

Article

Distribution Characteristics and Source Apportionment of Winter Carbonaceous Aerosols in a Rural Area in Shandong, China

Changwei Zou ^{1,2} , Jiayi Wang ^{1,2}, Kuanyun Hu ¹, Jianlong Li ^{1,2}, Chenglong Yu ³, Fangxu Zhu ⁴ and Hong Huang ^{1,2,*} 

¹ School of Resources & Environment, Nanchang University, Nanchang 330031, China

² Key Laboratory of Poyang Lake Environment and Resource Utilisation, Ministry of Education, Nanchang 330031, China

³ School of Land Resources and Environment, Jiangxi Agricultural University, Nanchang 330045, China

⁴ No.270 Research Institute of Nuclear Industry, Nanchang 330200, China

* Correspondence: honghuang@ncu.edu.cn

Abstract: PM_{2.5} samples were collected for 15 consecutive days in a rural area in Shandong from January to February 2022. The carbon components and water-soluble ions in PM_{2.5} were measured, and the distribution characteristics and sources of the carbonaceous aerosols were analysed. It was found that the concentrations of PM_{2.5} in the region were high in winter (55.79–236.11 µg/m³). Organic carbon (OC) and elemental carbon (EC) accounted for 11.61% and 4.57% of PM_{2.5}, respectively. The average concentrations of OC (19.01 µg/m³) and EC (7.49 µg/m³) in PM_{2.5} were high. The mean value of secondary organic carbon (SOC), estimated by the minimum R squared (MRS) method, was 14.76 µg/m³, accounting for a high proportion of OC (79.41%). Four OC fractions (OC₁, OC₂, OC₃, and OC₄) were significantly correlated with SOC, indicating that the OC components contained a large amount of SOC. OC₃, OC₄, EC₁, and OC₂ dominated (accounting for 80% of TC) among the eight carbon fractions. Water-soluble organic carbon (WSOC, 12.82 µg/m³) and methanol-soluble organic carbon (MSOC) (16.28 µg/m³) accounted for 67.47% and 84.99% of OC, respectively, indicating that SOC accounted for a high proportion of OC. The proportion of eight water-soluble ions in PM_{2.5} was 47.48%. NH₄⁺ can neutralise most of the SO₄^{2−} and NO₃[−], forming (NH₄)₂SO₄ and NH₄NO₃, while Cl[−] mainly exists in the form of KCl and MgCl₂. The ratios of some typical components showed that PM_{2.5} was not only affected by local combustion sources, but also by mobile sources. The cluster analysis results of the backward trajectory model showed that primary and secondary sources in Shandong Province had a great impact on PM_{2.5} (64%). The analysis results of the positive matrix factorisation (PMF) model showed that the sources of PM_{2.5} in the region included mobile sources, primary combustion sources, secondary sources, and dust sources, among which secondary sources contributed the most (60.46%).

Keywords: carbonaceous aerosol; chemical components; source apportionment



Citation: Zou, C.; Wang, J.; Hu, K.; Li, J.; Yu, C.; Zhu, F.; Huang, H. Distribution Characteristics and Source Apportionment of Winter Carbonaceous Aerosols in a Rural Area in Shandong, China. *Atmosphere* **2022**, *13*, 1858. <https://doi.org/10.3390/atmos13111858>

Academic Editor: Andrés Alastuey Urós

Received: 17 October 2022

Accepted: 4 November 2022

Published: 8 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In the rural areas of North China, coal and biomass are the main energy sources for heating and cooking in winter. They are used by families and are consumed in large quantities. The emission sources are scattered and the carbonaceous aerosol emission is large [1].

The main components of carbonaceous aerosols include organic carbon (OC), elemental carbon (EC), and water-soluble ions [2,3]. In recent years, many achievements have been made in the study of the distribution characteristics of carbonaceous aerosols and their chemical components in urban areas of China [4–6], but less attention has been paid to those in rural areas. In winter, fuels such as coal and biomass are widely used in rural areas of North China, which can easily lead to atmospheric pollution. The studies on the

distribution and sources of carbonaceous aerosols and their chemical components in rural areas are still limited and they are not thorough enough. There would be a large deviation if the research results in urban areas were analogised to those in rural areas.

In this study, the carbon components and water-soluble ions of fine particulate aerosol ($PM_{2.5}$) in a rural area in Shandong, China, were measured, and the distribution characteristics and influencing factors of carbonaceous aerosols and their components were analysed and discussed. The characteristic component ratio method, backward trajectory model, and positive matrix factorisation (PMF) model were used to analyse the sources of $PM_{2.5}$. Under the background of many coal- and biomass-burning primary emission sources in rural winter, the distribution characteristics of carbonaceous aerosols in rural areas far from urban areas in winter were studied, and the sources of regional $PM_{2.5}$ (primary source and secondary source) were quantitatively analysed. This provides basic data and a scientific basis for the study of carbonaceous aerosols and pollution control in rural areas, and contributes to the scientific formulation of regional air pollution prevention and control and air quality optimisation policies.

2. Material and Methods

2.1. Sampling Site

The sampling site was located in a village in Shandong Province, China ($34^{\circ}37'12''$ N, $117^{\circ}43'48''$ E), which is a 400×500 m² area surrounded by farmland. Other villages are distributed in different directions outside the farmland around the village; the distance from this sampling village is different, the nearest of which is about 500 m. The village is about 4 km away from the nearest city boundary. The village has a population of about 700 people. In winter, villagers mainly use coal or biomass such as corn stalks and firewood as fuel for heating and cooking. There is a biomass-burning power plant about 7 km away to the east of the village and a coal-fired power plant about 8 km away to the south of the village.

2.2. Sample Collection

Quartz filters (Whatman, UK, 47 mm) were used as the sampling filter, which was pre-treated at 900 °C for 3 h in a muffle furnace [4]. After 24 h of constant temperature and humidity, it was weighed with an electronic balance (Mettler Toledo, Switzerland, 0.01 mg accuracy) and then stored in the refrigerator until sampling.

The sampler was a portable aerosol sampler (Minivol, Airmetrics, Springfield, OR, USA) with a sampling flow rate of 5 L/min. The sampling height of the sample in this study was 1.5 m above the ground, taking into account the human respiratory height. Each sample was continuously sampled for 24 h. After the sampling filter was weighted, it was stored at 4 °C until the chemical composition determination.

Meteorological data (air pressure, air temperature, relative humidity, and wind speed) during the sampling period were quoted from the official website of the Central Meteorological Observatory [7].

2.3. The Determination of Chemical Components in $PM_{2.5}$

2.3.1. Determination of Carbon Fractions

The carbon components in the $PM_{2.5}$ samples were measured using a multi-wavelength thermal/optical carbon analyser (DRI-2015, Desert Research Institute, USA) with the IMPROVE_A TOR protocol. Four OC fractions (OC_1 , OC_2 , OC_3 , and OC_4) were measured at 140 °C, 280 °C, 480 °C, and 580 °C in a pure He environment. Three EC components (EC_1 , EC_2 , and EC_3) were measured at 580 °C, 740 °C, and 850 °C under 2% O₂ and 98% He atmospheres. In the process of measuring OC, a part of OC may be cracked to form optical pyrolyzed carbon (OPC), which may make the filter black in the absence of oxygen. The change in the filter blackening was detected by the reflection signal of the 635 nm laser. When oxygen was introduced, the combustion of OPC and EC increased the laser reflection signal. When the 635 nm laser reflection signal returned to its initial value, the corresponding carbon

content was defined as OPC, which was deducted from the measured EC_1 [8]. Therefore, the calculation equations of OC and EC were taken from Equations (1) and (2).

$$OC = OC_1 + OC_2 + OC_3 + OC_4 + OPC \quad (1)$$

$$EC = EC_1 - OPC + EC_2 + EC_3 \quad (2)$$

Han et al. [9] further divided the EC into char and soot.

$$\text{char} = EC_1 - OPC \quad (3)$$

$$\text{soot} = EC_2 + EC_3 \quad (4)$$

2.3.2. Determination of WSOC and MSOC

Two small circular filters (0.495 cm^2) were punched from the loaded filter. The two small circle filters were extracted by ultrapure water and ultrasonic methanol, respectively. After extraction, the small circle filters were dried by vacuum freeze-drying. The residual OC on the small circle filter extracted was measured using a DRI-2015 carbon analyser. Then, the OC that was not extracted from the same sampling filter was subtracted by the OC after extraction using ultrapure water and by the OC after extraction using methanol, to obtain WSOC and MSOC, respectively.

2.3.3. Determination of Water-Soluble Ions

Three anions (SO_4^{2-} , NO_3^- , and Cl^-) and five cations (Na^+ , NH_4^+ , Mg^{2+} , K^+ , and Ca^{2+}) were measured. A quarter of the loaded filter was cut and extracted by ultrapure water for ultrasonic extraction for 1 h. Ion chromatography (DIONEX ISC-1100, Thermo, Waltham, MA, USA) was used to measure the cations and another ion chromatography (DIONEX ICS-5000 + DC, Thermo Fisher, Waltham, MA, USA) was used to measure the anions in the extraction.

2.4. Minimum R Squared (MRS) Method

The MRS method was introduced by Wu et al. [10] to calculate the SOC, and its accuracy for SOC estimation was higher than the traditional OC/EC minimum method. In principle, the EC is a tracer of a primary source, OC is a mixture of primary source and secondary source, and SOC and EC are independent of each other. The equations used to calculate the POC and SOC were Equations (5) and (6), respectively.

$$POC = \left(\frac{OC}{EC} \right)_{\text{pri}} \times EC \quad (5)$$

$$SOC = OC_{\text{mix}} - \left(\frac{OC}{EC} \right)_{\text{pri}} \times EC \quad (6)$$

2.5. Backward Trajectory Model (HYSPPLIT)

The analysis of the air mass trajectories during sampling was performed using hybrid single-particle Lagrangian integrated trajectory (HYSPPLIT) [11]. This study used the 5.2.0 computer client version released in January 2022. The meteorological data used in the simulation were GDAS1° meteorological data provided by the National Centres for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS). In this study, the initial height of the trajectory was 100 m [12], and the backward trajectory simulation period was UTC from 15:00 on 26 January 2022 to 15:00 on 10 February 2022, and the airflow trajectory arriving at the sampling site in the backward direction for 48 h was tracked. The airflow trajectory was calculated for every hour, and the trajectory results were clustered and analysed.

2.6. Positive Matrix Factorisation (PMF)

Receptor-based source apportionment techniques have become significant tools for estimating the sources of atmospheric particulate matter (PM). The U.S. Environmental Protection Agency (US-EPA) PMF 5.0 software was used in the current study to achieve the PM source apportionment. Details of this model have been previously documented [13].

3. Results and Discussion

3.1. Distribution Characteristics of PM_{2.5}

Figure 1 shows the distribution of PM_{2.5} concentrations and meteorological factors during sampling. The daily PM_{2.5} concentrations during the sampling period ranged from 55.79 to 236.11 $\mu\text{g}/\text{m}^3$, with an average of $163.70 \pm 41.53 \mu\text{g}/\text{m}^3$. Compared with the daily average PM_{2.5} concentration limit of the China Ambient Air Quality Standards (GB3095-2012) ($75 \mu\text{g}/\text{m}^3$) [14], the exceedance rate was 93.33% and the maximum exceedance amount was 3.15 times, indicating that fine particulate pollution was serious during the sampling period. Compared with the PM_{2.5} concentration in other regions in winter, the PM_{2.5} concentration in this sampling site was higher than those in some urban areas and significantly higher than that in Hong Kong ($33\text{--}69 \mu\text{g}/\text{m}^3$) [15], Beijing ($93.9 \mu\text{g}/\text{m}^3$) [16], and Fuzhou ($59.81 \mu\text{g}/\text{m}^3$) [17], slightly higher than that in Tianjin ($140.59 \mu\text{g}/\text{m}^3$) [18] and Czech Ostrava-Radvanice ($159.00 \mu\text{g}/\text{m}^3$) [19]. The comparison results showed that the pollution of fine particulate matter in winter at the rural sampling sites in this study was more serious than those in some urban areas.

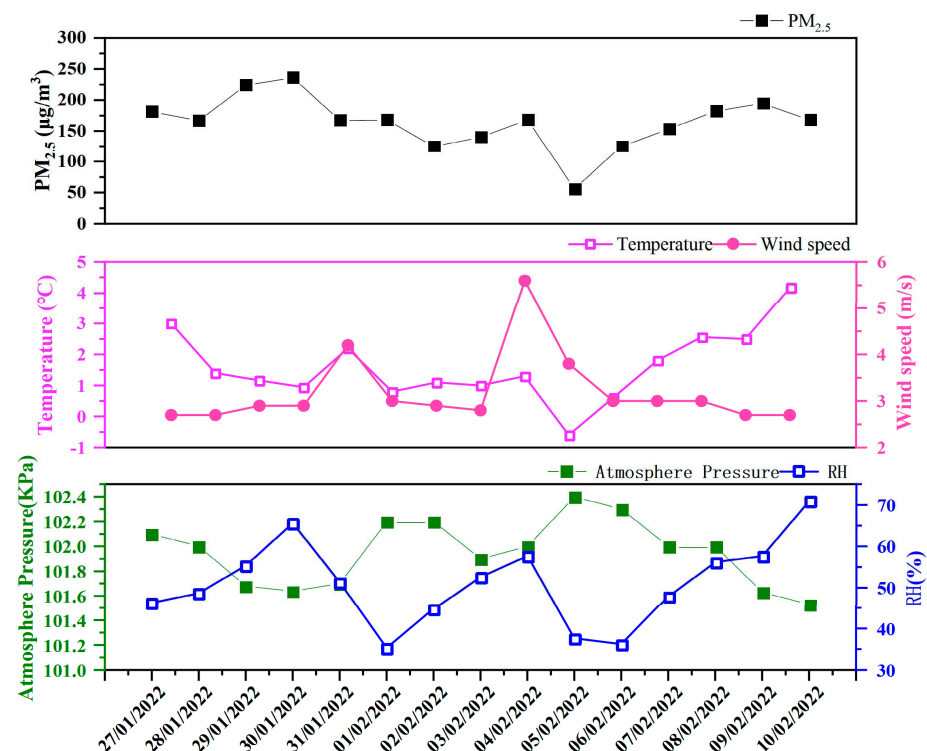


Figure 1. The distribution of PM_{2.5} and meteorological factors during the sampling period.

PM_{2.5} was negatively correlated with air pressure and wind speed ($<4 \text{ m/s}$), indicating that it contributed to the diffusion of PM_{2.5} when the ground was controlled by a high pressure or when the wind speed was large [20]. PM_{2.5} was positively correlated with relative humidity, reflecting that the high-humidity conditions in winter contributed to the accumulation of PM_{2.5} [21].

3.2. Distribution Characteristics of Carbon Components in $PM_{2.5}$

3.2.1. OC and EC

During the sampling period, the concentrations of OC in $PM_{2.5}$ ranged from 9.94 to 28.15 $\mu\text{g}/\text{m}^3$, with an average of $19.01 \pm 5.15 \mu\text{g}/\text{m}^3$ (See Figure 2). The EC concentrations in $PM_{2.5}$ ranged from 3.27 to 8.03 $\mu\text{g}/\text{m}^3$, with an average of $7.49 \pm 4.76 \mu\text{g}/\text{m}^3$. The average values of OC/ $PM_{2.5}$ and EC/ $PM_{2.5}$ were 11.6% and 4.6%, respectively, while the average value of TC/ $PM_{2.5}$ was 16.2%. Compared with the research results in other places, the average concentrations of OC and EC in this study were lower than those in Baoding (70.2 and 13.5 $\mu\text{g}/\text{m}^3$) and Wangdu (57.2 and 11.4 $\mu\text{g}/\text{m}^3$), similar to those in Beijing (28.6 and 5.5 $\mu\text{g}/\text{m}^3$) [5] and higher than those in Chengdu (14.50 and 2.19 $\mu\text{g}/\text{m}^3$) [6]. The comparison with OC and EC concentrations in other regions in the literature showed that the pollution status of $PM_{2.5}$ was related to the distribution of the carbon components.

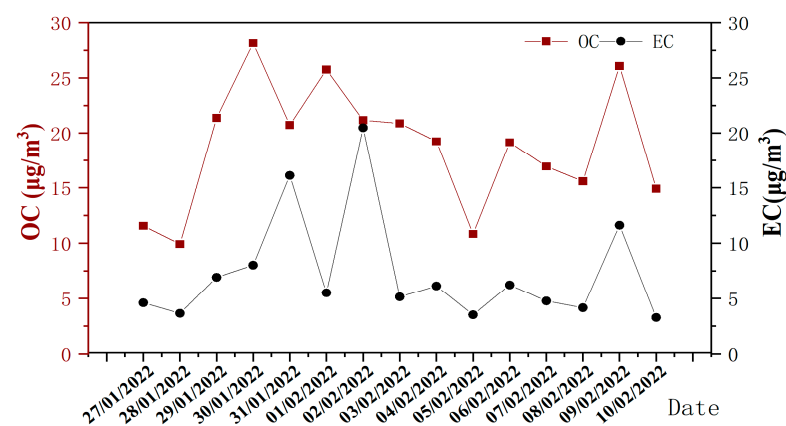


Figure 2. Distribution of OC and EC in $PM_{2.5}$ during the sampling period.

3.2.2. SOC

The results of $(OC/EC)_{pri}$ simulated by the MRS method are shown in Figure 3. According to the value or $(OC/EC)_{pri}$ fitted by the MRS method, the SOC concentrations were calculated using Equation (6). The average SOC concentration was 14.76 $\mu\text{g}/\text{m}^3$, and the proportion of SOC to OC was 79.41%. The SOC/OC estimated by the MRS method in this study was greater than that estimated by the MRS method in other regions, such as the suburbs of Guangzhou (41%) [22], rural Guangzhou (47%) [23], and Shanghai (48%) [24]. The above comparison results showed that the formation of secondary organic carbonaceous aerosols was significant in rural areas of Shandong in winter.

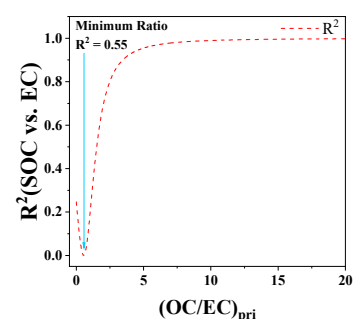


Figure 3. Relationship between the correlation coefficient R^2 of SOC and EC and the assumed $(OC/EC)_{pri}$.

3.2.3. Eight Carbon Fractions

The proportions of the eight carbon fractions in TC are shown in Figure 4. The four carbon fractions with high proportions were OC₄, OC₃, EC₁, and OC₂, accounting

for 23.76, 22.48, 18.97, and 14.74% of TC, respectively. The average concentrations were 5.96, 6.30, 5.47, and 3.91 $\mu\text{g}/\text{m}^3$, respectively. One part of OC₂, OC₃, and OC₄ originated from the secondary generation, and the other part was from the primary emission of the coal combustion. EC₁ was mainly from incomplete combustion of the coal and biomass. Therefore, it was considered that the carbonaceous aerosol in the sampling area was affected by the secondary sources and primary sources of the coal and biomass combustion.

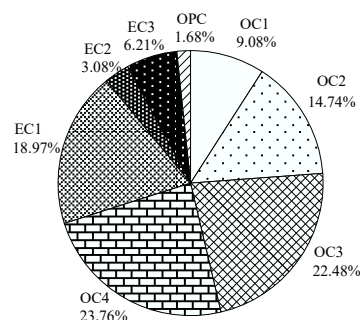


Figure 4. Percentage of eight carbon components in TC.

Figure 5 shows the correlation between the different carbon fractions. There was a strong correlation between the four OC fractions and SOC ($p < 0.01$), indicating that the four OC fractions were significantly affected by the secondary sources. In addition, the strong correlation between char, EC₁, and the four OC fractions also indicated that local primary emission sources have an impact on char, EC₁, and the four OC fractions in carbonaceous aerosols. The results of the correlation between the eight carbon components in this study were similar to the high correlations between char and OC in rural winters in the Ganges Plain, India, which were related to the burning of raw coal and biomass [25].

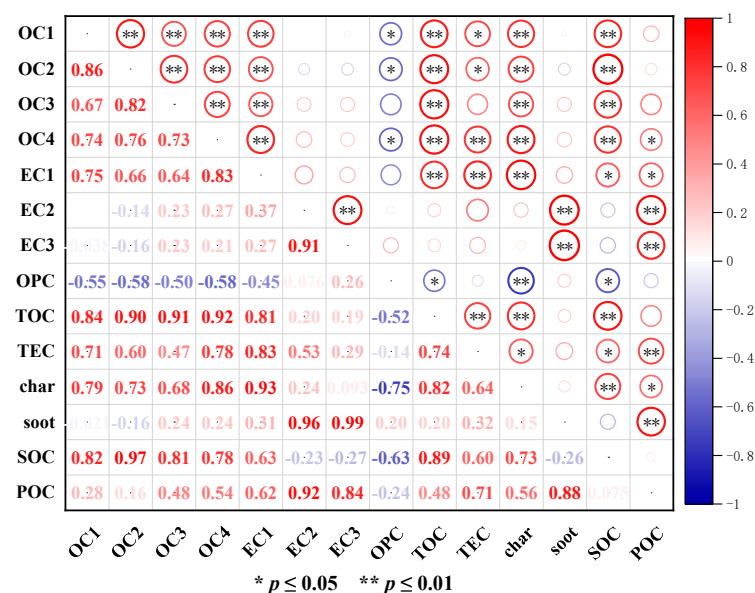


Figure 5. Correlation heat map between different carbon components.

3.2.4. WSOC and MSOC

Table 1 shows the correlation between MSOC, WSOC, SOC, and POC. The correlation between WSOC and MSOC was strong ($r = 0.911$, $p < 0.01$), reflecting that most of the substances in MSOC and WSOC were the same, and the organic matter extracted by methanol included both water-soluble OC and water-insoluble OC [26,27]. In addition, the correlation between SOC and MSOC ($r = 0.896$, $p < 0.01$) and the correlation between

SOC and WSOC ($r = 0.807$, $p < 0.01$) were significant, while the correlation between POC and MSOC ($r = 0.418$) and the correlation between POC and WSOC ($r = 0.527$) was weak, indicating that WSOC and MSOC could represent SOC.

Table 1. Correlation between MSOC, WSOC, SOC, and POC.

	MSOC	WSOC	SOC	POC
MSOC	1			
WSOC	0.911 **	1		
SOC	0.896 **	0.807 **	1	
POC	0.418	0.527 *	0.075	1

* significant correlation at 0.05 level (two-tailed), ** significant correlation at 0.01 level (two-tailed).

Figure 6 shows the concentrations of WSOC and MSOC in $PM_{2.5}$ and their proportions in OC during the sampling period. On most sampling days, the MSOC concentrations were markedly higher than the WSOC concentrations, except for the three sampling days of 27 January 2022, 30 January 2022, and 5 February 2022, when the MSOC concentrations were slightly higher than WSOC concentrations. During the sampling period, the concentrations of WSOC were from 6.39 to 19.54 $\mu\text{g}/\text{m}^3$, with an average of 12.82 $\mu\text{g}/\text{m}^3$, accounting for 60.15–77.89% of OC, and the average WSOC/OC was 67.47%. The concentrations of MSOC were from 7.95 to 23.89 $\mu\text{g}/\text{m}^3$, with an average of 16.28 $\mu\text{g}/\text{m}^3$, accounting for 70.02–93.21% of OC, and the average MSOC/OC was 84.99%. The proportions of WSOC/OC and MSOC/OC (64.47%, 84.9%) were high, which is consistent with the results of the high proportion of SOC/OC in Section 3.2.3.

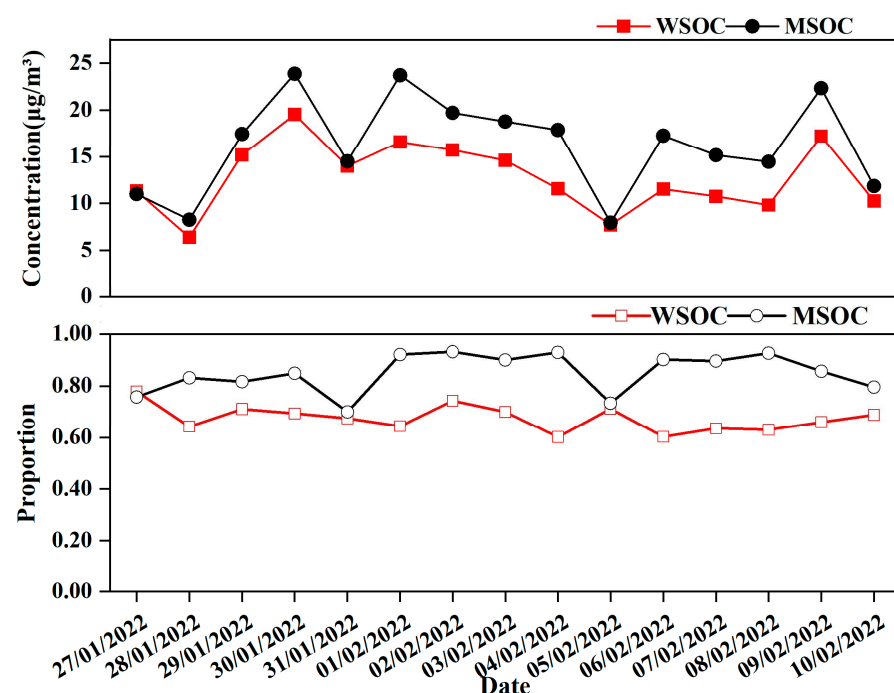


Figure 6. Variations of WSOC and MSOC concentrations and their proportion in TOC.

Table 2 shows the WSOC and MSOC concentrations and their proportions in OC in other studies. The average concentrations and proportions of WSOC and MSOC in this study were similar to those of other studies.

Table 2. The concentrations and proportions of WSOC and MSOC in other studies.

Location	Sampling Time	Component	Concentration ($\mu\text{g}\cdot\text{m}^{-3}$)	Proportion (%)	Reference
Beijing	7 December 2011– 31 December 2011	WSOC	8.15	40%	[28]
		MSOC	17.54	85%	
Kathmandu	12 April 2012–20 May 2014	WSOC	1.66	55%	[29]
Indo-Gangetic Plains	8 November 2017– 24 January 2018	WSOC	22.7	66%	[25]
		WSOC	17.4	50%	
Kathmandu Valley	April 2013–January 2018	WSOC	17.4	50%	[30]
Xi'an	15 November 2018– 15 December 2018	WSOC	8.9	58%	[31]
		MSOC	14.4	79%	

3.3. Distribution Characteristics of Water-Soluble Ions in $\text{PM}_{2.5}$

3.3.1. Concentrations and Proportions of Cations and Anions

In this study, the proportion of water-soluble ions in $\text{PM}_{2.5}$ was 47.48%, indicating that water-soluble ions were important chemical components in $\text{PM}_{2.5}$. The highest average concentration of cations was Na^+ ($12.88 \mu\text{g}/\text{m}^3$), followed by NH_4^+ ($11.03 \mu\text{g}/\text{m}^3$). The average concentrations of Ca^{2+} , K^+ , and Mg^{2+} were 5.62, 4.09, and $0.94 \mu\text{g}/\text{m}^3$, respectively. The highest average concentration of anions was NO_3^- ($22.29 \mu\text{g}/\text{m}^3$), followed by SO_4^{2-} ($15.64 \mu\text{g}/\text{m}^3$). The average concentration of Cl^- was $5.45 \mu\text{g}/\text{m}^3$. Table 3 shows the proportion of water-soluble ions in $\text{PM}_{2.5}$ in some urban and rural areas of China. The proportion of water-soluble ions in $\text{PM}_{2.5}$ in this study was slightly higher than that in Taiyuan (46.09%) and slightly less than that in Beijing (51%) and Shenzhen (53.10%).

Table 3. The proportion of water-soluble ions in $\text{PM}_{2.5}$ in some urban and rural areas of China.

Location	Sampling Site Type	Sampling Time	Season	Proportion (%)	Reference
A village in Shandong	rural	27 January 2022–10 February 2022	Winter	47.48%	This study
Beijing	urban area	4 December 2006– 27 December 2006	Winter	51%	[32]
		2009–2010	Winter	46.09%	
Taiyuan	urban area	2009–2010	Winter	46.09%	[33]
Shenzhen	suburban	November 2009–December 2010	Winter	53.10%	[34]

3.3.2. Analysis of the Combination Form of Anion and Cation

The equivalent relationship between anions and cations can reflect the combination form of ions in $\text{PM}_{2.5}$. The combination of NO_3^- and NH_4^+ is only in the form of NH_4NO_3 , while the combination of SO_4^{2-} and NH_4^+ may be in the form of NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$ [33]. SO_4^{2-} in the atmosphere reacts preferentially with NH_4^+ , forming $(\text{NH}_4)_2\text{SO}_4$ in excess of NH_4^+ and NH_4HSO_4 in deficiency of NH_4^+ [35,36].

Figure 7 shows that the scatter points (purple dots) of the equivalent concentration of NH_4^+ and SO_4^{2-} were distributed above the 1:1 line, indicating that NH_4^+ was sufficient to neutralise SO_4^{2-} , and both mainly existed in the form of $(\text{NH}_4)_2\text{SO}_4$. The equivalent concentration scatter points (blue dots) of NH_4^+ and $\text{SO}_4^{2-} + \text{NO}_3^-$ were partly distributed above the 1:1 line and the other part were below the 1:1 line, so NH_4^+ was not enough to neutralise all NO_3^- .

Figure 8 shows the fitting relationship between the equivalent concentration of three cations and the equivalent concentration of some anions. When the cation was $\text{NH}_4^+ + \text{K}^+$, the scatter points were distributed far below the 1:1 line and were far away from the 1:1 line. The slope of the fitting line was 0.92 and the correlation was strong ($R^2 = 0.94$). When the cation was $\text{NH}_4^+ + \text{K}^+ + \text{Ca}^{2+}$, most of the scatter points were distributed above the 1:1 line and the slope of the fitted line was 0.91, but the correlation coefficient ($R^2 = 0.65$) was smaller. When the cation was $\text{NH}_4^+ + \text{K}^+ + \text{Mg}^{2+}$, the slope of the fitted straight line of the equivalent concentration of the three anions and the three cations was closest to 1:1 ($R^2 = 0.96$), showing that the equivalent of the anions and the cations was almost balanced. Therefore, the combination of anions and cations was likely

to result in NH_4^+ being able to neutralise most of SO_4^{2-} and NO_3^- to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 , while K^+ and Mg^{2+} existed in the form of KCl and MgCl_2 .

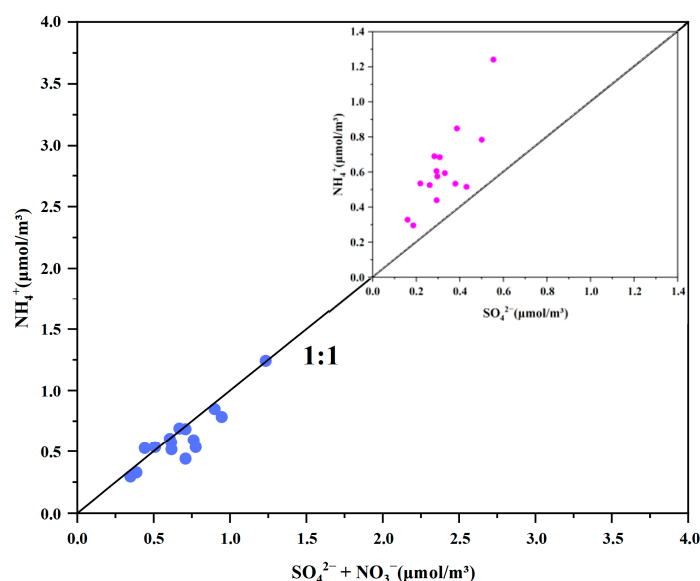


Figure 7. Scatter plot of NH_4^+ and $\text{SO}_4^{2-} + \text{NO}_3^-$.

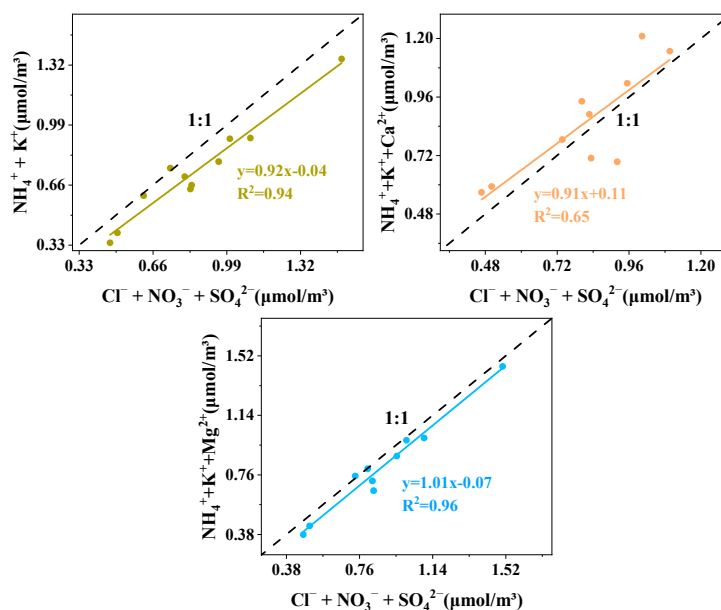


Figure 8. Scatter plot of some cations and $\text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-}$.

3.3.3. Analysis of the Formation of Secondary Ions

SO_4^{2-} , NO_3^- , and NH_4^+ are called secondary inorganic aerosols (SIA). The ratio of SIA to the total ions measured in this study was 55.55%. The formation pathways of secondary inorganic ions mainly include homogeneous reactions and heterogeneous reactions. On the one hand, SO_4^{2-} can be formed by a homogeneous reaction of SO_2 in the gas phase, such as SO_2 , oxide O_3 , and hydroxyl radical ($\cdot\text{OH}$) in the atmosphere. On the other hand, SO_4^{2-} can be formed by a heterogeneous reaction of SO_2 at the interface between the gas phase and liquid phase, and the gas phase and solid phase [37–39]. The homogeneous reaction of NO_3^- formation is the oxidation of NO_2 with $\cdot\text{OH}$ in the atmosphere to form HNO_3 which then reacts with NH_3 to form NH_4NO_3 , while the heterogeneous reaction is the hydrolysis

of N_2O_5 on the aerosol surface to form NO_3^- [40]. NH_4^+ is mostly produced by the reaction of NH_3 with acidic gases in the atmosphere [41], such as H_2SO_4 , HNO_3 , and HCl .

The correlation between SIA and $\text{PM}_{2.5}$ and the correlation between SIA and meteorological factors were used to explain these secondary ions formation pathways to some extent. NO_3^- was significantly correlated with relative humidity ($r = 0.777$, $p < 0.01$) and $\text{PM}_{2.5}$ ($r = 0.833$, $p < 0.01$). The study of Gržinić [42], Wang [43], and McDuffie et al. [44] showed that the heterogeneous uptake coefficient of N_2O_5 was significantly positively correlated with the relative humidity of the atmosphere, while Meng et al. [40] pointed out that the relative humidity increased the water content and surface area of the atmospheric particulate matter, which could promote the attachment of N_2O_5 to particulate matter. Relative humidity was significantly positively correlated with NO_3^- , and the heterogeneous reaction was the main generation pathway of NO_3^- . The results of this study were consistent with the results of Meng et al. Therefore, NO_3^- was most likely to be produced by the heterogeneous reaction, while the correlation between SO_4^{2-} and relative humidity, as well as the correlation between SO_4^{2-} and $\text{PM}_{2.5}$, were not obvious, indicating that their formation may be the result of both homogeneous and heterogeneous reactions.

3.4. Source Apportionment of $\text{PM}_{2.5}$

3.4.1. Source Apportionment Based on the Ratios of Some Typical Components

1. Based on the ratios of OC/EC and char/soot

The OC/EC ratios in this study ranged from 1.03 to 4.67, with an average of 3.06. When the OC/EC ratio is between 2.5 and 10.5, it reflects the strong contribution of coal combustion sources [45]. When the OC/EC ratio is between 3.8 and 13.2, it reflects the strong contribution of biomass combustion sources [46]. When the OC/EC ratio is between 0.3 and 2.9, it reflects the strong contribution of mobile sources [47]. SOC is generally considered to be generated when OC/EC is greater than 2, reflecting the effects of secondary sources [48]. The OC/EC ratio in this study was between the characteristic OC/EC ratios of the above primary sources and secondary sources, suggesting that the source of carbonaceous aerosol during the sampling period was complex and that multiple sources contributed. Wang et al. [49] proposed analysing the source of carbonaceous aerosol based on the char/soot ratio. Studies have shown that the char/soot ratios of the biomass combustion source, coal combustion source, and mobile source are 22.6, 1.3 and 0.6, respectively [50]. Cao et al. found that the char/soot ratios of diesel, gasoline, and coal combustion sources were 0.3, 0.7 [51], and 1.90 [52], respectively. The char/soot ratios in this study were between 0.37–271.88 with an average of 39.29, which was in the middle of the char/soot characteristic ratios of coal combustion and biomass combustion sources, indicating that the $\text{PM}_{2.5}$ in this sampling site was affected by coal and biomass combustion.

2. Based on the ratios of different ions

The ratios of different ions in particulate matter can be used to analyse sources [33,53–55]. The $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio is often used to analyse the contribution of mobile sources and stationary sources. A $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio greater than 1 indicates that the contribution of mobile sources is higher than the stationary sources. The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio is often used to analyse the contribution of soil sources. The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in the soil is about 0.09. The $\text{SO}_4^{2-}/\text{K}^+$ ratio is usually used to analyse the contribution of coal-fired sources and biomass combustion sources. The greater the $\text{SO}_4^{2-}/\text{K}^+$ ratio, the greater the contribution of coal-fired sources compared with that of biomass combustion sources. The $\text{Mg}^{2+}/\text{Na}^+$ ratio is often used to analyse the contribution of sea salt sources, which is usually 0.12 in sea salt aerosols [56].

The typical ion ratios in this study are shown in Figure 9. The average ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ was 1.44, which indicates that the $\text{PM}_{2.5}$ in the region was not only affected by local sources, but also by the increasing mobile sources of motor vehicles at the end of the year and during the Spring Festival. In addition, the sampling site was surrounded

by farmland, the terrain was flat, and there was no large shelter around. There was a provincial road 1.5 km away from the south of the sampling site, and there were rural roads 100 m away from the east, west, south, and north of the sampling site. The influence of motor vehicle exhaust cannot be ignored. The average ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ was 0.18, which was higher than that of soil (0.09). It has been shown that Mg^{2+} and K^+ also had a good correlation; therefore, the reason for the high $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio might be that some Mg^{2+} came from biomass combustion sources [57].

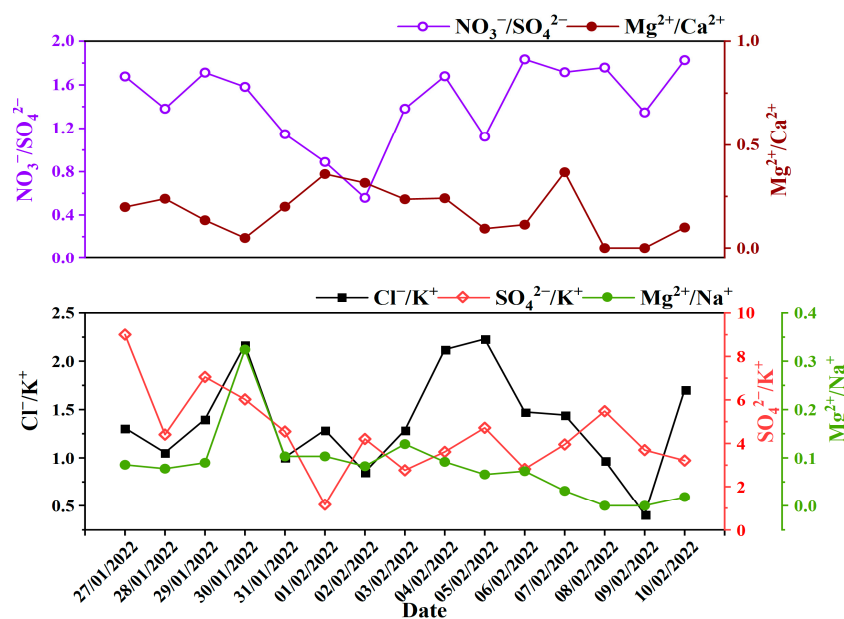


Figure 9. Distribution of multiple ion ratios.

3.4.2. Source Apportionment Based on HYSPLIT Model

A total of 360 backward trajectories were obtained after 48 h of backward trajectory simulation. After the clustering analysis, there were five clusters classified. As shown in Figure 10, Cluster 1 accounted for 29% of the total atmosphere mass, mainly from Binzhou City near the Bohai Sea in the northern part of Shandong Province. It went south through Shandong Province to reach the sampling site, and the initial height was less than 500 m, which belongs to the low atmosphere mass, and the height change was small during the movement. Cluster 2 accounted for 19% of the total atmosphere mass, mainly from Inner Mongolia. It passed through the Beijing–Tianjin–Hebei region and the Bohai Sea, and then went south to the sampling site. The initial height of the atmospheric mass was about 1000 m, which belongs to the middle- and high-altitude atmosphere mass. Cluster 3 and Cluster 5 together accounted for 17% of the total atmosphere mass, and both originated from Outer Mongolia. The initial height of Cluster 3 was 1000 m, and the initial height of Cluster 5 was about 3000 m. Cluster 4 accounted for the largest proportion of 35%, mainly from the junction of Shandong and Jiangsu, with a lower starting height (500 m) similar to Cluster 1.

According to the moving distance of the atmospheric mass, the above five trajectories were divided into three categories. First, the long-distance atmosphere mass included Cluster 3 and Cluster 5, which moved fast and could carry a large amount of dust through Inner Mongolia, accounting for 17%. The second was the middle-distance atmosphere mass, mainly including Cluster 2, which moved faster and accounted for 19%. The third was the local atmosphere mass, including Cluster 1 and Cluster 4—the atmosphere flow trajectory of which was short and the movement speed was slow, accounting for 64%. It showed that the primary emission source and the secondary source in Shandong Province had an important impact on the aerosol in the sampling area.

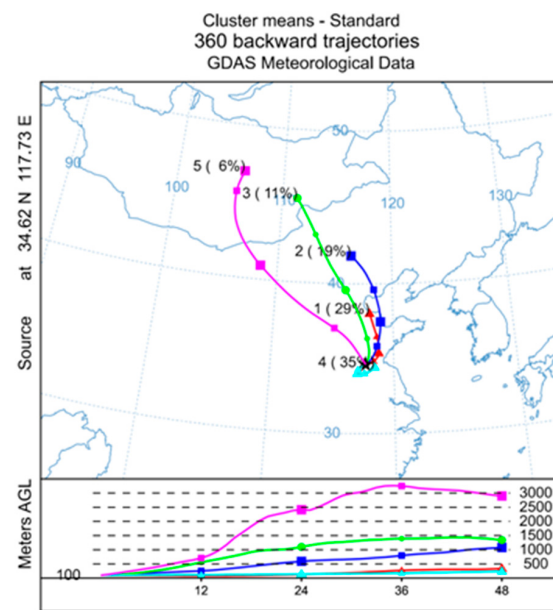


Figure 10. Cluster analysis of 48 h backward trajectories during the sampling period.

3.4.3. Source Apportionment Based on the PMF Model

Figures 11 and 12 show the source component spectrum and the source contribution rate of the PMF model analysis. The characteristic components of the first factor included EC_2 and EC_3 . EC_2 and EC_3 are often considered tracers of diesel vehicles [52], so they were identified as the contribution of mobile sources (4.59%). The characteristic components of the second factor were Cl^- , K^+ , and Na^+ , which could be identified as the contribution of the primary combustion source (12.68%). The characteristic components of the third factor included OC_1 , OC_2 , OC_3 , OC_4 , EC_1 , NO_3^- , SO_4^{2-} , and NH_4^+ . The four OC fractions were significantly correlated with SOC (see Section 3.2.3), while NO_3^- , SO_4^{2-} , and NH_4^+ were secondary inorganic ions. Therefore, the third factor was identified as the contribution of secondary sources that bring secondary organic and secondary inorganic aerosols (60.46%). The fourth factor was characterised by Ca^{2+} and Mg^{2+} , which can be identified as dust source contributions (22.26%).

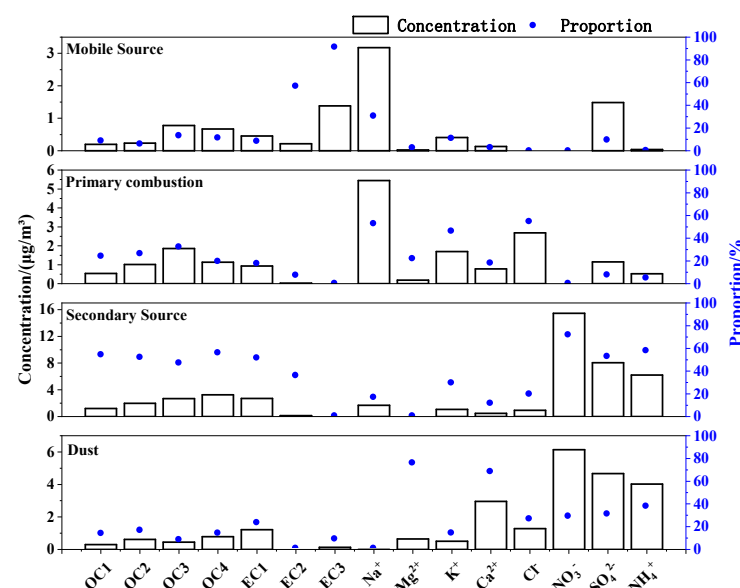


Figure 11. The source component spectra were resolved by the PMF model.

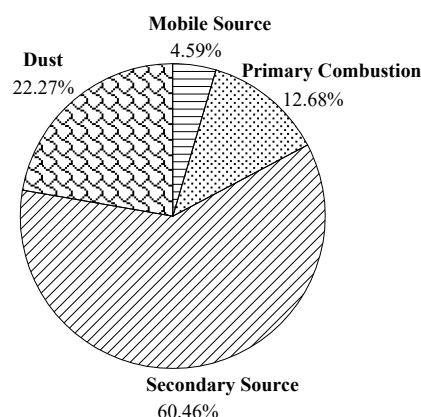


Figure 12. The source contribution rate from the PMF model.

4. Conclusions

In winter, the concentration of $PM_{2.5}$ (55.79 – $236.11 \mu\text{g}/\text{m}^3$) in rural areas of North China seriously exceeded the standard (the over-standard rate was 93.33% and the maximum over-standard multiple was 3.15). The negative correlation between $PM_{2.5}$ and air pressure and wind speed ($<4 \text{ m/s}$) reflected that high pressure and strong wind contributed to the diffusion of $PM_{2.5}$. The positive correlation between $PM_{2.5}$ and relative humidity reflected that high humidity conditions led to the accumulation of $PM_{2.5}$. OC ($19.01 \mu\text{g}/\text{m}^3$) and EC ($7.49 \mu\text{g}/\text{m}^3$) accounted for 11.61% and 4.57% of $PM_{2.5}$, respectively, which were important chemical components in $PM_{2.5}$. The proportion of SOC was high ($\text{SOC}/\text{OC} = 79.41\%$). OC_3 , OC_4 , EC_1 , and OC_2 were the dominant fractions among the eight carbon fractions. The four OC fractions were significantly correlated with SOC, indicating that OC components contained a large amount of SOC. WSOC ($12.82 \mu\text{g}/\text{m}^3$) and MSOC ($16.28 \mu\text{g}/\text{m}^3$) accounted for 67.47% and 84.99% of OC, respectively, indicating that a large part of OC was SOC. Water-soluble ions accounted for 47.48% of $PM_{2.5}$. The analysis of the combination form of ions showed that NH_4^+ can neutralise most of SO_4^{2-} and NO_3^- to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 , while Cl^- mainly existed in the form of KCl and MgCl_2 . The analysis of the secondary ion formation pathway showed that NO_3^- was mainly formed by a homogeneous reaction, while SO_4^{2-} was formed by both homogeneous and heterogeneous reactions. The OC/EC ratio (mean 3.06) and char/soot ratio (mean 39.27) indicated that regional $PM_{2.5}$ was affected by various sources. The analysis of typical ratios of different ions showed that $PM_{2.5}$ was not only affected by local combustion sources, but also by mobile sources. The cluster analysis of the backward trajectory model showed that the primary emission sources and secondary sources in Shandong Province had a great impact on $PM_{2.5}$ (64%). The PMF model analysis results showed that the main sources of $PM_{2.5}$ in the region were primary combustion sources, secondary sources, and dust sources, among which secondary sources contributed the most (60.46%). The results of various source apportionment methods supported each other.

Author Contributions: Conceptualisation, C.Z., J.W., K.H., C.Y. and F.Z.; software, J.W. and K.H.; validation, C.Z. and H.H.; data curation, J.W. and H.H.; writing—original draft preparation, C.Z., J.W., K.H. and H.H.; writing—review and editing, C.Z., J.W., C.Y., J.L., F.Z. and H.H.; supervision, H.H.; funding acquisition, H.H., J.L. and CL. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (42265011 and 52064037), the Natural Science Foundation of Jiangxi Province (20202BAB204030), and the Training Programme for Academic and Technical Leaders of Major Disciplines in Jiangxi Province (20212BCJL23054).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Zhang, Y.M.; Zhang, X.Y.; Zhong, J.T.; Sun, J.Y.; Shen, X.J.; Zhang, Z.X.; Xu, W.Y.; Liang, L.L.; Liu, Y.S.; Hu, X.Y.; et al. On the fossil and non-fossil fuel sources of carbonaceous aerosol with radiocarbon and AMS-PMF methods during winter hazy days in a rural area of North China plain. *Environ. Res.* **2022**, *208*, 112672. [CrossRef] [PubMed]
2. Pyta, H.; Rogula-Kozłowska, W.; Mathews, B. Co-occurrence of PM_{2.5}-bound mercury and carbon in rural areas affected by coal combustion. *Atmos. Pollut. Res.* **2017**, *8*, 127–135. [CrossRef]
3. Yin, L.Q.; Niu, Z.C.; Chen, X.Q.; Chen, J.S.; Xu, L.L.; Zhang, F.W. Chemical compositions of PM_{2.5} aerosol during haze periods in the mountainous city of Yong'an, China. *J. Environ. Sci.* **2012**, *24*, 1225–1233. [CrossRef]
4. Cao, J.J.; Shen, Z.X.; Chow, J.C.; Watson, J.G.; Lee, S.C.; Tie, X.X.; Ho, K.F.; Wang, G.H.; Han, Y.M. Winter and summer PM_{2.5} chemical compositions in fourteen Chinese cities. *J. Air Waste Manag. Assoc.* **2012**, *62*, 1214–1226. [CrossRef] [PubMed]
5. Liu, P.; Zhang, C.; Xue, C.; Mu, Y.J.; Liu, J.F.; Zhan, Y.Y.; Tian, D.; Ye, C.; Zhang, H.X.; Guan, J. The contribution of residential coal combustion to atmospheric PM_{2.5} in northern China during winter. *Atmos. Chem. Phys.* **2017**, *17*, 11503–11520. [CrossRef]
6. Shi, H.B.; Huang, Y.; Chen, X.; Li, T.; He, M.; Wang, J.J. Pollution characteristics and source apportionment of carbon components in PM_{2.5} in winter in Chengdu. *J. Ecol. Environ.* **2021**, *30*, 1420–1427.
7. Central Meteorological Station. 24-Hour Live Curve [EB/OL]. Available online: <http://www.nmc.cn/> (accessed on 5 April 2022).
8. Han, Y.M.; Han, Z.W.; Cao, J.J.; Chow, J.C.; Watson, J.G.; An, Z.S.; Liu, S.X.; Zhang, R.J. Distribution and origin of carbonaceous aerosol over a rural high-mountain lake area, Northern China and its transport significance. *Atmos. Environ.* **2008**, *42*, 2405–2414. [CrossRef]
9. Han, Y.M.; Cao, J.J.; Chow, J.C.; Watson, J.G.; An, Z.S.; Jin, Z.D.; Fung, K.; Liu, S.X. Evaluation of the thermal/optical reflectance method for discrimination between char- and soot-EC. *Chemosphere* **2007**, *69*, 569–574. [CrossRef]
10. Wu, C.; Yu, J.Z. Determination of primary combustion source organic carbon-to-elemental carbon (OC/EC) ratio using ambient OC and EC measurements: Secondary OC-EC correlation minimization method. *Atmos. Chem. Phys.* **2016**, *16*, 5453–5465. [CrossRef]
11. Stein, A.F.; Draxler, R.R.; Rolph, G.D.; Stunder, B.J.B.; Cohen, M.D.; Ngan, F. NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. *Bull. Am. Meteorol. Soc.* **2015**, *96*, 2059–2077. [CrossRef]
12. Liu, B.S.; Wu, J.H.; Zhang, J.Y.; Wang, L.; Yang, J.M.; Liang, D.N.; Dai, Q.L.; Bi, X.H.; Feng, Y.C.; Zhang, Y.F.; et al. Characterization and source apportionment of PM_{2.5} based on error estimation from EPA PMF 5.0 model at a medium city in China. *Environ. Pollut.* **2017**, *222*, 10–22. [CrossRef] [PubMed]
13. Benchrif, A.; Tahri, M.; Guinot, B.; Chakir, E.M.; Zahry, F.; Baghdad, B.; Bounakhla, M.; Cachier, H.; Costabile, F. Aerosols in Northern Morocco-2: Chemical Characterization and PMF Source Apportionment of Ambient PM_{2.5}. *Atmosphere* **2022**, *13*, 1701. [CrossRef]
14. Wang, H.L.; Miao, Q.; Shen, L.J.; Yang, Q.; Wu, Y.Z.; Wei, H. Air pollutant variations in Suzhou during the 2019 novel coronavirus (COVID-19) lockdown of 2020: High time-resolution measurements of aerosol chemical compositions and source apportionment. *Environ. Pollut.* **2021**, *271*, 116298. [CrossRef] [PubMed]
15. Louie PK, K.; Watson, J.G.; Chow, J.C.; Chen, A.; Sin, D.W.M.; Lau, A.K.H. Seasonal characteristics and regional transport of PM_{2.5} in Hong Kong. *Atmos. Environ.* **2005**, *39*, 1695–1710.
16. Meng, Z.Y.; Wu, L.Y.; Xu, X.D.; Xu, W.Y.; Zhang, R.J.; Jia, X.F.; Liang, L.L.; Miao, Y.C.; Cheng, H.B.; Xie, Y.L.; et al. Changes in ammonia and its effects on PM_{2.5} chemical property in three winter seasons in Beijing, China. *Sci. Total Environ.* **2020**, *749*, 142208. [CrossRef]
17. Xu, L.L.; Chen, X.Q.; Chen, J.S.; Zhang, F.W.; He, C.; Zhao, J.P.; Yin, L.Q. Seasonal variations and chemical compositions of PM_{2.5} aerosol in the urban area of Fuzhou, China. *Atmos. Res.* **2012**, *104–105*, 264–272. [CrossRef]
18. Tian, Y.Z.; Wang, J.; Peng, X.; Shi, G.L.; Feng, Y.C. Estimation of the direct and indirect impacts of fireworks on the physicochemical characteristics of atmospheric PM₁₀ and PM_{2.5}. *Atmos. Chem. Phys.* **2014**, *14*, 9469–9479. [CrossRef]
19. Mikuška, P.; Krůmal, K.; Večeřa, Z. Characterization of organic compounds in the PM_{2.5} aerosols in winter in an industrial urban area. *Atmos. Environmen.* **2015**, *105*, 97–108. [CrossRef]
20. Zhang, X.X.; Xu, H.D.; Liang, D. Spatiotemporal variations and connections of single and multiple meteorological factors on PM_{2.5} concentrations in Xi'an, China. *Atmos. Environ.* **2022**, *275*, 119015. [CrossRef]
21. Xu, Y.L.; Xue, W.B.; Lei, Y.; Zhao, Y.; Cheng, S.Y.; Ren, Z.H.; Huang, Q. Impact of Meteorological Conditions on PM_{2.5} Pollution in China during Winter. *Atmosphere* **2018**, *9*, 429. [CrossRef]
22. Wu, C.; Wu, D.; Yu, J.Z. Estimation and Uncertainty Analysis of Secondary Organic Carbon Using 1 Year of Hourly Organic and Elemental Carbon Data. *J. Geophys. Res. Atmos.* **2019**, *124*, 2774–2795. [CrossRef]
23. Hu, W.W.; Hu, M.; Deng, Z.Q.; Xiao, R.; Kondo, Y.; Takegawa, N.; Zhao, Y.J.; Guo, S.; Zhang, Y.H. The characteristics and origins of carbonaceous aerosol at a rural site of PRD in summer of 2006. *Atmos. Chem. Phys.* **2012**, *12*, 1811–1822. [CrossRef]
24. Xu, J.; Wang, Q.Z.; Deng, C.R.; McNeill, V.F.; Fankhauser, A.; Wang, F.W.; Zheng, X.J.; Shen, J.D.; Huang, K.; Zhuang, G.S. Insights into the characteristics and sources of primary and secondary organic carbon: High time resolution observation in urban Shanghai. *Environ. Pollut.* **2018**, *233*, 1177–1187. [CrossRef]

25. Izhar, S.; Gupta, T.; Panday, A.K. Improved method to apportion optical absorption by black and brown carbon under the influence of haze and fog at Lumbini, Nepal, on the Indo-Gangetic Plains. *Environ. Pollut.* **2020**, *263*, 114640. [[CrossRef](#)]
26. Yan, C.Q.; Zheng, M.; Bosch, C.; Andersson, A.; Desyaterik, Y.; Sullivan, A.P.; Collett, J.L.; Zhao, B.; Wang, S.X.; He, K.B.; et al. Important fossil source contribution to brown carbon in Beijing during winter. *Sci. Rep.* **2017**, *7*, 43182. [[CrossRef](#)] [[PubMed](#)]
27. Martinsson, J.; Eriksson, A.C.; Nielsen, I.E.; Malmberg, V.B.; Ahlberg, E.; Andersen, C.; Lindgren, R.; Nyström, R.; Nordin, E.Z.; Brune, W.H.; et al. Impacts of Combustion Conditions and Photochemical Processing on the Light Absorption of Biomass Combustion Aerosol. *Environ. Sci. Technol.* **2015**, *49*, 14663–14671. [[CrossRef](#)] [[PubMed](#)]
28. Cheng, Y.; He, K.B.; Du, Z.Y.; Engling, G.; Liu, J.M.; Ma, Y.L.; Zheng, M.; Weber, R.J. The characteristics of brown carbon aerosol during winter in Beijing. *Atmos. Environ.* **2016**, *127*, 355–364. [[CrossRef](#)]
29. Wu, G.M.; Ram, K.; Fu, P.Q.; Wang, W.; Zhang, Y.L.; Liu, X.Y.; Stone, E.A.; Pradhan, B.B.; Dangol, P.M.; Panday, A.; et al. Water-Soluble Brown Carbon in Atmospheric Aerosols from Godavari (Nepal), a Regional Representative of South Asia. *Environ. Sci. Technol.* **2019**, *53*, 3471–3479. [[CrossRef](#)]
30. Chen, P. Light absorption properties of elemental carbon (EC) and water-soluble brown carbon (WS-BrC) in the Kathmandu Valley, Nepal: A 5-year study. *Environ. Pollut.* **2020**, *261*, 114239. [[CrossRef](#)]
31. Wang, T.; Li, D.; Xue, S.P.; Wang, Y.S. Light absorption characteristics and source apportionment of multiphase particles of brown carbonaceous aerosol in Xi'an winter. *J. Eng. Thermophys.* **2021**, *42*, 2010–2016.
32. Tan, J.H.; Duan, J.C.; Zhen, N.J.; He, K.B.; Hao, J.M. Chemical characteristics and source of size-fractionated atmospheric particle in haze episode in Beijing. *Atmos. Res.* **2016**, *167*, 24–33. [[CrossRef](#)]
33. He, Q.S.; Yan, Y.L.; Guo, L.L.; Zhang, Y.L.; Zhang, G.X.; Wang, X.M. Characterization and source analysis of water-soluble inorganic ionic species in PM_{2.5} in Taiyuan city, China. *Atmos. Res.* **2017**, *184*, 48–55. [[CrossRef](#)]
34. Dai, W.; Gao, J.Q.; Cao, G.; Feng, O.Y. Chemical composition and source identification of PM_{2.5} in the suburb of Shenzhen, China. *Atmos. Res.* **2013**, *122*, 391–400. [[CrossRef](#)]
35. Li, H.; Tang, G.Q.; Zhang, J.K.; Liu, Q.; Yan, G.X.; Chen, M.T.; Gao, W.K.; Wang, Y.H.; Wang, Y.S. Characteristics of water-soluble inorganic ions in atmospheric PM_{2.5} in Beijing from 2017 to 2018. *Environ. Sci.* **2020**, *41*, 4364–4373.
36. Yang, L.M.; Wang, S.B.; Hao, Q.; Han, S.J.; Li, C.; Zhao, Q.Y.; Yan, Q.S.; Zhang, R.Q. Characteristics and source analysis of water-soluble ions in PM_{2.5} in Zhengzhou. *Environ. Sci.* **2019**, *40*, 2977–2984.
37. Cheng, C.; Shi, M.M.; Liu, W.J.; Mao, Y.; Hu, J.X.; Tian, Q.; Chen, Z.L.; Hu, T.P.; Xing, X.L.; Qi, S.H. Characteristics and source apportionment of water-soluble inorganic ions in PM_{2.5} during a wintertime haze event in Huanggang, central China. *Atmos. Pollut. Res.* **2021**, *12*, 111–123. [[CrossRef](#)]
38. Zhang, L.; Vet, R.; Wiebe, A.; Mihele, C.; Sukloff, B.; Chan, E.; Moran, M.D.; Iqbal, S. Characterization of the size-segregated water-soluble inorganic ions at eight Canadian rural sites. *Atmos. Chem. Phys.* **2008**, *8*, 7133–7151. [[CrossRef](#)]
39. Zheng, B.; Zhang, Q.; Zhang, Y.; He, K.B.; Wang, K.; Zheng, G.J.; Duan, F.K.; Ma, Y.L.; Kimoto, T. Heterogeneous chemistry: A mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China. *Atmos. Chem. Phys.* **2015**, *15*, 2031–2049. [[CrossRef](#)]
40. Meng, C.C.; Wang, L.T.; Zhang, F.F.; Wei, Z.; Ma, S.M.; Ma, X.; Yang, J. Characteristics of concentrations and water-soluble inorganic ions in PM_{2.5} in Handan City, Hebei province, China. *Atmos. Res.* **2016**, *171*, 133–146. [[CrossRef](#)]
41. Liu, K.; Ren, J. Seasonal characteristics of PM_{2.5} and its chemical species in the northern rural China. *Atmos. Pollut. Res.* **2020**, *11*, 1891–1901. [[CrossRef](#)]
42. Gržinić, G.; Bartels-Rausch, T.; Berkemeier, T.; Türler, A.; Ammann, M. Viscosity controls humidity dependence of N₂O₅ uptake to citric acid aerosol. *Atmos. Chem. Phys.* **2015**, *15*, 13615–13625. [[CrossRef](#)]
43. Wang, X.F.; Wang, H.; Xue, L.K.; Wang, T.; Wang, L.W.; Gu, R.R.; Wang, W.H.; Tham, Y.J.; Wang, Z.; Yang, L.X.; et al. Observations of N₂O₅ and ClNO₂ at a polluted urban surface site in North China: High N₂O₅ uptake coefficients and low ClNO₂ product yields. *Atmos. Environ.* **2017**, *156*, 125–134. [[CrossRef](#)]
44. McDuffie, E.E.; Fibiger, D.L.; Dubé, W.P.; Felipe, L.H.; Lee, B.H.; Thornton, J.A.; Shah, V.; Jaeglé, L.; Guo, H.Y.; Weber, R.J.; et al. Heterogeneous N₂O₅ uptake during winter: Aircraft measurements during the 2015 WINTER campaign and critical evaluation of current parameterizations. *J. Geophys. Res. Atmos.* **2018**, *123*, 4345–4372. [[CrossRef](#)]
45. Chen, Y.J.; Sheng, G.Y.; Bi, X.H.; Feng, Y.L.; Mai, B.X.; Fu, J.M. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environ. Sci. Technol.* **2005**, *39*, 1861–1867. [[CrossRef](#)]
46. Zhang, Y.X.; Shao, M.; Zhang, Y.H.; Zeng, L.M.; He, L.Y.; Zhu, B.; Wei, Y.J.; Zhu, X.L. Source profiles of particulate organic matters emitted from cereal straw burnings. *J. Environ. Sci.* **2007**, *19*, 167–175. [[CrossRef](#)]
47. Pio, C.; Cerqueira, M.; Harrison, R.M.; Nunes, T.; Mirante, F.; Alves, C.; Oliveira, C.; Campa, A.S.; Artíñano, B.; Matos, M. OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. *Atmos. Environ.* **2011**, *45*, 6121–6232. [[CrossRef](#)]
48. Huang, H.; Ho, K.F.; Lee, S.C.; Tsang, P.K.; Ho, S.S.H.; Zou, C.W.; Zou, S.C.; Cao, J.J.; Xu, H.M. Characteristics of carbonaceous aerosol in PM_{2.5}: Pearl Delta River Region, China. *Atmos. Res.* **2012**, *104–105*, 227–236. [[CrossRef](#)]
49. Wang, F.W.; Feng, T.; Guo, Z.G.; Li, Y.Y.; Lin, T.; Rose, N.L. Sources and dry deposition of carbonaceous aerosols over the coastal East China Sea: Implications for anthropogenic pollutant pathways and deposition. *Environ. Pollut.* **2019**, *245*, 771–779. [[CrossRef](#)]

50. Chow, J.C.; Watson, J.G.; Kuhns, H.; Etyemezian, V.; Lowenthal, D.H.; Crow, D.; Kohl, S.D.; Engelbrecht, J.P.; Green, M.C. Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational study. *Chemosphere* **2004**, *54*, 185–208. [[CrossRef](#)]
51. Cao, J.; Lee, S.; Ho, K.; Fung, K.; Chow, J.C.; Watson, J.G. Characterization of roadside fine particulate carbon and its eight fractions in Hong Kong. *Aerosol Air Qual. Res.* **2006**, *6*, 106–122. [[CrossRef](#)]
52. Cao, J.J.; Wu, F.; Chow, J.C.; Lee, S.C.; Li, Y.; Chen, S.W.; An, Z.S.; Fung, K.K.; Watson, J.G.; Zhu, C.S.; et al. Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmos. Chem. Phys.* **2005**, *5*, 3127–3137. [[CrossRef](#)]
53. Shen, Z.X.; Cao, J.J.; Arimoto, R.; Han, Z.W.; Zhang, R.J.; Han, Y.M.; Liu, S.X.; Okuda, T.; Naka, S.; Tanaka, S. Ionic composition of TSP and PM_{2.5} during dust storms and air pollution episodes at Xi'an, China. *Atmos. Environ.* **2009**, *43*, 2911–2918. [[CrossRef](#)]
54. Wang, H.J.; Wang, X.H.; Zhou, H.J.; Ma, H.; Xie, F.; Zhou, X.J.; Fan, Q.Y.; Lü, C.W.; He, J. Stoichiometric characteristics and economic implications of water-soluble ions in PM_{2.5} from a resource-dependent city. *Environ. Res.* **2021**, *193*, 110522. [[CrossRef](#)] [[PubMed](#)]
55. Mu, L.; Zheng, L.; Liang, M.; Tian, M.; Li, X.; Jing, D. Characterization and Source Analysis of Water-soluble Ions in Atmospheric Particles in Jinzhong, China. *Aerosol Air Qual. Res.* **2019**, *19*, 2396–2409. [[CrossRef](#)]
56. Xu, M.J.; Wang, Y.H.; Tang, L.L.; Zhang, X.Z.; Tang, L.; Li, X.W.; Cui, Y.X.; Cheng, M.N. Characteristics of water-soluble ions in PM₁₀ in urban and suburban Nanjing in autumn. *Environ. Eng.* **2012**, *30*, 108–113.
57. Park, S.S.; Sim, S.Y.; Bae, M.S.; Schauer, J.J. Size distribution of water-soluble components in particulate matter emitted from biomass burning. *Atmos. Environ.* **2013**, *73*, 62–72. [[CrossRef](#)]