Quantifying the seasonal variations and regional transport of PM$_{2.5}$ in the Yangtze River Delta region, China: Characteristics, sources, and health risks

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Abstract. Given the increasing complexity of the chemical composition of PM$_{2.5}$, identifying and quantitatively assessing the contributions of pollution sources has played an important role in formulating policies to control particle pollution. This study provides a comprehensive assessment between PM$_{2.5}$ chemical characteristics, sources, and health risks based on sampling data conducted over one year (March 2018 to February 2019) in Nanjing. Results show that PM$_{2.5}$ exhibits a distinct variation across different seasons, which is primarily driven by emissions, meteorological conditions, and chemical conversion of gaseous pollutants. First, the chemical mass reconstruction shows that secondary inorganic aerosols (SIA, 62.5 %) and carbonaceous aerosols (21.3%) contributed most to the PM$_{2.5}$ mass. The increasing oxidation rates of SO$_2$ and NO$_2$ from summer to winter indicate that the secondary transformation of gaseous pollutants is strongly positively correlated with relative humidity. Second, the positive matrix factorization (PMF) method shows that identified PM$_{2.5}$ sources include SIA (42.5%), coal combustion (CC, 22.4%), industry source (IS, 17.3%), vehicle emission (VE, 10.7%), fugitive dust (FD, 5.8%) and other sources (1.3%). The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model and the concentration-weighted trajectory (CWT) analysis are used to further explore different spatial distributions and regional transport of sources. High emissions (10-11 μg·m$^{-3}$) of SIA and CC distribute in Nanjing and central China in winter. Moderate emissions (8-9 μg·m$^{-3}$) of IS and VE are potentially located in the north of Jiangsu, Anhui, and Jiangxi. The PM$_{2.5}$ pollution from long-range transport is attenuated by meteorological conditions and ocean air masses. Finally, the health risk assessment indicates that the carcinogenic and non-carcinogenic risks of toxic elements (Cr, As, Ni, Mn, V, and Pb) mainly come from IS, VE, and CC, which are within the tolerance or acceptable level. Although the main source of pollution in Nanjing is SIA at present, we should pay more attention to the health burden of vehicle emissions, coal combustion, and industrial processes.

1. Introduction
PM$_{2.5}$ is particulate matter with an aerodynamic equivalent diameter less than or equal to 2.5 μm, and one of the most important air pollutants, which can affect air quality (Sharma et al., 2020), atmospheric visibility (Tseng et al., 2019) and ecosystems (Li et al., 2021). PM$_{2.5}$ can directly enter the human body through the respiratory system and lead to increased health risks (Kumar et al., 2019; Sulaymon et al., 2021). PM$_{2.5}$ concentrations in the United States and Europe have begun to decrease since the 1980s, and those in Japan gradually decreased after 2012 (Zhang et al., 2020). In China, the annual average concentration of PM$_{2.5}$ has decreased by 50% with the implementation of the Air Pollution Prevention and Control Action Plan (APPCAP) in 2013 (Zeng et al., 2019). However, PM$_{2.5}$ pollution levels remain higher than the World Health Organization recommendation (35 μg·m$^{-3}$), and the number of deaths caused by PM$_{2.5}$ exceeds one million per year (Zhu et al., 2020). It indicates that a comprehensive assessment between PM$_{2.5}$ chemical characteristics, sources, and health risks is significant for pollution control measures in the key regions of China.

Understanding the chemical composition of PM$_{2.5}$ is important for formulating control strategies. Sulfate, nitrate, and ammonium (SNA) are the major secondary inorganic aerosols, whose chemical conversion occurs in homogeneous and heterogeneous reactions (Fan et al., 2020; Chow et al., 2022). Variations in the form of SO$_4^{2-}$ and NH$_3$ lead to variations in the acid-base balance of aerosols (Roper et al., 2019). The organic carbon (OC) and elemental carbon (EC) in PM$_{2.5}$ are mainly derived from thousands of organic compounds and primary sources of combustion products (Wu et al., 2020). Both NO$_3$/SO$_4^{2-}$ and OC/EC ratios can be reasonably used to evaluate the contribution of mobile and stationary sources to PM$_{2.5}$ in the atmosphere (Zhan et al., 2021). To identify the sources of PM$_{2.5}$, receptor modelings have been developed, which include positive matrix factorization (PMF), chemical mass balance (CMB), and principal component analysis (PCA) (Zong et al., 2016; Lv et al., 2020). Recently, the combination of the PMF model and trajectory modeling has proven to be powerful to identify source regions and quantify chemical compositions for a receptor site (Zheng et al., 2019). In addition, the health risks of air exposure through the inhalation of PM$_{2.5}$ are beyond acceptable levels (Jiang et al., 2018; Xie et al., 2020). Air exposure models have been widely used to further assess the non-carcinogenic and carcinogenic health risks of toxic elements in PM$_{2.5}$ (Behrooz et al., 2021; Fang et al., 2021; Li et al., 2022).

Chemical characteristics of PM$_{2.5}$ have been widely investigated in the Beijing-Tianjin-Hebei (BTH), the Yangtze River Delta (YRD), and the Pearl River Delta (PRD) during the last decade (Huang et al., 2017; Liu et al., 2017; Sun et al., 2020). Source apportionment studies mainly focus on the relative importance of local emission and regional transportation on PM$_{2.5}$ at a specific site using the PMF model and the backward trajectory analysis (Zheng et al., 2019; Yan et al., 2021; Lv et al., 2022). Compared with other methods, the PMF model can provide both the source profiles and contributions of various sources as a model outcome (Li et al., 2020). Some studies involved the health risks of toxic elements in PM$_{2.5}$ (Zhang et al., 2019; Fang et al., 2021), and only a few studies discussed the classification of toxic elements according to PMF results (Wang et al., 2019; Wang et al., 2020). However, there were two shortcomings in previous studies: (1) Given the uneven geographical distribution of observation sites and difficulties in data collection, most studies were based on short-term data comparisons and lacked systematic comparisons of the distinctive seasonality, regional transport, and meteorological effects.
of various elements and sources. (2) A comprehensive assessment of the health risks of toxic elements in each source of PM$_{2.5}$ was still scarce, which limited the implementation of long-term pollution control measures in megacities.

The YRD region is China's scientific research base and comprehensive transportation hub. The annual PM$_{2.5}$ concentration in the YRD has been reduced by 45.6% from 2016 to 2018. However, as a mega-city in the YRD, the PM$_{2.5}$ in Nanjing still exceeds the National Ambient Air Quality Standard (35 μg m$^{-3}$ as an annual average) by more than 38% (Nie et al., 2018). In this work, we provide high-quality composition data for PM$_{2.5}$ in the typical YRD city, including their chemical characteristics and diurnal variations. Besides, the measured PM$_{2.5}$ in its entirety is successfully apportioned to various contributing sources by PMF and CWT methods. Finally, potential risks associated with exposure to airborne toxic elements are identified based on the health risk assessment. The results can systematically assess the relationship between chemical characteristics, sources, and health risks of PM$_{2.5}$, and serve to guide PM$_{2.5}$ control measures for other megacities.

2. Data and Methodology
2.1 Chemical component sampling, air quality and meteorological data

Hourly concentrations of particulate matter (PM) components from December 2018 to February 2019 in Nanjing were used in this study. The elemental carbon (EC), organic carbon (OC), 30 trace elements (Si, Al, As, Ca, K, Co, Mo, Ag, Sc, Ti, Pd, Br, Te, Ga, Cs, Pb, Se, Hg, Cr, Cd, Zn, Cu, Ni, Fe, Mn, Ti, Sb, Sn, and V) and the 8 inorganic components in aerosols (Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$) were quantified in each PM$_{2.5}$ sample. PM$_{2.5}$ samples were collected on the rooftop of the School of Atmospheric Sciences, Xianlin Campus, Nanjing University (32.12 °N, 118.96 °E). OC and EC were analyzed by the online carbon fraction Monitor (EA-32, Everiseth Co., Beijing). OC and EC were separated by step heating and then determined by the non-dispersive infrared method. The components of heavy metals were collected by the atmospheric heavy metal Monitor (AMS-100, Fpigroup Co., Hangzhou). The volumetric concentration of heavy elements (ng·m$^{-3}$) was obtained by detecting the concentration of PM enriched on the filter membrane using the β ray absorption principle (Wang et al., 2020). The inorganic components sampling instrument was the In-situ Gas and Aerosol Compositions Monitor (IGAC, Fortelice International Co., Taiwan). It consisted of the wet concentric circular tube, the gas gel processor, and the ion chromatograph. The sampling inlet was about 20 m above the ground and the flow rate was 16.67 L·min$^{-1}$. The collected liquid samples were filtered by defoaming and then injected into the ion chromatography analyzers to analyze the ion components from the gases and the aerosols.

Air pollutants, including PM$_{2.5}$, PM$_{10}$, O$_3$, NO$_2$, SO$_2$, and CO, were monitored by the National Environmental Monitoring Center (NEMC) of China. These data were issued hourly on the national urban air quality real-time publishing platform (https://air.cnemc.cn:18007/, last access: 7 April 2023). The detection limits were below 0.12 μg·m$^{-3}$ and the collection efficiency was higher than 90% (Zhan et al., 2021). Meteorological parameters included air pressure, air temperature, relative humidity, wind speed, and boundary layer height. We collected hourly data from the National Climatic Data Center (NCDC) of the University of Wyoming website (http://weather.uwyo.edu/surface/, last access: 7 April 2023).
Regarding boundary layer height, daily sounding vertical profiles were extracted from the national benchmark climate Nanjing station 58238 (32.00 °N, 118.48 °E) and were also acquired from this website. The quality assurance and quality control (QA/QC) procedures were used at each site according to the method of Xie et al. (2016) and Gao et al. (2021). In this study, we defined the blank sampling of atmospheric pollutant data as -999 to facilitate PMF processing. The chemical mass reconstruction method was used to correct potential measurement errors, which was described in detail in Section 2.2. The QA/QC procedures have passed the artificial random inspection of extreme value and time consistency.

2.2 Mass and chemical composition determination for PM_{2.5}

Due to the limitation in sampling location and equipment, the sum of measured species was often lower than the gravimetric mass. Chemical mass reconstruction (CMR) attempted to achieve closure between the gravitational mass and the sum of components and correct potential measurement errors. In this study, the reconstructed result and the gravimetric result exhibited a significant correlation, with a mean R² of 0.93, indicating that the chemical reconstruction method had strong reliability. Following the work of Xu et al. (2021), eight categories of chemical components in chemically reconstructed PM_{2.5} can be expressed as follows:

\[
PM_{2.5} = OM + EC + MD + TM + SO_{4}^{2-} + NO_{3}^{-} + NH_{4}^{+} + Cl^{-} \tag{1}
\]

where OM refers to the organic matter. The OC to OM conversion coefficient at urban sites is 1.6 (Brokamp et al., 2017).

The calculation of mineral dust (MD) is based on crustal element oxides (Yan et al., 2020):

\[
MD = 2.14 \times Si + 1.67 \times Ti + 1.89 \times Al + 1.40 \times Ca + 1.58 \times Mn + 1.43 \times Fe + 1.21 \times K + 1.67 \times Mg \tag{2}
\]

where Si is estimated as multiplying Al in crustal material by a converting factor (3.14) (Zheng et al., 2019). Trace metals (TM) represent the sum of 30 different types of heavy metals:

\[
TM = As + Co + Mo + Ag + Sc + Ti + Pd + Br + Te + Ga + Cs + Pb \\
+ Se + Hg + Cr + Cd + Zn + Cu + Ni + Sb + Sn + V + Ba \tag{3}
\]

2.3 Identification of source by the positive matrix factorization (PMF) model

The positive matrix factorization (PMF) was developed by the Environmental Protection Agency (EPA) and has been widely adopted to classify PM_{2.5} into different factors (Zong et al., 2016). The basic principle of the PMF model was to calculate the weight error of each chemical component in the particulate matter and then determined its main pollution source and contribution rate by the least square method (Paatero and Tapper, 1994). The equation of the PMF model can be expressed as follow:

\[
X_{ij} = \sum_{k=1}^{n} g_{ik}f_{kj} + e_{ij} \tag{4}
\]

where \( X_{ij} \) is the concentration of the \( ij \)th sample; \( g_{ik} \) represents the contribution of the \( ik \)th sample; \( f_{kj} \) represents the mass fraction of the \( jk \)th and \( e_{ij} \) is the residual between the measured mass concentration of the \( ij \)th sample and its analytical
The purpose of the PMF model is to find the minimum Q value with the concentration file and uncertainty file \( u_{ij} \) introduced into the model. The objective function Q is defined as follows:

\[
Q_{ij} = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{X_{ij} - \sum_{k=1}^{p} g_{ik} f_{kij}}{u_{ij}} \right]^2
\]

(5)

where Q is the sum of all sample residuals and their uncertainties u. In this study, the fitting species included 41 types of chemical species of PM\(_{2.5}\) that were selected and validated to ensure that the value of the objective function Q was minimized.

First, we excluded more than 50% of the dataset for species below the method detection limit (MDL) and retained 23 species that were significantly correlated with PM\(_{2.5}\). Second, we calculated the uncertainty (Unc) for each species based on the concentration fraction and MDL (Taylor et al., 2020). Third, different numbers of factors were tested with random seeds in 20 iterations of each run. When the number of factors was set to six, the fitting degree of the model calculation results was the highest, with a correlation coefficient of 0.93, and the species almost showed a normal curve. Finally, the bootstrap (BS) and displacement (DISP), and BS-DISP diagnostic analysis were also used to evaluate the rationality of the apportioned factor profiles and contributions. BS is used to detect and estimate the disproportionate effects of a small set of observations on the solution and also, to a lesser extent, the effects of rotational ambiguity. The value of the F-peak strength was ensured to be 0.5 to eliminate the rotation ambiguity. The mapping for each factor in this study was more than 80% from the BS run, indicating the six-factor solution was appropriate.

2.4 Source apportionment by backward trajectory calculation and CWT analysis

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model was developed by the National Oceanic and Atmospheric Administration (NOAA) and the Bureau of Meteorology Australia to simulate and analyze the movement, deposition, and diffusion of airflow. The reanalysis data with a spatial resolution of one degree and a temporal resolution of 6 h (00:00, 06:00, 12:00, and 18:00 UTC) were obtained from the Global Data Assimilation System (GDAS) (https://rda.ucar.edu/datasets/, last access: 7 April 2023). To locate the potential source areas for the corresponding components, we used the HYSPLIT model to analyze the backward trajectory of airflow from March 2018 to February 2019. 48-hour backward trajectories terminated at a height of 100 m above ground level were calculated at the starting point (32.07 °N, 118.78 °E). Due to the high uncertainty of a single backward trajectory, we drew multiple trajectories and performed cluster analysis. The cluster analysis was a multivariate statistical technique using the Angle Distance algorithm, which could quantify the relationship among the pollution concentrations in each source area (Shu et al., 2017).

The concentration-weighted trajectory (CWT) analysis was further used to determine the relative contribution of different areas. The CWT analysis was conducted by the TrajStat software, which was a GIS (geographic information system) application that enabled the user to visualize and analyze the spatial and meteorological data with multiple data formats
(Feng et al., 2021). In this study, the meteorological data used for the HYSPLIT model and the CWT method remained the same. The CWT method divided the research area into small equal grids, set a standard value for the research object, and defined the trajectory exceeding the standard value as the pollution trajectory. The spatial resolution was 0.5×0.5 (Liu et al., 2018). The CWT method reflected the pollution degree of different trajectories by calculating the weight concentration of the airflow trajectory in potential source areas:

\[ C_{ij} = \frac{1}{\sum_{l=1}^{M} \tau_{ijl}} \sum_{l=1}^{M} C_{l} \tau_{ijl} \]  

(6)

where \( C_{ij} \) is the average weight concentration of grid \( ij \), \( C_{l} \) is the pollutant concentration based on trajectory \( l \) that passes through grid \( ij \), and \( \tau_{ij} \) is the residence time of trajectory \( l \) in grid \( ij \). Similarly, to reduce the uncertainty caused by the smaller \( n_{ij} \), the CWT value is multiplied by the weight function as well (Wong et al., 2022):

\[ W_{ij} = \begin{cases} 1.00 & (80 < n_{ij}) \\ 0.72 & (20 < n_{ij} \leq 80) \\ 0.42 & (10 < n_{ij} \leq 20) \\ 0.05 & (n_{ij} \leq 10) \end{cases} \]  

(7)

where \( n_{ij} \) is the number of trajectories that pass through the \( ij \)-th cell. \( W_{ij} \) is an empirical weight function to reduce the undue influence of small \( n_{ij} \) on the CWT values (Fan et al., 2019). In this study, the CWT value of each identified source derived from the PMF model was calculated.

2.5 Health risk assessment

The human health risk from heavy metals in PM2.5 may occur through exposure to ambient air (Zhang et al., 2019). Based on the PMF analysis, we selected six toxic elements (Cr, As, Ni, Mn, V, and Pb) for the exposure risk assessment. Cr, Ni and As have both carcinogenic and non-carcinogenic effects, Mn and V mainly have non-carcinogenic effects, and Pb mainly produces a carcinogenic effect (Jiang et al., 2018). The non-carcinogenic and carcinogenic risks from the toxic species of PM2.5 were evaluated by the hazard quotient (HQ) and lifetime carcinogenic risk (LCR), respectively. The US EPA human health risk assessment models were used to conduct carcinogenic and non-carcinogenic risk assessments (Khan et al., 2016):

\[ EC_{inh} = \frac{GA \times ET \times EF \times ED}{AT} \]  

(8)

\[ HQ = \frac{EC_{inh}}{RfC_{i} \times 1000 \mu g \cdot mg^{-1}} \]  

(9)
where \( EC_{inh} \) is the average daily exposure concentration of toxic elements inhaled through respiration. \( GA \) is the concentration of toxic elements in each source composition. \( ET \), \( EF \), \( ED \) and \( AT \) are the exposure time, exposure frequency, exposure duration and average exposure time, respectively. \( RfC_i \) is the inhalation reference concentration (mg·m\(^{-3}\)). \( IUR \) is the inhalation unit risk((μg·m\(^{-3}\))\(^{-1}\)). HQ greater than 1 indicated a non-carcinogenic risk to human health. For carcinogenic risk, \( LCR < 10^{-6} \) means no cancer risk, \( LCR \) between \( 10^{-6} \) and \( 10^{-4} \) is acceptable or tolerable, and \( LCR > 10^{-4} \) is intolerable. The exposure parameters were shown in Table 1 (Jiang et al., 2018; Zhang et al., 2019).

### Table 1. Exposure parameters of toxic elements through inhalation route in health risk assessments.

<table>
<thead>
<tr>
<th>Toxic elements</th>
<th>( RfC_i ) (μg·m(^{-3}))(^{-1} )</th>
<th>IUR (mg·m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.0×10(^{-4} )</td>
<td>1.2×10(^{-2} )</td>
</tr>
<tr>
<td>As</td>
<td>1.5×10(^{-5} )</td>
<td>4.3×10(^{-3} )</td>
</tr>
<tr>
<td>Ni</td>
<td>1.4×10(^{-5} )</td>
<td>2.4×10(^{-4} )</td>
</tr>
<tr>
<td>Mn</td>
<td>5.0×10(^{-5} )</td>
<td>—</td>
</tr>
<tr>
<td>V</td>
<td>1.0×10(^{-4} )</td>
<td>—</td>
</tr>
<tr>
<td>Pb</td>
<td>—</td>
<td>1.2×10(^{-5} )</td>
</tr>
</tbody>
</table>

### 3. Results and discussions

#### 3.1 Chemical components, meteorological parameters and diurnal variations

Table 2 shows the seasonal average of chemical components and meteorological parameters from March 2018 to February 2019. In this study, March to May 2018 is defined as spring, June to August 2018 is defined as summer, September to November 2018 is defined as fall, and December 2018 to February 2019 is defined as winter. The concentration of PM\(_{2.5} \) ranged from 6.7 to 234.0 μg·m\(^{-3} \), with an annual average of 68.7 μg·m\(^{-3} \). The order of average concentrations of PM\(_{2.5} \) in each season was winter (113.9 μg·m\(^{-3} \)) > spring (99.1 μg·m\(^{-3} \)) > autumn (38.9 μg·m\(^{-3} \)) > summer (23.7 μg·m\(^{-3} \)). Seasonal variations of PM\(_{2.5} \) were closely related to meteorological conditions. In spring, the wind speed (WS) was higher in spring (3.5 m·s\(^{-1} \)) than those in other seasons. Pearson correlation showed that PM\(_{2.5} \) concentrations were significantly (p<0.01) correlated to WS (\( r=-0.36 \)) in spring. In summer, high boundary layer height (BLH) (520.4m) significantly reduced PM\(_{2.5} \) concentrations. In autumn and winter, PM\(_{2.5} \) showed significant correlations between temperature (\( r=-0.53 \)) and relative humidity (\( r=0.62 \)). High humidity (79.6%) and low temperature (4.9°C) in winter promoted the accumulation of pollutants.

The seasonal variation of anthropogenic emissions also considerably affected PM\(_{2.5} \) concentrations. The order of the major components in PM\(_{2.5} \) was NO\(_3^- \) (20-31%) > SO\(_4^{2-} \) (16-27%) > NH\(_4^+ \) (11-19%) > mineral dust (8-14%) > OM (6-14%) > EC (2-4%) > trace metals (2-3%) > Cl\(^- \) (1-3%). Sulfate, nitrate, and ammonium (SNA) accounted for 60% of the
total PM$_{2.5}$ and were closely related to the secondary transformation of gaseous precursors. The concentration ratio of NO$_3^-$ to SO$_4^{2-}$ (NO$_3^-$/SO$_4^{2-}$) was used to differentiate the relative importance of nitrogen (generally affected by vehicles) and sulfur (normally affected by stationary sources) in the atmosphere (Liu et al., 2019). Over the past few years, the mass ratio of NO$_3^-$/SO$_4^{2-}$ was 2.13 in Ningbo, 1.89 in Hangzhou, and 1.21 in Beijing (Huang et al., 2017; Wang et al., 2018). In this study, the average ratios of NO$_3^-$/SO$_4^{2-}$ in the four seasons were 1.81, 1.20, 2.34, and 1.59, indicating that the contribution of mobile sources was greater than that of stationary sources throughout the year. Carbonaceous aerosols (OM and EC) accounted for 12% and 14% in spring and winter. The large increase in the number of coal fires used for residential heating in winter may increase the abundance of carbon-containing emissions, including OC, EC, and VOCs (Islam et al., 2020). Compared with 2015, the concentrations of OM and EC decreased from 22.9% to 12.8% (Chen et al., 2017). This may be related to policies to control coal combustion and motor vehicle emissions, considering similar meteorological conditions in the two periods.

Table 2. Average of components of PM$_{2.5}$ and meteorological parameters in each season (μg·m$^{-3}$). T, RH, WS, and BLH represent air temperature, relative humidity, wind speed and boundary layer height, respectively.

<table>
<thead>
<tr>
<th>Average concentrations: μg·m$^{-3}$ (component percentages: %)</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>99.1</td>
<td>23.7</td>
<td>38.9</td>
<td>113.9</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>20.5 (20.7)</td>
<td>5.2 (21.9)</td>
<td>7.3 (18.8)</td>
<td>31.5 (27.7)</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>16.9 (17.1)</td>
<td>5.3 (22.4)</td>
<td>9.8 (25.2)</td>
<td>27.2 (23.9)</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>15.1 (15.2)</td>
<td>3.2 (13.5)</td>
<td>7.1 (18.3)</td>
<td>11.5 (10.1)</td>
</tr>
<tr>
<td>OM</td>
<td>11.7 (11.8)</td>
<td>1.6 (6.8)</td>
<td>4.1 (10.5)</td>
<td>11.0 (9.7)</td>
</tr>
<tr>
<td>EC</td>
<td>2.3 (2.3)</td>
<td>0.8 (3.4)</td>
<td>1.6 (4.1)</td>
<td>3.6 (3.2)</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>13.2 (13.3)</td>
<td>2.3 (9.7)</td>
<td>2.7 (6.9)</td>
<td>8.7 (7.6)</td>
</tr>
<tr>
<td>Trace metals</td>
<td>2.7 (2.7)</td>
<td>0.5 (2.1)</td>
<td>0.5 (1.3)</td>
<td>1.6 (1.4)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>2.7 (2.7)</td>
<td>1.6 (6.8)</td>
<td>0.8 (2.1)</td>
<td>1.7 (1.5)</td>
</tr>
<tr>
<td>T (°C)</td>
<td>18.8</td>
<td>27.6</td>
<td>19.4</td>
<td>4.9</td>
</tr>
<tr>
<td>RH (%)</td>
<td>86.5</td>
<td>58.2</td>
<td>73.1</td>
<td>79.6</td>
</tr>
<tr>
<td>WS (m·s$^{-1}$)</td>
<td>3.5</td>
<td>2.9</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td>BLH (m)</td>
<td>469.7</td>
<td>520.4</td>
<td>443.6</td>
<td>419.7</td>
</tr>
</tbody>
</table>

Figure 1 shows the diurnal variation of chemical components in PM$_{2.5}$. The seasonal differences were mainly reflected in the variation in the timing of peak values. The lowest PM$_{2.5}$ concentrations were 94.8 μg·m$^{-3}$ at 17:00 in spring and 120.3 μg·m$^{-3}$ at 14:00 in winter, which were related to the meteorological conditions. In spring (Fig. 1a), the concentration of SNA had obvious diurnal variations. From 6:00 to 18:00, the average concentration of NO$_3^-$ increased from 17.6 to 21.8 μg·m$^{-3}$,
while the average concentration of \( \text{SO}_4^{2-} \) decreased from 23.2 to 15.9 \( \mu g \cdot m^{-3} \). In summer (Fig. 1b), the highest and lowest pollution concentrations were 23.5 \( \mu g \cdot m^{-3} \) at 9:00 and 14.2 \( \mu g \cdot m^{-3} \) at 14:00, respectively. The maximum difference in concentration between day and night was less than 10 \( \mu g \cdot m^{-3} \), indicating the study area was in a relatively stable background field. Generally, high humidity, low wind speed, and low temperature tend to promote the secondary transformation of gaseous pollutants (Chen et al., 2018). In addition, the occurrence time of the daily minimum values of PM\(_{2.5}\) concentrations in winter was earlier than those in spring. The height of the atmospheric boundary layer decreased early in the winter afternoons due to less solar radiation. As shown in Figure 1d, from 18:00 to 23:00, the concentration of SNA increased from 74.5 \( \mu g \cdot m^{-3} \) to 108.7 \( \mu g \cdot m^{-3} \), with increasing rates of 8.5 \( \mu g \cdot m^{-3} \cdot h^{-1} \). The values of PM\(_{2.5}\) in winter were higher at night due to the coal combustion and biomass burning for residential heating (Zou et al., 2017). In summary, compared with the spring and winter, PM\(_{2.5}\) presented similar and relatively flat diurnal patterns in both autumn and summer. Although the seasonal variations of mass concentrations and aerosol compositions were substantially different, the concentrations of aerosol species showed similar diurnal variation patterns during all the sampling days with higher values in the nighttime and early morning, suggesting that the factors driving the diurnal variations were similar.

![Diurnal variations in the major chemical components of PM\(_{2.5}\).](https://doi.org/10.5194/egusphere-2023-489)

**Figure 1.** Diurnal variations in the major chemical components of PM\(_{2.5}\).

### 3.2 Variation of PM\(_{2.5}\) chemical compositions at different pollution levels

Figure 2 presents the PM\(_{2.5}\) concentrations and components at different pollution levels. In this study, it was defined as the clean day (C) when the daily average PM\(_{2.5}\) concentration < 75 \( \mu g \cdot m^{-3} \), the moderate pollution day (MP) when 75 \( \mu g \cdot m^{-3} \) \( \leq \) PM\(_{2.5}\) < 150 \( \mu g \cdot m^{-3} \), and the heavy pollution day (HP) when PM\(_{2.5}\) \( \geq \) 150 \( \mu g \cdot m^{-3} \). As shown in Figure 3a, the WSIIs were largely responsible for the variability in PM\(_{2.5}\). The contributions of SNA in spring and winter were similar, with ratios of 65.0% for clean days, 75.0% for moderate pollution days, and 83.9% for heavy pollution days. With the degradation of air...
quality, the contribution of NO$_3^-$ noticeably increased from 27.5% to 47.8% in spring and from 28.9% to 44.7% in autumn.

To understand the oxidation rates of SO$_2$ and NO$_2$, the sulfur oxidation rate and nitrogen oxidation rate (defined as SOR = SO$_2^+$/(SO$_2^+$+SO$_2$) and NOR = NO$_x^+/$(NO$_3^-$+NO$_2$)) were calculated. The critical value of SOR and NOR in the atmosphere are both 0.1 (Win et al., 2020). The order of the seasonal average NOR was winter (0.21) > spring (0.18) > autumn (0.17) > summer (0.15), while the order of the seasonal average SOR was winter (0.51) > spring (0.43) > autumn (0.42) > summer (0.36). SOR and NOR showed a strong positive correlation with relative humidity, with a correlation coefficient of 0.53 and 0.61, respectively. The increase in relative humidity is conducive to the growth of aerosol moisture absorption and heterogeneous oxidation on the surface of aerosol droplets, which is positively correlated with PM$_{2.5}$ concentrations (Islam et al., 2020). From summer to winter, the NOR and SOR values increased by 40.0% and 41.6%, respectively. Due to the high humidity (79.6%) and low temperature (4.9°C) in winter, meteorological conditions provided favorable conditions for the transformation of gaseous precursors.

Coal combustion, biomass burning, and motor vehicle emissions all lead to a remarkable increase in carbonaceous aerosols (Zhou et al., 2017). As shown in Figure 2b, carbonaceous species also had a significantly enhanced contribution in the colder season compared to the warmer season. The differences in different seasons might be related to the effects of meteorological conditions and source emissions. Pearson correlation showed that the relationships between OM and EC and meteorological parameters (T, RH, WS, and BLH) were not significant (Table 2). To explore the possible pollution sources, it is feasible to study the mass ratio of OC/EC under different pollution levels. OC is generally formed by photochemical reactions or emitted directly. EC is mainly derived from combustion processes (Zheng et al., 2019). The OC/EC mass ratio of motor vehicle emissions (1.1) is lower than that of coal combustion (2.7) and biomass burning (9.0) (Xu et al., 2021). In this study, the OC/EC ratios continuously decreased as air pollution got worse, and the values ranged from 6.1 (C), 4.1 (MP) to 3.9 (HP) in spring, from 6.2 (C) to 4.8 (MP) in autumn and from 4.3 (C), 2.7 (MP) to 1.3 (HP) in winter. The annual average ratio of OC/EC decreased by 56.1% from clean days to heavy pollution days. The variation in the OC/EC ratio was mainly due to the change in traffic and coal emission sources.
Figure 2. Chemical compositions of PM$_{2.5}$ and mass ratio of OC/EC at different pollution levels. “%” represents the proportion of the filter sample quantity at each pollution level out of the total samples.

3.3 Source identification and apportionment

3.3.1 Elemental profile and source apportionment from the PMF model

To further quantitatively determine the source apportionment of PM$_{2.5}$, the EPA PMF5.0 model was adopted. Figure 3 presents the source profiles and relative contributions of six sources to each species, including secondary inorganic aerosol (SIA), coal combustion (CC), industry source (IS), vehicle emission (VE), fugitive dust (FD), and other sources. As shown in Figure 3a, the compositions of SIA were more clear than other sources. NO$_3^-$ and SO$_4^{2-}$ are mainly from the oxidation of NO$_x$ and SO$_x$, while NH$_4^+$ probably comes from the conversion processes between ammonia and sulfuric and nitric acid (Win et al., 2020). Factor 1 was identified as the SIA with distinctly high loads of NH$_4^+$ (66.9%), NO$_3^-$ (61.9%), SO$_4^{2-}$ (63.8%) and Cl$^-$ (55.3%). In Figure 3b, the high proportion of Pb (38.2%) and Se (45.1%) was identified in Factor 2, associating with moderate weighting on As (14.3%), SO$_4^{2-}$ (20.5%), and Cl$^-$ (22.2%). Pb and As are important identifying elements of coal combustion and are used as tracers (Xie et al., 2020). SO$_4^{2-}$ is formed by the photochemical oxidation of sulfur-containing precursors (SO$_2$ and H$_2$S) released by coal combustion (Zong et al., 2016). Factor 2 was relevant to the CC. In Figure 3c, the compositions with large contributions included heavy metal pollutants such as As (42.8%), Pb (33.8%), Cr (61.1%), Zn (58.9%), Cu (59.4%), Fe (38.3%), and Mn (40.1%). As, Pb, Cr, Fe and Mn are related to metal smelting and processing (Fang et al., 2021). Cu, Zn, and OC are used as tracers of a mixed source of traffic and industrial (Wang et al., 2020). However, OC was the major pollutant in the vehicle exhaust while the contribution of OC was not significant in Figure 3c. Cu and Zn in Figure 3c were mainly from industrial process sources. As discussed above, Factor 3 was attributed to the IS. In figure 3d, the higher proportions of Ni (54.7%), V (80.5%), OC (55.4%), and EC (79.8%) in Factor 4 indicated the source of vehicle emission. OC and EC are mainly from the vehicle exhaust, and Ni and V are generally regarded as tracer elements for engine oil combustion (Wu et al., 2020). In addition, Factor 4 also showed a high loading on NO$_3^-$ (20.3%). The combustion of gasoline and diesel is an important source of NO$_x$ and VOCs, which in turn affects the transformation of NO$_3^-$ from gas to particles (Guevara et al., 2021). In Figure 3e, this factor had relatively high proportions of Fe (31.1%), Ti (78.2%), K$^+$ (55.8%), Ca$^{2+}$ (60.5%), and Mg$^{2+}$ (48.3%). Ti, Fe, and Mg are both common crustal elements that can represent the source of mineral dust. K$^+$ and Ca$^{2+}$ are considered to be significant tracers of biomass burning, which have obvious seasonal variations (Tong et al., 2020; Yan et al., 2020). Factor 5 was classified as the FD, including road dust, industrial dust, and soil dust. Factor 6 (Fig. 3f) was unidentified and could be affected by coal combustion, industrial processes, and biomass burning.
Table 3 and Figure 4 show the comparisons of our PMF results with the previous findings. For all studies, the secondary aerosols were the biggest contributor to PM$_{2.5}$ in China from 2014 to 2018. In the YED region, SIA contributed about 42.5% to PM$_{2.5}$ in Nanjing in this study, which was higher than that reported by Sun et al. (2020), while the contributions of CC and IS were lower. However, other sources of PM$_{2.5}$ in different cities were more complicated. In the BTH, IS was crucial source and contributed about 30% of Tianjin and Shijiazhuang (Huang et al., 2017). In contrast, IS in Nanjing contributed only 17.3% of PM$_{2.5}$ pollution. Recent emission control policies in the YRD have had positive effects on reducing industrial pollution. In the PRD, SIA, VE, and biomass burning were identified as the major sources of PM$_{2.5}$. VE showed noteworthy local emission characteristics (Zhou et al., 2017). In this study, CC contributed 22.4% and VE contributed only 10.7% in Nanjing. It is worth noting that the PMF model assumes that source profiles do not change significantly over time and that species do not undergo chemical reactions (Paatero and Tapper, 1994). The human activities under seasonal variations in this study made the actual pollution incompatible with the ideal assumption. For example, emissions from coal combustion in winter increased the contribution of CC significantly in winter (Xu et al., 2021). In addition, the sources of air masses in each season also created uncertainties. All of these required detailed discussions of regional transport conditions in each season.
Table 3. Comparisons of source apportionment among different cities.

<table>
<thead>
<tr>
<th>Location</th>
<th>Time</th>
<th>Main pollution sources (proportion)</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>YRD</td>
<td>Nanjing</td>
<td>2018</td>
<td>SIA (42.5%); Coal combustion (22.4%); Industry source (17.3%)</td>
</tr>
<tr>
<td></td>
<td>Nanjing</td>
<td>2015</td>
<td>SIA (37.8%); Coal combustion (27.2%); Vehicle emission (16.4%)</td>
</tr>
<tr>
<td></td>
<td>Ningbo</td>
<td>2015</td>
<td>SIA (27.6%); Vehicle emission (18.7%); Industry source (19.4%)</td>
</tr>
<tr>
<td>BTH</td>
<td>Beijing</td>
<td>2017</td>
<td>SIA (35.6%); Coal combustion (30.8%); Biomass burning (12.5%)</td>
</tr>
<tr>
<td></td>
<td>Tianjin</td>
<td>2014</td>
<td>SIA (29.2%); Industry source (25.9%); Vehicle emission (15.7%)</td>
</tr>
<tr>
<td></td>
<td>Shijiazhuang</td>
<td>2014</td>
<td>SIA (36.4%); Industry source (29.3%); Vehicle emission (17.9%)</td>
</tr>
<tr>
<td>PRD</td>
<td>Hong Kong</td>
<td>2015</td>
<td>SIA (49.9%); Industry source (13.5%); Biomass burning (10.8%)</td>
</tr>
<tr>
<td></td>
<td>Shenzhen</td>
<td>2014</td>
<td>SIA (30.0%); Vehicle emission (21.6%); Biomass burning (11.5%)</td>
</tr>
<tr>
<td></td>
<td>Guangzhou</td>
<td>2014</td>
<td>SIA (34.6%); Vehicle emission (28.6%); Biomass burning (23.1%)</td>
</tr>
</tbody>
</table>

Figure 4. The annual contribution of each source to PM2.5.

3.3.2 Source identification by backward air mass trajectory analysis

The regional transport of air pollutants exerts a profound impact on local air quality (Shu et al., 2017). Figure 5 shows the quantified contributions of PM$_{2.5}$ with 48-h backward trajectories. In spring (Fig 5a), nearly half of the air masses (cluster a3) stemmed from northern Jiangxi, passed over Anhui Province before arriving at the sampling sites, and had the highest PM$_{2.5}$ average value (127.2 μg·m$^{-3}$). CC from cluster a3 had the highest contribution with mass and percentage contributions being 41.0 μg·m$^{-3}$ and 32.3%, respectively. Considering that the largest coal-fired thermal power plant in Jiangxi was located in the northern city of Jiujian (Wang et al., 2018) and there were many industrial cities located along this pathway, regional transport from these areas would have a potentially high impact on the formation of severe particle pollution in Nanjing. In summer (Fig 5b), the most obvious characteristic of regional transport was significantly influenced by the ocean. Clusters b2 and b3 were relatively clean with low concentrations of PM$_{2.5}$ (28.2 μg·m$^{-3}$ for b2 and 32.4 μg·m$^{-3}$ for b3). These clusters passed over the ocean areas and accounted for more than half of all trajectories. The magnitude of total CC, IS and VE exhibited a descending order from clusters b1 to b3. The dilution effects of clean ocean air masses played a vital role in
particulate pollution. In autumn (Fig 5c), there were the highest concentrations of PM$_{2.5}$ in cluster c1, with an average value of 84.6 μg·m$^{-3}$. CC (23.1%) and IS (27.6%) contributed relatively highly in cluster c1, indicating that regional transport from industrial regions might play an important role. For SIA, the proportion of NH$_4^+$ in these air masses was significantly higher in autumn than those in other seasons (Table 2). As a tracer of the biomass burning source, the increase in the proportion of NH$_4^+$ indicated that air pollution masses were heavily affected by nearby agricultural activities. In winter (Fig 7d), clusters d1 (108.3 μg·m$^{-3}$) and d3 (122.6 μg·m$^{-3}$) originated from Shandong Province and the BTH, accounting for more than three-quarters of the air masses. These air masses, which moved at high altitudes with a slow speed, could have carried abundant air pollutants. Cluster d2 (153.9 μg·m$^{-3}$) was short-distance transport and derived from Jiangsu Province. The contribution of SIA exhibited a descending order from clusters d1 (22.9%) to d3 (43.4%) to d2 (55.5%), corresponding to the transition from long-range transport air masses to short-distance transport air masses.

Figure 6 shows the spatial distribution of the contribution from each source of PM$_{2.5}$ by the CWT method and highlighted the potential geographic origins. For SIA (Fig. 6a), the high levels (10-15 μg·m$^{-3}$) of this source mainly originated from local emissions in Jiangsu and regional transport from Shandong Province. For CC (Fig. 6b), the high emissions (10-11 μg·m$^{-3}$) were distributed in the YRD and central China. The weighted concentration values of CC were lower than those of the SIA. High concentrations near the center area are associated with local sources, while those far away from the center area are indicative of regional transport (Shu et al., 2017). The secondary aerosol source was probably from the accumulation of precursors emitted by local emissions. For IS and VE (Fig. 6c and d), there were no high potential areas for these sources. The moderate weighted concentration values of IS (8-9 μg·m$^{-3}$) were potentially located in the north of Jiangsu, Anhui, and Jiangxi, which were the most important industrial base in China. However, the industrial pollution derived from long-range transport was attenuated by meteorological conditions (Table 2). In addition, after the implementation of relevant control policies, many factories in the YRD were shut down and backward capacities in heavy industries were cut down (Zheng et al., 2019). The potential source regions identified after the source weighting could better reflect the spatial variations of source contribution.
Figure 5. Source contributions to PM$_{2.5}$ grouped by air masses associated with different 48-h backward trajectory clusters. The pie charts show the source contributions for corresponding clusters.
Figure 6. Potential source regions for individual sources of PM$_{2.5}$ identified by the CWT method from March 2018 to February 2019.

3.4 Non-carcinogenic and carcinogenic health risks of toxic metal elements in each source of PM$_{2.5}$

Figure 7 shows the HQ values of non-carcinogenic and the LCR values of carcinogenic risks in PM$_{2.5}$ and their total health risk in each source. For non-carcinogenic risk (Fig. 7a), the order of the average HQ values was Mn(0.47) > Ni (0.32) > As (0.14) > Cr (0.04) > V (0.02). The HQ values of toxic elements were all less than one, which indicated that there was no significant non-carcinogenic risk. However, the summation of five HQ values was higher than one, indicating that the combined exposure to the pollutant class still had adverse effects. The carcinogenic risk (Fig. 7b) posed by Ni ($2.3 \times 10^{-7}$) and Pb ($6.8 \times 10^{-8}$) were lower than $1 \times 10^{-6}$ and could be acceptable. The carcinogenic risk level of Cr ($1.0 \times 10^{-7}$) and As ($1.8 \times 10^{-5}$) were within the tolerance or acceptable level ($1 \times 10^{-6}$-$1 \times 10^{-4}$). Figures 7c and d show the integrated assessment of the source apportionment in toxic elements. IS accounted for the largest proportion of the non-carcinogenic and carcinogenic risk, with the HQ of 0.83 and the LCR of $5.8 \times 10^{-6}$, respectively. Although the PMF results indicated that SIA had the highest contribution to PM$_{2.5}$ (Fig. 4), the health risk results showed that the health risks of toxic elements from IS and CC were much higher than those from SIA. Previous studies showed that coal combustion sources in Beijing, Shanxi, and Jinan had higher respiratory exposure health risks, while the fugitive dust source in Liaoning contained higher levels of Pb, As, and Co (Zeng et al., 2021). It was related to the differences in PM$_{2.5}$ pollution characteristics and source contributions in different cities. The ingestion exposure may result in the potential health risk from IS, CC, and VE. Based
on the implementation of energy conservation and emission reduction policies, the main source of pollution in Nanjing is SIA at present, and the health risk has been alleviated. However, we should pay more attention to the health burden of vehicle emissions, coal combustion, and industrial processes.

Figure 7. Non-carcinogenic (a) and Carcinogenic (b) health risks of toxic elements and their total health risk (c and d) in each source.

3. Conclusions

Identifying and quantitatively assessing the contributions and health risks of pollution sources has played an important role in formulating policies to control particle pollution. We have derived a high-quality PM$_{2.5}$ composition data set, based on a chemical component monitoring from March 2018 to February 2019 in Nanjing. The PMF and back-trajectory results were adopted to investigate the chemical characteristics and regional transports of each source. The health risk assessment was used to explore non-carcinogenic and carcinogenic risks of toxic elements.

The results showed that PM$_{2.5}$ concentrations ranged from 6.7 to 234.0 $\mu$g·m$^{-3}$, with an annual average of 68.7 $\mu$g·m$^{-3}$. Water-soluble ions contributed the most to PM$_{2.5}$. From summer to winter, the increase of NOR and SOR indicated that the secondary transformation of gaseous pollutants was strongly positively correlated with RH. Based on values of NO$_3^-$/SO$_4^{2-}$ and OC/EC ratio, dominant vehicle emission occurred during the heavily polluted period, and the contribution of coal combustion increased in winter. Based on the PMF model, the source variations and health risks were assessed. The
contribution of identified sources (including SIA (42.5%), CC (22.4%), IS (17.3%), VE (10.7%), FD (5.8%), and other sources (1.3%)) had different spatial distributions and seasonal variations. The CWT analysis indicated that high emissions (10-11 μg·m⁻³) of SIA and CC were distributed in the YRD and central China in winter. Moderate emissions (8-9 μg·m⁻³) of IS and VE were potentially located in the north of Jiangsu, Anhui, and Jiangxi. PM$_{2.5}$ pollution from long-range transport was attenuated by meteorological conditions. The carcinogenic and non-carcinogenic risks of toxic elements (Cr, As, Ni, Mn, V, and Pb) mainly came from IS, VE, and CC, which were within the tolerance or acceptable level. Based on the implementation of energy conservation and emission reduction policies, the main source of pollution in Nanjing is SIA at present, and the health risk has been alleviated. However, we should pay more attention to the health burden of vehicle emissions, coal combustion, and industrial processes.

This study provided new insight for PM$_{2.5}$ research between the source apportionment and health risk. The results presented characteristics of chemical components, pinpointed secondary transformation processes leading to the high PM$_{2.5}$ concentrations, revealed spatial variations of source contribution, and provided new references for mega-cities to conduct health risk analysis on air pollution control measures.

Data Availability.

Air quality monitoring data were acquired from the official NEMC real-time publishing platform (https://air.cnemc.cn:18007/, last access: 7 April 2023). Meteorological data were obtained from the University of Wyoming website (http://weather.uwyo.edu/, last access: 7 April 2023). The NCEP FNL data were taken from the NCEP (https://rda.ucar.edu/datasets/, last access: 7 April 2023). These data can be downloaded for free as long as one agrees to the official instructions.

Author contributions.

YZ and MX had the original ideas, designed the research, collected the data, and prepared the original draft. YZ, YL, and RZ performed PMF experiments and carried out the data analysis. MX acquired financial support for the project leading to this publication. TW, SL, BZ, and ML reviewed the initial draft and checked the English of the original paper.

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Competing interests.

The contact author has declared that neither they nor their co-author has any competing interests.
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