Chemical characteristics and source apportionment of PM$_{2.5}$ in a petrochemical city: Implications for primary and secondary carbonaceous component

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**Abstract**

To study the pollution features and underlying mechanism of PM$_{2.5}$ in Luoyang, a typical developing urban site in the central plain of China, 303 PM$_{2.5}$ samples were collected from April 16 to December 29, 2015 to analyze the elements, water soluble inorganic ions, organic carbon and elemental carbon. The annual mean concentration of PM$_{2.5}$ was $142.3 \mu g/m^3$, and 75% of the daily PM$_{2.5}$ concentrations exceeded the $75 \mu g/m^3$. The secondary inorganic ions, organic matter and mineral dust were the most abundant species, accounting for 39.6%, 19.2% and 9.3% of the total mass concentration, respectively. But the major chemical components showed clear seasonal dependence. SO$_4^{2-}$ was most abundant specie in spring and summer, which related to intensive photochemical reaction under high O$_3$ concentration. In contrast, the secondary organic carbon and ammonium while primary organic carbon and ammonium significantly contributed to haze formation in autumn and winter, respectively. This indicated that the collaboration effect of secondary inorganic aerosols and carbonaceous matters result in heavy haze in autumn and winter. Six main sources were identified by positive matrix factorization model: industrial emission, combustion sources, traffic emission, mineral dust, oil combustion and secondary sulfate, with the annual contribution of 24%, 20%, 24%, 4%, 5% and 23%, respectively. The potential source contribution function analysis pointed that the contribution of the local and short-range regional transportation...
had significant impact. This result highlighted that local primary carbonaceous and precursor of secondary carbonaceous mitigation would be key to reduce PM$_{2.5}$ and O$_3$ during heavy haze episodes in winter and autumn.

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Introduction

The rapid industrialization and urbanization have led to the increasing air pollution in China in recent decades. Severe haze episodes, which are defined as the weather pollution phenomenon with the horizontal visibility of less than 10 km due to dense accumulation of fine particulate matter (particles with an aerodynamic diameter smaller than 2.5 μm, or PM$_{2.5}$), were frequently observed, especially in the megacities or dense regions (An et al., 2019). It seemed to copy the trajectories of many developed countries. However, it was different from the London and Los Angeles smog which was predominantly caused by the coal burning or photochemical oxidation of the automobile exhaust (Zhang et al., 2015). Haze pollution in China is more complicated, where the types of pollutants change from the traditional total suspended particulate matter (TSP) and inhalable particulate matter (PM$_{10}$) to the composite air pollution formed by the fine particulate matter (PM$_{2.5}$) and gaseous pollutants (O$_3$, SO$_2$, and NO$_x$). Intensive studies focused on the mega cities and some developed regions in China, such as Beijing-Tianjin-Hebei region, Yangtze River Delta and Pearl River Delta, which were characterized by a long duration and wide range with extremely high concentrations of PM$_{2.5}$ (An et al., 2019). Those studies found that the primary particles emitted directly into the atmosphere and the secondary particles produced by the gas-to-particle conversion in atmosphere jointly contributed to the PM$_{2.5}$ formation (Huang et al., 2019; Huang et al., 2014a; Sun et al., 2013; Wang et al., 2016). SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ are the main components of secondary inorganic aerosols, and their concentration are related to the level of their gaseous precursors (SO$_2$, NO and NH$_3$) and the rate at which they are converted into particles in the atmosphere. Sulphur and nitrogen oxidation ratio are used to estimate the degree of secondary formation of Sulphur and nitrogen (Behera and Sharma, 2010), they are usually affected by temperature and humidity, meanwhile these three ions also interact with each other (Baek et al., 2004; Saraswati et al., 2019), therefore it is an important way to explore the complexity of air pollution by considering the time series characteristics and evolution rules of water-soluble ions. Severe regional haze now become a serious problem in China, which is relevant to the air quality, human health, climate and ecosystems. However, the occurrence of extreme haze is both a challenge and an opportunity for us. Through the study of multiple sources of the particulate matter, formation of secondary pollution process, regional transport and the impacts of meteorological conditions in different cities and regions, the understanding of the haze problem and the processes of the atmospheric chemistry and physics can be improved.

To solve the increasingly severe haze concern, China has made series of measures to reduce the emission of pollution sources. Those short-term control measures had achieved remarkable results during the international events, such as the Beijing Olympic Game (Xu et al., 2016), Shanghai Expo (Huang et al., 2013), APEC 2014 (Xu et al., 2019), Nanjing Youth Olympic Game (Zhou et al., 2017) and some special events like fireworks regulation in Spring Festival (Yao et al., 2019). However, those emergency measures could not really solve the haze problem because of the complexity of the haze pollution. An effective and sustained pollution control plan is needed to solve the problem completely. Therefore, the long-term monitoring of the regional haze is very important to reveal the formulation of haze. A relatively accurate composition spectrum was obtained by off-line analysis of the chemical composition in PM$_{2.5}$, which would improve the understanding of the aerosol transformation process in haze episodes. In addition, the off-line data facilitated us to identify representative monitoring sites as well as improve the local model parameterization.

Luoyang, which suffered from severe haze problem recently years, is located in Fenwei Plain and adheres east to the North China Plain (Liu et al., 2018). The terrain in the southwest is higher than that in the northeast, which makes it more difficult for particles to diffuse from Beijing-Tianjin-Hebei region and transmit in the horizontal direction. In addition, Luoyang is the second largest economy production city in Henan province, with a population of around 3.4 million in urban and an area of 194 km$^2$. The GDP was $49 billion and its secondary industry was $25 billion in 2015. The total energy consumption was 16 Mt of the standard coal equivalent and the amount of vehicle was 0.71 million by the end of 2015 (jiang et al., 2017). The high intensity of the local industrial emissions and traffic pollution could contribute to the formation of the haze pollution. There are several publications available over the NCP regions on source apportionment study recently, however, most of studies concentrated on the megacities such as Beijing, Tianjin, Shijiazhuang and Xi’an(Cui et al., 2020; Huang et al., 2017b; Ji et al., 2018; Wang et al., 2015). Though Luoyang is not as developed as these cities above, the air pollution problem it faced was quite serious. Therefore, systematic studies on PM$_{2.5}$ in Luoyang is significant and urgent. Through a comprehensive analysis for inorganic ions, carbonaceous materials and elements, a whole year field experiment was carried out to explore the emission sources of the pollutants, chemical composition characteristics, reasons on formation of haze and the factors of meteorological conditions. That would improve the understanding of the local haze pollution and provide scientific basis for reasonable control and supervision measures in the future.
1. Materials and methods

1.1. Sampling

To collect the particulate matter samples with spatial and temporal representation, filter sampling was conducted at five sites of Luoyang, taking into account the characteristics of different functional areas in Luoyang (Fig. 1). SZ is located on the rooftop of six-story building within the Luoyang Environmental Protection Agency (15m above ground), which is in the middle part of Luoyang. DX is located in the western part of Luoyang, which is surrounded by several industrial areas. YX is located in the eastern part of Luoyang, which is a main residential area. SW was conducted at the new urban districts with good conditions of afforestation, located in the south of the city. XLD is in a scenic area of reservoir, on the north edge of Luoyang. Based on the seasonal characteristics of the particle matter emission sources and the periodic variation pattern of the meteorological conditions, representative receptor samples in spring, summer, autumn and winter were collected in April, July, October and December, respectively. Relevant sampling information was listed in the supplementary materials (Table S1).

Daily PM$_{2.5}$ samples were collected on quartz filters by TH-150 medium volume air samplers (Wuhan Tianhong Ltd., China) from 9:00 a.m. to 8:00 a.m. (23 hr) at a flow rate of 100 L/min (Wang et al., 2017). All quartz filters were prebaked at 450°C for 4 hr. Before and after sampling, the filters were conditioned at 23 °C and relative humidity of 50% for 48 hr and then weighted and stored at -18°C until pretreatment.

1.2. Chemical analysis

The chemical analysis processes were described in the previous research (Kong et al., 2015). A quarter of each PM-laden filter was cut for the digestion with an acid mixture (6 mL HNO$_3$ + 2 mL H$_2$O$_2$ + 0.6 mL HF) using microwave digestion system. As, Be, Cd, Co, Cr, Cu, K, Mn, Na, Ni, Pb, V and Zn were measured by inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500a). Al, Ba, Ca, Fe, Mg and Ti were analyzed by inductively couple plasma-optical emission spectrometer (ICP-OES, Agilent). The pretreatment by ultrasonic extraction was performed to make sure the water-soluble inorganic ions (WSII) on filter could dissolve into the deionized water, and then the extract liquid that through a 0.22 μm membrane pore aims to remove the impurity, before analyzed by the ion chromatograph system (Dionex ICS-1100, USA). Eight species of the WSII were analyzed, including Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, SO$_4^{2-}$ and NO$_3^-$.

A 0.495 cm$^2$ punch area from the filter was applied for the detection of organic carbon (OC) and elemental carbon (EC), by using a thermal/optical carbon aerosol analyzer (DRI Model 2001A, USA), the method was described in detail in the reports by Chow et al. (2007), and the secondary organic carbon was calculated by Eq. (5), more details could find in previous study (Ji et al., 2019).

An external calibration method was adopted to calibrate the instrument before and after the analysis of elements. By repeated analysis of the same sample three times, the reproducibility of extraction concentration was investigated (Xie et al., 2019). The correlation coefficients of the work curves for all analyzed elements reached above 0.999. Before the analysis of eight ions, the standard curve was made by external

Fig. 1 – (a) Map showing Luoyang and (b) the PM$_{2.5}$ sampling site, windrose with PM$_{2.5}$ concentrations.
standard solutions (Merck, Germany) with the correlation coefficients greater than 0.999. The relative standard deviation was less than 5% for the reproducibility test (Huang et al., 2016). During the measurement of OC and EC, the sucrose and potassium acid phthalate standard solutions were used to establish the calibration curve of the analyzer semiannually (Xin et al., 2015). Field blanks were analyzed with the samples, and reproducibility tests were performed by a duplicate sample analysis every ten samples. The concentrations of gaseous species (SO$_2$ and NO$_2$) were recorded from the website of China National Environmental Monitoring Center (http://www.cnemc.cn/), and the meteorological data including ambient temperature (T), relative humidity (RH), wind speed (WS), wind direction (WD) and barometric pressure (P) during sampling time were obtained from the website https://www.data.cma.cn/. The relevant information is shown in Fig. S1.

1.3. Data analysis methods

The chemically reconstructed mass concentration of PM$_{2.5}$ including mineral dust (MD), trace elements (Trace), secondary inorganic aerosol (SIA), organic matter (OM), EC and unidentified matter (UN) was calculated according to the previous study (Kong et al., 2015; Xie et al., 2019) as follows:

\[
\text{MD} = \text{Ca} \times 1.95 + \text{Al} \times 1.89 + \text{Mg} \times 1.67 + \text{Ti} \times 1.67 + \text{Mn} \times 1.59 + \text{Fe} \times 1.43 + \text{Na} \times 1.35 + \text{K} \times 1.21 
\]

(1)

\[
\text{Trace} = \text{As} + \text{Cd} + \text{Cr} + \text{Cu} + \text{Ni} + \text{Pb} + \text{V} + \text{Zn} 
\]

(2)

\[
\text{SIA} = [\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{NH}_4^+] 
\]

(3)

\[
\text{OM} = \text{OC} \times 1.6 
\]

(4)

\[
\text{SOC} = \text{OC} - \text{POC} = \text{OC} \times (\text{OC} / \text{EC})_{\text{min}} 
\]

(5)

where, (OC/EC)$_{\text{min}}$ is the minimum ratio of OC/EC in each season. The enrichment factor was calculated to differentiate the natural sources or anthropogenic sources of elements according to the following equation:

\[
EF_i = \frac{(E_i / E_r)_{\text{PM}_{2.5}}}{(E_i / E_r)_{\text{Crust}}} 
\]

(6)

where, $E_i/E_r$ is the concentration ratio of a target elements ($E_i$) to the reference element ($E_r$). Reference elements are the plentiful species in the crust and not susceptible to anthropogenic influence. In this study, Al was chosen as the reference elements (Zheng et al., 2019).

1.4. Positive matrix factorization

PMF is an effective source apportionment receptor model that does not require the source profiles prior to the analysis and has no limitation on the source numbers (Bressi et al., 2014). The principles of PMF were described elsewhere in detail (Paatero and Tapper, 1994). In this study, EPA PMF 5.0 model was performed by inputting the data of chemical species, which were pre-tested and validated: Finally, 21 species (15 elements, 4 ions, OC and EC) were used. After testing the PMF results between 4 and 8 factors, the six factors were chosen by comparing PMF factor profiles, and the F peak value was set as -0.5, based on the Displacement and Bootstrap-Displacement results.

1.5. Backward trajectory, potential source contribution functions (PSCF) analysis

The air mass backward trajectories for 24 hr were calculated at the sampling site (112.45°E, 34.62°N) by using the HYSPLIT-4 model. By starting the height at the altitude of 500 m, the model was run once for each hour during the sampling periods. The cluster analysis was based on the 24 hr backward trajectories and categorized into four clusters for each season. The PSCF analysis was used to explore the potential geographic origins of PM$_{2.5}$. It can probability describe the trajectories with pollutant concentrations over the threshold reach the receptor site (Polissar et al., 1999). The PSCF model are defined as:

\[
\text{PSCF}_{ij} = \frac{m_{ij}}{n_{ij}} 
\]

(6a)

\[
\text{WPSCF}_{ij} = W(n_{ij}) \times \text{PSCF}_{ij} 
\]

(7)

where, $n_{ij}$ represents the total number of end points falling in the i,jth cell; $m_{ij}$ is designated as the number of “polluted” end points in the same cell; (Zheng et al., 2019). To reflect the uncertainty, the calculated values were modified by a weighting function $W(n_{ij})$:

\[
W(n_{ij}) = \begin{cases} 
1.00 & n_{ij} > 3n_{ave} \\
0.703 & 1.5n_{ave} > n_{ij} > 1.5n_{ave} \\
0.40 & 0.5n_{ave} > n_{ij} > n_{ave} \\
0.17 & n_{ij} < 0.5n_{ave} 
\end{cases} 
\]

(8)

where, $n_{ave}$ is the average number of trajectory end points.

2. Results and discussion

2.1. Annual and seasonal mass concentrations of PM$_{2.5}$

The temporal dynamic of PM$_{2.5}$ mass concentration is shown in Fig. 2. The annual average concentration of PM$_{2.5}$ was 142.3 $\mu$g/m$^3$, which was approximate two times the Chinese National Ambient Air Quality Standard (GB3095-2012, 75 $\mu$g/m$^3$). Compared to European, American and Southeast Asia cities in the same period, such as Malaysia (Khan et al., 2016), Oporto of Portugal (Custodio et al., 2016) and Alberta of Canada (Landis et al., 2019), it was 4–18 times higher than those cities (Table S2). Moreover, it showed clearly higher concentration than domestic megacities in the south of China, such as Nanjing and Shanghai, which consistent to the decrease trend form north to south in a previous study (Zhang et al., 2012). However, compared to the cites in Fenwei Plain and Beijing-Tianjin-Hebei regions, the annual mass concentration was
comparable to Zhengzhou (jiang et al., 2017), a megacity near Luoyang, and other three megacities (xi’an (niu et al., 2016), Beijing (huang et al., 2017c), shijiazhuang (xie et al., 2019)). the results indicated that severe haze pollution was still a big concern in this densely populated city with developed industrial, though lots progresses have been made in the megacities by Chinese government.

the daily average concentrations of PM$_{2.5}$ were 90.5, 91.7, 190.8 and 204.3 μg/m$^3$ for spring, summer, autumn and winter, respectively. It showed highest in the winter, followed by autumn, and lowest in the spring and summer (Fig. 2). The seasonal pattern has been intensively documented in most cities of northern China, especially in North China plain (liu et al., 2018). Generally, the disadvantage meteorological conditions, such as the relative humidity (RH: 58%), average mixing layer height (MLH: 240 m), and wind speed (WS: 2.1 m/sec) in this study (Table 1), were significantly related to PM$_{2.5}$, and were conductive to PM$_{2.5}$ accumulation in wintertime (Table S3). In contrast, higher MLH (587 m) and frequent rainfall were facilitated to PM$_{2.5}$ diluted or wet deposition in the summertime. In addition, the lower average ventilation coefficients (VC) in the winter and autumn (655.7 and 705.3 m$^3$/sec, respectively) and higher VC in the spring and summer (1002.4 and 1032.7 m$^3$/s, respectively) also support to this seasonal variation. However, compared to the cities in Fenwei plain and Beijing-Tianjin-Hebei regions, the average mass concentration in autumn and winter were clear high in this study (Table S4), which was most likely attributed to higher PM$_{2.5}$ emission from primary or secondary formation due to the higher ratio of PM$_{2.5}$ to VC (zheng et al., 2019).

2.2. Temporal and spatial variation of chemical components

Temporal dynamics mass concentration of chemical components of PM$_{2.5}$ during the sample period are illustrated in Fig. 3. The annual mean secondary inorganic aerosol (SIA), carbonaceous materials (OM + EC) and elements (MD + Trace) accounted for 39%, 23% and 9% to PM$_{2.5}$, respectively. This was consistent to most cities of Fenwei Plain and Beijing-Tianjin-Hebei region, while the mass concentration and fractions of major chemical components showed clear seasonal variation (Fig. 3).

2.2.1. Water-soluble ions

Most water-soluble ions showed the same seasonal pattern as PM$_{2.5}$ variation, that was higher concentration in autumn and winter. SIA accounted for a large proportion of PM$_{2.5}$ in Luoyang, this is similar to previous studies of other megacities in Beijing-Tianjin-Hebei region (Beijing: 44%, Tianjin: 44%, Handan: 40%). NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ showed the maximum value in winter with values of 26.52, 28.59 and 25.42 μg/m$^3$ for NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$, respectively. The minimum value of NO$_3^-$ and NH$_4^+$ was exhibited in summer with value of 8.83 and 0.06 μg/m$^3$, respectively (Fig. 4). The proportion of SO$_4^{2-}$ was the largest in summer (22%), which was related to the high oxidant concentration and temperature in summer. The strong photochemical reaction promotes the secondary formation of sulfuric acid, making it the main pollutant in summer. It was worth noting that SO$_4^{2-}$ showed a high concentration level throughout the sampling period, reaching 20.74 μg/m$^3$, especially in summer when the other ion concentrations were usually low. The same seasonal variation was also observed in other cities, while the difference was in the concentration level and the dominant species. For example, the annual concentrations of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ were 16.6 μg/m$^3$22.4 μg/m$^3$ and 11.4 μg/m$^3$ in an industrial city in the north, while the dominant specie in SIA was NO$_3^-$ (18.0 μg/m$^3$) in Shanghai. In a semi-arid and petrochemical-industrialized city, the annual concentrations of NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ were 7.9 μg/m$^3$, 8.2 μg/m$^3$ and 5.3 μg/m$^3$ respectively. This indicates that the formation of pollutants in the

![Fig. 2 – Mass concentration of PM$_{2.5}$ in different seasons. Boxes and whiskers mark the 5th, 25th, 50th, 75th and 95th percentiles.](image-url)

**Table 1 – Meteorological parameters during the sampling period.**

<table>
<thead>
<tr>
<th></th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Annual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>2.90 ± 1.67</td>
<td>19.61 ± 2.07</td>
<td>27.09 ± 2.08</td>
<td>15.15 ± 3.47</td>
<td>16.60 ± 9.30</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>57.67 ± 17.74</td>
<td>59.20 ± 12.58</td>
<td>74.95 ± 8.16</td>
<td>67.40 ± 16.19</td>
<td>65.64 ± 15.46</td>
</tr>
<tr>
<td>Pressure (hPa)</td>
<td>988.46 ± 3.71</td>
<td>974.91 ± 4.22</td>
<td>967.02 ± 2.70</td>
<td>981.41 ± 3.18</td>
<td>977.58 ± 8.86</td>
</tr>
<tr>
<td>Wind speed (m/sec)</td>
<td>2.14 ± 1.28</td>
<td>1.96 ± 0.51</td>
<td>1.74 ± 0.60</td>
<td>1.99 ± 0.75</td>
<td>1.95 ± 0.83</td>
</tr>
<tr>
<td>Mixing layer height (m)</td>
<td>240.35 ± 127.42</td>
<td>513.55 ± 90.60</td>
<td>587.15 ± 101.78</td>
<td>335.49 ± 123.77</td>
<td>422.09 ± 178.92</td>
</tr>
<tr>
<td>Ventilation coefficient x</td>
<td>655.70 ± 820.43</td>
<td>1002.41 ± 308.35</td>
<td>1032.69 ± 433.14</td>
<td>705.27 ± 465.46</td>
<td>848.84 ± 557.64</td>
</tr>
<tr>
<td>PM$_{2.5}$/VC</td>
<td>0.85 ± 0.78</td>
<td>0.09 ± 0.03</td>
<td>0.11 ± 0.06</td>
<td>0.37 ± 0.26</td>
<td>0.35 ± 0.50</td>
</tr>
</tbody>
</table>

*Ventilation coefficient (m$^3$/sec) is calculated by: VC = MLH × WS, while MLH is mixing layer height and WS is wind speed.*
atmosphere of different cities are different, due to the social factors, atmospheric conditions and geographical locations.

The sulfur oxidation and nitrogen oxidation rates (defined as SOR = nSO3^- / (nSO4^- + nSO2) and NOR = nNO3^- / (nNO2^- + nNO3)) in four seasons, as shown in Fig. S3, were calculated to estimate the secondary inorganic production rate (Sun et al., 2006). The SOR in decreasing order for each season was 0.66 (summer), 0.39 (autumn), 0.34 (winter and spring), which were far more than 0.1, indicating that strong photochemical oxidation occurred, especially in summer. Interestingly, positive correlation was observed between SOR with RH ($r = 0.57$, $p < 0.01$, Fig. S2) and temperature ($r = 0.62$, $p < 0.01$, Fig. S2), NOR was only weak correlated to RH ($r = 0.31$, $p < 0.01$).

The highest concentration of Cl^- was 7.7 $\mu$g/m^3 in winter, accounting for 3%, which was much higher than the contribution in other seasons (0.6–3.1 $\mu$g/m^3, 1–2%). K^+ was a tracer of the biomass burning (Huang et al., 2014b) with the concentration of 10.4 $\mu$g/m^3 in winter and 5.2 $\mu$g/m^3 in autumn. These two ions were generally considered as tracers of the coal consumption and biomass burning and exhibited the season-dependence with the high concentration in heating seasons.

2.2.2. Carbonaceous species

The mass concentration of OC and EC had clearly seasonal variations (Fig. 3). The maximum of OC and EC occurred in winter with values of 28.42 and 11.31 $\mu$g/m^3, respectively, and minimum appeared in summer with values of 4.94 and 2.44 $\mu$g/m^3, respectively. OC and EC totally occupied 23% of annual mass concentration of PM$_{2.5}$ in Luoyang, which was the second predominant component (Fig. 3). That is in the range of 20–50% in China (Huang et al., 2017a; Tan et al., 2017; Zheng et al., 2019). Clearly, the proportion of carbonaceous materials in Luoyang was lower, compared to other megacities, like Beijing (44%), Xi’an (35%), Shanghai (50%) and Guangzhou (38%) (An et al., 2019). The seasonal variation of OM and EC were similar to that of PM$_{2.5}$. OM and EC are the dominant species in winter (45.47 and 11.8 $\mu$g/m^3, 23% and 5% of PM$_{2.5}$). The increase of coal and biomass combustion for household heating in winter led to the emission of large
amount of carbonaceous pollutants, meanwhile, the low temperature in winter is conducive to the formation from semi-volatile organic compounds.

2.2.3. Mineral dust and elements
As shown in Fig. 3, the concentration of mineral dust in spring is relatively high, contributing 20% to PM$_{2.5}$, which is significantly higher than the other three seasons (4%-13%). K as a tracer of biomass burning (Huang et al., 2014b), had a high level in spring and winter, which may be related with the increase of open biomass burning emission in the two seasons. The enrichment factor showed that Cd as a tracer of industrial processes (Zong et al., 2016), was the highest (Fig. S3b) with the value exceeding 1000 in all seasons. The elements of Zn, Pb, Cu, As, Ni and Cr ranged from 10 to 1000, indicating severe anthropogenic activities’ contributions like vehicle emission or industrial coal combustion (Tian et al., 2015). The rest elements ranged from 1 to 10, indicating that the dusts emitted from extensive constructions contributed largely to the composition of PM$_{2.5}$ in Luoyang.

2.2.4. Spatial distribution of chemical components
The annual mean concentration of PM$_{2.5}$ in five sites were 153.1, 153.7, 150.7, 150.3 and 133.3 µg/m$^3$ for YX, DX, SW, SZ and XLD, respectively. The mass concentration of PM$_{2.5}$ in four urban sites were higher than that in the suburban site (XLD), but there is no significant difference in the concentration of four urban sites. The spatial distribution of chemical components in PM$_{2.5}$ are shown in Table S5, the concentration of OC, EC, SO$_4^{2-}$ and crust elements like Ca, Al and Fe were relatively higher in YX site, this might because YX located in the residential area, with high contributions from vehicles and cooking activities. For most parts of components, the rural site (i.e., XLD) had a lower concentration than urban sites, however, the concentration of NO$_3^-$ and SO$_4^{2-}$ in XLD were in a high level in five sampling sites. Besides, it was noteworthy that SO$_4^{2-}$ was the dominant species in YX, DX and SZ in terms of SO$_4^{2-}$ and NO$_3^-$, while in SW and XLD, the average annual mass concentration of NO$_3^-$ and SO$_4^{2-}$ were in the same level. The concentration of OC, EC and Cl$^-$ were the lowest in XLD, which means the pollution level from primary emission was lower than other sites, while the highest concentration of NO$_3^-$ indicated that the pollution of secondary inorganic aerosols was severe in this site. For inorganic elements, the concentration of potassium was the highest in SW site, this might because it located in the south of Luoyang closing to the farming area.

2.3. Mechanisms for the evolution of pollution episodes
Haze episodes analysis was employed to understand possible mechanisms during the haze evolution process in this study. Fig. 5 shows the pollution classes in the observation period
Fig. 6 - (a) $\text{SO}_4^{2-}$ concentrations and SOR at different levels of each season, (b) $\text{NO}_3^{-}$ concentrations and NOR at different levels of each season, (c) the value of $\text{SO}_4^{2-}$ / EC in different periods, (d) the value of $\text{NO}_3^{-}$ / EC in different periods.

were divided into four categories according to the daily concentration of PM$_{2.5}$: clean days (PM$_{2.5}$ < 75 $\mu$g/m$^3$), slightly polluted days (75 $\leq$ PM$_{2.5}$ < 150 $\mu$g/m$^3$), moderate polluted days (150 $\leq$ PM$_{2.5}$ < 250 $\mu$g/m$^3$), heavily polluted days (250 $\mu$g/m$^3$ $\leq$ PM$_{2.5}$).

In spring and summer, the peak of PM$_{2.5}$ was relatively low compared to that in autumn and winter, there were only slightly haze episodes in these two seasons. During slightly polluted days, the dominant specie in both spring and summer was SO$_4^{2-}$, which accounted for 23% and 43% of the total mass, respectively. It was worth noting that the contribution of OM decreased gradually with the increase of pollution level. The increased concentration of SO$_4^{2-}$ may come from homogeneous reaction or heterogeneous reactions. In spring and summer, SOR increased by 0.07 and 0.19 from clean to slightly polluted days, in order to eliminate meteorological factors effect, EC-scaled SO$_4^{2-}$ also was calculated (Fig. 6). The ratios increased by 0.49 and 0.9 as polluted level increased. This pointed to the secondary formation contributed to the increased SO$_4^{2-}$ in these two seasons. Meanwhile, high O$_3$ concentration in the spring and summer give support to high SO$_4^{2-}$ may come from enhanced photochemical reaction of gaseous SO$_2$ under high atmospheric oxidation capacity (Xie et al., 2019).

Compared to spring and summer, the increase of OC and NH$_4^+$ was significant and the concentration of EC increased gradually with the enhancement of pollution level in autumn, but not for NO$_3^{-}$ and SO$_4^{2-}$. The results suggested the enhanced role of enhancing organic carbon accompany with ammonium formation as pollution level increased occurred in autumn. The contribution of carbonaceous aerosols was more prominent in autumn, it can also emitted directly from primary emissions and generated from volatile organic compounds (VOCs) oxidation (Kanakidou et al., 2005). Secondary organic carbon was estimated by using the EC-tracer method (Turpin and Huntzicker, 1995). As shown in Fig. 7, both secondary organic carbon (SOC) and primary organic carbon (POC) concentrations increased gradually. With the increase of PM$_{2.5}$ concentration, the SOC contribution to OC increased from 18% (1.1 $\mu$g/m$^3$) to 36% (11.9 $\mu$g/m$^3$). The value of normalized SOC increased from 1 to 10.6 for clean and heavily polluted days. Moreover, the EC-scaled SOC also increased significantly from clean (0.5) to heavily polluted days (1.3). This suggested that aerosol aging or secondary organic aerosol formation was contributed to haze evolution under benefit atmospheric conditions in autumn. In fact, the increase in O$_3$ concentration pointed to the enhancement of secondary formation most likely come from VOCs oxidation process. More interesting, NH$_4^+$ concentration was accompanying as SOC increased, this could be relevant to organic acid formed by atmospheric oxidation process through oxidants (such as O$_3$, •OH) could facilitate to convert NH$_3$•H$_2$O to NH$_4^+$ in the surface of
particles. Our results highlighted that VOCs would be as a priority proxy to synergy mitigation haze and O₃ formation in autumn.

In winter, NO₃⁻, NH₄⁺, Cl⁻, and carbon contents increased markedly as pollution increased (Fig. 5), which related to increasing precursor emissions from coal consumption and the static stability condition (i.e. a low level of MLH and low wind speed). In winter, photochemical reactions were weakened on severe pollution periods with lower value of O₃ (31 μg/m³). Accordingly, the values of NOR did not increase significantly, with the increase of pollution levels, they were maintained at 0.25, it indicated the atmospheric oxidative capacity was stable in winter. In fact, NOR demonstrated only weak correlations with relative humidity (r = 0.31). And the values of NO₃⁻/EC decreased with the increase of pollution level indicated the contribution of heterogeneous reaction might be not a major contribution process. The mass concentration of SOC in winter increased from 3.5 μg/m³ in clean period to 19.7 μg/m³ in heavy polluted days, while the SOC percentage to OC decreased from 51.3% to 41.5% and the EC- scaled SOC also decreased gradually, which indicated the secondary formation of organic aerosols was not significant. In contrast, normalized POC increased by 6.4 times in heavy pollution days compared to clean days, which most likely related to coal combustion for domestic heating. It should be noted that NH₄⁺ also increased as POC increased. It is reported that the particle size of carbonaceous aerosols produced from combustion is usually smaller than 1 μm (Liang et al., 2019), these fine particles are in Aitken nuclei mode and accumulation mode, with the increase of RH, inorganic compositions like NO₃⁻ and NH₄⁺ are conductive to be absorbed and accumulated on the surface of these fine carbonaceous particles with a low temperature (Duan et al., 2005). The cooperative effect of primary carbonaceous species, inorganic compositions and meteorology condition was the dominant factor, which drive the formation of polluted events in wintertime.

2.4. Source apportionment

Six main sources were identified through PMF runs, including industrial emission (IE), mineral dust (MD), combustion source (CS), traffic emission (TE), secondary sulfate (SS) and oil combustion (Fig. 8). Table 2 summarizes the sources apportionment results of the relative contributions of each source to PM₂.₅ in four seasons. The first source, IE is typically characterized by Cr, Cd, Mn, V and Zn, these tracer species have been used to identify industrial pollution (Jain et al., 2017). The seasonal pattern exhibited the highest contributions in winter and autumn, while the lowest in summer. Strengthening the industrial production restriction in these seasons is necessary. The second source is the mineral dust, which is identified mainly by the high loadings of Al, Ca, Fe, Mg and Ti. Al, Ca and Mg are well known as the earth crust elements (Hope, 1994). The time series exhibited the seasonal variations with higher values in spring, its annual proportion of 11.43% was consistent with that of the chemical mass closure as 9%. This consistency verifies the reliability of PMF results to some extent. The combustion source mainly includes coal combustion and biomass burning, characterized by Cl⁻, As, K, OC and EC. Extraordinarily high contribution of Cl⁻ and As associated with fine aerosols in winter is a distinctive feature in China, which is ascribed to the coal combustion (Zhang et al., 2013), meanwhile K is an excellent tracer of biomass-burning aerosols (Amit et al., 2016). The time series of the modeled concentration for combustion sources exhibited the seasonal pattern with the highest value in autumn and winter, while the lowest in spring and summer. It is associated with the increased demands for coal-combustion heating during the heating periods. The fourth source is the traffic emissions, which is characterized by OC, EC, NO₃⁻, Cu, Pb and Zn. These species are all enriched in vehicles and the combustion of fossil fuel emissions (Li et al., 2012). And the seasonal variation is not significant which was similar with Beijing (Zhang et al., 2013). The fifth source is relevant to the secondary aerosols with the high contribution of SO₄²⁻, and the seasonal pattern displayed an extremely high profile in summer (46.53%), this was consistent with the higher SOR in this season. V was regarded as the tracer element for oil combustion, they usually emitted from the incomplete combustion of diesel fuel and metal processing to improve the quality of steel (Waked et al., 2014).

The source apportionment is vital to effectively mitigate the local PM₂.₅ pollution. In this study, the contributions of
Fig. 8 – Profiles of six sources modeled by PMF in Luoyang. (MD: mineral dust; TE: traffic emission; IE: industrial pollution)

Table 2 – Relative contributions from six identified sources of PM$_{2.5}$ in four seasons.

<table>
<thead>
<tr>
<th>Season</th>
<th>Industrial emission</th>
<th>Mineral dust</th>
<th>Combustion sources</th>
<th>Traffic emission</th>
<th>Secondary Sulfate</th>
<th>Oil combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>33.50%</td>
<td>11.43%</td>
<td>2.84%</td>
<td>29.28%</td>
<td>19.24%</td>
<td>3.71%</td>
</tr>
<tr>
<td>Summer</td>
<td>6.75%</td>
<td>0.33%</td>
<td>4.27%</td>
<td>28.62%</td>
<td>46.53%</td>
<td>13.50%</td>
</tr>
<tr>
<td>Autumn</td>
<td>33.05%</td>
<td>1.70%</td>
<td>23.10%</td>
<td>28.85%</td>
<td>11.84%</td>
<td>1.47%</td>
</tr>
<tr>
<td>Winter</td>
<td>20.93%</td>
<td>4.24%</td>
<td>50.29%</td>
<td>9.41%</td>
<td>12.95%</td>
<td>2.19%</td>
</tr>
<tr>
<td>Annual</td>
<td>23.56%</td>
<td>4.23%</td>
<td>20.13%</td>
<td>24.04%</td>
<td>22.64%</td>
<td>5.21%</td>
</tr>
</tbody>
</table>

combustion sources, industrial pollution, the mobile source and secondary sulfate were significant. This was different from the studies in southern city, secondary pollution was the major source in Shanghai and Guangzhou, which contributed more than 60% of the mass of PM$_{2.5}$. Coal combustion, traffic emission and secondary inorganic aerosol were the three dominant sources in Beijing-Tianjin-Hebei region (Huang et al., 2017a; Ji et al., 2018), with the total contributions above 60%. Compared with the source results in other cities (Table S6), the contribution of secondary inorganic aerosols in Beijing was significant, with the highest contribution in surrounding areas and vehicle emission was the second contributor in Beijing. The contribution of combustion and industrial processes were relatively low, this phenomenon was relevant to the control measures in Beijing, which moved the industries and coal-fired power plants to the suburbs. The contribution of coal combustion had tended to increase southward from Beijing to Zhengzhou, which increased from 5.6% to 21.6%. And the contribution of biomass burning in Xi’an was greater than that in other cities. In Luoyang, the contribution of industrial processes was significant with the highest proportion of 23.6% compared to other cities, this indicated that the clean production for industrial processes should be improved in Luoyang. The contribution of four main sources (Secondary aerosols, Coal combustion, Industrial processes and Vehicle emission) were all above 20%, which indicated the secondary and primary sources were both critical in Luoyang.

2.5. Regional transport

The backward trajectories were calculated in four seasons and gathered into four clusters (Fig. S4). In spring, the west and east air masses (i.e., Shanxi province and Zhengzhou) contributed 33.47% and 33.05%, respectively. Contrast to spring, predominate air mass came from the northeast in summer (35.89%) and winter (53.60%) and south in autumn (30.73%).
Combined with PSCF analysis, the potential pollution origins of PM$_{2.5}$ in different seasons are shown in Fig. 9. In spring, the areas with high WPSCF values (WPSCF$>$0.6) were larger than the other seasons, mainly located in surrounding areas such as eastern Luoyang and southern Shanxi Province, these both belong to the Fenwei-Plain. The high WPSCF result areas of OC, EC and SO$_4^{2-}$ were consistent with the spatial distributions of PM$_{2.5}$, these components were usually associated with petrochemical and combustion source emissions. In summer, a more extensive area was also found in west and north parts of Henan for OC, which indicated there was sufficient fossil fuel carbon combustion transport. WPSCF results area was relatively small for SO$_4^{2-}$ in summer, meanwhile in the WSII section, we showed that the SOR was extremely high in Luoyang for this season. Thus, the local formation of sulfate during summer is critical. In autumn and winter, the areas with high values were mainly located in central and north of Henan, a transmission route linking southern Hebei, northern Henan and western Henan was obvious, as fact, this region was an important industry source for PM$_{2.5}$ in north China (Xie et al., 2019). The results showed that the potential pollution origins covered Anyang-Xinxiang-Zhengzhou-Xuchang area as well as the local parts of Luoyang, which all belong to the central plain urban agglomeration, exhibiting severe haze pollution in those districts (Liu et al., 2019). The results revealed that the air quality was mostly affected by local emissions as well as partly from Fenwei channel in spring and partly from Beijing-Tianjin-Hebei channel in the other seasons of the central urban agglomeration. Therefore, it’s critical to strengthen the overall regional joint prevention and treatment.
3. Conclusions

The annual average concentration of PM$_{2.5}$ was 142.3 $\mu$g/m$^3$ in Luoyang, and the proportion of pollution days was approximately 75% in 2015. The high concentrations of PM$_{2.5}$ and frequent occurrence implicated that haze pollution was extremely severe in Luoyang, especially in autumn and winter. For the compositions, the secondary inorganic ions, organic matter and mineral dust were the most abundant species, accounting for 39.6%, 19.2% and 9.3% of the total mass concentration, respectively. In spring and summer, only slightly polluted episodes were observed, and SO$_4^{2-}$ was the major component contributing 20% and 22% to the total mass of PM$_{2.5}$, respectively. The enhanced photochemical reactions were the main contributor to the high fraction of SO$_4^{2-}$ under a high O$_3$ concentration in these two seasons. Contrast to spring and summer, an increase in the proportion and concentration of carbonaceous matters and NH$_4^+$ were significant in autumn and winter. However, the contribution of SOC was significant with an increasing trend of O$_3$ in autumn, while POC was most contribution to the formation of heavy haze episodes in wintertime. This indicated that the collaboration effect of secondary inorganic aerosols and carbonaceous matters result in heavy haze in autumn and winter. By utilizing the PMF model with these components data, six sources were identified, among which industrial pollution, combustion sources, traffic emission, mineral dust, oil combustion and secondary sulfate were the main sources in Luoyang, with the annual contribution of 24%, 20%, 24%, 4%, 5% and 23%, respectively. Seasonally, the contribution of mineral dust, mainly consist of road dust and construction dust, was significant in spring (11%). Secondary sulfate was the main source in summer, which accounted for 47%. In autumn, the contribution of industry emission and traffic emission were significant, with the proportion of 33% and 29% respectively. In winter, coal combustion contributed 50%. The backward trajectory of air mass and PSCF analysis showed the transport effect of Fenwei channel was dominant in spring, while the impact of Beijing-Tianjin-Hebei channel was significant in other seasons. However, the hot spots of potential sources of pollution were mainly concentrated in the regions of central plain urban agglomeration, including Luoyang. This result highlighted that the control measures of local primary carbonaceous in wintertime was crucial for PM$_{2.5}$ reduction. Furthermore, the control of precursor for secondary carbonaceous matters in autumn would be beneficial to the reduction of PM$_{2.5}$ and O$_3$.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.11.012.

Reference


Declaration of Competing Interest

None.

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