

## Article

# Chemical Characteristics and Sources Analysis of PM<sub>2.5</sub> in Shaoxing in Winter

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**Abstract:** By analyzing the mass concentrations and compositions of atmospheric PM<sub>2.5</sub> in Shaoxing from December 2019 to February 2020, the characteristics of carbon-containing components, water-soluble ions and metal elements were obtained. NO<sub>3</sub><sup>-</sup>, OC, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> were the main components of PM<sub>2.5</sub> in winter. The OC/EC ratio was 3.27, which proved the existence of SOC. The proportion of SOC in OC was 47.3%, which showed that secondary sources made a significant contribution. The values of OC/EC and NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> indicated that vehicle exhaust emissions also made a significant contribution to PM<sub>2.5</sub>. Trace elements of Na, Ca, K and Cd had higher enrichment factor values and were enriched due to human activities. Finally, PM<sub>2.5</sub> sources analysis was performed by the positive matrix factorization model. The results showed that secondary inorganic salts (49.3%), motor vehicles and industrial sources (21.3%) and dust sources (17.0%) were the important sources of PM<sub>2.5</sub> pollution.

**Keywords:** PM<sub>2.5</sub>; metal elements; water-soluble ions; carbonaceous species; sources analysis



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## 1. Introduction

At present, PM<sub>2.5</sub> has become the primary pollutant in most cities in China [1]. The primary aerosol particles and gaseous pollutants emitted by industry, transportation and fossil fuel combustion, as well as the secondary aerosols transformed by primary aerosols, are the main causes of PM<sub>2.5</sub> pollution [2]. The chemical components of PM<sub>2.5</sub> are complex, including water-soluble ions, organic carbon, elemental carbon and metal elements, mainly derived from human activities [3]. Water-soluble ions, especially secondary inorganic ions NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, have become the main components of PM<sub>2.5</sub> in most cities in China [4].

In recent years, Zhejiang Province has successively conducted research on the components and sources of PM<sub>2.5</sub>, mainly focusing on rapidly developing cities such as Hangzhou, Wenzhou and Ningbo. Li et al. focused on analyzing the pollution characteristics of carbon-containing components of PM<sub>2.5</sub> in winter in Hangzhou [5] and found that organic carbon accounted for a relatively high proportion. The compositional characteristics of water-soluble ions in PM<sub>2.5</sub> in Hangzhou were analyzed separately by Chen et al., and the results showed that SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> were the main components [6]. Ge et al. analyzed the pollution characteristics of water-soluble ions in PM<sub>2.5</sub> in Wenzhou and found that SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were also the main components, mainly sourced from coal

combustion, motor vehicle exhaust and biomass combustion [7]. Wang et al. conducted a study on the characteristics and sources of PM<sub>2.5</sub> pollution in Ningbo and found that the source categories that made significant contributions to PM<sub>2.5</sub> were secondary nitrates, secondary sulfates, marine sources, biomass combustion, high chlorine sources, heavy oil combustion, motor vehicle emissions, industrial smelting and mixed dust [8]. A targeted analysis on the spatiotemporal distribution of carbon-containing components in PM<sub>2.5</sub> was conducted by Du et al., also in Ningbo. The results showed that secondary organic carbon contributed significantly to the carbon components [9]. Xu et al. compared the pollution characteristics of polycyclic aromatic hydrocarbons in PM<sub>2.5</sub> in Hangzhou and Ningbo, and the results showed that the concentration of polycyclic aromatic hydrocarbons exceeded the national standard [10]. In addition, some scholars have begun to pay attention to the PM<sub>2.5</sub> pollution characteristics of small and medium-sized cities in Zhejiang Province. For example, Fang et al. studied the distribution characteristics of secondary organic aerosol indicators in PM<sub>2.5</sub> in Lanxi, which is a small city in Zhejiang Province [11]. Isoprene and toluene made significant contributions to secondary organic carbon (SOC).

Although extensive research has been conducted in many cities, there is still a lack of comprehensive studies on the chemical components and sources of PM<sub>2.5</sub> in Shaoxing. Shaoxing is a typical industrial city in Zhejiang Province. Zhang et al. detected the pollution characteristics of metal elements in PM<sub>2.5</sub> in Shaoxing [12]. Zhu et al. also analyzed the characteristics of organic carbon (OC) and elemental carbon (EC) since Shaoxing belongs to the urban agglomeration around Hangzhou Bay, which is the area with the most serious PM<sub>2.5</sub> pollution in the Yangtze River Delta [13]. The impact of anthropogenic sources on PM<sub>2.5</sub> pollution in Shaoxing is obvious.

Since 2013, due to the frequent occurrence of winter haze pollution, China has been committed to controlling particulate matter pollution, and the concentration of PM<sub>2.5</sub> has continued to decrease in recent years. However, according to the online monitoring data of air pollutants in China on <http://www.aqistudy.cn/> (accessed on 26 July 2023), PM<sub>2.5</sub> pollution is still the most serious in winter. In winter, a PM<sub>2.5</sub> concentration exceeding the national standard limit often occurs in Shaoxing.

Therefore, this study focused on analyzing the chemical characteristics and sources of PM<sub>2.5</sub> in the atmosphere of Shaoxing from December 2019 to February 2020 by detecting the components such as carbon-containing components, water-soluble ions and metal elements. It would provide scientific support for the management of PM<sub>2.5</sub> pollution in Shaoxing during the winter.

## 2. Materials and Methods

### 2.1. Field Measurement

Considering urban functional area distribution, population density, environmental sensitivity and other factors, the environmental monitoring station of Shaoxing was selected as the sampling site. Shaoxing Environmental Monitoring Station is located at No. 38 Shuxiawang Road, which is a central area of commerce, transportation and residences.

Samples were collected from December 2019 to February 2020. Teflon filter membrane and quartz filter membrane were used for synchronous collection for 23 h. A 4-channel small-flow sampler and a medium-flow sampler were used to collect PM<sub>2.5</sub> samples, with sampling flow rates of 16.7 L/min and 100 L/min, respectively. The small-flow sampler collected four parallel samples (two quartz filter samples and two Teflon filter samples), and the medium-flow sampler synchronously collected one quartz filter sample, the brand of which was Waterman. A total of 25 groups of samples were collected.

### 2.2. Chemical Analysis

#### 2.2.1. PM<sub>2.5</sub> Mass Concentration

Before sampling, a filter membrane was placed in a constant temperature and humidity chamber (temperature 20 °C and humidity 50%) for 24 h, and then an automatic weighing system (CR-4; Chinese Intelligent Manufacturing, Hangzhou, China) was used to weigh

this filter membrane, and its mass was recorded. After sampling, the same instrument was used to weigh the same filter membrane and the mass was also recorded under the same conditions. The difference in mass was used to determine the mass concentration of PM<sub>2.5</sub>.

### 2.2.2. Analysis of Water-Soluble Ions and Elemental Components

The concentrations of water-soluble ions were determined by ion chromatography. A 1/4 of one sample filter was taken and put into the sample bottle. The water-soluble components were extracted from the filter into 20.0 mL of deionized water, entered the sample bottle and soaked for 30 min. Then, the sample bottle was put into the ultrasonic instrument for ultrasonic extraction for 20 min. Ice was added into the ultrasonic instrument to ensure that the temperature was not higher than 20 °C. This could reduce the component loss. The extract was filtered by 0.45 µm microporous membrane filter and then sent to ion chromatograph (Ics-5000; Thermo Fisher, Waltham, USA) for analysis.

A filter sample collected by a small-flow sampler was put into a dry and clean sample box, and then analyzed by the WD-XRF wavelength dispersive X-ray fluorescence spectrometer (S4 pioneer; Bruker, Saarbrücken, Germany). Then, the concentrations of element components were determined.

### 2.2.3. Carbon-Containing Components Analysis

According to the Technical and Methodological Guidelines for Analytical Monitoring of Ambient Air Particulate Matter Sources (trial) (Second Edition) [14], the carbon-containing components were determined by the thermo-photometry method. A certain area of quartz sample filter membrane was put into a quartz boat and analyzed by the thermal optical carbon analyzer (DRI Model 2015; Desert Research Institute, Reno, USA). Firstly, under the condition of pure He, heated in temperature gradients of 140 °C (OC<sub>1</sub>), 280 °C (OC<sub>2</sub>), 480 °C (OC<sub>3</sub>) and 580 °C (OC<sub>4</sub>), all organic carbon in the sample was evaporated or decomposed, left the filter membrane and entered the oxidation furnace with the He gas flow (900 °C). The carbon element in the organic matter was oxidized to CO<sub>2</sub> by MnO<sub>2</sub>. The CO<sub>2</sub> flowed out of the oxidation furnace with the He gas flow and was mixed with H<sub>2</sub>. The mixture entered the reduction furnace (420 °C) and was reduced to CH<sub>4</sub> by Ni. Finally, the generated CH<sub>4</sub> was detected by flame ion detector (FID) to calculate the carbon content.

Then, He/O<sub>2</sub> mixed gas containing 10% O<sub>2</sub> was introduced, and the sample furnace was gradually heated up again. The sample was heated at 580 °C (EC<sub>1</sub>), 740 °C (EC<sub>2</sub>) and 840 °C (EC<sub>3</sub>). In this process, the elemental carbon was oxidized in the oxidation furnace. The carbonaceous material was oxidized to CO<sub>2</sub>, and then reduced to CH<sub>4</sub>. Finally, the carbon-containing contents were calculated by detecting the generated CH<sub>4</sub> by FID. The total carbon (TC) mass concentration was the sum of the mass concentrations of OC and EC.

### 2.2.4. Quality Control and Quality Assurance

The testing process strictly followed the testing methods and procedures. Before injection, a solvent blank test and an experimental process blank test were conducted. The samples were injected in the order of PM<sub>2.5</sub> mass concentration, and no target compounds were detected in the blank test.

Recovery experiments were conducted during the detection of water-soluble ions. The standard solution was dropped onto the blank filter membrane. After the solution was air dried, the pretreatment process was performed following the sample operation process. Then, the blank filter membrane was tested on the machine. The added amount was equivalent to the actual concentration of the sample, and the results showed the recovery rates ranging from 80.0% to 120%.

### 2.3. Analysis Methods

#### 2.3.1. Estimation of Enrichment Factor (EF)

The EF method was used to assess the man-made influence on metal elements. The calculation formula was shown as follows:

$$EF = \frac{(C_X/C_R)_{\text{aerosol}}}{(C_X/C_R)_{\text{crust}}} \quad (1)$$

where  $C_X$  was the mass concentration of element X,  $\mu\text{g}/\text{m}^3$ ;  $C_R$  was the mass concentration of the reference element,  $\mu\text{g}/\text{m}^3$ . The subscripts aerosol and crust referred to the recipient sample and crust sample, respectively.

In this study, Al, which experiences less interference from human pollution, was used as the reference element [15]. When EF is less than 10, it indicates that these elements are not enriched and might be unaffected by human activities. When EF is larger than 10 and less than 100, it indicates that these elements are enriched to different degrees. When EF is larger than 100, it indicates that these elements are seriously enriched due to human activities [16].

#### 2.3.2. Estimation of Sulfur Oxidation Rate (SOR) and Nitrogen Oxidation Rate (NOR)

SOR and NOR were used to characterize the conversion rates of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in  $\text{PM}_{2.5}$ . The larger the SOR and NOR, the higher the secondary conversion efficiency [16]. The calculation equations were as follows:

$$\text{SOR} = \frac{C_{\text{SO}_4^{2-}}}{C_{\text{SO}_4^{2-}} + C_{\text{SO}_2}} \quad (2)$$

$$\text{NOR} = \frac{C_{\text{NO}_3^-}}{C_{\text{NO}_3^-} + C_{\text{NO}_2}} \quad (3)$$

where  $C_{\text{SO}_4^{2-}}$  was the mass concentration of water-soluble sulfate ion,  $\mu\text{g}/\text{m}^3$ ;  $C_{\text{NO}_3^-}$  was the mass concentration of water-soluble nitrate ion,  $\mu\text{g}/\text{m}^3$ ;  $C_{\text{SO}_2}$  was the mass concentration of  $\text{SO}_2$  in the atmosphere,  $\mu\text{g}/\text{m}^3$ ;  $C_{\text{NO}_2}$  was the mass concentration of  $\text{NO}_2$  in the atmosphere,  $\mu\text{g}/\text{m}^3$ .

#### 2.3.3. Calculation of Secondary Organic Carbon

The minimum OC/EC ratio was used to evaluate and verify the contribution of SOC to total organic carbon, and the specific calculation equation [17] was as follows:

$$\text{SOC} = \text{OC} - \text{EC} \times (\text{OC}/\text{EC})_{\text{min}} \quad (4)$$

where  $(\text{OC}/\text{EC})_{\text{min}}$  was the minimum OC/EC value of the detection results of OC and EC.

## 3. Results and Discussion

### 3.1. $\text{PM}_{2.5}$ Mass Concentrations

During the sampling period, the average mass concentration of  $\text{PM}_{2.5}$  in Shaoxing was  $45.3 \mu\text{g}/\text{m}^3$ , which exceeded the national standard limit ( $35 \mu\text{g}/\text{m}^3$ , GB3095-2012) of  $10.3 \mu\text{g}/\text{m}^3$ . The daily variation sequence of  $\text{PM}_{2.5}$  concentrations manually sampled is shown in Figure 1. During the sampling period, there were a total of 15 days in which the daily average concentration of  $\text{PM}_{2.5}$  exceeded the national standard limit, accounting for 60% of the total sampling days. The high daily average concentration ultimately led to exceeding the standard limit of the average concentration of  $\text{PM}_{2.5}$  in winter.

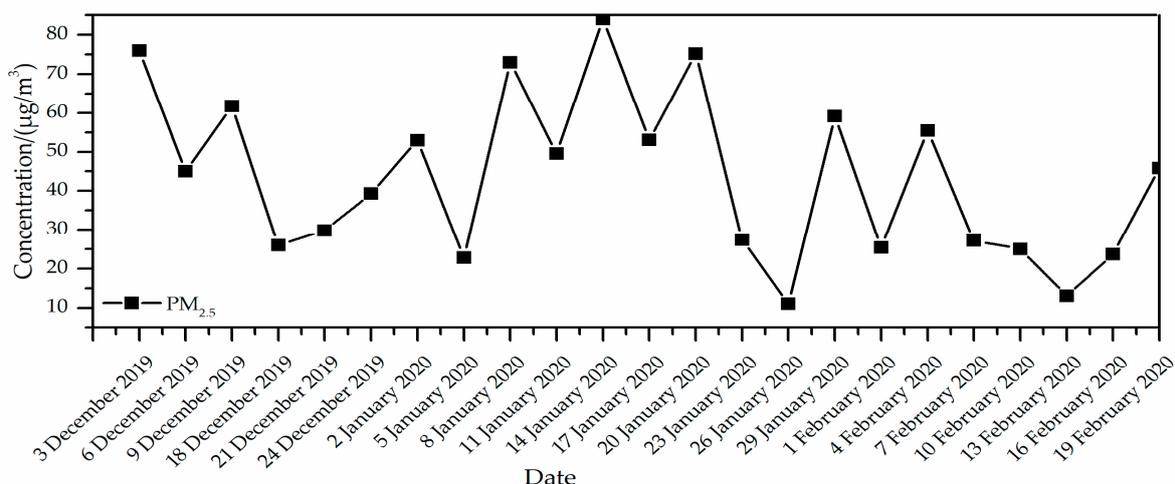


Figure 1. Daily variation sequence of PM<sub>2.5</sub> concentrations during the sampling period.

### 3.2. Carbon-Containing Components Characteristics

The daily variations in TC, OC and EC mass concentrations in winter in Shaoxing are shown in Figure 2. The average concentrations of TC, OC and EC were 9.86 µg/m<sup>3</sup>, 7.41 µg/m<sup>3</sup> and 2.45 µg/m<sup>3</sup>, accounting for 21.8%, 16.4% and 5.41% of PM<sub>2.5</sub> concentration, respectively. It could be seen that OC was the important component of PM<sub>2.5</sub>.

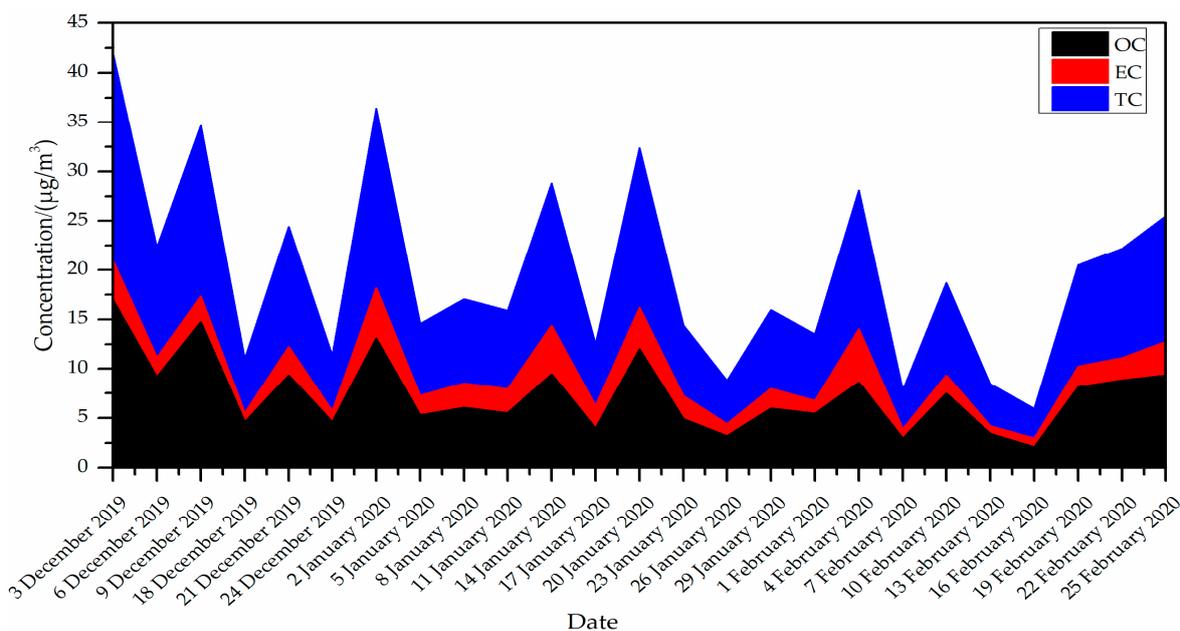
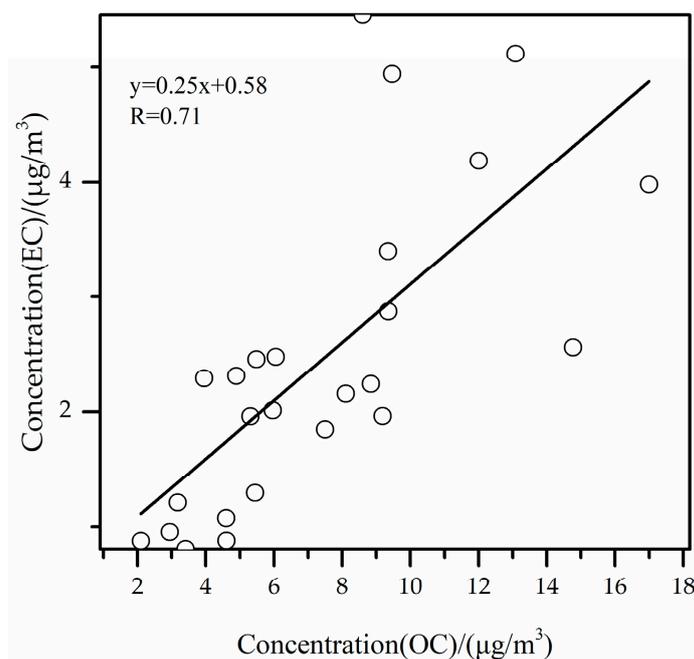


Figure 2. The daily variations in TC, OC and EC during the sampling period.

EC mainly comes from the incomplete combustion of fossil fuels or biomass, and only exists in the primary sources. OC sources include primary organic carbon (POC) emitted from coal, fuel and biomass combustion, and SOC formed by the conversion of VOCs and SVOCs [18]. That is to say, the POC sources in OC are consistent with EC sources. Therefore, the correlation analysis between OC and EC could be used to preliminarily determine the sources of carbon-containing components [19]. If the correlation coefficient between OC and EC is close to 1, it indicates that the OC and EC sources are consistent, both from primary sources [20]. If the correlation coefficient is less than 0.5, it indicates that the OC and EC sources are not consistent. As shown in Figure 3, the correlation coefficient R between OC and EC was only 0.71, indicating that the main sources of OC and EC in Shaoxing were not consistent. OC was more affected by SOC.



**Figure 3.** The correlation between OC and EC.

The ratio of OC/EC could reveal carbon-containing components' sources to some extent, and an OC/EC of 2.0 is often used as a basis for determining the presence of SOC [21]. The OC/EC ratio in this study was 3.27, indicating the presence of SOC in the carbon components of PM<sub>2.5</sub>. The SOC was calculated using Equation (4), and the result is shown in Table 1. The average concentration of SOC was 3.54 µg/m<sup>3</sup>, accounting for 47.8% of OC concentration and 7.82% of PM<sub>2.5</sub> concentration. This indicated that the contribution and impact of SOC were significant. Therefore, a more detailed analysis of the SOC characteristics should be conducted in the future, which will help to deepen the understanding of the PM<sub>2.5</sub> pollution characteristics in Shaoxing.

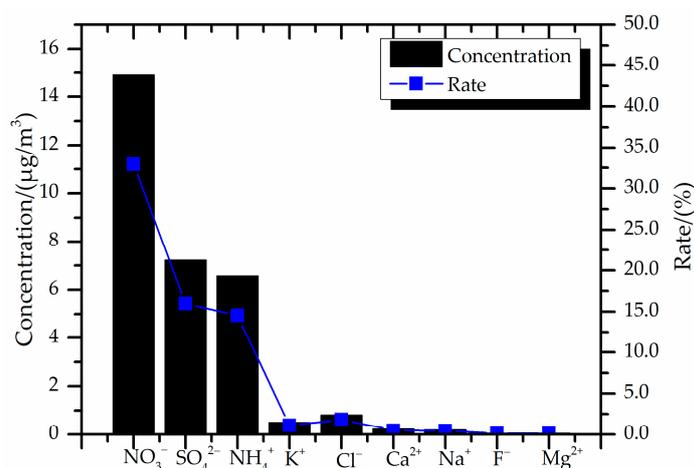
**Table 1.** The characteristics of SOC in winter in Shaoxing.

Season	OC (µg/m <sup>3</sup> )	EC (µg/m <sup>3</sup> )	OC/EC <sub>min</sub>	SOC (µg/m <sup>3</sup> )	SOC/OC
Winter	7.41	2.45	1.58	3.54	47.8%

Additionally, OC/EC is commonly used to preliminarily determine the types of primary and secondary sources of carbon-containing components. Through calculation, the OC/EC of Shaoxing was 3.27. According to the literature, when the OC/EC ratio is between 1.0 and 4.2, it indicates that exhaust emissions from diesel and gasoline vehicles exist [22,23]; meanwhile, 2.5 to 10.5 indicates coal-fired emissions contribute to carbon components [24]. Therefore, diesel vehicles, gasoline vehicles and coal-fired emissions all contributed to the carbon-containing contents of PM<sub>2.5</sub> in Shaoxing.

### 3.3. Variation Characteristics of Water-Soluble Ions

The water-soluble ions detected in this study included SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, etc. The mass concentrations of these ions are shown in Figure 4. The average total concentration of water-soluble ions during the sampling period was 30.6 µg/m<sup>3</sup>. The highest average concentrations of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> were 14.9, 7.23 and 6.58 µg/m<sup>3</sup>, respectively.



**Figure 4.** The average mass concentrations of water-soluble ions.

The total concentration of water-soluble ions accounted for 67.5% of PM<sub>2.5</sub> concentration. NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> accounted for the highest proportions, accounting for 32.9%, 16.0% and 14.5%, respectively. This illustrated that NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> had become the important components of PM<sub>2.5</sub> in Shaoxing. K<sup>+</sup> and Cl<sup>-</sup>, as representative elements of coal-fired combustion, also had a place in PM<sub>2.5</sub> (a total of 2.94%). K<sup>+</sup> is also usually considered as a marker for biomass combustion. This proved that coal and biomass combustion made contributions to PM<sub>2.5</sub> in winter.

In Shaoxing, the proportion of NO<sub>3</sub><sup>-</sup> was higher than that of SO<sub>4</sub><sup>2-</sup>. This result was different from the reports about Hangzhou and Wenzhou [6,7]. The possible reason was that the emission sources had changed. The research about Wenzhou and Hangzhou was conducted in 2014 and 2015. According to the statistical yearbooks of these three cities, the numbers of vehicles in Hangzhou and Wenzhou in 2014 were 2.18 million and 1.57 million [25,26], respectively. Between 2014 and 2019, the number of vehicles in Shaoxing increased from 851,200 to 1.67 million [27,28]. Therefore, based on the large increase in the number of vehicles, the proportion of NO<sub>3</sub><sup>-</sup> from vehicle exhaust in Shaoxing significantly increased.

NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, known as the secondary inorganic aerosols, are secondary reactions of primary pollutants such as SO<sub>2</sub> and NO<sub>2</sub> emitted into the atmosphere. In the past decade, due to the pollution problems caused by coal-fired sources (such as acid rain and particulate matter pollution), China has increased its efforts to govern SO<sub>2</sub> from coal-fired sources. The sources of NO<sub>2</sub> are more complex. The governance effect on NO<sub>2</sub> is not as good as SO<sub>2</sub>. Therefore, the concentration of SO<sub>2</sub> has been maintained at a low level. According to the data from <http://www.aqistudy.cn/> (accessed on 26 July 2023), the average concentration of SO<sub>2</sub> in the atmosphere of Shaoxing was only 7 µg/m<sup>3</sup> and the average concentration of NO<sub>2</sub> was 32 µg/m<sup>3</sup>. This inevitably led to a significant increase in NO<sub>3</sub><sup>-</sup>.

SOR and NOR reflect the conversion degrees of SO<sub>2</sub> and NO<sub>2</sub> into SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in the atmosphere, respectively. If NOR and SOR are larger than 0.1, it indicates that sulfates and nitrates are mainly produced by the photochemical oxidation of SO<sub>2</sub> and NO<sub>2</sub>. Therefore, secondary pollution exists [29]. The higher the SOR and NOR, the higher the conversion efficiency. Thus, in this study, the SOR and NOR values were calculated using Equations (2) and (3), with average values of 0.61 and 0.34, respectively. This indicates that the conversion effect of SO<sub>2</sub> was stronger than that of NO<sub>2</sub>.

Usually, with the concentration of particulate matter increasing, SO<sub>2</sub> is more likely to adsorb onto the surface of the particulate matter and undergo various homogeneous and heterogeneous reactions to generate secondary ions [30]. This might be the reason for the higher conversion rate of SO<sub>2</sub> in winter. There is a negative correlation between NOR and temperature [31], leading to a poor conversion of NO<sub>2</sub> under low temperature conditions in winter.

The correlations between various inorganic water-soluble ions in PM<sub>2.5</sub> can reflect the similarity in properties and sources between each ion [32]. NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> had high correlations and the R values were 0.98 and 0.86, respectively (Figure 5). It indicates that these three ions mainly existed in the forms of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> [32,33].

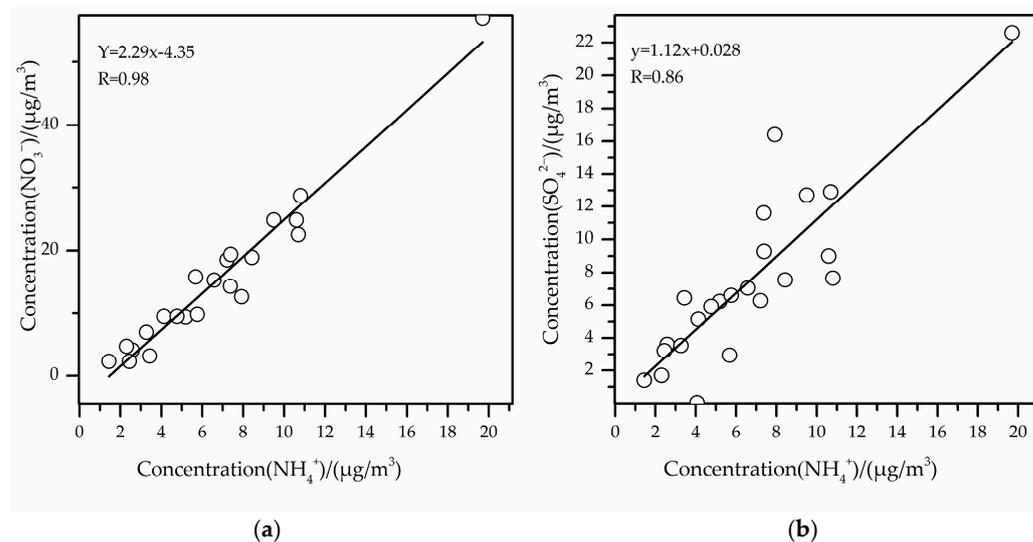


Figure 5. The correlations between NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> (a), NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> (b).

The NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ratio could reflect the situation of vehicle exhaust and fixed combustion sources to some extent [31]. If the NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ratio is larger than 1, it indicates that the effect of vehicle exhaust is more obvious than that of fixed combustion sources; if the NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ratio is less than 1, it suggests that the contribution of fixed combustion sources is greater than that of vehicle exhaust [18]. The average ratio of NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> was 2.06, suggesting that there were more sources to PM<sub>2.5</sub> emissions from vehicle exhaust compared to fixed combustion sources in the winter in Shaoxing.

### 3.4. Characteristics of Metal Elements

The mass concentrations and proportions of metal elements in PM<sub>2.5</sub> are shown in Table 2. K had the highest proportion, followed by Fe and Si. The background values of soil elements in Zhejiang Province [34] were selected to calculate the enrichment factors of metal elements, as shown in Figure 6. The EF values of Na, Ca, K and Cd were greater than 10, indicating that the impact of human activities was obvious and enriched these elements.

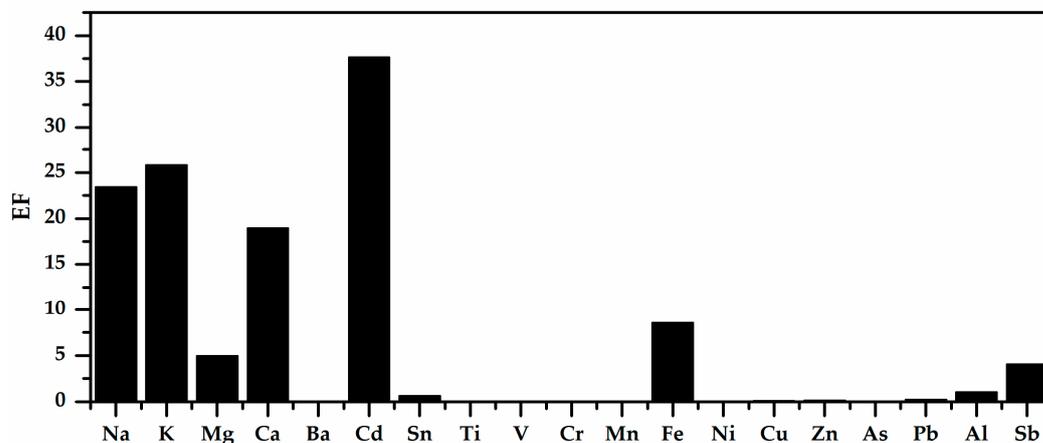


Figure 6. The EF values of metal elements.

**Table 2.** The mass concentrations and proportions of metal elements in PM<sub>2.5</sub>.

Metal Element	Mass Concentration (µg/m <sup>3</sup> )	Proportion in Metal Element (%)	Proportion in PM <sub>2.5</sub> (%)
K	0.514	10.72%	1.14%
Fe	0.300	6.26%	0.66%
Si	0.284	5.92%	0.63%
Na	0.159	3.31%	0.35%
Ca	0.152	3.16%	0.33%
Al	0.109	2.27%	0.24%
Zn	0.084	1.76%	0.19%
Pb	0.058	1.21%	0.13%
Cd	0.055	1.15%	0.12%
Mg	0.045	0.95%	0.10%
Ba	0.039	0.81%	0.09%
Mn	0.030	0.62%	0.07%
Sn	0.027	0.56%	0.06%
Sb	0.024	0.50%	0.05%
Cr	0.016	0.34%	0.04%
Ti	0.015	0.31%	0.03%
Cu	0.011	0.22%	0.02%

The sources of K were consistent with K<sup>+</sup> and might come from coal or biomass combustion. Coal or biomass combustion belong to anthropogenic sources. Na, Fe, Al and Si were crustal elements, mainly derived from crustal sources such as ground dust and soil fly ash. Although most of Fe came from crustal sources, it might be also influenced by human activities, such as steel smelting. In this study, the EF value of Na was greater than 10, indicating that crustal sources have caused Na to be enriched. Similarly, Ca was an indicator element for building construction [35]. The construction dust in Shaoxing has also enriched Ca. The EF value of Fe was less than 10, suggesting the influence of anthropogenic sources was weak. It indicates that Fe in PM<sub>2.5</sub> in Shaoxing was mainly from crustal sources.

Except for the above elements, the EF values of the other elements were all less than 10, indicating that they were not enriched.

### 3.5. PM<sub>2.5</sub> Sources Analysis

The positive matrix factorization (PMF) model was used to analyze the PM<sub>2.5</sub> sources in winter in Shaoxing. Based on the stability of the PMF analysis results, seven factors were identified as the optimal components spectra for various compounds in PM<sub>2.5</sub> (Figure 7).

The main contributions of factor 1 were Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, which were inferred as the dusts from construction sites and roads. The main contributors to factor 2 were NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, which were secondary nitrates. The main contributor to factor 3 was L-glycan, which was inferred as biomass combustion [36]. Factor 4 was characterized by Cl<sup>-</sup>, which was believed to mainly come from coal combustion in addition to natural sources. Therefore, factor 4 was inferred as the coal-fired source. Factor 5 was characterized by OC and EC, which were related to motor exhaust emissions. It also enriched metal elements such as Mn, Zn, Fe and Cu, which were related to industrial production activities [37]. Therefore, factor 5 was inferred as industrial sources and automotive exhaust. Factor 6 was characterized by Ti, Al and Si, which was inferred as soil dust. In this study, the dusts included road dust and construction dust, which belonged to man-made dust. The main contributors to factor 7 were NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, which were secondary sulfates.

Among them, factors 1 and 6 were both related to the dusts, and factors 2 and 7 represented secondary inorganic salts. Thus, these factors were merged. As a result, the sources of PM<sub>2.5</sub> in Shaoxing were simplified into five categories: coal combustion, dust, biomass combustion, motor vehicle exhaust and industrial sources and secondary inorganic salts.

Figure 8 shows secondary inorganic salts had the highest proportion to PM<sub>2.5</sub> in winter in Shaoxing, with a contribution value of 49.3%. The proportions of motor vehicles and industrial sources and dust sources were 21.3% and 17.0%, respectively. Biomass burning also made a contribution, accounting for 7.79%, perhaps because of the biomass burning in autumn and winter in Shaoxing.

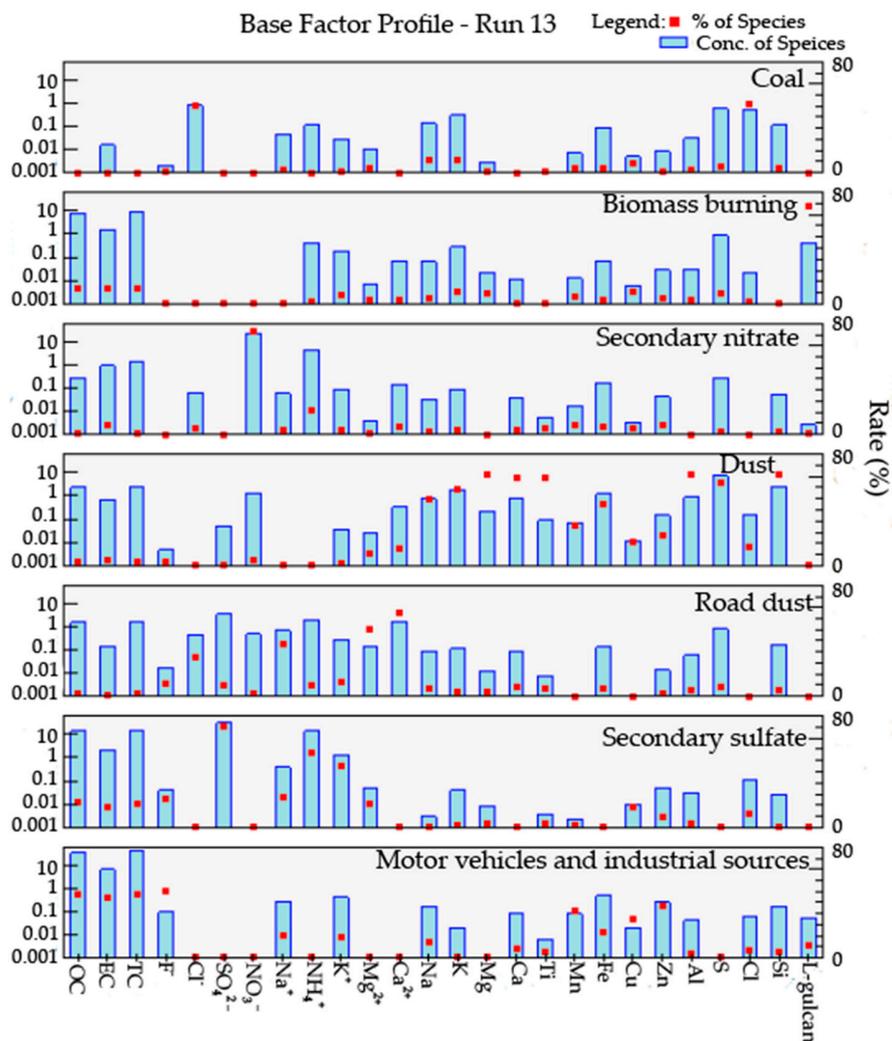


Figure 7. Factor profiles (% of species) of each source for the PMF model for PM<sub>2.5</sub>.

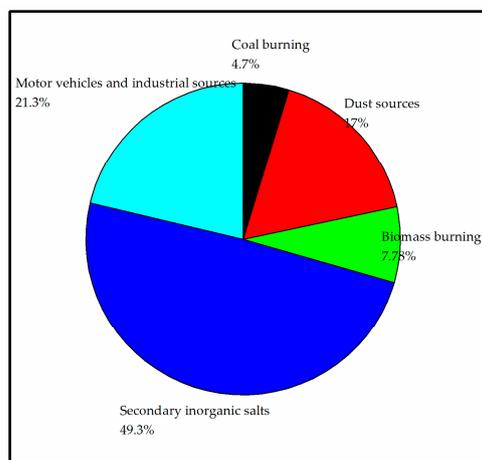


Figure 8. The result of sources analysis.

#### 4. Conclusions

A total of 25 groups of PM<sub>2.5</sub> samples were collected to analyze the components in Shaoxing in winter. During the sampling period, the average concentration of PM<sub>2.5</sub> was 45.3 µg/m<sup>3</sup>. There was an obvious pollution phenomenon. The chemical composition of PM<sub>2.5</sub> in winter was mainly composed of water-soluble ions and carbon-containing components.

Among all water-soluble ions, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> were three main components accounting for 63.4% totally of PM<sub>2.5</sub>. These three ions mainly existed in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub>. Through the calculation of SOR and NOR, it could be found that a considerable portion of NO<sub>2</sub> and SO<sub>2</sub> in the air was converted into NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The secondary conversion was very obvious. Based on the ratio of NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup>, it could be determined that the impact of vehicle exhaust on PM<sub>2.5</sub> pollution was more obvious than that of fixed combustion emission.

OC was the main component among the carbon-containing components. The OC/EC ratio was 3.27, indicating secondary aerosols existed in PM<sub>2.5</sub>. After calculation, the average concentration of SOC was 3.54 µg/m<sup>3</sup>, accounting for 47.8% of OC. The proportion of SOC in OC was relatively high.

The concentrations of metal elements in PM<sub>2.5</sub> were relatively low compared with carbon-containing components and water-soluble ions. However, the EF values of Na, Ca, K and Cd exceeded 10, indicating that these elements were obviously enriched due to human activities.

Finally, this study used the PMF model to analyze the sources of PM<sub>2.5</sub> in Shaoxing in winter. The result indicated that the PM<sub>2.5</sub> primary source was secondary inorganic salts (49.3%), followed by motor vehicles and industrial sources (21.3%) and dust sources (17.0%).

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