Reapportioning the sources of secondary components of PM$_{2.5}$: A combined application of positive matrix factorization and isotopic evidence

Zeyu Sun [a,c,d], Zheng Zong [a,c], Chongguo Tian [a,c,*], Jun Li [b,**], Rong Sun [b,d], Wenwen Ma [a,c,d], Tingting Li [b,d], Gan Zhang [b]

[a] CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai 264003, China
[b] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[c] Center for Ocean Mega-Science, Chinese Academy of Sciences, Qingdao 266071, China
[d] University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- A method to reapportion secondary sources of PM$_{2.5}$ solved by PMF is proposed.
- Utilizing stable isotopes as tracers of secondary components to reapportion
- Biomass burning and vehicle exhausts contribute the most to the secondary source.
- Comparison between improved results and ^{14}C measurements indicates its feasibility.

GRAPHICAL ABSTRACT
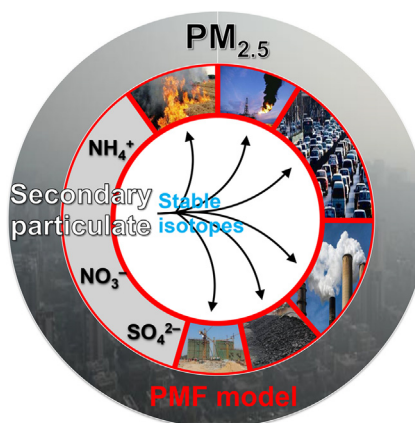
ARTICLE INFO

ABSTRACT

Secondary particles account for a considerable proportion of fine particles (PM$_{2.5}$) and reasonable reapportioning them to primary sources is critical for designing effective strategies for air quality improvement. This study developed a method which can reapportion secondary sources of PM$_{2.5}$ solved by positive matrix factorization (PMF) to primary sources based on the isotopic signals of nitrate, ammonium and sulfate. Actual PM$_{2.5}$ data in Beijing were used as a case study to assess the feasibility and capacity of this method. In the case, 20 chemical components were used to apportion PM$_{2.5}$ sources and source contributions of nitrate were applied to reapportion secondary source to primary sources. The model performance was also estimated by radiocarbon measurement (^{14}C) of organic (OC) and elemental (EC) carbons of eight samples. The PMF apportioned seven sources: the secondary source (36.1%), vehicle exhausts (18.7%), industrial sources (13.6%), biomass burning (11.4%), coal combustion (8.10%), construction dust (7.93%) and fuel oil combustion (4.24%). After the reapportionment of the secondary source, vehicle exhausts (28.7%) contributed the most to PM$_{2.5}$, followed by biomass burning (25.1%) and industrial sources (18.9%). Fossil oil combustion and coal combustion increased to 8.00% and 11.4%, respectively, and construction dust contributed the least. The average gap between contributions of

 * Correspondence to: C. Tian, Yantai Institute of Coastal Zone Research, CAS, China.
 ** Correspondence to: Jun Li, Guangzhou Institute of Geochemistry, CAS, China.
 E-mail addresses: cgtian@yic.ac.cn (C. Tian), junli@gig.ac.cn (J. Li).

identified sources to OC and EC and the ^{14}C measurements decreased $2.5 \pm 1.2\%$ after the reapportionment than $13.2 \pm 10.8\%$, indicating the good performance of the developed method.

1. Introduction

Fine particles (PM$_{2.5}$) attracted significant focus by its strong adverse effects on human health, visibility, and direct or indirect effects on weather and climate (Lu et al., 2015; Pui et al., 2014; M. Tao et al., 2014). Feasible source apportionment of PM$_{2.5}$ is critical for the control strategy of PM$_{2.5}$ pollution. Thus, multiple methods, such as the receptor model (e.g., the positive matrix factorization (PMF), the chemical mass balance, the principal component analysis), 3D numerical simulation and other tracer methods, have been developed and used to assess PM$_{2.5}$ sources (Liang et al., 2016). Among these methods, PMF has been widely used in those studies that quantitatively apportioned sources of PM$_{2.5}$ because it does not need prepared source profiles. Its results indicate that high secondary aerosol usually contributes most to the particulate pollution in China, consistent with the results estimated by other methods (Liu et al., 2019). For instance, secondary components accounted for 51.1%, 73.7%, 77.1% of PM$_{2.5}$ during haze events in the metropolitan Beijing, Shanghai and Guangzhou respectively (Huang et al., 2014). However, the secondary particulate solved by PMF model does not point to an actual type of pollution source, which limits the practical significance for the management and control of air pollution. Therefore, how to apportion these secondary components to primary sources is an urgent problem in the current PM$_{2.5}$ source apportionment.

The secondary components of PM$_{2.5}$ are mainly composed of sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$) and ammonium (NH$_4^+$), which are transformed from the sulfur dioxide (SO$_2$), nitric oxides (NO$_x$), and ammonia (NH$_3$), respectively. These secondary components possess their respective signatures of stable isotopes, which can be used to trace their sources. For example, the N isotopic signature of NO$_3^-$ and NH$_4^+$ was widely used to assess the contribution of coal combustion, mobile sources, biomass burning and biogenic soil emissions (Chang et al., 2019; Felix et al., 2012; Pan et al., 2016; Walters et al., 2015; Zhang et al., 2020); the S isotopes of SO$_4^{2-}$ were also adopted to assess its multitudinous sources (Han et al., 2016; Norman et al., 2006). Thus the isotopic signatures may provide a pathway to further reapportion these secondary components identified by PMF model to primary sources. It is necessary to take the isotopes apportioning results of NO$_3^-$, NH$_4^+$ and SO$_4^{2-}$ into the source analysis of PMF model, and subsequently, apportioning the secondary particulate source to check whether the simulation results are improved.

In this study, we integrated the isotopic source results of NO$_3^-$ into the simulation of source apportionment by PMF with the assumption that NO$_3^-$, NH$_4^+$ and SO$_4^{2-}$ had the same linear proportion of primary source contribution. In addition, specific assessment in Beijing was also made to verify the feasibility. The main aims of this study are (1) to develop a method to embed the isotopic apportioning results of NO$_3^-$, NH$_4^+$ and SO$_4^{2-}$ into the source apportionment of PMF; (2) to reapportion the secondary particulate source in PMF using the isotopic results of NO$_3^-$; (3) to assess the reapportionment performance by the comparison between the apportionment results of carbonaceous components in PMF and ^{14}C measurements.

2. Methods and materials

2.1. Method of source apportionment

2.1.1. Basic source apportionment of PM$_{2.5}$

The EPA PMF 5.0 model was used to apportion sources of PM$_{2.5}$ in this study (Hopke, 2003; Paatero et al., 2014). The factor analysis model of PMF where a data matrix (V) is decomposed into two matrices (W and H) can be written as Eq. (1).

$$V_{ij} = \sum_{r=1}^{p} W_{ir}H_{rj} + e_{ij} \tag{1}$$

where V_{ij} is the concentration of jth component in ith sample; W_{ir} is the relative contribution of the rth source to the ith sample; H_{rj} is the content of jth component in the rth source; p is the number of sources and e_{ij} is the residual. Taking the non-negative elements in W (pollution source load) and H (source profile) as constraint conditions, the PMF algorithm minimizes an objective function (Q_{PMF}) by weighted least square method and the decomposition is performed as Eq. (2).

$$\min Q_{PMF} = f(W, H) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\left(V_{ij} - \sum_{r=1}^{p} W_{ir}H_{rj} \right) / u_{ij} \right]^2 = \left\| \frac{V - WH}{u} \right\|_F^2 \tag{2}$$

where u is the uncertainty matrix, and $\|\cdot\|_F$ is the Frobenius norm.

2.1.2. Reapportionment of secondary sources

The secondary particulate source identified by PMF was apportioned to sources related to fossil fuel combustion, mobile sources and agriculture-related emission (such as biomass burning, agricultural fertilization, and livestock farming) (Li et al., 2016; J. Tao et al., 2014), and other sources in PMF results were also divided into these three parts. Assuming that the relative contribution of sources identified by PMF in each part to the secondary particulate source was the same as that to secondary components in PM$_{2.5}$, the secondary particulate source was apportioned to each source in PMF (taking sources related to fossil fuel combustion identified by PMF as an example) as shown in Eq. (3):

$$\begin{cases} F_1' = F_1 + S \times x_f \times \dfrac{F_1}{\sum_{k=1}^{f} F_k} \\ F_2' = F_2 + S \times x_f \times \dfrac{F_2}{\sum_{k=1}^{f} F_k} \\ \quad \vdots \\ F_f' = F_c + S \times x_f \times \dfrac{F_f}{\sum_{k=1}^{f} F_k} \end{cases} \tag{3}$$

where F and F' refer to the contribution rate (%) of sources in PMF results related to fossil fuel combustion to secondary components before and after the apportionment of secondary particulate, respectively; S is the contribution rate (%) of the secondary particulate source to secondary components in PM$_{2.5}$; f is the number of sources related to fossil fuel combustion identified by PMF, such as coal combustion and industrial sources; x_f is the proportion of secondary particulate source allocated to fossil fuel combustion. The rightmost term of the equation is the ratio that the secondary particulate source was apportioned to the fth source related to fossil fuel combustion. Similarly, the secondary particulate source was apportioned to the sources related to mobile sources and agriculture-related emission sources and the apportionment proportion to each initial source was calculated. The secondary source identified by PMF was further refined.

To find out the proportion of secondary particulate source allocated to fossil fuel combustion, mobile sources and agriculture-related emission sources, it was assumed that the ratio of contribution to each component in the secondary particulate was the same as that to NO$_3^-$. Then the apportionment results of atmospheric NO$_3^-$ based on the nitrogen isotope were

introduced, which were derived by the improved Bayesian mixing model (Zong et al., 2017). The model considered four sources: coal combustion (C), mobile sources (M), biomass burning (BB), and biogenic soil emissions (BSE) and the fractionation of the equilibrium/Leighton reaction was merged into MixSIR (Moore and Semmens, 2008). For minute calculation methods and model frames of the Bayesian mixing model (Zong et al., 2020), readers should refer to the SI Text S4.

Sources identified by the improved Bayesian mixing model were also divided into three parts same as the sources in PMF for the combining of the two models: coal combustion belonged to fossil fuel combustion and biomass burning as well as biogenic soil emissions were merged into agriculture-related emission sources. NO_3^- concentrations for each part followed an equal relationship as expressed by Eq. (4).

$$
\begin{cases}
\sum_{r=1}^{f} W_{ir}H_{rj} + x_f W_{iSP}H_{SPj} = N_C \\
\sum_{r=1}^{m} W_{ir}H_{rj} + x_m W_{iSP}H_{SPj} = N_M \\
\sum_{r=1}^{a} W_{ir}H_{rj} + x_a W_{iSP}H_{SPj} = N_{BB} + N_{BSE}
\end{cases}
\tag{4}
$$

where the left and right sides are results of PMF and the improved Bayesian mixing model, respectively; W and H are the same as in Eq. (1); i is a specified sample, j is the NO_3^- species; f, m and a represent the number of sources identified by PMF that related to fossil fuel combustion, mobile sources and agriculture-related emission, respectively; SP represents the secondary particulate source; N is the NO_3^- concentration contributed by each source of the improved Bayesian mixing model.

Taking the NO_3^- concentration contributed by the secondary components ($W_{iSP}H_{SPj}$) as the independent variable, and the difference of NO_3^- concentrations between sources of the improved Bayesian mixing model and the PMF model for each part as the dependent variable, the linear regression in SPSS (Statistical Product and Service Solutions) was performed in turn. The method was "Enter" and the unstandardized coefficients were apportionment coefficients (x_f, x_m and x_a). This means that $100 * x_f\%$, $100 * x_m\%$ and $100 * x_a\%$ of NO_3^- in the secondary particulate source were from fossil fuel combination, mobile sources and agriculture-related emission sources, respectively, and the sum of these three apportionment coefficients was 1 in theory. According to the significance of F test and the value of adjusted R^2 in the output of SPSS, the regression effect was judged; the unstandardized coefficients were summed to check if the secondary components in $PM_{2.5}$ were pro-rated into three parts well.

2.2. Experimental setup

$PM_{2.5}$ samples collected at the National Research Center for Geoanalysis in Beijing were used to verify the feasibility and capacity of the improved source apportionment method (Liu et al., 2020). The sampling schedule was one month selected for each season and a total of 104 $PM_{2.5}$ samples were collected. OC and EC were obtained with an offline carbon analyzer (Sunset Laboratory, Inc., USA) following the thermal-optical transmittance (TOT) protocol (Birch and Cary, 1996). The concentrations of water-soluble ions - NH_4^+, NO_3^-, SO_4^{2-}, chloride (Cl^-), potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}) were determined using ion chromatography (Dionex ICS3000, Dionex Ltd., America) based on the analysis method reported by Shahsavani et al. (2012). The concentrations of metal elements - iron (Fe), manganese (Mn), arsenic (As), chromium (Cr), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), vanadium (V) and uranium (U) were determined by inductively coupled plasma mass spectrometry (ICP-MS of ELAN DRCII type, Perkin Elmer Ltd., Hong Kong) according to the previous method (Wang et al., 2006). The nitrous oxide (N_2O) isotope analysis method was employed to admeasure the stable nitrogen isotope ($\delta^{15}N$) and stable oxygen isotope ($\delta^{18}O$) values for NO_3^- (McIlvin and Altabet,

2005). ^{14}C measurement of OC and EC was performed at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, and the analytical processes were detailed in the previous studies (Wacker et al., 2013; Xu et al., 2007; Zhang et al., 2010). Detailed sample information and chemical analysis are displayed in the SI Text S1-S3 and concentrations of $PM_{2.5}$ and chemical components are summarized in Table S1.

In this study, 20 chemical species (including OC, EC, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, V, Mn, Fe, Cr, Ni, Cu, Zn, As, U and Pb) were loaded into the model to quantitatively apportion $PM_{2.5}$, of which the concentration data formed the matrix V and the associated uncertainty formed the matrix u. In the input concentration data set, the data below species-specific method detection limit (MDL) were replaced with half of the MDL, and the missing species data were replaced with the arithmetic mean of corresponding elements (Polissar et al., 1998). The uncertainty of the variables was calculated based on MDL and the concentration of each sample. For details of the method, please refer to the SI Text S5.

2.3. Assessment of apportionment performance

To further confirm this apportionment result of secondary particulate in $PM_{2.5}$, the improved source contribution results to OC and EC were examined by ^{14}C measurement. The role that ^{14}C measurements play in distinguishing fossil (F) and non-fossil (NF) carbonaceous particles sources has been found in recent researches (Liu et al., 2014; Zong et al., 2015). In view of its half-life of 5730 years, ^{14}C has been completely exhausted in fossil fuel emissions, while ^{14}C levels of non-fossil carbon sources (e.g., from biomass burning or biogenic emissions) are similar to those of atmospheric CO_2 (Liu et al., 2013; Zhang et al., 2015). Thus, contributions of fossil and non-fossil sources to OC and EC in $PM_{2.5}$ can be quantified by ^{14}C measurements.

For the comparison, the modeled source contributions were classified into two carbon source groups based on the characteristic of fossil and non-fossil. The contribution fractions (R) of non-fossil or fossil sources to OC or EC, classified from PMF results and apportionment results of secondary particulate, were determined using the formula shown in Eq. (5).

$$
R_{ij} = \left(\sum_{r=1}^{q} W_{ir}H_{rj} + l W_{iSP}H_{SPj} \right) / \sum_{r=1}^{p} W_{ir}H_{rj}
\tag{5}
$$

where W, H, i and SP are the same as in Eq. (4), j is the OC or EC species; q is the number of fossil or non-fossil carbon sources, p is the total number of sources; l is the ratio of fossil (fossil fuel combustion as well as mobile sources) or non-fossil (agriculture-related emission sources) parts to the secondary particulate source. Values of R were subsequently compared with the ^{14}C measurement of specified samples, which were expressed with the modern carbon fraction (f_m).

3. Results and discussion

3.1. Source apportionment of $PM_{2.5}$

The concentrations of $PM_{2.5}$ and its component elements during the sampling period were listed in the SI Table S1. The range of daily $PM_{2.5}$ mass concentration was 70.8–518 μg/m³, and the average concentration was 181 ± 79.3 μg/m³. The concentrations of water-soluble ions, carbonaceous fraction and metal elements in $PM_{2.5}$ were 70.1 ± 55.6 μg/m³, 23.2 ± 15.8 μg/m³ and 5.10 ± 3.39 μg/m³, respectively, accounting for 36.9 ± 19.8%, 12.5 ± 4.71% and 2.73 ± 1.35% of the $PM_{2.5}$ concentration. The concentrations of SO_4^{2-}, NO_3^-, OC and NH_4^+ among the 20 analyzed components were significantly higher than those of other components, accounting for 12.7 ± 9.04%, 12.6 ± 9.35%, 11.1 ± 4.21% and 4.83 ± 3.49% of the $PM_{2.5}$ concentration, respectively. Such the composition intuitively showed the significant role played by the secondary particulate in atmospheric $PM_{2.5}$ pollution. In other studies of $PM_{2.5}$ in Beijing in

similar years (Gao et al., 2018; Liu et al., 2019; Ma et al., 2017; Yu et al., 2019), the average mass concentration of $PM_{2.5}$ was also up to 110–140 μg/m³, in which secondary ions (NO_3^-, SO_4^{2-} and NH_4^+) and OC occupied the largest proportion. The level of $PM_{2.5}$ in this study is basically comparable to the existing research results and the high average concentration may be caused by several severe haze days in winter.

To find the apportionment results with the most optimal factor numbers and profiles in PMF model, five to nine factor solutions were considered with each model experiment running 100 times from a random starting point. The solution with the minimum Q (robust) value of each experiment was determined as the best solution. Besides, PMF was run numerous times with different Fpeak. Finally, the pattern of seven factors was identified, which reasonably explained the pollution source category with the lowest Q value (2891.93) and no rotation was selected (Fpeak = 0). The uncertainty of the PMF solution was examined by three PMF error estimation methods in the SI Text S5. The seven sources were secondary particulate, vehicle exhausts, industrial sources, biomass burning, coal combustion, construction dust, and fuel oil combustion. The detailed recognizing process is described in the SI Text S6 and characteristics of the seven sources are shown in Figs. S1 and S2.

Contributions of sources identified by PMF to $PM_{2.5}$ and NO_3^- are shown in Fig. 1. Among the seven sources (secondary particulate, vehicle exhausts, industrial sources, biomass burning, coal combustion, construction dust, and fuel oil combustion), secondary particulate contributed the most to $PM_{2.5}$ during the sampling period, accounting for 36.1%; followed by vehicle exhausts (18.7%), industrial sources (13.6%), biomass burning (11.4%), coal combustion (8.10%), construction dust (7.93%) and fuel oil combustion (4.24%). Basically, this result is similar to those found in other $PM_{2.5}$ source studies of Beijing (Gao et al., 2016; Gao et al., 2018; Huang et al., 2014; Liu et al., 2019; Ma et al., 2017; Yang et al., 2016; Yu et al., 2019; Zikova et al., 2016) (SI Table S3, Text S6). For NO_3^-, the contribution of secondary particulate (71.3%) was significant, followed by vehicle exhausts, industrial sources, fuel oil combustion, coal combustion and biomass burning, accounting for 12.1%, 6.50%, 4.67%, 4.16% and 1.26%, respectively.

3.2. Reapportionment of secondary sources

In order to quantify the contribution of different sources to NO_3^- in $PM_{2.5}$, the improved Bayesian mixing model was run in four cases.

Related results showed that coal combustion was the main source of NO_3^- in Beijing which contributed 38.5% ± 16.0% to NO_3^- in the atmosphere, followed by mobile sources (25.3% ± 6.44%), biomass burning (21.3% ± 6.86%) and biogenic soil emissions (14.9% ± 8.07%). However, corresponding sources of coal combustion, vehicle exhausts and biomass burning identified by PMF only contributed 4.16%, 12.1% and 1.26% to NO_3^-, respectively, which is far less than the simulation results of Bayesian model. According to the apportionment results of PMF, secondary particulate contributed up to 71.3%, 35.7% and 53.4% to NO_3^-, NH_4^+ and SO_4^{2-}, respectively, which confirmed that a large part of NO_3^- emissions was classified as secondary sources in the PMF model.

Based on source apportionment of $PM_{2.5}$ described in Section 3.1, sources identified by PMF were divided into three parts (fossil fuel combustion, mobile sources and agriculture-related emission sources) for linear regression. Therein, coal combustion, fossil oil combustion and industrial sources were classified together as fossil fuel combustion due to their origins from fossil fuel burning; vehicle exhausts and biomass burning belonged to mobile sources and agriculture-related emission sources, respectively; construction dust was not classified due to its complexity. According to Eq. (4), NO_3^- concentrations contributed by seven sources were calculated based on the output table of the PMF model and linear regression in SPSS was performed with the method described in Section 2.1.2. The regression results of fossil fuel combustion, mobile sources and agriculture-related emission sources are shown in Table 1 after selectively excluding outliers with standard residuals >3 in "Casewise diagnostics".

In the output results, the significance level of the set test F in the linear regression model (the P value) was less than 0.05, indicating that the linear relationship was obvious and the regression model established had statistical significance; values of adjusted R^2 of three linear regression models were all higher than 0.674, proving the satisfactory regression effect. Values of regression coefficients x_f, x_m and x_a were 0.348, 0.282 and 0.387, respectively and the sum of the three was 1.02, close to 1. Results showed that the secondary particulate source was reasonably reapportioned to fossil fuel combustion, motor sources and agriculture-related emission sources by this method.

According to the reapportionment results, 34.8% of the contribution of secondary particulate to $PM_{2.5}$ was related to fossil fuel combustion. As precursors of secondary particulate, SO_2, NO_2, NO and other harmful gases produced by coal as well as fossil oil combustion are discharged into the atmosphere along with the smoke and dust. The secondary particles are subsequently generated after a series of photochemical
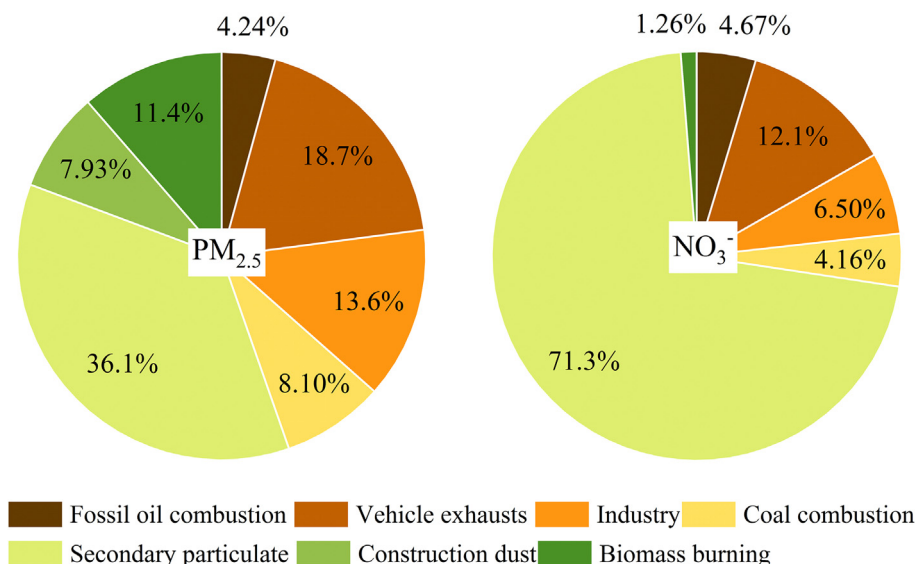

Fig. 1. The relative contributions of seven sources to $PM_{2.5}$ and NO_3^-.

Table 1

Linear regression results of NO_3^- concentrations of fossil fuel combustion (Model 1), mobile sources (Model 2) and agriculture-related emission sources (Model 3).

Model	Independent variable	Dependent variable	Unstandardized coefficients (x_r)	Adjusted R^2	Standard error of estimate	F	P
1	$W_{iSP}H_{SPj}$	$N_C - \sum_{r=1}^{f} W_{ir}H_{rj}$	0.348	0.674	4.97	208	<0.05
2		$N_M - \sum_{r=1}^{m} W_{ir}H_{rj}$	0.282	0.892	2.11	823	
3		$N_{BB} + N_{BSE} - \sum_{r=1}^{a} W_{ir}H_{rj}$	0.387	0.767	4.52	340	

reactions, causing serious air pollution. In addition to the direct emission of $PM_{2.5}$, the motor vehicle is also an important source of gaseous pollutants such as VOC and NO_x, which has an important contribution to the secondary organic compounds and secondary NO_3^- in $PM_{2.5}$. After linear regression, 28.2% of the secondary source was allocated to mobile sources. Analogously, pollutants generated by the complete combustion of biofuels such as NO_x, SO_2, acid gases, dioxins, etc. are also contributors to secondary particulates in $PM_{2.5}$. And 38.7% of the secondary source was reapportioned to agricultural emission sources that were closely related to biomass combustion.

After the process of reapportionment, 34.8%, 28.2% and 38.7% of the contribution ratio of secondary particulate source to $PM_{2.5}$ were allocated to fossil fuel combustion, mobile sources and agriculture-related emission sources, respectively. In the apportionment results of PMF, the contribution of coal combustion, fossil oil combustion and industrial sources to NO_3^- were 4.16%, 4.67% and 6.50%, respectively. According to the method described in Eq. (3), 34.8% of the secondary particulate source was apportioned to coal combustion, fossil oil combustion and industrial sources as the ratio of 9.44%, 10.6% and 14.8%, respectively. As mobile sources and agriculture-related emission sources only referred to one source in the PMF model results, 28.2% and 38.7% of the secondary particulate source were all apportioned to vehicle exhausts and biomass burning, respectively. Finally, the secondary particulate source identified by PMF was legitimately reapportioned to five sources: coal combustion, fossil oil combustion, industrial sources, vehicle exhausts and biomass burning, with the allocation ratio of 9.44%, 10.6%, 14.8%, 28.2% and 38.7%, respectively.

Zhang et al. (2012) applied the source-oriented chemical transport model to the apportionment of NO_3^- and SO_4^{2-} in $PM_{2.5}$ and demonstrated that power sector was the dominating source, followed by transportation sector and industry sector. The high contribution of power plants may be caused by the large proportion of coal-fired power plants and low level of coal emission control technology in China around 2009. Vehicle exhausts and industrial sources made great contributions to NO_3^- and SO_4^{2-} in $PM_{2.5}$, which is consistent with the results in this study. Simultaneously, Wang et al. (2018) utilized a regional source-oriented chemical transport model and two emission inventories to apportion sources of secondary organic aerosol in 2013. The conclusions of both emission inventories emphasized contributions of biogenic emissions and industrial sources, followed by transportation sector and residential sources. Hence, it is comparatively reasonable to reapportion the secondary particulate source identified by PMF mainly to biomass burning, vehicle exhausts and industrial sources herein in consideration of these previous studies.

The number of sources obtained from the PMF model was finally reduced to 6 and contributions of these final sources to $PM_{2.5}$ were calculated as shown in Fig. 2. After adding the contribution of the secondary particulate source to $PM_{2.5}$ (the shadow part in the pie), vehicle exhausts (28.7%) contributed the most to $PM_{2.5}$ and biomass burning (25.1%) became the second largest source, surpassing industrial sources (18.9%). Fossil oil combustion and coal combustion increased to 8.00% and 11.4%, respectively, and construction dust contributed the least.

3.3. Comparison of the source apportionment with ¹⁴C measurement

The contributions of coal combustion, fossil oil combustion, vehicle exhausts, and industrial sources derived from the PMF modeling to OC and EC were classified as fossil fuel combustion; biomass burning was taken as non-fossil source contribution. However, construction dust was not considered in this classification because they originated from hybrid sources of fossil and non-fossil carbon emissions. Calculated by the reapportionment results of the secondary particulate source, values of l in Eq. (5) were 0.630 ($x_f + x_m$) and 0.387 (x_a) for fossil and non-fossil carbon emissions, respectively. Contributions of fossil and non-fossil sources to the carbon content before and after the reapportionment of secondary particulate were calculated based on Eq. (5) and then compared with measured values of ¹⁴C, which were selected for eight days. The comparison results are shown in the SI Table S4 and Fig. S3.

As shown in Table S4, the average contribution of fossil (F) and non-fossil (NF) sources to OC accounted for 36.8 ± 18.5% and 37.1 ± 11.1% in the original results of the PMF model, which were 6.62% and 19.5% lower than the average measured values of ¹⁴C (43.4 ± 13.1% and 56.6 ± 13.1%), respectively. In general, contributions to the carbon content in the source apportionment results of PMF were lower than the measured values of ¹⁴C because the contribution of construction dust to OC and EC was unallowable to be neglected (Wang et al., 2017). After the secondary particulate source identified by PMF was reapportioned, the average contribution of fossil and non-fossil sources, including the fossil and non-fossil part of the secondary particulate, to OC increased to 41.0 ± 17.5% and 39.7 ± 12.1%, respectively, which were more approximate to the average measured values. The average contribution rates to EC were 45.4 ± 16.6% and 28.0 ± 9.30%, respectively. The former was 24.9% lower than the average measured values of ¹⁴C (70.3 ± 11.5%), while the latter was very close to the measured value. Simultaneously, the reapportionment of the secondary particulate source made the contribution rates to EC closer to the measured values of ¹⁴C, which increased to 47.4 ± 17.0% and 29.3 ± 9.63%, respectively. It can be seen more intuitively from Fig. S3 that OC (orange column) and EC (yellow column), representing contribution fractions of fossil and non-fossil sources identified by PMF to OC and EC, respectively, were generally lower (except a small number of abnormal samples) than ¹⁴C measured results (horizontal line); after adding the green column, representing contribution fractions of fossil and non-fossil part in the secondary particulate source (SP), the model analysis results matched measured values to a greater extent. Therefore, the reapportionment of the secondary particulate source made the PMF results more consistent with the real situation, showing
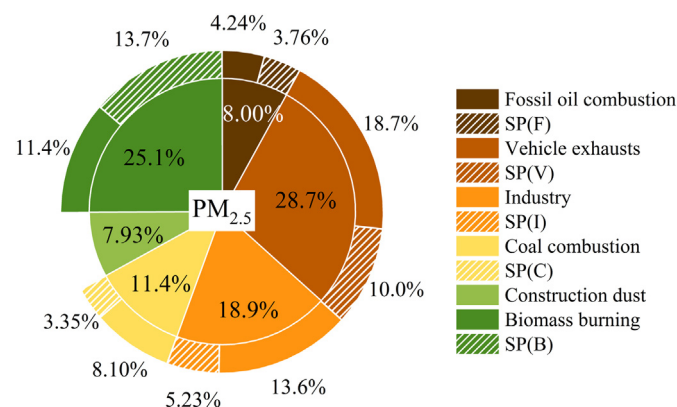

Fig. 2. The relative contributions to $PM_{2.5}$ of six sources after the reapportionment of the secondary particulate. "SP" (the shadow part in each source) refers to the contribution of related secondary particle source: fossil oil combustion (F), vehicle exhausts (V), industrial sources (I), coal combustion (C) and biomass burning (B).

that it was reasonable and feasible to reapportion secondary particulate to primary sources combining the PMF model with the improved Bayesian mixing model.

4. Conclusion

A method to reapportion the secondary source of $PM_{2.5}$ identified by PMF to primary sources with source contributions of NO_3^-, NH_4^+ and SO_4^{2-} in $PM_{2.5}$ estimated by their isotopes was proposed in this study. Based on the practical $PM_{2.5}$ data of Beijing, the feasibility and capacity of the model were evaluated. In this study, 20 chemical species were loaded into the PMF model to quantitatively apportion $PM_{2.5}$ and source contributions of NO_3^- were applied to reapportion secondary source to primary sources. Seven sources (secondary particulate, vehicle exhausts, industrial sources, biomass burning, coal combustion, construction dust, and fuel oil combustion) of $PM_{2.5}$ were identified by PMF, among which secondary particulate (36.1%) contributed the most, followed by vehicle exhausts (18.7%), industrial sources (13.6%), biomass burning (11.4%), coal combustion (8.10%), construction dust (7.93%) and fuel oil combustion (4.24%).

Utilizing the isotopes apportioning results of NO_3^- by the improved Bayesian mixing model, the secondary particulate source identified by PMF was reapportioned to coal combustion, fossil oil combustion, industrial sources, vehicle exhausts and biomass burning with the ratio of 9.44%, 10.6%, 14.8%, 28.2% and 38.7%, respectively. The number of contribution sources obtained from PMF simulation was finally reduced to 6. After the improvement that apportioning the secondary particulate source, vehicle exhausts (28.7%) contributed the most to $PM_{2.5}$ and biomass burning (25.1%) became the second largest source, surpassing industrial sources (18.9%). Fossil oil combustion and coal combustion increased to 8.00% and 11.4%, respectively, and construction dust contributed the least.

The apportionment performance was also assessed by comparing the source apportionment results of OC and EC in $PM_{2.5}$ with ^{14}C measurements in 8 $PM_{2.5}$ samples. The average gap between contributions of identified sources to OC and EC and the ^{14}C measurements decreased $2.5 \pm 1.2\%$ after the reapportionment of secondary particulate source than $13.2 \pm 10.8\%$, indicating that the reapportionment was reasonable and feasible. In addition, this method is based on the assumption that the contributions of each primary source identified by PMF to all components in the secondary particulate of $PM_{2.5}$ are the same. The apportionment results of the secondary particulate source will be more logical if the isotopic source analysis results of SO_4^{2-} and NH_4^+ are considered at the same time, which can be of great significance to the formulation of $PM_{2.5}$ control strategy.

CRediT authorship contribution statement

Zeyu Sun: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. **Zheng Zong:** Conceptualization, Investigation, Writing - review & editing. **Chongguo Tian:** Conceptualization, Methodology, Resources, Funding acquisition, Writing - review & editing. **Jun Li:** Resources, Funding acquisition. **Rong Sun:** Writing - review & editing. **Wenwen Ma:** Writing - review & editing. **Tingting Li:** Investigation. **Gan Zhang:** Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Appendix A. Supplementary data

References

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci. Technol. 25, 221–241.

Chang, Y., Zou, Z., Zhang, Y., Deng, C., Hu, J., Shi, Z., et al., 2019. Assessing contributions of agricultural and nonagricultural emissions to atmospheric ammonia in a Chinese megacity. Environmental Science & Technology 53, 1822–1833.

Felix, J.D., Elliott, E.M., Shaw, S.L., 2012. Nitrogen isotopic composition of coal-fired power plant NOx: influence of emission controls and implications for global emission inventories. Environmental Science & Technology 46, 3528–3535.

Gao, J., Peng, X., Chen, G., Xu, J., Shi, G.-L., Zhang, Y.-C., et al., 2016. Insights into the chemical characterization and sources of PM2.5 in Beijing at a 1-h time resolution. Sci. Total Environ. 542, 162–171.

Gao, J., Wang, K., Wang, Y., Liu, S., Zhu, C., Hao, J., et al., 2018. Temporal-spatial characteristics and source apportionment of PM2.5 as well as its associated chemical species in the Beijing-Tianjin-Hebei region of China. Environ. Pollut. 233, 714–724.

Han, X., Guo, Q., Liu, C., Fu, P., Strauss, H., Yang, J., et al., 2016. Using stable isotopes to trace sources and formation processes of sulfate aerosols from Beijing, China. Sci. Rep. 6.

Hopke, P.K., 2003. Recent developments in receptor modeling. J. Chemom. 17, 255–265.

Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., et al., 2014. High secondary aerosol contribution to particulate pollution during haze events in China. Nature 514, 218–222.

Li, H., Wang, Qg, Yang, M., Li, F., Wang, J., Sun, Y., et al., 2016. Chemical characterization and source apportionment of PM2.5 aerosols in a megacity of Southeast China. Atmos. Res. 181, 288–299.

Liang, C.-S., Duan, F.-K., He, K.-B., Ma, Y.-L., 2016. Review on recent progress in observations, source identifications and countermeasures of PM2.5. Environ. Int. 86, 150–170.

Liu, D., Li, J., Zhang, Y., Xu, Y., Liu, X., Ding, P., et al., 2013. The use of levoglucosan and radiocarbon for source apportionment of PM2.5 carbonaceous aerosols at a background site in East China. Environmental Science & Technology 47, 10454–10461.

Liu, J., Li, J., Zhang, Y., Liu, D., Ding, P., Shen, C., et al., 2014. Source apportionment using radiocarbon and organic tracers for PM2.5 carbonaceous aerosols in Guangzhou, South China: contrasting local- and regional-scale haze events. Environmental Science & Technology 48, 12002–12011.

Liu, Y., Zheng, M., Yu, M., Cai, X., Du, H., Li, J., et al., 2019. High-time-resolution source apportionment of PM2.5 in Beijing with multiple models. Atmos. Chem. Phys. 19, 6595–6609.

Liu, D., Vonwiller, M., Li, J., Liu, J., Szidat, S., Zhang, Y., et al., 2020. Fossil and non-fossil fuel sources of organic and elemental carbon aerosols in Beijing, Shanghai and Guangzhou: seasonal carbon-source variation. Aerosol Air Qual. Res. 20.

Lu, F., Xu, D., Cheng, Y., Dong, S., Guo, C., Jiang, X., et al., 2015. Systematic review and meta-analysis of the adverse health effects of ambient PM2.5 and PM10 pollution in the Chinese population. Environ. Res. 136, 196–204.

Ma, Q., Wu, Y., Tao, J., Xia, Y., Liu, X., Zhang, D., et al., 2017. Variations of chemical composition and source apportionment of PM2.5 during winter haze episodes in Beijing. Aerosol Air Qual. Res. 17, 2791–2803.

McIlvin, M.R., Altabet, M.A., 2005. Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. Anal. Chem. 77, 5589–5595.

Moore, J.W., Semmens, B.X., 2008. Incorporating uncertainty and prior information into stable isotope mixing models. Ecol. Lett. 11, 470–480.

Norman, A.L., Anlauf, K., Hayden, K., Thompson, B., Brook, J.R., Li, S.M., et al., 2006. Aerosol sulphate and its oxidation on the Pacific NW coast: S and O isotopes in PM2.5. Atmos. Environ. 40, 2676–2689.

Paatero, P., Eberly, S., Brown, S.G., Norris, G.A., 2014. Methods for estimating uncertainty in factor analytic solutions. Atmospheric Measurement Techniques 7, 781–797.

Pan, Y., Tian, S., Liu, D., Fang, Y., Zhu, X., Zhang, Q., et al., 2016. Fossil fuel combustion-related emissions dominate atmospheric ammonia sources during severe haze episodes: evidence from N-15-stable isotope in size-resolved aerosol ammonium. Environmental Science & Technology 50, 8049–8056.

Polissar, A.V., Hopke, P.K., Paatero, P., 1998. Atmospheric aerosol over Alaska - 2. Elemental composition and sources. J. Geophys. Res.-Atmos. 103, 19045–19057.

Pui, D.Y.H., Chen, S.-C., Zuo, Z., 2014. PM2.5 in China: measurements, sources, visibility and health effects, and mitigation. Particuology 13, 1–26.

Shahsavani, A., Naddafi, K., Haghighifard, N.J., Mesdaghinia, A., Yunesian, M., Nabizadeh, R., et al., 2012. Characterization of ionic composition of TSP and PM10 during the Middle Eastern Dust (MED) storms in Ahvaz, Iran. Environ. Monit. Assess. 184, 6683–6692.

Tao, J., Zhang, L., Ho, K., Zhang, R., Lin, Z., Zhang, Z., et al., 2014a. Impact of PM2.5 chemical compositions on aerosol light scattering in Guangzhou - the largest megacity in South China. Atmos. Res. 135, 48–58.

Tao, M., Chen, L., Xiong, X., Zhang, M., Ma, P., Tao, J., et al., 2014b. Formation process of the widespread extreme haze pollution over northern China in January 2013: implications for regional air quality and climate. Atmos. Environ. 98, 417–425.

Wacker, L., Fahrni, S.M., Hajdas, I., Molnar, M., Synal, H.A., Szidat, S., et al., 2013. A versatile gas interface for routine radiocarbon analysis with a gas ion source. Nuclear Instruments & Methods In Physics Research Section B-Beam Interactions with Materials And Atoms 294, 315–319.

Walters, W.W., Tharp, B.D., Fang, H., Kozak, B.J., Michalski, G., 2015. Nitrogen isotope composition of thermally produced NOx from various fossil-fuel combustion sources. Environmental Science & Technology 49, 11363–11371.

Wang, X., Bi, X., Sheng, G., Fu, H., 2006. Hospital indoor PM10/PM2.5 and associated trace elements in Guangzhou, China. Sci. Total Environ. 366, 124–135.

Wang, X., Zong, Z., Tian, C., Chen, Y., Luo, C., Li, J., et al., 2017. Combining positive matrix factorization and radiocarbon measurements for source apportionment of PM2.5 from a national background site in North China. Sci. Rep. 7.

Wang, P., Wang, Q., Zhang, H., Hu, J., Lin, Y., Mao, H., 2018. Source apportionment of secondary organic aerosol in China using a regional source-oriented chemical transport model and two emission inventories. Environ. Pollut. 237, 756–766.

Xu, X., Trumbore, S.E., Zheng, S., Southon, J.R., McDuffee, K.E., Luttgen, M., et al., 2007. Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: reducing background and attaining high precision. Nuclear Instruments & Methods In Physics Research Section B-Beam Interactions with Materials And Atoms 259, 320–329.

Yang, H., Chen, J., Wen, J., Tian, H., Liu, X., 2016. Composition and sources of PM2.5 around the heating periods of 2013 and 2014 in Beijing: implications for efficient mitigation measures. Atmos. Environ. 124, 378–386.

Yu, S., Liu, W., Xu, Y., Yi, K., Zhou, M., Tao, S., et al., 2019. Characteristics and oxidative potential of atmospheric PM2.5 in Beijing: source apportionment and seasonal variation. Sci. Total Environ. 650, 277–287.

Zhang, Y.L., Liu, D., Shen, C.D., Ding, P., Zhang, G., 2010. Development of a preparation system for the radiocarbon analysis of organic carbon in carbonaceous aerosols in China. Nuclear Instruments & Methods In Physics Research Section B-Beam Interactions with Materials And Atoms 268, 2831–2834.

Zhang, H., Li, J., Ying, Q., Yu, J.Z., Wu, D., Cheng, Y., et al., 2012. Source apportionment of PM2.5 nitrate and sulfate in China using a source-oriented chemical transport model. Atmos. Environ. 62, 228–242.

Zhang, Y.-L., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Zotter, P., Shen, R.-r., et al., 2015. Source apportionment of elemental carbon in Beijing, China: insights from radiocarbon and organic marker measurements. Environmental Science & Technology 49, 8408–8415.

Zhang, Y., Benedict, K.B., Tang, A., Sun, Y., Fang, Y., Liu, X., 2020. Persistent nonagricultural and periodic agricultural emissions dominate sources of ammonia in urban Beijing: evidence from N-15 stable isotope in vertical profiles. Environmental Science & Technology 54, 102–109.

Zikova, N., Wang, Y., Yang, F., Li, X., Tian, M., Hopke, P.K., 2016. On the source contribution to Beijing PM2.5 concentrations. Atmos. Environ. 134, 84–95.

Zong, Z., Chen, Y., Tian, C., Fang, Y., Wang, X., Huang, G., et al., 2015. Radiocarbon-based impact assessment of open biomass burning on regional carbonaceous aerosols in North China. Sci. Total Environ. 518, 1–7.

Zong, Z., Wang, X., Tian, C., Chen, Y., Fang, Y., Zhang, F., et al., 2017. First assessment of NOx sources at a regional background site in North China using isotopic analysis linked with modeling. Environmental Science & Technology 51, 5923–5931.

Zong, Z., Tan, Y., Wang, X., Tian, C., Li, J., Fang, Y., et al., 2020. Dual-modelling-based source apportionment of NOx in five Chinese megacities: providing the isotopic footprint from 2013 to 2014. Environ. Int. 137.