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Pollution Characteristics and Health Risk Assessment of Heavy Metals in $PM_{2.5}$ during Winter in the Suburb of Cangzhou, China

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Abstract

The heavy metals in atmospheric fine particles are of great concern to human health. To understand the pollution characteristics and health risks of heavy metals in particulate matter with an aerodynamic equivalent diameter ≤2.5 μm ($PM_{2.5}$) during winter in the suburb of Cangzhou, $PM_{2.5}$ samples were collected with an intelligent medium-flow atmospheric particulate matter sampler from January to February 2019. The Fe, Cu, Mn, Pb and Zn contents in $PM_{2.5}$ were determined via inductively coupled plasma optical emission spectrometry (ICP-OES). The sources and health risks of heavy metals in $PM_{2.5}$ were analysed via the enrichment factor (EF) method and the United States Environmental Protection Agency (US EPA) health risk assessment model. The results showed that the average $PM_{2.5}$ concentration in the suburb of Cangzhou reached 71.6 μg/m^3, ranging from 23.7 to 169.5 μg/m^3. The exceeding standard rate was 29.4% during the sampling period. The $PM_{2.5}$ concentration during the nighttime was higher than that during the daytime. The heavy metal concentrations in $PM_{2.5}$ decreased in the order of Fe > Mn > Zn > Cu > Pb, and the Fe, Mn, Pb and Zn concentrations decreased in the order of clean days < pollution days < heavy pollution days. The Fe and Mn concentrations were higher during the daytime than those during the nighttime, while the Cu, Pb and Zn concentrations were higher during the nighttime than those during the daytime. EF analysis revealed that Zn, Pb and Cu were significantly enriched, and Pb was highly enriched on heavy pollution days with increasing pollution degree. The enrichment level of heavy metals during the nighttime was higher than that during the daytime. Health risk assessment demonstrated that Mn posed non-carcinogenic risks to both adults and children, following the sequence of clean days < pollution days < heavy pollution days. Pb posed a carcinogenic risk to adults on heavy pollution days. The study revealed that the pollution levels of heavy metals in $PM_{2.5}$ in the suburb of Cangzhou were low, and Pb and Mn in $PM_{2.5}$ posed certain health risks to the population.

Keywords

Fine Particles, Enrichment Factor, Atmospheric Pollution, Different Pollution Levels

1. Introduction

$PM_{2.5}$ is particulate matter with an aerodynamic equivalent diameter ≤2.5 μm, which has attracted increasing attention because of its impact on climate change, ecosystems, atmospheric visibility and human health (Chen et al., 2021; Li et al., 2016; Shen et al., 2019). $PM_{2.5}$ exhibits the characteristics of a small particle size and large specific surface area and can enter the human alveolar area and further migrate into blood, affecting whole-body function and even causing respiratory system, cerebrovascular and cardiovascular diseases (Juda-Rezler et al., 2021; Wang et al., 2019). Toxicological and epidemiological studies have demonstrated that the toxicity of $PM_{2.5}$ is mainly related to the toxic metals adsorbed onto $PM_{2.5}$ (Sah et al., 2019). Heavy metals are important chemical components of $PM_{2.5}$. Although the proportion of heavy metals in $PM_{2.5}$ is small, they can enter the human body through breathing. The human health effects of heavy metals cannot be ignored. Studies have shown that heavy metals in $PM_{2.5}$ can cause acute and chronic health damage, acute changes in cardiopulmonary function, and even cancer (Luo et al., 2019). Hence, it is of great significance to study the pollution characteristics, sources and health risks of heavy metals in $PM_{2.5}$.

At present, a large number of studies on heavy metals in $PM_{2.5}$ have been conducted in China. He et al. (2019) studied the pollution characteristics, potential ecological risks and health risks of heavy metals in $PM_{2.5}$ in Zhengzhou and found that the concentrations of heavy metals in autumn and winter were generally higher than those in spring and summer, and the enrichment level and potential ecological hazard index of Cd were the highest. Cd, As and Cr posed carcinogenic risks, while Mn posed a non-carcinogenic risk. Zheng et al. (2020) studied the pollution characteristics, sources and health risks of heavy metals in $PM_{2.5}$ in Guizhou and found that the Zn and Mn concentrations were higher in winter than those in autumn, the Ni, Mn, Zn and Cu concentrations were higher during the daytime than those during the nighttime, and the Pb concentration was lower during the daytime than that during the nighttime. The main sources of heavy metals included transportation, coal combustion, industrial metallurgy and soil dust. Cd and Mn posed a carcinogenic risk to children. Overall, studies on heavy metals in $PM_{2.5}$ have mainly focused on pollution characteristics, source analysis, ecological risk and health risk assessment, but there are few studies on heavy metals considering different pollution levels (Qiao et al., 2017; Xu et al., 2015). The research area of heavy metals in $PM_{2.5}$ mainly involves urban areas, while research on metal elements in suburban areas is relatively limited (Luo et al., 2019; Yang et al., 2019). In recent years, atmospheric haze pollution incidents have frequently occurred in the Beijing-Tianjin-Hebei (BTH) region. Cangzhou is located in southeastern Hebei Province, which is an important coastal open city near the Bohai Sea with obvious location advantages. It is necessary to deeply analyse the pollution characteristics and health risks of heavy metals in $PM_{2.5}$ in this area. However, there are few documents on this situation. For this reason, the author performed membrane sampling in the suburb of Cangzhou, collected $PM_{2.5}$ samples, and analysed the concentration level, enrichment characteristics and health risks of heavy metals in $PM_{2.5}$ at different pollution levels to provide references for the prevention and control of atmospheric heavy metal pollution and associated health effect evaluation in this region.

2. Materials and Methods

2.1. Sample Collection and Analysis

The sampling site is located on the roof of a building on the campus of the Cangzhou Normal University in the suburb of Cangzhou, China, as shown in Figure 1. There are no tall buildings or typical pollution sources around the sampling site. The sampling site is mainly surrounded by residential areas and public green spaces. Samples were continuously collected twice a day with an intelligent medium-flow atmospheric $PM_{2.5}$ sampler (TH-150C, Wuhan Tianhong Instrument Co., Ltd.) from January 19 to February 21, 2019. Sampling was performed for 11.5 h, and the sampling periods were 08:00-19:30 during the day

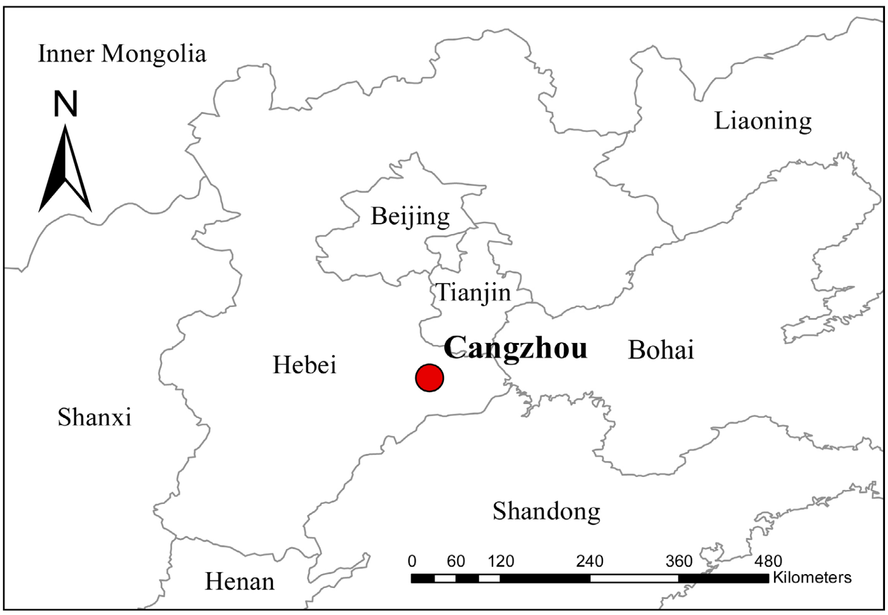

Figure 1. Location of the sampling site in the suburb of Cangzhou, China.

time and 20:00-7:30 during the nighttime. Mixed cellulose membrane filters with a diameter of 90 mm were employed in the $PM_{2.5}$ sampler, and a sampling flow of 100 L/min was used. After each sampling, the samples were wrapped with aluminium foil paper and stored in a refrigerator (−18˚C) prior to analysis.

One-quarter of each cellulose membrane filter was cut into small pieces with plastic scissors and placed in a digestion vessel containing 5.00 mL 65% HNO_3 and 2.00 mL 30% H_2O_2, ensuring that all filter membranes were soaked in this acid system. The samples were digested via a microwave dissolver (WX-8000, Shanghai Yiyao Instrument Technology Development Co., Ltd.) using a three-stage temperature procedure. After digestion, the digestion solution was subjected to acid-driving operation for 15 min at 100˚C and transferred into polyethylene terephthalate (PET) bottles by washing the digestion vessel with ultrapure water 3 times with a constant volume of 25 mL. The Fe, Cu, Mn, Pb and Zn contents in the samples were determined via inductively coupled plasma atomic emission spectrometry (ICP-OES 5100, Agilent). The corresponding optimal wavelengths were 259.940, 324.754, 257.610, 220.353 and 213.857 nm, respectively. The correlation coefficients of the standard curves of the different elements exceeded 0.999. The samples were analysed three times, and the relative standard deviation (RSD) was less than 5%.

2.2. Enrichment Factors

To quantitatively evaluate the enrichment degree of metal elements in atmospheric particulate matter, enrichment factors (EFs) were calculated, choosing soil or crust as the reference medium. According to its value, the contribution level of natural and man-made sources to metal elements can be determined (Hong et al., 2010; Qin et al., 2020; Wei et al., 2011). *EF* can be calculated with Equation (1) as follows:

$$EF = \frac{(C_i/C_r)_{air}}{(C_i/C_r)_{crust}} \tag{1}$$

where *EF* is the enrichment factor, C_i is the concentration of the investigated element *i*, C_r is the concentration of the reference element *r*, $(C_i/C_r)_{\text{air}}$ is the concentration ratio of elements *i* to *r* in particulate matter, and $(C_i/C_r)_{\text{crust}}$ is the ratio of elements *i* to *r* in the crust. In this study, Fe was selected as the reference element, and the element abundance in the crust is the global average concentration (Taylor, 1964).

2.3. Health Risk Assessment

According to the pollutant health risk assessment model recommended by the United States Environmental Protection Agency (US EPA), the health risks of heavy metals in $PM_{2.5}$ via the respiratory route were calculated. Health risk assessment mainly includes non-carcinogenic and carcinogenic risks and is conducted considering both adults and children (Li et al., 2016; Sah et al., 2019). Health risk assessment largely entails four steps: hazard identification, dose-response assessment, exposure assessment and risk characterization (Taner et al., 2013). In combination with the elements determined in this study, the US EPA Integrated Risk Information System (IRIS) database was queried. Mn was selected in non-carcinogenic risk assessment, and Pb was selected in carcinogenic risk assessment. The exposure concentrations of non-carcinogenic and carcinogenic risk elements among adults and children were computed using Equation (2) (Li et al., 2016; Taner et al., 2013):

$$EC = \frac{C \times ET \times EF \times ED}{AT} \quad (2)$$

where EC is the exposure concentration via the respiratory route (μg/m^3), C is the element concentration (μg/m^3), ET is the exposure time (24 h/day), EF is the exposure frequency (365 days/year), ED is the exposure duration (24 years for adults and 6 years for children), and AT is the average time (for non-carcinogenic elements, $AT = ED \times 24$ h/day × 365 days/year, and for carcinogenic elements, $AT = 70$ years × 24 h/day × 365 days/year).

Finally, the non-carcinogenic risk of Mn and carcinogenic risk of Pb in $PM_{2.5}$ were calculated using Equations (3) and (4), respectively (Hu et al., 2012; Taner et al., 2013):

$$HQ = \frac{EC}{RfC \times 1000\ \mu g \cdot mg^{-1}} \quad (3)$$

$$CR = IUR \times EC \quad (4)$$

where HQ is the hazard quotient, representing the non-carcinogenic risk, CR denotes the carcinogenic risk, RfC is the respiratory reference concentration (for Mn, $RfC = 5 \times 10^{-5}$ mg/m^3), and IUR is inhalation unit risk (for Pb, $IUR = 8 \times 10^{-5}$ (μg/m^3)$^{-1}$). If HQ is less than 1, this suggests that the non-carcinogenic risk of the element is low or negligible. Conversely, a non-carcinogenic risk exists. If CR is less than 1×10^{-6}, this indicates that there is no carcinogenic risk. Conversely, there exists a carcinogenic risk.

3. Results and Discussion

3.1. $PM_{2.5}$ Mass Concentration Level

Figure 2 shows the daily and diurnal changes in the $PM_{2.5}$ mass concentration during the sampling period. The daily average $PM_{2.5}$ concentration varied greatly, with maximum and minimum values of 169.5 and 23.7 μg/m^3, respectively. The maximum value was 7.2 times the minimum value, and the maximum value was 2.3 times the Grade II level of the Chinese Ambient Air Quality Standard (CAAQS, GB 3095-2012) (75 μg/m^3). The mean value of the $PM_{2.5}$ concentration during the sampling period was 71.6 μg·m^{-3}, which was lower than the CAAQS Grade II standard but 1.1 times higher than the CAAQS Grade I standard (35 μg/m^3). If the CAAQS Grade II standard were selected as the reference level, the daily average $PM_{2.5}$ concentration exceeded the standard for 10 days during the observation period, and the exceeding rate was 29.4%. The variation range of the

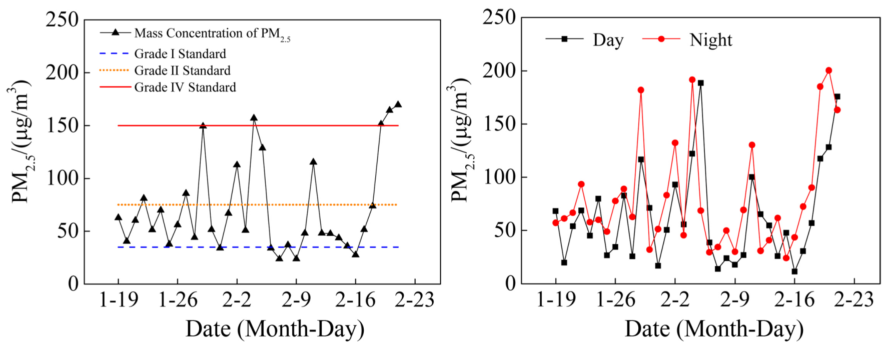

Figure 2. Daily and diurnal variations in the $PM_{2.5}$ mass concentration in the suburb of Cangzhou.

$PM_{2.5}$ concentration during the daytime and nighttime was 11.5 - 188.7 μg/m^3 and 24.1 - 200.3 μg/m^3, respectively, with mean values of 63.4 and 79.9 μg·m^{-3}, respectively. The $PM_{2.5}$ concentration during the nighttime was 1.3 times that during the daytime, and it exceeded the CAAQS Grade II standard. The research results indicated that the $PM_{2.5}$ concentration during the nighttime was higher than that during the daytime, which is consistent with the research results for northern cities such as Beijing (Xu et al., 2019) and Baoding (Lei et al., 2021). This may be largely due to the low temperature at night. The near-surface atmosphere is prone to inversion, and atmospheric stratification remains relatively stable, which is not conducive to the diffusion of air pollutants. During the daytime, the ground temperature is higher, the solar radiation is enhanced, the height of the mixed layer is increased, and the atmospheric diffusion conditions are better, which facilitates air pollutant diffusion.

3.2. Mass Concentrations of Heavy Metals in $PM_{2.5}$

The concentrations of heavy metals in $PM_{2.5}$ in the suburb of Cangzhou in winter followed the descending order of Fe > Mn > Zn > Cu > Pb, as indicated in **Table 1**. Among them, Fe was the main element, accounting for 81.5% of all elements. The Mn, Zn and Cu concentrations were comparable, accounting for 4.3% - 5.7% of all elements. The Pb concentration was the lowest, accounting for 1.2% of all elements. China has not yet established standard limits for the concentration of metal elements in atmospheric $PM_{2.5}$, and CAAQS stipulates that the annual average concentration limit of Pb in ambient air is 0.5 μg/m^3, and the seasonal average concentration limit is 1 μg/m^3 (Qi et al., 2017). The World Health Organization (WHO) has stipulated that the reference limits of Mn and Pb are 150 and 500 ng/m^3, respectively (Yang et al., 2019). The Pb concentration in atmospheric $PM_{2.5}$ in the suburb of Cangzhou did not exceed the standard, but the Mn concentration was 153.6 ng/m^3, slightly higher than the reference limit (150 ng/m^3).

To explain the pollution level of heavy metals in $PM_{2.5}$ in the suburb of Cangzhou in winter, the five heavy metals in $PM_{2.5}$ were also compared to winter research results for certain cities, as listed in **Table 1**. The Fe concentration was

Table 1. Mass concentrations of heavy metals in $PM_{2.5}$ in winter in select cities in China (ng/m^3).

Site	Fe	Mn	Pb	Zn	Cu	Reference
Cangzhou, China	2195.8	153.6	31.3	148.7	116.4	This study
Beijing, China	1323.1	58.8	154.3	185.3	185.2	(Qiao et al., 2017)
Tianjin, China	1310	100	230	730	120	(Zhao et al., 2013)
Shijiazhuang, China	1840	160	430	810	60	(Zhao et al., 2013)
Baoding, China	/	38.6	158.9	226.5	99.6	(Lei et al., 2021)
Zhengzhou, China	301.9	41.3	63.2	97.5	30.5	(Yan et al., 2019)
Nanchang, China	/	226.1	468.7	1141.1	343.4	(Zheng et al., 2018)
Guilin, China	/	173	102	132	8.9	(Mo et al., 2019)
Guiyang, China	/	18	20	34	8.8	(Zheng et al., 2020)
Fuzhou, China	563.2	47.6	46.6	232.6	164.9	(Xu et al., 2012)

higher than that in Beijing, Tianjin and Shijiazhuang and significantly higher than that in Zhengzhou and Fuzhou. The Mn concentration was comparable to that in Shijiazhuang but was significantly higher than that in Guiyang, Zhengzhou, Fuzhou, Beijing and Baoding. The Pb concentration was significantly lower than that in surrounding cities. The Zn concentration was obviously lower than that in Tianjin, Shijiazhuang and Baoding and higher than that in Zhengzhou and Guiyang. The Cu concentration was comparable to that in Tianjin and Baoding and significantly higher than that in Guilin and Guiyang. The concentration of heavy metals varied significantly among the different cities, which may be caused by different sources of heavy metals and different contribution levels of the various emission sources in the different cities.

With the use of different pollution levels, the variation characteristics of heavy metals in $PM_{2.5}$ vary (Fang et al., 2020; Xu et al., 2015). Due to the limited observation data, days with a $PM_{2.5}$ concentration below 75 $\mu g/m^3$ were defined as clean days, days with a $PM_{2.5}$ concentration ranging from 75 - 150 $\mu g \cdot m^{-3}$ were defined as pollution days, and days with a $PM_{2.5}$ concentration higher than 150 $\mu g \cdot m^{-3}$ were defined as heavy pollution days (Zhang et al., 2020), as shown in **Figure 2**. During the observation period, the corresponding numbers of clean, pollution and heavy pollution days were 24, 6 and 4 days, respectively, with occurrence rates of 70.6%, 17.6% and 11.8%, respectively, and the corresponding $PM_{2.5}$ concentrations were 47.1, 104.7 and 160.5 $\mu g/m^3$, respectively. The $PM_{2.5}$ concentration on pollution and heavy pollution days was 2.2 and 3.4 times, respectively, that on clean days, showing an increasing trend of clean days < pollution days < heavy pollution days, and there was a significant difference in the

$PM_{2.5}$ concentration between these three pollution conditions ($p < 0.01$). The total concentration of the five heavy metals in $PM_{2.5}$ on clean, pollution and heavy pollution days was calculated, as shown in **Figure 3**. The corresponding concentration of clean, pollution and heavy pollution days were 2534.9, 2725.2 and 3164.2 ng/m^3, respectively, showing an increasing trend of clean days < pollution days < heavy pollution days, and the concentration ratios of pollution days to clean days, heavy pollution days to clean days were 1.1 and 1.3, respectively. It was consistent with the change trend of the $PM_{2.5}$ concentration, but significantly lower than the increase proportion of $PM_{2.5}$ concentration, and the concentration difference under the three pollution states was not significant ($p > 0.05$). This shows that with increasing pollution degree, although the total concentration of heavy metals in $PM_{2.5}$ increased, the contribution to $PM_{2.5}$ decreased, which is consistent with the research results of Qiao et al. (2017), indicating that when pollution or heavy pollution events occur, the main reason for the increase in the $PM_{2.5}$ concentration is the contribution of water-soluble ions and other main components, but the increase in the heavy metal concentration is not the main reason for the increase in the $PM_{2.5}$ concentration (Juda-Rezler et al., 2021).

From the point of view of a single element, with increasing pollution degree, the Fe, Mn, Pb and Zn concentrations also decreased in the order of clean days < pollution days < heavy pollution days. The increase proportion of Pb was the largest. Compared to clean days, the daily concentration on pollution and heavy pollution days increased by 0.5 and 2.8 times, respectively. The Pb concentration on heavy pollution days was significantly higher than that on pollution and clean days ($p < 0.01$), indicating that Pb was more likely to be enriched with increasing pollution degree. The variation trends of the Fe, Mn, Pb, Zn and $PM_{2.5}$ concentrations were consistent. Correlation analysis showed that the Pb and Zn

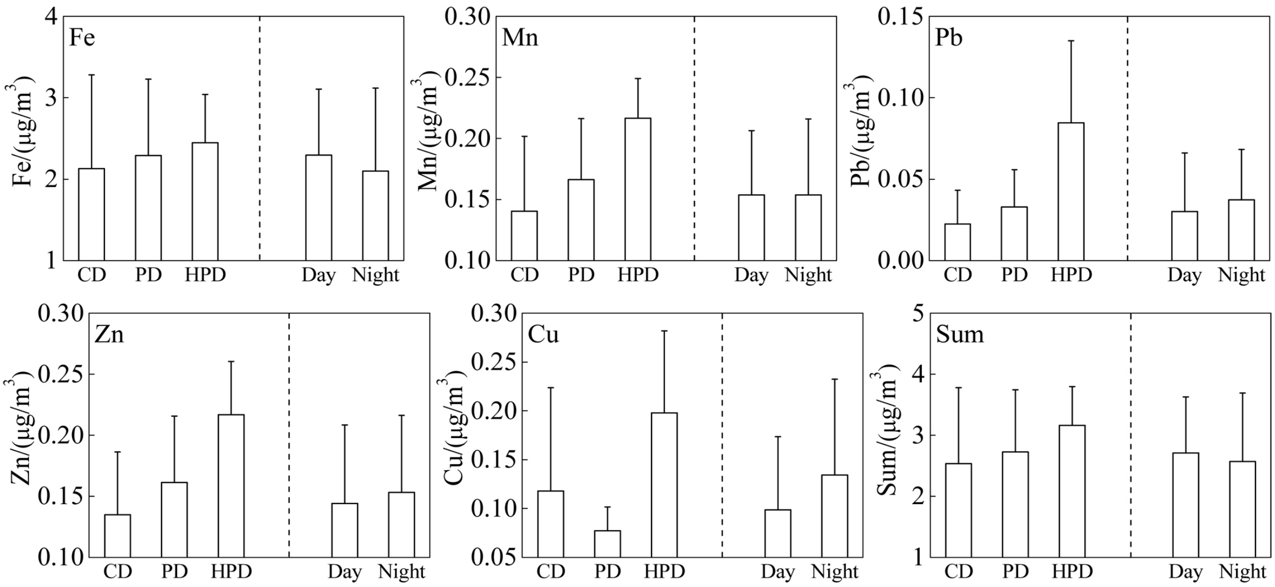

Figure 3. Mass concentrations of heavy metals in $PM_{2.5}$ in the suburb of Cangzhou.

concentrations were significantly correlated with the $PM_{2.5}$ concentration ($p < 0.01$), indicating that the sources of these elements are similar to those of $PM_{2.5}$. Cu differed from the other elements, and the Cu concentration decreased in the order of pollution days < clean days < heavy pollution days. Compared to clean days, the concentration on pollution days decreased by 34.4%, and the level on heavy pollution days increased by 68.0%. In general, with increasing pollution degree, the concentrations of the five heavy metals reached a maximum value on heavy pollution days. The absolute value of the increase in Fe was the largest, while the proportion of the increase in Pb was the largest, but the absolute increase value was the smallest.

Figure 3 also shows the daytime and nighttime concentrations of the various heavy metals in $PM_{2.5}$. The total concentration of the five heavy metals reached 2709.4 and 2568.1 $ng \cdot m^{-3}$ during the daytime and nighttime, respectively, which were higher during the daytime than that during the nighttime. By comparing the daytime and nighttime concentrations of the different elements, it could be found that the Fe and Mn concentrations were higher during the daytime than those during the nighttime, and the Cu, Pb and Zn concentrations were higher during the nighttime than those during the daytime ($p > 0.05$), indicating that the pollution elements during the nighttime were more likely to be enriched, which is consistent with the research results of Qiao et al. (2017). The mean values of the $PM_{2.5}$ concentrations during the daytime and nighttime were 63.4 and 79.9 $\mu g/m^3$, respectively, and the value during the nighttime was higher than that during the daytime. The diurnal variation trends of the Cu, Pb, Zn and $PM_{2.5}$ concentrations were consistent. The higher concentrations of Cu, Pb and Zn during the nighttime could be related to the increase in heavy vehicle activities at night (Lei et al., 2021; Zheng et al., 2020). At night, the atmosphere is mostly temperature inverted, with notable atmospheric stability. Heavy metals emitted by pollution sources are more likely to be enriched, resulting in an increase in the concentration (Qiao et al., 2017).

3.3. Enrichment Level of Heavy Metals in $PM_{2.5}$

According to the EF method, the order of Mn < Cu < Zn < Pb could be obtained. Among them, the EF value of Mn was less than 10, indicating that this element mainly originated from the crust. The EF values of Cu, Zn and Pb were greater than 10, showing moderate enrichment. These elements mainly stemmed from anthropogenic sources (Wang et al., 2019). Studies have shown that the sources of Cu, Zn and Pb are mainly related to traffic sources and the metallurgical industry (Arditsoglou & Samara, 2005; Hieu & Lee, 2010). To better understand the changes in heavy metal concentrations in $PM_{2.5}$ at different pollution levels, the EF values of four heavy metals on clean, pollution and heavy pollution days were calculated, as shown in **Figure 4**. The enrichment degree of Mn, Zn and Pb indicated the order of clean days < pollution days < heavy pollution days, but the EF value of Mn was less than 10, indicating that this element was also

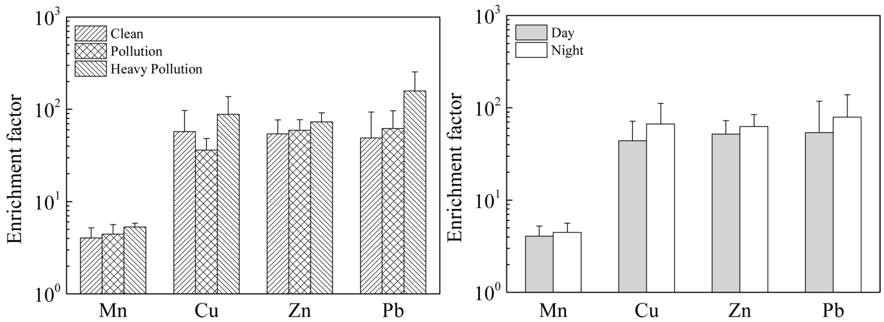

Figure 4. Enrichment factors of heavy metals in $PM_{2.5}$ in the suburb of Cangzhou.

mainly affected by natural sources on pollution and heavy pollution days. The EF values of Zn and Pb on clean, pollution and heavy pollution days were all greater than 10, and the EF value of Pb on heavy pollution days increased the most. Compared to clean days, the EF value of Pb increased by 2.2 times, and EF reached a value of 158.0, which was highly enriched and significantly higher than that on clean and polluted days ($p < 0.05$), indicating that the enrichment of polluting elements occurred more easily with increasing pollution degree. The change in the EF value of Cu was significantly different from that in the EF values of Mn, Zn and Pb. Notably, the EF value of Cu decreased on pollution days and reached a maximum on heavy pollution days, which was significantly higher than that on pollution days ($p < 0.05$). During heavy pollution events, the EF value of anthropogenic source elements (Cu, Zn and Pb) significantly increases, while the EF value of natural source elements (Mn) changes slightly (Xu et al., 2015).

Figure 4 also shows the EF values of heavy metals in $PM_{2.5}$ during the daytime and nighttime. The EF values of Mn during the daytime and nighttime were less than 10, indicating that Mn was mainly affected by crustal sources. The EF values of Cu, Zn and Pb were greater than 10, indicating that they were mainly affected by anthropogenic sources. The ratios of EF values of Mn, Cu, Zn and Pb during the nighttime and daytime were 1.1, 1.5, 1.2 and 1.5, respectively, demonstrating the EF values during the nighttime were greater than those during the daytime. Among them, the EF values of Cu and Pb during the nighttime and daytime were the greatest, and the EF values during the nighttime were significantly higher than those during the daytime ($p < 0.05$), indicating that pollution elements were more prone to enrichment during the nighttime.

3.4. Health Risk Level of Heavy Metals in $PM_{2.5}$

Figure 5 shows the non-carcinogenic and carcinogenic risks of Mn and Pb in $PM_{2.5}$ via the respiratory pathway. The non-carcinogenic risk of Mn was higher than 1, indicating that Mn posed a non-carcinogenic risk to human health (Duan et al., 2021). With increasing pollution degree, the non-carcinogenic risk decreased in the order of clean days < pollution days < heavy pollution days. The non-carcinogenic risk on heavy pollution days was the highest, and the

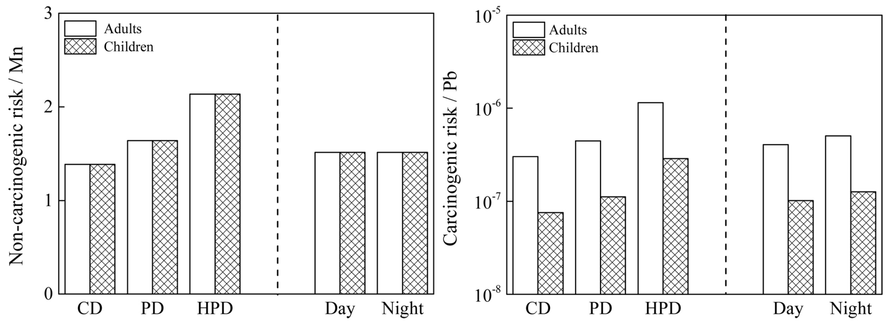

Figure 5. Non-carcinogenic risk of Mn and carcinogenic risk of Pb in $PM_{2.5}$ in the suburb of Cangzhou.

non-carcinogenic risk to adults and children reached 2.1. The difference in the non-carcinogenic risk of Mn between the daytime and nighttime was not obvious, but both were higher than 1. Relevant studies have also found that Mn poses a high non-carcinogenic risk. He et al. (2019) found that the non-carcinogenic risk of Mn in $PM_{2.5}$ in a residential area of Zhengzhou to children, adult men and adult women was 6.3, 2.6 and 2.5, respectively. Zhang et al. (2014) found that the non-carcinogenic risk of Mn in $PM_{2.5}$ in Tianjin in winter and summer was 4.9 and 2.8, respectively. Mn is the main contributor to the non-carcinogenic risk of heavy metals, which may cause harmful health effects on the human body (Zheng et al., 2020). The EF value of Mn in this study was less than 10, indicating that Mn mainly originated from crustal sources and that natural sources such as dust may also increase the non-carcinogenic risk to humans (Cao et al., 2019; Duan et al., 2021).

The carcinogenic risk of Pb to adults and children was 4.2×10^{-7} and 1.1×10^{-7}, respectively, and the risk to adults was higher than that to children, both lower than the human acceptable risk level (1×10^{-6}) (Li et al., 2016). With increasing degree of pollution, the carcinogenic risk also decreased in the order of clean days < pollution days < heavy pollution days, and the carcinogenic risk to children was lower than 1×10^{-6}. The carcinogenic risk to adults on clean and pollution days was lower than 1×10^{-6}. The carcinogenic risk to adults on heavy pollution days was 2.3×10^{-6}, higher than the acceptable human level. The carcinogenic risk of Pb during the nighttime was higher than that during the daytime, and the carcinogenic risk to adults was higher than that to children, but both were lower than 1×10^{-6}. In general, Pb poses a high carcinogenic risk to adults on heavy pollution days, and long-term exposure to the outdoor environment should be reduced during heavy pollution periods.

4. Conclusion

1) The average $PM_{2.5}$ concentration reached 71.6 μg/m^3 in the suburb of Cangzhou, ranging from 23.7 - 169.5 μg/m^3, exceeding the CAAQS Grade II standard (75 μg/m^3) for 10 days, and the exceeding standard rate was 29.4%. The corresponding $PM_{2.5}$ concentrations on clean, pollution and heavy pollution days

were 47.1, 104.7 and 160.5 μg/m^3, respectively, and the $PM_{2.5}$ concentration at the three pollution levels significantly differed ($p < 0.01$). The $PM_{2.5}$ concentration during the nighttime was higher than that during the daytime.

2) The concentration of heavy metals in $PM_{2.5}$ presented the order of Fe > Mn > Zn > Cu > Pb. With increasing pollution degree, the Fe, Mn, Pb and Zn concentrations decreased in the order of clean days < pollution days < heavy pollution days. The Fe and Mn concentrations were higher during the daytime than those during the nighttime, and the Cu, Pb and Zn concentrations were higher during the nighttime than those during the daytime, which was consistent with the change trend of $PM_{2.5}$.

3) EF analysis showed that Mn mainly stemmed from the crust, and Zn, Pb and Cu mainly originated from anthropogenic sources. With increasing pollution degree, Mn was not obviously enriched, but Zn, Pb and Cu were obviously enriched. Pb was highly enriched on heavy pollution days, and the Pb enrichment degree was significantly higher than that on clean and pollution days. The concentrations of the four heavy metals during the nighttime were higher than those during the daytime.

4) Health risk assessment showed that Mn posed a non-carcinogenic risk to adults and children, which was manifested as cleaning day < pollution day < heavy pollution day. Pb on heavy pollution days posed a carcinogenic risk to adults. The carcinogenic risk of Pb to adults was higher than that to children and higher during the nighttime than that during the daytime. The risk to both adults and children was less than 1×10^{-6}, indicating no carcinogenic risk.

5) The result revealed that the pollution levels of heavy metals in $PM_{2.5}$ in the suburb of Cangzhou were low, and Pb and Mn in $PM_{2.5}$ posed certain health risks to the population. It is quite necessary for further research to increase the sampling time and the number of sampling sites so as to make a more comprehensive assessment of atmospheric heavy metal pollution in the study area.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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