RESEARCH ARTICLE

Characteristics, source and risk assessment of heavy metals in size-separated particulate matter in Tianjin, China

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In recent years, serious short-term air pollution events have occurred in Beijing-Tianjin-Hebei region of China. The metal pollution in atmosphere particles has a serious negative impact on human health and public life. Though many studies have investigated the metals in fine particles, the distribution characteristics, source, and risk assessment of metal elements in $PM_{0.5}$, $PM_{0.5\text{-}1.0}$, $PM_{1.0\text{-}2.0}$, and $PM_{2.0\text{-}2.5}$ are rarely reported. In this study, atmospheric particles with different particle size were collected in Tianjin, China in 2018 and analyzed for the concentration of metals by Inductively Coupled Plasma-Mass Spectrometer in order to investigate the size distribution. In addition, the source apportionment was also accessed for these metals using Enrichment Factor. Finally, the potential ecological risk index method and the health risk assessment model proposed by the US National Environmental Protection Agency were used to evaluate the potential ecological risk and health risk of potential metals. The results showed that the mass concentration of heavy metals in different particle sizes was high in winter and spring, but low in summer and autumn. Most heavy metal elements were relatively low in $PM_{0.5\text{-}1.0}$ and $PM_{1.0\text{-}2.0}$. It is generally believed that particles with smaller particle size pose a greater threat to human health, so the health risks of heavy metal pollution in $PM_{0.5\text{-}1.0}$ and $PM_{1.0\text{-}2.0}$ cannot be ignored. The results of enrichment factor analysis showed that the small particle size was greatly affected by artificial sources. In addition, long-distance transport of pollutants contributed to air pollution in Tianjin. Compared with other particle sizes, the carcinogenic risk of $PM_{2.0\text{-}2.5}$ heavy metals was higher, indicating that while paying attention to the health risk of finer particle sizes, it was still necessary to pay attention to the harm caused by larger particle sizes.

Keywords: heavy metal; distribution characteristic; source apportionment; risk assessment.

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Introduction

Atmospheric particulate matter is a kind of uniformly dispersed small particles in solid or liquid, and its composition is mainly in different chemical forms of metal elements, carbon aerosols, and inorganic substances such as ammonium salts, nitrates, and sulfates. According to the particle size of atmospheric particles, particles can usually be divided into four levels including total suspended particulate matter (TSP), inhalable particulate matter (PM_{10}), fine particulate matter ($PM_{2.5}$), and sub-micron particulate matter (PM_1) [1]. A certain number of heavy metals can be attached to the surface of particulate matter, which will cause certain harm to the human body and the external environment after being absorbed by the human body. Guo *et al*. found that the metal elements in particles with smaller particle size tended to produce greater toxicity and greater harm to human health [2]. Yao *et al*. evaluated the ecological risk of heavy metals in atmospheric fine particulate matter in Tianjin, China during the heating period

and found that Cu, Zn, Pb, Cd, and other elements had high potential ecological risks, among which Cd was extremely harmful [3]. Zhao *et al*. assessed the health risks of different heavy metals in Tianjin and found that As, Cd, and Cr have potential carcinogenic risks [4].

In recent years, domestic and foreign scholars have done a lot of research on the spatial and temporal distribution characteristics, sources, and health risk assessment of metal concentration in different particle size segments. Wang *et al*. found that the concentrations of Mg, Th, Ba, Mn, Ca, Fe, Al, and other elements in the crust were usually the highest in spring [5]. Liu *et al*. assessed the health risks of different heavy metals in $PM_{2.5}$ and TSP in Nanjing, Jiangsu, China and found that the harm caused by heavy metals to human health varied with particle size distribution [6]. Yang *et al.* analyzed the sources of heavy metals in fine particulate matter and found that motor vehicles, coal burning, dust, and industrial sources contributed more to the heavy metals in particulate matter in Beijing, China [7]. Cui *et al*. studied the potential ecological hazards of heavy metals in atmospheric particulate matter in Shijiazhuang, Hebei, China and found that Cd was the strongest one followed by Hg, while the hazards of As, Cr, Pb, Cu, Zn, and Ni were relatively light [8]. Gao *et al*. assessed the health risks of different heavy metals in Beijing and found that Pb in particulate matter had certain non-carcinogenic risks [9].

Tianjin is located in the mid-latitude region of the Northern Hemisphere, close to the Bohai Sea, and is strongly affected by Marine climate. In recent years, domestic and foreign scholars have conducted a large number of studies on the concentration characteristics, sources, and risk assessment of heavy metals in particulate matter and have achieved certain results, but there is still a lack of systematic research on the information related to heavy metals of $PM_{0.5}$, $PM_{0.5\text{-}1.0}$, $PM_{1.0\text{-}2.0}$, and $PM_{2.0\text{-}2.5}$. In view of this problem, the heavy metals of $PM_{0.5}$, $PM_{0.5\text{-}1.0}$, $PM_{1.0\text{-}2.0}$, and $PM_{2.0\text{-}2.5}$ in Tianjin were studied in this paper. The sources of heavy metals in atmospheric particulate matter were analyzed more accurately, and the potential ecological risks and health risks were assessed to provide a more comprehensive and detailed understanding of the atmospheric pollution situation in Tianjin. The results of this study would pave the way and guide the air pollution control work in Tianjin area.

Materials and methods

Sample collection

The sampling sites were located on the roof of the 19 teaching building of Tianjin University in Nankai District, downtown of Tianjin, China about 20 m from the ground. Winter samples were obtained in December, January, and February while spring samples were obtained in March, April, and May. The summer samples were collected in June, July, August, and autumn samples were obtained in September, October, and November. The samples were collected by impinging sampling method with sampling pump speed 10 L/min, sampling days of 7 days, and sampling volume of 110 m^3. During the hierarchical sampling process, the vacuum pump sucked the air into the Teflon sampler, and the atmospheric particles of different particle sizes ($PM_{0.5}$, $PM_{0.5\text{-}1.0}$, $PM_{1.0\text{-}2.0}$, $PM_{2.0\text{-}2.5}$) were successively adsorb through the slit at a diameter of 25 mm. Millipore nitrate fiber filter membrane with a pore size of 0.45 μm was used to achieve the classification effect. All nitrate fiber filter membranes were weighed before and after sampling to determine the quality of particulate matter and were always stored in the capsule after soaking in 1% HCl for 24 hours and repeatedly washing and drying with Milli-Q ultra-pure water to reduce the influence of blank space on the determination.

Sample analysis

Inductively coupled plasma-mass spectrometer (ICP-MS) technology was employed to analyze commonly used elements including sodium (Na), manganese (Mn), potassium (K), aluminum (Al), chromium (Cr), magnesium (Mg), zinc (Zn),

titanium (Ti), cadmium (Cd), calcium (Ca), iron (Fe), nickel (Ni), copper (Cu), barium (Ba), and lead (Pb). The influence of blank sample film was deducted during the experiment, and the sample error was less than 3%. The error between parallel samples was less than 5%, and the recovery rate of standard samples according to National Institute of Standards and Technology (NIST) 1648a was 80%-120%.

Enrichment factor

Enrichment factor method is an important method used to evaluate the influence of man-made and natural sources on the outside world. The influence of human activities on different elements in atmospheric particles can be judged by the size of enrichment factor [10], and the source of elements in atmospheric particles can be qualitatively judged. The enrichment factor (EF) formula can be expressed as:

$$EF=(C_i/C_n)_{sample}/(C_i/C_n)_{background} \quad (1)$$

where the $(C_i/C_n)_{sample}$ was the ratio of the concentration of element (C_i) in the sample to the concentration of reference element (C_n). The $(C_i/C_n)_{background}$ was the ratio of the element (C_i) to the reference element (C_n) in the soil background value. Ti was the reference element, which was less disturbed by human activities and abundant in the crust. In this study, the local soil background value of Tianjin was used as the crustal element concentration. Normally, when the enrichment factor EF < 10, it is considered that there is no enrichment of elements, and the natural source has the great influence on the elements. When 10 < EF < 100, it is considered that the element is enriched to a certain extent, and both natural and anthropogenic sources have influence on the element. When EF > 100, the element is highly enriched, and human activities have a relatively great influence on the element [11, 12].

Results

Seasonal distribution characteristics of heavy metals

The seasonal distribution characteristics of heavy metal elements of different particle sizes were shown in Figure 1. There were obvious differences in the seasonal distribution of elements in different particle sizes. In $PM_{0.5}$, the seasonal distribution characteristics of heavy metal concentrations were winter > Spring > Summer > Autumn. In $PM_{0.5\text{-}1.0}$ and $PM_{2.0\text{-}2.5}$, there were significant differences in the content of different elements, but the overall performance was Spring and Winter exceed Summer and Autumn. In $PM_{1.0\text{-}2.0}$, the contents of Zn and Cr were the highest in Summer, while the contents of Pb, Cu, Ni, Cd, and Mn were the highest in Spring, and the content of 7 heavy metal elements were higher in Spring than that in Winter.

Seasonal distribution of heavy metal particle size

The seasonal variation characteristics of the proportion of heavy metals in $PM_{2.5}$ in particulate matter with different particle sizes were shown in Table 1. Zn was mainly distributed in $PM_{0.5}$ and $PM_{2.0\text{-}2.5}$ in Winter, and in $PM_{2.0\text{-}2.5}$ in other seasons. The particle size distribution characteristics of Cr and Mn were basically the same, except that the highest concentration of Cr in Winter was distributed in $PM_{0.5}$, and the two elements were concentrated in $PM_{0.5}$ and $PM_{2.0\text{-}2.5}$ in different seasons, of which the proportion was the highest in Autumn with the size of 47.5% and 53.9%, respectively, which was much higher than that in other particle sizes. Ni and Cu showed the same distribution characteristics as Cr and Mn in Autumn, and the highest values were distributed in $PM_{0.5}$ in Spring and Winter. The distributions of Cd and Pb elements were significantly different from that of other elements and were mainly distributed in $PM_{0.5}$ and $PM_{0.5\text{-}1.0}$ in different seasons. The proportion of the two elements in different particle sizes reached the highest value in Winter with the sizes of 56.4% and 52.1%, respectively, and the lowest values appeared in Autumn with the sizes of 26.4% and 20.9%, respectively.

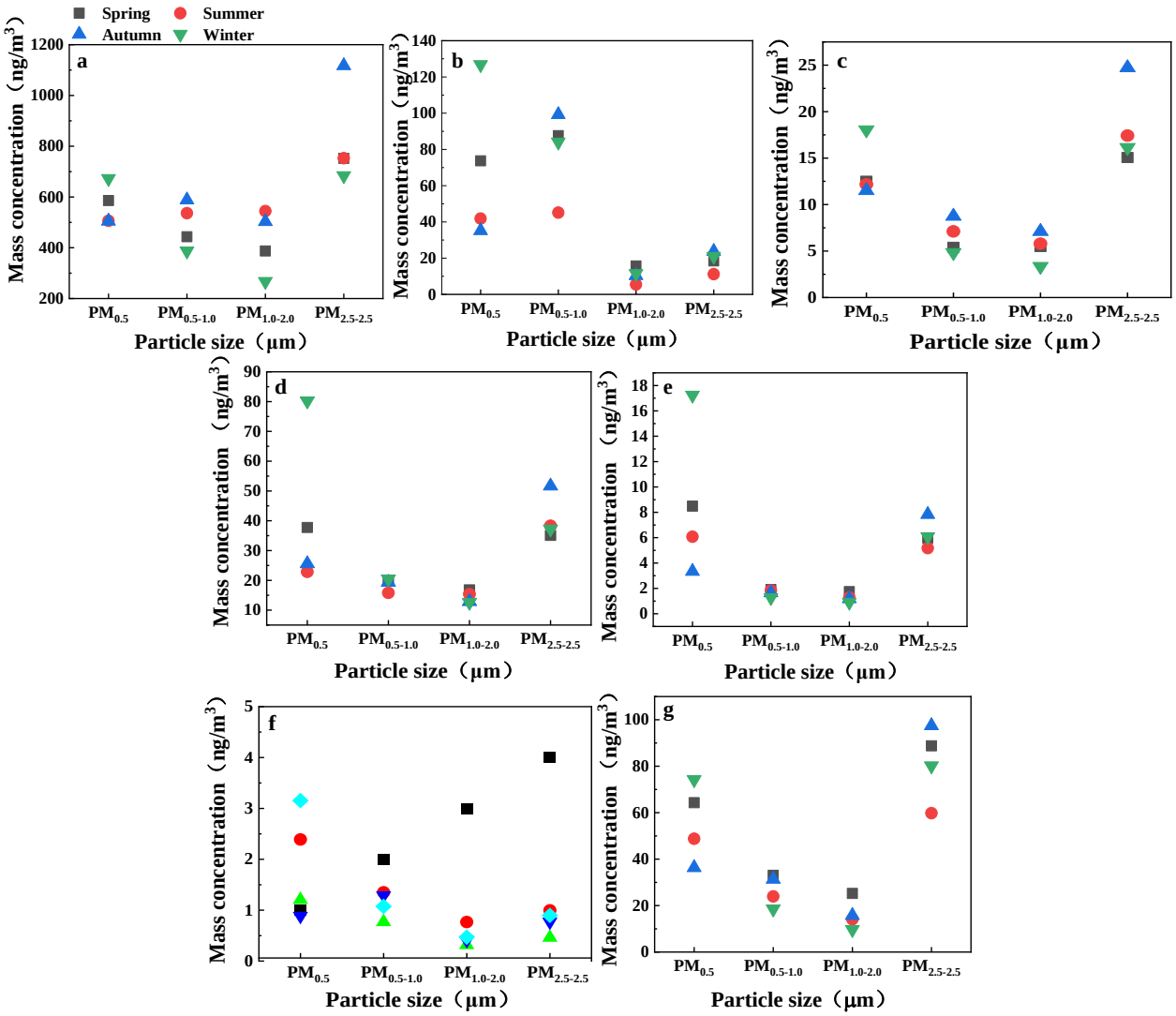

Figure 1. Seasonal distribution characteristics of Zn (a), Pb (b), Cr (c), Cu (d), Ni (e), Cd (f), and Mn (g) mass concentrations in particles with different particle sizes.

Enrichment factor analysis

Through the analysis of each element enrichment factor, the source of elements could be divided into three categories including man-made source, natural source, man-made source and natural source mixture, so as to have a clearer understanding of the source of elements. The EF values of Cu, Zn, Cd, Ba, and Pb in $PM_{0.5}$ were greater than 100 (Table 2), indicating obvious enrichment degree of elements, and the influence of human activities on these elements was relatively great. The EF values of Na, K, Cr, Mn, and Ni were in the range of 10-100, and the elements were enriched to a certain extent, which was influenced by human activities and natural sources. The EF values of Mg, Al, Ca, and Fe were less than 10 and were mainly influenced by natural sources. In $PM_{0.5\text{-}1.0}$, the EF values of Cu, Zn, Cd, and Pb were all greater than 100, and the enrichment degree of these elements was obvious, and the influence of human activities on these elements was relatively great. The EF values of Na, Cr, Ni, and Ba ranged from 10-100, and the elements were enriched to a certain extent, which was influenced by both human activities and natural sources. The elements Mg,

Table 1. Seasonal variation characteristics of the proportion of heavy metals in $PM_{2.5}$ with different particle sizes (%).

		Cr	Mn	Ni	Cu	Zn	Cd	Pb
Spring	$PM_{0.5}$	32.5	30.4	46.9	34.5	27.0	43.4	37.7
	$PM_{0.5-1.0}$	14.0	15.6	10.6	18.2	20.4	24.6	44.8
	$PM_{1.0-2.0}$	14.3	11.9	9.6	15.4	17.9	13.9	8.0
	$PM_{2.0-2.5}$	39.2	42.0	32.9	32.0	34.7	18.1	9.4
Summer	$PM_{0.5}$	28.6	33.3	42.3	24.7	21.6	43.8	40.4
	$PM_{0.5-1.0}$	16.7	16.3	12.8	17.1	22.9	27.9	43.6
	$PM_{1.0-2.0}$	13.6	9.6	8.9	16.6	23.3	11.5	5.3
	$PM_{2.0-2.5}$	41.0	40.8	36.0	41.5	32.2	16.8	10.8
Autumn	$PM_{0.5}$	22.1	20.1	23.8	23.4	18.6	26.4	20.9
	$PM_{0.5-1.0}$	16.8	17.3	11.8	17.7	21.7	38.5	58.9
	$PM_{1.0-2.0}$	13.6	8.7	8.4	11.7	18.5	12.1	6.2
	$PM_{2.0-2.5}$	47.5	53.9	55.9	47.2	41.2	23.0	14.1
Winter	$PM_{0.5}$	42.6	40.6	67.6	53.3	33.4	56.4	52.1
	$PM_{0.5-1.0}$	11.4	10.2	5.0	13.6	19.3	19.2	34.5
	$PM_{1.0-2.0}$	7.9	5.3	3.6	8.4	13.3	8.4	4.7
	$PM_{2.0-2.5}$	38.1	43.9	23.9	24.7	34.0	16.0	8.6

Table 2. Enrichment factors of elements in different particle size segments.

	$PM_{0.5}$	$PM_{0.5-1.0}$	$PM_{1.0-2.0}$	$PM_{2.0-2.5}$
Na	50.76	33.43	26.28	11.80
Mg	3.57	2.38	1.97	1.93
Al	1.55	1.01	1.07	0.89
K	23.81	9.39	3.79	1.78
Ca	1.14	0.87	0.83	0.79
Cr	41.65	16.83	11.05	5.35
Mn	18.52	8.33	3.69	2.22
Fe	4.13	2.25	1.80	1.79
Ni	49.80	11.30	6.35	3.82
Cu	307.42	148.22	85.57	38.57
Zn	1923.66	1323.97	940.03	300.60
Cd	484.67	2671.72	827.89	257.92
Ba	160.39	98.21	106.72	43.75
Pb	761.57	797.17	76.44	24.46

Al, K, Ca, Mn, and F had EF values less than 10 and were mainly influenced by natural sources. In $PM_{1.0-2.0}$, EF values of Zn, Cd, and Ba were greater than 100, and the enrichment degree of these elements was obvious, and the influence of human activities on these elements was relatively great. The EF values of Na, Cr, Cu, and Pb ranged from 10-100, and the elements were enriched to a certain extent, which was influenced by both human activities and natural sources. The EF values of Mg, Al, K, Ca, Mn, Fe, and Ni were less than 10 and were mainly influenced by natural sources. In $PM_{2.0-2.5}$, EF values of Zn and Cd were greater than 100, and

the enrichment degree of these elements was obvious, and the influence of human activities on these elements was relatively great. The EF values of Na, Cu, Ba, and Pb ranged from 10-100, and the elements were enriched to a certain extent, which was influenced by both human activities and natural sources. The EF values of Mg, Al, K, Ca, Cr, Mn, Fe, and Ni were less than 10 and were mainly affected by natural source with the decrease of particle size, the enrichment factors of different elements basically showed a gradually increasing trend, indicating that the particles with small particle size were more influenced by human sources. The elements with enrichment factor greater than 100 were the most abundant in $PM_{0.5}$ particle size segment, and the least in $PM_{2.0\text{-}2.5}$. The enrichment factors of Mg, Al, Fe, and Mn in particles with different particle sizes were small, which was mainly related to crustal sources [13, 14], while the enrichment factors of Na and K were relatively high, which might be related to the biomass burning events still existing in some areas of Tianjin. Ba is a marker of motor vehicle source. Brake and tire wear process will produce Ba [15]. The high enrichment factor might be because the sampling point was close to the intersection and the large traffic flow led to Ba enrichment. The high Pb enrichment factor might be related to the burning of coal for heating in winter [16].

Potential source contribution factor analysis

In this paper, backward trajectory analysis was used to analyze the origin and trace quantity of $PM_{2.5}$ in different seasons in Tianjin, so as to clearly understand the pollution situation in Tianjin from the macro level. Samples from January, April, July, and October were used to represent the spring, summer, autumn, and winter seasons.

(1) Spring backward trajectory model analysis

The backward trajectory analysis results of Tianjin in spring 2018 were shown in Figure 2. According to the backward track chart in April, Cluster 1 came from the northwest, passing through Russia, Mongolia, Inner Mongolia, Hebei, and Beijing, and finally reaching Tianjin, with the number of tracks accounting for 24.48% of the total number of tracks. Cluster 2 came from the northwest, passing through Russia, Mongolia, Inner Mongolia, Hebei, and Beijing, and finally reaching Tianjin, accounting for 19.27% of the total. Cluster 3 came from the northwest, passing through Mongolia, Inner Mongolia, Hebei, and Beijing, and finally reaching Tianjin, where the number of tracks accounted for the highest proportion of 31.25% of the total number of tracks. This cluster had the greatest impact on the concentration of pollutants in $PM_{2.5}$ in Tianjin. Cluster 4 came from the south, passing through Shandong, Hebei, and Tianjin, and its tracks accounted for 15.63% of the total tracks. Cluster 5 came from the north, passing through Russia, Inner Mongolia, Hebei, and Beijing, and finally reaching Tianjin, where the number of tracks accounted for the lowest proportion of 9.38% of the total number of tracks. This cluster had the least impact on the concentration of pollutants in $PM_{2.5}$ in Tianjin. Cluster 2 had the largest track length and Cluster 3 had the smallest track length. To sum up, the air pollutants in spring in Tianjin mainly came from inland areas, such as Russia, Mongolia, and Inner Mongolia, and long-distance transmission contributed to air pollution to some extent.

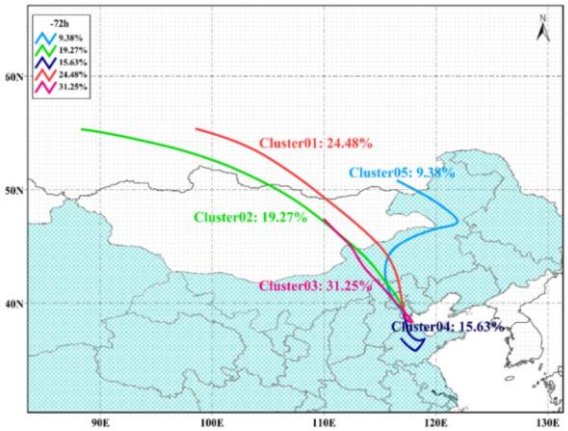

Figure 2. Backward trajectory map of spring.

(2) Summer backward trajectory model analysis

The backward trajectory analysis results of Tianjin in summer 2018 were shown in Figure 3.

According to the backward track chart in July, Cluster 1 came from the west, passing through Jiangsu, Shandong, Hebei, and Tianjin, and its track number accounted for 16.15% of the total track number. Cluster 2 came from the southeast, passing through Shanghai, Jiangsu, Shandong, Hebei, and Tianjin, and its number of tracks accounted for the highest proportion, up to 35.42%. This cluster had the greatest impact on the concentration of $PM_{2.5}$ pollutants in Tianjin. Cluster 3 came from the southeast direction, passing through the East China Sea, Yellow Sea, Shandong, and Tianjin, and its tracks accounted for 17.19% of the total tracks. Cluster 4 came from the east, passing through South Korea, North Korea, Liaoning, Shandong, and Tianjin, and its number of tracks accounted for the smallest proportion of 15.63% of the total number of tracks. This cluster had little impact on the concentration of pollutants in $PM_{2.5}$ in Tianjin. Cluster 5 came from the east, passing through Korea, Yellow Sea, Bohai Sea, and Tianjin, and its tracks accounted for 15.63% of the total tracks. Cluster 4 and Cluster 5 clustering had little effects on the concentration of $PM_{2.5}$ pollutants in Tianjin. Cluster 3 had the longest track length and Cluster 1 had the shortest track length. To sum up, the Marine air mass had an impact on Tianjin in summer, which was mainly caused by the monsoon climate in summer. Under the influence of monsoon, pollutants discharged by shipping might be carried to Tianjin.

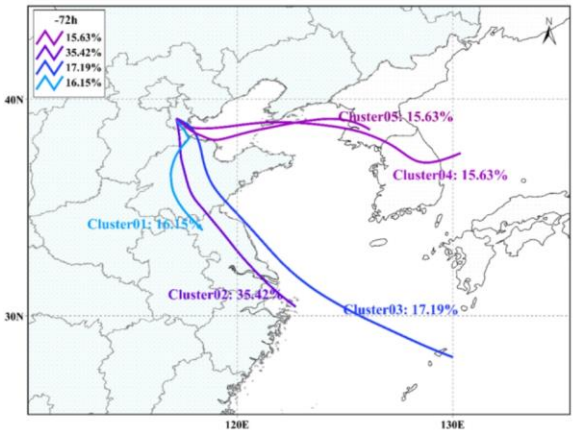

Figure 3. Backward trajectory map of summer.

(3) Autumn backward trajectory pattern analysis

The analysis results of Tianjin backward trajectory in autumn 2018 were shown in Figure 4. According to the backward track chart in October, Cluster 1 came from the north, passing through Russia, Mongolia, Inner Mongolia, Hebei, Beijing, and Tianjin, and its track number accounted for 30.73% of the total track number. Cluster 2 came from the south, passing through Jiangsu, Shandong, Hebei, and Tianjin, and its number of tracks accounted for 28.13% of the total number of tracks. This cluster had the least influence on the concentration of $PM_{2.5}$ pollutants in Tianjin. Cluster 3 came from the north and passed through Inner Mongolia, Mongolia, Inner Mongolia, Hebei, and Tianjin with the highest number of tracks, accounting for 41.15% of the total number of tracks. This cluster had the greatest impact on the concentration of $PM_{2.5}$ pollutants in Tianjin. Cluster 1 had the longest track length and Cluster 2 had the smallest track length. In conclusion, all the air pollutants in autumn of Tianjin came from inland areas, but the meteorological track characteristics were different from those in spring.

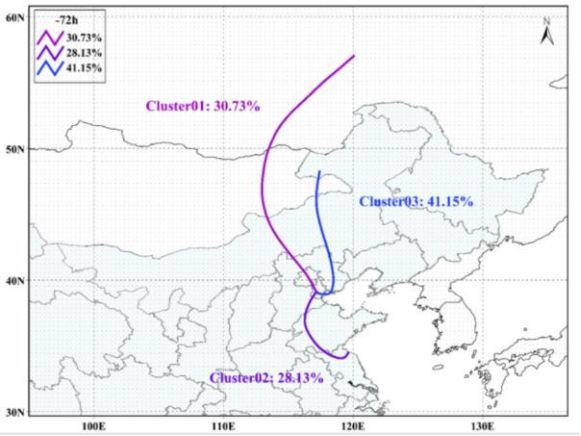

Figure 4. Backward trajectory map of autumn.

(4) Analysis of backward track model in winter

The analysis results of the backward trajectory of Tianjin in winter 2018 were shown in Figure 5. According to the backward track chart in January,

Cluster 1 came from the northwest, passing through Russia, Mongolia, Inner Mongolia, Hebei, Beijing, and Tianjin. The number of tracks accounted for the smallest proportion of 22.92% of the total number of tracks, and this cluster had the smallest impact on the concentration of $PM_{2.5}$ pollutants in Tianjin. Cluster 2 came from the northwest and passed through Russia, Mongolia, Inner Mongolia, Hebei, and Tianjin. The number of tracks accounted for the highest proportion of 44.27% of the total number of tracks. This cluster had the greatest impact on the concentration of $PM_{2.5}$ pollutants in Tianjin. Cluster 3 came from the northwest, passing through Beijing and Tianjin, and its tracks accounted for 32.81% of the total tracks. The track lengths of Cluster 1 and Cluster 2 were equal, and the track length of Cluster 3 was the least. In summary, the air pollutants in Tianjin in winter mainly came from inland areas, and the meteorological track characteristics were basically similar to those in spring.

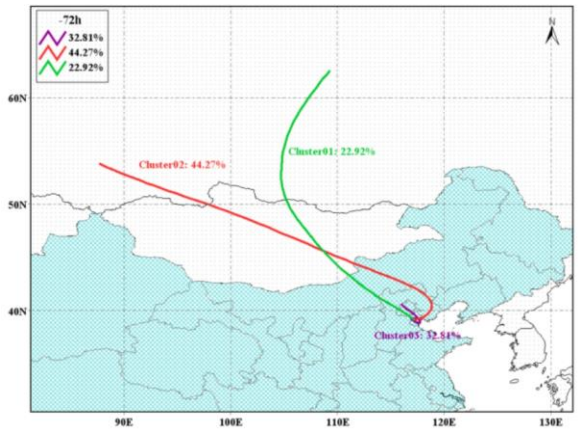

Figure 5. Backward trajectory map of winter.

Combined with the meteorological track characteristics of air pollutants in different seasons, the direction of pollution sources in different seasons was very different. In Tianjin, northwest winds prevail in winter and southeast winds dominate in summer. However, the source of air mass in winter is relatively simple, mainly in the northwest direction, and in summer, it is mainly in the southeast direction, indicating that the air pollution in Tianjin is greatly affected by the monsoon. In addition, the track length of different seasons is generally longer, indicating that the long-distance transport of pollutants has a certain contribution to the air pollution in Tianjin.

Discussion

Comparison of heavy metal concentrations with standard limits and cities in other countries

The concentrations of Pb, Ni, and Cd in particles of different particle sizes were added together to obtain the total concentrations of these elements in $PM_{2.5}$. The comparison between the concentrations of these elements in different months and the World Health Organization (WHO) standard limits were shown in Figure 6. The annual average concentration of Pb was 178.6 ng/m^3, which was lower than the WHO standard value of 500 ng/m^3 and might be related to the unleaded gasoline policy implemented in China since 2000. The concentration of Ni was 18.4 ng/m^3, which was lower than the WHO reference value of 25.0 ng/m^3. The concentration of Cd was 4.4 ng/m^3, which was equivalent to the WHO standard value of 5.0 ng/m^3. Compared with cities in South Asia, the average concentration of most heavy metals in the atmospheric particles in Tianjin was lower, but higher than the average of cities in Europe, East Asia, Japan, South Korea, and the Americas (Table 3). In addition, as far as a single city was concerned, the heavy metal content of atmospheric particulate matter in Tianjin was much higher than that in most cities in Europe and the Americas, especially in New York, New Jersey, Toronto, Los Angeles, and Oakland. Among them, China and some developing countries in South Asia such as India and Pakistan were relatively backward in air pollution control work compared to developed countries such as Japan, South Korea, Europe, and the United States. To sum up, the prevention and control of heavy metal pollution in atmospheric particulate matter in Tianjin was relatively severe, and the prevention and control of heavy metal in

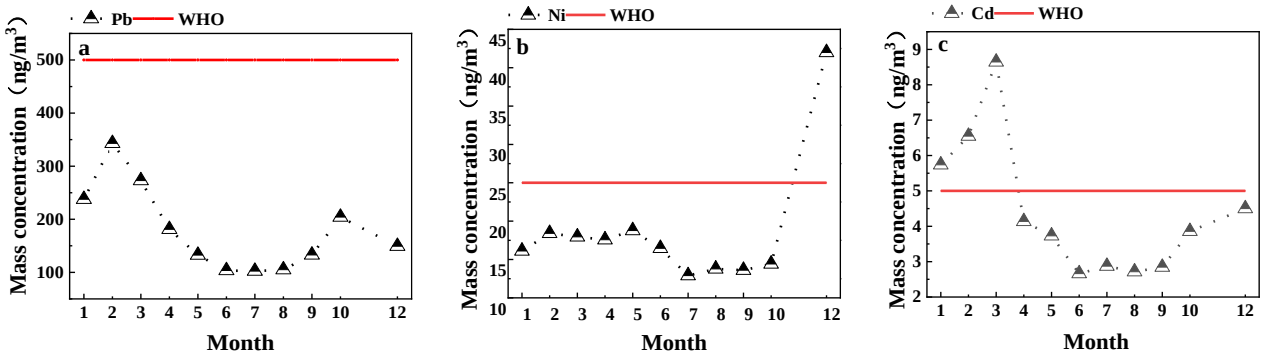

Figure 6. Comparison of Pb(a), Ni(b), and Cd(c) concentration values with WHO limit values.

Table 3. Summary of atmospheric heavy metal content in foreign cities (Unit: ng/m^3).

City	Pb	Cd	Cr	Cu	Ni
Tianjin	178.6	4.4	43.1	116	18.4
East Asia	110.7	1.5	9.8	-	10.8
North Asia	1881.3	40.5	113.7	-	80.7
Europe	58.4	0.3	12.1	25.5	9.7
America	28.2	14.5	8.9	11.5	2.4

atmospheric particulate matter in Tianjin still needs to be strengthened.

Distribution characteristics

The grain size distribution characteristics of most heavy metals in different seasons are basically consistent with the distribution characteristics of the whole year. That is, the content of most elements is relatively high in $PM_{0.5}$ and $PM_{2.0\text{-}2.5}$, while the content is low in $PM_{0.5\text{-}1.0}$ and $PM_{1.0\text{-}2.0}$, among which Cd and Pb are relatively high in $PM_{0.5\text{-}1.0}$ in some seasons. Although most heavy metal elements occupy a relatively low proportion in $PM_{0.5\text{-}1.0}$ and $PM_{1.0\text{-}2.0}$, it is generally believed that particles with smaller particle size pose a greater threat to human health [17], so the pollution of heavy metals in $PM_{0.5\text{-}1.0}$ and $PM_{1.0\text{-}2.0}$ cannot be ignored. In addition, there are certain differences in the concentration of each element in different seasons, so it is of great significance to treat the heavy metal elements according to the particle size distribution characteristics in different seasons. In general, although the seasonal variation characteristics of element concentration in the four particle size particles are different, it basically conforms to the characteristics that spring and winter are higher than summer and autumn, and the seasonal variation of particle size concentrations shows synchronization. Coal burning in winter and spring will release a large amount of Pb and Cd elements. In spring, there are a lot of dust weather, and a large number of dust source elements are brought into the atmosphere, resulting in a high concentration of dust source related elements in atmospheric particles. The temperature inversion layer prevents the diffusion of atmospheric particles and increases the concentration of heavy metals. The rainfall in summer is sufficient, and the atmospheric wet sedimentation is relatively serious and intense [18]. Summer and autumn pollutants are more easily dispersed, and the corresponding heavy metal concentration in the atmosphere is correspondingly lower. The above factors lead to the difference in the distribution of heavy metal concentration between different seasons.

Potential ecological risk assessment

The formula for calculating the potential

ecological harm index of heavy metals was as follows:

$$EI = CI \times TI = \frac{C_V}{C_{V0}} \times TI \quad (2)$$

In equation 2, the risk of heavy metal concentration in atmospheric particulate matter could be characterized by pollution index (C_I), and its value could be calculated by the ratio of heavy metal concentration to standard value or base value, the calculation formula was $C_I = C_V/C_{V0}$, the actual measured value of heavy metal concentration was represented by C_V, and the standard value or base value of heavy metal was represented by C_{V0}. The concentration of heavy metals in the soil of Tianjin was selected as the standard value and the base value. TI represented the toxicity of heavy metals and the sensitivity of organisms to heavy metals.

The formula for calculating the potential ecological harm index of various heavy metals was as follows:

$$RI = \sum EI \quad (3)$$

In Formula 3, EI represented the potential ecological harm index of a single heavy metal.

The biological toxicity coefficient and the baseline values of heavy metals was listed in Table 4 and the classification criteria for potential ecological risk factors of RI and EI was listed in Table 5.

Evaluation of potential ecological hazards

According to formula 2, the potential ecological hazard index of each element was calculated by combining the toxicity coefficient and background value of each heavy metal element, and the calculation results were shown in Table 6. The potential ecological risk level of each heavy metal element could be determined by EI classification table. The EI of each element in atmospheric particulate matter in Tianjin was Pb (35) > Zn (26.1) > Cu (17.0) > Ni (2.0) > Cr (0.9) > Mn (0.2). According to the analysis results of Table 6, the risk levels of Pb, Zn, and Cu in the study area were low risk, the risk levels of Cr, Mn, and Ni were no risk, and the overall risk levels of test elements were low risk. The potential ecological risk contribution of each element was shown in Figure 7. Pb, Zn, and Cu contributed more, accounting for 43.1%, 32.1%, and 20.9% respectively, while Cr, Mn, and Ni contributed less, accounting for 1.1%, 0.2%, and 2.5% respectively. It showed that Pb, Zn, and Cu had great influences on ecological risk in the study area.

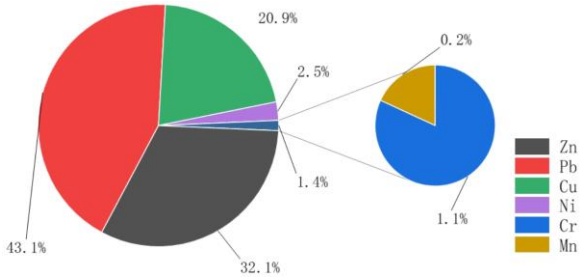

Figure 7. Proportion of potential ecological risk contribution of elements.

Health risk assessment of heavy metals

Compared with most elements, Zn, Ni, Cu, Pb, Cr, Cd, and other elements are more harmful to human health. Therefore, this paper used the health risk assessment model proposed by EPA to evaluate the human health risk of these heavy metal elements. The main ways of heavy metal elements entering the human body are "hand-mouth, breath, and skin". Previous studies found that hand-mouth intake was the most important way leading to non-carcinogenic risks [19-21]. Therefore, this paper focused on the health risks to adults and children caused by the intake of heavy metals in particles of different particle sizes through "hand-mouth" to put forward reasonable suggestions for better prevention and control of heavy metal hazards.

(1) Health risk assessment

The average daily human exposure through hand-mouth ingestion was calculated as follows:

Table 4. Baseline values (mg/kg) and biotoxicity coefficients of heavy metal elements.

Heavy metal	Zn	Pb	Cr	Cu	Ni	Mn
Biological toxicity coefficient	1	5	2	5	5	1
Baseline values	79.3	21	84.2	28.8	33.3	686

Table 5. Ranking table of potential ecological risk factors EI and RI.

EI	Risk level	RI	Risk level
100 ≤ EI	Extremely high risk	600 < RI	Extremely high risk
70 ≤ EI < 100	High risk	300 < RI < 600	High risk
40 ≤ EI < 70	Medium risk	150 ≤ RI < 300	Medium risk
10 ≤ EI < 40	Low risk	RI < 150	Low risk
EI < 10	Nontoxic		

Table 6. Potential ecological risk index of different heavy metals.

	Zn	Pb	Cr	Cu	Ni	Mn
Concentration mean	26.1	35	0.9	17	2	0.2
Pollution level	Low risk	Low risk	Nontoxic	Low risk	Nontoxic	Nontoxic

Table 7. The meaning and value of the calculation parameters for the average daily exposure to heavy metals.

	Parameter	Meaning	Unit	Children	Adult
Basic parameter	C	Heavy metal concentration	mg /kg		
	EF	Exposure frequency	d/a	180	180
	ED	Exposure period	a	6	24
Exposure behavior parameter	AT	Mean exposure time	d	365×ED (Non-carcinogenic effect) 365×70 (carcinogenic effect)	365×ED (Non-carcinogenic effect) 365×70 (carcinogenic effect)
	BW	Average weight unit conversion	kg	15	70
	CF		kg/mg	1/1,000,000	1/1,000,000
Hand-mouth feeding	IRoral	grazing rate	mg/d	200	100

$$ADDoral = C \times \frac{IRoral \times EF \times CF \times ED}{BW \times AT} \quad (4)$$

where ADDoral represented the daily average exposure through hand-oral ingestion, and the specific meanings and values of other parameters in the formula were shown in Table 7.

The safety valve dose of chronic poisoning could be used to evaluate the health risk caused by each heavy metal element to the human body. The formula was as follows:

$$HQ = \frac{ADD}{RfD} \quad (5)$$

Table 8. RfD and SF of different exposure routes.

	Ni	Cu	Zn	Cd	Pb	Cr
RfD	0.02	0.04	0.3	0.001	0.0035	0.003
SF	0.84	-	-	6.3	-	42

Table 9. Non-carcinogenic exposure dose of heavy metals (mg/kg·d).

	$PM_{0.5}$		$PM_{0.5-1.0}$		$PM_{1.0-2.0}$		$PM_{2.0-2.5}$	
	Children	Adult	Children	Adult	Children	Adult	Children	Adult
Ni	2.04E-05	2.19E-06	1.22E-05	1.31E-06	9.66E-06	1.03E-06	4.45E-05	4.77E-06
Cu	1.03E-04	1.11E-05	1.40E-04	1.50E-05	1.09E-04	1.17E-05	2.89E-04	3.10E-05
Zn	1.27E-03	1.36E-04	3.47E-03	3.72E-04	3.10E-03	3.32E-04	5.76E-03	6.17E-04
Cd	4.66E-06	4.99E-07	8.14E-06	8.72E-07	3.75E-06	4.01E-07	5.79E-06	6.20E-07
Pb	1.72E-04	1.85E-05	5.74E-04	6.15E-05	8.22E-05	8.81E-06	1.33E-04	1.43E-05
Cr	3.12E-05	3.34E-06	4.59E-05	4.92E-06	3.89E-05	4.17E-06	1.27E-04	1.36E-05
Mn	1.27E-04	1.37E-05	1.91E-04	2.04E-05	1.21E-04	1.30E-05	5.85E-04	6.27E-05

Table 10. Heavy metal hazard.

	$PM_{0.5}$		$PM_{0.5-1.0}$		$PM_{1.0-2.0}$		$PM_{2.0-2.5}$	
	Children	Adult	Children	Adult	Children	Adult	Children	Adult
Ni	1.02E-03	1.09E-04	6.13E-04	6.57E-05	4.83E-04	5.17E-05	2.22E-03	2.38E-04
Cu	2.59E-03	2.77E-04	3.52E-03	3.77E-04	2.73E-03	2.92E-04	7.24E-03	7.75E-04
Zn	4.24E-03	4.54E-04	1.15E-02	1.24E-03	1.03E-02	1.10E-03	1.92E-02	2.05E-03
Cd	4.66E-03	4.99E-04	8.14E-03	8.72E-04	3.75E-03	4.01E-04	5.79E-03	6.20E-04
Pb	4.93E-02	5.29E-03	1.64E-01	1.75E-02	2.35E-02	2.51E-03	3.82E-02	4.09E-03
Cr	1.04E-02	1.11E-03	1.53E-02	1.64E-03	1.29E-02	1.39E-03	4.26E-02	4.56E-03
Mn	2.78E-03	2.97E-04	4.15E-03	4.45E-04	2.63E-03	2.82E-04	1.27E-02	1.36E-03

where ADD was the exposure amount of each heavy metal element in children and adults, and RfD represented the reference dose of each heavy metal element by hand and mouth. When HQ was less than 1, it indicated that the heavy metal element was lower than the safety threshold and did not pose a non-carcinogenic risk to human health. When HQ was greater than 1, it indicated that the heavy metal element exceeded the safety threshold and posed a non-carcinogenic risk to human health. The total non-carcinogenic risk was obtained by adding the heavy metal HQ. The carcinogenic risk of each heavy metal was calculated as follows:

$$\left(Risk\right)_i = ADD_{inh} \times SF \quad (6)$$

where ADD_{inh} was the exposure dose corresponding to carcinogens, and the specific values of carcinogenic slope factor (*SF*) were shown in Table 8.

Non-carcinogenic risk assessment

According to formula 4 and 5 and the calculation parameters in Tables 7 and 8, the non-carcinogenic exposure dose and hazard quotient were calculated and shown in Tables 9 and 10. In both children and adults, the average daily exposure dose of children was higher than that of adults, which was consistent with previous research results [19-21]. There were some differences in the ranking of non-carcinogenic risk daily mean exposure dose of heavy metals in

Table 11. Carcinogenic exposure dose of heavy metals (mg/kg·d).

	$PM_{0.5}$		$PM_{0.5-1.0}$		$PM_{1.0-2.0}$		$PM_{2.0-2.5}$	
	Children	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
Ni	1.75E-06	7.51E-07	1.05E-06	4.51E-07	8.28E-07	3.55E-07	3.82E-06	1.63E-06
Cd	3.99E-07	1.71E-07	6.97E-07	2.99E-07	3.21E-07	1.37E-07	4.96E-07	2.12E-07
Cr	2.67E-06	1.14E-06	3.93E-06	1.68E-06	3.33E-06	1.43E-06	1.09E-05	4.69E-06

Table 12. Carcinogenic risk index of heavy metals.

	$PM_{0.5}$		$PM_{0.5-1.0}$		$PM_{1.0-2.0}$		$PM_{2.0-2.5}$	
	Children	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
Ni	1.47E-06	6.30E-07	8.84E-07	3.78E-07	6.96E-07	2.98E-07	3.20E-06	1.37E-06
Cd	2.51E-06	1.07E-06	4.39E-06	1.88E-06	2.02E-06	8.68E-07	3.12E-06	1.34E-06
Cr	1.12E-04	4.82E-05	1.65E-04	7.08E-05	1.40E-04	6.01E-05	4.60E-04	1.97E-04

particulate matter with different particle sizes. The non-carcinogenic risk of heavy metal elements in particles of different particle sizes was less than 1, and the total non-carcinogenic risk was less than 1, which did not exceed the safety threshold that could cause the health of contacts, and there was no non-carcinogenic risk. Among all elements, the non-carcinogenic risk of Pb was greater than that of other elements, which was consistent with the results of Jian *et al*. on the health risk of Pb in Shenyang fine particles [21], indicating that the protection against the non-carcinogenic risk of Pb had been further strengthened. The total non-carcinogenic risk of different elements was greater in children than that in adults, indicating that children's health was more severely affected by heavy metals than adults. Therefore, it is important to focus on the cultivation of children's health habits and enhance children's health awareness.

Carcinogenic risk assessment

Carcinogenic exposure dose and carcinogenic risk index were calculated according to Formula 4 and 6 and the parameters in Tables 8 and 9. The results were shown in Tables 11 and 12. The average daily exposure dose of the three elements was Cr > Ni > Cd, and the average daily exposure dose of children was higher than that of adults, and the carcinogenic risk index of heavy metal elements in different particle sizes was different. In $PM_{0.5}$, except for Ni, which had a carcinogenic risk for children and did not have a carcinogenic risk for adults, the remaining elements had a carcinogenic risk for children and adults. In $PM_{0.5-1.0}$, Ni did not pose a carcinogenic risk to children and adults, and the remaining elements posed a carcinogenic risk to children and adults. In $PM_{1.0-2.0}$, Ni had no carcinogenic risk for children and adults, Cd had a carcinogenic risk for children but no carcinogenic risk for adults, and Cr had a carcinogenic risk for children and adults. All elements in $PM_{2.0-2.5}$ posed carcinogenic risks to both children and adults. Compared with other particle size particles, $PM_{2.0-2.5}$ had a greater risk of carcinogenesis of heavy metals, followed by $PM_{0.5}$, $PM_{0.5-1.0}$, and $PM_{1.0-2.0}$, which was somewhat different from the conclusion of previous studies that particles with smaller particle size were more harmful to human body [2], indicating that while paying attention to the health risks of particles with smaller particle size, there was still a need to pay attention to the hazards of oversized particles. In addition, the carcinogenic risk index of Cr element in different particle size particles was relatively high, and the protection of Cr element carcinogenic risk should be strengthened. The carcinogenic risk index of all kinds of heavy metals to children was higher than that of adults, therefore, children need to strengthen prevention of carcinogenic metal elements.

Conclusion

The characteristics of concentration distribution, source, and potential ecological and health risks of metal elements in particles of different particle sizes in Tianjin, China in 2018 were analyzed. The seasonal variation of heavy metal mass concentration in particles with different particle sizes was higher in Winter and Spring than that in Summer and Autumn. The concentrations of heavy metals were not mainly concentrated in $PM_{0.5}$, and the concentrations of some elements in $PM_{0.5\text{-}1.0}$ and $PM_{2.0\text{-}2.5}$ were also relatively high. It is generally believed that particles with smaller particle size pose a greater threat to human health, so the pollution of heavy metals in $PM_{0.5\text{-}1.0}$ and $PM_{1.0\text{-}2.0}$ cannot be ignored. Enrichment factor analysis showed that the small particle size was greatly affected by human sources. In addition, long-distance transport of pollutants contributed to air pollution in Tianjin. Elements such as Pb, Zn, and Cu in the study area had a great impact on ecological risks. It is necessary to conduct targeted management and protection of the hazards brought by these elements. Compared with other particle size particles, $PM_{2.0\text{-}2.5}$ had a higher cancer risk indicating that while paying attention to the health risks of finer particle size particles, it is still necessary to pay attention to the harm caused by particles with larger particle size.

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