Pollution Characteristics and Sources of Fine Particles During a Heavy Haze Episode in Winter: A Case Study of Weinan City

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Abstract. Single Particle Aerosol Mass Spectrometry (SPAMS) is used to investigate a heavy haze process in Weinan, 2017. Firstly, the fine particles (PM₂.⁵) using ART-2a was analysed and clustered into 8 classes: organic carbon (OC), organics and elemental carbon combined particles (ECOC), elemental carbon (EC), heavy metal (HM), high molecular organic carbon (HOC), K-rich, levoglucosan (Lev) and dust. Secondly, positive matrix factorization (PMF) was used to identify the sources of PM₂.⁵. Results from PMF showed that the main six sources of PM₂.⁵ were coal-fired (38.48%), secondary (19.19%), biomass burning (15.04%), industry (9.28%), traffic (5.02%), and dust (5.00%). And it is obvious that the major cause of the atmospheric heavy haze is an unfavorable meteorological conditions such as high humidity and low wind speed, as well as coal-fired pollution and secondary pollution caused by heating and industrial production.

1. Introduction
PM₂.⁵ pollution has become an increasingly serious environmental challenge in recent years, with the rapid development of industrialization and urbanization in China. PM₂.⁵ with many toxic and harmful components can stay in the atmosphere for a long time, which has a direct and important impact on human health and environmental quality [1]-[3]. Therefore, China has been making many efforts in air pollution control. There are already many scholars to analyze characteristics, formation mechanism of haze episodes in Guangzhou [4], Beijing [5], Shanghai [6], Xi’an [7] and other places, from different angles.

However, in the traditional research methods, most of the atmospheric particulate matter is collected through the filter membrane, and then carried out various chemical composition analysis [8]. This method has a long sampling time, a large amount of sample demand and low time resolution. Therefore, it is unable to reflect the concentration variation characteristics of trace elements in one day and it is difficult to judge sources and evolution processes of particle matters. SPAMS is capable of detecting the particle size and corresponding chemical composition of individual particles with very high time resolution, which avoids changes of sample properties on the monitoring results [9]. It was widely applied in the field of characterizing emission sources [10], physical and chemical properties [11], and mixing states of particulate matter [12].

Weinan is one of eleven cities in the Fenwei Plain, which is listed as a key area for air pollution control in 2017. It is the main thoroughfare of the Central Plains to Shaanxi and even the northwest
area, and is also an important part of the New Eurasia Continental Bridge as well as the starting point of the Silk Road Economic Belt. In 2017, it was reported that annual average concentration of PM$_{2.5}$ reached 68µg/m$^3$ in the Fenwei Plain, in which the Weinan is one of the most polluted areas, its air quality has been ranked in the back all the time. However, there were few studies on the Weinan, and most of studies previously focused on megacities like Xi’an, Guangzhou, Shanghai and so on. Chen et al. (2016) used SPAMS to analyze the chemical composition and mixing state of urban PM$_{2.5}$ in Xi’an during winter haze period [13]. Hu et al. (2017) analysed mixing state of aerosol during different fog/haze pollution episodes in Nanjing [14]. Zhang et al. (2014) analysed source and mixing state of iron-containing particles in Shanghai by individual particle analysis [15]. Therefore, in order to investigate the source and characteristics of particulate pollution in Weinan more quickly, accurately and in real-time, we selected the severe pollution process in Winter, Weinan as the subject. Based on SPAMS, supplemented by PMF and HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) mode, analyzes the chemical composition, pollution characteristics and sources of PM$_{2.5}$.

2. Experimental methods

2.1. Field measurements

In this study, the SPAMS-0525 was used to monitor the chemical composition of PM$_{2.5}$. The observation site (34°29′42″ N, 109°27′32″ E) is on the ground level in the Weinan Normal University. The site is surrounded by residential communities, exists serious non-point source pollution. There are high traffic carrying pressure around the site. The observation time is from 11/27/2017 to 12/8/2017. The data such as PM$_{2.5}$ mass concentration and meteorological parameters come from the national control site.

2.2. Analysis method

The sample data from the SPAMS-0525 were imported into the SPAMS Data Analysis V3.0 software run in Matlab 2012b for analysis. An adaptive resonance theory based neural network algorithm (ART-2a) was applied to cluster the particles by setting some parameters including a vigilance factor of 0.75, a learning rate of 0.05, and 19 iterations [16]. Then, based on the characteristics of data quality and elements, we screened the samples and chemical components involved in the simulation, and a total of 216 environmental samples were included in the PMF model, excluding several components that do not have significant source traceability, and including Al$^+$, Ca$^+$, Cl$^-$, Fe$^+$ and NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, SiO$_2^-$, K$^+$ plasma and chemical components after ART-2a classification. Finally, the HYSPLIT model was used to simulate possible origins of air masses. The meteorological data select the relevant data in the GDAS database (Global Data Assimilation System). Forty - eight - hr backward trajectories were calculated every 6h (0:00; 6:00; 12:00; 18:00), and the trajectory simulation starting height is set to 500 meters.

3. Results and discussion

3.1. Overall pollution status

During observation, we have collected 635,803 particles. Among them, 182,587 particles were successfully attacked and analyzed. The analysis rate was 28.72%. The PM$_{2.5}$ concentrations agreed well with the particulate matter collected and successfully measured numbers by SPAMS ($R^2$=0.733, see Figure 1). Thus, we believed that the data collected by SPAMS can reflect the pollution status of PM$_{2.5}$ in the atmosphere at that time.

Figure 2 shows the time series of meteorological conditions from 11/27/2017 to 12/8/2017. It can be seen that the southwesterly wind was dominant from 11/29/2017 to 12/842017. The relative humidity (RH) was in the high ranges (RH>59%), the wind speed was below 1.2 m/s, and the weather is static. Severe on occurred near the ground. At 1:00 on December 3, the highest concentration of PM$_{10}$ was 394 µg/m$^3$, the concentration of PM$_{2.5}$ was over 250 µg/m$^3$. During this period, PM$_{2.5}$/PM$_{10}$
concentrated on more than 60%, the air pollution was serious. From 9:00 to 12:00 on December 4, the wind direction changed from north to southeast in Weinan, the wind speed was higher than 3.5 m/s, the RH was getting lower. At the same time, the air pollution improved significantly.

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure 1.** Correlation between hourly size particles by SPAMS and hourly mass concentration of PM$_{2.5}$.

**Figure 2.** Time series of meteorological conditions from November to December 2017.

3.2. Chemical composition analysis of PM$_{2.5}$

Combined with the PM$_{2.5}$ data (Figure 1) and the HYSPLIT4 model (Figure 3), the observation period is divided into the pollution period (15:00, 11/27 to 12:00, 12/4) and the clean period (12:00, 12/4 to 10:00, 12/8). After data processing, it was determined that Lev, k-rich, OC and ECOC particles were the main types of PM$_{2.5}$ in Weinan in winter, accounting for 74.80%. Secondary ion components appear frequently in the spectrum of the particles, indicating that the particles have undergone different secondary reactions or mixed with secondary components in varying degrees [17].

In Figure 4(a), the OC showed the peaks m/z=27,37,43,63 and so on. The peaks of C$_2$H$_4$O$^+$ / C$_3$H$_5$N$^+$ (m/z=43) is the characteristic peak of SOA generated by photochemical reaction [18]. In Figure 4(b), EC has C$_n^+$ peaks in the positive spectrum. In the negative spectrum, the organic nitrogen, nitrates and sulfates had obvious signal peaks, it shows that the EC is once discharged into the atmosphere and mixed with the secondary components to rapidly age. In Figure 4(c), ECOC was dominated by elemental carbon peaks and organic carbon peaks. We believed that volatile organic compounds (VOC) present in the air can be converted into semi-volatile oxygenated organic compounds by photochemical oxidation reaction. Then the ECOC is formed. In Figure 4(d), the K-rich showed a significant peak of K$^+$. The nitrate and sulfate peaks were seen in the negative spectrum. It has been accepted that K$^+$ is a tracer of biomass burning. Therefore, these are derived from biomass burning [19]. In Figure 4(e), the HM showed the typical m/z of metal ion in the positive spectrum, such as Na$^+$, K$^+$, Fe$^+$, and Pb$^+$. Cl$^-$ peaks were observed in the negative spectrum. The HM was mainly from industrial emissions. In Figure 4(f), the HOC was dominated by low molecular organic carbon peaks in the positive spectrum. The particles containing signals of peaks (m/z = 163, 178, 202, 228). The negative spectrum was dominated by m/z = -26, -45 peaks. The sources of HOC are possibly from polycyclic aromatic hydrocarbons produced by biomass burning [20]. In Figure 4(g), the Lev mainly contains a fragment peak generated by thermal cracking of cellulose, such as the m/z=45, -59, -73 peaks, which is derived from biomass burning. In Figure 4(h), the dust showed signals of Al$^+$, Fe$^+$, Ca$^+$ and Mn$^+$ in the positive spectrum. In the negative spectrum, SiO$_3^-$ and SiO$_2^-$ peaks were observed. It is the same as the dust spectrum in most studies [21].

3.3. Analysis of source of PM$_{2.5}$ pollution

3.3.1. Backward trajectory analysis. It can be seen from Figure 5(a) that during the period from 11/25
to 11/27, the reverse trajectory of Weinan City is short, the wind speed is small, and the diffusion conditions are poor. The pollutants are mainly from the south to the west, from Hubei and Chongqing to Hanzhong, Shangluo Xi’an and other places arrived in Weinan. Weinan is located in the Guanzhong Basin. High south and north terrain, low middle terrain. When the high concentration pollutants in the southern region are transported into the unfavorable meteorological conditions with high RH, strong temperature, and low wind speed, these result in a regional cumulative pollution process in calm weather. It can be seen from Figure 5(b) that the trajectory becomes longer after 48h in December 2 to 4, the wind speed becomes larger, the wind direction changes. The air mass is mainly from the northwestern direction of Weinan, and is passed by Xinjiang, Gansu and other places, finally arrived in Weinan. The high air currents above 500 meters are frequent, the boundary layer is elevated, and the atmospheric diffusion conditions are better.

![Figure 3](image-url)  
*Figure 3. Time series of particulate mass concentrations, percentage of main types of particles observed and source.*

![Figure 4](image-url)  
*Figure 4. Average mass spectrograms for the top eight particle types.*

3.3.2. PMF source analysis. As shown in figure 6. Factor a has the highest contribution rate to OC, reaching 65.98%, which is considered to be a characteristic component of coal combustion [22]. The contribution rate to secondary ions [SO$_4^{2-}$, NO$_3^-$], Cl$^-$, and Br is also large. Therefore, it is determined to be coal-fired source. Factor b contributes a lot to metal elements such as Pb, Li, Ti, and Al. It is determined to be industrial source. The contribution of factor c to EC particles was up to 90.66%. And it has a significant contribution to the secondary ions and dust. It is determined as source of traffic. The contribution of factor d to secondary inorganic ions SO$_4^{2-}$, NO$_3^-$, NO$_2^-$ and NH$_4^+$ is 17.43%, 24.27%, 26.51%, and 50.55%. The contribution to ECOC is very high. It is determined as secondary inorganic ions and secondary organic substances generated by photochemical reactions, which can be determined as secondary sources. The contribution rate of factor e to Lev is very high at 54.93%. At
the same time, the contribution to Qxalic, CNO\(^{-}\), K\(_2\)Cl\(^{-}\) plasma contained in biomass itself is higher than other factors, and it is determined as biomass burning source. The characteristic elements of factor f are crust elements such as Al, Si, Ca, Fe, etc., and the contribution rate to dust is also quite large, and it also contributes to EC and OC. This factor represents the multi-mixed secondary source characteristics of the dust source. Therefore, it is determined to be dust source.

According to PMF analysis, the sources of particulate matter pollution and their proportions were coal-fired (38.48%), secondary (19.19%), biomass burning (15.04%), industrial (9.28%), traffic (5.02%), dust (5.00%), and others (7.98%). Among them, coal-fired, secondary and biomass burning are the three major pollution sources in the local area, totaling 72.71%.

It can be seen from figure 3 that the main types of pollution period are Lev, K-rich, ECOC, and OC, accounting for 25.78%, 23.02%, 12.73% and 12.73%. The contribution of secondary and coal-fired is 34.86% and 22.83%, which is the main cause of serious particulate pollution. This result is related to the start of the winter heating period in Weinan.

![Image](image.png)

**Figure 5.** The 48-hour backward air trajectories of 25\(^{th}\), November and 48\(^{th}\), December.

![Image](image.png)

**Figure 6.** Contribution of the six pollution sources resolved by PMF model.

4. **Conclusion**

This paper studies a severe pollution process in Weinan from 11/27/2017 to 12/8/2017. We use SPAMS, combined with PMF model and HYSPLIT model to explore the chemical composition, pollution characteristics and the sources of PM\(_{2.5}\) in the pollution process. The results are as follows:

1. The main chemical components in PM\(_{2.5}\) include EC, ECOC, HM, HOC, K-rich, Lev, OC, and SiO\(_{2}\). These eight kinds of particles have aged for a certain period of time.
2. The air mass during the heavy haze episode mainly came from Hanzhong and Shangluo in the southwest of Weinan. Unfavorable meteorological conditions and special topography with high north, south and low middle caused the accumulation of this pollutant.
3. Coal-fired, secondary, and biomass burning are the three major sources of air pollution in Weinan in winter. This is related to the winter heating in Weinan, the large amount of SO\(_2\) emissions from the gas precursor and the accumulation of secondary pollutants.
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