Chemical Composition of PM$_{2.5}$ and its Impact on Inhalation Health Risk Evaluation in a City with Light Industry in Central China

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Abstract: A city with light industry in China was selected for the study of the chemical characteristics of PM$_{2.5}$ and to assess its impact on inhalation health risks. During the period from May 2017 to February 2018, a total of 382 PM$_{2.5}$ filter samples were collected across four seasons (15–20 days for each season). The results showed that the daily average PM$_{2.5}$ concentration ranged from 21 to 255 µg/m$^3$, with an annual average of 73 ± 49 µg/m$^3$. SO$_2^-$, NO$_x$, NH$_4^+$, and organic matter (OM) were the dominant components, accounting for 13%, 20%, 11%, and 20% of annual PM$_{2.5}$ mass loading, respectively. Compared with the clean periods, the meteorology of the pollution periods were mostly characterized by high relatively humidity, high temperature, and low wind speeds. Based on positive matrix factorization (PMF), the major source of PM$_{2.5}$ was identified as secondary aerosols, contributing 28% and 49% on clean days and polluted days, respectively. The health risk assessment of heavy metals showed that non-carcinogenic hazard is not expected to occur, while Cr contributed the highest cancer risk. This study is helpful for the advancement of our scientific understanding of PM$_{2.5}$ pollution and its impact on health in cities with light industries.

Keywords: PM$_{2.5}$; chemical composition; source apportionment; health risk assessment

1. Introduction

Numerous studies have indicated PM$_{2.5}$ (particle with an aerodynamic diameter of 2.5 µm or less) is the major cause of haze in most areas [1,2] and has adverse effects on human health [3,4]. Many cities have carried out a source analysis and health risk assessment of PM$_{2.5}$.

Atmospheric PM$_{2.5}$ is a complex mixture from many sources. The automobile exhaust and coal-fired emissions were the main anthropogenic sources of the PM$_{2.5}$ [5]. The secondary sources (secondary sulfate, secondary nitrate, and secondary organic aerosol) are also considered to be the main sources in most cities [5–7]. Depending on the natural condition and industrial structure, each city has its specific sources for PM$_{2.5}$, such as dust, biomass burning, ironmaking, glass manufacturing, steel plants, and so on [5–11]. Therefore, to find the PM$_{2.5}$ sources in a specific city, source apportionment should be done.

Fine particles can penetrate into the gas exchange regions of the lung and can cause serious health problems [12–15]. Heavy metals are one of the major concerns. For example, a study on metals in PM$_{2.5}$ at the campus of Agra, the capital of India showed chromium and manganese show the highest carcinogenic and non-carcinogenic risks [5]. Zhang et al. [11] conducted a health risk assessment of five sites in four cities in Shandong Province. Studies showed that there was a non-
carcinogenic risk of Cd in adults and Pb and Co in children, and there was a carcinogenic risk of As and Pb in both adults and children. Therefore, to protect human health, it is necessary to study the health effects of heavy metals in PM$_{2.5}$ in more cities.

In recent years, with the rapid industrialization and urbanization of China, haze events have raised great concern among the public [16,17]. Though the concentration of PM$_{2.5}$ has decreased significantly, it is still high in many cities in China and is often the primary pollutant on polluted days [18]. It is highly important to study the characteristics of components, sources, and the environmental and health effects of PM$_{2.5}$. A large number of previous studies focus on many well-developed regions such as Beijing–Tianjin–Hebei, the Yangtze River Delta, and the Pearl River Delta [10,11]. There has been little research that focuses on other cities. Although some cities have small built-up areas and are underdeveloped in terms of industry, their populations are relatively dense and PM$_{2.5}$ exceeds the standard. These cities may also have suffered from environmental problems and have health risks. Therefore, they are also a potential research object that should be focused on.

In this study, a city (Luohe) with light industry as the main industry was selected. Chemical characteristics, source apportionment, and risk assessment of PM$_{2.5}$ were measured. The main objectives of this study are as follows: 1) to quantify seasonal PM$_{2.5}$ concentration and chemical composition; 2) to analyze the source apportionment of PM$_{2.5}$; 3) to assess the impact of heavy elements in PM$_{2.5}$ on inhalation health risks. This study is a comprehensive study on the characteristics of the chemical composition and sources of PM$_{2.5}$ as well as the impacts on health in a light industry city.

2. Method

2.1. Sample Collection

This research is conducted in the urban area of Luohe City, which is located in the middle of Henan Province in China. The terrain is high in the northwest (~102 m above sea level) and low in the southeast (~50 m above sea level). It has a warm and humid monsoon climate. The total area is 2617 km$^2$ and the urban area is 72 km$^2$. The resident population is 2,650,000 and the urban resident population is 1,350,000 (Henan Statistical Yearbook, 2018, China Statistics Press [19]). The main industry in Luohe city is food processing—including meat processing, beverage production, instant noodle production, and so on. It is representative of a light industrial city, typically characterized by more consumer-oriented goods [20].

Three sampling sites were selected: the Luohe Water Control Bureau (114.03E, 33.59N), the Party School of the Municipal Party Committee (114.07E, 33.60N) and the 3515 factory (114.06E, 33.57N), which are shown in Figure 1. These sampling points are located in the centre of the city, no more than 5 km between any two sampling sites. The sampling times were as follows: (1) Spring: 10–24 May 2017; (2) Summer: 12–26 July 2017; (3) Autumn: 31 October–19 November 2017; (4) Winter: 19 January–7 February 2018. PM$_{2.5}$ membranes were collected from 11:00 a.m. to 10:00 a.m. the next day. The particulate membrane sampler (16.7 L/min) meets the European standard and the American standard (DERENDA PNS, Germany) Samples were collected simultaneously using a quartz filter and a Teflon filter, which are 47 mm in diameter. A total of 382 filters were collected. Among them, the quartz filters were used to analyse ions and carbon components, and the Teflon filters were used to analyze elemental components. The filter samples were weighed with a filter automatic weighing system (Commodore AWS-1, Germany) before and after sampling.
To understand the divergence of PM$_{2.5}$ and its chemical composition between different sampling sites, the coefficient of divergence (COD) was calculated.

$$\text{COD}_{jk} = \sqrt{\frac{\sum_{i=1}^{P} \left( x_{ij} - x_{ik} \right)^2}{\sum_{i=1}^{P} x_{ij} + x_{ik}}}$$

where \(\text{COD}_{jk}\) is the coefficient of divergence, \(j\) and \(k\) are the component spectrum numbers participating in the calculation, \(P\) is the number of chemical components participating in the calculation, and \(x_{ij}\) and \(x_{ik}\) represent the average concentration for a chemical component \(i\) at site \(j\) and \(k\), respectively. It has been reported that if COD approaches 0, concentrations can be considered to be spatially homogeneous; if the COD was close to 1, the difference was more significant [21,22]. Results showed that the COD value ranged from 0.07 to 0.18 in this study. Therefore, the spatial variation of PM$_{2.5}$ and its chemical composition was not significant. The average value from three sites is thus used in subsequent discussions.

2.2. Chemical Composition Analysis

The organic carbon (OC) and elemental carbon (EC) were analysed by a thermal/optical carbon analyser (2001A, the American Desert Research Institute, USA) and the IMPROVE programmed temperature method was used [23].

Ion chromatography (ICS-2100, ICS-1100, Dionex, USA) was used to analyse four anions (F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$) and five cations (Na$^+$, K$^+$, NH$_4^+$, Ca$^{2+}$, Mg$^{2+}$) [24]. Cation concentrations were determined using a CS12-A (4 × 250 mm), with 20 mmol/L methane sulfonate as an eluent. The anions were separated using an AS11-HC (4 × 250 mm), with 1 to 30 mmol/L KOH as an eluent. The specific method is described in detail in previous research [25].
Elements (Li, Be, Na, P, K, Sc, As, Rb, Y, Mo, Cd, Sn, Sb, Cs, La, V, Cr, Mn, Co, Ni, Cu, Zn, Ce, Sm, W, Ti, Pb, Bi, Th, U) were analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500a, USA) while other elements (Zr, Al, Sr, Mg, Ti, Ca, Fe, Ba, Si) were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-OES, USA) [26].

For the elements, mineral dust (MD) was calculated using formula (2) [27,28].

\[ \text{MD} = 1.89 \rho(\text{Al}) + 2.14 \rho(\text{Si}) + 1.4 \rho(\text{Ca}) + 1.43 \rho(\text{Fe}) + 1.67 \rho(\text{Ti}) + 1.2 \rho(\text{Mg}) + 1.66 \rho(\text{Mg}) \]

where \( \rho(\text{Al}), \rho(\text{Si}), \rho(\text{Ca}), \rho(\text{Fe}), \rho(\text{Ti}), \rho(\text{Mg}) \) are the concentrations of Al, Si, Ca, Fe, Ti, K, and Mg (\( \mu g/m^3 \)), respectively. TE is a simple addition of trace elements other than crustal elements and sea salt elements [29].

In order to analyze ions, the testing of a standard solution and a blank was performed before the targeted sample analysis, and the correlation coefficients of the standard samples were above 0.999. The method detection limits of F, Cl, NO\textsubscript{3}, SO\textsubscript{4}\textsuperscript{2-}, Na\textsuperscript{+}, K\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+} were 0.026, 0.058, 0.013, 0.010, 0.013, 0.087, 0.048, and 0.067 mg L\textsuperscript{-1}, respectively. With regard to the analysis of the trace elements, the relative standard deviations between the real values of the standard materials and the analysis results were within a range of 2~15%, and the detection limits ranged from 0.00001 to 0.0005 \( \mu g \) L\textsuperscript{-1}. For carbonaceous species, 1 in every 10 samples was detected twice and the precision was less than 1%. Standard concentrations of CH\textsubscript{4}/CO\textsubscript{2} mixed gases were used to calibrate the analyzer each day before and after the sample analysis. All the reported data for water-soluble ions, trace elements, and carbonaceous species were corrected by the filter blanks.

2.3. PMF Model

PMF (positive matrix factorization) is a multivariate receptor model, which is often used to study the PM source apportionment to obtain the type of pollution source and its contribution to PM [30–32].

In this work, Model PMF 5.0 (EPA, DurhamNC, USA) was used to conduct the receptor-based source apportionment for PM\textsubscript{2.5}. The recommended approach in previous studies was used to come to a suitable solution [33]. The PMF model was run several times with the number of source factors ranging from three to seven. A higher number improved the fit marginally, but also resulted in factors that contributed little to the total PM\textsubscript{2.5} mass. Meanwhile, the possible sources impacting PM\textsubscript{2.5} mass concentration in the study area was considered [34,35].

2.4. Health Risk Estimation

According to the method described by the US Environmental Protection Agency (USEPA, 1989 [36]), several steps were used to develop the risk evaluation of metals in PM\textsubscript{2.5}, including the calculation for the 95% upper confidence limit (UCL) of the arithmetic mean concentration, evaluating the exposure, and calculating the risk [31]. Nine heavy metals are considered in this study: Pb, Cr, Co, Ni, Zn, As, Cd, V, and Mn. Due to incomplete data on hand-feeding and skin contact, this study only considered the carcinogenic and non-carcinogenic risks of respiratory pathways.

The heavy metal exposure intake (\( D_{\text{inh}} \)) is calculated as in formula (3)

\[ D_{\text{inh}} = \frac{C \times \text{InhR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \]

where \( D_{\text{inh}} \) is the heavy metal exposure intake through breath inhalation, mg kg\textsuperscript{-1} day\textsuperscript{-1}. \( C \) is the heavy metal exposure concentration, generally taking the 95% confidence interval upper limit, mg/m\textsuperscript{3}. \( \text{InhR} \) is the inhalation rate (m\textsuperscript{3}/day). \( \text{EF} \) is the exposure frequency, day/year. \( \text{ED} \) is the exposure duration (year). \( \text{BW} \) is the body weight (kg). \( \text{AT} \) is the averaging time, \( \text{AT} = \text{ED} \times 365 \) (days) for non-carcinogenic risk and \( \text{AT} = 70 \times 365 \) (days) for cancer risk. The parameters involved in the exposure assessment are described in Table S1 [37–40].

The hazard quotient (HQ) represents the health risk value of non-carcinogenic metals. The hazard index (HI) is the sum of the risk quotients of metals through various pathways. If \( \text{HI} > 1 \), it
indicates that a non-carcinogenic toxic risk exists. If $HI \leq 1$, it indicates that the non-carcinogenic effect is inappreciable. The calculation formulas are as [11]

$$HQ = \frac{D_{inh}}{R_{fd}}$$ (4)

$$HI = \sum HQ_i$$ (5)

where $R_{fd}$ is the reference dose, mg kg$^{-1}$ day$^{-1}$ (Table S2) [41].

As a step towards calculating the carcinogenic risk, lifetime average daily dose (LADD) for heavy metal exposure are calculated (Equation 6).

$$LADD = \frac{C \times EF}{AT} \times \left( \frac{\text{InhR}_{child} \times \text{ED}_{child}}{\text{BW}_{child}} + \frac{\text{InhR}_{adult} \times \text{ED}_{adult}}{\text{BW}_{adult}} \right)$$ (6)

To evaluate the health risk for carcinogenic metals, incremental lifetime cancer risk (ILCRi) value was used. If the ILCR is greater than $10^{-6}$, it is considered to be a carcinogenic risk [42]. The calculation formula is

$$ILCRi = LADD \times SFa$$ (7)

$$ILCR = \sum ILCRi$$ (8)

where SFa is the slope factor in mg kg$^{-1}$ day$^{-1}$ (Table S2).

3. Results and Discussion

3.1. Chemical Composition

Figure 2 shows the variations of meteorological parameters, gaseous pollutants, and PM$_{2.5}$ during the campaign. There were several pollution episodes during the campaign. These pollution periods (PP) were defined as daily PM$_{2.5}$ concentrations being above 75 µg/m$^3$. Meanwhile, the days with PM$_{2.5}$ concentrations below 75 µg/m$^3$ were defined as clean periods (CP). Seven pollution episodes were identified during the campaign. There were three long-lasting pollution episodes that occurred between 6–9 November 2017; 13–16 November 2017; and 19–23 January 2018. The number of polluted days was 0, 1, 12, and 7 in the spring, summer, autumn, and winter, accounting for 0%, 6.7%, 60%, and 46.7% of the total sampling days in each season, respectively.
Figure 2. Variation in ambient PM$_{2.5}$ and gaseous pollutants as well as meteorological parameters during the study. The light brown bar represents the pollution period and is marked as PP1-PP7; 75 µg/m$^3$ is the Grade II limit for the PM$_{2.5}$ daily average stated by the Chinese National Ambient Air Quality Standard (GB 3096-2012). WS: wind speed; Tem.: temperature; RH: relative humidity.

Table 1 presents seasonal and annual mean concentrations of PM$_{2.5}$ and its major chemical components during the sampling periods. During the sampling period, the mean temperature was 16.2 ± 11.1 °C and the RH was 66.0 ± 12.8% on average. The average wind speed was 1.7 ± 0.8 m/s over the whole sampling period. Daily PM$_{2.5}$ ranged from 21 to 255 µg/m$^3$, with an annual average of 73 ± 49 µg/m$^3$. The average concentrations of PM$_{2.5}$ in autumn (97 µg/m$^3$) and winter (96 µg/m$^3$) were much higher than that in spring (51 µg/m$^3$) and summer (38 µg/m$^3$).

### Table 1. Seasonal and annual average concentrations of PM$_{2.5}$ and of the major chemical species, as well as meteorological parameters and the concentrations of gaseous pollutants during the sampling period

| Species | Spring | Summer | Autumn | Winter | Annual |
|---------|--------|--------|--------|--------|--------|
| Tem.\(^{(°C)}\) | 22.8 ± 3 | 30.3 ± 1.7 | 12.2 ± 3.6 | -0.1 ± 2.2 | 16.2 ± 11.1 |
| RH/% | 65.3 ± 6.1 | 77.6 ± 6.6 | 60.2 ± 11.4 | 58.1 ± 13.9 | 66.0 ± 12.8 |
| WS/(m/s) | 1.8 ± 0.9 | 1.8 ± 0.7 | 1.6 ± 0.9 | 1.9 ± 0.8 | 1.7 ± 0.8 |
| Concentrations of gaseous pollutants (µg/m$^3$) | | | | | |
| O$_3$ | 99 ± 16 | 68 ± 14 | 48 ± 20 | 42 ± 9 | 63 ± 27 |
| SO$_2$ | 15 ± 4 | 7 ± 1 | 18 ± 6 | 18 ± 5 | 15 ± 6 |
| NO$_2$ | 30 ± 6 | 18 ± 3 | 56 ± 14 | 44 ± 9 | 39 ± 18 |
| Concentrations of PM$_{2.5}$ and chemical compositions (µg/m$^3$) | | | | | |
| PM$_{2.5}$ | 51 ± 13 | 38 ± 22 | 97 ± 47 | 96 ± 61 | 73 ± 49 |
| SO$_{4}^-$ | 8.6 ± 3.7 | 9 ± 7.8 | 9.3 ± 5.7 | 12.3 ± 11.2 | 9.8 ± 7.7 |
| NO$_3^-$ | 5.2 ± 2.4 | 3.6 ± 5.3 | 22.9 ± 14.1 | 22.4 ± 17 | 14.4 ± 14.9 |
| NH$_4^+$ | 4.4 ± 1.9 | 4.6 ± 4.3 | 9.5 ± 5.3 | 11.2 ± 8.5 | 7.7 ± 6.3 |
| Cl$^-$ | 0.2 ± 0.1 | 0.2 ± 0.2 | 1.8 ± 1.6 | 2.8 ± 1.5 | 1.3 ± 1.6 |
| K$^+$ | 0.9 ± 0.5 | 0.3 ± 0.1 | 1.1 ± 0.6 | 1.3 ± 0.7 | 0.9 ± 0.6 |
| OC | 7.9 ± 2.0 | 5.2 ± 1.2 | 14 ± 6.6 | 13.2 ± 5.5 | 10.4 ± 6 |
| EC | 4.1 ± 1.2 | 2.9 ± 0.7 | 6.8 ± 2.8 | 6.1 ± 3 | 5.1 ± 2.7 |
| MD | 10.7 ± 2.4 | 8.1 ± 0.8 | 11.3 ± 2.7 | 8.6 ± 2.2 | 9.8 ± 2.6 |
| TE | 0.5 ± 0.1 | 0.3 ± 0.1 | 0.6 ± 0.2 | 0.7 ± 0.2 | 0.6 ± 0.2 |
The contribution of different compositions to PM$_{2.5}$ varied widely (Figure S1). For water soluble ions, SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ were the main ions, accounting for 13%, 20%, and 11% of PM$_{2.5}$ mass in terms of an annual average, respectively. The sum of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ (SNA) was 31.9 µg/m$^3$, contributing 44% to PM$_{2.5}$ mass. For carbonaceous components, organic matter (OM) was the most abundant species in PM$_{2.5}$. OM was estimated from OC using a conversion factor of 1.4 to account for other elements presented in organic compounds [43], and accounted for 20% of PM$_{2.5}$ mass. Meanwhile, the EC proportion was relatively low and only accounted for around 7%. MD was 9.8 µg/m$^3$ and accounted for 13% of PM$_{2.5}$ mass. The other portions of PM$_{2.5}$ reached 17%, which were likely related to the uncertainties in the multiplication factors used for estimating OM and MD, other unidentified species, and measurement uncertainties. In total, the sum of the secondary inorganic ions and carbonaceous species accounted for 64% of PM$_{2.5}$ mass and were the main component.

Table 1 also shows the seasonal average concentrations of PM$_{2.5}$ and its major chemical components during the sampling periods. Meanwhile, Figure 3 shows the seasonal distributions of PM$_{2.5}$ and its major chemical components. PM$_{2.5}$ mass in winter and autumn was 0.9–1.6 time higher (interquartile ranges) than those in the other seasons, and there was not much difference in these two seasons. The chemical components basically follow the seasonal variation of the PM$_{2.5}$ mass concentration. In terms of MD, its concentration was highest in autumn, followed by spring, winter, and summer. Regarding SO$_4^{2-}$, its average concentration was highest in winter and the difference in the other three seasons was not significant. The average temperature in the winter was $-0.1 \pm 2.2$ °C. Though no central heating exists in the urban area, residential coal combustion for heating is absolutely necessary. Therefore, residential coal combustion might be the main reason for the high sulphate concentrations in winter.

It should also be noted that the seasonal variation of NO$_3^-$ was much larger than those of SO$_4^{2-}$ and NH$_4^+$. The average concentration of NO$_3^-$ in autumn and winter was 4.1 times higher than in the spring and the summer. Atmospheric physicochemical processes played an important role [44]. The concentration of NO$_3^-$ might have been enhanced in the winter under high RH through heterogeneous aqueous processes and decreased in the summer due to the volatilization of NH$_4$NO$_3$ under high temperatures.

Note: WS—wind speed; Tem.—temperature; RH—relative humidity; MD—mineral dust, TE—trace elements.
To investigate the source of carbon compositions, the correlation between OC and EC was analyzed (Figure 4). As reported in the literature, OC was mainly derived from fossil fuel combustion, biomass burning and secondary organic aerosols generated by atmospheric chemical reactions, which were susceptible to weather conditions and emission sources [30,45]. EC was mainly derived from fossil fuel combustion and it was an inert pollutant. If the correlation coefficient between OC and EC was greater than 0.65, the source of OC and EC was considered to be consistent [46]; otherwise, the source of the two was complicated. In this study, there was good correlation for OC and EC in spring, autumn, and winter, indicating the same pollution sources. Regarding summer, the relatively low correlation between OC and EC indicated the different sources of OC and EC in the summer, which was related to the fact that OC was partly derived from secondary aerosol generation in the summer.
3.2. Comparison of Chemical Composition on Clean and Polluted Days

The concentrations of PM$_{2.5}$ and major chemical components increased dramatically on polluted days compared with clean days (Table 2). The average concentrations of PM$_{2.5}$ on polluted days (130 µg/m$^3$) were 1.8 times higher than on clean days (46 µg/m$^3$), and the concentrations of the two dominant groups of components, SNA and OM, were 2.7 and 2.3 times higher than on clean days. The contribution of SNA to PM$_{2.5}$ on polluted days was 48%, which was higher than that on clean days (36%). Compared with clean days, concentrations of the individual SNA species (SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$) increased by a factor of 1.4–4.7 on polluted days. However, the proportion of each chemical composition differed across different days with increasing NO$_3^-$ and decreasing SO$_4^{2-}$ on polluted days. The proportion of OM in PM$_{2.5}$ decreased from 23% on clean days to 18% on polluted days.

Table 2. Average concentration of major chemical components in PM$_{2.5}$ on clean days and polluted days

| Period      | Concentration | PM$_{2.5}$ | SO$_4^{2-}$ | NO$_3^-$ | NH$_4^+$ | Cl | K | OM | EC | MD | Other |
|-------------|---------------|------------|-------------|-----------|----------|----|---|----|----|----|-------|
| Clean day   | Mass concentration (µg/m$^3$) | 46 | 7.0 | 5.5 | 4.2 | 0.8 | 0.6 | 10.5 | 4.0 | 10.2 | 3.2 |
|             | Proportion (%) | / | 15 | 12 | 9 | 2 | 1 | 23 | 9 | 22 | 7 |
| Polluted day| Mass concentration (µg/m$^3$) | 130 | 16.5 | 31.4 | 14.7 | 2.5 | 1.5 | 23.7 | 8.3 | 12.1 | 19.3 |
|             | Proportion (%) | / | 13 | 24 | 11 | 2 | 1 | 18 | 6 | 9 | 15 |

Note: MD—mineral dust.

Stagnant atmospheric conditions and high RH were important factors causing PM$_{2.5}$ pollution events [47–49]. Weak winds suppressed pollutant dispersion vertically and horizontally [50].
RH was also conducive for aqueous-phase reactions and resulted in the rapid elevation of \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) concentrations \([51-53]\). Compared with the clean periods in the same season, the pollution periods were usually characterized by high temperatures and weak wind speeds in this study. For RH, the seasonal variation was small, ranging from 58.1\% (in winter) to 77.6\% (in summer) with an annual average of 66.0\%. This high humidity was favorable for aqueous-phase reactions.

In order to characterise the conversion degree of gaseous \( \text{SO}_2 \) and \( \text{NO}_2 \) to \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) ions, SOR (sulfur oxidation rate) and NOR (nitrogen oxidation rate) are usually used \([54]\). Studies have shown that when the values of SOR and NOR were < 0.1, the pollutants mainly stemmed from direct discharge, and when the value was > 0.1, it means that there was a secondary conversion of primary pollutants \([55,56]\). In this study, the values of NOR and SOR in different PM\(_{2.5}\) concentrations are shown in Figure 5. The average values of NOR were 0.30 (on polluted days) and 0.12 (on clean days), respectively. The average values of SOR were 0.40 (on polluted days) and 0.28 (on clean days), respectively. All the SOR and NOR values were greater than 0.1 on polluted days, and the increase in NOR on polluted days was greater than SOR. This explained the large variation of \( \text{NO}_3^- \) in the four seasons and the high proportion of \( \text{NO}_3^- \) on polluted days.

**Figure 5.** The values of the nitrogen oxidation rate (NOR) and sulfur oxidation rate (SOR) in different PM\(_{2.5}\) concentrations. The horizontal dash line represents 0.1. The vertical dash line represents PM\(_{2.5}\) = 75 \( \mu \text{g/m}^3 \).

### 3.3. Sources Apportionment of PM\(_{2.5}\)

The positive matrix factorization (PMF, version 5.0) was applied to elucidate the source–receptor relationship of PM\(_{2.5}\). We examined a wide range of factor solutions (4–7). The recommended approach in previous studies was used to come to a suitable solution \([33]\). Six factors were identified by PMF analysis, and the factor profiles are shown in Figure 6. The correlation coefficient \( R^2 \) between the fitted value and the measured value of PM\(_{2.5}\) was 0.68, indicating that the analytical result was reasonable.
Atmosphere combustion, vehicle exhaust, livestock and
part in each season. The secondary sulf
element also ac
tion on livestock and poultry breeding, therefore, this factor was determined to be a mixed source (construction dust, metal industry,
metal parts wear of batteries and metal parts could be attributed to metal industry activities
dust and road dust, construction dust is an important source
loads of Fe (23%), Cu (18%), Pb (18%), Ni (14%), and NH₄⁺ (14%). Cr is a tracer of dust. As well as soil dust and road dust, construction dust is an important source of dust. The presence of many metals could be attributed to metal industry activities [62,63]. Aside from secondary aerosols, NH₄⁺ is related to the source emissions from agriculture, livestock, and poultry. Because of the food processing industry in this city, there were several atmospheric pollutant emission sources such as animal feeding, the use of spices, packaging material production, fossil fuel combustion, and so on. Therefore, this factor was determined to be a mixed source (construction dust, metal industry, livestock and poultry breeding, food processing industry, and so on). Factor 6 displays a high proportion of Cl⁻ (73%), NO₃⁻ (33%), V (24%), and OC (22%). Cl⁻ is a tracer of coal combustion in inland areas [64]. NO₃⁻ is mainly converted from NOₓ, which was emitted from fossil fuel combustion. The V element also acted as a typical tracer of fossil fuel combustion [65]. Therefore, this factor is determined to be coal combustion.

Seasonal contributions of each source are shown in Figure 7. Secondary sources are the largest part in each season. The secondary sulfate, nitrate, and ammonia salt are likely to be associated with the formation of primary pollutants emitted from coal combustion, vehicle exhaust, livestock and

Figure 6. The results of the source profile of six factors identified by positive matrix factorization (PMF).

In factor 1, Ti (83%) and Si (36%) accounted for high proportions. These elements were mainly crust elements [57], so this factor was judged to be a soil dust source. Factor 2 was remarkably characterized by NO₃⁻ (59%), SO₄²⁻ (49%), and NH₄⁺ (51%), and was determined to be a secondary source. In factor 3, Mg (43%), Ca (36%), Si (36%), Fe (39%), and Zn (22%) accounted for high proportions. Mg, Ca, and Si were mainly crust elements [58]. Fe and Zn may come from tire wear and metal parts wear [41,59,60]. Therefore, this factor was judged to be a dust source. Factor 4 contains a high proportion of Zn (59%), Sn (56%), Pb (59%), Cu (45%), and K (55%). The metallic elements were usually derived from traffic pollution sources such as fuel combustion, tire wear, oil leakage, and wear of batteries and metal parts [41,59–61]. K is often used as a tracer of biomass burning. Considering the biomass burning in the suburban area, this factor is determined to be a mixed source of vehicle exhaust and biomass burning. Factor 5 displays high loadings for Cr (47%), with median loads of Fe (23%), Cu (18%), Pb (18%), Ni (14%), and NH₄⁺ (14%). Cr is a tracer of dust.

The atmospheric pollutant sources were identified by positive matrix factorization (PMF) and positive matrix factorization (PMF). Figure 6 shows the results of the source profile of six factors identified by PMF. In factor 1, Ti and Si accounted for high proportions. These elements were mainly crust elements, so this factor was judged to be a soil dust source. Factor 2 was remarkably characterized by NO₃⁻ (59%), SO₄²⁻ (49%), and NH₄⁺ (51%), and was determined to be a secondary source. In factor 3, Mg (43%), Ca (36%), Si (36%), Fe (39%), and Zn (22%) accounted for high proportions. Mg, Ca, and Si were mainly crust elements. Fe and Zn may come from tire wear and metal parts wear. Therefore, this factor was judged to be a dust source. Factor 4 contains a high proportion of Zn (59%), Sn (56%), Pb (59%), Cu (45%), and K (55%). The metallic elements were usually derived from traffic pollution sources such as fuel combustion, tire wear, oil leakage, and wear of batteries and metal parts. K is often used as a tracer of biomass burning. Considering the biomass burning in the suburban area, this factor is determined to be a mixed source of vehicle exhaust and biomass burning. Factor 5 displays high loadings for Cr (47%), with median loads of Fe (23%), Cu (18%), Pb (18%), Ni (14%), and NH₄⁺ (14%). Cr is a tracer of dust. As well as soil dust and road dust, construction dust is an important source of dust. The presence of many metals could be attributed to metal industry activities. Aside from secondary aerosols, NH₄⁺ is related to the source emissions from agriculture, livestock, and poultry. Because of the food processing industry in this city, there were several atmospheric pollutant emission sources such as animal feeding, the use of spices, packaging material production, fossil fuel combustion, and so on. Therefore, this factor was determined to be a mixed source (construction dust, metal industry, livestock and poultry breeding, food processing industry, and so on). Factor 6 displays a high proportion of Cl⁻ (73%), NO₃⁻ (33%), V (24%), and OC (22%). Cl⁻ is a tracer of coal combustion in inland areas. NO₃⁻ is mainly converted from NOₓ, which was emitted from fossil fuel combustion. The V element also acted as a typical tracer of fossil fuel combustion. Therefore, this factor is determined to be coal combustion.

Seasonal contributions of each source are shown in Figure 7. Secondary sources are the largest part in each season. The secondary sulfate, nitrate, and ammonia salt are likely to be associated with the formation of primary pollutants emitted from coal combustion, vehicle exhaust, livestock and
poultry breeding, and so on. Emissions from livestock and poultry were the most important source in the summer and the spring when the temperature was high. In the autumn and the winter, the appearance of adverse meteorological conditions usually occurred, which led to atmospheric pollution as well as the formation and accumulation of secondary pollutants. In line with the volatilization of NH₄NO₃ under high temperatures in the summer, the contribution of secondary sources was low in the summer.

Luohe city is located in Henan province, which is an agriculture province. Therefore, in the spring and the summer, the contribution of soil dust is relatively high because of agricultural activity. Road dust and vehicle exhaust sources are steady across the four seasons. Because of the need for heating in late autumn and the winter, coal combustion and biomass burning played an important role. Vehicle exhaust and biomass sources increased slightly and coal combustion sources increased significantly in the autumn and the winter. Except metal industry, the other parts in the mixed source (construction dust, metal industry, livestock and poultry breeding, food processing industry, and so on) are active in the spring and the summer. Therefore, the mixed sources in the spring and the summer were much higher than in the autumn and the winter.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Contribution percentage of the identified sources to PM₂.₅ in the four seasons.

The source percentage contributions of each source to PM₂.₅ are shown in Table 3. For comparison, source apportionment results on polluted and clean days as well as other cities are also listed in Table 3. The most important source of PM₂.₅ was secondary aerosols both on clean days (28%) and polluted days (49%). Coal combustion made a relatively low contribution to PM₂.₅, which was in line with the light industry characteristics. Soil dust and road dust contributed 11–25% to PM₂.₅, which was similar to many cities such as Zhengzhou [66], Lanzhou [67], and Xian [68] in China, as well as New York in USA [34]. The contribution proportion of secondary aerosol sources to PM₂.₅ on polluted days was 1.75 times that of clean days, while coal combustion and dust (soil dust and road dust) sources contributed a lower proportion to PM₂.₅ on polluted days than on clean days. Certain identified sources, such as coal combustion and vehicle exhaust, could also promote the production of secondary inorganic and organic aerosols through the precursor gases [17]. These source apportionment results confirmed the importance of the chemical reaction process to secondary aerosol formation.
### Table 3. Comparison of source apportionment with other cities

| City            | Method          | Source contribution (%) | Reference                                      |
|-----------------|-----------------|-------------------------|------------------------------------------------|
| Luohe, China    | 2017–2018, Urban, clean days | PMF 11 | 28 | Soil dust: 12 | Road dust: 13 | Mixed source (husbandry and food procession industry): 21 | This study |
|                 | 2017–2018, Urban, pollution days | PMF 2 | 49 | Soil dust: 6 | Road dust: 5 | Mixed source (husbandry and food procession industry): 21 | This study |
| Zhengzhou, China| 2013–2015 Pollution days | CMB 14 | 8 | Nitrate: 13 | 8 | 7 | 12 | carbon + refractory material: 2 | [66] |
|                 | 2013–2015 Other days | CMB 27 | 9 | Nitrate: 20 | Sulfate: 18 | 14 | 15 | 9 | carbon + refractory material: 2 | |
| Xiangtan, China | 2016–2017 urban | PMF 6-9 | Secondary inorganic aerosols: 25-27 | 16-18 | 21-22 | | coal combustion + secondary aerosols: 19-21 | steel industry: 8-9 | [69] |
| Lanzhou, China  | 2012 winter urban | PMF 28.7 | 33.0 | 13.3 | 8.8 | | Steel industry: 7.1 | Power plant: 3.12 | [67] |
|                 | 2013 summer urban | PMF 3.1 | 14.8 | 11.6 | 25.2 | | Steel industry: 6.7 | Power plant: 3.4 | Smelting industry: 35.2 |
| Xian, China     | 1.1–2.28. 2006, urban | PMF 31.2 | 9.8 | 20.9 | 12.8 | 19.3 | 6.0 |
|                 | 1.1–2.28. 2008, urban | PMF 27.6 | 11.5 | 23.2 | 11.7 | 20.9 | 5.1 |
|                 | 1.1–2.28. 2010, urban | PMF 24.1 | 12.6 | 17.5 | 19.4 | 21.3 | 5.1 |
| Taian, China    | 8–9.11. 2014, urban | PMF 17.94 | 9.41 | 27.47 | 16.65 | | Metal manufacturing: 19.06% | [70] |
### Atmospheric Composition

| Location          | Collection Period | PMF/Matrix Factorization | Other Components |
|-------------------|-------------------|---------------------------|------------------|
| **New York, U.S.A.** | June–July 2009, 2010, urban | PMF: sulfate:35, nitrate:14 | Aged sea-salt:9, residual oil: < 5, fresh sea-salt: < 5 |
| **Dongguan, China** | 2014 Suburb | PMF: sulfate:5–8, nitrate: 5–8 | secondary organic:10, Ship emission: 5–8 |
| **Fort McKay, Canada** | March 2009–January 2011 suburb | PMF: Secondary sulfate: 30.77, Fugitive dust: 32.4 | Secondary nitrate/biomass burning: 26.4, Mining / mobile: 10.1, Other: 0.4 |

**Note:** PMF—positive matrix factorization. CMB—chemical mass balance.
3.4. Health Risk Evaluation of Heavy Metals

Some health effects of atmospheric particulate matter can be recognized by assessing the exposure of heavy metals to human bodies. Because of individual differences, these estimations are preliminary estimations and can only be regarded for screening purposes [72].

The daily exposure concentration and health risk value of heavy metals in PM$_{2.5}$ are shown in Table 4. For a non-carcinogenic risk assessment, the risk index (HI) of non-carcinogenic heavy metals through the respiratory route were $1.86 \times 10^{-5}$-0.261 and $9.26 \times 10^{-6}$-0.130 for children and adults, respectively. Since the risk index (HI) does not exceed 1, non-carcinogenic hazard is not expected to occur for people. In terms of carcinogenic hazard, Cr, Co, Ni, As, and Cd exceeded the risk threshold of $10^{-6}$ and had carcinogenic hazard. Among them, the carcinogenic risk of Cr was at its highest at $3.11 \times 10^{-4}$. Therefore, we should pay special attention to these heavy metals in PM$_{2.5}$ with high carcinogenic risks for residents.

| Table 4. Annual heavy metal inhalation exposure concentrations and health risks |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Element** | **Child intake (Child)** | **Adult intake (Adult)** | **Lifetime intake** | **Child risk index** | **Adult risk index** | **Carcinogenic risk** |
| | mg kg$^{-1}$ day$^{-1}$ | mg kg$^{-1}$ day$^{-1}$ | mg kg$^{-1}$ day$^{-1}$ | | | mg kg$^{-1}$ day$^{-1}$ |
| V | $7.31 \times 10^{-4}$ | $3.65 \times 10^{-4}$ | | | | |
| Cr | $2.11 \times 10^{-4}$ | $1.05 \times 10^{-4}$ | $7.42 \times 10^{-5}$ | $1.04 \times 10^{-4}$ | $5.21 \times 10^{-5}$ | |
| Mn | $3.65 \times 10^{-4}$ | $1.82 \times 10^{-4}$ | | | | |
| Co | $4.12 \times 10^{-4}$ | $2.05 \times 10^{-4}$ | $1.45 \times 10^{-4}$ | $2.61 \times 10^{-5}$ | $1.30 \times 10^{-5}$ | |
| Ni | $3.82 \times 10^{-4}$ | $1.91 \times 10^{-4}$ | $1.34 \times 10^{-4}$ | $1.86 \times 10^{-5}$ | $9.26 \times 10^{-6}$ | $1.13 \times 10^{-5}$ |
| Zn | $2.61 \times 10^{-4}$ | $1.30 \times 10^{-4}$ | | $8.66 \times 10^{-5}$ | $4.32 \times 10^{-5}$ | |
| As | $4.98 \times 10^{-4}$ | $2.48 \times 10^{-4}$ | $1.75 \times 10^{-4}$ | $1.65 \times 10^{-5}$ | $8.25 \times 10^{-6}$ | $2.64 \times 10^{-5}$ |
| Cd | $4.46 \times 10^{-4}$ | $2.23 \times 10^{-4}$ | $1.57 \times 10^{-4}$ | $4.46 \times 10^{-5}$ | $2.23 \times 10^{-5}$ | $1.00 \times 10^{-5}$ |
| Pb | $7.68 \times 10^{-4}$ | $3.83 \times 10^{-4}$ | | $2.18 \times 10^{-5}$ | $1.09 \times 10^{-5}$ | |
| ∑ | $4.16 \times 10^{-4}$ | $2.08 \times 10^{-4}$ | $1.22 \times 10^{-4}$ | $3.46 \times 10^{-5}$ | $1.73 \times 10^{-5}$ | $3.50 \times 10^{-5}$ |

As shown in Table 5, vehicle exhaust sources are the largest HI contributor, accounting for 54%. Vehicle exhaust and mixed sources are the main Rt contributor, accounting for 36% and 45%, respectively. Similar findings have been reported by previous studies [72,73]. The contribution of sources to PM$_{2.5}$ mass concentration was also listed in Table 5. It is obvious that the source contribution for mass and health risks are different. Secondary sulfate contributed the most (37%) to PM$_{2.5}$ mass and only accounted for 6% of HI and 4% of Rt. However, vehicle sources contributed 16% to PM$_{2.5}$ mass and accounted for 54% of HI and 36% of Rt. Therefore, PM control strategies should highlight sources with more toxic components such as trace heavy metals.

| Table 5. Annual mass, risk index HI, and carcinogenic risk Rt of six identified sources of PM$_{2.5}$ |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Sources** | **soil dust** | **secondary aerosol** | **road dust** | **vehicle exhaust** | **mixed source** | **coal combustion** |
| **Mass concentration (µg/m$^3$)** | **5.75** | **23.33** | **5.81** | **10.03** | **4.42** | **12.97** |
| **HI Child** | $9.25 \times 10^{-4}$ | $2.08 \times 10^{-4}$ | $7.54 \times 10^{-4}$ | $1.85 \times 10^{-5}$ | $5.86 \times 10^{-6}$ | $5.35 \times 10^{-5}$ |
| **HI Adult** | $4.62 \times 10^{-4}$ | $1.04 \times 10^{-4}$ | $3.76 \times 10^{-5}$ | $9.23 \times 10^{-6}$ | $2.92 \times 10^{-6}$ | $2.67 \times 10^{-5}$ |
| **Rt** | $4.29 \times 10^{-4}$ | $1.35 \times 10^{-4}$ | $4.50 \times 10^{-5}$ | $1.26 \times 10^{-5}$ | $1.58 \times 10^{-5}$ | $4.35 \times 10^{-5}$ |

4. Conclusions

To study the chemical composition and health risk of PM$_{2.5}$ in a city with light industry as its main industry, a total of 382 PM$_{2.5}$ filter samples were collected in four seasons (15–20 days for each season) from May 2017 to February 2018 in the urban area of Luohe city. PM$_{2.5}$ concentrations and chemical compositions were analyzed. Representative elemental components (V, Cr, Mn, Co, Ni, Zn, As, Cd, P) of PM$_{2.5}$ were applied to assess health risk.

During the sampling period, the annual PM$_{2.5}$ value was $73 \pm 49$ µg/m$^3$. Seasonal variations of PM$_{2.5}$ concentrations and major chemical components were significant, usually with high mass concentrations in the autumn (97 µg/m$^3$) and the winter (96 µg/m$^3$), and with low mass concentrations...
in the spring (51 µg/m³) and the summer (38 µg/m³). SNA (SO\(_4^{2-}\), NO\(_x\), and NH\(_3\)) was the most abundant component, and the sum of the SNA was 31.9 µg/m³, contributing 43.8% to PM\(_{2.5}\) mass. PM\(_{2.5}\) concentrations were more than two times higher on polluted days than on clean days, and the two dominant groups of components (SNA and OC) were 2.3–3.7 times higher than on clean days. The values of SOR were 0.40 (on polluted days) and 0.28 (on clean days), respectively. The most important source of PM\(_{2.5}\) was secondary aerosols, both on clean days (28%) and polluted days (49%). A stagnant atmosphere and high relative humidity were the meteorological conditions for the formation of pollution. Secondary aerosol generation was one main reason for the variation of chemical composition proportions on different polluted days.

The health risk assessment of heavy metals showed that non-carcinogenic risk was not appreciable, while the carcinogenic risk exceeded the risk threshold of 10\(^{-6}\). Vehicle exhaust and mixed sources (construction dust, metal industry, livestock and poultry breeding, and food processing industries) are the main Rt contributor, accounting for 36% and 45%, respectively. Therefore, we should pay special attention to the heavy metal elements in PM\(_{2.5}\). In the future, more research needs to be conducted in order to master the pollution characteristics of such cities and to provide scientific support for the government to make policies for atmospheric pollution prevention and control.

**Supplementary Materials:** The following are available online at www.mdpi.com/2073-4433/11/4/340/s1, Table S1: Exposure parameter values used in the risk assessment calculations, Table S2: The reference dose of non-carcinogenic metals and the slope factor of carcinogenic metals, Figure S1: Seasonal and annual contributions of individual chemical components to PM\(_{2.5}\). OM is short for “organic matter”, TE is short for “trace elements”, MD is short for “mine dust”.

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