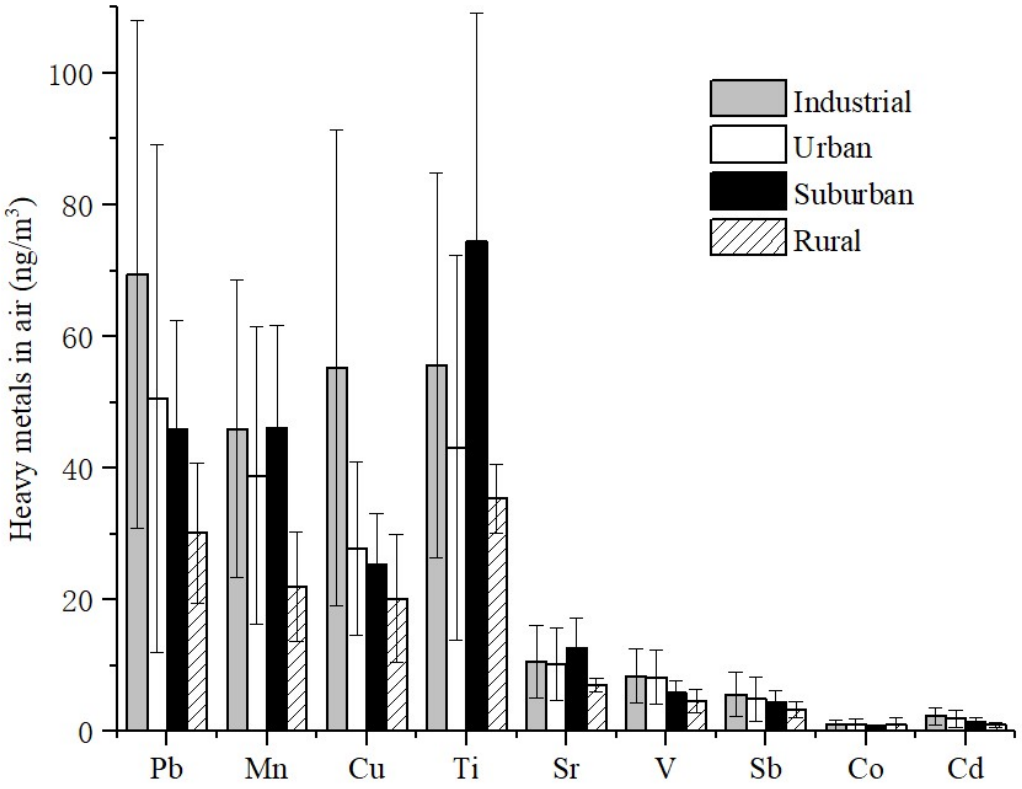

Figure 5. Comparison of the concentrations of $PM_{2.5}$-bound heavy metals (ng/m^3) in air among four different functional regions in Nanjing city during 2016.

Pb, Mn, Cu, and Ti are of higher concentrations compared with other heavy metals [26]. However, there was no clear unified spatial pattern in metal levels among the studied regions. The concentrations of six metals (Sb, Pb, Cd, V, Mn, and Cu) were highest in the industrial area, while Co was highest in the urban area. Although the remarkable role of $PM_{2.5}$ concentrations in atmospheric metal levels was observed in most studies, there were still some deviations for metal patterns in different areas [20]. Heavy metal levels were higher in winter than in summer (Table 3), similar to other air pollutants in Nanjing [21]. However, some metals, such as Pb, Cu, V, Co, and Cd, were highest in spring in the industrial area.

Table 3. Seasonal average concentrations (ng/m^3) of $PM_{2.5}$-bound heavy metals in industrial and urban sites of Nanjing city during 2016.

Location	Season	Pb	Mn	Cu	Ti	Sr	V	Sb	Co	Cd
Industrial area	Spring (n = 34)	79.9	45.9	48.8	50.2	8.14	8.29	5.98	0.80	2.12
	Summer (n = 28)	54.3	36.3	39.1	44.0	9.54	7.72	4.81	0.82	2.19
	Autumn (n = 22)	79.5	53.2	41.5	47.6	11.3	10.0	5.31	1.56	2.97
	Winter (n = 28)	63.0	52.5	86.9	93.9	16.2	7.95	5.04	1.08	2.24
Urban area	Spring (n = 34)	47.9	36.0	26.3	40.7	8.00	8.67	4.93	1.14	1.61
	Summer (n = 28)	39.7	27.3	21.4	33.2	6.95	7.17	4.57	0.92	1.67
	Autumn (n = 22)	42.6	38.0	25.6	40.8	9.60	7.62	4.74	1.11	2.04
	Winter (n = 28)	70.8	48.9	70.3	82.4	12.6	8.48	5.13	1.21	2.32

3.3. Source Identification of Airborne Metals in Different Urban Functional Areas

3.3.1. Sources Implied by EFs

The EFs of Cd, Sb, Pb, and Cu were greater than 10 for the whole year, indicating their anthropogenic enrichments, while the EFs of Mg, V, Sr, Mn, Co, and Ti were less than 10, suggesting they were less affected by human activity sources (Figures 6 and 7).

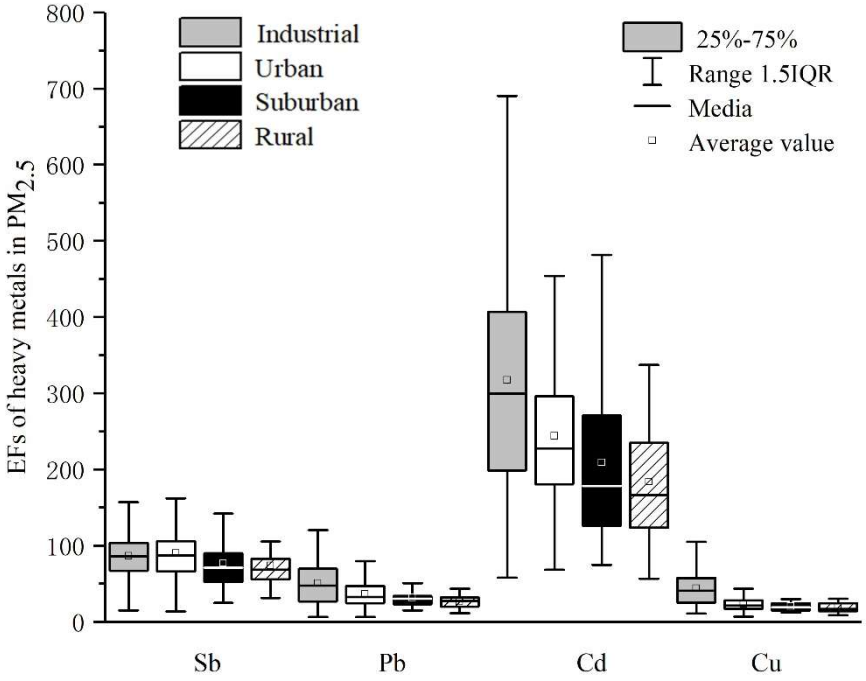

Figure 6. Comparison of the enrichment factors (EFs) of $PM_{2.5}$-bound heavy metals (EF > 10) in air among four different functional regions in Nanjing city during 2016.

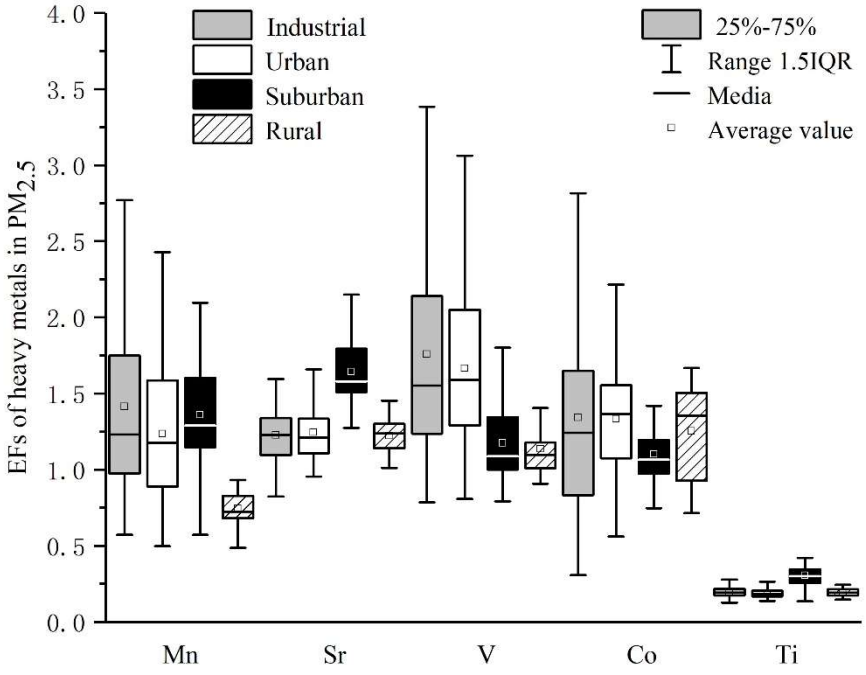

Figure 7. Comparison of the EFs of $PM_{2.5}$-bound heavy metals (EF < 10) in air among four different functional regions in Nanjing city during 2016.

The average EFs of $PM_{2.5}$-bound heavy metals in industrial areas were Cd > Sb > Pb > Cu > 10 > V > Sr > Mn > Co > Ti, and the EF of Cd was quite high. However, the concentration of air Cd was not high compared with other heavy metals, indicating that it was heavily enriched from anthropogenic sources, such as coal-fired and metallurgical chemical industries. The Sb was the marking component of coal burning, and Pb was often used as a marker for vehicle exhaust and coal combustion sources. Therefore, the main sources of airborne heavy metals in industrial areas were coal combustion, metallurgical chemical industries, and motor vehicle exhaust. The EFs of Cd, Sb, Pb, and Cu were all >10 in the urban area, where traffic emissions greatly contributed to this [35]. No significant difference was found in EFs of any measured elements between the suburban and rural areas.

3.3.2. Sources Implied by PCA

In order to further clarify the sources of heavy metals in $PM_{2.5}$, the PCA results are shown in Table 4. For the industrial area, all variables were divided into three factors by PCA, with a cumulative contribution of 74.6%. The PC1 was linked to Sr, Al, and Ti (Table 4). As indicated by the relatively low EF values of Sr and Ti, they were mainly from natural sources, such as soil and dust. PC2 was mainly related to Co, V, and Mn, which might have been mainly from petrochemicals. PC3 was mainly related to Sb, Pb, Cd, and Cu, which were contributed by metallurgical chemical dust and traffic [36].

Table 4. Results of principal component analysis (PCA) of heavy metals in $PM_{2.5}$ from industrial, urban, suburban, and rural areas of Nanjing, China.

Elements	Industrial Area			Urban Area				Suburban Area			Rural Area			
	PC1	PC2	PC3	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC1	PC2	PC3	PC4
Sb	0.353	0.009	0.678	0.191	0.363	**0.758**	0.129	0.165	0.383	**0.656**	0.050	**0.728**	0.215	0.071
Pb	0.064	0.254	**0.796**	0.042	0.054	**0.884**	0.187	0.112	0.085	**0.843**	0.097	**0.720**	0.023	0.482
Co	0.210	**0.868**	0.033	0.204	**0.724**	0.123	0.229	**0.790**	0.221	0.202	0.031	0.045	**0.896**	0.133
Cd	0.268	0.069	**0.826**	0.554	0.221	0.499	0.159	0.041	0.051	**0.879**	0.109	0.030	0.154	**0.940**
Mn	0.162	**0.856**	0.349	0.165	0.322	0.149	**0.769**	0.276	**0.756**	0.201	0.412	**0.835**	0.049	0.029
V	0.433	**0.670**	0.264	0.268	**0.758**	0.072	0.079	**0.799**	0.043	0.261	0.311	0.484	**0.696**	0.053
Cu	0.100	0.347	**0.701**	0.106	**0.611**	0.534	0.161	**0.841**	0.150	0.323	**0.718**	0.028	0.265	0.298
Ti	**0.844** *	0.102	0.107	**0.790**	0.303	0.048	0.303	0.155	**0.891**	0.159	**0.906**	0.161	0.150	0.276
Al	**0.794**	0.404	0.339	**0.861**	0.405	0.094	0.185	**0.893**	0.290	0.118	**0.958**	0.168	0.155	0.046
Sr	**0.848**	0.315	0.205	**0.840**	0.118	0.002	0.331	**0.849**	0.376	0.016	**0.948**	0.218	0.083	0.155
Eigenvalue > 1	3.27	2.86	2.82	3.228	2.32	1.99	1.77	4.51	2.69	2.24	4.92	2.37	1.53	1.44
Variance %	27.2	23.9	23.5	26.9	19.3	16.7	14.7	37.6	22.4	18.7	40.9	19.7	12.8	11.9
Cumulative %	27.2	51.1	74.6	26.9	46.2	62.9	77.6	37.6	60.0	78.7	40.9	60.7	73.4	85.4
Source	Natural source Metallurgical chemical dust			Natural source Automobile exhaust				Natural source Automobile exhaust			Natural source			

* Bold numbers (>0.6) indicate a significant association in an analyzed principle component.

All variables were divided into four factors in the urban area, with an additional source for Mn, which mainly came from natural sources. The results of sources implied by PCA indicated that the sources of heavy metals in the suburban area were natural and traffic sources. In addition, the heavy metals in the rural area mainly came from natural sources.

3.4. Spatial Characteristics of Human Health Risks of Airborne Metals

Heavy metals such as Cd are classified as class A carcinogenic, Pb as class 2A, Co as class 2B, and Mn and Cu are not carcinogenic. Although the noncarcinogenic hazards to adults were greater than those to children, that of $PM_{2.5}$-bound heavy metals in Nanjing were below the threshold value 1 (Table 5), comparable to Jinan city [37] and Mexico [38]. Among the five metals, Mn had the highest HQ and should be monitored. The ILCR values of Cd were slightly higher than Co and both exceeded 1×10^{-6} in most areas; thus, their emissions should be strictly controlled. Compared with the risks

found in other studies [39–41], the noncarcinogenic risk of airborne metals to adults and the cancer risks of Cd and Co in Nanjing are an environmental issue, especially in the industrial and urban areas.

Table 5. Hazard quotient (HQ) and increased lifetime cancer risk (ILCR) for heavy metals in $PM_{2.5}$ from industrial, urban, suburban, and rural areas during 2016.

Health Risk	Elements	Industrial Area		Urban Area		Suburban Area		Rural Area	
		Adult	Children	Adult	Children	Adult	Children	Adult	Children
Noncarcinogenic Hazard	Pb	1.52×10^{-3}	8.16×10^{-4}	1.10×10^{-3}	5.94×10^{-4}	1.00×10^{-3}	5.38×10^{-4}	6.57×10^{-4}	3.54×10^{-4}
	Co	1.37×10^{-2}	7.35×10^{-3}	1.42×10^{-2}	7.64×10^{-3}	1.10×10^{-2}	5.91×10^{-3}	1.37×10^{-2}	7.35×10^{-3}
	Cd	1.79×10^{-4}	9.62×10^{-5}	1.49×10^{-4}	8.01×10^{-5}	1.12×10^{-4}	6.04×10^{-5}	7.71×10^{-5}	4.15×10^{-5}
	Mn	2.50×10^{-1}	1.35×10^{-1}	2.12×10^{-1}	1.14×10^{-1}	2.51×10^{-1}	1.35×10^{-1}	1.20×10^{-1}	6.45×10^{-2}
	Cu	1.05×10^{-4}	5.68×10^{-5}	5.30×10^{-5}	2.85×10^{-5}	4.84×10^{-5}	2.61×10^{-5}	3.85×10^{-5}	2.07×10^{-5}
Carcinogenic Risk	Co	1.17×10^{-6}		1.22×10^{-6}		9.44×10^{-7}		1.17×10^{-6}	
	Cd	1.73×10^{-6}		1.44×10^{-6}		1.09×10^{-6}		7.47×10^{-7}	

4. Conclusions

The characteristics for concentrations and health risks of $PM_{2.5}$ and associated heavy metals showed spatial and seasonal patterns in different urban functional areas owing to various sources and components. Although heavy metals are minor components accumulated in atmospheric PM, their distribution patterns are not always consistent with the overall PM. Therefore, both human health risk assessments and air quality guidelines for PM pollution control should consider and include these key pollutants. More detailed and accurate source investigations for ambient aerosols and associated heavy metals are needed in future research. Besides strengthening emission controls for clean air, we recommend reducing outdoor activities in industrial and traffic areas, especially in spring and winter.

Author Contributions: X.-S.L. designed the overall project; L.W. and Z.Z. conceived and carried out the experiments; L.W. and X.-S.L. led the writing of the manuscript; L.C., J.Y., M.T., and J.Y. performed the sampling; H.L. performed sample analysis.

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