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 $55.8 \pm 22.7 \mu\text{g m}^{-3}$ and $56.5 \pm 24.5 \mu\text{g m}^{-3}$ 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 SO₂, 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 SO₂ 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

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(Agrawal *et al.*, 2009). Similar downward trends of shipping emission contributions to $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ in port cities is important for taking effective $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ concentrations in port cities. In a recent review (Viana *et al.*, 2014), shipping emissions were estimated to contribute to 1–14% of $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$. Using the linear relation between emission rates of $\text{PM}_{2.5}$ and V in ship fuels established by Agarawal *et al.* (2009), Zhao *et al.* (2013), Cesari *et al.* (2014), and Zhang *et al.* (2014) estimated the contribution of shipping emissions to primary $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ level showed only a slight reduction from $29 \mu\text{g m}^{-3}$ in 2015 to $27 \mu\text{g m}^{-3}$ in 2017, although strict emission control policies, including desulfurization and denitration 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 $\text{PM}_{2.5}$ from fuel oil combustion and the high population density near Xiamen Port, it is necessary to quantify the impacts of this source on $\text{PM}_{2.5}$.

In this study, a 2.5-year $\text{PM}_{2.5}$ 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

contributions and to evaluate the primary and secondary contribution of shipping emissions to $PM_{2.5}$.

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.

during the sampling periods were obtained from the websites of www.aqistudy.cn and <https://rp5.ru>, respectively. No significant difference was found between the PM_{2.5} concentration from our gravimetric analysis of high-volume quartz fiber filters and the real-time PM_{2.5} concentration based on the paired sample *t*-test ($p < 0.001$, $n = 138$). Xiamen's climate is influenced significantly by the East-Asian monsoon system with prevailing northeastern winds in fall and winter and southwestern winds in summer (Fig. S1).

Chemical Analysis

A punch (3.14 cm²) from the quartz filter was extracted in water and analyzed for water-soluble ions of Cl[−], NO₃[−], SO₄^{2−}, 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 SO₄^{2−}. Because the sea-salt sulfate (ssSO₄^{2−}; calculated as $0.25 \times \text{Na}^+$) (Prodi et al., 2009) contributed less than 3% to the total sulfate, the measured sulfate was regarded as non-sea-salt (nssSO₄^{2−}) 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: the 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 $0.57 \pm 0.42 \mu\text{gC m}^{-3}$, $0.08 \pm 0.10 \mu\text{gC m}^{-3}$, and $0.15 \pm 0.22 \mu\text{gC m}^{-3}$ 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[−], SO₄^{2−}, Na⁺, NH₄⁺, and K⁺), 3 carbonaceous species (WSOC, WIOC, and EC), 15 elements (excluding Be and K), and PM_{2.5}, 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 $1/2 \times \text{MDL}$ and the overall uncertainties were set as $5/6 \times \text{MDL}$. 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:

$$\text{Unc} = \sqrt{(\text{Error Fraction} \times C_i)^2 + (0.5 \times \text{MDL})^2} \quad (1)$$

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 PM_{2.5}. 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 (HYSPPLIT4) 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.arl.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:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (2)$$

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):

$$W_{ij} = \begin{cases} 1.00; & n_{ij} > 3n_{ave} \\ 0.70; & 1.5n_{ave} < n_{ij} \leq 3n_{ave} \\ 0.42; & n_{ave} < n_{ij} \leq 1.5n_{ave} \\ 0.17 & n_{ij} \leq n_{ave} \end{cases} \quad (3)$$

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 $55.8 \pm 22.7 \mu\text{g m}^{-3}$ with a range of 12.0 to $113.2 \mu\text{g m}^{-3}$ at the urban site and $56.5 \pm 24.5 \mu\text{g m}^{-3}$ with a range of 9.5 to $105.1 \mu\text{g m}^{-3}$ at the suburban site. The daily $PM_{2.5}$ values at the urban site 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 ($35 \mu\text{g m}^{-3}$) 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 ($51.5 \pm 20.4 \mu\text{g m}^{-3}$; Wu *et al.*, 2015) and urban Guangzhou ($48 \pm 22 \mu\text{g m}^{-3}$; Tao *et al.*, 2017), lower than those in Shanghai ($62.6 \mu\text{g m}^{-3}$; Zhao *et al.*, 2013) and Qinhuangdao ($70.1 \mu\text{g m}^{-3}$; Lang *et al.*, 2017), China, and the port area in Thessaloniki, Greece ($66 \mu\text{g m}^{-3}$; Tolis *et al.*, 2015), but much higher than those in some coastal harbor sites, such as Hong Kong, China ($30.5 \mu\text{g m}^{-3}$; Yai *et al.*, 2013); Marseille, France ($35.5 \mu\text{g m}^{-3}$ during pollution episodes; Salameh *et al.*, 2018); Busan, Korea ($26.1 \pm 15.3 \mu\text{g m}^{-3}$; Jeong *et al.*, 2017); Brindisi, Italy ($15.1 \pm 5.4 \mu\text{g m}^{-3}$; Cesari *et al.*, 2016); Rotterdam, Netherlands ($19.5 \mu\text{g m}^{-3}$; Mooibroek *et al.*, 2011); Bay of Algeciras, Spain ($21.8\text{--}24.2 \mu\text{g m}^{-3}$; Pandolfi *et al.*, 2011); and Los Angeles ($7.0 \mu\text{g m}^{-3}$) and Seattle ($10.6 \mu\text{g m}^{-3}$), 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 $\pm$ standard deviation) and at the urban and suburban sites.

Component ($\mu\text{g m}^{-3}$)	Siming campus of XMU (urban)				Xiangnan campus of XMU (suburban)					
	Spring (n = 22)	Summer (n = 40)	Fall (n = 31)	Winter (n = 47)	Annual (n = 140)	Spring (n = 22)	Summer (n = 40)	Fall (n = 31)	Winter (n = 47)	Annual (n = 140)
PM _{2.5}	61.6 ± 23.4	39.4 ± 17.3	53.7 ± 19.6	62.6 ± 21.2	55.8 ± 22.6	66.0 ± 20.4	38.8 ± 18.6	54.9 ± 19.9	60.9 ± 27.1	56.5 ± 24.5
Cl ⁻	0.61 ± 0.56	0.39 ± 0.22	0.49 ± 0.31	1.0 ± 0.78	0.68 ± 0.61	0.81 ± 0.59	0.4 ± 0.34	0.51 ± 0.5	1.1 ± 1.13	0.77 ± 0.82
NO ₃ ⁻	6.62 ± 6.86	1.35 ± 0.79	2.33 ± 1.56	7.42 ± 5.26	5.09 ± 5.48	5.76 ± 5.42	2.02 ± 2.01	1.90 ± 1.3	6.41 ± 5.7	4.58 ± 4.95
SO ₄ ²⁻	8.83 ± 3.57	7.07 ± 3.68	4.72 ± 1.72	7.19 ± 4.15	7.28 ± 3.80	8.09 ± 4.06	6.47 ± 4.60	4.54 ± 2.0	6.42 ± 3.98	6.64 ± 4.06
Na ⁺	0.68 ± 0.60	0.63 ± 0.27	0.57 ± 0.37	0.47 ± 0.32	0.58 ± 0.42	0.56 ± 0.45	0.71 ± 0.40	0.61 ± 0.3	0.47 ± 0.33	0.58 ± 0.36
NH ₄ ⁺	3.93 ± 2.45	2.35 ± 1.17	1.36 ± 0.64	3.33 ± 2.06	3.0 ± 2.07	3.50 ± 1.66	2.32 ± 1.72	1.59 ± 0.74	3.37 ± 2.45	2.91 ± 2.01
K ⁺	0.37 ± 0.29	0.25 ± 0.14	0.35 ± 0.12	0.42 ± 0.31	0.36 ± 0.26	0.34 ± 0.32	0.23 ± 0.16	0.29 ± 0.10	0.35 ± 0.24	0.31 ± 0.24
Mg ²⁺	0.13 ± 0.08	0.12 ± 0.06	0.17 ± 0.06	0.12 ± 0.05	0.13 ± 0.06	0.13 ± 0.09	0.12 ± 0.06	0.17 ± 0.05	0.13 ± 0.06	0.13 ± 0.07
Ca ²⁺	0.82 ± 0.47	0.79 ± 0.66	1.37 ± 0.70	1.05 ± 1.57	0.97 ± 0.66	1.03 ± 0.73	0.71 ± 0.61	1.45 ± 0.55	0.96 ± 0.73	0.99 ± 0.71
WSOC	3.02 ± 1.50	1.89 ± 0.93	2.42 ± 0.68	3.27 ± 1.57	2.77 ± 1.42	2.94 ± 1.38	1.55 ± 1.04	2.29 ± 0.81	3.31 ± 1.52	2.66 ± 1.45
WIOC	2.87 ± 2.04	1.96 ± 1.11	2.49 ± 1.89	4.56 ± 3.47	3.18 ± 2.66	3.63 ± 2.54	2.13 ± 1.41	2.26 ± 1.26	3.41 ± 1.52	3.02 ± 1.92
OC	5.89 ± 2.67	3.85 ± 1.27	4.90 ± 2.09	7.83 ± 4.05	5.95 ± 3.29	6.57 ± 3.21	3.68 ± 1.62	4.55 ± 1.48	6.72 ± 2.87	5.66 ± 2.88
EC	2.91 ± 1.22	2.22 ± 1.26	1.84 ± 0.99	3.13 ± 1.69	2.67 ± 1.45	2.78 ± 1.37	1.83 ± 1.27	1.46 ± 0.61	2.64 ± 1.59	2.33 ± 1.43
Mg	0.12 ± 0.12	0.20 ± 0.18	0.32 ± 0.21	0.23 ± 0.21	0.21 ± 0.19	0.18 ± 0.17	0.21 ± 0.19	0.33 ± 0.27	0.17 ± 0.12	0.21 ± 0.19
Al	0.44 ± 0.31	0.67 ± 0.73	1.26 ± 0.92	0.83 ± 0.72	0.74 ± 0.71	0.74 ± 0.57	0.68 ± 0.57	1.43 ± 1.11	0.71 ± 0.52	0.82 ± 0.70
K	0.29 ± 0.21	0.24 ± 0.24	0.44 ± 0.22	0.50 ± 0.27	0.37 ± 0.26	0.37 ± 0.27	0.20 ± 0.17	0.48 ± 0.29	0.42 ± 0.25	0.37 ± 0.26
Ca	0.94 ± 0.69	1.19 ± 1.16	3.03 ± 2.09	2.17 ± 1.93	1.72 ± 1.69	1.44 ± 0.95	0.98 ± 0.72	2.29 ± 1.97	1.37 ± 0.92	1.44 ± 1.16
Fe	0.58 ± 0.35	0.69 ± 0.56	1.29 ± 0.86	1.14 ± 0.95	0.90 ± 0.77	0.68 ± 0.51	0.57 ± 0.48	1.14 ± 0.74	0.71 ± 0.47	0.73 ± 0.55
Be [*]	0.04 ± 0.04	0.07 ± 0.14	0.10 ± 0.09	0.07 ± 0.08	0.06 ± 0.09	0.06 ± 0.06	0.07 ± 0.08	0.13 ± 0.11	0.08 ± 0.10	0.08 ± 0.09
V [*]	21 ± 13	18 ± 11	10 ± 14	10 ± 8	15 ± 12	14 ± 10	12 ± 7	6 ± 5	4 ± 2	9 ± 8
Cr [*]	8 ± 7	15 ± 14	13 ± 9	16 ± 16	13 ± 13	9 ± 6	10 ± 13	15 ± 17	11 ± 12	11 ± 12
Mn [*]	21 ± 13	20 ± 18	44 ± 25	44 ± 27	32 ± 24	24 ± 16	14 ± 14	40 ± 25	28 ± 17	25 ± 19
Ni [*]	11 ± 8	14 ± 9	10 ± 7	10 ± 9	11 ± 9	8 ± 5	10 ± 8	11 ± 10	6 ± 6	8 ± 7
Cu [*]	12 ± 8	12 ± 9	21 ± 8	17 ± 9	15 ± 9	10 ± 6	11 ± 7	14 ± 7	13 ± 5	12 ± 6
Zn [*]	156 ± 91	92 ± 61	177 ± 68	191 ± 88	157 ± 89	139 ± 74	68 ± 46	131 ± 74	146 ± 94	124 ± 82
As [*]	1.8 ± 0.9	1.5 ± 1.3	2.4 ± 1.4	2.6 ± 1.3	2.1 ± 1.3	2.0 ± 1.1	1.2 ± 1.0	2.2 ± 1.4	2.4 ± 1.7	2.0 ± 1.4
Se [*]	2.9 ± 1.7	2.0 ± 1.9	3.4 ± 1.9	4.2 ± 2.2	3.2 ± 2.1	3.1 ± 1.6	1.7 ± 1.5	2.8 ± 1.7	3.7 ± 2.2	2.9 ± 2.0
Cd [*]	0.6 ± 0.4	0.5 ± 0.6	1.1 ± 0.7	1.0 ± 0.5	0.8 ± 0.6	0.7 ± 0.5	0.5 ± 0.5	0.9 ± 0.7	0.9 ± 0.5	0.8 ± 0.6
Ba [*]	14 ± 17	15 ± 13	23 ± 13	20 ± 12	18 ± 14	16 ± 21	11 ± 10	20 ± 13	17 ± 11	16 ± 15
Pb [*]	35 ± 24	25 ± 22	36 ± 19	49 ± 28	38 ± 26	38 ± 30	23 ± 23	30 ± 20	42 ± 32	35 ± 29
Cl ⁻ /Na ⁺	1.3 ± 1.4	0.67 ± 0.29	0.95 ± 0.56	3.16 ± 4.11	1.74 ± 2.72	1.98 ± 1.49	0.68 ± 0.72	0.87 ± 0.54	3.64 ± 4.59	2.09 ± 3.06
NO ₃ ⁻ /SO ₄ ²⁻	0.73 ± 0.63	0.22 ± 0.14	0.53 ± 0.35	1.07 ± 0.63	0.70 ± 0.61	0.77 ± 0.67	0.48 ± 0.39	0.50 ± 0.32	0.96 ± 0.59	0.73 ± 0.70
OC/EC	2.12 ± 0.81	2.31 ± 1.31	3.31 ± 1.95	2.79 ± 1.03	2.56 ± 1.27	2.57 ± 1.08	2.64 ± 1.37	3.40 ± 0.98	3.00 ± 1.04	2.85 ± 1.15
WSOC/EC	1.07 ± 0.44	1.02 ± 0.54	1.93 ± 0.88	1.19 ± 0.18	1.22 ± 0.90	1.14 ± 0.46	0.99 ± 0.62	1.76 ± 0.73	1.49 ± 0.61	1.32 ± 0.65
WSOC/TC	0.35 ± 0.11	0.31 ± 0.10	0.40 ± 0.16	0.32 ± 0.11	0.34 ± 0.12	0.33 ± 0.11	0.29 ± 0.13	0.40 ± 0.13	0.36 ± 0.07	0.34 ± 0.11
V/Ni	2.5 ± 0.66	1.64 ± 1.06	1.08 ± 0.74	1.32 ± 0.75	1.57 ± 0.87	1.72 ± 0.68	1.95 ± 1.49	1.08 ± 1.14	1.01 ± 0.63	1.44 ± 1.04
Concentration in the units of ng m ⁻³ .										

* Concentration in the units of ng 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 SO₂ and NO₂ 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 SO₄²⁻, NO₃⁻, WIOC, NH₄⁺, WSOC, and EC, which contributed more than 40% of the total mass on annual average. For the water-soluble ions, significant differences between urban and suburban sites were only observed for K⁺ ($p = 0.001$) and SO₄²⁻ ($p = 0.015$) 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 NO₃⁻ to SO₄²⁻ (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 1). Similar seasonal variations have also been reported in Chinese cities such as Qinhuaogdao (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 NO₃⁻ 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 ; $r = -0.366$ and -0.42 for NO₃⁻ vs. T ; $p < 0.001$), quite likely due to the loss of NH₄NO₃ 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 Qinhuaogdao (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 NH₄⁺ and Cl⁻ was lower than that between NH₄⁺ and NO₃⁻ or SO₄²⁻ (Table S2), suggesting that most of NH₄⁺ was likely in the form of NH₄NO₃, (NH₄)₂SO₄, or NH₄HSO₄ rather than NH₄Cl. In addition, Cl⁻ showed a positive correlation with Na⁺ ($r = 0.239$, $p = 0.002$) and Mg²⁺ ($r = 0.191$, $p = 0.012$) 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 Mg²⁺ and Ca²⁺, which could indicate a crustal source. The much higher levels of Mg²⁺ and Ca²⁺ 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 $16 \pm 6\%$ and $15 \pm 5\%$ 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 WSOC/EC ratios in fall can be used as indicators for aged aerosol.

For crustal elements in PM_{2.5}, Ca was the most abundant element ($> 1.4 \mu\text{g m}^{-3}$), followed by Fe, Al, K, and Mg

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

t-test pair ^a	t_s^b	Sig. level	t-test pair	t_s	Sig. level
EC	3.700	< 0.001	Fe	2.533	0.012
V	7.559	< 0.001	Ca	2.052	0.042
Ni	3.806	< 0.001	SO ₄ ²⁻	2.474	0.015
Cu	5.149	< 0.001	OC/EC	-3.291	0.001
Zn	4.015	< 0.001	Fe/Mn	-2.103	0.037
K ⁺	3.441	0.001	V/EC	3.963	< 0.001
Mn	3.187	0.002	V/SO ₄ ²⁻	4.398	< 0.001

^a Paired difference of urban minus suburban;

^b t -test statistics is calculated according to $t_s = \bar{D} \times \sqrt{n}/S_D$, where $\bar{D}$ 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 .

(0.2–0.9 $\mu\text{g m}^{-3}$) 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 $\text{PM}_{2.5}$ ($> 100 \text{ ng m}^{-3}$), followed by Mn, Pb, Ba, and Cu ($10\text{--}50 \text{ ng m}^{-3}$) and then As, Se, and Cd ($1\text{--}5 \text{ ng m}^{-3}$). Be was at even lower concentrations ($< 0.1 \text{ ng m}^{-3}$). 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 that resuspended dust correlated more with vehicles at the urban site. The average concentrations of V and Ni, which are good marker elements for oil-fired power plants and oil combustion, were $15 \pm 12 \text{ ng m}^{-3}$ and $11 \pm 9 \text{ ng m}^{-3}$, respectively, at the urban site and were $9 \pm 8 \text{ ng m}^{-3}$ and $8 \pm 7 \text{ ng m}^{-3}$, respectively, at the suburban site. These average values were comparable with those measured in coastal cities such as Guangzhou, Busan, and Genoa; higher than those in Changhua, Seattle, Toronto, Brindisi, the New York–New Jersey Harbor Estuary, Shanghai’s Yangshan Port in 2016, and Tuoji Island in Baohai Sea; and much lower than those in Shanghai’s Yangshan Port in 2011 and the Strait of Gibraltar (Table S5).

The tracer ratio V/Ni has been recommended for the identification of shipping traffic $\text{PM}_{2.5}$ in port areas without significant amounts of land-based oil combustion (Agrawal *et al.*, 2008; Viana *et al.*, 2009; Zhao *et al.*, 2013; Tao *et al.*, 2017; Wen *et al.*, 2018). In this study, strong positive correlations were obtained between V and Ni at both sites ($p < 0.001$), and the V/Ni ratio as well as their concentrations at the urban site exhibited high values in spring and summer with respect to those in fall and winter (Table 1). According to the economic statistics of Xiamen (<http://www.stats-xm.gov.cn/>), the port’s cargo and container throughput showed no significant seasonal

variations. In addition, the seasonal patterns of V and Ni were different from those of other trace heavy metals, such as Mn, Cu, Zn, and Pb, with higher values in fall with respect to those in spring (Table 1). Consequently, we interpret the seasonal variation as due to the enhanced west and southwest winds from harbor sector in spring and summer carrying more shipping emission to the sampling sites (Fig. S1). As illustrated in Table S5, the seasonal patterns of V and Ni in different location were different due to the changing wind direction. V/Ni ratios in HFO and PM from ship engine using HFO in literatures were summarized in Table S6. The wide range of V/Ni in HFO could complicate the source identification of shipping traffic $\text{PM}_{2.5}$. Therefore, the V/Ni ratio obtained in $\text{PM}_{2.5}$ from the port area cannot be used in a straightforward way to compare with the reported values in HFO in other areas. Note that neither V nor Ni has significant correlation with Pb (Table S4), which has been interpreted as a tracer of traffic emissions rather than shipping (Tao *et al.*, 2017; He *et al.*, 2008). Nevertheless, there was no significant difference for the ratio V/Ni between the two sites ($p = 0.18$), indicating 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 $(X/\text{Al})_{\text{aerosol}}/(X/\text{Al})_{\text{soil}}$, where $(X/\text{Al})_{\text{aerosol}}$ is the concentration ratio of element X to Al in aerosol, and $(X/\text{Al})_{\text{soil}}$ 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 $\text{PM}_{2.5}$ 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, V, Cr, Se, Ni, Cu, and Pb were moderately enriched ($\text{EF} < 100$), while Zn and Cd ($\text{EF} > 100$) 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 $\text{PM}_{2.5}$

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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ (Fig. S8). The $\text{PM}_{2.5}$ mass concentration was reconstructed according to the sum of the six factors.

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.

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 SO₄²⁻ 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 ($r = 0.39\text{--}0.43$, $p < 0.001$) and SO₄²⁻ concentration ($r = 0.68\text{--}0.74$, $p < 0.001$), and the PSCF analysis and wind rose identified the potential source areas to the south and southeast (Figs. 3(a) and S8(a)). The transport and transformation of SO₂ from ocean-going vessels as well as the sea-to-air exchange of dimethyl sulfide might affect the secondary SO₄²⁻ level at the receptor site.

The second factor was distinguished by the high loading of NO₃⁻, NH₄⁺, 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 NH₄NO₃ and NH₄Cl 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 NO₃⁻ to NH₄⁺ was in the range of 0.81–0.89, suggesting the existence of NH₄NO₃. 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. S1, S2, S7, and S8(c)). 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. 3. Results of PSCF analysis showing the potential source areas of each source of $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 (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 Xiamen, suggesting local vehicle emissions (Fig. 3(f)). Overall, the six identified sources contributed $96 \pm 21\%$ and $95 \pm 23\%$ to the ambient PM_{2.5} at the urban and suburban sites, respectively. The measured PM_{2.5} concentration and the reconstructed PM_{2.5} concentration derived from the PMF model exhibited extremely strong positive correlations at both sites ($r = 0.86$, $p < 0.001$) (Fig. S9). However, the PMF analysis did not separate shipping emissions from secondary sulfate. The contribution to 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):

$$PM_a = \langle r \rangle \times V_a / \langle F_{V,HFO} \rangle \quad (4)$$

where PM_a is primary PM_{2.5} concentration ($\mu\text{g m}^{-3}$) estimated from shipping traffic, $\langle r \rangle$ is the average ratio of PM_{2.5} to the normalized V emitted (in ppm) according to HFO burning experiments, V_a is in situ ambient V concentration ($\mu\text{g m}^{-3}$), and $\langle F_{V,HFO} \rangle$ 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 $\langle F_{V,HFO} \rangle$ 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 primary PM_{2.5} concentrations contributed by shipping emissions ranged from 0.11 to $8.7 \mu\text{g m}^{-3}$ with an average of $1.90 \pm 1.54 \mu\text{g m}^{-3}$, corresponding to a range of 0.3% to 17.5% and an average of $3.9 \pm 3.6\%$ of the PM_{2.5} at the urban site. At the suburban site, the shipping emission contribution ranged from

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.

0.04 to $5.5 \mu\text{g m}^{-3}$ with an average of $1.13 \pm 1.03 \mu\text{g m}^{-3}$, corresponding to a range of 0.3% to 12.9% and an average of $2.5 \pm 3.1\%$ of the PM_{2.5}. The estimated primary contributions of PM_{2.5} 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 $3.58 \mu\text{g m}^{-3}$ with an average of $1.96 \mu\text{g m}^{-3}$ in 2011, but much higher than those reported by Mamoudou *et al.* (2018), 0.02 to $0.73 \mu\text{g m}^{-3}$ with an average of $0.10 \mu\text{g m}^{-3}$ 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 (MOT, 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 shipping traffic would be $1.33 \mu\text{g m}^{-3}$ and 2.8% at the urban site and $0.79 \mu\text{g m}^{-3}$ and 1.7% at the suburban site, respectively.

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 *et al.*, 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 $1 \mu\text{g m}^{-3}$ of primary shipping emission particles, there was $1.25 \mu\text{g m}^{-3}$ of secondary sulfate, implying that shipping emissions give a secondary

Fig. 5. Primary $\text{PM}_{2.5}$ contribution from V-based method plotted against the secondary sulfate concentrations at the urban and suburban sites in Xiamen.

contribution to $\text{PM}_{2.5}$ higher than the primary contribution. This relation indicated that, on average, $2.38 \mu\text{g m}^{-3}$ and $1.42 \mu\text{g m}^{-3}$ secondary sulfate were estimated to be formed from the primary $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$, on average, rise to $4.28 \pm 3.46 \mu\text{g m}^{-3}$ ($8.9 \pm 8.1\%$) and $2.55 \pm 2.31 \mu\text{g m}^{-3}$ ($5.5 \pm 7.0\%$) 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 ($r = 0.439\text{--}0.459$, $p < 0.001$, 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 $\text{SO}_4^{2-}/\text{V}$ ratio for the HFO combustion aerosols to estimate $1.2 \mu\text{g m}^{-3}$ (representing $\sim 30\%$) SO_4^{2-} associated with HFO combustion in summer at the island of Lampedusa in the Mediterranean. Taking $\text{SO}_4^{2-}/\text{V} = 200$ as a lower limit for particle mass originating from HFO combustion in Xiamen Port, shipping emissions accounted for, on average, at least $3.01 \pm 2.43 \mu\text{g m}^{-3}$ and $1.79 \pm 1.63 \mu\text{g m}^{-3}$, representing $45 \pm 33\%$ and $31 \pm 30\%$ of the total SO_4^{2-} at the urban and suburban sites, respectively. The contributions of sulfate from shipping emissions based on the characteristic $\text{SO}_4^{2-}/\text{V}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ in shipping emissions, 138 pairs of $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ concentrations were $55.8 \mu\text{g m}^{-3}$ and $56.5 \mu\text{g m}^{-3}$ 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 $\text{PM}_{2.5}$ concentrations exceeded the limit specified by the Chinese NAAQS ($35 \mu\text{g m}^{-3}$). Based on the analysis of the air mass back trajectories in combination with that of meteorological factors, the $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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.aaqr.org>.

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