Source Apportionment of PM$_{2.5}$ at Urban and Suburban Sites in a Port City of Southeastern China

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ABSTRACT

Shipping emissions potentially contribute to the degradation of air quality in port cities. In this study, PM$_{2.5}$ samples were collected from two sites at different distances from the shipping channel of Xiamen Port in southeastern China between November 2015 and May 2018 and analyzed for their chemical compositions, which included water-soluble ions, carbonaceous species, and elements. The average annual PM$_{2.5}$ mass concentrations were 55.8 ± 22.7 µg m$^{-3}$ and 56.5 ± 24.5 µg m$^{-3}$ at the urban and suburban sites, respectively, with the lowest values in summer and the highest in winter/spring. Significantly higher values for vanadium (V) and nickel (Ni) were found at the urban site due to the shorter distance between this location and the shipping channel. Using a PMF model, six source factors were identified: sulfate and shipping emissions (16.6–20.9%), secondary nitrate and chloride (14.7–17.3%), fugitive dust (16.9–23.0%), industrial emissions (5.5–7.0%), primary organic aerosol (14.1–14.8%), and traffic emissions and biomass burning (23.8–24.6%). Potential source contribution function analysis indicated that air masses from the South China Sea contributed significantly to the shipping emissions. The PMF-based method did not distinguish primary shipping emissions from secondary sulfate. When a V-based method was used, the primary PM$_{2.5}$ from shipping emissions plus its associated secondary sulfate was shown to contribute 5.5–8.9% of the ambient PM$_{2.5}$ on average. The results from the V-based method exhibited strong positive correlations with those of the PMF-based method. Considering the potential negative effect on air quality and the expanding international maritime trade in the long term, our research indicates that policies and regulations for controlling shipping emissions are necessary in all major port cities, including those outside the domestic emission control areas of China.

Keywords: Shipping emissions; PM$_{2.5}$; Source apportionment; PMF; Vanadium.

INTRODUCTION

With the increase of global trade, ocean-going ships are becoming a significant and growing contributor to SO$_2$, NO$_x$, and fine particulate matter (PM$_{2.5}$) in the coastal atmospheric environment, and in particular in port cities with heavy ship traffic (Erying et al., 2010; Viana et al., 2014; Zhang et al., 2017). Ports are not only important transport hubs of economic activity but also important hot pots of atmospheric pollutants. The oxidation of SO$_2$ and NO$_x$ produces secondary sulfate and nitrate aerosol and also contributes to PM$_{2.5}$. In addition, NO$_x$ contributes to ozone pollution, which has an effect on people’s health and the quality of the vegetation. The enhanced PM$_{2.5}$ has been strongly related to the degradation of visibility, adverse health effects, and radiative forcing (Erying et al., 2010; Hu and Jiang, 2014; Wu et al., 2015). In northwestern Europe, a clear pattern of decreasing concentration of vanadium (V), which is taken as a representative and conservative marker of heavy fuel oil (HFO) combustion emission associated with fine particles, was observed from the coastline to about 400 km inland during the period 2005 to 2008 (Visschedijk et al., 2013). In southern California, primary PM$_{2.5}$ contributions from ocean-going vessels were found to range from 8.8% of the total PM$_{2.5}$ at the monitoring location closest to the Port of Long Beach to 1.4% of the total PM$_{2.5}$ at the monitoring location 80 km inland...
(Agrawal et al., 2009). Similar downward trends of shipping emission contributions to PM$_{2.5}$ from harbor regions to inland regions were also observed in Qingdao, the Yangtze River Delta (YRD), and the Pearl River Delta (PRD), China, based on shipping emission inventories and air quality models (Chen et al., 2017; Liu et al., 2018; Chen et al., 2019). Moreover, the influence of shipping emissions on air quality depends on both meteorological factors and emission intensities (including fuel type) from ships and land-based sources. Given that ports are often close to heavily populated urban areas, ports are becoming a target for air pollution control measures in port cities. Thus, understanding the contribution of shipping emissions to PM$_{2.5}$ in port cities is important for taking effective PM$_{2.5}$ pollution mitigation measures.

Dispersion and receptor models as well as chemical tracer methods are commonly used to estimate the contribution of shipping emissions or oil combustion to PM$_{2.5}$ concentrations in port cities. In a recent review (Viana et al., 2014), shipping emissions were estimated to contribute to 1–14% of PM$_{2.5}$ in European coastal areas based on positive matrix factorization (PMF) and chemical tracer methods. In Busan, Korea, PMF results indicated that on average, 7% of PM$_{2.5}$ was attributed to ships in 2013 (Jeong et al., 2017). In China, assessment studies on the role of shipping emissions are so far based on inventories and air quality model analyses (Fan et al., 2016; Chen et al., 2017; Lang et al., 2017, Chen et al., 2018; Liu et al., 2018; Chen et al., 2019), as well as receptor models and tracer marker methods (Zhao et al., 2013; Zhang et al., 2014; Tao et al., 2017; Mamoudou et al., 2018). However, the uncertainties in ship and other anthropogenic emissions might seriously affect the accuracy of the research results.

With rapid development of the economy and the shipping industry in China, the ambient V concentration in port cities has been increasing over time. For example, the concentration of V increased from 2.4 ng m$^{-3}$ in 2008 to 4.9 ng m$^{-3}$ in 2009–2010 in Tianjin, China (Gu et al., 2011; Zhao et al., 2013), and increased from 13 ng m$^{-3}$ in 2002 to 70 ng m$^{-3}$ in 2011–2012 in Qingdao (Guo et al., 2004; Wu et al., 2013). In Korea, the concentration of V in PM$_{2.5}$ observed in Jeju Island increased rapidly from 1.1 ng m$^{-3}$ in 2001 to 8.5 ng m$^{-3}$ in 2006 (Kim et al., 2006; Moon et al., 2008; Nguyen et al., 2009). The observed concentration of V for the port of Rotterdam showed significant decrease due to the ban of HFO use by ships since 2008 because fuels now in use contain much less sulfur and vanadium (Visschedijk et al., 2013). Therefore, the ambient V concentration in port cities can be used to investigate the impact of shipping emissions on primary PM$_{2.5}$. Using the linear relation between emission rates of PM$_{2.5}$ and V in ship fuels established by Agrawal et al. (2009), Zhao et al. (2013), Cesari et al. (2014), and Zhang et al. (2014) estimated the contribution of shipping emissions to primary PM$_{2.5}$ at Shanghai Port (China), on an island in the Bohai Sea strait (China), and in the harbor-industrial area of Brindisi (Italy), respectively.

In addition, as described by Kim and Hopke (2008), the secondary sulfate associated with primary shipping emissions could be quantified by plotting the daily contributions from the primary shipping source with those from the secondary aerosol source obtained by PMF. Based on this method, shipping emissions were estimated to give a secondary contribution to atmospheric aerosol significantly higher than their primary contribution in port cities such as Seattle (Kim and Hopke, 2008), Gibraltar (Pandolfi et al., 2011), Melilla (Viana et al., 2009), Hong Kong (Yau et al., 2013), and Brindisi (Cesari et al., 2014). Mamoudou et al. (2018) reported that the primary PM$_{2.5}$ from shipping emissions by V-based method was much lower than the values calculated by using a PMF-based method in Yangshan Harbor, Shanghai. In a recent review (Zhang et al., 2017), the contribution of shipping emissions to PM$_{2.5}$ concentration ranged from 2% to 25% in Chinese port cities. In China, however, most of previous studies were carried out in PRD, YRD and Bohai-Sea rim areas, and few long-term studies on contribution of shipping emissions to PM$_{2.5}$ were conducted in other regions (Xu et al., 2018).

Driven by the economic globalization and activity in the ocean shipping industry, shipping emissions in ports and along shipping channels are expected to increase and potentially worsen the current severe air pollution along the coastline in China. In order to reduce harmful emissions from ships, the Chinese Ministry of Transport (MOT) has set up the domestic emission control areas (DECAs) in PRD, YRD, and the Bohai-Sea rim (MOT, 2015). From 2017 onwards, the sulfur content of the fuel oil shall not exceed 0.5% at all ports in these regions. Based on the WRF/CMAQ modeling system and DECA policy, reductions of 2.7% in PM$_{2.5}$ and 9.54% in SO$_2$ concentrations in 2013 in the ports in PRD, China, were predicted (Liu et al., 2018). Furthermore, expanding the DECAs along the whole coastline is expected to improve air quality even more. Thus, the air quality in currently unregulated port regions will benefit from an expansion of the DECA policy. Even without low sulfur fuel oil regulation in Xiamen Port, some berths have begun to supply shore power to ships at berth since 2017 as a solution for cutting shipping emissions. According to the Xiamen Environmental Quality Bulletin in 2017, the annual PM$_{2.5}$ level showed only a slight reduction from 29 µg m$^{-3}$ in 2015 to 27 µg m$^{-3}$ in 2017, although strict emission control policies, including desulfurization and denitrification for coal-fired boilers and the State IV Emission Standard for the motor vehicles in the fourth stage, were implemented (Xiamen Environmental Protection Bureau, 2017). As a regional hub port in southeastern China, Xiamen Port handled a total of 10.38 million TEU (twenty-foot equivalent unit) and ranked 14th in the world in 2017 (www.stats-xm.gov.cn). Considering the significant emissions of SO$_2$, NO$_x$, and PM$_{2.5}$ from fuel oil combustion and the high population density near Xiamen Port, it is necessary to quantify the impacts of this source on PM$_{2.5}$.

In this study, a 2.5-year PM$_{2.5}$ monitoring program at an urban site near the shipping channel of Xiamen Port and a suburban site away from the port was carried out to quantify the shipping emissions by using PMF and tracer marker methods. The main purpose of the study is to distinguish shipping emissions from the other anthropogenic
METHODS

Sample Collection

The measurements were carried out at an urban site (24.45°N, 118.08°E) and a suburban site (24.62°N, 118.23°E) every month from November 2015 to May 2018 (Fig. 1). The urban site is located on the roof of an office building in the Siming campus of Xiamen University at the southern end of Xiamen Island, 18 m above the ground. It is situated between two busy roads and close to the shipping channels of Xiamen Port. There are two coal-fired power plants in the vicinity of this site. Songyu generating station is about 6 km west of the urban site, and Housi generating station is about 15 km south of the site. The suburban site is located on the roof of an office building in the Xiangan campus of Xiamen University to the northeast of Xiamen Island, 15 m above the ground. The site is surrounded by villages and cropland with few nearby stationary sources of PM$_{2.5}$ and is about 30 km northeast of the urban site. However, factories and automobile exhaust from Quanzhou urban area to the northeast during the northeastern monsoon season might become significant.

PM$_{2.5}$ samples from a 24-h period (8:00 a.m–8:00 a.m.) were collected using a high-volume PM$_{2.5}$ sampler (1.05 m$^3$ min$^{-1}$, TH1000C; Wuhan Tianhong Instruments, China) and quartz filters (Tissuquartz 2500QAT-UP; Pall Corp.). The quartz filters were pre-baked in an oven at 600°C for 4 h to remove impurities. The concentrations of PM$_{2.5}$ ($\mu$g m$^{-3}$) were determined according to the mass difference before and after sampling and the sampling volume. A total of 140 pairs of the available samples were successfully collected for chemical analysis. 2 pairs of these samples collected on May 8, 2017, and April 16, 2018, were removed from source analysis due to the sand-dust storms from North China, which resulted in a total of 138 pairs. The daily mean concentrations of criteria air pollutants (PM$_{2.5}$, SO$_2$, NO$_2$, and O$_3$) and meteorological factors, including temperature (T), relative humidity (RH), pressure (P), wind speed (WS), wind direction (WD), visibility (Vis), and rainfall (RF), at the air quality auto monitoring stations of Xiamen Environmental Protection Bureau near the sampling sites.

**Fig. 1.** Location of the sampling sites (red dots) and berth of Xiamen Port (red rectangle) to the west of Taiwan Strait, China. The triangles represent the coal-fired power plants. The density map for marine traffic in the left up corner was a screenshot from https://www.marinetraffic.com. The Yangtze River Delta (YRD) and the Pearl River Delta (PRD) as well as marginal seas in China are labelled in the marine traffic density map.
Chemical Analysis

A punch (3.14 cm²) from the quartz filter was extracted in water and analyzed for water-soluble ions of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ by ion chromatography (PIC-10; Qingdao Puren Instruments Co., China) (Wu et al., 2015). The individual method detection limits (MDL) were calculated as three times of the standard deviations of species concentrations in the blank filters. The MDLs ranged from 0.033 µg m⁻³ for Cl⁻ to 0.165 µg m⁻³ for SO₄²⁻. Because the sea-salt sulfate (ssSO₄²⁻; calculated as 0.25 × Na⁺) (Prodi et al., 2009) contributed less than 3% to the total sulfate, the measured sulfate was regarded as non-sea-salt (nssSO₄²⁻) completely.

A 2 cm × 2 cm portion of each quartz filter sample was cut into fragments using ceramic scissors and placed into a conical Teflon tube. Acid solutions (10 mL 65% HNO₃ and 5 mL 35% H₂O₂) were added into the tube for digestion using a closed microwave digester (TOPEX; PreeKem Scientific Instruments Co., Ltd., China). After being completely digested, the solution was diluted to 20 mL with deionized water for the analysis of Be, V, Cr, Mn, Ni, Cu, Zn, As, Se, Cd, Ba, and Pb by inductively coupled plasma mass spectrometry (ICP-MS) (7700X; Agilent). A separate aliquot solution was diluted an additional 100-fold with deionized water for K, Ca, Mg, Al, and Fe analysis since their concentrations in the 20 mL samples were beyond the linear ranges. MDLs of elements ranged from 0.03 ng m⁻³ for Be to 124.8 ng m⁻³ for Ca.

Organic carbon (OC) and elemental carbon (EC) were analyzed using a DRI Model 2001 carbon analyzer (Atmoslytic, Calabasas, CA). An area of 0.49 cm² punched from each quartz filter was analyzed for four OC fractions (OC1, OC2, OC3, and OC4), OP (optical pyrolyzed carbon determined when the reflectance returns to its original value in a 2%-oxygen/98%-helium mixture), and three EC fractions (EC1, EC2, and EC3). The IMPROVE_A thermal/optical reflectance (TOR) protocol defines total OC and total EC as follows: OC = OC1 + OC2 + OC3 + OC4 + OP and EC = EC1 + EC2 + EC3 – OP (Chow et al., 1993; Cao et al., 2003; Wu et al., 2015). The organic carbon can be classified into two fractions based on water solubility: water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC). In this study, a 1.57 cm² punch of filter was extracted with 20 mL deionized water for WSOC analysis by a Total Organic Carbon Analyzer (TOC-VCPH; Shimadzu Co., Ltd., Beijing, China). The difference between OC and WSOC was defined as the WIOC, and the sum of WSOC, WIOC, and EC was defined as the total carbon (TC).

MDLs were 0.57 ± 0.42 µgC m⁻³, 0.08 ± 0.10 µgC m⁻³, and 0.15 ± 0.22 µgC m⁻³ for OC, EC, and WSOC, respectively. The data were corrected for average field blanks and recovery rates. A random duplication of measurements was carried out every 10 samples and the relative standard deviation (RSD) associated with instruments fell within 15%.

Positive Matrix Factorization (PMF)

PMF is a multivariate receptor model based on the analysis of the correlation between measured concentrations and source emissions of chemical species. The model utilizes nonnegative factor elements, which has advantages over principal component analysis (PCA) and chemical mass balance (CMB). The principles of PMF have been described in detail in the PMF 5.0 User Guide (Norris et al., 2014). The measured concentrations and their uncertainties were used as inputs to the model. In order to prevent double counting, Mg, Ca, and K⁺ instead of Mg²⁺, Ca²⁺, and K⁺ were included in PMF analysis. Moreover, the trace element of Be (beryllium) with more than 50% of samples below MDL was screened out. As illustrated in the user guide, the chemical species are considered as “strong” if the signal-to-noise ratio is greater than 2.0, “good” if it is between 1.0 and 2.0, and “weak” if it is between 0.5 and 1.0. Finally, a total of 25 parameters, including 6 water-soluble ions (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, and K⁺), 3 carbonaceous species (WSOC, WIOC, and EC), 15 elements (excluding Be and K), and PM2.5, were included in the data matrix in the source apportionment analysis using EPA PMF 5.0 (http://www.epa.gov/heasd/research/pmf.html).

Values below the MDL were replaced with the value of 1/2 × MDL and the overall uncertainties were set as 5/6 × MDL. For the values above the MDL, the uncertainty (Unc) was calculated based on the error fraction (determined by the RSD associated with instruments used for chemical analysis), the concentration, and MDL for the application of PMF as follows:

\[ Unc = \sqrt{\left(\frac{Error\ Fraction \times C}{1}\right)^2 + \left(0.5 \times MDL\right)^2} \] (1)

Because the number of factors depends on the air shed, number of samples, sampling frequency, and species characteristic (Norris et al., 2014), it is not straightforward to deduce the number of sources contributing to PM2.5. Based on previous PMF results in harbor areas and the atmospheric pollutant emission inventory in Fujian, China (Cesari et al., 2014; Lu et al., 2014; Wu et al., 2016; Jeong et al., 2017; Tao et al., 2017), we carried out a detailed examination of the features of PMF solutions for models with 4 to 8 factors (Text S1). In this study, the best solution was obtained with 6 factors.

Backward Trajectory Analysis and the Potential Source Contribution Function (PSCF)

The 72-h backward trajectories were calculated by using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (https://ready.arl.noaa.gov/) every 6 h (0, 6, 12, 18 UTC) at 100 m above the ground at
both sites. The meteorological data were derived from the NOAA GDAS (Global Data Assimilation System) database at a resolution of \(1^\circ \times 1^\circ\) (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1). The final types of transport clusters were categorized based on the distance between a trajectory endpoint and the corresponding cluster mean endpoint (Dorling et al., 1992).

PSCF analysis was used to identify the PM\(_{2.5}\) potential source areas. The PSCF values for the grid cells in the study domain are calculated by counting the trajectory segment endpoints that terminate within each cell by the following equation:

\[
PSCF_{ij} = \frac{m_{ij}}{n_{ij}}
\]

where \(n_{ij}\) is the number of endpoints that fall in the \(ij\)th cell and \(m_{ij}\) is the number of times that a source concentration was higher than a criterion value when the trajectories passed through the \(ij\)th cell. In this study, the geographic information system (GIS)-based software, TrajStat 1.4.5 (http://meteothink.org/products/index.html), was used to compute the PSCF values with threshold criteria of 75th percentile concentration of a source resolved by PMF (Yao et al., 2016; Jeong et al., 2017). That is, a higher PSCF value indicates that this region has a high potential to influence the air pollution concentration observed at a receptor site. These cells are indicative of areas of “high potential” contributions for the constituent. Due to a higher uncertainty associated with small value of \(n_{ij}\), the PSCF values are multiplied by an arbitrary weight function, \(W_{ij}\), to reduce the effect of small values of \(n_{ij}\). \(W_{ij}\) was applied when the total number of the endpoints in a particular cell was less than about 3 times the average values \(n_{ave}\) of the end points per cell (Wang et al., 2009):

\[
W_{ij} = \begin{cases} 
1.00 & \text{if } n_{ij} > 3n_{ave} \\
0.70 & \text{if } 1.5n_{ave} < n_{ij} \leq 3n_{ave} \\
0.42 & \text{if } n_{ave} < n_{ij} \leq 1.5n_{ave} \\
0.17 & \text{if } n_{ij} \leq n_{ave}
\end{cases}
\]

RESULTS AND DISCUSSION

Seasonal Variation of PM\(_{2.5}\)

Table 1 presents the mean levels and standard deviations of PM\(_{2.5}\) mass, and major and trace element concentrations at both sites. The average PM\(_{2.5}\) mass concentrations were 55.8 ± 22.7 µg m\(^{-3}\) with a range of 12.0 to 113.2 µg m\(^{-3}\) at the urban site and 56.5 ± 24.5 µg m\(^{-3}\) with a range of 9.5 to 105.1 µg m\(^{-3}\) at the suburban site. The daily PM\(_{2.5}\) values at the urban site were correlated well with those at the suburban site (1-tailed, \(r = 0.624, p < 0.001, n = 138\)) and the paired \(t\)-test showed no significant difference between the two sites (2-tailed, \(p = 0.683, n = 138\)), probably due to the influence of regional meteorological fields. The maximum value was about 9 times higher than the minimum, with a wide variation of PM\(_{2.5}\) at both sites. The lowest PM\(_{2.5}\) values were typically observed on rainy days, and the highest values were observed on foggy calm days. Pearson correlation analysis revealed that PM\(_{2.5}\) concentrations were strongly correlated with atmospheric pressure (P) but anti-correlated with temperature (T), relative humidity (RH), rainfall (RF), and visibility (Vis) at both sites throughout the sampling period (Table S1). However, the PM\(_{2.5}\) concentration was not negatively correlated with WS, suggesting the non-dominant role of local sources. Strong winds flush pollutants out of the system, whereas low winds cause air pollution to remain in one area.

These annual average values of PM\(_{2.5}\) at the two sites were around 60% higher than the PM\(_{2.5}\) standard (35 µg m\(^{-3}\)) of the National Ambient Air Quality Standard (NAAQS) of China (Grade I, GB3095-2012). PM\(_{2.5}\) concentrations observed at the urban site were slightly higher than previously reported at the same site in Xiamen in 2011–2013 (51.5 ± 20.4 µg m\(^{-3}\); Wu et al., 2015) and urban Guangzhou (48 ± 22 µg m\(^{-3}\); Tao et al., 2017), lower than those in Shanghai (62.6 µg m\(^{-3}\); Zhao et al., 2013) and Qinhuangdao (70.1 µg m\(^{-3}\); Lang et al., 2017), China, and the port area in Thessaloniki, Greece (66 µg m\(^{-3}\); Tolis et al., 2015), but much higher than those in some coastal harbor sites, such as Hong Kong, China (30.5 µg m\(^{-3}\); Yai et al., 2013); Marseille, France (35.5 µg m\(^{-3}\) during pollution episodes; Salameh et al., 2018); Busan, Korea (26.1 ± 15.3 µg m\(^{-3}\); Jeong et al., 2017); Brindisi, Italy (15.1 ± 5.4 µg m\(^{-3}\); Cesari et al., 2016); Rotterdam, Netherlands (19.5 µg m\(^{-3}\); Mooibroek et al., 2011); Bay of Algeciras, Spain (21.8–24.2 µg m\(^{-3}\); Pandolfi et al., 2011); and Los Angeles (7.0 µg m\(^{-3}\)) and Seattle (10.6 µg m\(^{-3}\)), United States (Kim et al., 2008; Minguillon et al., 2008).

The average PM\(_{2.5}\) concentrations at both sites exhibited clear seasonal variations with the lowest values in summer (June–September) and the highest values in winter (December–February) and spring (March–May) (Table 1). This behavior is similar to previous studies in port cities such as Shanghai, Guangzhou, Hong Kong, and Qinhuangdao in China (Yau et al., 2013; Zhao et al., 2013; Wu et al., 2015; Lang et al., 2017; Tao et al., 2017) and is largely due to the regional meteorology of the Asian Monsoon. Mean 72-h backward trajectory clusters in four seasons showed that the air masses originating from the YRD city cluster could carry the coastal urban air pollutants to the sampling sites and result in high PM\(_{2.5}\) concentrations, while the air masses originating from the South China Sea and Taiwan Strait might dilute the air pollutants to a great extent (Fig. S1). The monthly variations of meteorological factors and gaseous precursors are shown in Figs. S2 and S3. In summer, the lower pressures facilitate the dispersion of air pollutants, the higher temperatures enhance the dissociation of \(NH_4NO_3\), and the lower concentrations of \(SO_2\) and \(NO_2\) limit the formation of secondary inorganic aerosols. The significant decrease of \(SO_2\) and \(NO_2\) in February with respect to that in January or March was mainly due to the Spring Festival homecoming as a secular pilgrim, resulting in fewer emissions from factories and vehicles in Xiamen. In fall, the prevailing northeasterly winds and lower
Table 1. Descriptive statistics of PM$_2.5$ and its associated chemical species (mean ± standard deviation) and at the urban and suburban sites.

<table>
<thead>
<tr>
<th>Component ( (\mu g \cdot m^{-3}) )</th>
<th>Siming campus of XMU (urban)</th>
<th>Xiangan campus of XMU (suburban)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spring ((n = 22))</td>
<td>Summer ((n = 40))</td>
</tr>
<tr>
<td>PM$_2.5$</td>
<td>61.6 ± 23.4</td>
<td>39.4 ± 17.3</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.61 ± 0.56</td>
<td>0.39 ± 0.22</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>6.62 ± 6.86</td>
<td>1.3 ± 0.79</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>8.83 ± 3.57</td>
<td>7.0 ± 3.68</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.68 ± 0.60</td>
<td>0.63 ± 0.27</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>3.93 ± 2.45</td>
<td>2.35 ± 1.17</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.37 ± 0.29</td>
<td>0.25 ± 0.14</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.13 ± 0.08</td>
<td>0.12 ± 0.06</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.82 ± 0.47</td>
<td>0.79 ± 0.66</td>
</tr>
<tr>
<td>WSOC</td>
<td>3.02 ± 1.50</td>
<td>1.89 ± 0.93</td>
</tr>
<tr>
<td>OC</td>
<td>5.28 ± 2.69</td>
<td>3.54 ± 1.7</td>
</tr>
<tr>
<td>EC</td>
<td>2.91 ± 1.22</td>
<td>2.22 ± 1.28</td>
</tr>
<tr>
<td>Mg$^+$</td>
<td>0.12 ± 0.12</td>
<td>0.12 ± 0.06</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>0.44 ± 0.32</td>
<td>0.67 ± 0.73</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.29 ± 0.21</td>
<td>0.22 ± 0.14</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.84 ± 0.65</td>
<td>0.69 ± 0.56</td>
</tr>
<tr>
<td>Be</td>
<td>0.04 ± 0.04</td>
<td>0.07 ± 0.08</td>
</tr>
<tr>
<td>V</td>
<td>2.1 ± 1.3</td>
<td>2.2 ± 1.6</td>
</tr>
<tr>
<td>Cr</td>
<td>0.33 ± 0.21</td>
<td>0.24 ± 0.14</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>0.44 ± 0.32</td>
<td>0.67 ± 0.73</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.84 ± 0.65</td>
<td>0.69 ± 0.56</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>1.2 ± 0.8</td>
<td>1.2 ± 0.9</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>1.56 ± 0.91</td>
<td>0.92 ± 0.61</td>
</tr>
<tr>
<td>As$^{3+}$</td>
<td>1.8 ± 0.9</td>
<td>1.5 ± 1.3</td>
</tr>
<tr>
<td>Se$^{4+}$</td>
<td>2.9 ± 1.7</td>
<td>2.0 ± 1.9</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>0.6 ± 0.4</td>
<td>0.5 ± 0.6</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>14 ± 17</td>
<td>15 ± 17</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>35 ± 24</td>
<td>25 ± 22</td>
</tr>
<tr>
<td>Cl$^-$/Na$^+$</td>
<td>1.3 ± 1.4</td>
<td>0.67 ± 0.29</td>
</tr>
<tr>
<td>NO$_3^-$/SO$_4^{2-}$</td>
<td>0.73 ± 0.63</td>
<td>0.24 ± 0.14</td>
</tr>
<tr>
<td>OC/EC</td>
<td>2.07 ± 0.81</td>
<td>1.1 ± 1.3</td>
</tr>
<tr>
<td>WSOC/TC</td>
<td>0.35 ± 0.11</td>
<td>0.31 ± 0.10</td>
</tr>
<tr>
<td>V/Ni</td>
<td>2.5 ± 0.66</td>
<td>1.64 ± 1.06</td>
</tr>
</tbody>
</table>

Concentration in the units of $ng \cdot m^{-3}$.
rainfall might play a more important role than wind speed in PM$_{2.5}$ variations with respect to those in summer. However, the wet and rainy weather in combination with low wind speed in spring limited local dispersion to a great extent, which resulted in the accumulation of air pollutants. As a result, the favorable weather conditions for secondary aerosol formation as well as higher concentrations of SO$_2$ and NO$_2$ contributed significantly to the higher levels of PM$_{2.5}$ in spring and winter.

**PM$_{2.5}$ Chemical Compositions**

As shown in Table 1, the most abundant species associated with PM$_{2.5}$ were SO$_4^{2-}$, NO$_3^-$, WIOC, NH$_4^+$, WSOC, and EC, which contributed more than 40% of the total mass on annual average. For the water-soluble ions, a significant difference between urban and suburban sites was only observed for K$^+$ (p = 0.001) and SO$_4^{2-}$ (p = 0.015) with 95% confidence interval based on the paired-sample t-test (Table 2), quite probably due to the additional contribution from joss paper and incense burning from the South Putuo temple only 800 m to the north and coal combustion from power plants to the west and south, respectively (Fig. 1). The ratio of NO$_3^-$ to SO$_4^{2-}$ (N/S) for PM$_{2.5}$ has been used as an indicator of the relative importance of mobile and stationary sources when compared to nitrogen and sulfur in the global atmosphere (Liu et al., 2016; Jeong et al., 2017). In this study, no significant spatial difference for the N/S ratio was found, suggesting that the two sites were affected by similar emission sources. However, the N/S ratio exhibited much higher values in winter than in summer (Table S1). Similar seasonal variations have also been reported in Chinese cities such as Qinhuangdao (Lang et al., 2017), Chengdu (Tao et al., 2013), Hangzhou (Cao et al., 2009), Nanjing (Li et al., 2016), Guangzhou (Tao et al., 2017), Xi’an (Wang et al., 2015), and four southeastern coastal cities (Wu et al., 2015). In our study, both the NO$_3^-$ concentration and the N/S ratio at both sites had significantly negative correlations with ambient temperature (r = −0.32 and −0.562 for N/S vs. T; p = 0.001), quite likely due to the loss of NH$_4$NO$_3$ at high temperature in summer and not the change of emission sources from mobile to stationary (Zhao et al., 2013). Nevertheless, the N/S ratios in Xiamen were comparable with Nanjing (0.46–0.68; Li et al., 2016), Toronto (0.81; Lee et al., 2003), Xi’an (0.69–0.88; Wang et al., 2015), and Qinhuangdao (0.94; Lang et al., 2017), indicating that vehicular emissions made a great contribution to the PM$_{2.5}$. The statistical results showed that the correlation coefficient between NH$_4^+$ and Cl$^-$ was lower than that between NH$_4^+$ and NO$_3^-$ or SO$_4^{2-}$ (Table S2), suggesting that most of NH$_4^+$ was likely in the form of NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, or NH$_4$HSO$_4$ rather than NH$_4$Cl. In addition, Cl$^-$ showed a positive correlation with Na$^+$ (r = 0.239, p = 0.002) and Mg$^{2+}$ (r = 0.191, p = 0.012) at the urban site, but there was no significant correlation between them at the suburban site. The urban site is only about 50 m away from the seaside and is likely influenced by sea sprays from the surf zone. Furthermore, a significant correlation has been observed between Mg$^{2+}$ and Ca$^{2+}$, which could indicate a crustal source. The much higher levels of Mg$^{2+}$ and Ca$^{2+}$ in fall provided further support for the enhanced wind-induced resuspension of fugitive dust (Fig. S2) (Liu et al., 2016).

The total carbon (TC) on average accounted for 16 ± 6% and 15 ± 5% of PM$_{2.5}$ at the urban and suburban sites, respectively, indicating that carbonaceous materials represent a significant component of PM$_{2.5}$. Both OC and EC showed higher concentrations in winter and spring due to the limited local dispersion and regional transport of air pollutants (Fig. S1). The OC/EC ratio exceeding 2.0–2.2 has been used as an indicator of secondary organic carbon (SOC) formation (Chow et al., 2006). The highest average ratios of OC/EC were observed in fall (3.31 and 3.40), which was more due to the lower EC concentrations than to the enhanced production of SOC in the atmosphere as a result of higher ozone concentrations (Chow et al., 2006; Turpin and Huntzicker, 1991) (Table 1 and Fig. S3). As shown in Table 2, the EC concentration was significantly higher at the urban site than the suburban site (p < 0.001), indicating that the urban site was more affected by vehicular and/or shipping emissions. The decrease of the OC/EC ratio at the urban site was essentially due to an increase of EC rather than to a decrease of SOC formation. A significant correlation between OC and EC (r = 0.732 and 0.745; p < 0.001) was obtained at both sites (Table S3), which suggested that OC and EC might be emitted from the same source. Besides, elevated WSO4/EC ratios in fall can be used as indicators for aged aerosol.

Crustal elements in PM$_{2.5}$, Ca was the most abundant element (> 1.4 µg m$^{-3}$), followed by Fe, Al, K, and Mg.

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**Table 2.** Paired sample t-test with 95% confidence interval of the difference test (2-tailed, $t_{0.05[137]} = 1.972$).

<table>
<thead>
<tr>
<th>t-test pair $^a$</th>
<th>$t_s$</th>
<th>Sig. level</th>
<th>t-test pair</th>
<th>$t_s$</th>
<th>Sig. level</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>3.700</td>
<td>&lt; 0.001</td>
<td>Fe</td>
<td>2.533</td>
<td>0.012</td>
</tr>
<tr>
<td>V</td>
<td>7.559</td>
<td>&lt; 0.001</td>
<td>Ca</td>
<td>2.052</td>
<td>0.042</td>
</tr>
<tr>
<td>Ni</td>
<td>3.806</td>
<td>&lt; 0.001</td>
<td>SO$_4^{2-}$</td>
<td>2.474</td>
<td>0.015</td>
</tr>
<tr>
<td>Cu</td>
<td>5.149</td>
<td>&lt; 0.001</td>
<td>OC/EC</td>
<td>–3.291</td>
<td>0.001</td>
</tr>
<tr>
<td>Zn</td>
<td>4.015</td>
<td>&lt; 0.001</td>
<td>Fe/Mn</td>
<td>–2.103</td>
<td>0.037</td>
</tr>
<tr>
<td>K$^+$</td>
<td>3.441</td>
<td>0.001</td>
<td>V/EC</td>
<td>3.963</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Mn</td>
<td>3.187</td>
<td>0.002</td>
<td>V/SO$_4^{2-}$</td>
<td>4.398</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

$^a$ Paired difference of urban minus suburban;  
$^b$ t-test statistics is calculated according to $t_s = \frac{D \times \sqrt{n}}{S_D}$, where $D$ is the arithmetic mean of difference between urban and suburban ($D_i$), $n$ is the sample number and $S_D$ is the standard deviation of $D_i$. 

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(0.2–0.9 µg m⁻³) in Xiamen. Nearly all the crustal elements had higher mean concentrations in fall (except K at the urban site), whereas most crustal metals showed the lowest mean concentrations in summer at the suburban site and in spring at the urban site. Both Fe and Ca showed significantly higher concentrations at the urban site than the suburban site (p = 0.012 and 0.042), this being consistent with the location of the urban site close to the construction site at Siming campus of XMU. The construction work occurred December 2015 to November 2017 within the sampling period. Regarding the trace elements, Zn was the most abundant trace metal in PM_{2.5} (> 100 ng m⁻³), followed by Mn, Pb, Ba, and Cu (10–50 ng m⁻³) and then As, Se, and Cd (1–5 ng m⁻³). Be was at even lower concentrations (<0.1 ng m⁻³). Zn is generally enriched in the aerosol as a result of emissions from motor vehicles, iron and steel works, and trash incinerator smelters and metallurgical industries (Qureshi et al., 2006). Similar profiles have been reported in Nanjing (Li et al., 2016), Brindisi (Cesari et al., 2014), Toronto (Lee et al., 2003), Seattle (Maykut et al., 2003), Guangzhou (Tao et al., 2017), Busan (Jeong et al., 2017), and the Strait of Gibraltar (Pandolfi et al., 2011). Seasonally, the mean concentrations of Mn, Ba, and Cu showed similar variations to the crustal elements, suggesting their common mixed crustal and anthropogenic sources. As shown in Table 2, trace metals, such as V, Ni, Cu, Zn, Mn, and Fe, were more often significantly elevated at the urban site, attributed to the site receiving greater influence of pollutant sources, such as vehicular emissions, power plants and shipping emissions. Interestingly, however, there was no significant difference for Pb between the two sites. Moreover, Pb showed much stronger correlation with crustal elements at the urban site than the suburban site (Table S4), implying the major contribution of marine vessels to V and Ni at the two sites (Fig. 1). An enrichment factor (EF) has commonly been used to evaluate the influences of anthropogenic sources on observed concentrations of elements. In this study, Al served as a reference element, and the EF of element X was calculated as \( (X/Al)_{aerosol} / (X/Al)_{soil} \), where \( (X/Al)_{aerosol} \) is the concentration ratio of element X to Al in aerosol, and \( (X/Al)_{soil} \) is the ratio in the local topsoil from Xiamen. Higher values of EF imply a greater extent of anthropogenic origin of a given element (Zhao et al., 2013; Liu et al., 2016). The EFs for elements in PM_{2.5} in Xiamen are shown in Fig. S4. The EFs for Fe, Mn, Be, K, Ca, and Mg were less than 20, likely derived from construction dust or resuspended road/soil dust (Cesari et al., 2014). The elements As, Cr, Se, Ni, Cu, and Pb were moderately enriched (EF <100), while Zn and Cd (EF >100) were highly enriched due to the contribution of nearby anthropogenic sources to aerosol composition. It should be noted that the EFs for V and Ni also showed clear seasonal variations with lower values in winter and fall (Fig. S4), which might be a result of less southern sea breeze in these seasons (Fig. S1).

### Source Apportionment of PM_{2.5}

The solution of six factors, namely, secondary sulfate and shipping emissions (F1), secondary nitrate and chloride (F2), fugitive dust (F3), industrial emissions (F4), primary organic aerosol (F5), and traffic emissions and biomass burning (F6), was identified as an optimal solution. The source profiles were shown in Figs. S5 and S6. The time series plot of daily contribution from each identified sources and the seasonal contribution of different sources to PM_{2.5} were shown in Fig. S7 and Fig. 2, respectively. The PMF diagnostics were summarized in Tables S7 and S8. In addition, the daily prevailing winds at SM site were also used to investigate their influence on the individual factor contribution to PM_{2.5} (Fig. S8). The PM_{2.5} mass concentration was reconstructed according to the sum of the six factors.
The first factor was distinguished by the relatively high contribution of V and Ni as well as sulfate and Na⁺ (Figs. S5 and S6). V and Ni are commonly associated with residual oil combustion (Pandolfi et al., 2011). This source factor accounted for 20.9% and 16.6%, on average, of the PM$_{2.5}$ mass concentrations at the urban and suburban sites, respectively. As mentioned above, V and Ni concentrations at the urban site were significantly higher than those at the suburban site due to shorter distances between the urban site and the shipping channel. The elevated contribution of SO$_4^{2-}$ and Na⁺ in this factor could be due to shipping emissions and sea spray, respectively. The resolved contribution of shipping emissions to PM$_{2.5}$ was comparable to those in Guangzhou and Zhuhai (17% and 18%, respectively) (Tao et al., 2017), Brindisi (15.3%) (Cesari et al., 2014), Hong Kong (19%) (Yau et al., 2013), and the Songyu container terminal of Xiamen Port (13.2–26.1%) (Xu et al., 2018) but higher than those in Busan (7.3%) (Jeong et al., 2017) and Shanghai’s Yangshan Port (2.7%) (Mamoudou et al., 2018), all resolved by using a PMF model. The seasonal variation of this factor was in line with the south and southwest prevailing winds from harbor and shipping channel in spring and summer (Figs. 1, 2, S1, and S7). As expected, shipping emissions were well correlated with V concentration ($r = 0.39–0.43$, $p < 0.001$) and SO$_4^{2-}$ concentration ($r = 0.68–0.74$, $p < 0.001$), and the PSCF analysis and wind rose identified the potential source areas to the south and southwest (Figs. 3(a) and S8(a)). The transport and transformation of SO$_2$ from ocean-going vessels as well as the sea-to-air exchange of dimethyl sulfide might affect the secondary SO$_4^{2-}$ level at the receptor site.

The second factor was distinguished by the high loading of NO$_3^-$, NH$_4^+$, and Cl⁻ with large seasonal variation peaking in spring and winter, which is consistent with the formation of secondary nitrate aerosol (Figs. S5–S7). This is because both NH$_3$NO$_3$ and NH$_4$Cl are unstable in high-temperature conditions. A similar factor has been identified in urban Guangzhou and suburban Zhuhai in PRD, China (Tao et al., 2017). The molar ratio of NO$_3^-$ to NH$_4^+$ was in the range of 0.81–0.89, suggesting the existence of NH$_4$NO$_3$. This factor accounted for 17.3% and 14.7% of the PM$_{2.5}$ mass concentration annually at the urban and suburban sites, respectively. High nitrate was usually observed in spring and winter when the ambient temperature and wind speed were low and the prevailing wind was northeasterly from eastern China and the East China Sea (Figs. 3(b), S7, and S8(b)).

The third factor of fugitive dust was identified by high concentrations of Al, Mg, Ca, Fe, Mn, and Ba, accounting for 16.9% and 23.0% of the PM$_{2.5}$ at the urban and suburban sites, respectively. All these elements are primarily of crustal origin. This factor might be a mixed source of soil dust, road dust, and construction dust. The EF values of these elements were all less than 20, indicative of the dominance of crustal origin. Moreover, the highest contribution of this factor to PM$_{2.5}$ was observed in fall, consistent with high surface wind speed and less precipitation (Figs. 2 and S8(b)). Dry windy conditions favor the emissions from fugitive dust resuspension. The two sites exhibit notable variation in the contribution from this source, probably due to a greater amount of fugitive dust from plowing and construction at the urban site, as well as fewer dust-reducing operations, such as road surface cleaning and spraying water mist in the air, near the suburban site. For fugitive dust, high PSCF values were evident in Bohai Sea, Yellow Sea, and YRD (Fig. 3(c)). Asian dust storm events were observed in Xiamen on May 8, 2017, and April 16, 2018; thus, most fugitive dust was likely from local sources instead of long-range transport. The spatial distribution characteristics of PSCF values and the north-northeasterly winds were relevant because the northeastern monsoon flow usually occurred during fall and winter (Figs. S1 and S8(c)).

The fourth factor, industrial sources, was identified by high loadings of As (44–51%), Se (62–66%), Cd (55–61%), Zn (48–57%), and Pb (51–61%) as well as high quantities of sulfate and OC (Watson et al., 2001; Zhang et al., 2016). The EF values of these trace elements were all greater than 20, indicative of the dominance of anthropogenic origin. The average contribution of industrial sources to PM$_{2.5}$ was relatively low (5.5–7.0%). As can be seen from Figs. 2 and S7, the contributions of this source in fall and winter were higher than in spring and summer, indicating that the sources were mainly inland emissions. In Fig. 3(d), PSCF analysis indicated that eastern China was a main source region, compatible with the spatial distribution of coal.

**Fig. 2.** Seasonal variation of source contribution to PM$_{2.5}$ derived from the PMF model at the two sites in Xiamen (F1, secondary sulfate and ship emissions; F2, secondary nitrate and chlorine; F3, fugitive dust; F4, industrial; F5, primary organic aerosol; F6, traffic emissions and biomass burning). The error bar represents the standard deviation.
Fig. 3. Results of PSCF analysis showing the potential source areas of each source of PM$_{2.5}$ in Xiamen between November 2015 and May 2018. The red solid star represents the location of Xiamen.

combustion, nonferrous metal smelting, iron and steel manufacturing, and construction materials production in China (Cheng et al., 2015; Wang et al., 2016). In addition, the northeastern monsoon winds accompanying this trajectory type could also favor the transport of pollutants along the coastline of mainland China (Fig. S8(d)).

The fifth factor, characterized by a high loading of WIOC (74–81%) but a low loading of EC (15–17%), was identified as primary organic aerosol (POA), including cooking oil fumes, sea spray, and resuspended dust, accounting for 14.1–14.8% of the PM$_{2.5}$ mass concentration. It was found that the OC fraction in cooking oil fumes (74.2%) and sea salt (31.5%) was much higher than that of EC (1.0% and 3.9%, respectively) (Zhang et al., 2016). In addition, increased organic matter content was found in the aged sea-salt aerosol compared with the fresh sea salt (Chi et al., 2015). PSCF analysis identified the potential source regions in eastern China and East China Sea to some extent.
extent (Figs. 3(e) and S8(e)), suggesting that sea salt could be an important contributor of POA in PM$_{2.5}$ at the receptor sites in Xiamen.

The sixth factor, characterized by a high loading of WSOC (48–61%), EC (40.2–65.4%), and K ($43.7–51.3\%$) and a moderate loading of Cu ($20.4–47.1\%$) and Pb ($22.2–26.6\%$), was identified as a mixed source of vehicular traffic emissions and biomass burning, accounting for $23.8–24.6\%$ of PM$_{2.5}$ mass concentration (Cesari et al., 2014; Tao et al., 2017). K$^+$ is known as a typical tracer of biomass burning. Cu is linked to brake wear, and Pb is linked to motor vehicle exhaust emissions although non-leaded gasoline was used in vehicles. The number of motor vehicles reached 1.1 million in 2016 in Xiamen with an annual growth rate of 13.5% over the past ten years (http://www.stats-xm.gov.cn/2017/), indicating that traffic emission will continue to be a major contributor of PM$_{2.5}$. The higher PSCF values mostly fell to the southwest of ambient PM$_{2.5}$ at the two sites in Xiamen.

The estimated primary contributions derived from shipping emissions in this study were comparable to those reported in Yangshan Port in the Port of Shanghai by Zhao et al. (2013), 0.63 to 3.58 µg m$^{-3}$ with an average of 1.96 µg m$^{-3}$ in 2011, but much higher than those reported by Mamoudou et al. (2018), 0.02 to 0.73 µg m$^{-3}$ with an average of 0.10 µg m$^{-3}$ in the same harbor in 2016. The setup of DECAs in YRD region might be the main cause of this downward trend of shipping emissions in Yangshan Port (MAT, 2015). The primary ship contribution to PM$_{2.5}$ in this study was also consistent with the $2.8 \pm 1.1\%$ reported in Brindisi (Cesari et al., 2014) and $2.9 \pm 1.2\%$ in Thessaloniki (Saraga et al., 2019). According to the data summarized in Table 1 (Zhao et al., 2013), the average V content in the international HFO (93 ± 77.9 ppm) was much higher than that in the domestic HFO (56 ± 35.6 ppm), with large standard deviation. If the V content of 93 ppm in the international HFO was used, the average primary PM$_{2.5}$ concentration and fraction from secondary sulfate associated with the primary emissions of shipping HFO combustion will be investigated in the next section.

**Comparison of the V-based Method and the PMF-based Method**

As noted in the introduction, primary PM$_{2.5}$ contributions from shipping HFO combustion can be calculated based on an empirical equation established by Agrawal et al. (2009) using V as a tracer of HFO (V-based method):

$$\text{PM}_a = \langle r \rangle \times V_a <F_{V,HFO}>$$  \hspace{1cm} (4)

where PM$_a$ is primary PM$_{2.5}$ concentration (µg m$^{-3}$) estimated from shipping traffic, $\langle r \rangle$ is the average ratio of PM$_{2.5}$ to the normalized V emitted (in ppm) from HFO burning experiments, $V_a$ is in situ ambient V concentration (µg m$^{-3}$), and $<F_{V,HFO}>$ is average V content (in ppm) of HFO from vessel. In this study, the value of $\langle r \rangle$ used was 8205.8 ppm, as suggested in Agrawal et al. (2009): the value of $<F_{V,HFO}>$ was 65.3 ppm, derived from the average V content in the 25 HFO samples collected from China Marine Bunker by Zhao et al. (2013); and all the measured V in PM$_{2.5}$ was assumed to come from shipping emissions. Fig. 4 shows the seasonal variation of primary PM$_{2.5}$ estimated from shipping emission and its relative contribution to ambient PM$_{2.5}$ at the two sites in Xiamen.

The result indicates that the primary PM$_{2.5}$ concentrations contributed by shipping emissions ranged from 0.11 to 8.7 µg m$^{-3}$ with an average of 1.90 ± 1.54 µg m$^{-3}$, corresponding to a range of 0.3% to 17.5% and an average of 3.9 ± 3.6% of the PM$_{2.5}$ at the urban site. At the suburban site, the shipping emission contribution ranged from 0.04 to 5.5 µg m$^{-3}$ with an average of 1.13 ± 0.13 µg m$^{-3}$, corresponding to a range of 0.3% to 12.9% and an average of 2.5 ± 3.1% of the PM$_{2.5}$. The estimated primary contributions of PM$_{2.5}$ from shipping emissions in this study were lower than those reported by Mamoudou et al. (2018), 0.02 to 0.73 µg m$^{-3}$ with an average of 0.10 µg m$^{-3}$ in the same harbor in 2016. The setup of DECAs in YRD region might be the main cause of this downward trend of shipping emissions in Yangshan Port (MAT, 2015). The primary ship contribution to PM$_{2.5}$ in this study was also consistent with the 2.8 ± 1.1% reported in Brindisi (Cesari et al., 2014) and 2.9 ± 1.2% in Thessaloniki (Saraga et al., 2019). According to the data summarized in Table 1 (Zhao et al., 2013), the average V content in the international HFO (93 ± 77.9 ppm) was much higher than that in the domestic HFO (56 ± 35.6 ppm), with large standard deviation. If the V content of 93 ppm in the international HFO was used, the average primary PM$_{2.5}$ concentration and fraction from secondary sulfate associated with the primary emissions of shipping HFO combustion will be investigated in the next section.

Since the PMF analysis did not separate shipping emissions from secondary sulfate, the primary PM$_{2.5}$ contribution from the V-based method was plotted against the secondary sulfate to investigate the contribution of sulfate associated with the primary shipping emission according to the method in Kim and Hopke (2008) (Fig. 5). This relationship between oil combustion resolved by PMF model and secondary sulfate was also obtained for Seattle (Kim and Hopke, 2008), Gibraltar (Pandolfi et al., 2011), Hong Kong (Yau et al., 2013), Brindisi (Cesari et al., 2014), and Thessaloniki (Saraga et al., 2019) with slopes of 1.21, 1.25, 2, 1.8, and 1.87, respectively. In this study, the plot resulted in an upper edge with a slope of 0.8. This slope is lower than the values reported in the above literatures because the oil combustion contributions derived from PMF contain V-/Ni-bearing particles and other secondary components. The slope of 0.8 means that for every 1 µg m$^{-3}$ of primary shipping emission particles, there was 1.25 µg m$^{-3}$ of secondary sulfate, implying that shipping emissions give a secondary

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Fig. 4. Concentration of primary PM$_{2.5}$ from ship emission and its contribution to the ambient PM$_{2.5}$ at the two sites in Xiamen.
contribution to PM$_{2.5}$ higher than the primary contribution. This relation indicated that, on average, 2.38 µg m$^{-3}$ and 1.42 µg m$^{-3}$ secondary sulfate were estimated to be formed from the primary PM$_{2.5}$ from shipping emissions at the urban and suburban sites, respectively. By adding the associated sulfate contributions to the primary shipping emissions (PM$_{a}$), the estimated total contributions from shipping emissions to ambient PM$_{2.5}$, on average, rise to 4.28 ± 3.46 µg m$^{-3}$ (8.9 ± 8.1%) and 2.55 ± 2.31 µg m$^{-3}$ (5.5 ± 7.0%) at the urban and suburban sites, respectively. Although the V-based method results underestimated the contribution from shipping emission with respect to the values calculated by using a PMF-based method, there existed strong positive correlations between the two methods (r = 0.439–0.459, p < 0.001, 1-tailed) (Fig. S10). Similar results were also reported by Mamoudou et al. (2018) and Cesari et al. (2014). Becagli et al. (2012) used the value of 200 for the characteristic SO$_{4}^{2-}$/V ratio for the HFO combustion aerosols to estimate 1.2 µg m$^{-3}$ (representing ~30%) SO$_{4}^{2-}$ associated with HFO combustion in summer at the island of Lampedusa in the Mediterranean. Taking SO$_{4}^{2-}$/V = 200 as a lower limit for particle mass originating from HFO combustion in Xiamen Port, shipping emissions accounted for, on average, at least 3.01 ± 2.43 µg m$^{-3}$ and 1.79 ± 1.63 µg m$^{-3}$, representing 45 ± 33% and 31 ± 30% of the total SO$_{4}^{2-}$ at the urban and suburban sites, respectively. The contributions of sulfate from shipping emissions based on the characteristic SO$_{4}^{2-}$/V ratio were slightly higher than those based on the correlations between SO$_{4}^{2-}$ and PM$_{a}$. These results suggest that shipping emissions play an important role among the sources of PM$_{2.5}$ in the region of Xiamen Port. Although control measures, such as shore power, have been implemented since 2017 to alleviate shipping emissions while berthing at Xiamen Port, this policy is not compulsory for shipping firms and will not affect the shipping emissions while entering and leaving the port. In view of the rapid growth of container freight and the lack of any requirement for the low-sulfur fuel oil in Xiamen Port, shipping emissions are expected to increase and have a greater impact on local and regional air quality. Therefore, it is important to distinguish the emissions of ships from other sources in the near future to provide scientific support for the health risk assessment, decision-making, and development of environmental protection policies.

**CONCLUSIONS**

Ports are hubs of economic activity, but they also represent a significant source of air pollution; therefore, they are now being targeted by air quality control measures. To identify and characterize the sources of PM$_{2.5}$ in shipping emissions, 138 pairs of PM$_{2.5}$ samples were collected during a 2.5-year (November 2015–May 2018) study at an urban site near the shipping channel of Xiamen Port and at a suburban site farther from the port. The average annual PM$_{2.5}$ concentrations were 55.8 µg m$^{-3}$ and 56.5 µg m$^{-3}$ at the urban and suburban sites, respectively, with the maximum concentrations occurring in spring/winter and the minimum concentrations in summer. Approximately 60% of the daily PM$_{2.5}$ concentrations exceeded the limit specified by the Chinese NAAQS (35 µg m$^{-3}$). Based on the analysis of the air mass back trajectories in combination with that of meteorological factors, the PM$_{2.5}$ concentrations in Xiamen were strongly influenced by variations in the East Asian monsoon. Compared to the suburban site, significantly higher levels of V and Ni were observed at the urban site due to its shorter distance to the shipping channel. However, the V/Ni ratio exhibited no significant difference between the two sites, indicating that shipping emissions were potentially the primary source of V and Ni at both locations.

Source apportionment based on PMF analysis identified secondary sulfate and shipping emissions as a mixed source of PM$_{2.5}$ at the urban and suburban sites, accounting for, on average, 20.9% and 16.6%, respectively, of its ambient concentration. PSCF analysis also traced the potential source area for this factor as the South China Sea when southwesterly and easterly winds prevailed. However, calculations based on the V-based method indicated contributions of 8.9% and 5.5% from shipping emissions (primary PM$_{2.5}$ emissions plus their associated secondary sulfate) at the urban and suburban sites, respectively. Although the magnitude differed, a strong positive correlation existed between the results obtained with these two methods. Thus, the effects of using low-sulfur fuel oil
in shipping and/or shore power can be tracked via long-term monitoring of V in areas surrounding major shipping ports, which will provide a basis for future policies.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aqar.org.

REFERENCES


Wu, S.P., Zhang, Y.J., Schwab, J.J., Huang, S., Wei, Y. and Yuan, C.S. (2016). Biomass burning contributions to urban PM$_{2.5}$ along the coastal lines of southeastern China Citation: Tellus B 68: 30666.


