Exploration of PM$_{2.5}$ sources on the regional scale in the Pearl River Delta based on ME-2 modeling

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Abstract:
The Pearl River Delta (PRD) of China, which has a population of more than 58 million people, is one of the largest agglomerations of cities in the world and ever experienced severe PM$_{2.5}$ pollution at the beginning of this century. Due to the implementation of strong pollution control in recent decades, PM$_{2.5}$ in the PRD has continuously decreased to relatively lower levels in China. To comprehensively understand the current PM$_{2.5}$ sources in the PRD to support future air pollution control strategy in similar regions, we performed regional-scale PM$_{2.5}$ field observations coupled with a state-of-the-art source apportionment model at six sites in four seasons in 2015. The regional annual average PM$_{2.5}$ concentration was determined to be 37 $\mu$g/m$^3$, which is still more than three times the WHO standard, with organic matter (36.9%) and SO$_4^{2-}$ (23.6%) as the most abundant species. A novel multilinear engine (ME-2) model was then applied to the PM$_{2.5}$ dataset in the PRD to perform source apportionment with predetermined constraints, which produced more environmentally meaningful results compared to those obtained using traditional positive matrix factorization (PMF) modeling. The regional annual average PM$_{2.5}$ source structure was retrieved to be secondary sulfate (21%), vehicle emissions (14%), industrial emissions (13%), secondary nitrate (11%), biomass burning (11%), secondary organic aerosol (SOA, 7%), coal burning (6%), fugitive dust (5%), ship emissions (3%) and aged sea salt (2%). Analyzing the spatial distribution of PM$_{2.5}$ sources under different weather conditions clearly identified the central PRD area as the key emission area for SO$_2$, NOx, coal burning, biomass burning, industrial emissions and vehicle emissions. It was further estimated that under the polluted northerly air flow in winter, local emissions in the central PRD area accounted for approximately 45% of the total PM$_{2.5}$, with secondary nitrate and biomass burning being most abundant; in contrast, the regional transport from outside the PRD accounted for more than half of PM$_{2.5}$, with secondary sulfate representing the most abundant transported species.

Keywords: source apportionment; ME-2; local emissions; regional transport; Pearl River Delta.

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1 Introduction

With China’s rapid economic growth and urbanization, air pollution has become a serious problem in recent decades. Due to its smaller size, fine particulate matter (PM$_{2.5}$) can carry toxic chemicals into human lungs and bronchi, causing respiratory diseases and cardiovascular diseases that can harm human health (Sarnat et al., 2008; Burnett et al., 2014). In particular, long-term exposure to high concentrations of fine particulate matter can also lead to premature death (Lelieveld et al., 2015). The Chinese government has attached great importance to improving air quality and issued the “Air Pollution Prevention and Control Action Plan” in September 2013, clearly requiring the concentrations levels of fine particulate matter in a few key regions, including the Pearl River Delta (PRD), to drop by 2017 from 15 to 25% of their values in 2012. The Pearl River Delta is one of the fastest-growing regions in China and the largest urban agglomeration in the world; it includes Guangzhou, Shenzhen, Zhuhai, Dongguan, Foshan, Huizhou, Zhongshan, Zhaoqing and Jiangmen provinces and contains more than 58 million people. The PM$_{2.5}$ concentration in this region reached a high level of 58 μg/m$^3$ in 2007 (Nanfang Daily, 2016); however, the air quality has significantly improved due to the implementation of strict air pollution control measures, which occurred here earlier than in other regions in China. The annual average concentration of PM$_{2.5}$ in the PRD dropped to 34 μg/m$^3$ in 2015 (Ministry of Environmental Protection, 2016).

In recent years, the receptor model method (commonly, positive matrix factorization) in the PRD was applied to perform the source apportionment of PM$_{2.5}$, which was carried out in several major cities, including Guangzhou (Gao et al., 2013; Liu et al., 2014; Wang et al., 2016), Shenzhen (Huang et al., 2014b), Dongguan (Wang et al., 2015b; Zou et al., 2017) and Foshan (Tan et al., 2016). However, the above source apportionment studies only focused on part of PM$_{2.5}$ (e.g., organic matter) or lacked the extensive representation of the PRD. Since the lifetime of PM$_{2.5}$ in the surface layer of the atmosphere is days to weeks and the cities in PRD are closely linked, the transport of PM$_{2.5}$ between cities should be specifically noteworthy (Hagler et al., 2006). On the other hand, although the positive matrix factorization (PMF) model has been successfully applied to source apportionment in the PRD, the apportionment with PMF has high rotational ambiguity and can output non-meaningful or mixed factors. Under such conditions, the multilinear engine (ME-2) model can guide the rotation toward a more objective optimal solution by utilizing a priori information (i.e., predetermined factor profiles). In recent years, ME-2, initiated and controlled via the Source Finder (SoFi) written by the Paul Scherrer Institute, was successfully developed to apportion the sources of organic aerosols (Canonaco et al., 2013). The novel ME-2 model has become a widely used and successful source analysis technique (e.g. Crippa et al., 2014; Fröhlich et al., 2015; Visser et al., 2015; Elser et al., 2016; Reyes-Villegas et al., 2016).

Accurately understanding the regional characteristics of PM$_{2.5}$ sources in the PRD can certainly guide the regional joint prevention and control of PM$_{2.5}$ in this region and provide useful references for future air pollution control strategies in China. Thus, in this study, the PM$_{2.5}$ mass and chemical compositions were measured during four seasons in 2015 at six sites in the PRD, which basically represent the pollution level of the PRD on a regional scale rather than on a city scale. The novel ME-2 model via the SoFi was applied to identify the sources of PM$_{2.5}$ in the PRD; then, the spatial locations of the sources were systematically explored using the analysis of weather conditions.
2 Experimental methodology

2.1 Sampling and chemical analysis

The PRD is located in south central Guangdong Province. Based on the layout of the cities in the PRD, six sampling sites were selected to represent urban, suburban, and background sites. Detailed descriptions of these sampling sites are listed in Table 1, and their locations are shown on the regional map in Fig. 1.

Table 1. Description of the sampling sites in the PRD.

<table>
<thead>
<tr>
<th>Site</th>
<th>Site code</th>
<th>Coordinates</th>
<th>Site description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doumen</td>
<td>DM</td>
<td>Lat: N 22.23</td>
<td>Suburban</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 113.30</td>
<td>Contains industrial areas</td>
</tr>
<tr>
<td>Qi-Ao island</td>
<td>QA</td>
<td>Lat: N 22.43</td>
<td>Background</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 113.63</td>
<td>An area for eco-tourism</td>
</tr>
<tr>
<td>Heshan</td>
<td>HS</td>
<td>Lat: N 22.73</td>
<td>Suburban</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 112.93</td>
<td>Contains industrial areas and farmlands</td>
</tr>
<tr>
<td>Modiesha</td>
<td>MDS</td>
<td>Lat: N 23.11</td>
<td>Urban</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 113.33</td>
<td>Contains dense urban traffic</td>
</tr>
<tr>
<td>University Town</td>
<td>UT</td>
<td>Lat: N 22.59</td>
<td>Urban</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 113.98</td>
<td>Contains urban traffic</td>
</tr>
<tr>
<td>Dapeng</td>
<td>DP</td>
<td>Lat: N 22.63</td>
<td>Background</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lon: E 114.41</td>
<td>An area for eco-tourism</td>
</tr>
</tbody>
</table>

Fig. 1. Spatial distribution of the sampling sites in the PRD.

Samples were collected every other day during the months of January—February (winter), April (spring), July (summer) and October—November (fall) in 2015. Each sampling period lasted for 24 h at each site. The sampling sites of University Town (UT) and Dapeng (DP) used Thermo 2300 PM$_{2.5}$ samplers (Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA, with a flowrate of 16.7 L/min for two channels and a flowrate of 10.0 L/min for the other two channels), while those in Modiesha (MDS), Heshan (HS), Qi-Ao Island (QA) and Doumen (DM) used TH-16A PM$_{2.5}$ samplers (Tianhong Corp., Wu Han, China, with a flow rate of 16.7 L/min for four
channels). Prior to the sampling campaigns, two different types of samplers sampled in parallel yielded a relative deviation of less than 5\% for PM$_{2.5}$ mass concentrations. The PM$_{2.5}$ mass can be obtained based on the difference in the weight of the Teflon filter before and after sampling in a cleanroom at conditions of 20°C and 50\% relative humidity. Teflon filters were analyzed for their major ion contents (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and Cl$^-$) via an ion chromatography system (ICS-2500, Dionex; Sunnyvale, California, USA), and their metal element contents (23 species) were analyzed via an inductively coupled plasma mass spectrometer (ICP-MS, auroraM90; Bruker, Germany). Quartz filters were analyzed for their organic carbon (OC) and elemental carbon (EC) contents using an OC/EC analyzer (Desert Research Institute, Reno, Nevada, USA). The overall organic mass (OM) was estimated as 1.8 × OC (He et al., 2011).

The meteorological conditions during the observation period, shown in Table 2, indicated that the PRD region experienced a hot and humid summer and a cool and dry winter, while spring and fall were two transition seasons. Furthermore, the back trajectories of the air masses obtained using the NOAA HYSPLIT model (Fig. S1) revealed that the air masses originated from the northern inland in winter, from the northern inland and the South China Sea in spring, from the South China Sea in summer, and from the northeast coast and the northern inland in fall.

<p>| Table 2. General meteorological conditions during the observation period in the PRD. |</p>
<table>
<thead>
<tr>
<th>Mean Temp. (°C)</th>
<th>Rainfall (mm)</th>
<th>Mean RH (%)</th>
<th>Mean wind speed (m/s)</th>
<th>Predominant wind direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter (Jan.10-Feb.9)</td>
<td>17</td>
<td>35</td>
<td>63</td>
<td>2.1</td>
</tr>
<tr>
<td>Spring (Apr.2-Apr.30)</td>
<td>23</td>
<td>61</td>
<td>72</td>
<td>1.8</td>
</tr>
<tr>
<td>Summer (Jul.1-Jul.29)</td>
<td>29</td>
<td>244</td>
<td>74</td>
<td>2.1</td>
</tr>
<tr>
<td>Fall (Oct.11-Nov.10)</td>
<td>25</td>
<td>92</td>
<td>68</td>
<td>1.7</td>
</tr>
</tbody>
</table>

2.2 Input data matrices for source apportionment modeling

PMF is a multivariate factor analysis tool widely used for aerosol source apportionment. The PMF algorithm groups the measured matrix X (Eq. (1)) into two non-negative constant matrices G (factor time series) and F (factor profiles), and E denotes the model residuals (Paatero and Tapper, 1994). The entries in G and F are fitted using a least-squares algorithm that iteratively minimizes the object function $Q$ in Eq. (2), where $e_{ij}$ are the elements of the residual matrix E, and $u_{ij}$ are the errors/uncertainties of the measured species $x_{ij}$.

$$X = G \cdot F + E \quad (1)$$

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

The multilinear engine (ME-2) was later developed by Paatero (1999) based on the PMF algorithm. In contrast to an unconstrained PMF analysis, ME-2 can utilize the constraints (i.e., predetermined factor profiles) provided by the user to enhance the control of rotation for a more objective solution. One or more factor profiles can be expediently input into ME-2, and the output profiles are allowed to vary from the input profiles to some extent. When using ME-2 modeling, the “mixed factors” can usually be better resolved.
In this study, both PMF and ME-2 models were run for the datasets observed in the PRD. We first need to determine the species input into the models. Species that may lead to high species residuals or lower R² values between measured and model-predicted or non-meaning factors were not included, such as those that fulfilled the following criteria: (1) species that were below detection in more than 40% of samples; (2) species that yielded R² values of less than 0.4 in inter-species correlation analysis; and (3) species that had little implication for pollution sources and lower concentrations. Therefore, 18 species were input into the models; these species accounted for 99.6% of the total measured species and included OM, EC, SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻, K, Ca, Na, Mg, Al, Zn, Fe, Cd, V, Ni, Ti and Pb.

The application of PMF or ME-2 also depends on the estimated realistic uncertainty \( u_{ij} \) of the individual data point of an input matrix, which determines the \( Q \) value in Eq. (2). Therefore, the estimation of uncertainty is an important component of the application of these models. There are many sources of uncertainty, including sampling, handling, transport, storage, preparation, and testing (Leiva et al., 2012). In this study, the sources of uncertainty that contributed little to the total uncertainty could be neglected. Therefore, we first considered the uncertainties introduced by sampling and analysis processes, such as sampling volume, repeatability analysis and ion extraction. The species uncertainties \( u_{ij} \) are estimated using Eq. (5), where \( \bar{u}_c \) is the error fraction of the species, which is estimated using the relative combined error formula Eq. (6) (Vazquez et al., 2008).

\[
\begin{align*}
\bar{u}_c &= \bar{u}_f \times x_{ij} \\
\bar{u}_c &= \frac{\bar{u}_f}{\sqrt{\bar{u}_s^2 + \bar{u}_i^2 + \bar{u}_e^2}}
\end{align*}
\]

where \( \bar{u}_f \) is the relative error of the sampling volume; \( \bar{u}_i \) is the relative error of the repeatability analysis of the standard species; and \( \bar{u}_e \) is the relative error of the ion extraction of multiple samples. When the concentration of the species is below the detection limit (DL), the concentration values were replaced by 1/2 of DL, and the corresponding uncertainties were set at 5/6 of DL. Missing values were replaced by the geometric mean of the species with corresponding uncertainties of 4 times their geometric mean (Polissar et al., 1998). To account for other uncertainties, the estimated uncertainties (\( \bar{u}_c \)) of all species were further increased by a factor of 2.

### 2.3 Constraint setup in ME-2 modeling

In this study, USEPA PMF (v5.0) was first applied with the concentration matrix and uncertainties matrix described above to identify the PM\(_{2.5}\) sources. After examining a range of factor numbers from 3 to 12, the nine-factor solution output by PMF (base run, \( Q_{true}/Q_{exp}=2.5 \)) was found to be the optimal solution, since the factor of biomass burning was not extracted in the eight-factor solution while the factor of fugitive dust was separated into two non-meaningful factors when more factors were set to run PMF. For the nine-factor solution, the source judgement based on tracers for each factor was identical to that of the ME-2 results detailed in Section 3.2. However, in Fig. S2, some factors seemed to be mixed by some unexpected components and were thus overestimated. For example, the secondary sulfate and secondary nitrate factors of PMF had certain species from primary particulates, such as EC, Zn, Al, K and Fe, among which EC had obvious EV values of 18.7% and 9.7%, respectively; the EV value of OM in the sea salt factor
(which was theoretically negligible) had a high value of 6.4%, and OM accounted for 37% of the total mass of this factor; the EV value of SO$_4^{2-}$ in the fugitive dust factor (which was theoretically negligible) had a high value of 8.6%, and the SO$_4^{2-}$ concentration accounted for 26% of the total mass of this factor.

Therefore, using the same species concentration matrix and uncertainties matrix, we ran the ME-2 model via SoFi for 9-12 factors with the four factors constrained as described above, as shown in Table 3. The following considerations were used. Secondary sulfate and secondary nitrate factors should theoretically not contain species from primary particulates, but they may contain secondary organic matter related to the secondary conversion process of SO$_2$ and NOx (He et al., 2011; Yuan et al., 2006b; Huang et al., 2014). Therefore, the contributions of the species from primary particulates were constrained to zero in the input secondary aerosol factors, while others were not constrained. In addition, the factors of sea salt and fugitive dust in primary aerosols could be understood based on the abundance of species in seawater and the upper crust (Mason, 1982; Taylor and McLennan, 1995). As seen in Table S1, the abundances of Cl$^-$, Na$^+$, SO$_4^{2-}$, Mg$^{2+}$, Ca$^{2+}$ and K$^+$ in sea salt were relatively high, as were the abundances of Al, Fe, Ca, Na, K, Mg and Ti in fugitive dust. Therefore, these high-abundance species were not constrained in the sea salt and fugitive dust factors, while the other species (with abundances of less than 0.1% in the particulates) were constrained to zero (Table 3). In addition, HNO$_3$ might react with sea salt to displace Cl$^-$ (Huang et al., 2006); thus, NO$_3^-$ was also not constrained in the sea salt factor.

### Table 3. The constraints of factor species for ME-2 modeling.

| Factors       | OM | EC | Cl$^-$ | NO$_3^-$ | SO$_4^{2-}$ | NH$_4^+$ | Ca | Ti | V | Ni | Zn | Cd | Pb | Na | Mg | Al | K | Fe |
|---------------|----|----|--------|----------|-------------|----------|-----|----|---|----|----|----|----|----|----|---|----|#####
| Secondary     | 0  | 0  | 0      | 0        | 0           | 0        | 0   | 0  | 0 | 0  | 0  | 0  | 0  | 0  | 0  | 0 | 0  |
| sulfate       | 0  | 0  | 0      | 0        | 0           | 0        | 0   | 0  | 0 | 0  | 0  | 0  | 0  | 0  | 0  | 0 | 0  |
| nitrate       | 0  | 0  | 0      | 0        | 0           | 0        | 0   | 0  | 0 | 0  | 0  | 0  | 0  | 0  | 0  | 0 | 0  |
| Sea salt      | 0  | 0  | 0      | 0        | 0           | 0        | 0   | 0  | 0 | 0  | 0  | 0  | 0  | 0  | 0  | 0 | 0  |
| Fugitive dust | 0  | 0  | 0      | 0        | 0           | 0        | 0   | 0  | 0 | 0  | 0  | 0  | 0  | 0  | 0  | 0 | 0  |

### 3 Results and discussion

#### 3.1 Temporal-spatial variations of PM$_{2.5}$ in the PRD

The 4-month average PM$_{2.5}$ concentration for all six sites in the PRD was 37 μg/m$^3$, which was slightly higher than the Grade II national standards for air quality (with an annual mean of 35 μg/m$^3$). The chemical compositions of PM$_{2.5}$ in the PRD are shown in Fig. 2. OM had the highest contribution of 36.9%, suggesting severe organic pollution in the PRD. Other important components included SO$_4^{2-}$ (23.6%), NH$_4^+$ (10.9%), NO$_3^-$ (9.3%), EC (6.6%) and Cl$^-$ (0.9%). The major metallic components included K (1.5%), Na (1.1%), Fe (0.7%), Al (0.6%), and Ca (0.6%), and trace elements accounted for 6.2%. Fig. 3a shows the spatial distribution of the PM$_{2.5}$ and chemical components between six sites. The PM$_{2.5}$ pollution level in the PRD was distinctly higher in the northwestern hinterland (HS and MDS) and lower in the southern coastal areas (DM and DP). The much lower PM$_{2.5}$ concentration at the background DP site (28 μg/m$^3$) indicated that the central PRD area was characterized by large contributions of pollution transported from outside this region. At the background DP site, the fractions of Cl$^-$ and NO$_3^-$ in PM$_{2.5}$ were the lowest of the six sites, i.e., 0.3% and 3.9%, respectively, suggesting that they had dominantly local sources in the PRD. The highest concentration level of PM$_{2.5}$ was observed at HS (suburban), which was...
influenced by the pollution transport of Foshan (industrial city) and Guangzhou (metropolis) under
the dominant northeastern wind the year. Fig. 3b shows that the seasonal variations in the major
components of PM$_{2.5}$ in the PRD were evidently higher in winter and lower in summer and that
they were correlated with monsoon characteristics. The back trajectories of the air masses (Fig. S1)
show that the northern monsoon prevails in winter and the southern monsoon prevails in summer
in the PRD. Under the northeast monsoon, the air masses mostly came from the inland and carried
higher concentrations of air pollutants. However, under the southwest monsoon, the air masses
largely originated from the South China Sea and were relatively clean. In addition, the frequent
rainfall and higher planetary boundary layer (PBL) in summer in the PRD also favored the
dispersion and removal of air pollutants (Huang et al., 2014b).

In 2002-2003, Hagler et al. (2006) also conducted observations and analysis of PM$_{2.5}$ in the
PRD and Hong Kong region, nearly 12 years before this study, as shown in Table 4. Compared
with Hagler’s results, the PM$_{2.5}$ concentrations in this study decreased by 42% in Guangzhou
(MDS) and 21% in Shenzhen (UT), especially OC, EC and SO$_4^{2-}$, which decreased significantly
by 20%—47%, indicating that the measures taken to desulfurize coal-fired power plants, improve
the fuel standards of motor vehicles and phase-out yellow label vehicles have played important
roles in improving the air quality in the PRD region (People's Government of Guangdong
Province, 2012). Compared with the PM$_{2.5}$ concentrations reported by other cities in China in
recent years, the PM$_{2.5}$ concentrations in urban Guangzhou and Shenzhen in this study were
63%—75% lower than those in Beijing and Tianjin in northern China, Hainan in eastern China, and
Deyang in western China. However, the PM$_{2.5}$ concentrations in urban Guangzhou and Shenzhen
observed in this study were clearly higher than those in famous mega-cities in developed countries,
such as Paris, London, and Los Angeles, while they were similar to those of Santiago and Incheon.
It should be highlighted that the higher concentration of SO$_4^{2-}$ in the urban atmosphere of the
PRD is one of the major reasons leading to the higher degree of PM$_{2.5}$ pollution in the PRD
compared to those in developed cities.

Fig. 2. Chemical composition of annual average PM$_{2.5}$ in the PRD region.
Fig. 3. The spatial distributions (a) and seasonal variations (b) of the PM$_{2.5}$ chemical compositions in the PRD (unit in brackets: μg/m$^3$).

<table>
<thead>
<tr>
<th>Cities</th>
<th>Periods</th>
<th>PM$_{2.5}$</th>
<th>OC</th>
<th>EC</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>Cl$^-$</th>
<th>Metal Elements</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhuhai (DM)</td>
<td>2015.1–2015.11</td>
<td>35</td>
<td>6.4</td>
<td>2.3</td>
<td>8.1</td>
<td>4.4</td>
<td>3.6</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Zhuhai (QA)</td>
<td>37</td>
<td>7.2</td>
<td>2.2</td>
<td>9.9</td>
<td>3.5</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Jiangmen (HS)</td>
<td>47</td>
<td>9.0</td>
<td>2.8</td>
<td>9.8</td>
<td>5.6</td>
<td>5.0</td>
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<td>Guangzhou (MDS)</td>
<td>41</td>
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<td>2.7</td>
<td>9.2</td>
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<td>4.6</td>
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<td>Shenzhen (UT)</td>
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<td>3.0</td>
<td>8.0</td>
<td>2.6</td>
<td>3.7</td>
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<td>Shenzhen (DP)</td>
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<td>1.8</td>
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<td>1.1</td>
<td>3.3</td>
<td></td>
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<tr>
<td>Hong Kong (Urban)</td>
<td>2002.10–2003.06</td>
<td>34.3</td>
<td>6.6</td>
<td>1.9</td>
<td>9.3</td>
<td>1.0</td>
<td>2.5</td>
<td></td>
<td>Hagler et al., 2006</td>
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<tr>
<td>Shenzhen (Urban)</td>
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<td>11.1</td>
<td>3.9</td>
<td>10.0</td>
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<td>3.2</td>
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<td>Guangzhou (Urban)</td>
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<td>17.6</td>
<td>4.4</td>
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<td>4.5</td>
<td></td>
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<tr>
<td>Beijing</td>
<td>2012.6–2013.4</td>
<td>112</td>
<td>17</td>
<td>6</td>
<td>24</td>
<td>20</td>
<td>16</td>
<td></td>
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<td></td>
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<tr>
<td>Wuxi/Tianjin</td>
<td>2012.11–2013.7</td>
<td>148.9</td>
<td>14.1</td>
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<td>24.2</td>
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<td>Deyang/Sichuan</td>
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<td>10.2</td>
<td>6.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paris/France</td>
<td>2009.9–2010.9</td>
<td>14.8</td>
<td>3.0</td>
<td>1.4</td>
<td>2.0</td>
<td>2.9</td>
<td>1.4</td>
<td></td>
<td>Breon et al., 2013</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Source apportionment of PM$_{2.5}$ using ME-2

The solutions of 9–12 factors of the ME-2 were modeled with the four factors constrained in Table 3, using the SoFi tool, an implementation of ME-2 (Canonaco et al., 2013). Again, the nine-factor solution provided the most reasonable source profiles, since non-interpretable factors were produced (e.g., a Ti-high factor) when more factors were set to run ME-2. Based on the percentage explained variations (EV) and the contributed concentrations of species in each factor shown in Fig. 4, the sources of PM$_{2.5}$ can be judged as follows: (1) The first factor was explained as secondary sulfate, which had large EV values of SO$_4^{2-}$ and NH$_4^+$. The high OM concentration was considered to represent low-volatilized oxygenated organic aerosol (LV-OOA, Jimenez et al., 2009; He et al., 2011). (2) The second factor was explained as secondary nitrate, which had significant EV values of NO$_3^-$ and NH$_4^+$, and its high OM concentration was considered to represent semi-volatile oxygenated organic aerosol (SV-OOA, Jimenez et al., 2009; He et al., 2011). (3) The third factor was related to sea salt due to the large EV values and concentrations of Na and Mg. However, the low Cl$^-$ concentration and high SO$_4^{2-}$ concentration implied that SO$_4^{2-}$ replaced Cl$^-$ during the sea salt aging process. Therefore, this factor was identified as aged sea salt (Yuan et al., 2006a). (4) The fourth factor was identified as fugitive dust due to its significant EV values of Al, Ca, Mg and Fe. In this study, the undetermined mass of O and Si in this factor was compensated using the elemental abundance in dust particles in Table S1 (Taylor and McLennan, 1995). (5) The fifth factor was identified as biomass burning due to its significant characteristic value of K (Yamasoe et al., 2000). (6) The sixth factor had high concentrations and large EV values of OM and EC, as well as a certain range of EV values of Fe and Zn, which were related to tires and the brake wear of motor vehicles (Yuan et al., 2006a; He et al., 2011). Therefore, this factor was identified as vehicle emissions. (7) The seventh factor had a high EV value of Cl$^-$ and certain concentrations of OM, EC, SO$_4^{2-}$ and NO$_3^-$, implying a combustion source. This factor was identified as coal burning, which was a major source of Cl$^-$ in the PRD (Wang et al., 2015b). (8) The eighth factor had large EV values of Zn, Cd and Pb, and certain concentrations of OM and EC. Zn, Cd and Pb had high enrichment factors (Table S2) of 821, 4121 and 663, respectively, and were thus considered to be related to industrial emissions (Wang et al., 2015b). (9) The last factor had large EV values of V and Ni. V and Ni were predominantly derived from heavy oil combustion, and they had high enrichment factors (Table S2) of 64 and 89, respectively. Heavy oil was related to ship emissions in the PRD (Chow et al., 2002; Huang et al., 2014b). In this study, secondary organic aerosol (SOA), which was not resolved as a single factor, can be extracted from the factors of secondary sulfate and secondary nitrate in the forms of LV-OOA and SV-OOA, respectively. Therefore, in terms of the mass balance of PM$_{2.5}$, SOA can be calculated as the sum of LV-OOA and SV-OOA (Yuan et al., 2006b). It is easy to see that, in comparison with the PMF modeling (Fig. S2), the ME-2 modeling indeed provided a better $Q_{true}/Q_{exp}$ (1.2) than the PMF modeling ($Q_{true}/Q_{exp}=2.5$), and the EV values of tracers (e.g., SO$_4^{2-}$, NO$_3^-$, OM, EC, Cl$^-$, V, Ni, Pb and Cd) were assigned more intensively. Therefore, it is concluded that the source apportionment results of ME-2 in this study were more environmentally meaningful and
statistically better than those of PMF modeling. Fig. 4. The factor profiles and explained variations of the ME-2 modeling.

Fig. 5 shows the 4-month average contributions of the PM$_{2.5}$ sources in the PRD in 2015 based on the source apportionment of ME-2. The total secondary aerosols accounted for 39% of PM$_{2.5}$ in the PRD, which were secondary sulfate (21%), secondary nitrate (11%) and SOA (7%). However, the identified primary particulates contributed 54% of PM$_{2.5}$, which comprised vehicle emissions (14%), industrial emissions (13%), biomass burning (11%), coal burning (6%), fugitive dust (5%), ship emissions (3%) and aged sea salt (2%). Unidentified sources accounted for 7%.

Fig. 5. The annual average contributions of PM$_{2.5}$ sources in the PRD.

3.3 Tempo-spatial variations of sources in the PRD

The spatial distributions of the PM$_{2.5}$ sources between six sites are shown in Fig. 6a. Secondary sulfate represented the largest fraction (31%) of PM$_{2.5}$ at DP, indicating that it was a major air pollutant in the air mass transported to the PRD. Vehicle emissions also contributed...
relatively highly to urban sites (18% in MDS and 17% in UT). Industrial emissions, biomass burning, secondary nitrate, and coal burning contributed larger fractions of PM$_{2.5}$ at HS, which could be attributed to both strong local sources (e.g., the surrounding township factories and farmlands) and regional transport from upwind cities at this site. Fugitive dust, which is primarily related to construction activities, was relatively high at DM (9%). The contributions of ship emissions and aged sea salt were the highest at QA due to its being located on Qi-Ao Island in the Pearl River Estuary, which records the greatest impact from the sea. SOA contributed similar amounts (7%–8%) at all sites. It should be noted that, although QA was a background site without local anthropogenic sources, its PM$_{2.5}$ level was moderate in the PRD, indicating that QA was impacted by severe regional transport from the surrounding cities.

Fig. 6b shows the seasonal variations of the major sources of PM$_{2.5}$ in the PRD. The contributions of most sources were higher in winter and lower in summer, e.g., secondary sulfate, secondary nitrate, fugitive dust, biomass burning, vehicle emissions, coal burning, industrial emissions and SOA; these sources were correlated with monsoon characteristics and rainfall and PBL variations. In contrast, the contributions of aged sea salt and ship emissions displayed little seasonal variations, which could be attributed to the fact that they played more important roles only when the wind came from the sea in the south, when the background levels of other air pollutants were lower.

Previous studies of the source apportionment of bulk PM$_{2.5}$ in the PRD have mainly focused on Guangzhou, Dongguan and Shenzhen, as seen in Table 5. It can be seen that in those studies, PM$_{2.5}$ was apportioned to 6–9 sources and that secondary sulfate was the prominent source, although the results of different studies exhibited certain differences due to the use of different models or data inputs. Compared with the study of Huang et al. (2014b) in Shenzhen in 2009, the contributions of secondary sulfate and vehicle emissions in Shenzhen in this study were obviously lower due to power plant desulfurization and motor vehicle oil upgrades in recent years (People’s Government of Shenzhen Municipality, 2013). Compared with previous studies in Guangzhou, this study attained more PM$_{2.5}$ sources, which can more clearly describe the source structure of PM$_{2.5}$ in this region, especially industrial emissions (11%). The PRD region has experienced a high degree of industrialization; thus, industrial sources should be a major source, contributing 8.1% of PM$_{2.5}$ reported by the Guangzhou Environmental Protection Bureau (2017), similar to our results. Tao et al. (2017) apportioned PM$_{2.5}$ to 6 sources using PMF in Guangzhou, including some mixed sources. For example, ship emissions in Tao’s study may not actually represent a primary source due to the significant existence of some secondary inorganics and sea salt in the source profile; thus, they obtained a significantly higher contribution (17%) than that in our study. Ship emissions were unidentified in Huang’s study (2014a) in Guangzhou.
Fig. 6. The spatial distributions (a) and seasonal variations (b) of PM$_{2.5}$ sources in the PRD (unit in brackets: μg/m³).

Table 5. Comparison of the results of source apportionment of PM$_{2.5}$ in the PRD.

<table>
<thead>
<tr>
<th>Cities</th>
<th>Periods</th>
<th>Model</th>
<th>Results</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guangzhou</td>
<td>2015.1—2015.11</td>
<td>ME-2</td>
<td>Secondary sulfate (23%), secondary nitrate (11%), SOA (7%), vehicle emissions (18%), industrial emissions (11%), biomass burning (8%), coal burning (6%), fugitive dust (3%), ship emissions (2%) and aged sea salt (1%).</td>
<td>This study</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>2015.1—2015.2</td>
<td>ME-2</td>
<td>Secondary sulfate (20%), secondary nitrate (16%), SOA (8%), vehicle emissions (11%), industrial emissions (13%), biomass burning (6%), coal burning (9%), fugitive dust (2%), ship emissions (1%) and aged sea salt (1%).</td>
<td>This study</td>
</tr>
<tr>
<td>Shenzhen</td>
<td>2015.1—2015.11</td>
<td>ME-2</td>
<td>Secondary sulfate (21%), secondary nitrate (8%) and SOA (7%), vehicle emissions (17%), industrial emissions (11%), biomass burning (9%), coal burning (3%), fugitive dust (6%), ship emissions (3%) and aged sea salt (1%).</td>
<td>This study</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>2014.1—2014.12</td>
<td>PMF</td>
<td>Secondary sulfate and biomass burning (38%), ship emissions (17%), coal combustion (15%), traffic emissions (10%), secondary nitrate and chloride (12%), soil dust (7%).</td>
<td>Tao et al. (2017)</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>2013.1</td>
<td>ME-1</td>
<td>Secondary inorganic-rich (59.0%), secondary organic-rich (38.1%), traffic (8.6%), coal burning (3.4%), biomass burning (6.7%), cooking (0.8%), dust related (3.4%).</td>
<td>Huang et al. (2014a)</td>
</tr>
</tbody>
</table>
3.4 Identification of high-emission areas in the PRD in typical meteorological conditions

Changes in meteorological conditions with the seasons have significant influences on the air quality in the PRD (Hagler et al., 2006). The same type of weather is often repeated. Physick et al. (2001) classified the weather over the region surrounding Hong Kong into seven categories based on surface pressure patterns, i.e., as northerly (winter monsoon), northeasterly (winter monsoon), easterly or southeasterly, trough, southerly or southwesterly (summer monsoon), cyclonic 1 and cyclonic 2 weather types. The PRD region, including Hong Kong, has nearly the similar weather patterns and similar meteorological conditions. In this study, the daily weather types during the observation period (excluding rainy days) were also classified into seven categories based on surface pressure patterns. However, according to the surface horizontal wind vectors, the PRD was mostly impacted by two types of airflow, i.e., southerly flow and northerly flow. Southerly flow, including the southeasterly and southerly or southwesterly (summer monsoon) weather types, was relatively clean and originated from the ocean (e.g., Fig. S3 and Fig. S5). Northerly flow, including the northerly (winter monsoon) and northeasterly (winter monsoon) weather types, was relatively polluted and originated from the north mainland (e.g., Fig. S4 and Fig. S6). Southerly flow and northerly flow appeared with the highest frequency in the PRD (i.e., above 80%). In this study, southerly flow days (PM$_{2.5} \leq 17 \, \mu g/m^3$, see Table 6) were selected to better reflect the local source regions in the PRD, and northerly flow days (PM$_{2.5} \geq 75 \, \mu g/m^3$, see Table 6) were selected to better understand the pollution accumulation process and regional transport characteristics of pollutants in the PRD. The sampling days for southerly flow and northerly flow are listed in Table 6.

**Table 6.** Sampling days categorized as southerly flow and northerly flow days.

<table>
<thead>
<tr>
<th>Southerly flow</th>
<th>Wind speed (m/s)</th>
<th>PM$_{2.5}$ (μg/m$^3$)</th>
<th>Northerly flow</th>
<th>Wind speed (m/s)</th>
<th>PM$_{2.5}$ (μg/m$^3$)</th>
</tr>
</thead>
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<tr>
<td>2015.07.01</td>
<td>2.6</td>
<td>16</td>
<td>2015.01.18</td>
<td>2.3</td>
<td>78</td>
</tr>
<tr>
<td>2015.07.03</td>
<td>3.6</td>
<td>17</td>
<td>2015.01.20</td>
<td>1.5</td>
<td>82</td>
</tr>
<tr>
<td>2015.07.15</td>
<td>1.9</td>
<td>17</td>
<td>2015.02.03</td>
<td>2</td>
<td>75</td>
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<td>2.6</td>
<td>12</td>
<td>2015.02.07</td>
<td>1.7</td>
<td>101</td>
</tr>
<tr>
<td>2015.07.25</td>
<td>2</td>
<td>13</td>
<td>2015.02.09</td>
<td>2.2</td>
<td>75</td>
</tr>
<tr>
<td>2015.07.29</td>
<td>1.3</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7 shows the contributions of PM$_{2.5}$ sources under southerly flow and northerly flow conditions in the PRD. Southerly flow primarily originated from the South China Sea and carried clean ocean air masses to the PRD with overall PM$_{2.5}$ values of 15 μg/m$^3$. As shown in Fig. 7(a), secondary sulfate (19%), vehicle emissions (15%) and biomass burning (11%) had higher
contributions under southerly flow. In contrast, in northerly flow, the level of PM$_{2.5}$ was 4.5 times higher than that of southerly flow due to the transport of polluted air masses southward from the north mainland. Under northerly flow, secondary sulfate (18%) and biomass burning (10%) were still the major sources, but secondary nitrate became the dominant source of PM$_{2.5}$, accounting for 20% of PM$_{2.5}$. In addition, industrial emissions also exhibited a relatively high contribution (14%).

Fig. 7. Source structures of PM$_{2.5}$ in the PRD: that in southerly flow (a) and that in northerly flow (b).

The spatial distributions of the PM$_{2.5}$ sources under southerly flow and northerly flow are shown in Fig. 8. The average concentrations of aged sea salt were similar in the summer southerly flow and winter northerly flow, reflecting the local release of surrounding sea salt. Moreover, a relatively high level of aged sea salt was observed at Qi-Ao Island (QA), which was consistent with the geographical features of the area, which faces the sea.

The influences of ship emissions exhibited large differences between six sites, showing significant local characteristics. The concentrations of ship emissions were the highest at DP under southerly flow, mainly due to the impact of vessels in the upwind Yiantian Port, while they were the highest at QA under northerly flow, primarily due to the effects of the upwind Nansha Port, as shown in Fig. 9. Yantian Port and Nansha Port are among the ten largest ports in the world (Hong Kong Marine Department, 2012).

The contributions of fugitive dust also exhibited significant differences between six sites, which is consistent with local construction activities. DM is located in a newly developed zone that has experienced relatively high levels of fugitive dust during southerly flow and northerly flow due to active construction activities. Sample records indicate that the high value of fugitive dust at UT under southerly flow maybe related to its surrounding short-term road construction project, while the high value at QA under northerly flow maybe related to the operations of the adjacent Nansha Port.

Motor vehicles are a common source of air pollution in the highly urbanized and industrialized PRD region. The average concentration of vehicle emissions during northerly flow was nearly 3-fold that during southerly flow. Under southerly flow, MDS, HS and UT, which are located in the hinterland of the PRD, had much higher levels of vehicle emissions than the other three sites; in particular, the highest level at the urban MDS site was caused by the high density of motor vehicles in Guangzhou. Under northerly flow, the highest concentration of vehicle emissions was still at the urban MDS site, while QA also recorded the prominent contribution of vehicle emissions, which was probably closely related to the container trucks in the neighboring

![Source structures of PM$_{2.5}$ in the PRD: (a) southerly flow and (b) northerly flow.](image-url)
Nansha Port. It should be noted that the concentration of vehicle emissions at the background DP site exceeded half the regional average value, approaching 4 μg/m³, thus indicating that vehicle emissions had a significant impact on the regional transport of air masses from the north.

During southerly air flow, the background DP and QA sites and the urban UT site all recorded similar concentrations of secondary sulfate, suggesting that the secondary sulfate at these sites was dominated by regional transport from the southern ocean with heavy vessel transport and had little to do with the urban emissions at UT. Kuang et al. (2015) also found that ship emissions could be a major source of secondary sulfate in the PRD in summer. HS and MDS had significantly higher concentrations than their upwind site, DM, suggesting that the area between MDS and HS could be a high-SO₂-emission area, which is consistent with the fact that this area is an intensive industrial area. During northerly air flow in winter, HS and DM had lower concentrations than the four upwind sites, i.e., MDS, QA, UT, and especially DP (the background site), indicating that secondary sulfate could mainly be derived from regional transport from outside the PRD in this season. Although the industrial area between HS and MDS could emit significant amounts of SO₂, the lower temperatures and dry air in winter did not appear to favor the quick conversion of SO₂ to secondary sulfate. On the other hand, the spatial distributions and source characteristics of secondary sulfate also reflected the corresponding characteristics of LV-OOA.

The spatial distributions of coal burning were significantly different between the six sites during periods of both south wind and north wind, thus showing conspicuous local characteristics. The contribution of coal burning was higher at MDS under southerly flow and higher at HS under northerly flow. Most of the coals in the PRD were consumed by thermal power plants, but there were no coal-fired power plants near the urban MDS and background DP sites. Therefore, it is speculated that the high-emission areas of coal burning sources mainly exist in the region between HS and MDS, as shown in Fig. 9. The distributions of coal-fired power plants in Guangdong (Wang et al. 2017) reveal that some important coal-fired power plants are distributed in this region. Additionally, DM also exhibited relatively obvious contributions of coal burning during southerly flow and northerly flow, which is also consistent with the distribution of coal-fired power plants in the vicinity.

The average concentration of secondary nitrate during northerly flow in winter was 40 times greater than that during southerly flow in summer; this occurred not only because of the unfavorable conditions of atmospheric diffusion in winter but also due to the high semi-volatility of ammonium nitrate, which cannot stably exist in fine particles in the PRD during hot summer (Huang et al. 2006). Under southerly flow conditions, the concentrations of secondary nitrate presented prominent differences between six sites, showing local characteristics. Moreover, the relatively low concentrations at the background DP site during northerly flow also indicated that secondary nitrate mainly originated from the interior of the PRD. The spatial distribution characteristics of secondary nitrate were very similar to those of coal burning, with the highest occurring at MDS under southerly flow, the highest occurring at HS under northerly flow and significantly high values occurring at DM under southerly and northerly flow, displaying that the NOx emissions produced by coal burning maybe the main reason for the high nitrate levels in those areas. In addition, the spatial distributions and source characteristics of secondary nitrate also reflected the corresponding characteristics of LV-OOA.

Under southerly flow, the influence of industrial emissions differed vastly between six sites,
showing obvious local characteristics. Under northerly flow, the average concentration of industrial emissions reached 14-fold that of southerly flow, and the high contributions at background DP suggested that regional transport probably dominated the industrial sources of fine particulate matter in the PRD in winter. HS had the highest concentration of industrial emissions during southerly flow and northerly flow conditions, which is consistent with the dense factories present in the surrounding area (Hu, 2004; Environmental Protection Agency of Jiangmen City, 2017). In addition, the contribution of industrial emissions was relatively high at MDS during southerly flow and relatively high at QA during northerly flow, which supports the inference that a high-emission region of industrial sources was located between MDS and QA, as seen in Fig. 9.

The impacts of biomass burning exhibited relatively large differences between six sites during both south and north wind conditions, presenting somewhat local characteristics. Suburban HS had relatively high biomass burning levels during southerly flow and northerly flow, which were related to the presence of more farmland in its vicinity and the frequent open-burning of crop residues. The concentrations of biomass burning were relatively high at the urban MDS site during southerly flow and relatively high at the background QA site during northerly flow, implying that there was a high-emission area of biomass burning between MDS and QA, as shown in Fig. 9. Those spatial distribution characteristics of biomass burning were similar to those of industrial emissions in the PRD, suggesting that not only the combustion of open-air biomass but also the use of industrial biomass-boilers could make important contributions to PM$_{2.5}$ in the PRD.

As a summary, the central PRD area, i.e., the middle region between MDS, HS and QA (the shaded region in Fig. 9), represents the most important pollutant emissions area in the PRD; these emissions include SO$_2$, NOx, coal burning, biomass burning, industrial emissions and vehicle emissions, thus leading to high pollution levels in the PRD. Therefore, this area is a key area for pollution control in the PRD. Primary fine particulate matter and SO$_2$ from ship emissions had significant impacts on PM$_{2.5}$ in the southern coastal area of the PRD during summer southerly flow, and special attention must be paid to them.
Fig. 8. The average contributions of PM$_{2.5}$ sources at six sites in the PRD: (a) those in southerly flow, (b) those in northerly flow.

Fig. 9. The schematic diagram of high-emission areas in the PRD (box colors correspond to those in Fig. 8, and shaded area indicates the key emission area).
3.5 Distinguishing local and regional PM$_{2.5}$ pollution in the PRD

The analyses presented in Section 3.4 indicate that the secondary sulfates at the four southern coastal sites (DM, QA, UT and DP) in the PRD were almost entirely derived from the conversion of SO$_2$ from the emissions of ships in the southern ocean during southerly flow, contributing approximately 20% of the average PM$_{2.5}$ (13 μg/m$^3$) at the four sites. Considering that the ship emissions directly contributed approximately 10% of the average PM$_{2.5}$ at the four sites, the total ship emissions contributed approximately 30% of PM$_{2.5}$ in the southern coastal PRD area and acted as the largest source of PM$_{2.5}$. Under northerly flow conditions, the background DP site, which was barely affected by pollution emissions within the PRD, reflected regional transport from the north air mass outside the PRD, while the background QA site reflected the superposition effect of regional background pollution and the input of the most serious pollution area in the PRD. The consistency of the secondary sulfate concentrations at the background QA and DP sites was interpreted to reflect almost the same regional background effect during northerly flow; thus, the differences in the six anthropogenic sources between the two background sites, including secondary nitrate (and SV-OOA), biomass burning, industrial emissions, coal burning, vehicle emissions and ship emissions, could be used to trace the internal inputs from the most serious pollution area within the PRD to the downwind area. The internal inputs of six anthropogenic sources to the corresponding sources of PM$_{2.5}$ at the background QA site were 66%, 67%, 28%, 76%, 59% and 75%, respectively, and the total internal input of 37.7 μg/m$^3$ accounted for 45% of PM$_{2.5}$ at the background QA site, showing that the local contributions of anthropogenic pollution emissions in the key source area of the PRD were still crucial in winter but lower than the contribution of the regional background. Ignoring natural sources, such as aged sea salt and fugitive dust, under northerly flow, the contributions of other anthropogenic sources to DP were considered to represent regional background pollution, and the differences in their corresponding source concentrations between QA and DP were expected to represent the local emissions of source areas in the PRD. Therefore, the source structures in the regional background air mass and local emissions of heavy pollution sources area in the PRD are shown in Fig. 10a and b. Secondary sulfate and LV-OOA occupied the vast majority (45.6%) of the regional background air mass from the northern mainland, followed by industrial emissions (17.8%), secondary nitrate and SV-OOA (15.5%). However, the major sources between the sources output by local emissions from the heavy pollution source area of the PRD were secondary nitrate and SV-OOA (37.3%), biomass burning (20.6%), vehicle emissions (14.9%) and coal burning (11.9%). Therefore, measures implemented for the effective control of PM$_{2.5}$ in the PRD should focus on local controls and regional joint prevention and control under winter northerly flow conditions.
Fig. 10. The PM$_{2.5}$ source structures: (a) those in regional background air and (b) locally produced pollution of the central PRD area under northerly flow.

4 Conclusions

The PRD is one of the largest agglomerations of cities in the world, and its air quality has largely improved in recent decade. To reveal the current PM$_{2.5}$ pollution characteristics on a regional scale in the PRD, six sampling sites were selected to conduct 4 months of sampling and chemical analysis in 2015; then, the source exploration of PM$_{2.5}$ was performed using a novel method. The conclusions are described below.

1. The 4-month average PM$_{2.5}$ concentration for all six sites in the PRD was 37 μg/m$^3$, of which OM, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, EC, metal elements, and Cl$^-$ contributed 36.9%, 23.6%, 10.9%, 9.3%, 6.6%, 6.5% and 0.9%, respectively. The tempo-spatial PM$_{2.5}$ variations were generally characterized as being higher in the north inland region and higher in winter.

2. This study revealed that theME-2 model produced more environmentally meaningful and statistically robust results of source apportionment than the traditional PMF model. Secondary sulfate was found to be the dominant source of PM$_{2.5}$ in the PRD, at 21%, followed by vehicle emissions (14%), industrial emissions (13%), secondary nitrate (11%), biomass burning (11%), SOA (7%), coal burning (6%), fugitive dust (5%), ship emissions (3%) and aged sea salt (2%). Only aged sea salt and ship emissions did not show obvious seasonal variations.

3. Based on the spatial distribution characteristics of PM$_{2.5}$ sources under typical southerly and northerly airflow conditions, the central PRD area between MDS, HS and QA is identified as a key area for source emissions, including SO$_2$, NOx, coal burning, biomass burning, industrial emissions and vehicle emissions, and thus deserves more attention when implementing local pollution control in the PRD. In addition, ship emissions should be controlled more strictly during summer due to its contribution of approximately 30% of PM$_{2.5}$ in the southern coastal area of the PRD under southerly air flow.

4. Under typical winter northerly flow, the contributions of anthropogenic pollution emissions in the central PRD area contributed 37.7 μg/m$^3$ (45% of PM$_{2.5}$) to the regional background air. Secondary sulfate (36.9%), industrial emissions (17.8%), and secondary nitrate SV-OOA (12.8%) were the major PM$_{2.5}$ sources for the PM$_{2.5}$ transported in the regional background air mass, while secondary nitrate (30.9%), biomass burning (20.6%), vehicle emissions (14.9%) and coal burning (11.9%) were the major sources for the PM$_{2.5}$ produced in the central PRD area. Therefore, effective control measures of PM$_{2.5}$ in the PRD in the future should pay more attention to both local controls and regional joint prevention.

Acknowledgments

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