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$PM_{2.5}$-Bound Heavy Metals in Southwestern China: Characterization, Sources, and Health Risks

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Abstract: The health risks of $PM_{2.5}$-bound heavy metals have attracted extensive attention recently. In order to evaluate those deleterious effects on human health more accurately, and to propose proper measures to reduce health risks of air pollution, the conduction of a source-specific health risk assessment is necessary. Based on daily collected $PM_{2.5}$ samples at different functional sites during winter 2019 in a megacity Chongqing, China, combining source apportionment results from PMF and health risk assessment from the U.S. EPA, the source-specific health risks from $PM_{2.5}$-bound heavy metals were given. Six types of $PM_{2.5}$ sources have been identified, coal burning (25.5%), motor vehicles (22.8%), industrial emissions (20.5%), biomass burning (15.9%), dust (7.8%), and ship emissions (7.5%). Results showed that the total hazard quotient (HQ) was 0.32 and the total carcinogenic risks (CR) were 2.09×10^{-6} for children and 8.36×10^{-6} for adults, implying certain risks for local residents. Industrial emissions related with Cr posed both the highest carcinogenic risk and noncarcinogenic risk (contributing 25% CR and 36% HQ). Coal combustion (associated with Cr, As, and Mn) contributed 15.46% CR and 20.64% HQ, while biomass burning and motor vehicles shared 19.99% and 19.05% of the total CR, respectively. This work indicated that health risks of air pollution sources were the combined effects of the source contribution and chemical components. In order to control the health risks of $PM_{2.5}$ to the local residents, the priority of targeted emission sources should be adopted for industrial emissions, biomass burning, vehicle emissions, and coal combustion sources.

Keywords: $PM_{2.5}$; heavy metal; health risk sources; air pollution

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1. Introduction

The components of atmospheric fine particulate matters ($PM_{2.5}$) are very complicated, including carbonaceous components (organic carbon, OC; elemental carbon, EC), major water-soluble inorganic ions, and trace elements [1,2]. Inhaled $PM_{2.5}$ can settle in the lungs and blood, causing harmful effects on human health, respiratory diseases such as bronchitis and asthma, as well as heart disease, which are more likely to occur or worsen in areas with high levels of $PM_{2.5}$ pollution [3–5]. Some $PM_{2.5}$ components can be highly deleterious at low concentrations, such as heavy metals (HMs), which have been shown to cause dysfunctions and carcinogenicity even though only at the level of nanograms per cubic meter in the air [6,7]. The inhaled $PM_{2.5}$ is an important approach for HMs get into human body and accumulate in the organs and blood [5]. Long-term human exposure to Pb may have adverse effects on the blood and central nervous system [8], e.g., pregnant women exposed to Pb, As, Cd, and Hg during the early and late gestation of pregnancy have an increased incidence of childhood asthma [9]; As, Cd, and $Cr_{(VI)}$ in the environment put children at a higher noncarcinogenic risk than adults [6].

Former studies have researched the pollution status of HMs in $PM_{2.5}$ in different polluted Chinese cities. Generally, HMs in $PM_{2.5}$ increased from southern to northern China. Northern cities such as Harbin, Taiyuan, Tianjin, Baoding, Xi'an, Lanzhou, and southern cities such as Kunming, Nanchang, and Wuhan [6,10] displayed relatively high HMs. According to Li et al. [6], the average concentrations of As and Cd have exceeded the annual limits of Chinese Ambient Air Quality Standard (GB3095-2012) by 74% and 33% in some cities; As was even 20 times over its limits (6 ng/m^3) in some cases, with both Xi'an and Kunming having concentrations of more than 105 ng/m^3. Baoding, Nanchang, Lanzhou, Taiyuan, Tianjin, and Kunming held high Pb concentrations in the range of 281 ng/m^3–433 ng/m^3 [10,11]. Li et al. [6] evaluated the pollution degree of $PM_{2.5}$-bound HMs in major cities of China, using enrichment factors (EFs) as the index. All obtained EFs were higher than 1; EFs of Cd, Hg, Pb, Zn, Cu, As, Cr, and Ni in major cities were greater than 40—EF > 20 is usually considered highly enriched and severely polluted by anthropogenic emissions; the relatively high EFs reflected the noteworthy pollution status of $PM_{2.5}$-bound HMs contributed by anthropogenic sources.

The sources of HMs are very complicated, mainly including crustal sources, coal combustion, traffic emissions, heavy-metal smelting, and other industrial emissions. Coal has been the major energy source for a long time in China. As and Cr are produced by coal burning, winter heating, and coal-dominated industrial emissions, which are the main related sources in northern and northwest China [12–14]. Cd and Ni pollution were related to heavy industrial emissions; Ni and V often share similar characteristics and are regarded as trace markers for heavy diesel burning in ship emissions [15], usually showing lower mass concentrations in inland cities than coastal areas [16,17]. Liu et al. [7] developed a provincial emission inventory of 13 HMs from 10 anthropogenic sources in China based on 2015 $PM_{2.5}$ emission and historical source profiles; the total emission of the mentioned 13 HMs was about 58,000 tons for the base year, and iron production was thought to be the main source of HMs. The northern and eastern regions have generally had a higher emission load, Chongqing's HMs emission was relatively low throughout the country, but emissions in the neighboring provinces like Sichuan (Cd, V, Ba, As, Cr, Sn), Guizhou (Cd, Sb, Co, Ni, Sn), Hubei (Zn, As, Pb, Cu, Mn), and Hunan (Co, As, Cr, Pb, Cu, Mn) were relatively high. $PM_{2.5}$-bound HMs can transport far away after being emitted from sources due to their stability in the atmosphere, yielding regional pollution [18]. Air-quality models and receptor models have been widely used in source apportionment of $PM_{2.5}$ and associated components. Wang et al. [19] used Positive Matrix Factorization (PMF) to analyze the sources of $PM_{2.5}$ from 1973 to 2010 in Chengdu; HMs were included in the factor identification of the PMF model. It was found that Pb and As were mainly contributed by burning coal, petroleum, and gas; Zn, Mn, As, Pb, and Cu were mostly associated with industrial emission in this area. Kong et al. [20] also studied the $PM_{2.5}$ sources by PMF in Chengdu and identified that coal combustion, biomass burning, vehicle emissions, dust, and industrial sources were the five main $PM_{2.5}$ sources.

In the present study, we focused on HM pollution in southwest China, an area topographically isolated as it is surrounded by highlands and characterized by high relative humidity and low wind speeds [21]. Sichuan–Chongqing is one of four highly polluted areas in China and one of the most heavily affected by acid rain, which still continues in some regions [22]. The relatively strong acidity of precipitation and particulate matters in southwest China would enhance the solubility of some HMs and then increase their bioavailability and bioaccumulation [23–25]. Considering the toxic properties of HMs, studying the HMs in $PM_{2.5}$ is of great significance for evaluating the health risk from air pollution emission sources. The research area, Jiangjin District, is located in Chongqing, which is a large city in southwest China and has a population of 32 million (National Bureau of Statistics, China. 1 November 2020). Jiangjin belongs to the eastern part of the Sichuan Basin (SCB; 25°~35° N, 95°~110° E); it is obviously influenced by pollution in the basin range and can represent the corresponding regional air quality. In this work, the characteristics and sources of $PM_{2.5}$-bound HMs (Cr, As, Pb, Cu, Zn, Ni, V, Mn) were studied and their health risks were evaluated. Although As is a nonmetal element, it has similar health effects with HMs; so, As is discussed in this work. The research conclusions can provide scientific support for environmental administration of the government to establish relevant policies for reducing atmospheric pollution emissions with high health risks.

2. Methods and Materials

2.1. $PM_{2.5}$ Sampling and Chemistry Analysis

Jiangjin District is located southwest of Chongqing and is a developed industrial area about 40 km away from the city center. This project examined 5 sampling sites, among which there were two central urban sites, Jiangjin Middle school (S1) and Yuanshuai Square (S2); one suburban site, Binjiang New City (S3); and two industrial sites, De-Gan industrial zone (S4) and Shuangfu industrial zone (S5). The Yangtze River flows through Jiangjin District for 127 km and includes 135 ferry piers, there are large cargo terminals and ports in the vicinities of four industrial zones (Degan, Luohuang, Baisha, and Shuangfu). The sampling sites' information is shown in Figure 1. BGI OMNI samplers (5 L/min) were used in the urban and suburban sites (S1, S2, S3), Dandong Bettersize automatic sampler (16.67 L/min) was employed in the two industrial sites (S4, S5). All $PM_{2.5}$ samplers were placed on the roof of the building, which was about 9–15 m above the ground. $PM_{2.5}$ samples were collected by Teflon filter membrane (Whatman Corp., 47 mm) from 6 January 2019 to 28 January 2019, and collected continuously for 23 h each time from 10:00 to 09:00 the next day. A total of 114 $PM_{2.5}$ samples and 15 blank samples were obtained. The collected samples were stored in a clean refrigerator environment of −18 °C to avoid contamination and volatilization.

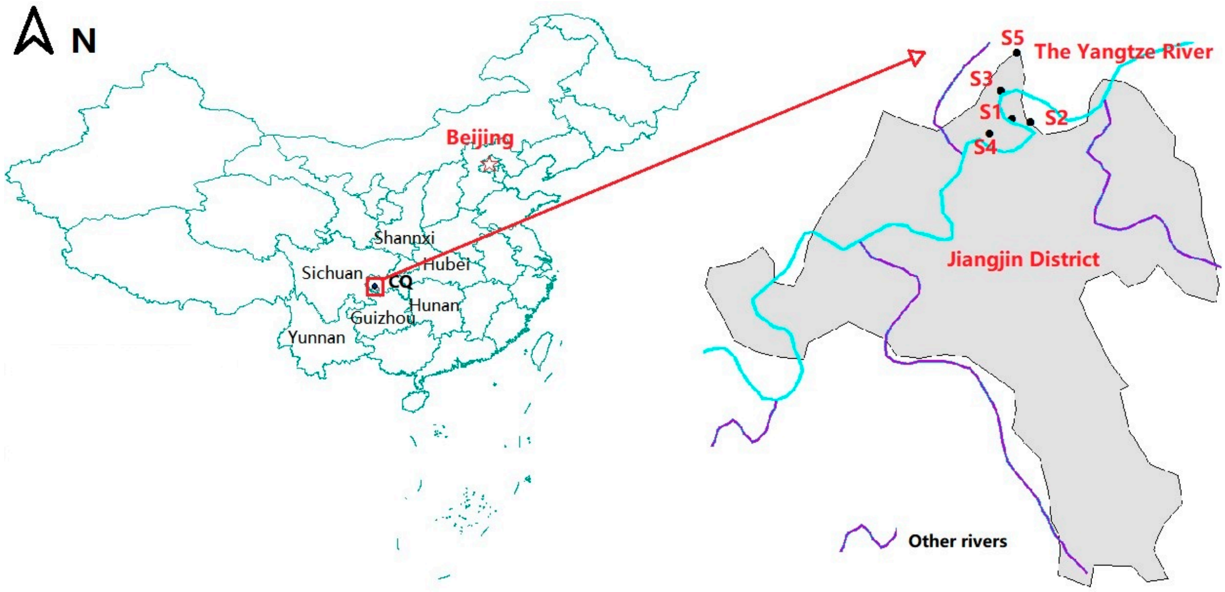

Figure 1. Location of the sampling sites in Jiangjin of Chongqing, China.

In this study, a weighing method was adopted to measure the mass of $PM_{2.5}$ samples. Before and after sampling, the Teflon filter membranes were placed in a relatively constant temperature (20–23 °C) and humidity (45–50%) environment for 48 h to reach equilibrium. Then, a microbalance (Sartorius, ME5-F, Goettingen, Germany) was used to weigh the filer membrane. The atmospheric $PM_{2.5}$ concentration can be obtained according to the ratio of $PM_{2.5}$ mass on each filter membrane and the sampling air volume. Major chemical components in $PM_{2.5}$ including water-soluble ions (SO_4^{2-}, NO_3^-, Cl^-, F^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, etc.), carbon-containing components (Organic Carbon, OC; Elemental Carbon, EC), and elements (V, Cr, Mn, Ni, Cu, Zn, As, Pb, Al, Si, Fe, Ti, etc.) have been analyzed. Water-soluble ions were analyzed by Ion Chromatography (ICS-600, Thermo Scientific, Shanghai, China); OC and EC were analyzed by Thermo-Optical Carbon Analyzer (Desert Research Institute Model 2015, Atmoslytic Inc. Calabasas, CA, USA) with Thermo-Optical Reflection (TOR) Method under IMPROVE-A (Interagency Monitoring of Protected Visual Environment) analysis protocol. Elements including HMs were analyzed by X-ray fluorescence spectrometer (Epsilon 5 ED-XRF, Palytical B.V., Netherlands). For methods of quality control and quality assurance, please refer to Wang et al. [26].

2.2. Health Risk Estimation of $PM_{2.5}$-Bound Heavy Metals

The carcinogenic and noncarcinogenic risks by $PM_{2.5}$-bound HMs via inhalation were calculated by adopting the U.S. Environmental Protection Agency (US EPA) human health risk assessment models (US EPA, 1989) [27]. The adverse effects of heavy metals were determined by their bioavailable toxicity, which were influenced by chemical form, solubility, active organic location, aerosol surface property, and so on. The method included calculation of the deposition fraction of $PM_{2.5}$ that can penetrate in lungs [28], the bioavailable concentration of each HM during the monitoring periods [29], the exposure concentration of $PM_{2.5}$-bound HMs (EC), hazard quotient (HQ, noncarcinogenic health risk), and carcinogenic risk (CR). This study referred to the bioavailable ratios of $PM_{2.5}$-bound HMs in another research in China—the detail can be seen in Huang et al. [29]. The sensitive residents were divided into two groups, adults and children, the inhalation reference concentration (RfC, mg m^{-3}) and inhalation unit risk (IUR, $(\mu g\ m^{-3})^{-1}$) were obtained from the Regional Screening Level (RSL) Resident Ambient Air Table (US EPA, 2021) [30]. The 8 HMs that induce noncarcinogenic risks are V, Cr, Mn, Ni, and As, those showing carcinogenic risks are V, Cr, Ni, As, and Pb. The carcinogenic health risks of each air pollution source were assessed by the sum of CR of carcinogenic HMs contributed by that source (CR_s), as were the noncarcinogenic health risks of that source (HQ_s). The CR_s and HQ_s are calculated by Equations (4) and (5), respectively.

$$EC = \frac{C_b \times E_i \times ET \times EF \times ED}{ATn} \tag{1}$$

$$CR_i = IUR_i \times EC \ (i = V, Cr_{(VI)}, Ni, As, Pb) \tag{2}$$

$$HQ_i = \frac{EC}{RfC \ \times 1000\ \mu g\ mg^{-1}} \ (i = V,\ Cr(_{VI}),\ Mn,\ Ni,\ As) \tag{3}$$

$$CR_{sj} = \sum(CR_i \times RC_{ij}) \ (i = V, Cr(_{VI}), Ni, As, Pb) \tag{4}$$

$$HQ_{sj} = \sum(HQ_i \times RC_{ij}) \ (i = V, Cr(_{VI}), Mn, Ni, As) \tag{5}$$

where C_b is the average bioavailable concentrations of particulate elements (referring to the bioavailable index of heavy metals in Huang et al. [29]); E_i is the deposition fraction of $PM_{2.5}$ that can penetrate in lungs [28] (Volckens and Leith, 2003); ET is the exposure time (24 h/day); EF is the exposure frequency (180 day/year); ED is the exposure duration (6 years for children and 24 years for adults); ATn is the averaging time (for noncarcinogens ATn = ED × 365 day/year × 24 h/day; for carcinogens ATn = 70 year × 365 day/year × 24 h/day); RC_{ij} is the contribution rate of air pollution source j to element i in $PM_{2.5}$, which was provided by $PM_{2.5}$ source apportionment results; CR_{sj} and HQ_{sj} are the CR and HQ of source j.

3. Results and Discussion

3.1. Pollution Characteristics of Heavy Metals in $PM_{2.5}$

The mean concentration of $PM_{2.5}$ and HMs in $PM_{2.5}$ during the observation period were shown in Table 1. The average $PM_{2.5}$ concentration was 97.06 μg/m^3, varied at each site from 84.56 ± 28.39 to 106.60 ± 36.11 μg/m^3; of the 114 samples, 83 had $PM_{2.5}$ concentrations above 75 μg/m^3 (the second level of Chinese Ambient Air Quality Standard, GB3095-2012). The highest $PM_{2.5}$ concentration was 168.77 μg/m^3, 2.25 times the second-level limit.

Table 1. The concentrations of $PM_{2.5}$ and $PM_{2.5}$-bound HMs (mean ± std).

Sites	S1	S2	S3	S4	S5	All
$PM_{2.5}$ (μg/m^3)	106.60 ± 36.11	92.92 ± 32.84	84.56 ± 28.39	101.25 ± 35.49	92.10 ± 32.48	97.06 ± 33.05
HMs (ng/m^3)	201.41 ± 34.03	193.95 ± 33.75	163.30 ± 26.82	329.53 ± 53.28	198.54 ± 29.35	220.46 ± 72.53
Zn (ng/m^3)	100.78 ± 65.46	100.17 ± 51.95	78.03 ± 33.62	104.08 ± 34.73	82.51 ± 24.94	94.22 ± 32.90
Mn (ng/m^3)	34.99 ± 15.94	30.69 ± 12.06	31.97 ± 14.89	142.17 ± 89.41	50.28 ± 20.51	58.63 ± 24.48
Pb (ng/m^3)	39.38 ± 13.50	38.32 ± 15.67	33.02 ± 11.16	40.48 ± 15.00	36.10 ± 13.48	37.93 ± 13.29
Cu (ng/m^3)	13.25 ± 6.38	12.44 ± 5.68	11.85 ± 5.14	25.63 ± 18.02	14.76 ± 6.05	15.83 ± 7.22
As (ng/m^3)	6.52 ± 4.55	8.05 ± 3.99	4.43 ± 3.86	8.15 ± 4.28	8.97 ± 5.75	7.56 ± 4.38
Cr (ng/m^3)	5.04 ± 2.55	2.92 ± 1.18	2.76 ± 1.46	6.21 ± 3.36	4.07 ± 2.14	4.29 ± 1.76
Ni (ng/m^3)	1.14 ± 1.33	1.00 ± 0.58	0.54 ± 0.68	1.82 ± 1.38	1.50 ± 0.54	1.39 ± 0.42
V (ng/m^3)	0.30 ± 0.20	0.36 ± 0.25	0.70 ± 0.68	1.00 ± 0.50	0.36 ± 0.28	0.60 ± 0.25

HMs—heavy metals; std—standard deviation.

The total concentration of 8 HMs was 220.46 ng/m^3 ranged from 163.30 to 329.53 ng/m^3 at five sites on average, which accounted for 0.19% to 0.33% of $PM_{2.5}$. Zn, Mn, and Pb were the three HMs with high concentrations, accounting for 42.74%, 26.60%, and 17.21% of the total HMs, respectively. The $PM_{2.5}$ and its chemical compositions of urban areas in Chongqing and Chengdu have been reported by Chen et al. [31] and Tao et al. [32], respectively. In their research, the concentrations of Zn, Mn, and Pb were also higher than those of Cu, As, Cr, Ni, and V. It has also been reported that Zn and Pb in $PM_{2.5}$ were higher than other HMs during winter in northern China such as Baoding and Beijing [10,11,33]. When compared with the results in 2012, obtained at an urban area of Chongqing by Chen et al. [31], the HMs' concentrations have decreased, except for Mn and As, which somehow indicate that the air quality in this region has been getting better.

The $PM_{2.5}$ concentrations generally showed urban > industrial zone > suburban, while $PM_{2.5}$-bound HMs were industrial zone > urban > suburban. HMs at the southern industrial site (S4, De-Gan Industrial zone) were the highest, accounting for 0.33% of $PM_{2.5}$, especially Mn, Cu, Ni, and V, maximally 4.63, 2.16, 3.37, and 3.33 times of that at other sampling sites, respectively. However, HM concentrations at the northern industrial site (S5, Shuangfu industrial zone) were similar to those at urban sites. A possible reason was that the Shuangfu industrial zone was only about 40 km southwest of the downtown area of Chongqing. Under the dominant northeast wind, S5 was significantly influenced by the air pollution from the upwind downtown area.

As shown in Figure 2, among all heavy metals, the time trend of Pb and $PM_{2.5}$ has the best correlation, and the correlation coefficients of the five sites are 0.8~0.91. According to the PMF results of $PM_{2.5}$ and $PM_{2.5}$-bound HMs, the proportions of Pb in source profiles of coal burning, motor vehicles, and industrial emission were quite close to each other, and these three sources contributed about 69% $PM_{2.5}$ and 58% of total Pb in $PM_{2.5}$, which can explain the high consistency between $PM_{2.5}$ and Pb. Except for S4, the correlation coefficients between Cu and $PM_{2.5}$ were 0.66~0.80. The correlation between as and $PM_{2.5}$ showed obvious differences between sites, poorly correlated in the central urban sites (0.37 and 0.34 at S1 and S2, respectively), while good in the suburbs and industrial sites (0.64, 0.70, and 0.77 in S3, S4, and S5, respectively). The correlation between Zn and $PM_{2.5}$ was quite similar to that of As. The concentrations of V at the five sites had relatively small changes, indicating that it may have stable local sources like industrial emissions and ship emissions. Generally, the different variation trend of $PM_{2.5}$-bound HMs among the five sites suggested differences in $PM_{2.5}$ sources.

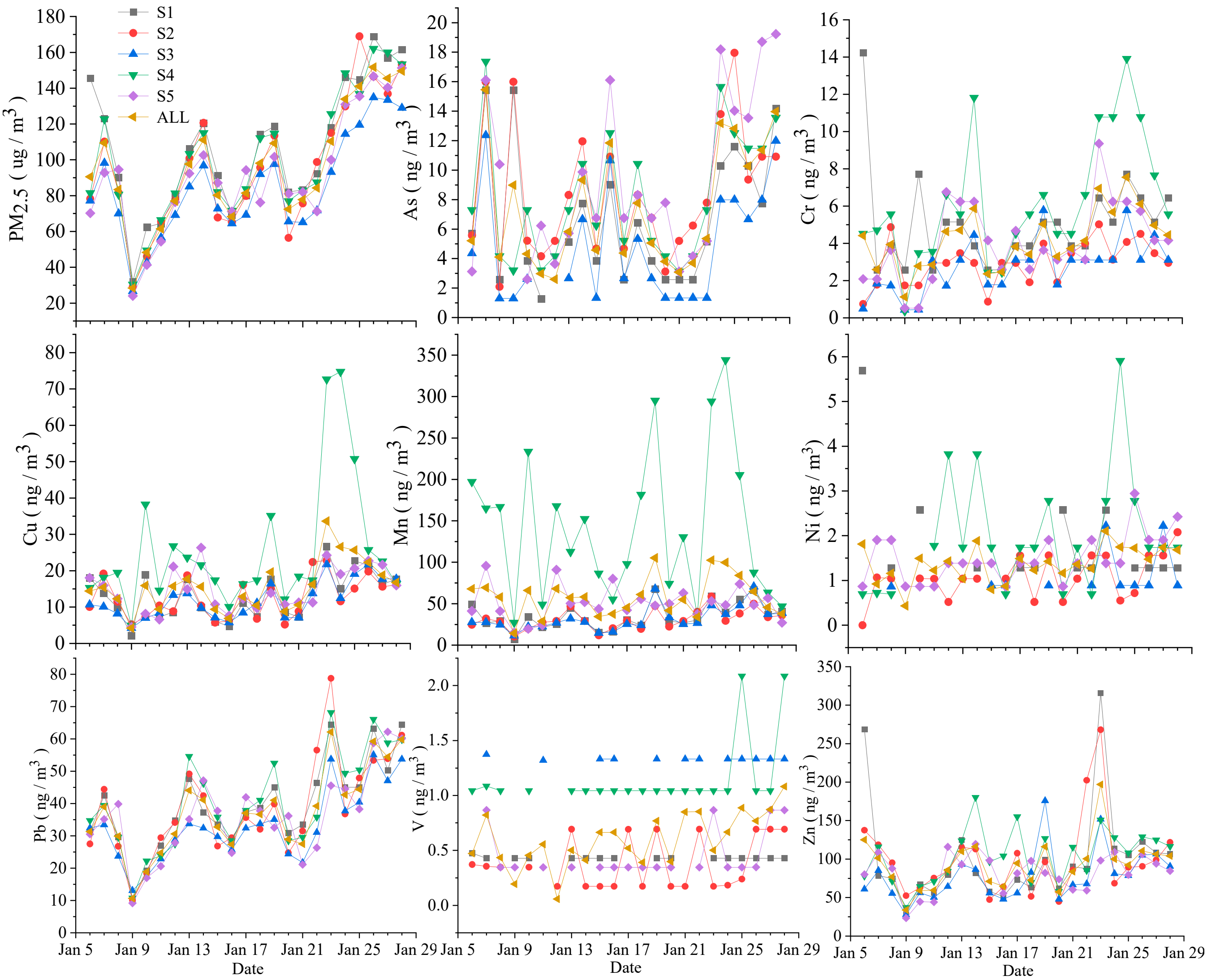

Figure 2. Temporal variation of $PM_{2.5}$-bound HMs at five sampling sites.

Table 2 lists the standard limits for heavy metals defined by China, WHO, the EU, and other countries. On average, As and Cr were the two HMs exceeding the standard limits of GB3095-2012 (As was 26% higher and Cr was 170 times higher) and WHO (As was 15% higher and Cr was 16 times higher). The concentration of $PM_{2.5}$-bound Mn at the De-Gan industrial zone was higher than GB3095-2012 and WHO limits in nearly half of the sampling time with the highest value of 344.17 ng/m^3. The HMs' pollution in this area was worthy of attention.

Table 2. Reference concentration limits for HMs in ambient air (ng/m^3).

Source	Pb	V	As	Mn	Ni	Cr ($_{VI}$)	Issued Year
GB3095-2012	500		6	150		0.025	2012
WHO	500	1000	6.6	150	25	0.25	2000
EU			6		20		2004
U.S. EPA	150						2016
India			6		20		2009

WHO—World Health Organization; EU—European Union; U.S. EPA—U.S. Environmental Protection Agency.

3.2. Sources of Fine Particulate Heavy Metals

3.2.1. Source Apportionment of $PM_{2.5}$

Positive Matrix Factorization (PMF) was used to identify the pollution sources of $PM_{2.5}$ and the related heavy metals in the study area (Q_{true}/Q_{exp} = 1.003; detailed method description is available in the literatures reported by Amato and Hopke [34] and Polissar et al. [35]. The other chemical components of $PM_{2.5}$, including OC, EC, major water-soluble inorganic ions (F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+), and other trace elements (Al, Si, Fe, Ti), have also been added into PMF to trace the possible sources. For the five sites on average, we identified the following 6 $PM_{2.5}$ sources in descending order: coal burning (25.5%), motor vehicles (22.8%), industrial emissions (20.5%), biomass burning (15.9%), dust (7.8%), ship emissions (7.5%) Figure 3. The first factor with high levels of SO_4^{2-}, NO_3^-, OC, EC, K^+, and NH_4^+ was recognized as coal burning [1,29]. Coal combustion plays a major role in Chinese energy consumption and air pollution, former studies have pointed out that coal combustion contributes over 1/3 of $PM_{2.5}$ [21] and was the highest air pollution source in Sichuan Basin. The second factor was characterized by high OC, EC, NO_3^-, and NH_4^+, this factor represented $PM_{2.5}$ from motor vehicles [1,36], which was correlated to the motor vehicle emissions from the vicinity of urban areas such as Chengdu and Chongqing. The sampling sites (29.25°~29.40° N, 106.21°~106.29° E) were located at the southeast Sichuan Basin and only about 40~60 km away from the central downtown of Chongqing, as shown in Figure 1. SCB is a lowland region with more than 11.3 million vehicles, the west and the north of Jiangjin District are generally plain cities, the south includes the Yunnan–Guizhou Plateau, and Wushan Mountains is to the east. under the combined action of disadvantageous diffusion conditions and high vehicle numbers, vehicle emissions have become the important $PM_{2.5}$ source of the study region. The third factor was dominated by metal elements such as Al, Fe, Mn, Ti, Ni, Cu, Cr, and Zn; OC, EC and NO_3^- also had significant proportions, which have been considered to be industrial emissions [37,38]. To the northwest of the sampling locations, the adjacent Sichuan province has about 15 steel industries. Chongqing also has a developed automobile manufacturing industry and iron and steel industry. In these factories, it often needs to be accompanied by high energy consumption such as coal combustion sources, so both metallic particulate matter and burning particles existed in this factor. The fourth factor was characterized by high levels of SO_4^{2-}, NO_3^-, NH_4^+, OC, K^+, and Cl^- and considered to be biomass burning [39,40]. The SCB is one of the most important grain-producing areas in China, as many local rural areas still rely on biomass as their main energy source. Early studies also have widely stated that biomass burning was one of the main sources of air pollution in this area, e.g., 12.8% in Wang et al. [19], 11.7% in Kong et al. [20], and even reached up to 56~65% in Zhou et al. [41,42] and Song et al. [43]. The last two factors were identified as dust and ship emissions, contributing roughly the same amount (less than 8%) to $PM_{2.5}$. The dust factor was characterized by Na, Ca, Mg, Si, and Al [44,45]. Due to the occlusive terrain, the dust was mostly from local sources such as road dust caused by vehicle movement, construction dust, and soil dust due to urban construction [29]. With the continuous advancement of urbanization process in China, there have been steady construction activities in Chinese cities, including many muck and slag trucks shuttling between the urban area and suburbs, which were thought to be the main dust origin of the sampling sites. The proportions of V, Ni, and Mg in the last factor's source profile from PMF results were the highest among all the recognized sources. Ni and V have been regarded as trace markers for heavy diesel burning in ship emissions [11,15], then they were identified as ship emissions, which were also characterized by EC and NO_3^- due to cargo ships generally running on diesel in this area. The sampling sites are located near the Jiangjin Port area along the Yangtze River, which is the main transit port for goods from western Chongqing, northern Guizhou, and southern Sichuan. Therefore, ship emissions would contribute a proportion of air pollution in Jiangjin.

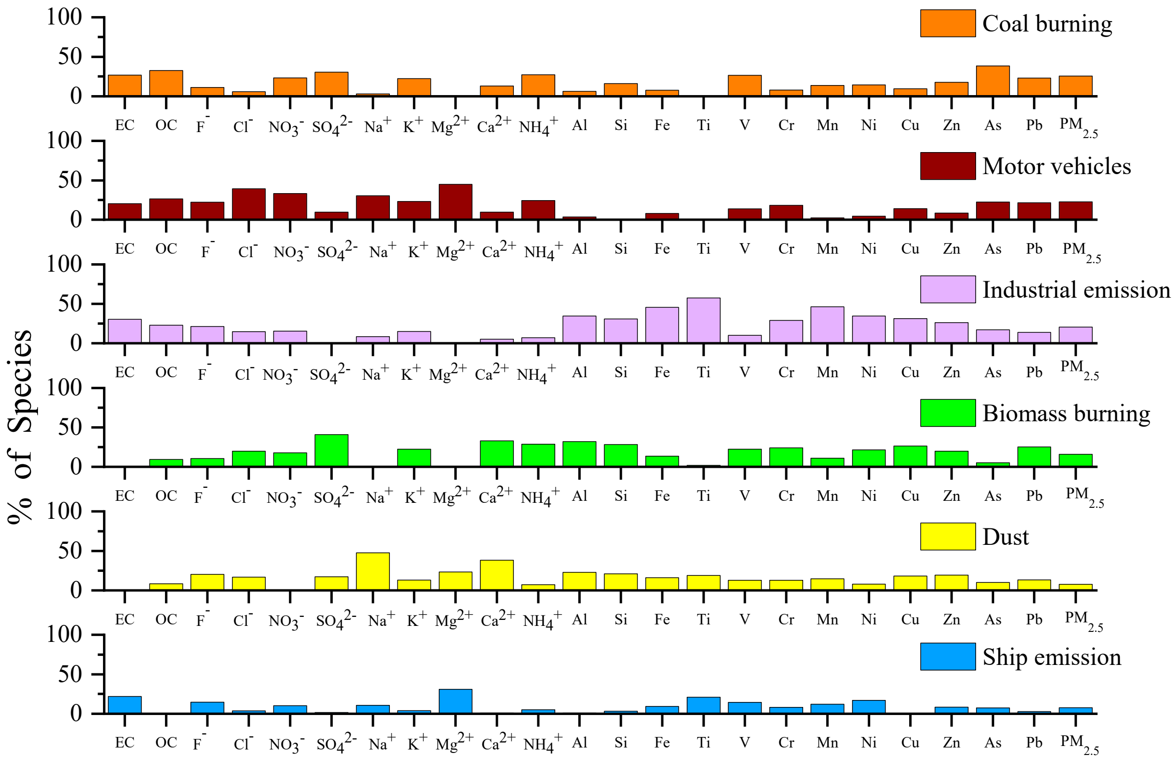

Figure 3. Relative source contributions to the measured $PM_{2.5}$ and associated components.

3.2.2. Source Apportionment of $PM_{2.5}$-Bound Heavy Metals

According to the PMF results, the relative contribution of the above sources to the 8 mentioned HMs was given in Figure 4. The contributors of heavy metals were different from $PM_{2.5}$, the order of source contributions to the 8 $PM_{2.5}$-bound HMs was industrial emissions (29.2%) > biomass burning (18.7%) > coal burning (17.7%) > dust (16.4%) > vehicle emissions (10.4%) > ship emissions (7.6%). Although coal burning was the largest $PM_{2.5}$ contributor, in total, industrial emissions contributed the most of the 8 HMs, and the sources of different metallic elements also varied. V was mainly contributed by coal burning and biomass burning, while motor vehicles, ship emissions, and dust also contributed certain amounts of V. The proportion of V in the ship emissions' $PM_{2.5}$ profile from PMF was highest and always used as a marker of heavy oil burning [46–48]. Cr was mainly contributed by industrial emissions and biomass burning; motor vehicles also took account of 18% of the total $PM_{2.5}$-bound Cr. Mn mainly originated from industrial emissions, such as the manganese steel production process [46,49]. The sources of Mn were dust, coal burning, and ship emissions. Ni, Cu, and Zn were mainly emitted from industrial emissions such as metal smelting, while the contribution of biomass burning should not be ignored. Ni can also be emitted from diesel exhausts [46,47,50]; the proportion of ship emissions and motor vehicles contributed about 21% of the total $PM_{2.5}$-bound Ni. Dust, biomass burning, and coal burning shared similar contribution proportions to $PM_{2.5}$-bound Zn. It has been reported that Zn accounted for about 1% in the $PM_{2.5}$ source profile of coal combustion [51]. As was mainly contributed by coal burning, which is used as a tracer for coal combustion [7,52]. Motor vehicles, biomass burning, and coal combustion were three major Pb sources in this study—this is consistent with the results of [11,53].

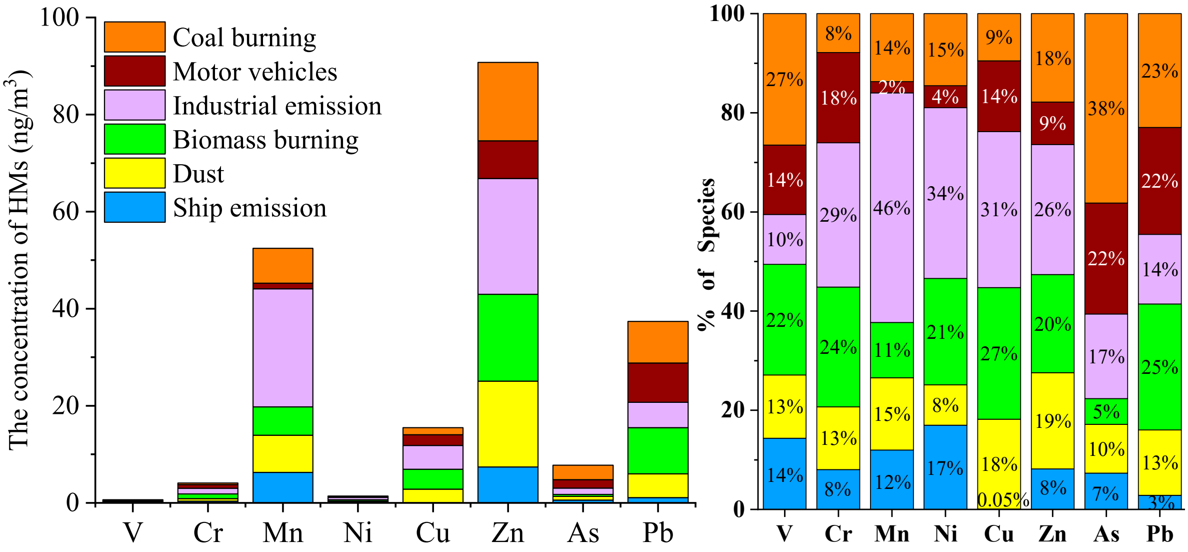

Figure 4. Absolute (**left**) and relative (**right**) source contributions to the 8 HMs in $PM_{2.5}$.

3.3. Health Risks of Heavy Metals from Pollution Sources

Since the components of $PM_{2.5}$ varied among different air pollution sources, so do the health risks from each source. Therefore, in order to control the health risk of $PM_{2.5}$ to the local residents, source apportionment should be integrated with health risk evaluations to estimate source-specific health risks. The corresponding calculation parameters (which have been introduced in 1.2) and health risks of $PM_{2.5}$-bound HMs were shown in Tables 3 and 4, respectively. The carcinogenic risk (CR) of $PM_{2.5}$-bound Cr was the highest among the studied metals in the wintertime of Chongqing due to its high IUR, contributing 72% CR originating from $PM_{2.5}$-bound HMs. Noncarcinogenic risk (HQ) of $PM_{2.5}$-bound Mn was the highest in all listed HMs because of its high exposure concentration (44.06 ng/m^3), accounting for 65% of the total HMs' HQ. $PM_{2.5}$-bound As was the second-highest CR and HQ element, which contributed 22% of the total CR and 26% of the total HQ. The noncarcinogenic risks resulted from $PM_{2.5}$-bound HMs were the same for adults and children, but $PM_{2.5}$-bound HMs were four times more likely to cause cancer in adults than in children, which might be due to HMs' bioaccumulation property in the human body.

Table 3. The calculated Ei, C, RfC, and IUR.

Elements	Ei	C (ng/m^3)	RfC (mg/m^3)	IUR (μg/m^3)$^{-1}$
V	0.48	0.41	7.00×10^{-6}	8.30×10^{-3}
Cr	0.48	0.89	1.00×10^{-4}	8.40×10^{-2}
Mn	0.48	44.06	5.00×10^{-5}	
Ni	0.48	0.64	1.40×10^{-5}	2.40×10^{-4}
As	0.48	5.27	1.50×10^{-5}	4.30×10^{-3}
Pb	0.48	32.62		8.00×10^{-5}

Ei—the deposition fraction of $PM_{2.5}$ that can penetrate in lung; C—the inhaled concentration of each HM during the monitoring periods; RfC—the inhalation reference concentration; IUR—inhalation unit risk.

Table 4. Carcinogenic risks and noncarcinogenic risks resulted from $PM_{2.5}$-bound HMs.

Elements	CR		HQ (Non-CR)	
	Adults	Children	Adults	Children
V	2.72×10^{-7}	6.81×10^{-8}	1.37×10^{-2}	1.37×10^{-2}
Cr	6.04×10^{-6}	1.51×10^{-6}	2.10×10^{-3}	2.10×10^{-3}
Mn			2.07×10^{-1}	2.07×10^{-1}
Ni	1.24×10^{-8}	3.10×10^{-9}	1.08×10^{-2}	1.08×10^{-2}
As	1.82×10^{-6}	4.56×10^{-7}	8.24×10^{-2}	8.24×10^{-2}
Pb	2.10×10^{-7}	5.25×10^{-8}		
Sum	8.36×10^{-6}	2.09×10^{-6}	3.16×10^{-1}	3.16×10^{-1}

HQ—hazard quotient; CR—carcinogenic risk.

Through combining the results of HMs' source apportionment and health risks assessment, the health risks of HMs from each $PM_{2.5}$ source were given in Table 5. Industrial emissions were the riskiest heavy metal sources at the study sites, contributing 25% CR and 36% HQ, which resulted from $PM_{2.5}$-bound HMs, even though industrial emissions are only the third contributors to $PM_{2.5}$. Biomass burning and vehicle emissions contributed about one fifth of CR, which is the same for industrial emissions; biomass burning was the fourth $PM_{2.5}$ source, but held similar health risks as the second $PM_{2.5}$ source. Coal combustion, as the biggest $PM_{2.5}$ source, only accounted for 15% CR and 21% HQ. All these phenomena indicate that health risks of air pollution sources are the combination effects of the source contribution factor and chemical components' characteristics. In order to control the health risk of $PM_{2.5}$ to the local residents, the pollutants from industrial emissions, biomass burning, vehicle emissions, and coal combustion sources should be given more attention in Sichuan Basin and similar regions.

Table 5. Carcinogenic and noncarcinogenic risks resulted from six emission sources via inhalation exposure to $PM_{2.5}$ in winter 2019 in Chongqing.

Sources	CR		HQ (Non-CR)	
	Adults	Children	Adults	Children
Coal combustion	1.29×10^{-6}	3.23×10^{-7}	6.52×10^{-2}	6.52×10^{-2}
Biomass burning	1.67×10^{-6}	4.18×10^{-7}	3.33×10^{-2}	3.33×10^{-2}
Industrial emission	2.13×10^{-6}	5.32×10^{-7}	1.16×10^{-1}	1.16×10^{-1}
Ship emission	6.67×10^{-7}	1.67×10^{-7}	3.48×10^{-2}	3.48×10^{-2}
Dust	1.01×10^{-6}	2.52×10^{-7}	4.11×10^{-2}	4.11×10^{-2}
Vehicle emission	1.59×10^{-6}	3.98×10^{-7}	2.59×10^{-2}	2.59×10^{-2}
Sum	8.36×10^{-6}	2.09×10^{-6}	3.16×10^{-1}	3.16×10^{-1}

HQ—hazard quotient; CR—carcinogenic risk.

4. Conclusions

In this study, $PM_{2.5}$ and associated heavy metals were measured from 6 January 2019 to 28 January 2019 in Chongqing, southwest China. The PMF model was adopted to conduct source apportionment of $PM_{2.5}$-bound HMs, and the health risks carried by 8 listed heavy metals in $PM_{2.5}$ were assessed with the U.S. EPA method. Finally, this work gave the source-specific health risks from $PM_{2.5}$-bound HMs by coupling the PMF source apportionment with the risk assessment results. The mean concentrations of $PM_{2.5}$ and HMs in $PM_{2.5}$ during the observation period were 97.06 $\mu g/m^3$ and 220.46 ng/m^3, respectively. The downwind industrial site had higher concentrations than the upwind industrial site and urban sites, while suburban was the lowest site. The concentration of Zn was the highest among the 8 heavy metals, followed by Mn and Pb. As and Cr were the two HMs that exceeded the standard limits of GB3095-2012 (As was 26% higher and Cr was 170 times higher) and WHO (As was 15% higher and Cr was 16 times higher). For the five sites on average, six $PM_{2.5}$ sources have been recognized: coal burning (25.5%), motor vehicles (22.8%), industrial emissions (20.5%), biomass burning (15.9%), dust (7.8%), ship emissions (7.5%). The larger contributors of $PM_{2.5}$ or $PM_{2.5}$-bound heavy metals might not be the higher health risk sources; the study results show that health risks of air pollution sources are the combination effects of the source contribution factor and chemical components' characteristics. Industrial emissions were the riskiest heavy metal sources at the study sites, contributing 25% CR and 36% HQ, which resulted from $PM_{2.5}$-bound HMs; biomass burning and vehicle emissions contributed about one fifth of CR; coal combustion only accounted for 15% CR and 21% HQ. In order to control the health risk of $PM_{2.5}$ to the local residents, the pollutants from industrial emissions, biomass burning, vehicle emissions, and coal combustion sources should be given more attention in Sichuan Basin and the similar regions.

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