Seasonal Variation and Source Apportionment of Inorganic and Organic Components in PM_{2.5}: Influence of Organic Markers Application on PMF Source Apportionment

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Research Article

Keywords: organic markers, PMF, PM_{2.5}, source apportionment

Posted Date: January 11th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1131595/v1>

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Abstract

PM_{2.5} samples collected over a 1-year period in a Chinese megacity were analyzed for organic carbon (OC), elemental carbon (EC), water soluble ions, elements and organic markers such as polycyclic aromatic hydrocarbons (PAHs), hopanes, steranes, and n-alkanes. In order to study the applicability of organic markers in source apportionment, this study analyzes the relationship between organic and inorganic components, and four scenarios were implemented by incorporating different combinations of organic and inorganic tracers. A positive correlation of SO_4^{2-} with 4 rings PAHs can prove that coal burning directly emits a portion of sulfate. A positive correlation of NO_3^- with 5-7 rings PAHs are found, implying collective impacts from the vehicle source. The concentrations of OC and EC positively correlate with the 5-7 rings PAHs and Cu and Zn, which proves that part of Cu and Zn comes from vehicle emissions. Five factors were identified by incorporating only conventional components, including secondary source (SS, 30%), urban fugitive dust (UFD, 14%), cement dust (CD, 4%), traffic source (TS, 19%) and coal combustion (CC, 14%). Six factors were identified by incorporating conventional components and PAHs, including SS (28%), UFD (15%), CD (4%), CC (13%), gasoline vehicles (GV, 12%) and diesel vehicles (DV, 10%). Eight factors were identified by incorporating conventional components, PAHs, hopanes, and n-alkanes, including SS (26%), UFD (17%), CD (3%), GV (14%), DV (8%), immature coal combustion (ICC, 5%), mature coal combustion (MCC, 10%) and biogenic source (BS, 1%).

1. Introduction

Source apportionment of PMs is the process to identify and quantify the contribution of the emission sources, and it is vital for formulating emission reduction policies for air pollution (Liu et al., 2017; Liu et al., 2016; Lu et al., 2018). However, it is more difficult to identify specific sources based on only the inorganic markers (Galvao et al., 2019; Lin et al., 2010; Xue et al., 2019). Organic compounds in source apportionment can be utilized to identify specific sources. For example, PAHs (polycyclic aromatic hydrocarbons) are generated due to incomplete combustion of organic material, which can be used as markers for the vehicle exhausts, combustion of coal and biomass (Chen et al., 2016; Esmaeilirad et al., 2020; Fraser et al., 2003; Galvao et al., 2019; Lin et al., 2010; Liu et al., 2012; Oros and Simoneit, 2000; Pereira et al., 2017; Xue et al., 2019). Hopanes and steranes are emitted by using lubricating oils in gasoline and diesel vehicles, while hopanes are also present in the smoke of coal combustion. Configurations of hopanes can also be employed to identify fossil fuels of different maturity (Krumal et al., 2013; Liu et al., 2012; Pereira et al., 2017). Alkanes with different carbon numbers can distinguish natural sources from anthropogenic sources (Kang et al., 2018; Lin et al., 2010; Wang et al., 2009).

There are some studies that using both organic and inorganic markers into PMF to improve factors interpretation (Belis et al., 2019; Choi et al., 2015; Esmaeilirad et al., 2020; Galvao et al., 2019; Wang et al., 2015; Wang et al., 2012; Xue et al., 2019). Some studies applied organic markers to identify the sources of OC (Kang et al., 2018; Krumal et al., 2013; Wang et al., 2009; Wang et al., 2017). Several approaches have previously summarized by using organic markers to distinguish the collinearity sources of PMs, e.g.

molecular marker chemical mass balance (MM-CMB) models (Ke et al., 2008; Schauer and Cass, 2000; Zheng et al., 2002), hybrid of positive matrix factorization (PMF) and MM-CMB models (Ke et al., 2008; Lu et al., 2018). PMF works by using sufficient identification information to apportion sources of PM (Dai et al., 2020; Ke et al., 2008). However, when the variables included model increase, the demand for sample size is also greater (Ke et al., 2008). Thus, the sample size is a limitation that has to be considered. Besides, PMF is unable to apportion particulate matter sources with large fractions of low signal-to-noise organic components and few inorganic makers well (Christensen and Schauer, 2008; Lu et al., 2018). Simultaneously inputting a large number of organic components and a small amount of inorganic components in the PMF model without screening may cause obvious deviations due to the collective influence of element and ions (Lu et al., 2018). And as the organics data set increases, the influence of organics closely resembles (Christensen and Schauer, 2008). However, how to better incorporate organic and inorganic markers into the PMF model for the purpose of source apportionment have been less investigated.

The co-linearity of the sources increases since the large correlation between some organic components, it may due to the time variation of some organics and the influence of other conditions (such as meteorological factors) is greater than the fingerprint of organics. Compared with inorganics, organics are more susceptible to meteorological factors (Al-Naiema et al., 2018; Kim et al., 2013). PAHs will undergo reactions such as photolysis, oxidation, desorption and resorption under the influence of temperature and luminosity (Al-Naiema et al., 2018; Huang et al., 2014; Kim et al., 2013; Mu et al., 2018). Therefore, the reaction activity of organics will affect whether it can be used as a marker (Lin et al., 2010).

To solve the above issues, one-year monitoring program to determine seasonal variations of $PM_{2.5}$. Conventional components including elements, ions, OC and EC, and organic components including PAHs, hopanes, steranes, and n-alkanes were analyzed. In order to fill the mentioned knowledge gap, four main objectives were established in this paper: (1) to explore the variation in concentrations and sources of inorganic and organic components in four seasons; (2) to identify the relations among organic and inorganic markers and the relationship between components and meteorological factors; (3) to carry out research on screening variables included in the PMF model; (4) to study the applicability of organic markers and inorganic markers in the PMF model.

2. Materials And Methods

2.1 Particulate matter sampling

The sampling site is located on the 7th floor in the Environmental Protection Building (104°04'E, 30°35'N), which is located in the central city of Chengdu and belongs to residential areas and office areas. There is no obvious pollution source around except for some subway construction around during in the sampling period. 83 $PM_{2.5}$ samples were collected using 90 mm quartz and polypropylene fiber filters from December 2017 to December 2018 by a medium-volume air sampler. Each sampling lasted for 22 h, with a flow rate of 100 L min^{-1} . Samples were divided into four parts: spring (April), summer (July), autumn

(October) and winter (January). Other conditions of quality control and quality assurance of sampling were the same as those in our previous reports (Xue et al., 2019).

2.2 Filter analysis

The detailed analysis method and instrument of 7 ions (Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , etc.), 17 inorganic elements (Na, Mg, Al, Si, K, etc.) and organic carbon (OC) and elemental carbon (EC) are provided in supplementary context I and Table S1. For organic components analyses, each filter was cut into a quarter for analysis of 18 PAHs, 7 hopanes, 2 steranes and 24 n-alkane. Samples were pretreated by ultrasound extraction for 15 minutes and repeated twice. Then, 10 ml of dichloromethane and 10 ml of N-hexane (1:1,v:v) were added to the tubes. Florisil solid phase extraction column (1g/12mL) was used to clean up the extract and the above fractions and then were eluted with 20 mL of DCM/hexane (1:1). Collected solution after the solid phase extraction was combined and reduced to less than 5 mL (about 2 or 3 mL) using the rotary evaporator. The extract was then solvent-exchanged to N-hexane and the volume was finally condensed to 1mL. The mixed recovery surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12, hexamethylbenzene and n-Tetracosane-d50) were spiked into the sample vial. The prepared samples need to be refrigerated at -20°C and analyzed within 30 days. The organic compounds were analyzed by a gas chromatography/mass spectrometer (GC/MS), which equipped with a DB-5MS fused-silica capillary column (30 m $\times$ 0.25 mm, 0.25 mm film thickness, Agilent Technology). 1 mL was injected into a splitless injector, and pure helium (purity of 99.99% or more) was used as a carrier gas at a constant flow rate of 1.0 mL min^{-1} .

2.3 Analytical procedure of GC/MS

To analyze PAHs, hopanes and steranes, inlet and temperature transmission line temperatures were set to 230°C and 280°C , the initial ionization temperature was set to 280°C . Chromatography temperature program was set as follows, the column oven temperature was initially held at 50°C for 2 min, increased to 240°C at a rate of $10^\circ\text{C min}^{-1}$, and finally increased to 280°C at 5°C min^{-1} and then held for 20 min. Mass spectrometry conditions was set as follows, the EI mode was selected, and the ionization energy level was 70eV. An internal standard (IS) (naphthalene-D8, acenaphthene-D10, phenanthrene-D10, phenanthrene-D12, pyrene-D10, Hexamethylbenzene) was applied to the samples to qualify actual volumes of the target compounds present. As for n-alkanes' analysis conditions, inlet and temperature transmission line temperatures were 300°C , the initial ionization temperature was 300°C . Chromatography temperature program followed the steps, column oven temperature was initially held at 50°C , increased to 60°C at a rate of $2.5^\circ\text{C min}^{-1}$, and then increased to 280°C at a rate of $22^\circ\text{C min}^{-1}$, and finally increased to 325°C at $30^\circ\text{C min}^{-1}$ and held for 11 min.

2.4. Quality assurance and quality control

Strict quality control procedures were implemented during the experiment. All samples were collected by one instrument and analyzed by the same methods. All instruments and glassware are pretreated before using. When analyzing each batch of samples, method/lab blanks and parallel samples are used to control the data quality. The concentration range of the calibration curve of the studied substance is

0.005–20 mg mL⁻¹, with the correlation coefficients (r) exceeding 0.99. The purity of the standards used is above 98%, and other basic information is shown in Table S2. The recovery rate of PAHs, hopanes and steranes and n-alkanes ranged from 66–110%, 90–130%, 60–130%, respectively. The limit of detection (LOD) for PAHs, hopanes, steranes and n-alkanes are given in Table S3.

2.5 Data analysis

SPSS19.0 performs descriptive analysis, principal component analysis, and cluster analysis, and R language performs correlation analysis and visualization. United States Environmental Protection Agency Positive matrix factorization (US EPA PMF5.0) was used to identify the source categories and estimate their contributions in our study, whose principle has been well introduced in other studies (Ikemori et al., 2021; Liu et al., 2017; Tian et al., 2016; Tian et al., 2014; Yu and Park, 2021).

In order to study the applicability of organic markers in source apportionment, four scenarios were implemented.

(1) PMF_{tra}: The first scenario was set by incorporating only conventional components (inorganic elements, ions, OC and EC) into the PMF, which is defined as PMF_{tra}.

(2) PMF_{more}: The second scenario was set by incorporating conventional components and all organic markers (PAHs, hopanes, and n-alkanes) into the PMF, which is defined as PMF_{more}. The purpose of the second scenario is to investigate how to include as many organic markers as possible, and whether there is a difference between the source apportionment results.

(3) PMF_{less}: In order to study whether the part organic markers can play a role in source apportionment, the third scenario was set by incorporating conventional components (inorganic elements, ions, OC and EC) and PAHs into the PMF, which is defined as PMF_{less}.

(4) PMF_{scr}: This scenario was set by incorporating conventional components (inorganic elements, ions, OC and EC) and organic markers (PAHs, hopanes, and n-alkanes) after screening into the PMF, which is defined as PMF_{scr}. The purpose is to minimize the variables included in the model.

3. Results And Discussion

3.1 Seasonal characteristics of PM_{2.5} levels and components

Seasonal trends of particulate and components with concentration during four seasons have been studied. The measured concentrations of PM_{2.5}, WSI, elements, OC, EC and the sum of organic species are shown in Fig. 1. Concentrations of PM_{2.5}, WSI, tracer elements, OC and EC are higher in the winter. The average concentrations of the daily PM_{2.5} are 114.2 ± 58.0 µg m⁻³ in the winter and 48.2 ± 14.3 µg m⁻³ in

the summer. The average concentrations of the WSI are $32.2 \pm 20.2 \mu\text{g m}^{-3}$ in the winter and $13.6 \pm 5.7 \mu\text{g m}^{-3}$ in the summer. Concentrations of NO_3^- are higher in autumn and winter than in spring and summer (Fig. S1), which might be caused by the NH_4NO_3 volatilization in the warmer spring and summer. The average concentrations of the elements are $12.2 \pm 7.9 \mu\text{g m}^{-3}$ in the winter and $5.2 \pm 1.8 \mu\text{g m}^{-3}$ in the summer. Al, Si, Ca, and Fe are the most inorganic elements (Fig. S2). However, a slight difference found in the seasonal variation of the sum of organic species (PAHs, hopanes, steranes and n-alkanes), which the lowest concentration is observed in autumn. The average concentrations of the sum of organic species are approximately equal to $0.6 \mu\text{g m}^{-3}$ in the four seasons.

3.2 Seasonal characteristics of organic components

The PAHs concentrations of four seasons are presented in Fig. 2. The annual concentration of total PAHs is 7.4 ng m^{-3} . The total PAHs is higher in winter (13.0 ng m^{-3}) than in spring (4.9 ng m^{-3}), autumn (3.9 ng m^{-3}) and summer (2.8 ng m^{-3}). DBA is the most abundant PAH (17%-23% of total PAHs) in four seasons, followed by BbF (6%-16%), BghiP (9%-13%). These results echo those of Ma et al. (2018), who found a higher concentration of PAHs in the winter period than in the spring and summer period. Hopanes and steranes are regarded as markers of fossil fuel combustion because they mainly come from lubricating oil residues.

The mean concentrations of hopanes, $\alpha\alpha(20R)$ -cholestane and $\alpha\alpha(20S)$ -cholestane in four seasons are shown in Fig. 3. The concentrations of hopanes and steranes are 7.7 ng m^{-3} , 7.6 ng m^{-3} , 5.5 ng m^{-3} and 4.6 ng m^{-3} in spring, winter, summer and autumn, respectively. Like PAHs, the high concentration due to larger emissions from coal combustion and poor dispersion in winter (e.g. weaker winds and lower temperature inversions). The concentration of hopanes is approximately 10 times that of steranes. $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane is the most abundant hopane, followed by $17\alpha(\text{H}), 21\beta(\text{H})$ -30-Norhopane. $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane can be used as a marker for mature fossil fuels, and $17\alpha(\text{H}), 21\beta(\text{H})$ -30-Norhopane can indicate the maturity coal combustion sources, such as anthracite.

Concentrations of the n-alkanes in four seasons are plotted in Fig. 4. A total of 18 n-alkanes (ranging from C14 to C33) are detected. The total n-alkane concentrations in $\text{PM}_{2.5}$ range from 161.3 to 2020.4 ng m^{-3} . The total concentrations of n-alkanes in summer (854.3 ng m^{-3}) are higher than those in spring (652.9 ng m^{-3}), autumn (651.2 ng m^{-3}) and winter (586.6 ng m^{-3}). Concentrations of C14 to C21 n-alkanes are higher in spring and winter than in summer and autumn (Fig. 4). Studies have shown that n-alkanes with lower carbon numbers ($\text{C} \leq 24$) are mainly from the combustion of fossil fuels, such as vehicle emission and coal combustion. Concentrations of C22-C33 n-alkanes are higher in summer than in autumn, spring and winter (Fig. 4). High-carbon n-alkanes ($\text{C} \geq 25$) are mainly from higher plant wax emissions and other biogenic sources such as pollen and spores.

3.3 Diagnostic ratios of organic components

The PAHs diagnostic ratios for four seasons (Table 1) are obtained since they can prove some emission sources, such as gasoline vehicles, diesel vehicles, coal or wood combustion (Krumal et al., 2013). The

values of PAHs ratios can also be changed by the phase, transport and degradation of PAHs (Ma et al., 2018). The ratio of BeP/BaP is related to the aerosol photolysis. BeP and BaP emissions from the local PAHs contain are similar. However, BaP is more unstable and is likely to undergo photolysis or oxidation (Oliveira et al., 2011; Pacheco et al., 2017; Pereira et al., 2017). The average BeP/BaP ratio is 1.4 in winter, 1.8 in autumn, 2.0 in spring and 2.1 in summer, respectively. The concentration of BeP is higher than that of BaP, especially in spring and summer, mainly due to the photolysis or oxidation of the PAHs in summer and spring caused by the high temperature and sufficient sunlight. (Pereira et al., 2017). This suggested that the PAHs found at the site are aged. The BaP/BghiP and IcdP/(IcdP+BghiP) ratios are close to 0.4-0.7 and 0.2-0.4, similar to the ratio for the gasoline vehicles and diesel vehicle presented in Table 1. The average Phe/Ant ratio ranged between 5.6 and 7.7 in the four seasons, also approaching that of the gasoline vehicles and diesel vehicle.

The homohopane indices ($22S / (22S + 22R)$) of hopanes are showed in Table 1, which is much greater in summer (0.5) than in spring (0.2), autumn (0.1) and winter (0.2). This implies vehicle exhausts contributed most to $PM_{2.5}$ in summer, however, coal combustion also contributed to $PM_{2.5}$ in other seasons. Diagnostic ratios of $C_{29}\alpha\beta/C_{30}\alpha\beta$ were 0.6-0.7 in four seasons, which were in the range of traffic emissions. As shown in Fig. 4 and Table 1, C_{max} of n-alkanes are C16, C18 and C28 in winter, while the C_{max} of n-alkanes are at C28 and C30 in summer. Above all, n-alkanes in Chengdu during spring and winter mainly come from coal combustion and vehicles emissions, while n-alkanes partly influenced by biogenic sources in summer and autumn. Previous studies showed that C29 and C31 mainly come from the emission of plant wax (Ling-Yan et al., 2008; Wang et al., 2009). The C_{max} of gasoline vehicles are mainly C18 and C25, and the C_{max} of diesel vehicles is C20 (Ling-Yan et al., 2008; Lyu et al., 2017; Wang et al., 2009).

3.4 Correlations of components in $PM_{2.5}$

Correlations were calculated to determine the relationships among the concentrations of conventional and organic components, and the relationships with meteorological factors (T (temperature), relative humidity (RH) and wind speed (WS)) during the sampling period were shown in Table 2. The meteorological parameters were downloaded from a website (<https://rp5.ru/>).

A positive correlation of NO_3^- (0.36, p value < 0.01) concentrations with 5-7 rings PAHs are found, presumably they are affected by the vehicle source. A positive correlation of SO_4^{2-} (0.38, p value < 0.01) concentrations with 4 rings PAHs has been found, like pyrene, benzo(a)anthracene can be used as markers for coal emissions (Lin et al., 2010; Liu et al., 2012; Oros and Simoneit, 2000), therefore, it can be proved that burning coal directly emits a portion of sulfate (Dai et al., 2019).

The concentrations of OC and EC correlate positively with the sum of 5-7 rings PAHs (0.52, p value < 0.05) and Cu and Zn (0.51 and 0.70, p value < 0.01), which prove that part of Cu and Zn comes from vehicle emissions. 5-7 rings PAHs are markers for traffic (Lin et al., 2010; Pereira et al., 2017; Xue et al., 2019),

which are released by incomplete combustion of fossil fuels. Unlike 5-7 rings PAHs, Cu and Zn are mainly from tire wear or other vehicle parts, not fuel combustion.

There is a negative correlation between the concentrations of ions (-0.38 , p value < 0.01) and PAHs (-0.48 , p value < 0.01) with temperature. Cl^- , NO_3^- , NH_4^+ and 2-4 rings PAHs are more significantly affected by temperature (Zang et al., 2021). At higher temperatures, the photochemical degradation of the most reactive PAHs species (such as 2-4 rings PAHs, NO_3^- and NH_4^+) or the G/P distribution of more volatile species (2-4 rings PAHs) are more likely to happen (Hsu et al., 2019).

However, high-carbon n-alkanes (C29-C33) have a positive correlation with temperature (0.23 , p value < 0.05). High-carbon n-alkanes are mainly from higher plant wax emissions and other biogenic sources such as pollen and spores, which mainly dominate in the higher temperature season. All components are negatively correlated with wind speed, and the conventional components are significantly negatively correlated. A negative correlation of crustal metal elements (-0.40 , p value < 0.01), PAHs (-0.30 , p value < 0.01) and hopanes (-0.33 , p value < 0.01) concentrations with relative humidity has been found. Si, Mg, K and 2-3 rings PAHs are more significantly affected by relative humidity.

3.5 Source characterization

3.5.1 Identification of PMF factors

US EPA PMF5.0 was used to realize source apportionment in four scenarios. Bootstrap (BS) and displacement of factor elements (DISP) were run to estimate the uncertainty of receptor modeling (Table S4). The results of Scenario 2 show that when a large number of components (conventional components and all organic markers without screening) are included, the co-linearity of the sources increases due to the large correlation between some organic components. That is, the model extracts organic components uniformly to one or two factors, thereby masking the identity of the organic components, making it impossible to distinguish the sources by its identity (Fig. S6). Therefore, based on the analysis of the correlation between organic and inorganic markers and between organic and organic markers, the components included in the PMF were screened. Fig. S7 shows the source profiles in three scenarios (PMF_{tra} , PMF_{less} and PMF_{scr}) periods by PMF. The source categories were identified as follows:

$\text{Factor}_{\text{tra } 1}$, $\text{Factor}_{\text{less } 6}$ and $\text{Factor}_{\text{scr } 5}$ are characterized by high loadings of SO_4^{2-} , NO_3^- , NH_4^+ and OC, which are considered as markers of secondary source (Dai et al., 2020; Xue et al., 2019). $\text{Factor}_{\text{tra } 2}$, $\text{Factor}_{\text{less } 2}$ and $\text{Factor}_{\text{scr } 3}$ are explained as urban fugitive dust due to its characteristic species of Si, Ca and Al, as well as some Fe, Cu and SO_4^{2-} (Bi et al., 2019; Dai et al., 2019; Liu et al., 2017). $\text{Factor}_{\text{tra } 3}$, $\text{Factor}_{\text{less } 1}$ and $\text{Factor}_{\text{scr } 8}$ are characterized as cement dust due to its characteristic species of Si and Ca as well as some Na, Mg and NO_3^- (Bi et al., 2019).

$\text{Factor}_{\text{tra } 4}$ presents high concentrations of OC and EC, because it also contains the markers of road dust such as Al, Si, Ca, Cu and Fe, the $\text{Factor}_{\text{tra } 4}$ is finally identified as the traffic source. By incorporating

PAHs, the PMF_{less} and PMF_{scr} model distinguishes motor vehicles into gasoline and diesel vehicles. Factor_{less 3} and Factor_{scr 4} present high concentrations of OC, EC and NO₃⁻, BbF, BkF, BaP and IcdP in Factor_{less 3} and BbF, BkF, BaP, 17α(H),21β(H)-Hopane, C16, C18 and C25 in Factor_{scr 4} are indicator of gasoline vehicles (Chen et al., 2016; Choi et al., 2015; Galvao et al., 2019; Lin et al., 2010; Wang et al., 2021). Factor_{less 5} and Factor_{scr 2} present high concentrations of OC and EC, IcdP, DBA, BghiP and Cor in Factor_{less 5} and IcdP, DBA, BghiP, Cor, 17α(H),21β(H)-Hopane, C16, C18, C20, C28 n-alkane in Factor_{scr 2} indicate the diesel vehicles (Chen et al., 2016; Fraser et al., 2003; Kang et al., 2018; Lin et al., 2010; Pereira et al., 2017). Therefore, Factor_{less 5} and Factor_{scr 2} are identified as the diesel vehicles source.

Factor_{tra 5} and Factor_{less 4} are characterized by high loadings of OC, EC and SO₄²⁻, as well as some Si and Ca (Belis et al., 2019; Bi et al., 2019). The main organic markers for Factor_{less 4} are Flt, Pyr, BaA and BbF. Therefore, Factor_{tra 5} and Factor_{less 4} are identified as the coal combustion. By incorporating hopanes and n-alkane, the PMF_{scr} model distinguishes coal combustion source into mature coal combustion and immature coal combustion sources. The Factor_{scr 6} is characterized by high loadings of OC, EC and SO₄²⁻, as well as some Si and Ca, the main organic markers are Flt, Pyr, BaA and BbF, 17α(H),21β(H)-30-Norhopane, 17α(H),21β(H)-Hopane, C24 and C27 n-alkane (Bi et al., 2008; Choi et al., 2015; Oros and Simoneit, 2000). 17α(H),21β(H)-30-Norhopane can identify the marker of combustion of maturity coal. The C_{max} of n-alkanes emitted by bituminous coal and anthracite are C27 and C24 (Choi et al., 2015; Galvao et al., 2019; Oros and Simoneit, 2000). Therefore, Factor_{scr 6} is identified as the mature coal combustion. The Factor_{scr 7} presents high concentrations of OC, EC and SO₄²⁻, as well as some Si and Ca, different from Factor_{scr 6}. The main organic markers for this factor are Flt, Pyr, BaA, BbF, 17β(H),21β(H)-Hopane, C16, C18 and C25, which indicates the factor was from immature coal combustion source (Bi et al., 2008; Choi et al., 2015; Lin et al., 2010; Wang et al., 2009; Wang et al., 2015).

In addition, the main organic markers for Factor_{scr 1} are high-carbon n-alkanes, especially C29, C30 and C31 n-alkanes, which are considered as markers of plant wax (Lin et al., 2010; Wang et al., 2009), the Factor_{scr 1} is finally identified as the biogenic source.

3.5.2 Comparison

Figure 5 presents the average percentage to PM_{2.5} mass concentrations estimated by the PMF for the three scenarios. The secondary sources, urban fugitive dust and cement dust share the same average percentage to PM_{2.5} in the three scenarios. As for the coal combustion source, the average percentage to PM_{2.5} mass concentrations obtained by PMF_{tra} is 14%, PMF_{less} incorporating PAHs and conventional components is 13%. The summed percentage of mature coal combustion and immature coal combustion source obtained by PMF_{scr} is 14%, that is, the apportionment results of coal combustion source in the three models are relatively consistent. The average percentage to PM_{2.5} mass concentrations of traffic source obtained by PMF_{tra} is 19%, the average percentage to PM_{2.5} of gasoline vehicles and diesel vehicles obtained by PMF_{less} is 22%. The summed percentage of gasoline and diesel vehicles source

obtained by PMF_{scr} is also 22%, that is, the apportionment results of traffic source in the three models are basically consistent.

PMF_{tra} , PMF_{less} and PMF_{scr} input different components to obtain relatively consistent results, indicating that the source apportionment results after incorporating organic markers are reliable. Correlation between modeled and measured $PM_{2.5}$ concentrations of the three scenarios are also exhibited in Fig. S8. Comparing the correlation between modeled and measured $PM_{2.5}$ concentrations of the three PMF models, the source apportionment results of the three models are all good. Therefore, by including the organic components such as PAHs, this study can well distinguish motor vehicle sources into diesel vehicle sources and gasoline vehicle sources. By including the organic components such as PAHs, hopane and n-alkanes, this study can well distinguish motor vehicle sources into diesel vehicle sources and gasoline vehicle sources. And at the same time can distinguish coal combustion sources into maturity coal combustion and immaturity coal combustion sources. What's more, the source apportionment results have a certain reliability.

4. Conclusions

This study explored the seasonal variations of inorganic and organic components in $PM_{2.5}$, and identified the relationship among organic markers, inorganic markers and meteorological factors. What's more, this study carried out research on the applicability of organic markers and inorganic markers in the PMF model.

The highest and lowest concentrations of conventional components ($PM_{2.5}$, WSI, tracer elements, OC and EC) were observed in the winter and summer, respectively. While the highest concentration of the sum of organic species (PAHs, hopanes, steranes and n-alkanes) was observed in winter and spring and the lowest concentration was in autumn.

By including the organic markers such as PAHs, this study can well distinguish motor vehicle sources into diesel vehicle sources and gasoline vehicle sources. If the organic markers (such as PAHs, hopane and n-alkanes) are included, this study can well distinguish motor vehicle sources into diesel vehicle and gasoline vehicle sources, and at the same time distinguish coal combustion sources into maturity coal combustion and immaturity coal combustion sources, and the source apportionment results have a certain reliability.

Declarations

Data availability

All relevant data are within the manuscript and available from the corresponding author upon request.

Statements and Declarations

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.

Funding

This study is supported by the National Natural Science Foundation of China (41977181), Young Elite Scientists Sponsorship Program by Tianjin (TJSQNTJ-2018-04), the Fundamental Research Funds for the Central Universities, Nankai University (63211064).

Authors Contributions

Qianqian Xue: Writing - original draft, Methodology. Yingze Tian: Methodology, Writing - review & editing. Yang Wei: Grammar check. Danlin Song and Fengxia Huang: Basic data support. Yinchang Feng: Resources, Supervision. All authors contributed toward revising and improving the manuscript.

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Ethical approval

Not applicable

Consent to participate

All authors participated in this work.

Consent to publish

All authors agree to publish.

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Tables

Due to technical limitations, table 1,2 is only available as a download in the Supplemental Files section.

Figures

Figure 1

Concentrations of PM_{2.5}, WSI (the sum of NH_4^+ , SO_4^{2-} , NO_3^- and Cl^-), tracer elements (the sum of Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Ti, V, and Zn), OC, EC and the sum of organic species (PAHs, hopanes, sterane, and n-alkane).

Figure 2

Concentrations of PAHs during four seasons.

Figure 3

Concentrations of hopanes during four seasons.

Figure 4

Concentrations of n-alkane during four seasons.

Figure 5

Percentage source contributions (%) to $PM_{2.5}$ mass concentrations estimated by the PMF model.

Figure (a), (b), (c) represent the result from PMF_{tra} , PMF_{less} and PMF_{scr} , respectively; CD: cement dust; SS: secondary source; UFD: urban fugitive dust; TS: traffic source; CC: coal combustion; GV: gasoline vehicles; DV: diesel vehicles; MCC: mature coal combustion; ICC: immature coal combustion; BS: biogenic source.

Supplementary Files

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