Characteristics and source apportionment of PM$_{2.5}$ on an island in Southeast China: Impact of sea-salt and monsoon

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ABSTRACT

To study the combined effects of the East Asian monsoon and ocean emissions on wintertime and summertime PM$_{2.5}$ in island cities, filter samples were collected simultaneously at four different functional sites. Based on the chemical compositions of PM$_{2.5}$ and positive matrix factorization (PMF) model analysis, the pollution characteristics and sources were determined. Insignificant differences, and no correlation in PM$_{2.5}$ reconstructed compositions were found among the sites ($P_{ANOVA}$ < 0.05, $P > .05$), while significant differences, and no correlation, were found between winter and summer ($P_{ANOVA}$ < 0.05, $P > .05$). There was more serious chloride depletion in summer (0.88 ± 0.05), caused by both significant Cl$^-$ depletion and Na$^+$ enrichment, than in winter (0.18 ± 0.10). The concentrations of non-sea-salt-SO$_4^{2-}$ in winter were close to those in summer, but the sulfate oxidation ratio (SOR) in winter was much lower than that in summer. The results could be explained by the fact that sea-salt-SO$_4^{2-}$ has an important contribution to secondary inorganic aerosol on island cities. From both air trajectory clustering and PMF analysis, it was found that there was significant aerosol aging and regional transport in the island city during the East Asian monsoon, and that continental air masses control the variation of air pollution in winter, while sea breezes dominate the characteristics of PM$_{2.5}$ in summer. This study helps to understand the characteristics and source mechanisms of PM$_{2.5}$ pollution under complex meteorological conditions in island cities.

1. Introduction

With rapid economic development and urban agglomeration, fine particulate matter (PM$_{2.5}$) in East Asia has gradually developed characteristics such as wide-ranging regional pollution, complex formation mechanisms and explosive growth (Luo et al., 2017; Weagle et al., 2014). High concentrations of PM$_{2.5}$ affect air quality, atmospheric visibility, climate change and human health (Posch, 2005; Zhou et al., 2016; Liu et al., 2016). Recently, pollution characteristics and sources of PM$_{2.5}$ were investigated not only for urban and suburban areas, but also for background or remote areas (Tao et al., 2014; Norris et al., 2014; Zhang et al., 2017; Wang et al., 2019). Haze development is predominantly caused by regional transport and local sources, and synoptic weather plays an important role in the evolution of haze in the East Asian continental outflow region (Seo et al., 2017; Yeh et al., 2017). Therefore, it is necessary to study further the interaction between air pollution and weather in these areas, especially in coastal cities (Li et al., 2017; Ding et al., 2017; Liu et al., 2018).

Air quality in subtropical coastal areas is influenced by the transport of pollution from East Asia during the monsoon season (Wang et al., 2019). Most previous studies relating to monsoons focused on the PM$_{2.5}$ concentration or gaseous species (Jeong and Park, 2017). The effects of northeasterly winds on the particle concentration and its size distributions in Bachok were analyzed, reflecting a mixture of local anthropogenic emissions, aging aerosol transported from East Asia and clean air masses from marine regions (Dominick et al., 2015). In addition, large differences in aerosol composition, including SO$_4^{2-}$ concentrations and Cl$^-$ depletion, were observed between marine air...
masses from the South China Sea and continental air masses affected by urban areas in East Asia (Farren et al., 2019). Higher nss-SO$_4^{2-}$, NH$_4^+$ and nss-SO$_4^{2-}$/NO$_3^-$ ratios were found in marine aerosols over the South China Sea, compared to remote open oceans and the western Pacific Ocean (Hsu et al., 2007). Chou et al. (2008) suggested that the Asian outflow aerosols, in which SO$_4^{2-}$ can be neutralized by NH$_4^+$, make NO$_3^-$ more abundant in Taiwan, and the chlorine deficiency is mainly caused by the reaction of NaCl and HNO$_3$. Bagtasa et al. (2018) found that long-range transport accounts for around one-third of the formation mechanism of PM$_{2.5}$ and internal and external influences in island cities of East Asia are still not fully understood.

Pingtan Island, located on the western side of the Taiwan Strait, is affected by the subtropical East Asian monsoon, sea and land breezes and typhoons. The monsoon wind flows from the subtropical ocean to the land in summer, while in winter the wind flows from the high-latitude continent to the ocean (Zhang et al., 2010; Jia et al., 2008; Webster et al., 1998). In our previous study, PM$_{2.5}$ concentrations in Pingtan occasionally appear to be high, up to 100 $\mu$g m$^{-3}$, resulting not only from the influence of local sources, but also from the contribution of the outflow from continental air pollutants (Hu et al., 2019). Pingtan offers an opportunity to study how the formation process and sources of PM$_{2.5}$ in an island area are controlled by the East Asian monsoon. Therefore, the aims of this study are: (1) to investigate the pollution characteristics of PM$_{2.5}$ on Pingtan Island during summer and winter; (2) to identify the potential sources of PM$_{2.5}$ using receptor modeling (PMF) and backward trajectories; and (3) to determine the impact of the monsoon and sea salt on the diurnal variations between winter and summer; by integrating the chemical components of PM$_{2.5}$ and identifying their sources. The results provide a scientific basis and comprehensive understanding of the formation mechanisms of PM$_{2.5}$ in island cities of East Asia.

2. Materials and methods

2.1. Sampling

Based on geographical location, distribution of anthropogenic activities, and dominant meteorological conditions, four sampling sites on Pingtan Island (Fig. 1 and Table S.1) were selected: 36-Foot Lake (FL), Jinjing Bay (JB), Jun Mountain (BG) and County Government (CG) (details are shown in Table S1 and Fig. S1). FL is a suburban site, close to a natural freshwater lake, and surrounded by emissions from traffic and agricultural activity. JB, a developing town, is mainly affected by emissions from construction, shipping and traffic, with the sampling site located at the rooftop of a 21-storey building. BG, a background site on the island, is located halfway up the Jun Mountain, which suffers less impact from anthropogenic emissions. BG is surrounded to the northeast by mountains, resulting in a southwestward wind throughout the year. The site is not representative, so no specific analysis was done, and it was only used as a background reference. CG, a developed town, is influenced by emissions from urban traffic and food preparation. Due to the “channeling effect” of the Taiwan Strait, the wind speed in Pingtan is high throughout the whole year. The maximum wind speed can reach 19.7 m s$^{-1}$ during the typhoon period. Generally, wind speeds in winter are higher than those in summer (except at BG), which is beneficial to the dispersion of air pollutants (Table S.1). Fig. S.1 shows wind rose plots for the four sites, by season. Apart from BG, southwestward and northeastward were the dominant wind directions for summer and winter, respectively. Daily PM$_{2.5}$ filter samples were collected (over 23 h, from 9:00 am to 8:00 am the next day), using two low-flow (5 L min$^{-1}$) air samplers (MiniVol, AirMetrics Corp., USA), in winter (from Jan. to Feb. 2017) and summer (from Jul. to Aug. 2017). Polycarbonate filters (Whatman, USA, 47 mm) were used to analyze metallic elements, while quartz filters (Whatman, USA, 47 mm) were used for water-soluble inorganic ions, organic carbon (OC) and elemental carbon (EC). In total, 50 sets of PM$_{2.5}$ samples (26 in winter and 24 in summer) and 4 sets of blank samples were collected at each site and strict quality control and assurance was applied to the measuring instruments throughout the sampling period. A schedule was applied to check the flow of the samplers and clean them regularly. We also regularly ran 2 or 3 samplers to start sampling at the same time and site, and the target compounds among these duplicate samples all differed by < 10%. In addition, different categories of air pollutant (PM$_{10}$, PM$_{2.5}$, NO$_2$, SO$_2$, CO, O$_3$) and meteorological parameters were measured at the monitoring sites.

2.2. Experiments

The mass concentrations of PM$_{2.5}$ were measured using the
The concentration of TE was determined using the sum of oxides method (Andrews et al., 2011):

$$\text{OC}_{\text{sec}} = \text{OC}_{\text{tot}} - \text{OC}_{\text{pri}} \tag{1}$$

$$\text{OC}_{\text{pri}} = \text{EC} \times \left( \frac{(\text{OC})_{\text{min}}}{\text{EC}} \right) \tag{2}$$

The elemental components of the PM$_{2.5}$ samples were analyzed using polycarbonate filters through wave dispersive X-ray fluorescence (WD-XRF) spectrometry (Axios-MAX, Panalytical, Holland). Thirteen elements (V, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Cu, Zn, As, Pb) were measured. The methods are described in detail in our previous study (Du et al., 2017).

2.3. PM$_{2.5}$ mass reconstruction

PM$_{2.5}$ can be reconstructed into nine groups: organic matter (OM), elemental carbon (EC), non-sea-salt-SO$_4^{2-}$ (nss-SO$_4^{2-}$), NO$_3^-$, NH$_4^+$, sea salt (SS), crustal elements (CE), trace elements (TE), and other (undetected) components.

The OM concentration was calculated by multiplying OC by a conversion factor. Based on OM oxidation, the OC multiplier was chosen within the range between 1.2 and 2.6. The multipliers of non-urban sites are expected to be highest, because of the level of oxidation and the conversion of secondary organic compounds during the process of transport (Chow et al., 2015; Jennerjahn, 2012). Therefore, 1.8 was chosen for BG and 1.6 for the other three sites in this study.

SS contains the components ss-Cl$^-$, ss-Na$^+$, ss-Ca$^{2+}$, ss-K$^+$, ss-Mg$^{2+}$, and ss-SO$_4^{2-}$. Assuming that all Na$^+$ is from SS, the concentrations of other species were calculated as ratios to Na$^+$ from the seawater chemistry: ss-Ca$^{2+}$ (1.8), ss-Ca$^{2+}$ (0.038), ss-K$^+$ (0.036), ss-Mg$^{2+}$ (0.12), ss-SO$_4^{2-}$ (0.252) (Li et al., 2017). The concentration of SS was then derived from:

$$\text{SS} = \text{Na}^+ + \text{Cl}^- + \text{ss} - \text{Ca}^{2+} + \text{ss} - \text{K}^+ + \text{ss} - \text{Mg}^{2+} + \text{ss} - \text{SO}_4^{2-} \tag{3}$$

where symbols refer to the concentration of the respective species. The concentrations of nss-SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and chemical elements (including EC) can be determined directly. The concentration of CE was derived using the sum of oxides method (Andrews et al., 2011):

$$\text{CE} = 2.145 \text{Si} + 1.89 \text{Al} + 1.43 \text{Fe} + 1.4 \text{ss} - \text{Ca} + 1.2 \text{SS} - \text{K} + 1.67 \text{Ti} \tag{4}$$

again, symbols refer to the concentration of the respective species. The concentration of TE was defined as the sum of the concentrations of As, Mn, Pb, Cu, Zn, V and nss-Mg. Lastly, “other components” was defined as the remaining portion of PM$_{2.5}$ and includes F$^-$. 

2.4. Data quality control and statistical analysis

Every filter was equilibrated at a temperature 25 ± 0.1 °C and relative humidity (RH) 52 ± 2%, and then weighed on an electronic microbalance (Sartorius 0.01 mg, Germany). The water used for pretreatment of the sample was ultra-pure (resistance coefficient > 18 MΩ cm). The method detection limits (MDLs) for F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ were 0.05, 0.03, 0.02, 0.02, 0.19, 0.19, 0.15, 0.31, and 0.45 μmol L$^{-1}$, respectively. When measuring the concentrations of water-soluble ions, a point concentration of ions was undetected. The methods are described in detail in our previous study (Du et al., 2017).

2.5. PMF analysis

In this paper, the US EPA (United States Environmental Protection Agency) PMF 5.0 (positive matrix factorization) model was used to identify the sources of the PM$_{2.5}$ samples in Pingtan, and its equation is (Norris et al., 2014; Paatero and Tapper, 1994; Paatero, 1997):

$$X = GF + E \tag{5}$$

where $X$ is the sample concentration matrix ($n \times m$, $n$ is the sample number, $m$ is the chemical composition number), $G$ is the factor (pollutant source) contribution matrix ($n \times p$, $p$ is the number of precipitation factors), $F$ is the factor profile matrix ($p \times m$) and $E$ is the residual matrix ($n \times m$), defined as:

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \tag{6}$$

$$Q(E) = \frac{\sum_{i=1}^{n} \sum_{j=1}^{m} \left( \frac{e_{ij}}{x_{ij}} \right)^2}{\sum_{i=1}^{n} \sum_{j=1}^{m} \left( \frac{g_{ik}}{g_{ik}} \right)} \tag{7}$$

where $x_{ij}$ is the standard deviation of $X$, and the elements in $G$ and $F$ are all non-negative. $Q(E)$ is one of the model criteria, and subsequent analysis can be carried out only when $Q(E)$ converges. The matrices $G$ and $F$ are determined when the optimization causes $Q(E)$ tend to the number of degrees of freedom.

The variables input to the PMF model in this study include the daily average concentration of OC, EC, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Na$^+$, Cl$^-$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Fe, Si, Al, Cu, Zn, Pb, Mn, Ti, As and V in PM$_{2.5}$. The number of each species was 187, meeting the operational requirements of PMF. Data inputs of PMF included the concentrations and uncertainties, and the uncertainties were calculated in detail from (Li et al., 2018; Polissar et al., 1998):

$$uij = \sqrt{(EF \times \text{conc.})^2 + (\text{MDL})^2} \tag{8}$$

where $EF$ is the error factor based on experience, ~10–20%, and MDL is the minimum detection limit of chemical concentration. However, when the concentrations were lower than the MDL, they were replaced by half the MDL, and the uncertainties were defined as 5/6 of the MDL. The signal-to-noise ratios (S/N) were > 1.0 for the 19 species (except V), and they were defined to be “strong” (Paatero and Hopke, 2003); $V$ was re-weighted as “weak” because the concentrations of a third of the samples were less than the MDL.

Based on experience and reference files, six to eight factors were tested. We compared the lowest $Q_{\text{obs}}/Q_{\text{expected}}$ at each step increase in number of factors (Brown et al., 2015). Table S2 shows that there was a decrease (0.64) in $Q_{\text{obs}}/Q_{\text{expected}}$ going from six to seven factors and a larger decrease (0.71) going from seven to eight factors. When changes...
in \( Q_{\text{robust}}/Q_{\text{expected}} \) become smaller with increasing number of factors, this can indicate that too many factors are being fitted, suggesting that eight factors may be the optimal solution here. The displacement of the factor elements (DISP) had no swaps for all factors, indicating that the solutions had no data errors and were well defined. The bootstrap (BS) for results with eight factors showed one factor of 55% mapping, and 10% of BS-DISP runs were rejected due to factor swaps. However, with seven factors, one factor of the BS had 70% mapping and 0% of BS-DISP runs were rejected. Combining uncertainty and source profiles, seven factors were retained for Pingtan after numerous runs.

2.6. Analysis of the backward trajectories of air masses

The backward trajectories of air masses arriving Pingtan in two seasons during the campaign were simulated and clustered by using MeteoInfo (Wang et al., 2014). 24-h backward trajectories were run every hour, with starting time 0:00 and ending time 23:00 (local time), at 100 m height, and located at 25.50°E, 119.79°N. Meteorological data were provided by NOAA ARL (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1).

2.7. Correlation and difference tests

The correlations and differences of chemical species among different sampling sites were investigated using Pearson correlation and paired sample t-tests, respectively. The method of paired sample t-tests must meet the condition that the differences between the pair-samples are normally distributed. The differences in source contributions among the trajectory clusters and between winter and summer were examined using an ANOVA test.

3. Results and discussion

3.1. Overview of PM\(_{2.5}\) concentration and chemical compositions

Table 1 shows the comparison of PM\(_{2.5}\) concentrations and their chemical components in this study, and at other major coastal cities worldwide. Similarly to Seoul, Mexico and Barcelona, the masses of PM\(_{2.5}\) in Pingtan were lower than in Xiamen, Fuzhou, Lin’an, Qingdao and Hong Kong, and higher than in Penghu, Toronto and Yokohama (Heo et al., 2009; Elizabeth et al., 2004; Querol et al., 2004; Zhang et al., 2012; Li et al., 2016; Zhang et al., 2017; Cao et al., 2012; Lee et al., 2003; Khan et al., 2010). In these studies, SO\(_4^{2-}\), NO\(_3^-\) and NH\(_4^+\) (SNA) were the predominant components, ranging from 25.2% to 46.3%. Apart from Haikou, the concentrations of NO\(_3^-\) were higher than those of NH\(_4^+\) in Chinese cities (Table 1), while two other cities (Mexico and Yokohama) showed the reverse pattern (Liu et al., 2017; Elizabeth et al., 2004; Khan et al., 2010). The higher NO\(_3^-\) has been explained by the rapid increase in the number of vehicles in recent years. OM was also an important component of PM\(_{2.5}\). The OM concentrations in the Chinese cities ranged from 14.9% to 31.9%, while the OM concentrations in other countries ranged from 21.8% to 62.4%. The lowest EC concentration was observed in Pingtan, followed by Toronto, indicating limited primary emissions impacts (Lee et al., 2003). Most previous studies have shown clear seasonal variations in PM\(_{2.5}\), especially for winter and summer, whereas this is not seen in suburban areas in Pingtan (Fig. 2) (Li et al., 2018; Wang et al., 2016; Zhang et al., 2017). PM\(_{2.5}\) concentrations were observed at the different sampling sites in the following order: JB (37.52 ± 16.26 μg m\(^{-3}\) ) > BG (37.10 ± 15.02 μg m\(^{-3}\) ) > FL (33.71 ± 9.99 μg m\(^{-3}\) ) > CG (29.73 ± 16.25 μg m\(^{-3}\) ). BG has the lowest wind speed (1.93 ± 1.61 m s\(^{-1}\)) and few local sources, so its second highest PM\(_{2.5}\) concentration indicates regional transport and accumulation of air pollutants. This analysis of seasonal and site variation makes it possible to correlate the results with the influence of meteorological conditions and anthropogenic factors.

As shown in Fig. 3(a), the OC and EC contributions to the PM\(_{2.5}\) concentration were higher in winter than in summer. Unlike inland cities, Pingtan has no industry and does not require heating for warmth.

### Table 1

Comparison of chemical components in PM\(_{2.5}\) in coastal areas (μg m\(^{-3}\)); locations in China except where otherwise stated.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling period (YY/MM)</th>
<th>PM(_{2.5})</th>
<th>SO(_4^{2-})</th>
<th>NO(_3^-)</th>
<th>NH(_4^+)</th>
<th>OM</th>
<th>EC</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuzhou (FL)</td>
<td>17/01-17/02, 17/07-17/08</td>
<td>33.7</td>
<td>6.0</td>
<td>3.0</td>
<td>1.4</td>
<td>7.2</td>
<td>0.4</td>
<td>This study (2019)</td>
</tr>
<tr>
<td>Fuzhou (JB)</td>
<td>37.5</td>
<td>37.1</td>
<td>5.7</td>
<td>2.7</td>
<td>1.3</td>
<td>7.0</td>
<td>0.3</td>
<td>This study (2019)</td>
</tr>
<tr>
<td>Fuzhou (CG)</td>
<td>29.7</td>
<td>23.3</td>
<td>4.7</td>
<td>1.6</td>
<td>1.7</td>
<td>5.3</td>
<td>1.6</td>
<td>This study (2019)</td>
</tr>
<tr>
<td>Haikou</td>
<td>15/01,15/05,15/07,15/09</td>
<td>86.2</td>
<td>11.2</td>
<td>6.0</td>
<td>4.5</td>
<td>27.5</td>
<td>3.0</td>
<td>Liu et al. (2017)</td>
</tr>
<tr>
<td>Xiamen</td>
<td>09/06-10/05</td>
<td>53.6</td>
<td>8.0</td>
<td>5.3</td>
<td>4.2</td>
<td>12.8</td>
<td>2.0</td>
<td>Li et al. (2016)</td>
</tr>
<tr>
<td>Penghu</td>
<td>13/07-15/04</td>
<td>23.6</td>
<td>3.9</td>
<td>2.1</td>
<td>0.9</td>
<td>4.6</td>
<td>1.1</td>
<td>Li et al. (2016)</td>
</tr>
<tr>
<td>Lin’an, Ningbo</td>
<td>2014-2015</td>
<td>68.9</td>
<td>16.9</td>
<td>9.2</td>
<td>5.8</td>
<td>17.4</td>
<td>2.7</td>
<td>Zhang et al. (2017)</td>
</tr>
<tr>
<td>Qingdao</td>
<td>03/01, 03/06-03/07</td>
<td>134.8</td>
<td>21.6</td>
<td>18.9</td>
<td>14.8</td>
<td>41.8</td>
<td>5.4</td>
<td>Cao et al. (2012)</td>
</tr>
<tr>
<td>Hong Kong</td>
<td>03/01, 03/06-03/07</td>
<td>88.4</td>
<td>21.2</td>
<td>9.7</td>
<td>7.1</td>
<td>22.1</td>
<td>6.2</td>
<td>Cao et al. (2012)</td>
</tr>
<tr>
<td>Seoul, Korea</td>
<td>03/06-12</td>
<td>37.6</td>
<td>5.8</td>
<td>5.2</td>
<td>3.7</td>
<td>11.4</td>
<td>2.9</td>
<td>Heo et al. (2009)</td>
</tr>
<tr>
<td>Mexico City, Mexico</td>
<td>2000-2002</td>
<td>35.1</td>
<td>5.9</td>
<td>2.7</td>
<td>3.0</td>
<td>21.9</td>
<td>8.4</td>
<td>Elizabeth et al. (2004)</td>
</tr>
<tr>
<td>Toronto, Canada</td>
<td>00-02-01/02</td>
<td>12.7</td>
<td>2.3</td>
<td>1.8</td>
<td>1.2</td>
<td>4.4</td>
<td>0.5</td>
<td>Lee et al. (2003)</td>
</tr>
<tr>
<td>Barcelona, Spain</td>
<td>1999-2001</td>
<td>27.6</td>
<td>4.2</td>
<td>2.3</td>
<td>1.2</td>
<td>12.2</td>
<td>NA</td>
<td>Querol et al. (2004)</td>
</tr>
<tr>
<td>Yokohama, Japan</td>
<td>07/09-08/09</td>
<td>20.6</td>
<td>3.8</td>
<td>1.0</td>
<td>2.3</td>
<td>4.5</td>
<td>1.9</td>
<td>Khan et al. (2010)</td>
</tr>
</tbody>
</table>

NA = data not available
in winter. The reason for the higher winter contributions is the dominant meteorological conditions, especially the East Asian monsoon (Zhang et al., 2013). These mean mainly northward winds and the Continental Asian Outflow leads to higher OC and EC concentrations in winter. Previous studies indicate that the ratio of OC to EC from coal combustion and biomass burning is estimated to be 8, while that from vehicle exhausts is estimated to be 4 (Safai et al., 2014; Shi et al., 2011; Watson et al., 2001; Zhao et al., 2013). In both summer and winter, the ratios of OC to EC in Pingtan are higher than 8 (Fig. 3(a)), showing that OC and EC come mainly from coal combustion and biomass burning. These results illustrate the importance of the regional transport. The percentage of POC (primary organic carbon) and SOC were calculated using Eqs. (1,2), as described in Section 2.2. SOC accounted for 70–90% of the total, suggesting the influence of aged aerosols. The aged aerosols could be associated with photochemical reactions of primary organic matter and regional transport. In winter, the predominant north-eastward wind brought more aged aerosols through the outflow of continental pollutants to the monitoring sites, while strong oxidation conditions in summer can enhance the formation of aged aerosols in an island area (Liu et al., 2016a). In this study, the ratio \( \text{NO}_3^-/\text{SO}_4^{2-} \) was higher in winter than in summer at all four sites, based on the seasonal distribution characteristics shown in Fig. 3(b). High concentrations of nitrate aerosol in the YRD region of China could elevate the concentrations of related air pollutants in coastal area of southeast China through long-range transport (Zhang et al., 2007). A previous study also found \( \text{NO}_3^- \) over East Asia in winter to significantly enhance \( \text{NO}_3^- \) concentrations in the downwind regions (such as the Pearl River Delta (PRD) region of China (Ying et al., 2014)).

The conversion efficiencies of \( \text{NO}_2 \) to \( \text{NO}_3^- \) and \( \text{SO}_2 \) to \( \text{SO}_4^{2-} \) were calculated from the formulas \( \text{NOR} = \frac{[\text{NO}_3^-]}{([\text{NO}_3^-] + [\text{NO}_2])} \) and \( \text{SOR} = \frac{[\text{SO}_4^{2-}]}{([\text{SO}_4^{2-}] + [\text{SO}_2])} \), respectively (Table S.3). The saturation of secondary transformation means \( \text{NO}_2 \) and \( \text{SO}_2 \) were negatively or non-correlated with NOR and SOR in Pingtan (Yin et al., 2014). Limited \( \text{NO}_2 \) and low concentrations of \( \text{NO}_3^- \) (winter: 3.39 \( \mu \text{g} \cdot \text{m}^{-3} \); summer: 1.31 \( \mu \text{g} \cdot \text{m}^{-3} \)) in Pingtan made NOR in winter (0.27 ± 0.14) higher than that in summer (0.22 ± 0.13). The concentrations of nss-\( \text{SO}_4^{2-} \) in winter (6.77 \( \mu \text{g} \cdot \text{m}^{-3} \)) and summer (6.65 \( \mu \text{g} \cdot \text{m}^{-3} \)) are close, while SOR in winter (0.55 ± 0.12) was much lower than in summer (0.63 ± 0.13), which can be explained by the fact that sea-salt-\( \text{SO}_4^{2-} \) has a more important contribution to secondary inorganic ions on islands than inland and in coastal cities (Yin et al., 2014; Zhang et al., 2017). A previous study has shown that when \( \text{SOR} > 0.25 \) and \( \text{NOR} > 0.1 \), this is representative of high oxidation values. The higher the values are (Table S.3), the higher the conversion strength (Colbeck and Harrison, 1984).

In this study, \( \text{Na}^+ \) and \( \text{Cl}^- \) concentrations were higher in summer than in winter, indicating that a large amount of sea salt enters the atmosphere from the ocean under the influence of the predominant southeastward wind and waves. From the ratio of \( \text{Na}^+ \) to \( \text{Cl}^- \) (Fig. 3(b)), it can be seen that there was chloride depletion. The chloride depletion was estimated using the equation \( \text{Cl}_{dep} = ([\text{Na}^+]/0.56 - [\text{Cl}^-]/[\text{Na}^+] \times 0.56 \) (Quinn et al., 2000). The chloride depletion in summer (0.88 ± 0.05) was larger than that in winter (0.18 ± 0.10). KCl and NaCl can form HCl by reacting with acidic gases (such as HNO3), and then react with NH4+ in particulates; higher temperatures (Table S.1) in summer promote the volatilization of \( \text{NH}_4\text{Cl} \), leading to a reduction in chloride salt (Hu et al., 2008; Martens et al., 1973). Although relative humidity had a negative effect on chloride depletion through its impact on heterogeneous reactions, photochemical reactions played a more important role in chloride depletion, so that more intense chloride depletion occurred in summer (Hsu et al., 2007). The ratio of \( \text{Na}^+ \) to \( \text{Cl}^- \) concentrations in seawater is close to 0.557 (Wang and Shooter, 2001), and the concentration of \( \text{Cl}^- \) in PM2.5 in winter showed a significant enrichment compared with this.

### 3.2. Inter-site and inter-seasonal analysis of PM2.5 mass reconstruction

Table 2 shows the correlations and differences for chemical species of PM2.5 between winter and summer and among sites FL, JB, and CG. The compositions were mostly characterized by insignificant correlations (\( P > 0.05 \)) and significant differences (\( P_{\text{ANOVA}} < 0.05 \)) between winter and summer at each site. Large differences in meteorological parameters (including monsoon, air temperature, relative humidity, radiation and boundary layer dynamics) lead to varying pollution sources between winter and summer (Hsu et al., 2017; Poschl, 2005). For a small number of components, the difference between winter and summer is insignificant, showing that these pollution emissions have seasonal stability. The CE (Si, Al, Fe, nss-Ca, nss-K, Ti), EC and TE (As, Mn, Pb, Cu, Zn, V, nss-Mg) components are thought to represent dust, vehicle exhaust and industry emissions (Amato et al., 2009; Hueglin et al., 2005; Zhang et al., 2013; Cao et al., 2008). There are dense road traffic and ship emissions all year round at developing region JB, while CG, a residential region, is affected by local residential activities. Compared with other sites, the highest nss-\( \text{SO}_4^{2-} \) concentration (winter: 7.32 \( \mu \text{g} \cdot \text{m}^{-3} \); summer: 10.26 \( \mu \text{g} \cdot \text{m}^{-3} \)) and proportion (winter: 17.63%; summer: 29.33%) at JB may be related to precursor emissions.
Table 2

<table>
<thead>
<tr>
<th></th>
<th>Correlation</th>
<th>Difference</th>
<th>Correlation</th>
<th>Difference</th>
<th>Correlation</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>Summer</td>
<td>FL</td>
<td>JB</td>
<td>CG</td>
<td>Summer</td>
<td>FL and JB</td>
</tr>
<tr>
<td>EC</td>
<td>0.367</td>
<td>0.240</td>
<td>0.000</td>
<td>−0.584</td>
<td>0.046</td>
<td>0.014</td>
</tr>
<tr>
<td>OM</td>
<td>−0.193</td>
<td>0.549</td>
<td>0.001</td>
<td>−0.433</td>
<td>0.159</td>
<td>0.000</td>
</tr>
<tr>
<td>nss-SO(_4)(^{2-})</td>
<td>0.153</td>
<td>0.635</td>
<td>0.003</td>
<td>0.005</td>
<td>0.987</td>
<td>0.323</td>
</tr>
<tr>
<td>NO(_3)(^-)</td>
<td>−0.099</td>
<td>0.761</td>
<td>0.000</td>
<td>−0.186</td>
<td>0.563</td>
<td>0.000</td>
</tr>
<tr>
<td>NH(_4)(^+)</td>
<td>−0.201</td>
<td>0.531</td>
<td>0.001</td>
<td>−0.161</td>
<td>0.618</td>
<td>0.002</td>
</tr>
<tr>
<td>SS</td>
<td>−0.186</td>
<td>0.563</td>
<td>0.000</td>
<td>−0.107</td>
<td>0.741</td>
<td>0.004</td>
</tr>
<tr>
<td>CE</td>
<td>0.632</td>
<td>0.050</td>
<td>0.383</td>
<td>0.000</td>
<td>1.000</td>
<td>0.484</td>
</tr>
<tr>
<td>TE</td>
<td>0.222</td>
<td>0.537</td>
<td>0.039</td>
<td>−0.353</td>
<td>0.352</td>
<td>0.051</td>
</tr>
</tbody>
</table>

\(\text{a} 2\)-tailed test of significance is used.
\(\text{b} \) Correlation and difference are analyzed at each site between winter and summer.
\(\text{c} \) Correlation and difference are analyzed between FL, JB and CG, in winter.
\(\text{d} \) Correlation and difference are analyzed between FL, JB and CG, in summer.
\(\text{e} \) Difference is analyzed by using an ANOVA test.
\(\text{f} \) Difference is analyzed by using a paired sample t-test.

(i.e., local industrial activities may emit SO\(_2\)).

Unlike the pair CG and FL, the correlations and differences between FL and JB, FL and JB and CG, are insignificant in winter (P > 0.05, Pt-test > 0.05). The correlations and differences between CG and FL can be divided into three groups. The first group has significant correlations (P < 0.01) and insignificant differences (Pt-test > 0.05). This group includes EC and OM, which are good tracers of incomplete combustion of fossil fuel and biomass burning in primary sources (Turpin and Huntzicker, 1995), and secondary transformation, respectively (Shi et al., 2011; Zhao et al., 2013). CG is ~3 km northeast of FL, and the prevailing wind direction at CG and FL is northeastward, which means that wind arriving at CG has passed through FL, having a regional impact. The second group was characterized by significant correlations (P < 0.01) and significant differences (Pt-test < 0.05), which are seen in nss-SO\(_4\)\(^{2-}\), NO\(_3\)\(^-\) and NH\(_4\)\(^+\). The concentrations of nss-SO\(_4\)\(^{2-}\), NO\(_3\)\(^-\) and NH\(_4\)\(^+\) at CG in winter were 6.85, 4.86, 2.59 (gm\(^{-3}\)), respectively, which were higher than those at FL (6.15, 4.02, 1.71 (gm\(^{-3}\))). These findings imply that there are similar secondary formation and short-range transport characteristics between FL and CG. The third group, consisting of SS and CE, was characterized by insignificant correlations (P > 0.05) and significant differences (Pt-test < 0.05). The CE include Si, Al, Fe, nss–Ca, nss-K and Ti, which could be emitted from coal combustion, industrial sources, biomass burning or dust. The pollution sources in urban and suburban areas are different, and agricultural activities occurred more frequently at FL. SS mainly includes Na\(^+\) and Cl\(^-\). Apart from marine sources, there are contributions from coal and wood combustion (Mcculloch et al., 1999; Morawksa and Zhang, 2002), mineral dusts (Li and Shao, 2009; Sun et al., 2006) and garbage burning (Zárnte et al., 2000) as the main sources of Cl\(^-\). The proportion of SS of PM\(_{2.5}\) is 7–13% in winter and 16–25% in summer. The Na\(^+\) concentration in summer is around 10.9 times than that in winter (because of sea freezing), while the Cl\(^-\) in winter is around 2.16 times than that in summer (because of lower Cl\(^-\) depletion). The Cl\(^-\) concentration at FL (1.33 \(\mu\)g m\(^{-3}\)) is higher than that at CG (1.06 \(\mu\)g m\(^{-3}\)). Because many agricultural activities of straw burning and biomass burning are happened at suburban FL, there are additional sources of Cl\(^-\) at FL.

The inter-site correlations and differences for SS, CE and TE in summer had P > 0.05, Pt-test > 0.05. Combining with the analysis above, it can be concluded that CE mainly represents dust in summer. However, dust may come from construction and road fugitive dust (Cesari et al., 2014; Han et al., 2007). Huang et al. (2017) indicate that soil dust is from long-range transport. The local construction and road dust lead to an insignificant correlation, and the regional transport leads to insignificant differences between sites. Similarly, for TE the combination of less industry-related activity and diffusion in small areas causes the same result. Hence, we cannot determine what the major controlling factor is. The Mg\(^2+\)/Na\(^+\) mass ratio was 0.04 ± 0.01 in summer, which was lower than 0.12, the bulk seawater ratio (Hsu et al., 2007). This result indicates that the high chloride depletion in summer is caused by both Cl-depletion and Na\(^+\) enrichment. An additional Na\(^+\) source causes the insignificant correlation for SS. Partly significant correlations or differences mainly appear for EC and secondary components (OM, nss-SO\(_4\)\(^{2-}\), NO\(_3\)\(^-\) and NH\(_4\)\(^+\)). Whether it is significant or insignificant depends on the dominant factor:
Fig. 4. Cluster results of air mass trajectories, relative contributions of chemical components and \( \text{PM}_{2.5} \) concentrations of each air mass to the \( \text{PM}_{2.5} \) concentrations, by season.
precursor emissions or the extent of the regional transport.

### 3.3. Effect of the monsoon on PM$_{2.5}$

Pingtan, a subtropical and coastal city in southeastern China, has a climate affected by the shifting of Asian Monsoon system, which causes significant seasonal differences in meteorological conditions. In summer, there are subtropical high pressures, typhoons, heavy monsoon rains, and the monsoon blows from the Pacific Ocean (Bagtasa et al., 2018; Li et al., 2017). In contrast, air transported from inland China, coupled with a strong temperature inversion and low air pressure in winter, can be favorable for the accumulation of particulate matter (Wang et al., 2019; Wang et al., 2014; Zheng et al., 2018). The back trajectories of air parcels show a clear picture in the two sampling periods. Fig. 4 presents the cluster results of air mass trajectories and chemical components of PM$_{2.5}$ in winter and summer. The PM$_{2.5}$ concentrations are indicated at the centers of the pie charts. It can be seen that air masses mainly originated from inland in winter, while all air masses originated from the marine environment in summer.

In winter, Air Mass 1 had the highest proportion (30.56%) of the total, transmitted via a short pathway from Zhejiang province. Air Mass 2 (25.69%) traveled via a long pathway from the northwest, with smaller proportions of most components than in the other three air masses and larger proportions of CE and others. This result indicates that long-range transport leads to a decline in dust and complicates aerosol structures. Air Mass 3 (27.08%) arrived from the west, originating from Jiangxi province. The pathways of Air masses 1, 2 and 3 all originated in southeastern China and passed over the sea. Air Mass 4 (16.67%) originated in the Taiwan Strait, carrying the second highest PM$_{2.5}$ concentration (38.7 μg m$^{-3}$). In summer, the air masses arriving at Pingtan had mostly marine origins. Air Mass 1 (55.99%) originated in the Taiwan Strait. Air Mass 2 (14.32%) was transmitted from the Taiwan Strait but arrived by hooking northward in a counterclockwise direction. Air Mass 3 (23.18%) began at the outer rim of Taiwan and carried the highest PM$_{2.5}$ concentration of 38.7 μg m$^{-3}$. Air Mass 4 (6.51%) originated from the outer rim of East China Sea, carrying a low proportion of CE, TC and EC.

The average PM$_{2.5}$ concentration of each air mass in winter (38.7 μg m$^{-3}$) was close to that in summer (35 μg m$^{-3}$). The percentages of secondary pollutants accounted for 56–70% in winter and 36–45% in summer, and sea salt 15–18% in summer. Furthermore, significant differences (PANOVA < 0.01) in compositions of PM$_{2.5}$ reconstruction among the trajectory clusters were obtained. Pingtan has few local pollution sources, and pollution is mainly controlled by air mass trajectories, so these results indicate that there was significant aerosol aging and regional transport in the island city during the East Asian monsoon, and that continental air masses control the variation of air pollution in winter, while sea breezes dominate the characteristics of PM$_{2.5}$ in summer.

### 3.4. Source apportionment of PM$_{2.5}$

Figs. 5 and 6 present the PMF factor profiles and the contribution of various sources to PM$_{2.5}$. The high contributions of OC, EC, Cl$^-$, and K$^+$ appear in Factor 1; OC, EC, and Cl$^-$ act as coal combustion tracers and OC, EC, and K$^+$ as biomass burning tracers (Xu et al., 2018; Li et al., 2018), indicating that there is a mixed source of coal combustion and biomass burning. Therefore, Factor 1 was identified as combustion emission. Factor 2 shows high contributions of Cu, Pb, Fe, Zn, Mn, Ti, As and V, which are generally indicators of vehicle exhaust. Cu, regarded as a good tracer of vehicle emissions, mainly originates from the wearing of tires and brakes (Amato et al., 2009), V originates mostly
from heavy oil combustion (Hueglin et al., 2005), and the lubricant oil that is used in the tire manufacturing process and in brake linings contains a high concentration of Zn (Zíková et al., 2016). Factor 3, contributing a high loading of metal elements (Zn, Pb, As, V and Mn), was characterized by industrial and ship emission sources (Moffet et al., 2008). Factor 4 was associated with secondary aerosol, with high loads of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ (Song et al., 2006). Factor 5 was dominated by Ca$^{2+}$ and Mg$^{2+}$, which are related to construction dust (Zhang et al., 2013). Factor 6, with the highest proportion of Na$^+$ loading, was associated with marine sources. Factor 7 was designated as crustal dust, and dominated by Al, Si, Ti, Zn, Pb and As (Cao et al., 2008).

As shown in Fig. 6, the contributions of various sources were similar among the four sites, but the differences between winter and summer were significant. Secondary formation was one of the largest sources and was five times larger in winter (55%) than in summer (12%). However, marine sources account for 43% in summer, and construction dust including high Ca$^{2+}$ and Mg$^{2+}$, an important part of which comes from sea salt in island cities, accounts for 11%. These results are consistent with the air trajectory clusters in Section 3.3. Secondary aerosols were generated mainly from secondary transformations during transport in winter, and both sea salt and secondary products were dominant factors in summer. The contributions from combustion emission (25%) were larger in winter. There was little contribution from biomass burning and coal combustion in Pingtan, which can be attributed to monsoon convection in winter. JB had a higher loading from industrial and ship emissions (22%) than the other three sites (12%), which were affected by a mixture of local industry activities, port activities and regional transport.

Overall, secondary aerosol, marine sources and combustion emissions, which are defined as mainly controlled by regional transport in the above analysis, show a higher proportion in summer or winter. However, soil dust, construction dust, industrial and ship emissions, and vehicle exhaust, for which it is not clear if the dominant factor is local sources or regional transport, show relatively stable proportions across summer and winter.

4. Conclusions

The pollution characteristics and sources of PM$_{2.5}$ in Pingtan were investigated in order to determine the relative contributions between primary emissions and secondary formation, and between local sources and regional transport. For individual reconstructed compositions of PM$_{2.5}$, significant differences and no correlations were found between winter and summer, and positive correlations and insignificant differences were observed among different sites. The predominant north-eastward wind in winter brought more aged aerosols through the outflow of continental pollutants to the monitoring sites, while strong oxidation conditions and sea salt carried by waves in summer affected the formation of aged aerosols and marine contributions in the island area. There was more serious chloride depletion in summer than in winter, and the high chloride depletion in summer is caused by both significant Cl$^-$ depletion and Na$^+$ enrichment.

Significant differences in compositions of PM$_{2.5}$ reconstruction among the trajectory clusters indicated that the elevated PM$_{2.5}$ concentrations in Pingtan are mainly controlled by air mass transport. In winter, three air masses were identified as originating mainly in southeastern China and passing over the sea, and one air mass as originating in the Taiwan Strait. In summer, the air masses arriving at Pingtan were mostly transmitted from marine regions and originated in the Taiwan Strait and the outer rim of the East China Sea. Overall, these
results indicate that there was significant aerosol aging and regional transport in an island country during the East Asian monsoon, and that while continental air masses control the variation of air pollution in winter, sea breezes dominate the characteristics of PM$_{2.5}$ in summer.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found at https://doi.org/10.1016/j.atmosres.2019.104786.

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