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Source apportionment of $PM_{2.5}$ in Shanghai based on hourly molecular organic markers and other source tracers

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Abstract

Identification of various sources and quantification of their contributions are a necessary step to formulating scientifically sound pollution control strategies. Receptor model is widely used in source apportionment of fine particles. However, most of the previous studies are based on traditional filter collection and lab analysis of aerosol chemical species (usually ions, elemental carbon (EC), organic carbon (OC) and elements) as inputs. In this study, we conducted robust online measurements of a range of organic molecular makers and trace elements, in addition to the major aerosol components (ions, OC and EC), in urban Shanghai in the Yangtze River Delta region, China. The large suite of molecular and elemental tracers, together with water-soluble ions, OC and EC, provide data for establishing measurement-based source apportionment methodology for $PM_{2.5}$. We conducted source apportionment using positive matrix factorization (PMF) and compared PMF solutions with molecular makers added (i.e. MM-PMF) and those without organic markers. MM-PMF identified 11 types of pollution sources, with biomass burning, cooking and secondary organic aerosol (SOA) as the additional sources identified. The three sources accounted for 4.9%, 2.6% and 14.7% of the total $PM_{2.5}$ mass, respectively. During the whole campaign, the secondary source is an important source of atmospheric pollution, the average contribution of secondary pollution sources is as high as 63.8% of the total $PM_{2.5}$ mass. Grouping different sources to secondary and primary, we note that SOC and POC contributed 45.1% and 54.9%, respectively. It is worth noting that the contribution of cooking to $PM_{2.5}$ mass only account for 2.6%, but it contributed to 10.7% of OC. Episodic analysis indicated that secondary nitrate was always the main cause of $PM_{2.5}$ pollution, while during non-episodic hours, vehicle exhaust made a significant

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contribution. Through the application of the above-mentioned techniques to the Yangtze River Delta, more insights are gained on the sources, formation mechanism and pollution characteristics of $PM_{2.5}$ in this region.

1. Introduction

In recent years, with the increasingly prominent problem of air quality, more and more attention has been paid to the research of air pollution, which focuses on the study of atmospheric particulate matter (PM), especially fine particulate matter ($PM_{2.5}$) (Chen et al., 2007; Zhang et al., 2009a). The study of chemical composition of atmospheric $PM_{2.5}$ is to help understand the source, formation mechanism, and environmental effects. $PM_{2.5}$ pollution reduces atmospheric visibility (Chow et al., 2004) and exposure to $PM_{2.5}$ is positively correlated with adverse health effects (Nel, 2005; Lippmann et al., 2009; Mimura et al., 2014; Liu et al., 2016; Jimenez et al., 2009). $PM_{2.5}$ in the atmosphere also affects the radiation balance on the ground by scattering or absorbing solar radiation and changing the properties of clouds, which has an impact on global climate (Foley et al., 2010; Ramanathan et al., 2001; Kanakidou et al., 2005). Therefore, $PM_{2.5}$ pollution has become the primary control target to improve air quality in urban environments. Studying the composition of $PM_{2.5}$ and identifying its sources have practical significance for the understanding of $PM_{2.5}$ pollution characteristics and environmental effects.

The analysis of the sources is of great significance for $PM_{2.5}$ emission reduction and pollution control (Huang et al., 2014; Wang et al., 2017). Generally, the sources of pollution can be qualitatively assessed according to presence of chemical components characteristic to specific sources. In addition, receptor models can be used to further identify and quantify the sources of atmospheric $PM_{2.5}$ (Hopke, 2016; Jaeckels et al., 2007; Lee et al., 2008; Sofowote et al., 2014;). Compared with other methods, Positive Matrix Factorization (PMF) (Paatero & Tapper, 1994) does not need to input the source profiles, and we can simultaneously analyze the source profiles and contributions of various sources. Hence, PMF has been widely used in the source analysis of $PM_{2.5}$ all over the world, for example, Beijing (Song et al., 2006; Yao et al., 2016), Shanghai (Wang et al., 2018; Wang et al., 2013; Feng et al., 2013; Feng et al., 2012; Wang et al., 2015; Wang et al., 2014; Zhao et al., 2015; Qiao et al., 2016), Hong Kong (Hu et al., 2010; Yuan et al., 2006), New York (Zhou et al., 2019; Masiol et al., 2017), and other regions (Ulbrich et al., 2009; Fang et al., 2015).

High time resolution measurements are inherently advantageous to the source analysis, because they are able to capture the diurnal variations of the main source activities (such as vehicle exhaust) and secondary formation processes. High time resolution data provide opportunities to study short-term source distributions. There are limited number of source apportionment studies exploring the combined high-time resolution data set including various aerosol components such as trace elements (Wang et al., 2018). Online-measurement based source apportionment studies in the past, so far, are mainly

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based on PM_1 Aerodyne aerosol mass spectrometer (AMS) or Aerosol chemical speciation monitoring (ACSM) (Al-Naiema et al., 2018). AMS or ACSM provide data on ion fragments, which only retain partial information for their parent molecules. Multiple parent molecules could lead to the same fragments during the ionization process in AMS or ACSM, which introduce ambiguity in relying on fragment ions for source differentiation. Accurate quantitative monitoring of atmospheric organic matter on the molecular level is critical to source analysis.

Shanghai is the financial center of China, with a large population and a total area of 6,340 km^2. Past source apportionment studies of $PM_{2.5}$ in Shanghai were either based on offline filters using receptor models (Du et al., 2017; Chang et al., 2018), or emissions with numerical models (Li et al., 2015; Shu et al., 2019; Li et al., 2019; Feng et al., 2019). The past receptor modeling studies relied on chemical composition data derived from 24-h time-integrated filter samples followed by off-line laboratory analysis. The off-line nature severely limits its utility in addressing episodic pollution events and in providing data to assess emission-based model evaluation of pollution sources and regional transport. Some researchers have conducted online $PM_{2.5}$ source apportionment, however, previous studies were mainly using the traditional aerosol species as inputs (Wang et al., 2018). Organic matter constitutes a considerable share of $PM_{2.5}$, while the online analytical techniques used in the past were not suitable for describing this fraction in full.

In this study, online monitoring of atmospheric $PM_{2.5}$ compositions, including inorganic ions, organic carbon (OC), elemental carbon (EC), trace elements and organic molecular markers, was conducted in Shanghai from November 9 to December 3, 2018. The purpose is to use the detailed high-time resolution speciation data (especially organic molecular markers) to identify the sources of $PM_{2.5}$ based on molecular-marker based PMF. This study gives insights into more detailed source contributions, changes of sources and effects of the air pollution control strategies.

2. Methodology

2.1 Online measurement

We conducted an observation for $PM_{2.5}$ and its major chemical compositions (including inorganic ions, OC, EC, elements, and organic tracers) from November 9 to December 3, 2018. The organic tracers were measured in Shanghai Academy of Environmental Sciences, which is a reprehensive site for the urban city. The inorganic ions, OC/EC, and elements were measured in Shanghai Pudong Environmental Monitoring Station, which is also a typical site for the urban city. Monitoring site locations are shown in Figure 1. The two sites are 12 km apart. We combined these data in order to obtain a more comprehensive chemical characterization of the urban $PM_{2.5}$ air pollution situation.

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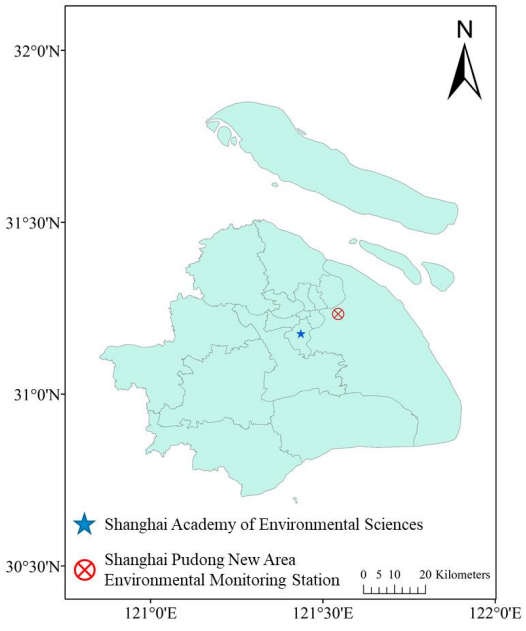

Figure 1. Locations of the two sampling sites in Shanghai, China

The concentration of $PM_{2.5}$ was measured by an online beta attenuation particulate monitor (FH 62 C14 series, Thermo Fisher Scientific) (Qiao et al., 2014). Carbonaceous materials (OC and EC) were monitored by a semi continuous OC/EC analyzer (model RT-4, Sunset Laboratory, Tigard, OR, USA) (Nicolosi et al., 2018; Zhang et al., 2017). The water-soluble inorganic ions were measured by Monitor for Aerosols and Gases (MARGA, Model ADI 2080, Applikon Analytical B.V.) (Makkonen et al., 2012; Griffith et al., 2015). Concentrations of 22 elements in $PM_{2.5}$ were measured by an ambient elemental monitor (Xact 625 Ambient Continuous Multi-metals Monitor, Cooper Environmental Services, Tigard, OR, USA) using nondispersive X-ray fluorescence (XRF) analysis (Battelle, 2012; Jeong et al., 2019). Quantification of hourly speciated organic compounds were achieved using a Thermal desorption Aerosol Gas Chromatograph (TAG) (Williams et al., 2014; Zhao et al., 2013a; Isaacman et al., 2014). The operation details and data quality are described in a separate paper (Wang et al., 2019). Figure S1 shows the comparison of reconstructed and measured $PM_{2.5}$ mass for samples collected for this study (Wang et al., 2016; Huang et al., 2014). The meteorological parameters are from the open data at Hongqiao airport (available at http://www.wunderground.com).

2.2 PMF receptor model

PMF is a bilinear factor analysis method, which is widely used to identify pollution sources and quantify the

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contribution of source sectors to the concentration of ambient air pollutants at receptor sites, with an assumption of mass conservation and a chemical mass balance between emission source and receptors. In this study, the Environmental Protection Agency (EPA) PMF version 5.0 (Norris et al., 2014) was applied to perform the analysis. PMF decomposes the measured data matrix, X_{ij}, into a factor profile matrix, f_{kj}, and a factor contribution matrix, g_{ik}, (Eq 1):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)$$

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij}/u_{ij})^2 \quad (2)$$

In eq 1, X_{ij} is the measured ambient concentration of target pollutants; g_{ik} is the source contribution of the k^{th} factor to the i_{th} sample, and f_{kj} is the factor profile of the j_{th} specie in the k_{th} factor; e_{ij} is the residual concentration for each data point. PMF seeks a solution that minimizes an object function Q (Eq 2), based on the uncertainties of each observation u_{ij}. The user provides the u_{ij} for each data point. The selection of the best factor in this study and the error estimation diagnostics for each model result are described in the supplement information (Figure S2, Figure S3, Table S1, Table S2).

PMF model assumes that the quantity of the input species is conserved, and the source profile is unchanged. In order to minimize the impact of organic matter degradation on the deviation of mass conservation hypothesis, organic species with low volatility and low reactivity are selected as input. The requirement of constant source profiles is not strictly met when the receptor model is applied to measurement data covering a long duration (e.g., months or longer). However, understanding/progress can be achieved despite the non-strict adherence to the requirements of the constant source profile. The source profile parsed by PMF can be viewed as the averaged profile over the entire sampling period. In an atmospheric environment, both primary organic aerosol (POA) and secondary organic aerosol (SOA) have the problem of changing source profiles. Therefore, it is necessary and vital to obtain high time resolution data, preferably several hours for a sample of data or shorter, as an input file for PMF model. The input files in this study are hourly data and the time span of whole campaign is less than one month. As such, the source type information will not change significantly.

In this study, a total of 289 samples has been collected. The hourly chemical species selected as input to PMF model contain 13 elements, 4 inorganic species, the carbon component (OC and EC), organic markers (including polycyclic aromatic hydrocarbons (PAHs) and anhydro sugars, etc.), and $PM_{2.5}$ mass concentration. Traditional PMF (PMFt, "t" refers to traditional) which include only $PM_{2.5}$ mass, elements, inorganic ions, OC and EC as inputs, and molecular marker based-PMF (MM-PMF) (Al-Naiema et al., 2018; Wang et al., 2017; Zhang et al., 2009b) with organic markers added as inputs on the basis of above species were performed separately to do source apportionment.

The uncertainty of each data point is calculated according to Eq 3:

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$$u_{ij} = \sqrt{(x_{ij} \times EF)^2 + (\frac{1}{2} \times MDL)^2} \quad (3)$$

where MDL is the method detection limit and EF is the error fraction determined by the user and associated with the measurement uncertainty. The concentration data of species below the detection limit were replaced by 1/2 of the MDL, and the u_{ij} was calculated by 5/6 of the MDL. For the concentration data of missing species, the missing value is the geometric average value of the concentration of this species, and its u_{ij} is four times the geometric average value.

2.3 Trajectory analysis

The backward trajectory analysis is a useful tool to identify the influence of air mass path on PMF resolved sources. 36-h duration backward trajectories arriving at an altitude of 100 m above ground level (AGL) over the site were calculated using the NOAA HYSPLIT model (https://ready.arl. noaa.gov/HYSPLIT.php), deploying the 0.5° Global Data Assimilation System (GDAS) meteorological data. The sampling days were then classified into four clusters according to the geographical origin and movement process of the trajectories, i.e., two oceanic trajectories, and two continental trajectories.

3. Results and discussion

The pollution episodes occurred mostly in winter, due to adverse atmospheric conditions（such as more frequent stagnation of atmospheric movement）and enhanced the impact on air quality from local and regional emissions. The hourly meteorological parameters and $PM_{2.5}$ concentration during the monitoring time is shown in Fig. 2. The concentration levels of the major species measured are provided in Table 1. The average temperature was 14℃, the relative humidity (RH) was 79.9%, the wind speed (WS) was 3m/s during the campaign. The average $PM_{2.5}$ concentrations were 46.3±33.8 μg/m^3, with organic matter contributing to 19.6% of the total mass. Nitrate, sulfate, and ammonium contributed to 32.0%, 16.5%, and 16.2% of $PM_{2.5}$, respectively. Measured total elements account for 3.5% of $PM_{2.5}$ mass on average.

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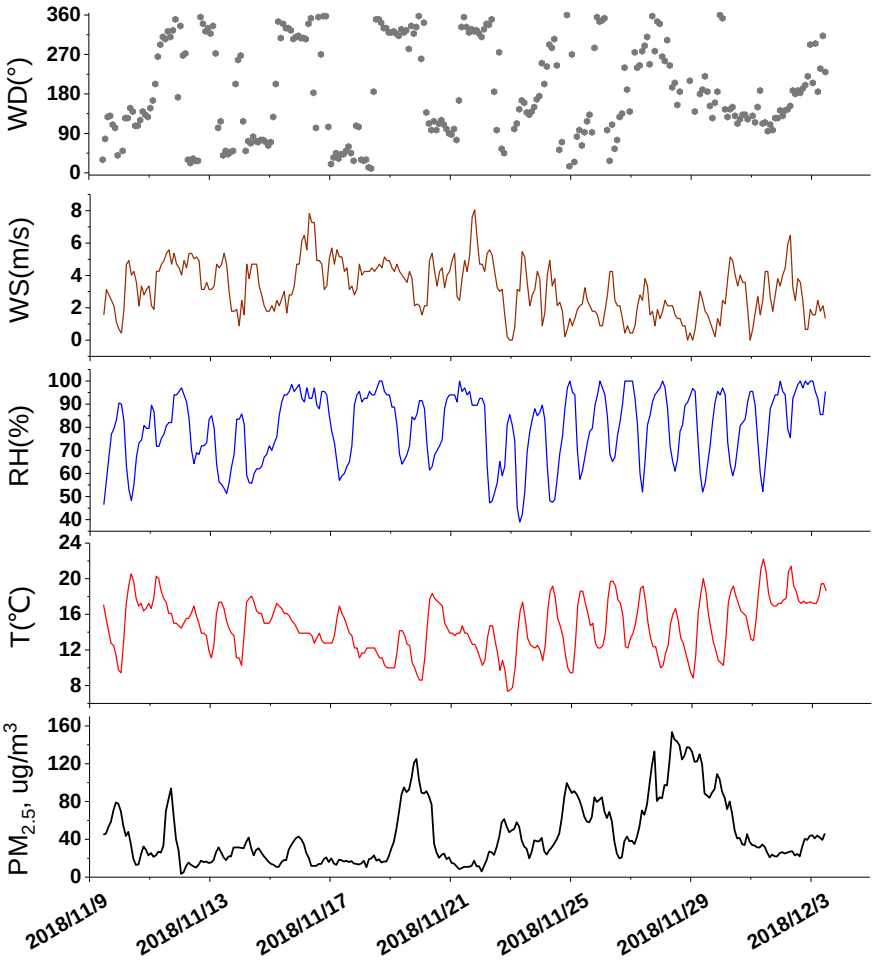

Figure 2. Time series of meteorological parameters and $PM_{2.5}$ during the field campaign.

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152 **Table 1. Measured $PM_{2.5}$ major components (μg/m^3) used in the PMF analysis in this study**

Compound	Average	Stdev
$PM_{2.5}$	46.3	33.8
Cl^-	0.78	0.52
Nitrate	14.81	15.12
Sulfate	7.65	4.31
Ammonium	7.47	6.25
EC	1.59	1.13
OC	6.48	2.79
As	0.006	0.005
Ba	0.024	0.017
Ca	0.137	0.104
Cr	0.004	0.005
Cu	0.012	0.008
Fe	0.445	0.627
K	0.381	0.196
Mn	0.065	0.069
Ni	0.004	0.003
Pb	0.025	0.026
Si	0.421	0.322
V	0.0031	0.0029
Zn	0.114	0.099

153

154 **Table 2. Abundance and naming of measured organic tracers (ng/m^3) used in the MM-PMF Analysis**

Naming	Grouping	Average	Stdev
PAHs252	benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, and benzo[a]pyrene	1.44	1.43
PAHs276	benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene	0.559	0.529
$C_{6\text{-}8}$ DICAs	Adipic acid, Pimelic acid, and Suberic acid	17.45	18.46
C_9-acids	9-Oxononanoic acid, and Azelaic acid	9.25	6.46
SFAs	Palmitic acid, and Stearic acid	71.57	60.86
Mannosan		1.54	1.51
Levoglucosan		45.91	39.17
OHBAs	3-hydroxybenzoic acid, and 4-hydroxybenzoic acid	1.05	0.85
α-pinT	Pinic acid,and 3-methyl-1,2,3-butanetricarboxylic acid	21.05	19.22
DHOPA	2,3-dihydroxy-4-oxopentanoic acid	3.93	4.92
Phthalic acid		9.13	10.28

155 **3.1 $PM_{2.5}$ source apportionment**

156 In this study, PMF source analysis was conducted in two scenarios. They were MM-PMF with organic tracers and

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157 PMFt without organic tracers included and the results were compared in detail. The abundance and nomenclature of the
158 organic tracers used are shown in Table 2. The priority input species for PMF analysis are those with high abundance and
159 characteristics of different sources, especially organic compounds with lower volatility and lower reactivity were selected
160 as input for MM-PMF. Highly correlated organic species (R> 0.8), indicating common sources, are clustered together to
161 reduce the number of species and to avoid collinearity problems in MM-PMF (Wang et al., 2017).

162 **3.1.1 MM-PMF results**

163 In PMF, the optimal number of factors is a compromise between identifying factors with the best physical explanations
164 and achieving a sufficiently good fit for all species. In PMF solutions of too few factors, different sources are combined
165 together, the resolved sources cannot fully explain the individual species; while too many factors may split one source into
166 multiple uninterpretable factors. Initially, 7 to 14 factors were tested, and the final factor numbers were determined by
167 examining the change in Q/Q_{exp}. Finally, the 11-factor solution for MM-PMF was selected as it gave the most reasonable
168 factor profiles (Figure S2). Table S1 shows the summary of error estimation diagnostics from BS, DISP and BS-DISP for
169 MM-PMF.The summary of the model performance for individual input species for the 11-factor solution in MM-PMF are
170 given in Table S3. Nevertheless, the base run results still have certain degrees of factor mixing. As the source specific
171 tracer compounds have similar temporal variations and the diversity of species components contained in the source,
172 chloride, sulfate and certain metal elements were found in different PMF-resolved profiles.

173 Factor recognition was based on the highest loaded species of each factor. The factor profiles of the 11-factor solution
174 are shown in Fig. 3. Secondary nitrate factor (F1) was identified by high concentrations of nitrate and ammonium, the
175 distribution of ammonium and nitrate in F1 is 48.1% and 66.2% respectively. The secondary sulfate factor (F2) is
176 characterized by the highest loading of sulfate (35.3%). In addition, ammonium in the secondary sulfate factor distribution
177 ranks the second among the eleven factors, less than F1. A small amount of organics acids and PAHs also appear in the two
178 factors. OC contribution from the secondary sulfate, secondary nitrate, and SOA factors were assumed as secondary OC
179 (SOC), whereas OC from the other factors was assumed to be primary OC (POC). The secondary sulfate factor contributes
180 the most to SOC, which can be seen from the correlation of the respective species with OC. Percentage contribution of
181 various source factors to $PM_{2.5}$ and to OC based on MM-PMF show in Fig.4. F1 and F2 contributed 33.5% and 15.6% to
182 total $PM_{2.5}$ mass, respectively. The SOC associated with secondary nitrate and sulfate factors accounted for 2.68 $\mu g/m^3$
183 (41.3%) on average across the whole observation period. The diurnal variation of F1 showed much higher contributions at
184 nighttime; while for F2, no obvious diurnal contrast was observed. F1 has the medium and highest correlation with NO_x

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(R =0.54) and CO (R = 0.79) while F2 showed moderate correlations with SO_2 (R = 0.32) and CO (R =0.36) (Table S4). These results suggest that F1 may represent condensation of oxidation products of local emissions in the nighttime plus regional transportation. Sun et al. (2006) observed increased sulfate formation under high RH in winter in urban city. During the observation period, the RH is high during the day and night, and the daytime temperature is higher than the nighttime. Therefore, the combined effects of aqueous phase oxidation and daytime photochemical reactions, leading to the not obvious daily variation of the secondary sulfate factor.

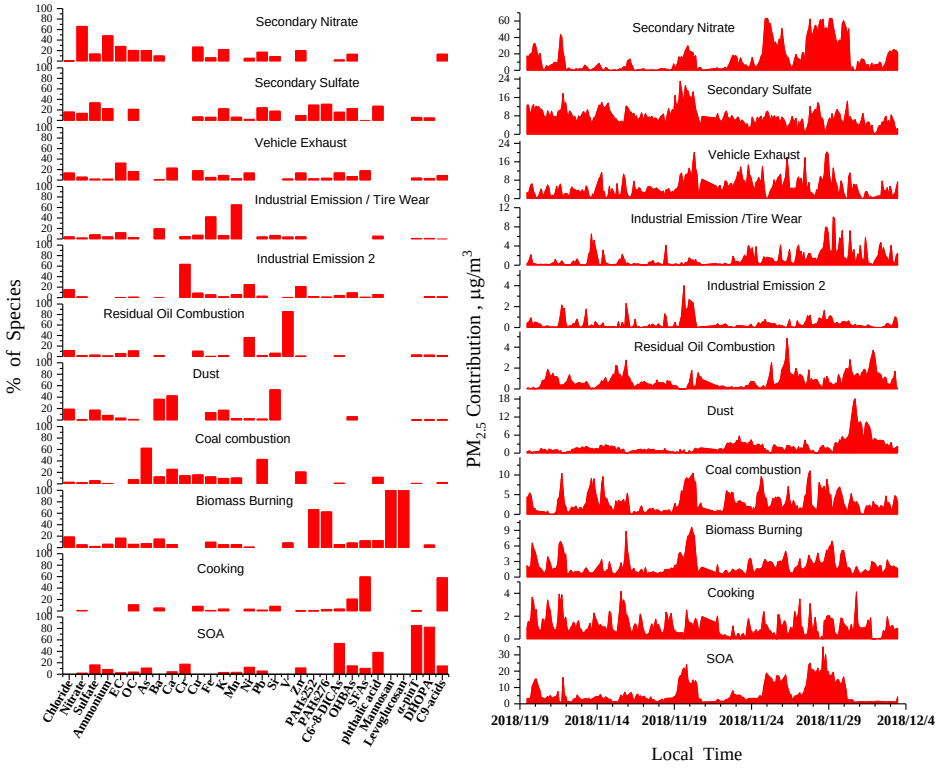

Figure 3. Resolved factor profiles (left) and factor contributions (right) in eleven-factor solution in MM-PMF

The third factor (F3) has a high abundance of EC, OC, Ca, Cu and also contains some organic tracers (PAHs and organic acids, etc.), contributing to 11.3% of the total $PM_{2.5}$ mass on average. The source of vehicle exhaust contributes the most to POC, accounting for 16.2% to OC. Vehicle exhaust is an important source for carbonaceous species, the presence of Cu may originate from both fuel/lubricant combustion and brake abrasions (Adachi and Tainosho, 2004; Pant and Harrison, 2013), and the element Ca may be derived from road dust. The influence of vehicle exhaust on this factor is supported by the peak hours at 7:00-9:00 am and 5:00-7:00 pm in daily variation (Fig. 5). In addition, the high correlation

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with NOx (R=67) and CO (R=58) indicate that vehicle exhaust have a significant impact on this factor. The higher nighttime than daytime contribution of this factor may suggest influence from the planetary boundary layer height variation. In the daytime, higher boundary height leads to more vertical mixing of the pollutants and facilitates dispersion, while the stagnant nighttime atmosphere easily accumulates pollutants (Liu and Liang, 2010).

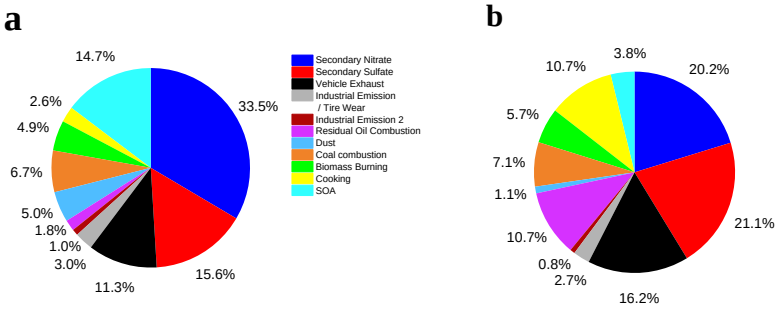

Figure 4. Percentage contribution of various source factors to $PM_{2.5}$ (a) and to OC (b) based on MM-PMF.

Factor 4 contains high loads of Fe and Mn as source tracers, in addition, it contains Ba as well. Most of these metal elements come from industries related to steel production. Although metallic elements are not exclusive tracers of industrial emissions, there are no other characteristic elements or compounds to track industrial emissions.In addition, the diurnal variation of F4 is similar to that of F3, which may be due to the tire wear in the morning and evening peak. Manganese-ferro, Zn, Cu and other elements have also been reported to be related to tire wear (Pant and Harrison, 2013), and Wang et al. (2018) also revealed this in their research on online data. While F2 showed moderate correlations with SO_2 (R = 0.52) , CO(R=0.35)and NO_X(R=49),therefore, F4 is considered as the industrial and Vehicle emission source.The factor contribution to total $PM_{2.5}$ mass and OC was minor, only 3.0% and 2.7%, respectively. Analysis of membrane samples in the area did not reveal this phenomenon (Du et al., 2017; Huang et al., 2014; Qiao et al., 2016), suggesting the benefit of the online high-resolution measurement.The fifth factor (F5) is characterized by high concentrations of Cr and Ni, which are often used in industrial processes such as plating, tanning, and metallurgy (Karar et al., 2006; Borai et al., 2002). This factor showed best correlation with CO (R = 59). No diurnal variation was observed. The factor contribution to total $PM_{2.5}$ and OC mass were minor, only 1.0% and 0.8%. The residual oil combustion factor (F6) was identified with V and Ni as tracers, of which V is often used as a tracer for residual oil combustion. The contribution of this factor mainly comes from ship transportation (Zhao et al., 2013b). The diurnal contribution at night was greater than that during daytime. The factor, residual oil combustion, were minor contributors to $PM_{2.5}$, accounting for 1.8%, but the contribution (10.7%) of this factor to OC is not negligible. The dust factor (F7) was distinguished by crustal elements Ca, Si, and Ba. The diurnal variation of

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this factor showed a broad peak during the daytime, and negative correlation with RH (R=-0.26), suggesting an influence from meteorological conditions. The factor (dust) contribution to total $PM_{2.5}$ and OC mass were 5.0% and 1.1%, respectively.

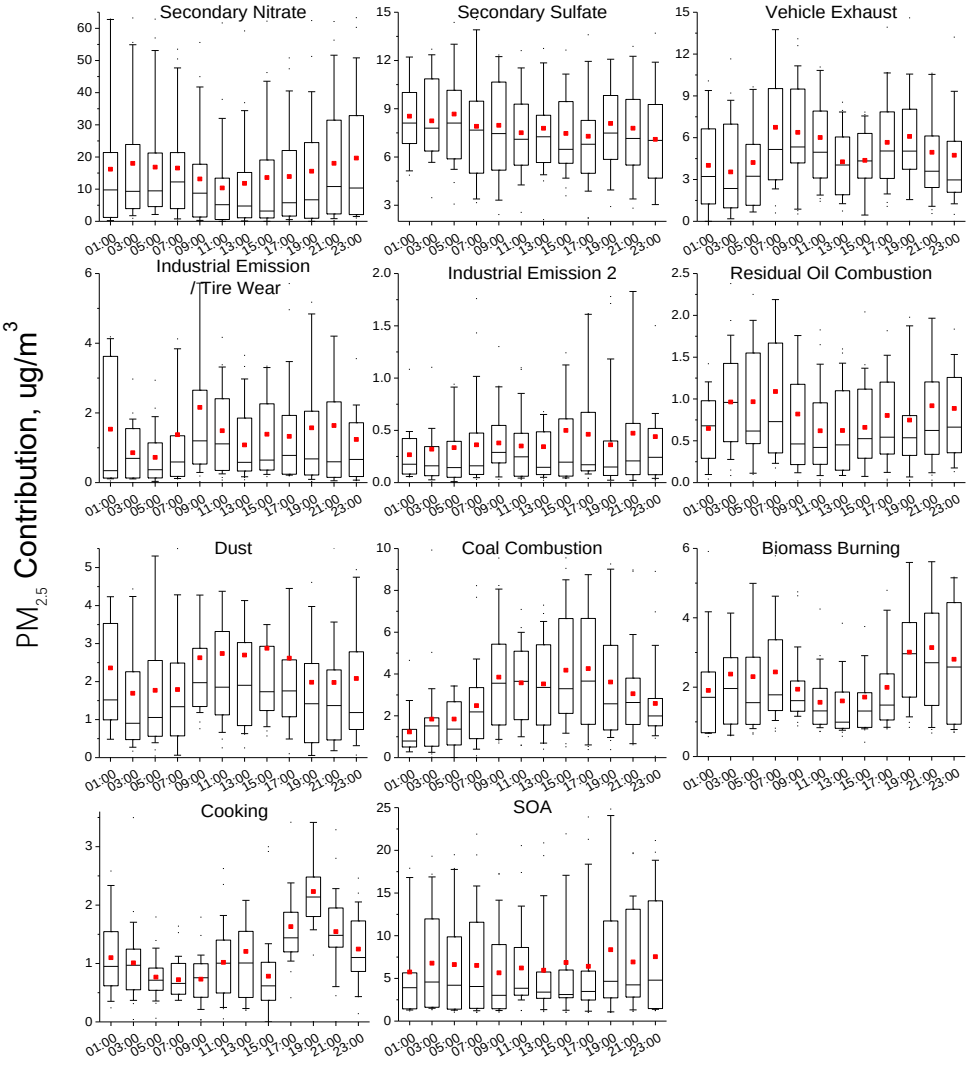

Figure 5. Diurnal variation of various source factors based on MM-PMF. (25th and 75th percentile boxes, 10th and 90th percentile whiskers; lines inside the boxes represent the hourly median and the red points represent the hourly mean)

The coal combustion factor (F8) contains high loading of metals As and Pb, accounting for 6.7 % of $PM_{2.5}$ mass on average and 7.1% to OC, it is mostly associated with coal combustion (Chen et al., 2013). Good correlations with SO_2 (R

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= 59) and CO (R =56) further support the identification of this factor. Based on analysis of MM-PMF, there is no specific organic tracers such as PAHs present in the source. The results are different from those of Wang et al. (2017) and Yu et al. (2016), which are related to regional differences in source classes.

The F9 and F10 were resolved, namely, biomass burning identified by levoglucosan and mannosan; cooking aerosol by SFAs (Palmitic acid, and Stearic acid) and C_9-acids (9-oxononanoic acid, and azelaic acid). Levoglucosan is uniquely emitted by biomass burning activities (Engling et al., 2006; Feng et al., 2013). Using Levoglucosan to indicate biomass burning may avoid the ambiguity of using K to determine the biomass burning source, which improves the accuracy of source analysis. This factor, contributed 4.9% and 5.7% of total $PM_{2.5}$ and OC mass on average, respectively. In addition, biomass burning contains high-loading of five-ring and six-ring PAHs that are considered to be derived from a mixed combustion source (including coal combustion, biomass burning, etc.). It is worth noting that the contribution of cooking to $PM_{2.5}$ mass only account for 2.6%, but it contributed 10.7% to OC. In addition, by analyzing the diurnal variation of biomass burning and cooking, the biomass burning emission at night is greater than at daytime, while cooking has an obvious peak value during 5:00-9:00 pm, which is consistent with the local dining consumption habits in Shanghai.

SOA was identified by toluene SOA tracer (2,3-dihydroxy-4-oxopentanoic acid) , α-pinene SOA tracers (pinic acid and 3-methyl-1,2,3-butanetricarboxylic acid) and phthalic acid. It is a major source of $PM_{2.5}$, accounting for 14.7%. SOC from the SOA factor accounted for 0.25 μg/m^3 (3.8%) on average to OC. SOA related to toluene was considered as anthropogenic SOA, and SOA containing pinic acid was considered as biogenic SOA. It was found that there was a similar daily changes between SOA and secondary nitrate factor, indicating some commonality in their formation processes. Many studies have documented the enhancement of biogenic SOA production by anthropogenic species through creating a more acidic environment in the aerosol (Jang et al., 2002; Wang et al., 2017).

Overall, the source apportionment results showed that secondary sources accounted for 63.9% of the total $PM_{2.5}$ mass from MM-PMF, and the contribution of secondary nitrate to $PM_{2.5}$ was greater than that of secondary sulfate. SOA is the third largest source of $PM_{2.5}$, followed by vehicle exhaust, which is the largest source of primary sources. The SOC associated with secondary nitrate, secondary sulfate and SOA factors accounted for 45.1% on average of the total OC mass across all the study period. The high loading of SOC in the secondary nitrate and sulfate factor compared with the SOA factor may indicate the potential mix of the SOA in secondary sulfate factor due to the limited organic tracers included. POC accounts for 3.55 μg/m^3 (54.8%) of the total OC. And vehicle exhaust contributes the most to POC. MM-PMF gives more detailed allocation of $PM_{2.5}$ to more accurate source factors.

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3.1.2. Back Trajectory Analysis of MM-PMF-Resolved Sources

Previous studies based on source models have shown the importance of regional transportation and local emissions to Shanghai haze events. Wang et al. (2014) identified two types of haze events in November 2010: local emission plays a dominant role in the case of weak wind (WS < 0.5m /s), while in the case of stroke (~ 2m /s), regional transport from the upwind region contributes the most. Li et al. (2015) found that local emission (~50%) in Shanghai in January 2013 was the most significant factor causing pollution. Wang et al. (2018) studied with online high-resolution data in December 2014, and found that local emission had an obvious impact on most pollution sources, while dust emission and coal combustion had a greater impact on the region.

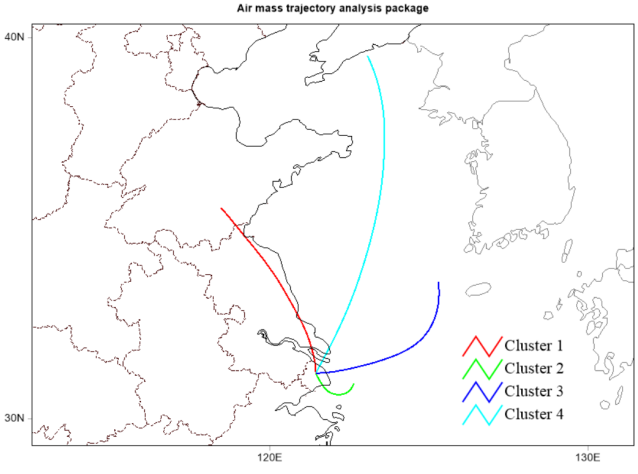

Figure 6. Clustering of air mass trajectories during observation

During the observation period, all the air mass trajectories at the receptor are shown in Figure S4. Fig.6 and table S5 show the clustering results of all air mass trajectories and the average $PM_{2.5}$ concentration measured at the sampling time represented by each cluster. These four clusters accounted for 16.1%, 40.7%, 14.3% and 28.9% of the total trajectory, respectively. It can be seen from Fig.7 that the composition varies with the source of the air mass. The average concentration of modeled $PM_{2.5}$ of each cluster analyzed by the model was 53.7 μg/m^3, 61.5 μg/m^3, 32.6 μg/m^3 and 23.0 μg/m^3, respectively. By comparing the four clusters, nitrate was the most important reason for PM pollution in Shanghai.

The effect of pollutant accumulation caused by air mass transport represented by cluster 1 and 2 on the average $PM_{2.5}$ concentration is significantly greater than the effect of cluster 3 and 4 air mass transport on $PM_{2.5}$. The average concentration of $PM_{2.5}$ in Cluster 1 is slightly larger than that of Cluster 2. According to the length and source of the trajectories of the respective clusters, cluster 1 is greatly affected by the urban transmission in North China. Coal

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combustion, biomass burning, vehicle exhaust and secondary sulfate contribution to $PM_{2.5}$ concentration are greater than cluster 2. Cluster 2 mainly represents the pollution caused by the accumulation of $PM_{2.5}$ concentration by local source emissions. In addition, the contribution of secondary nitrate to $PM_{2.5}$ in cluster 2 is much larger than that of cluster 1. The contribution of secondary source to $PM_{2.5}$ concentration is as high as 67.8%, and the secondary conversion of local source emission is more obvious. In clusters 1 and 2, SOA is a source of high contribution to total $PM_{2.5}$ concentration. Both regional and local source emissions contain a large amount of organic matter, which is an important component of secondary source pollution. The dust source is also an important source of pollution caused by local emissions leading to atmospheric $PM_{2.5}$ pollution.

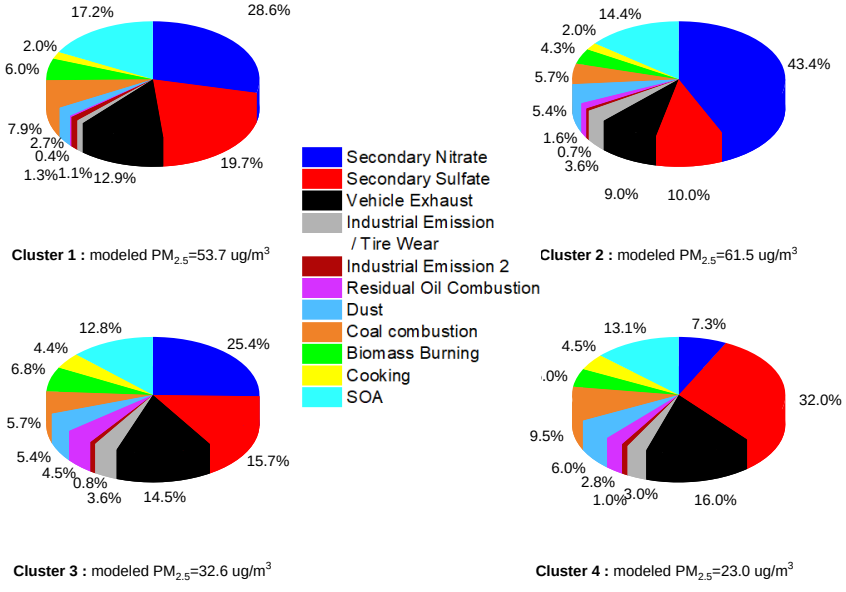

Figure 7. The percentage of sources under different air mass clusters.

Under cluster 3 and 4, $PM_{2.5}$ concentrations are relatively lower. Their biggest difference is the contribution of secondary sulfate and secondary nitrate in cluster 3 and cluster 4. Under the influence of the northern air mass transport, the proportion of secondary sulfate in cluster 4 is much larger than that of secondary nitrate, and also greater than the proportion of secondary sulfate in cluster 3. It indicates that cluster 4 is discharged from coal combustion in winter in northern China. And cluster 4 is a long-distance air mass transport, nitrogen oxides are more active in the atmosphere, and secondary nitrate contributes less in cluster 4 than in cluster 3. In general, in the winter, the coal combustion in the north of China and the biomass burning will affect the increase of $PM_{2.5}$ concentration in Shanghai under the action of air mass

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movement. The accumulation of pollutants caused by local source emissions in Shanghai is also an important cause of $PM_{2.5}$ pollution in winter.

3.1.3. Source contribution under different episodes

In order to better understand the source composition characteristics of atmospheric particulates during pollution ($PM_{2.5}$>75μg/m^3), we selected three time periods for further analysis, $PM_{2.5}$ concentration in the three periods is over 75μg/m^3 continuously or most of the time, as shown in Fig.8 (shaded area). The first episode (EP1) took place from 9 a.m. to 9 a.m. on November 19, 2018, and lasted 24 hours. The second episode (EP2) took place between 19 p.m. on November 24 and 1 p.m. on November 26, 2018, during which the $PM_{2.5}$ concentration decreased, but soon began to rebound. The third episode (EP3) lasts for a long time period, from 13 p.m. on November 27, 2018 to 7 a.m. on November 30, 2018, and the $PM_{2.5}$ average concentration was the highest among the three episodes. It is worth noting that the pollution episode that occurred from November 9 to 12 was not selected because the concentration of $PM_{2.5}$ was only over 75μg/m^3 for a few hours.

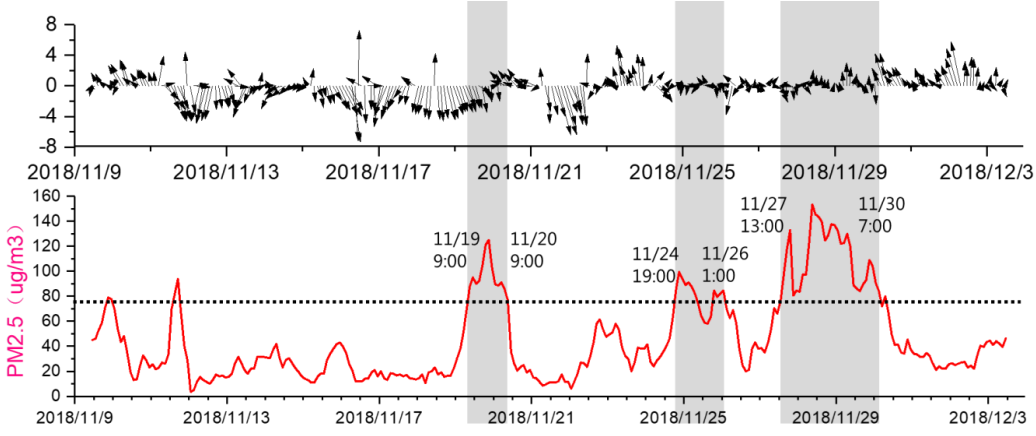

Figure 8. Pollution episodes and its $PM_{2.5}$ concentration level

The chemical characteristics of the selected three episodes are shown in Figure S5. It can be seen that the percentage of each component of $PM_{2.5}$ in the total $PM_{2.5}$ under three episodes has little difference, indicating that the component will not change much in a short time period. By analyzing the sources of $PM_{2.5}$ in the three selected periods, it is found that the sources of $PM_{2.5}$ do not follow this rule, as shown in Fig.9. To better understand the influence of regional sources on factors analyzed by PMF model, using the NOAA HYSPLIT model (https://ready.arl) for the three episodes, the 36-hour duration backward trajectory of the 100-meter AGL was calculated. 0.5 global data assimilation system meteorological data was

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deployed every 6 hours.

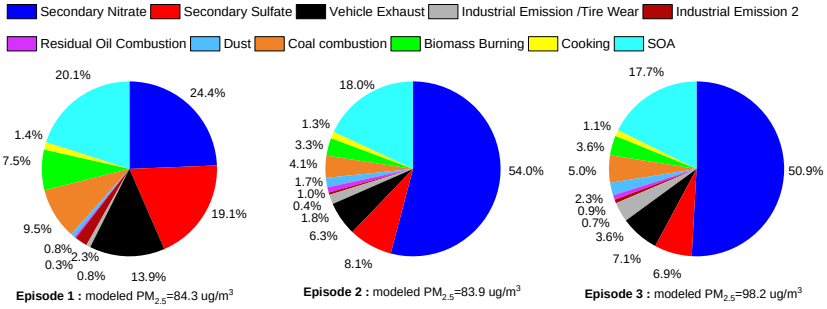

Figure 9. Source contributions under different episodes.

Combining the trajectories of the three episodes (EP1: a; EP2: b; EP3: c& d, Fig.10), the process from pollution occurrence to pollution dissipation is a process that centers around the monitoring site, and the air mass entering the monitoring point from the north turns clockwise from the east to the south and enters the monitoring area. And with the increase of air mass movement in the vertical direction.

The average $PM_{2.5}$ concentrations observed during the three episodes were EP1: 96.2 μg/m^3, EP2: 79.8μg/m^3, and EP3: 109.1μg/m^3, EP3>EP1>EP2. Generally speaking, $PM_{2.5}$ concentrations are highest when the airflow originates from the mainland under prevailing northerly winds. When easterly and southerly winds prevail, the $PM_{2.5}$ concentration observed under the influence of oceanic air mass is lower than that of air mass originating from the north. EP3 is greatly affected by the transition air mass, and the diffusion of adverse pollutants caused by the weak air flow in the vertical direction and small local wind speed leads to the accumulation of pollutants, resulting in the highest concentration of $PM_{2.5}$. EP2 is mainly affected by the clean air flow from the south and some ocean air masses, and the vertical movement of the existing air flow is greater than EP3. Compared with EP2 and EP3, EP1 has a greater contribution to secondary sulphate factor under the influence of the northern continental air mass, which was close to the study of Hua et al. (2018) on the source analysis of $PM_{2.5}$ in Beijing area. Additionally, secondary sulfate factor may also be affected by primary emission of coal combustion. Under the influence of the air quality of marine air mass and transition air mass, EP2 and EP3 show considerable contribution of secondary nitrates (EP2: 54.0% and EP3: 50.7%), while when the land air mass is dominant, the contribution rate is much lower (EP1: 24.1%). The contribution of biomass burning and coal combustion source factors show a changing pattern similar to that of secondary sulfate factors, the average contribution is the highest under the influence of northern air mass, followed by transitional and marine air mass. Under the influence of the southern air mass, the contribution of biomass burning and coal combustion source factors is the smallest, while the dust source is more

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affected by local and short-distance air mass transport.

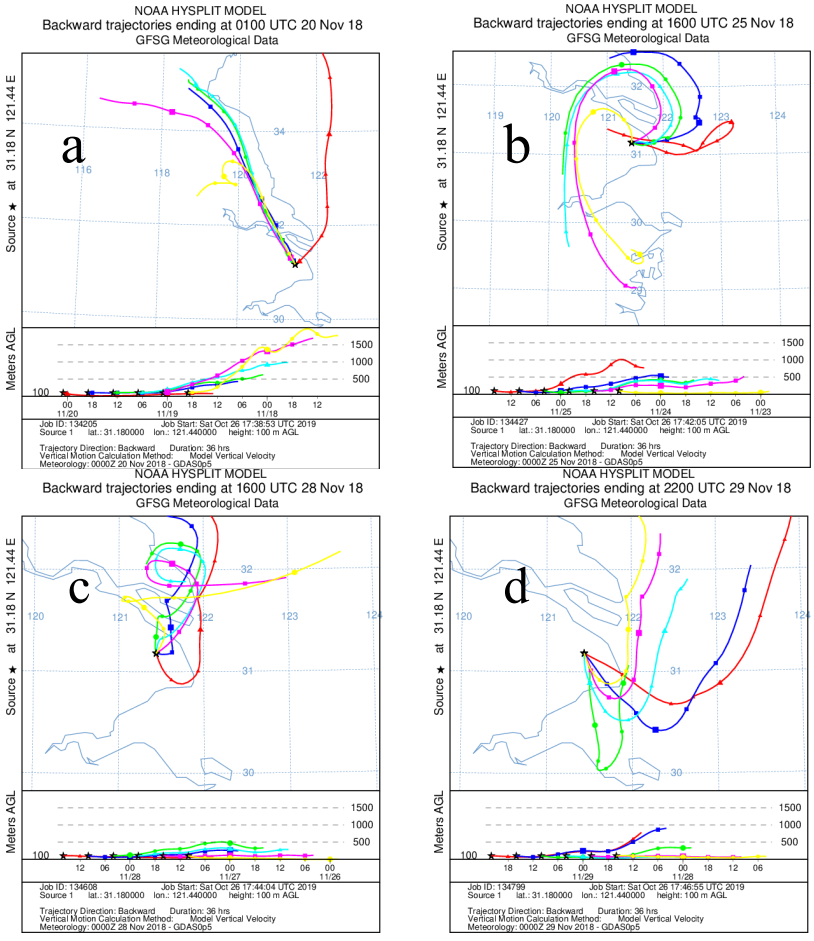

Figure 10. The backward trajectory by each episode.

In EP1, SOA is the largest contributor to the combined effects of anthropogenic and biogenic sources (19.8%), mainly affected by the secondary conversion of OM carried by long-distance air mass from the north, while vehicle exhaust is mainly affected by the continental air mass, the secondary conversion is not obvious, and other factors have little effect. In general, due to differences in energy structure and production and living habits, biomass burning and coal combustion sources are greatly affected by airflow from the north, which indirectly affects the proportion of secondary sulfate and secondary nitrate in $PM_{2.5}$. Air mass from the south and ocean is cleaner than air mass from the north. $PM_{2.5}$ pollution is also affected by the vertical movement of air mass and horizontal wind speed.

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3.2 Impact of organic tracers on source apportionment

We also tested the PMF model without including the organic tracers to compare with the base PMF (MM-PMF), which includes the organic tracers. The input data for PMFt are given in Table S6. In PMFt, eight factors were resolved (see source profiles in Figure S6), and the three factors, biomass burning, cooking, and SOA could not be extracted due to the lack of the corresponding organic tracers. The correlation of the common factor contributions for each factor between PMFt and MM-PMF is shown in Table 3. Generally, the eight common factors, except for secondary sulfate and vehicle exhaust, the other six factors correlated well between the two runs (R = 0.906-0.993), indicating the robustness of the resolved factors. The secondary sulfate adds more organic matter (PAHs, organic acids, etc.) to the MM-PMF factor profile, showed a moderate correlation (R=0.665) between PMFt and MM-PMF.

Table 3. Correlation (R) of common source factors between PMFt and MM-PMF

MM-PMF \ PMFt	Secondary Nitrate	Secondary Sulfate	Vehicle Exhaust	Industrial Emission /Tire Wear	Industrial Emission 2	Residual Oil Combustion	Dust	Coal Combustion
Secondary Nitrate	**0.906**	0.256	0.674	0.388	0.407	-0.036	-0.086	0.458
Secondary Sulfate	0.187	**0.665**	-0.011	-0.311	0.387	-0.337	-0.377	0.29
Vehicle Exhaust	0.352	-0.265	**0.562**	0.315	0.321	-0.063	0.094	0.514
Industry / Tire Wear	0.413	-0.225	0.412	**0.991**	0.151	0.072	0.346	0.236
Industry 2	0.523	-0.033	0.289	0.061	**0.983**	-0.144	-0.17	0.582
Residual Oil Combustion	-0.064	-0.346	-0.072	0.069	-0.167	**0.993**	0.264	-0.115
Dust	-0.169	-0.376	-0.196	0.277	-0.181	0.223	**0.98**	-0.026
Coal combustion	0.573	-0.027	0.436	0.153	0.636	-0.122	-0.013	**0.967**

The factor profiles of PMFt of the 8-factor solution is shown in Figure S6, and the difference of individual factor contribution to $PM_{2.5}$ and to OC from MM-PMF and PMFt are show in Fig.11. And, among MM-PMF and PMFt results, the concentrations of reconstructed $PM_{2.5}$ and OC are shown in Table S7.Compare the factor profiles and contributions of MM-PMF and PMFt, it can be found that the contribution from the secondary sources changed from (29.1 μg/m^3) 63.8% of MM-PMF to (28.5 μg/m^3) 63.9% of PMFt, while SOC changed from (2.9 μg/m^3) 46.1% to (3.1 μg/m^3) 48.9% of the total OC mass. The change in the factor profile of the secondary nitrate to $PM_{2.5}$ is not obvious, and the contribution of secondary nitrate to $PM_{2.5}$ was greater than that of secondary sulfate. While for OC, the contribution of secondary sulfate was greater than that of secondary nitrate in the two PMF analysis results. In addition, the source apportionment results under two scenarios showed that secondary sources accounted for 63.9% and 63.8% of the total mass of $PM_{2.5}$ in PMFt and MM-PMF, respectively.

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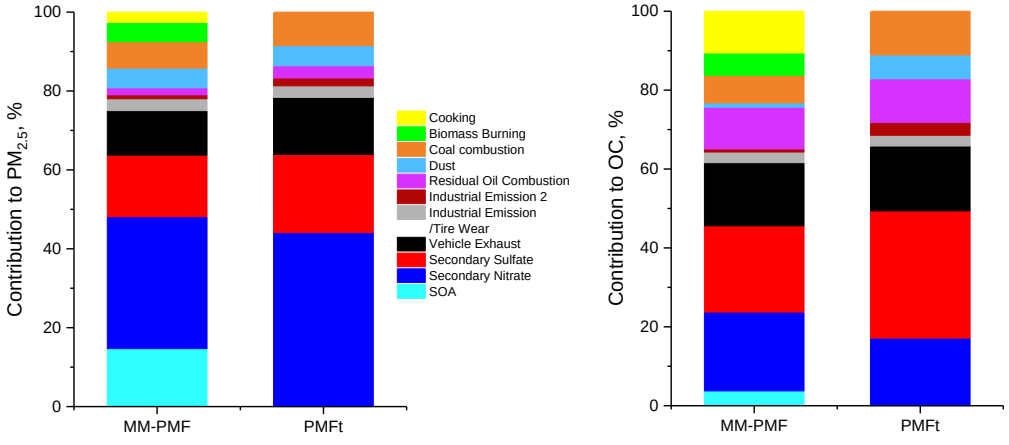
368 With the addition of organic tracers, contribuiton from vehicle exhaust dropped from 14.5% to 11.3% of MM-PMF,
369 the correlation (R) of the vehicle exhaust between MM-PMF and PMFt was only 0.562 (Table 3), which is mainly because
370 organic matters were added to the vehicle exhaust factor of MM-PMF, and the factor contribution time series diagram has
371 changed. There was no significant change in the contribution of vehicle exhaust to OC.

372 The contribution of industrial emission 2 and residual oil combustion sources to $PM_{2.5}$ mass changed from 2.0% and
373 3.1% in PMFt to 1.0% and 1.8% in MM-PMF. This is mainly because OC shifted from these two factors to the newly added
374 source of MM-PMF. Due to the transfer of OC and other elements (Ca, and Zn, etc.) in the coal combustion, the proportion
375 of this factor in $PM_{2.5}$ decreased from 8.5% of PMFt to 6.7% of MM-PMF. Compared with MM-PMF, the concentration
376 of OC in industrial emission 2, residual oil combustion and coal combustion in PMFt increased by 0.16, 0.14 and 0.25
377 μg/m^3, respectively.Generally, for the eight factors, the factor industrial emission /tire wear and dust were more stable,
378 contributions of these two factors to total $PM_{2.5}$ were relatively small, with little differences between MM-PMF and PMFt
379 results (3.0% vs 2.9% and 5.0% vs 5.1%), whereas the contribution from dust to the total OC mass changed from (0.10
380 μg/m^3) 1.1% of MM-PMF to (0.24 μg/m^3) 3.8% of PMFt. Compare the difference of individual factor contribution to OC
381 from MM-PMF and PMFt, POC changed from 53.9% to 51.1% of PMFt of the total OC mass.



382
383 **Figure 11. Difference of individual factor contribution to PM2.5 and to OC from MM-PMF and PMFt.**

384 **4. Conclusions**

385 In this study, an intensive observation campaign was organized in winter to gain more insights into the sources and

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formation of $PM_{2.5}$ in Shanghai, a typical city in the Yangtze River Delta region. $PM_{2.5}$ and its chemical components, including water-soluble inorganic ions, carbonaceous species, trace elements and organic markers (PAHs, sugars, organic acids, etc.) were measured with 1-h time resolution. By combining comprehensive data sets of chemical species into the PMF model for source analysis, the average contribution of secondary pollution sources is more than 60%. The MM-PMF with organic tracers added was further compared with the traditional PMF without organic tracers. MM-PMF further resolved the source contributions from SOA, biomass burning and cooking factors, which can't be separated without organic tracers.

Comparing the contributions of different sources to OC mass from MM-PMF, it can be seen that SOC and POC contributed 45.1% and 54.9%, respectively. The SOC associated with secondary nitrate and sulfate factors accounted for 2.68 μg/m3 (41.3%) on average across all the study. The source of vehicle exhaust contributes the most to POC, in addition, it is worth noting that the contribution of cooking to PM2.5 mass only account for 2.6%, but it contribute 10.7% to OC.

Comparisons of $PM_{2.5}$ source composition under different air quality shows that the secondary nitrate contribution is much higher when $PM_{2.5}$ concentrations are high. The data during the whole observation period were analyzed by backward trajectory clustering and four types of backward trajectories were analyzed separately. It was found that secondary nitrate was the main cause of air pollution in Shanghai. In addition, in the absence of pollution, vehicle exhaust sources still make a significant contribution. In winter, Shanghai area is greatly affected by the air mass from the northern area, which is an important cause of particulate pollution. In addition, adverse meteorological conditions may also cause the accumulation of particulate matter, resulting in air pollution.

Competing interest. The authors declare that they have no conflict of interest.

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References

Adachi, K. and Tainosho, Y.: Characterization of heavy metal particles embedded in tire dust, Environ. Int., 30(8), 1009-1017, 2004.

Al-Naiema, I. M., Hettiyadura, A. P. S., Wallace, H. W., Sanchez, N. P., Madler, C. J., Cevik, B. K., Bui, A. A. T., Kettler,

https://doi.org/10.5194/acp-2019-951
Preprint. Discussion started: 31 January 2020

Atmospheric Chemistry and Physics Discussions

J., Griffin, R. J., and Stone, E. A.: Source apportionment of fine particulate matter in Houston, Texas: insights to secondary organic aerosols, Atmos. Chem. Phys., 18(21), 15601-15622, https://doi.org/10.5194/acp-18-15601-2018, 2018.

Battelle, (2012). Environmental technology verification report. Retrieved from http://cooperenvironmental.com/wp-content/uploads/2014/09/Xact625_ETVReport-full.pdf.

Borai, E. H., El-Sofany, E. A., Abdel-Halim, A. S., and Soliman, A. A.: Speciation of hexavalent chromium in atmospheric particulate samplesby selective extraction and ion chromatographic determination, Trac-Trend. Anal. Chem., 21(11), 741-745, 2002.

Chang, Y. H., Huang, K., Xie, M. J., Deng, C. R., Zou, Z., Liu, S. D., and Zhang, Y. L.: First long-term and near real-time measurement of trace elements in China's urban atmosphere: temporal variability, source apportionment and precipitation effect, Atmos. Chem. Phys., 18(16), 11793-11812, doi:10.5194/acp-18-11793-2018, 2018.

Chen, J., Liu, G. J., Kang, Y., Wu, B., Sun, R. Y., Zhou, C. C., and Wu, D.: Atmospheric emissions of F, As, Se, Hg, and Sb from coal-fired power and heat generation in China, Chemosphere, 90(6), 1925-1932, 2013.

Chen, L. W. A.; Watson, J. G.; Chow, J. C.; and Magliano, K. L.: Quantifying $PM_{2.5}$ source contributions for the San Joaquin Valley with multivariate receptor models, Environ. Sci. Technol., 41(8), 2818-2826, 2007.

Chow, J. C., Watson, J. G., Kuhns, H., Etyemezian , V., Lowenthal, D. H., Crow, D., Kohl, S. D., Engelbrecht, J. P., and Green, M. C.: Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational study, Chemosphere., 54(2), 185-208, 2004.

Du, W. J., Zhang, Y. R., Chen, Y. T., Xu, L. L., Chen, J. S., Deng, J. J., Hong, Y. W., and Xiao, H.: Chemical Characterization and Source Apportionment of $PM_{2.5}$ during Spring and Winter in the Yangtze River Delta, China, Aerosol. Air. Qual. Res., 17(9), 2165-2180, 2017.

Engling, G., Carrico, C. M., Kreldenweis, S. M., Collett, J. L., Day, D. E., Malm, W. C., Lincoln, E., Hao, W. M., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection, Atmos. Environ., 40, S299-S311, 2006.

Fang, T., Guo, H., Verma, V., Peltier, R., and Weber, R.: $PM_{2.5}$ water-soluble elements in the southeastern united states: Automated analytical method development, spatiotemporal distributions, source apportionment, and implications for heath studies, Atmos. Chem. Phys., 15(20), 11667-11682. doi:10.5194/acp-15-11667-2015, 2015.

Feng, J. L., Sun, P., Hu, X. L., Zhao, W., Wu, M. H., and Fu, J. M.: The chemical composition and sources of $PM_{2.5}$ during the 2009 Chinese New Year's holiday in Shanghai, Atmos. Res., 118, 435-444, 2012.

Feng, J. L., Li, M., Zhang, P., Gong, S. Y., Zhong, M. A., Wu, M. H., Zheng, M., Chen, C. H., Wang, H. L., and Lou, S. R.: Investigation of the sources and seasonal variations of secondary organic aerosols in $PM_{2.5}$ in Shanghai with organic tracers, Atmos. Environ., 79, 614-622, 2013.

Feng, J. L., Zhang, Y., Li, S. S., Mao, J. B., Patton, A. P., Zhou, Y. Y., Ma, W. C., Liu, C., Kan, H. D., Huang, C., An, J. Y., Li, L., Shen, Y., Fu, Q. Y., Wang, X. N., Liu, J., Wang, S. X., Ding, D., Cheng, J., Ge, W. Q., Zhu, H., and Walker, K.: The influence of spatiality on shipping emissions, air quality and potential human exposure in the Yangtze River Delta/Shanghai, China, Atmos. Chem. Phys., 19(9), 6167-9183, doi:10.5194/acp-19-6167-2019, 2019.

Foley, K. M., Roselle, S. J., Appel, K. W., Bhave, P. V., Pleim, J. E., Otte, T. L., M athur, R., Sarwar, G., Young, J. O., Gilliam, R. C., Nolte, C. G., Kelly, J. T., Gilliland, A. B., and Bash, J. O.: Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7, Geosci. Model Dev., 3, 205 226, https://doi.org/10.5194/gmd-3-205-2010, 2010.

Griffith, S. M., Huang, X. H. H., Louie, P. K. K., and Yu, J. Z.: Characterizing the thermodynamic and chemical composition factors controlling $PM_{2.5}$ nitrate: Insights gained from two years of online measurements in Hong Kong, Atmos. Environ.,

https://doi.org/10.5194/acp-2019-951
Preprint. Discussion started: 31 January 2020

122, 864-875, 2015.

Hopke, P. K.: Review of receptor modeling methods for source apportionment, J. Air Waste Manage., 66, 237-259, https://doi.org/10.1080/10962247.2016.1140693, 2016.

Hu, D., Bian, Q. J., Lau, A. K. H., and Yu, J. Z.: Source apportioning of primary and secondary organic carbon in summer $PM_{2.5}$ in Hong Kong using positive matrix factorization of secondary and primary organic tracer data, J. Geophys. Res-Atmos., 115, D16204, 2010.

Hua, Y., Wang, S. X., Jiang, J. K., Zhou, W., Xu, Q. C., Li, X. X., Liu, B. X., Zhang, D. W., and Zheng, M.: Characteristics and sources of aerosol pollution at a polluted rural site southwest in Beijing, China, Sci. Total. Environ., 626, 519-527, 2018.

Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z. S., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514(7521), 218-222, 2014.

Isaacman, G., Kreisberg, N. M., Yee, L. D., Worton, D. R., Chan, A. W. H., Moss, J. A., Hering, S. V., and Goldstein, A. H.: Online derivatization for hourly measurements of gas- and particle-phase semi-volatile oxygenated organic compounds by thermal desorption aerosol gas chromatography (SV-TAG), Atmos. Meas. Tech., 7(12), 4417-4429, 2014.

Jang, M. S., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, Science, 298(5594), 814-817, 2002.

Jaeckels, J. M., Bae, M. S., and Schauer, J. J.: Positive matrix factorization (PMF) analysis of molecular marker measurements to quantify the sources of organic aerosols, Environ. Sci. Technol., 41(16), 5763-5769, 2007.

Jeong, C. H., Wang, J. M., Hilker, N., Debosz, J., Sofowote, U., Su, Y. S., Noble, M., Healy, R. M., Munoz, T., Dabek-Zlotorzynska, E., Celo, V., White, L., Audette, C., Herod, D., and Evans, G. J.: Temporal and spatial variability of traffic-related $PM_{2.5}$ sources: Comparison of exhaust and non-exhaust emissions, Atmos. Environ., 198, 55-69, 2019.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326(5959), 1525-1529, 2009.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., and Nielsen, C. J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, 2005.

Karar, K., Gupta, A. K., Kumar, A., and Biswas, A. K.: Characterization and identification of the sources of chromium, zinc, lead, cadmium, nickel, manganese and iron in PM_{10} particulates at the two sites of Kolkata, India, Environ. Monit. Assess., 120(1-3), 347-360, 2006.

Lee, S., Liu, W., Wang, Y. H., Russell, A. G., and Edgerton, E. S.: Source apportionment of $PM_{2.5}$: Comparing PMF and CMB results for four ambient monitoring sites in the southeastern United States, Atmos. Environ., 42(18), 4126-4137, 2008.

Li, L., An, J. Y., Zhou, M., Yan, R. S., Huang, C., Lu, Q., Lin, L., Wang, Y. J., Tao, S. K., Qiao, L. P., Zhu, S. H., and Chen, C. H.: Source apportionment of fine particles and its chemical components over the Yangtze River Delta, China during a heavy haze pollution episode, Atmos. Environ., 123, 415-429, 2015.

Li, R., Mei, X., Wei, L. F., Han, X., Zhang, M. G., and Jing, Y. Y.: Study on the contribution of transport to $PM_{2.5}$ in typical regions of China using the regional air quality model RAMS-CMAQ, Atmos. Environ., 214, 116856, 2019.

Lippmann, M., Chen, L.C.: Health effects of concentrated. ambient air particulate matter (CAPs) and its components, Crit. Rev. Toxicol., 39(10), 865-913, 2009.

https://doi.org/10.5194/acp-2019-951
Preprint. Discussion started: 31 January 2020

Atmospheric Chemistry and Physics Discussions

498 Liu, B., Song, N., Dai, Q., Mei, R., Sui, B., Bi, X., and Feng, Y.: Chemical composition and source apportionment of
499 ambient $PM_{2.5}$ during the non-heating period in Tai'an, China, Atmos. Res., 170, 23-33, 2016.
500 Liu, S. Y. and Liang, X. Z.: Observed diurnal cycle climatology of planetary boundary layer height, J. Climate, 23(21),
501 5790-5809, 2010.
502 Masiol, M., Hopke, P. K., Felton, H. D., Frank, B. P., Rattigan, O. V., Wurth, M. J., and LaDuke, G. H.: Source
503 apportionment of $PM_{2.5}$ chemically speciated mass and particle number concentrations in New York City, Atmos.
504 Environ., 148, 215-229, 2017.
505 Makkonen, U., Virkkula, A., Mantykentta, J., Hakola, H., Keronen, P., Vakkari, V., and Aalto, P. P.: Semi-continuous gas
506 and inorganic aerosol measurements at a Finnish urban site: Comparisons with filters, nitrogen in aerosol and gas phases,
507 and aerosol acidity, Atmos. Chem. Phys.,12(12), 5617-5631, https://doi.org/10.5194/acp-12-5617-2012, 2012.
508 Mimura, T., Ichinose, T., Yamagami, S., Fujishima, H., Kamei, Y., Goto, M., and Matsubara, M.: Airborne particulate matter
509 ($PM_{2.5}$) and the prevalence of allergic conjunctivitis in japan, Sci. Total. Environ., 487(1), 493-499, 2014.
510 Nel, A.: Air pollution-related illness: Effects of particles, Science, 308(5723), 804-806, 2005.
511 Nicolosi, E. M. G., Quincey, P., Font, A., and Fuller, G. W.: Light attenuation versus evolved carbon (AVEC) – A new way
512 to look at elemental and organic carbon analysis. Atmos. Environ., 175, 145-153, 2018.
513 Norris, G., Duvall, R., Brown, S., and Bai, S.: EPA positive matrix factorization (PMF) 5.0 fundamentals and user guide,
514 U.S. Environmental Protection Agency, Washington, DC, EPA/600/R- 14/108 (NTIS PB2015-105147), 2014.
515 Paatero, P. and Tapper, U.: Positive matrix factorization: A nonnegative factor model with optimal utilization of error
516 estimates of data values, Environmetrics, 5, 111-126, 1994.
517 Pant, P. and Harrison, R. M.: Estimation of the contribution of road traffic emissions to particulate matter concentrations
518 from field measurements: A review, Atmos. Environ., 77, 78-97, 2013.
519 Qiao, L. P., Cai, J., Wang, H. L., Wang, W. B., Zhou, M., Lou, S. R., Lou, S. R., Chen, R. J., Dai, H. X., Chen, C. H., and
520 Kan, H. D.: $PM_{2.5}$ constituents and hospital emergency-room visits in Shanghai, China, Environ. Sci. Technol., 48(17),
521 10406-10414, 2014.
522 Qiao, T., Zhao, M. F., Xiu, G. L., and Yu, J. Z.: Simultaneous monitoring and compositions analysis of PM_1 and $PM_{2.5}$ in
523 Shanghai: Implications for characterization of haze pollution and source apportionment, Sci. Total. Environ., 557, 386-
524 394, 2016.
525 Ramanathan, V.; Crutzen, P. J.; Kiehl, J. T.; Rosenfeld, D. Atmosphere - Aerosols, climate, and the hydrological cycle,
526 Science, 294 (5549), 2119 2124, 2001.
527 Shu, L., Wang, T. J., Xie, M., Li, M. M., Zhao, M., Zhang, M., and Zhao, X. Y.: Episode study of fine particle and ozone
528 during the CAPUM-YRD over Yangtze River Delta of China: Characteristics and source attribution, Atmos. Environ.,
529 203, 87-101, 2019.
530 Sofowote, U. M., Rastogi, A. K., Debosz, J., and Hopke, P. K.: Advanced receptor modeling of near-real-time, ambient
531 $PM_{2.5}$ and its associated components collected at an urban-industrial site in Toronto, Ontario. Atmos. Pollut. Res., 5(1),
532 13-23, 2014.
533 Song, Y., Zhang, Y. H., Xie, S. D., Zeng, L. M., Zheng, M., Salmon, L. G., Shao, M., and Slanina, S.: Source apportionment
534 of $PM_{2.5}$ in Beijing by positive matrix factorization, Atmos. Environ., 40, 1526-1537, 2006
535 Sun, Y. L., Zhuang, G. S., Tang, A. H., Wang, Y., and An, Z. S.: Chemical characteristics of $PM_{2.5}$ and PM_{10} in haze-fog
536 episodes in Beijing, Environ. Sci. Technol., 40(10), 3148-3155, 2006.
537 Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components
538 from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos. Chem. Phys., 9, 2891-2918,
539 doi:10.5194/acp-9-2891-2009, 2009.

https://doi.org/10.5194/acp-2019-951
Preprint. Discussion started: 31 January 2020

Atmospheric Chemistry and Physics Discussions

Wang, H. L., Qiao, L. P., Lou, S. R., Zhou, M., Chen, J. M., and Wang, Q.: $PM_{2.5}$ pollution episode and its contributors from 2011 to 2013 in urban Shanghai, China, Atmos. Environ., 123, 298-305, 2015.

Wang, J., Hu, Z. M., Chen, Y. Y., Chen, Z. L., and Xu, S. Y.: Contamination characteristics and possible sources of PM_{10} and $PM_{2.5}$ in different unfunctional areas of Shanghai, China, Atmos. Environ., 68, 221229, 2013.

Wang, Q. Q., Feng, Y. M., Huang, X. H. H., Griffith, S. M., Zhang, T., Zhang, Q. Y., Wu, D., and Yu, J. Z.: Nonpolar organic compounds as $PM_{2.5}$ source tracers: Investigation of their sources and degradation in the Pearl River Delta, China, J. Geophys. Res-Atmos., 121(19), 11862-11879, 2016.

Wang, Q. Q., He, X., Huang, X. H. H., Griffith, S. M., Feng, Y. M., Zhang, T., Zhang, Q. Y., Wu, D., and Yu, J. Z.: Impact of secondary organic aerosol tracers on tracer-based source apportionment of organic carbon and $PM_{2.5}$: A Case Study in the Pearl River Delta, China, Acs. Earth. Space. Chem., 1(9), 562-571, 2017.

Wang, Q. Q., Qiao, L. P., Zhou, M., Zhu, S. H., Griffith, S., Li, L., and Yu, J. Z.: Source apportionment of $PM_{2.5}$ using hourly measurements of elemental tracers and major constituents in an urban environment: investigation of time-resolution influence, J. Geophys. Res-Atmos., 123(10), 5284-5300, 2018.

Wang, Q. Q., He, X., Zhou,M., Huang, D.D., Qiao, L. P., Zhu, S. H., Ma, Y.G., Wang, H. L., Li L, Huang, H., Xu, W., Worsnop, D.,. Goldstein,∇ Hai Guo,# Jian Zhen Yu: Primary organic aerosol source identification and aging observed by hourly measurements of organic molecular markers in urban Shanghai, China, under preparation, 2019.

Wang, Y. J., Li, L., Chen, C. H., Huang, C., Huang, H. Y., Feng, J. L., Wang, S. X., Wang, H. L., Zhang, G., Zhou, M., Cheng, P., Wu, M. H., Sheng, G. Y., Fu, J. M., Hu, Y., Russell, A. G., and Wumaer, A.: Source apportionment of fine particulate matter during autumn haze episodes in Shanghai, China, J. Geophys. Res-Atmos., 119(4), 1903-1914, 2014.

Williams, B. J., Jayne, J. T., Lambe, A. T., Hohaus, T., Kimmel, J. R., Sueper, D., Brooks, W., Williams, L. R., Trimborn, A. M., Martinez, R. E., Hayes, P. L., Jimenez, J. L., Kreisberg, N. M., Hering, S. V., Worton, D. R., Goldstein, A. H., and Worsnop, D. R.: The first combined thermal desorption aerosol gas chromatograph-aerosol mass spectrometer (TAG-AMS), Aerosol. Sci. Tech., 48(4), 358-370, 2014.

Yao, L., Yang, L., Yuan, Q., Yan, C., Dong, C., and Meng, C.: Sources apportionment of $PM_{2.5}$ in a background site in the north china plain, Sci. Total. Environ., 541, 590-598, 2016.

Yu, Q. Q., Gao, B., Li, G. H., Zhang, Y. L., He, Q. F., Deng, W., Huang, Z. H., Ding, X., Hu, Q. H., Huang, Z. Z., Wang, Y. J., Bi, X. H., and Wang, X. M.: Attributing risk burden of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons to major emission sources: Case study in Guangzhou, south China, Atmos. Environ., 142, 313-323, 2016.

Yuan, Z.B., Yu, J.Z., Lau, A.K.H., Louie, P.K.K., and Fung, J.C.H.: Application of positive matrix factorization in estimating aerosol secondary organic carbon in Hong Kong and its relationship with secondary sulfate, Atmos. Chem. Phys., 6 (1), 25-34, 2006.

Zhang, Q., Ning, Z., Shen, Z. X., Li, G. L., Zhang, J. K., Lei, Y. L., Xu, H. M., Sun, J., Zhang, L. M., Westerdahl, D., Gali, N. K., and Gong, X. S.: Variations of aerosol size distribution, chemical composition and optical properties from roadside to ambient environment: A case study in Hong Kong, china, Atmos. Environ., 166, 234-243, 2017.

Zhang, Y. X., Sheesley, R. J., Bae, M. S., and Schauer, J. J.: Sensitivity of a molecular marker based positive matrix factorization model to the number of receptor observations, Atmos. Environ., 43(32), 4951-4958, 2009a.

Zhang, Y., Sheesley, R. J., Schauer, J. J., Lewandowski, M., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., and Edney, E. O.: Source apportionment of primary and secondary organic aerosols using positive matrix factorization (PMF) of molecular markers, Atmos. Environ., 43(34), 5567-5574, doi:10.1016/j.atmosenv.2009.02.047., 2009b.

Zhao, M. F., Huang, Z. S., Qiao, T., Zhang, Y. K., Xiu, G. L., and Yu, J. Z.: Chemical characterization, the transport pathways and potential sources of PM2.5 in Shanghai: Seasonal variations, Atmos. Res., 158, 66-78, 2015.

Zhao, M. J., Zhang, Y., Ma, W. C., Fu, Q. Y., Yang, X., Li, C. L.,Zhou, B., Yu, Q., and Chen, L. M.: Characteristics and

https://doi.org/10.5194/acp-2019-951
Preprint. Discussion started: 31 January 2020

Atmospheric Chemistry and Physics Discussions

ship traffic source identification of air pollutants in China's largest port. Atmos. Environ., 64, 277-286, 2013b.

Zhao, Y. L., Kreisberg, N. M., Worton, D. R., Teng, A. P., Hering, S. V., and Goldstein, A. H.: Development of an in situ thermal desorption gas chromatography instrument for quantifying atmospheric semi-volatile organic compounds, Aerosol. Sci. Tech., 47(3), 258-266, 2013a.

Zhou, H., Hopke, P. K., Zhou, C. L., and Holsenc, T. M.: Ambient mercury source identification at a New York State urban site: Rochester, NY, Sci. Total. Environ., 650, 1327-1337, 2019.