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Source apportionment of $PM_{2.5}$ at urban and suburban areas of the Pearl River Delta region, south China - With emphasis on ship emissions

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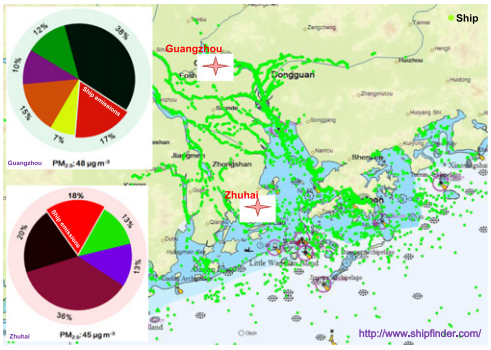
HIGHLIGHTS

- Elevated ship emission tracer elements (Ni and V) were found in PRD.
- Contributions of ship emissions to $PM_{2.5}$ were significant and were quantified.
- Interregional and intraregional transport of pollutants are both important sources.

GRAPHICAL ABSTRACT



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ABSTRACT

Daily $PM_{2.5}$ samples were collected at an urban site in Guangzhou in 2014 and at a suburban site in Zhuhai in 2014–2015. Samples were subject to chemical analysis for various chemical components including organic carbon (OC), element carbon (EC), major water-soluble inorganic ions, and trace elements. The annual average $PM_{2.5}$ mass concentration was 48 ± 22 μg $m^{-3}$and 45 ± 25 μg m^{-3} in Guangzhou and Zhuhai, respectively, with the highest seasonal average concentration in winter and the lowest in summer at both sites. Regional transport of pollutants accompanied with different air mass origins arriving at the two sites and pollution sources in between the two cities caused larger seasonal variations in Zhuhai (>a factor of 3.5) than in Guangzhou (<a factor of 2.0). Positive matrix factorization (PMF) analysis identified six and five major source factors for $PM_{2.5}$ in Guangzhou and Zhuhai, respectively. Ship emissions, a source factor previously ignored in making emission control policies in the Pearl River Delta region of south China, were among the top contributors to $PM_{2.5}$ at both sites, accounting for >17% of $PM_{2.5}$ mass concentrations.

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1. Introduction

The impact of fine particulate matter ($PM_{2.5}$) on human health, climate and visibility not only depends on its concentration level but also on its chemical composition (Li et al., 2011; Pui et al., 2014; Watson, 2002). $PM_{2.5}$ is known to compose of water-soluble inorganic salts, organic matter, element carbon and mineral dust, trace element oxide, and water, but the relative contributions of these chemical components depend on source origins and many other factors (Turpin and Lim, 2001). In urban areas, $PM_{2.5}$ is mainly produced from anthropogenic sources including both primary and secondary particles, the latter group is formed from chemical conversion of gaseous precursor pollutants (Zhang et al., 2015a). Source-apportionment analysis worldwide frequently revealed major source factors for urban $PM_{2.5}$, which were categorized into secondary inorganic and organic aerosols, coal combustion, industrial emission, traffic emission, biomass burning, and soil dust (Almeida et al., 2005; Amato and Hopke, 2012; Heo et al., 2009).

Severe $PM_{2.5}$ pollution in China, especially in the northern regions, has spurred extensive studies on $PM_{2.5}$ composition and source apportionment in the most recent decade (He et al., 2011; Huang et al., 2014; Tao et al., 2014a; Wang et al., 2014; Zhang et al., 2013). Results from these earlier studies have provided solid scientific evidences for making emission control policies. However, for the Pearl River Delta (PRD) region, one source region for $PM_{2.5}$ – ship emissions, seemed to have been neglected in the source-apportionment studies (He et al., 2011; Yau et al., 2013). The three biggest ports in PRD (Hong Kong, Shenzhen and Guangzhou) are among the top-ten list of the world's largest ports. The number of ships arrival at and departure from ports in PRD (not including the Hong Kong port) reached about 1.5 million in 2010. The duration between arrival and departure was larger than 30 h for most of cargo ships (Ye, 2014). Ship emissions ranked the third and fourth largest contributor of the total SO_2 and NOx emissions, respectively, in PRD during 2000–2009, and there is an increasing trend in ship emissions in this region (Lu et al., 2013). In Hong Kong, ship emission contributed 11%, 17% and 16% of the total SO_2, NOx and PM_{10} emissions, respectively (Yau et al., 2012).

Strict emission control policies, such as desulfurization and dedusting for coal combustion boilers initiated in 2005, denitration for all power plants finished in 2013, and the state IV standard for vehicle emission started in 2010, have improved local air quality significantly. As a result, the $PM_{2.5}$ level in PRD has mostly met the National Ambient Air Quality Standards (NAAQS) (annual average: 35 μg m^{-3}) since 2015 (http://www.gdep.gov.cn/). However, annual $PM_{2.5}$ in PRD was still two to three times higher than the World Health Organization (WHO) Air Quality Guidelines (annual average: 10 μg m^{-3}). Considering the significant contributions of ship emissions to the total SO_2 and NOx emissions in PRD, it is necessary to quantify the contributions of this source origin to $PM_{2.5}$. To fill this knowledge gap, chemically-resolved $PM_{2.5}$ data were collected at an urban site in Guangzhou and a suburban site in Zhuhai during 2014 and 2015 for subsequent source-apportionment analysis. The two cities have a population of 8.4 and 1.6 million, respectively. They are situated next to the Tropic of Cancer zone and impacted by both tropical and subtropical air masses (Domrös and Peng, 1988). Interregional and intraregional pollutant transports are both important contributors to the observed PM pollution in these cities (Cheng et al., 2013).

In this study, $PM_{2.5}$ and its major chemical components were first briefly characterized (Section 3.1), followed by discussions on ship emission tracer elements (Section 3.2). Source factors contributing to $PM_{2.5}$ were quantified using PMF model (Section 3.3). Implications of the results for future research and policy activities are then provided (Section 3.4).

2. Methodology

2.1. Site description

Two monitoring sites were selected in this study, one urban site in Guangzhou situated inside the South China Institute of Environmental

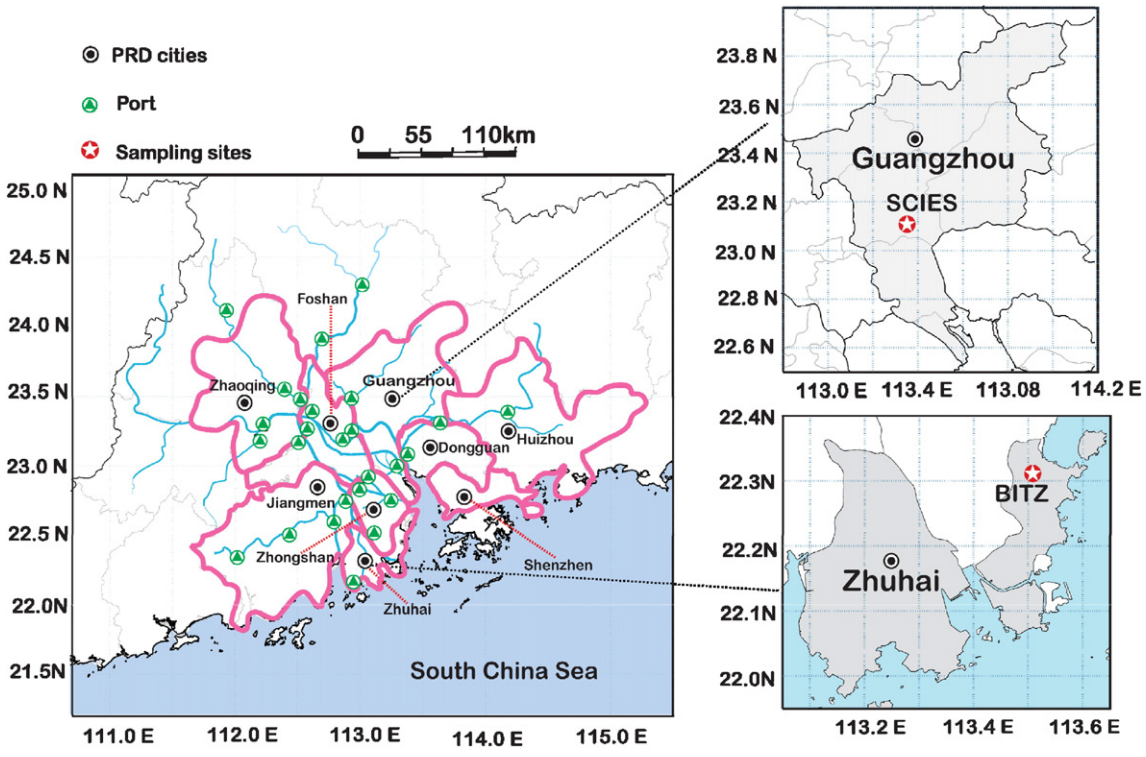

Fig. 1. The sampling locations in urban Guangzhou and suburban Zhuhai in PRD.

Science (SCIES) (23°07′N, 113°21′E) and another suburban site in Zhuhai situated inside the Beijing Institute of Technology, Zhuhai (BITZ) (22°22′N, 113°32′E) (Fig. 1). There is no obvious industrial activity in the vicinity of the two monitoring stations. The instruments used in this study were installed on the roof of a building 50 m above ground in the SCIES and 18 m above ground in the BITZ.

2.2. Sampling

$PM_{2.5}$ samples in urban Guangzhou were collected using two Gravisol Sequential Ambient Particulate Monitor (APM Inc., Korea) at a flow rate of 16.7 L min^{-1}, and in suburban Zhuhai using two low-flow air samplers (MiniVol TAC, AirMetrics Corp., Eugene, OR, USA) at a flow rate of 5.0 L min^{-1}. Samples were collected on two types of filters: 47 mm quartz fiber filter (Whatman QM-A) and 47 mm Teflon filter (Whatman PTFE). Sampling duration was 24 h, starting at 10:00 local time each day and ending at 10:00 local time the following day. A total of 119 sets of daily $PM_{2.5}$ samples (one in every three days) and 12 sets of blank samples were collected in Guangzhou during four seasons: March–May 2014 (spring), June–August 2014 (summer), September–November 2014 (autumn), and January, February and December 2014 (representative of winter). A total of 124 daily $PM_{2.5}$ samples and 11 sets blank samples were collected in Zhuhai during the four seasons: 1–30 April 2014 (spring), 20 June–21 July 2014 (summer), 8 October–8 November 2014 (autumn), and 24 December 2014–24 January 2015 (winter). Field blanks were used to account for any artifacts caused by gas absorption and background filters. The aerosol-loaded filter samples were stored in a freezer at −18 °C before analysis to prevent volatilization of particles. Teflon filters were measured gravimetrically for calculating $PM_{2.5}$ mass concentration.

2.3. Chemical analysis

Twenty-one elements including Si, S, K, Ca, Fe, Zn, Na, Al, Cl, Ti, V, Cr, Mn, Cu, Sb, Ba, Pb, Mg, Co, Ni and Rb were quantified using an energy-dispersive X-ray fluorescence analysis (ED-XRF, Epsilon5, PANalytical Company, Netherlands) on Teflon filters. Quality assurance and control (QA/QC) of ED-XRF measurement was guaranteed by the analysis of a certified standard, Standard Reference Material® 2783 (Air Particulate on Filter Media) of National Institute of Standards & Technology. The certified standards of elements include Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Ti, V and Zn. Moreover, the reference standards of elements include Ce, Rb, S, Sc, Si, Sm, Th, U and W. The analysis uncertainties were <10% for Si, S, K, Ca, Fe and Zn, 10–20% for Na, Al, Cl, Ti, V, Cr, Mn, Cu, Sb, Ba and Pb, and 20–30% for Mg, Co, Ni and Rb. Average field blanks were subtracted from each sample filter. Generally, method detection limits (MDL) of elements were within the range of 0.002 to 0.116 μg cm^{-2}.

After elements analysis, Teflon filter samples were used to determine water-soluble inorganic ions. The extraction of water-soluble species from each filter were put into a separate 4 mL bottles, followed by 4 mL distilled-deionized water (with a resistivity of >18 MΩ), and then subjected to ultrasonic agitation for 1 h for complete extraction of the ionic compounds. The extract solutions were filtered (0.25 μm, PTFE, Whatman, USA) and stored at 4 °C in pre-cleaned tubes until analysis. Cation (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) concentrations were determined by ion chromatography (Dionex ICS-1600) using a CS12A column with 20 mM Methanesulfonic Acid eluent. Anions (SO_4^{2-}, NO_3^-, Cl^-, and F^-) were separated on an AS19 column in ion chromatography (Dionex ICS-2100), using 20 mM KOH as the eluent. A calibration was performed for each analytical sequence. Procedural blank values were subtracted from sample concentrations. MDL of ions were within the range of 0.001 to 0.002 mg L^{-1}.

OC and EC were analyzed using a DRI model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA, USA). An area of 0.526 cm^2 punched from each quartz filter was analyzed for four OC fractions (OC1, OC2, OC3, and OC4 at 140 °C, 280 °C, 480 °C, and 580 °C, respectively, in a helium [He] atmosphere); OP (a pyrolyzed carbon fraction determined when transmitted laser light attained its original intensity after oxygen [O_2] was added to the analysis atmosphere); and three EC fractions (EC1, EC2, and EC3 at 580 °C, 740 °C, and 840 °C, respectively, in a 2% O_2/98% He atmosphere). IMPROVE_TOR OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as EC1 + EC2 + EC3-OP. Average field blanks were subtracted from each sample filter. MDLs of OC and EC were 0.41 ± 0.2 μgC cm^{-2} and 0.03 ± 0.2 μgC cm^{-2}, respectively.

2.4. Data analysis

To evaluate if the determined chemical components represent the measured $PM_{2.5}$, the measured $PM_{2.5}$ mass was reconstructed based on $(NH_4)_2SO_4$, NH_4NO_3, OM, EC and fine soil (FS) (Pitchford et al., 2007). The converting factor between OC and OM was 1.6 according to the previous studies in PRD (Cao et al., 2004; Lai et al., 2016).

The reconstructed $PM_{2.5}$ mass was calculated according to:

$$[PM_{2.5}] = [(NH_4)_2SO_4] + [NH_4NO_3] + [OM] + [EC] + [FS] \quad (1)$$

The FS component is often estimated through the following formula (Malm et al., 1994):

$$[FS] = 2.20[Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti] \quad (2)$$

Good correlations ($R^2 > 0.93$) were found between the reconstructed and measured $PM_{2.5}$ mass concentrations at both sites. The reconstructed $PM_{2.5}$ explained 74 ± 7% and 76 ± 5% of the measured $PM_{2.5}$ in Guangzhou and Zhuhai, respectively, suggesting that about 25% of the measured $PM_{2.5}$ mass was unidentified, which may include water, non-combustion organic matter and trace elements oxides. Despite the missing portion of $PM_{2.5}$, the identified chemical compositions are believed to represent the general characteristics of $PM_{2.5}$ at both sites. Based on the reconstructed chemical components, $(NH_4)_2SO_4$, NH_4NO_3, OM, EC and FS accounted for 26 ± 9%, 5 ± 5%, 28 ± 4%, 9 ± 2% and 7 ± 2%, respectively, of $PM_{2.5}$ on annual average in Guangzhou, and 23 ± 10%, 6 ± 5%, 36 ± 8%, 6 ± 2% and 6 ± 3%, respectively, in Zhuhai. Trace elements only accounted for <1%.

Source apportionment analysis of $PM_{2.5}$ was conducted using the U.S. Environmental Protection Agency PMF model version 5.0. For organic carbon, element carbon, water-soluble inorganic ions and trace elements detected in the blanks and samples, the uncertainty was calculated from the square root of the sum of the squares of the standard deviation of the blanks and analytical uncertainty. The analytical uncertainty for each compound was calculated as the measured values multiply the relative uncertainty of the compound in the replicate measurements of the standard reference materials.

Considering the similar chemical compositions, for example Na^+ and Na, Ca^{2+} and Ca, K^+ and K, etc., only one of them was chosen for PMF analysis. Moreover, some of the water-soluble inorganic ions and trace elements having concentrations below or close to the detection limit were ignored in the input data of PMF model. As a result, OC, EC, Na^+, NH_4^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sb, Ba and Pb were selected for PMF analysis using database at both sites. The above chemical compositions were categorized as "strong" if the S/N ratio is larger than 2.0, "good" if between 1.0 and 2.0, and "weak" if between 0.5 and 1.0.

To investigate the air mass origins of the air pollutants arriving at PRD, 48 h backward trajectories (including 2:00, 8:00, 14:00, and 20:00) were calculated at an elevation of 50 m for every day in 2014 at the Guangzhou urban site and during April 2014–January 2015 at the Zhuhai suburban site using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) 4 model (http://ready.arl.noaa.gov/HYSPLIT.php). The meteorological inputs to HYSPLIT model were from the Global Data Assimilation System (GDAS) at a resolution of 1° × 1° (ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1).

Table 1
Statistics of $PM_{2.5}$ mass concentrations and chemical constituents in urban Guangzhou and suburban Zhuhai.

	Guangzhou (urban)					Zhuhai (suburban)				
	Annual (n = 119)	Spring (n = 31)	Summer (n = 29)	Autumn (n = 31)	Winter (n = 28)	Annual (n = 124)	Spring (n = 30)	Summer (n = 32)	Autumn (n = 31)	Winter (n = 31)
$PM_{2.5}$/μg m^{-3}	48 ± 22	44 ± 18	37 ± 16	48 ± 17	63 ± 28	45 ± 25	35 ± 10	19 ± 10	56 ± 18	71 ± 19
OC/μgC m^{-3}	8.2 ± 4.1	7.5 ± 3.3	6.1 ± 2.2	7.9 ± 3.0	11.6 ± 5.5	9.4 ± 4.6	7.4 ± 2.0	5.1 ± 2.0	10.3 ± 2.8	14.7 ± 4.1
EC/μgC m^{-3}	4.0 ± 1.9	4.2 ± 1.9	3.5 ± 1.4	3.6 ± 1.3	5.0 ± 2.5	2.6 ± 1.6	2.2 ± 0.9	1.1 ± 0.8	3.1 ± 1.2	4.2 ± 1.4
Na^+/μg m^{-3}	0.4 ± 0.2	0.4 ± 0.2	0.4 ± 0.1	0.3 ± 0.2	0.3 ± 0.2	0.3 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.3 ± 0.2	0.4 ± 0.2
NH_4^+/μg m^{-3}	3.8 ± 2.5	3.6 ± 2.2	2.6 ± 2.4	4.4 ± 2.1	4.8 ± 2.7	3.6 ± 2.5	3.2 ± 1.3	0.8 ± 1.1	5.1 ± 2.2	5.5 ± 1.8
K^+/μg m^{-3}	0.7 ± 0.5	0.6 ± 0.3	0.5 ± 0.3	0.6 ± 0.3	1.0 ± 0.7	0.4 ± 0.4	0.2 ± 0.1	0.1 ± 0.2	0.6 ± 0.3	0.8 ± 0.4
Ca^{2+}/μg m^{-3}	0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.0	0.1 ± 0.1	0.3 ± 0.2	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.1	0.2 ± 0.2
Cl^-/μg m^{-3}	0.2 ± 0.6	0.3 ± 0.8	0.0 ± 0.0	0.1 ± 0.1	0.5 ± 0.7	0.3 ± 0.4	0.2 ± 0.3	0.1 ± 0.1	0.2 ± 0.4	0.6 ± 0.5
NO_3^-/μg m^{-3}	2.2 ± 3.1	2.4 ± 2.4	0.3 ± 0.2	1.0 ± 1.3	5.5 ± 4.0	2.7 ± 3.1	2.1 ± 2.1	0.3 ± 0.2	2.4 ± 2.4	6.1 ± 3.1
SO_4^{2-}/μg m^{-3}	9.3 ± 5.4	8.2 ± 4.7	7.6 ± 6.5	11.4 ± 5.3	9.8 ± 4.5	8.1 ± 5.6	7.0 ± 2.4	2.1 ± 2.7	12.6 ± 5.8	10.6 ± 3.6
Al/ng m^{-3}	305 ± 190	253 ± 150	276 ± 178	265 ± 114	436 ± 248	309 ± 179	223 ± 87	256 ± 144	349 ± 181	405 ± 220
Si/ng m^{-3}	543 ± 327	461 ± 212	498 ± 223	469 ± 198	763 ± 565	342 ± 205	226 ± 88	202 ± 114	417 ± 163	525 ± 223
Fe/ng m^{-3}	353 ± 174	339 ± 131	331 ± 140	326 ± 135	423 ± 258	212 ± 132	158 ± 68	100 ± 53	262 ± 128	330 ± 120
Ca/ng m^{-3}	195 ± 140	176 ± 72	160 ± 56	157 ± 65	296 ± 241	122 ± 78	87 ± 27	77 ± 28	143 ± 61	179 ± 110
Ti/ng m^{-3}	24 ± 13	24 ± 10	25 ± 12	21 ± 10	28 ± 19	18 ± 12	13 ± 8	10 ± 6	21 ± 11	27 ± 13
V/ng m^{-3}	9 ± 6	11 ± 8	11 ± 4	7 ± 5	8 ± 6	12 ± 10	22 ± 10	5 ± 5	11 ± 9	10 ± 9
Cr/ng m^{-3}	9 ± 6	9 ± 5	9 ± 5	8 ± 5	11 ± 9	6 ± 3	4 ± 3	4 ± 3	7 ± 3	7 ± 3
Mn/ng m^{-3}	34 ± 17	34 ± 13	34 ± 15	31 ± 13	37 ± 24	28 ± 16	22 ± 12	17 ± 10	31 ± 16	42 ± 13
Ni/ng m^{-3}	4 ± 2	5 ± 2	5 ± 2	4 ± 2	4 ± 3	7 ± 3	9 ± 3	5 ± 2	7 ± 3	7 ± 4
Cu/ng m^{-3}	37 ± 29	30 ± 22	33 ± 20	37 ± 20	50 ± 44	20 ± 17	11 ± 10	7 ± 6	28 ± 18	36 ± 12
Zn/ng m^{-3}	225 ± 124	207 ± 86	214 ± 138	228 ± 75	253 ± 177	149 ± 122	96 ± 69	42 ± 50	199 ± 106	263 ± 106
Sb/ng m^{-3}	20 ± 9	17 ± 5	17 ± 5	21 ± 5	27 ± 15	22 ± 15	22 ± 15	19 ± 16	23 ± 14	22 ± 15
Ba/ng m^{-3}	46 ± 22	43 ± 17	44 ± 9	40 ± 11	60 ± 37	48 ± 28	42 ± 24	41 ± 22	56 ± 30	54 ± 34
Pb/ng m^{-3}	77 ± 47	62 ± 22	55 ± 32	78 ± 31	113 ± 71	59 ± 46	41 ± 22	20 ± 14	75 ± 42	102 ± 44

3. Results and discussion

3.1. Overview of $PM_{2.5}$ and its major chemical components

Annual average $PM_{2.5}$ mass concentration was 48 ± 22 μg m^{-3} and 45 ± 25 μg m^{-3}, respectively, in urban Guangzhou and suburban Zhuhai (Table 1), which was about 30% higher than the NAAQS for annual $PM_{2.5}$ (35 μg m^{-3}). A similar seasonal pattern was seen at the two sites with the highest seasonal average concentration in winter and the lowest in summer. However, the magnitude of the seasonal variations was different, e.g., <2.0 in Guangzhou, but larger than 3.5 in Zhuhai. Thus, while with similar annual average at the two sites, $PM_{2.5}$ was 26% lower in spring, 95% lower in summer, but 11–14% higher in autumn and winter at the suburban than at the urban site. Since the PRD region is in a transitional climate region presenting characteristics of both tropical and subtropical air masses, significant differences of

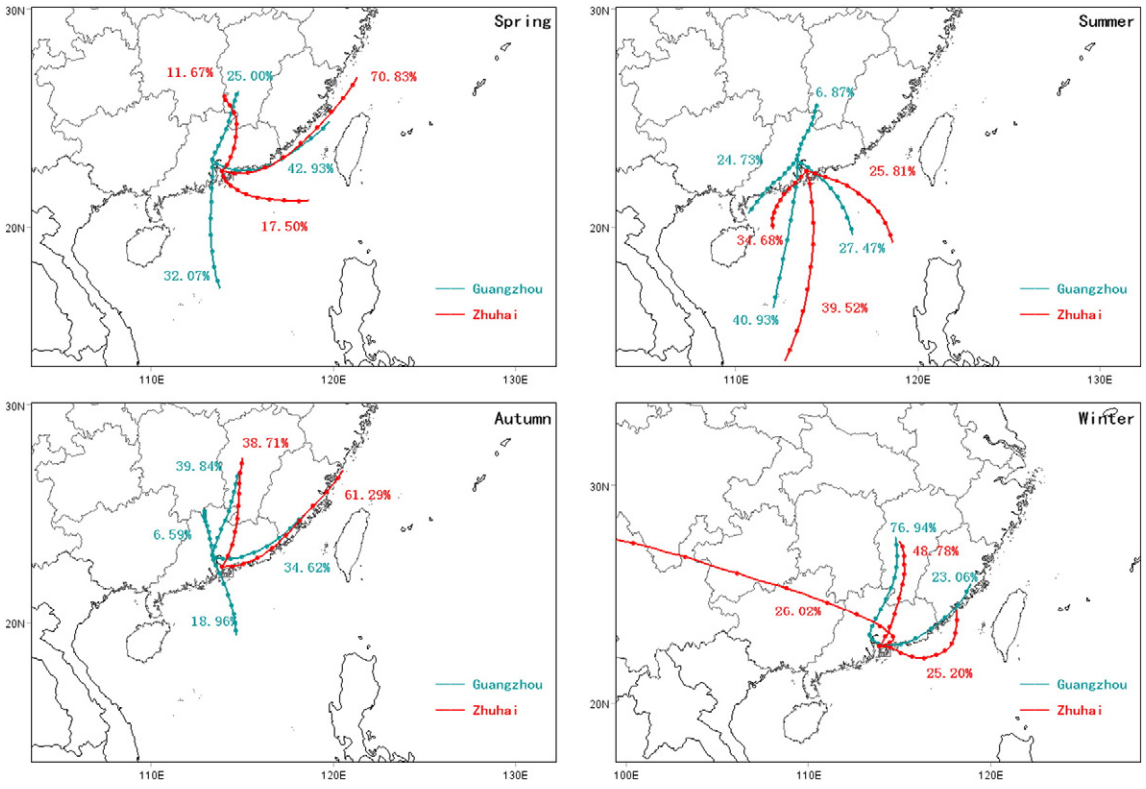

Fig. 2. Analytical results of 48 h air mass back trajectories arriving at 50 m elevation at the two sites in four seasons.

air masses between Guangzhou and Zhuhai were found in four seasons (Fig. 2). Thus, the seasonal differences in $PM_{2.5}$ between the two sites were found to be partially caused by the different air mass origins as shown by the back trajectory analysis. For example, the higher $PM_{2.5}$ in Guangzhou in spring and summer can be explained by the air masses originated from the southwest to southeast directions, which passed over many cities in PRD including Jiangmen, Foshan, Zhuhai, Dongguan and Shenzhen. The lowest $PM_{2.5}$ in Zhuhai in summer was due to almost 100% of air masses from the China South Sea where few pollutant sources exist except ship emissions. In contrast, air masses arriving at Zhuhai in autumn and winter were mainly originated from the north and northeastern directions, often passing over the cities of Shenzhen and Dongguan, and Shenzhen, Dongguan, Guangzhou and Foshan, respectively, where numerous pollutant sources exist (Zheng et al., 2009). Air masses arriving at Guangzhou in autumn and winter were also mainly originated from the north and northeastern directions. However, a small fraction of air masses originated from southwest and southeast directions, as shown in a previous study in urban Guangzhou in 2006 (Cheng et al., 2013).

Annual average $PM_{2.5}$ in urban Guangzhou decreased by 38% in 2014 when compared with that (77 μg m^{-3}) measured in 2009–2010 at the same site (Tao et al., 2014b), mainly due to the decreae of the dominant chemical components including OC, EC, SO_4^{2-}, NO_3^- and NH_4^+. For example, SO_4^{2-} and NO_3^- decreased by about 50%, which can be explained by the decrease of their respective gaseous precursors, e.g., annual concentration of SO_2 and NO_2 in Guangzhou decreased by more than 50% and 10%, respectively, in 2014 compared with those in 2009.

OC and EC decreased by <30% in Guangzhou in 2014 compared with 2009–2010. A good correlation ($R^2 = 0.81$) was found between OC and EC with a regression slope of 1.96 in 2014, suggesting vehicle emissions as the dominant source of carbonaceous aerosols. Although the number of vehicles in Guangzhou increased in recent years, the concentration of carbonaceous aerosols decreased due to the successful control measures for vehicle emissions (Hagler et al., 2006; Tao et al., 2014b; Lai et al., 2016). Historical studies on $PM_{2.5}$ were limited in Zhuhai compared with those in Guangzhou, and relevant studies only covered summer and winter seasons in Zhuhai in 2002 (Cao et al., 2004; Lai et al., 2007). Comparing the data from the present study (2014–2015) with the 2002 measurements (summer - 31 μg m^{-3} and winter - 59 μg m^{-3} for $PM_{2.5}$ mass), it was found that seasonal average $PM_{2.5}$ decreased in summer but increased in winter. Several dominant chemical components (e.g. EC, SO_4^{2-} and NO_3^-) decreased in summer and winter, but OC only slightly decreased in summer and increased in winter. A good correlation ($R^2 = 0.93$) was found between OC and EC with a regression slope of 2.76, suggesting coal combustion as the dominant source of carbonaceous aerosols. In fact, SO_2 emission intensity (representing coal combustion) in Zhuhai was lower than in other PRD cities (Zheng et al., 2009), and the high $PM_{2.5}$ in winter was due to the pollutants transport from other cities as shown in Fig. 2 and discussed above.

In conclusion, $PM_{2.5}$ pollution in PRD was alleviated in recent years due to the reduction of secondary inorganic aerosols and carbonaceous aerosols. Regional transport of pollutants resulted in similar levels of secondary inorganic aerosols between urban and suburban sites. However, the two sites have different dominant sources of carbonaceous aerosols, with vehicle emissions in urban and coal combustion in suburban.

3.2. Elevated ship emission tracer elements

The annual average $PM_{2.5}$ mass, the dominant chemical components (water soluble inorganic salts and carbon fraction), crustal elements, and most of the abundant trace elements (e.g. Cu, Zn and Pb) were much lower in PRD than in those inland cities in China; however, Ni and V concentrations were evidently higher. Ni and V are the dominant metal elements from crude oil and crude oil combustion emissions (Agrawal et al., 2008; Hays et al., 2009). Residual or crude oil has been widely used by big commercial container vessels (Yau et al., 2013). As expected, high concentrations of Ni and V in ambient $PM_{2.5}$ have been observed near ports (Agrawal et al., 2009; Peltier and Lippmann, 2010; Yau et al., 2013; Zhao et al., 2013). Ni and V are thus believed to be robust tracer elements of ship emissions in coast areas without significant amounts of coal and oil combustion (Agrawal et al., 2009).

Annual average Ni and V in $PM_{2.5}$ mass concentrations were 4 ng m^{-3} and 9 ng m^{-3}, respectively, in urban Guangzhou, and were evidently higher, e.g., 7 ng m^{-3} and 12 ng m^{-3}, respectively, in suburban Zhuhai. The higher values in Zhuhai were comparable with those (5 ng m^{-3} and 13 ng m^{-3}, respectively) measured in Hong Kong, a typical coast city in PRD during 2000–2001. The concentrations of V in PRD were close to these measured in other big ports neighboring cities such as Southern California, New York, Barcelona and Shanghai (Agrawal et al., 2009; Chen et al., 2008; Moreno et al., 2011; Peltier and Lippmann, 2010), but were slightly lower than that (15 ng m^{-3}) measured in Yangshan port of Shanghai, the largest port of China (Zhao et al., 2013). The concentrations of Ni in PRD were close to that measured in Southern California, but were evidently lower than those measured in urban Shanghai (about 10 ng m^{-3}), Yangshan port (about 80 ng m^{-3}) and New York (ranged from 6 ng m^{-3} to 25 ng m^{-3}). The V/Ni ratio is larger than 2.2 in general in heavy fuel oil (Agrawal et al., 2009). The low values of V/Ni ratio in Shanghai, Yangshan port and New York suggested excessive Ni from other sources (especially oil combustion) than just ship emissions (Peltier and Lippmann, 2010). In contrast, Ni and V mass concentrations in $PM_{2.5}$ in inland cites (e.g. Beijing, Chengdu and Zürich) were mostly <5 ng m^{-3}, which were much lower than those in coast cities (Tao et al., 2014a; Tao et al., 2016; Richard et al., 2011). The elevated Ni and V in PRD was likely caused by ship emissions, as further discussed below.

3.3. Source apportionments of $PM_{2.5}$ in PRD

PMF analysis was conducted to investigate the sources (especially ship emissions) of $PM_{2.5}$ in PRD. Five, six and seven sources were separately tested in the PMF analysis for optimum results. The scaled residuals of chemical components for the selected results were mainly distributed around 0 with a range between −4 to +3. The selected results were then run with different F_{peak} strengths (±0.5, ±1.0, and 1.5) to assess the stabilities of the selected results. A value of −0.5 for the F_{peak} strength provided the most physically reasonable source profiles in both Guangzhou and Zhuhai.

Six main sources were identified using PMF model in urban Guangzhou including (1) ship emissions, (2) soil dust, (3) coal combustion, (4) traffic emissions, (5) secondary nitrate and chloride, and (6) secondary sulfate and biomass burning. The profiles of these sources are shown in Fig. 3 and Fig. 4 and their contributions are shown in Fig. 5(a) and they are discussed in detail below.

The first source is ship emissions, characterized by high Ni and V concentrations, as discussed in Section 3.2. This source factor accounted for 17% of the $PM_{2.5}$ mass concentration. Certain amounts of Na^+, SO_4^{2-}, OC and EC concentrations were also observed in this factor, since residual oil also emit SO_2/SO_4^{2-}, Cl/Cl^- and carbonaceous aerosols. The extra Na^+ should be related with aged sea salts (e.g. $NaNO_3$, Na_2SO_4) produced by reactions between fresh sea salt NaCl and acids (Chen et al., 2005). As expected, ship emission and V concentration were correlated with R^2 of 0.85.

The second source is soil dust, characterized by high concentrations of typical crustal elements including Al, Si, Ca, Ti, and Fe. This source factor accounted for 7% of the $PM_{2.5}$ mass concentration. Al, Si, Fe, Ca, and Ti were the dominant chemical components in soil dust profiles (Zhang et al., 2014). The absolute contribution of soil dust to $PM_{2.5}$ mass concentration in winter (5.4 μg m^{-3}) was slightly higher than that in other seasons (2.5–3.1 μg m^{-3}) due to lower precipitation amount in winter in

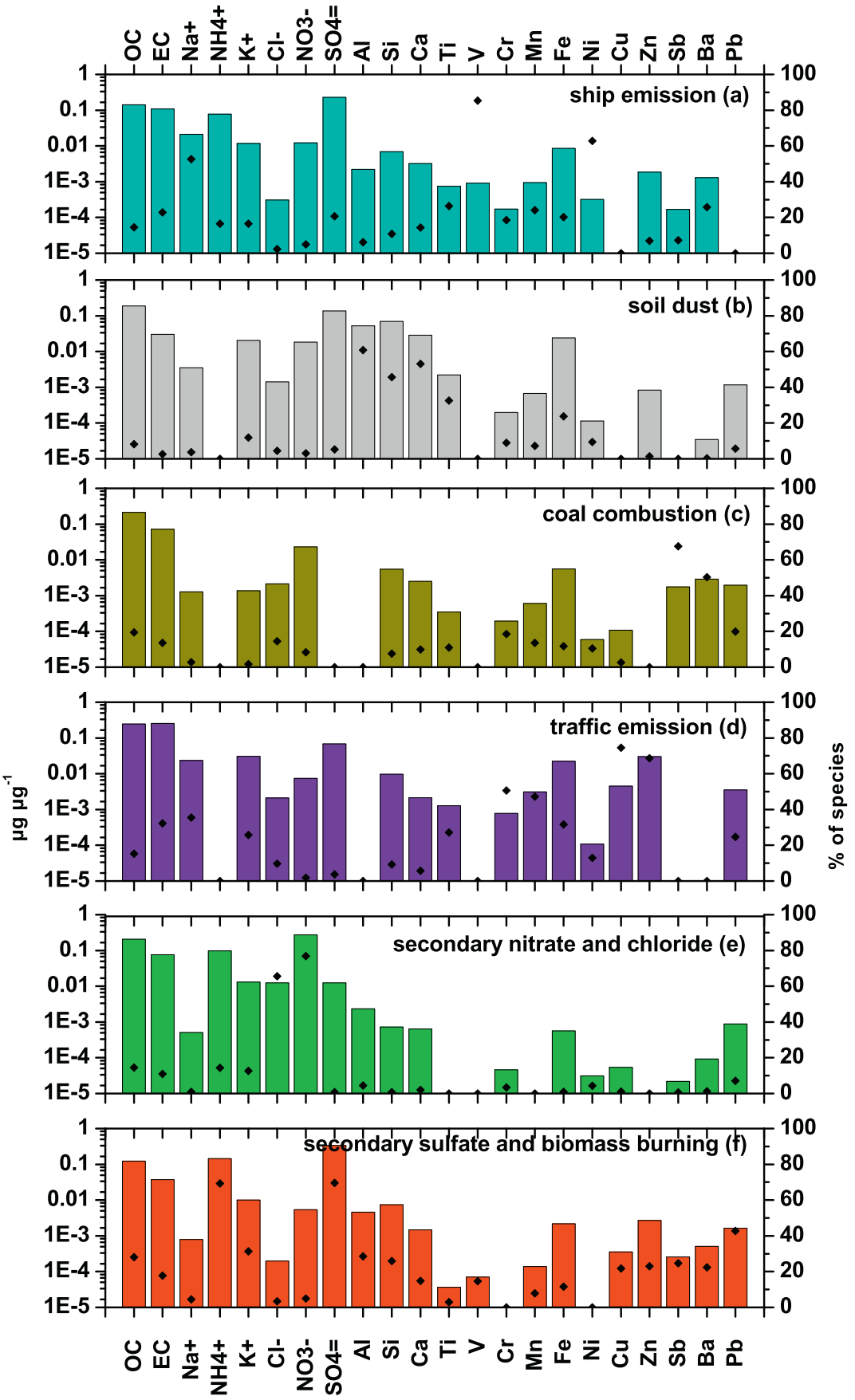

Fig. 3. Six source profiles (bars and left y-axis) and percentage contributions (dots and right y-axis) of each chemical component resolved from PMF model analysis in urban Guangzhou.

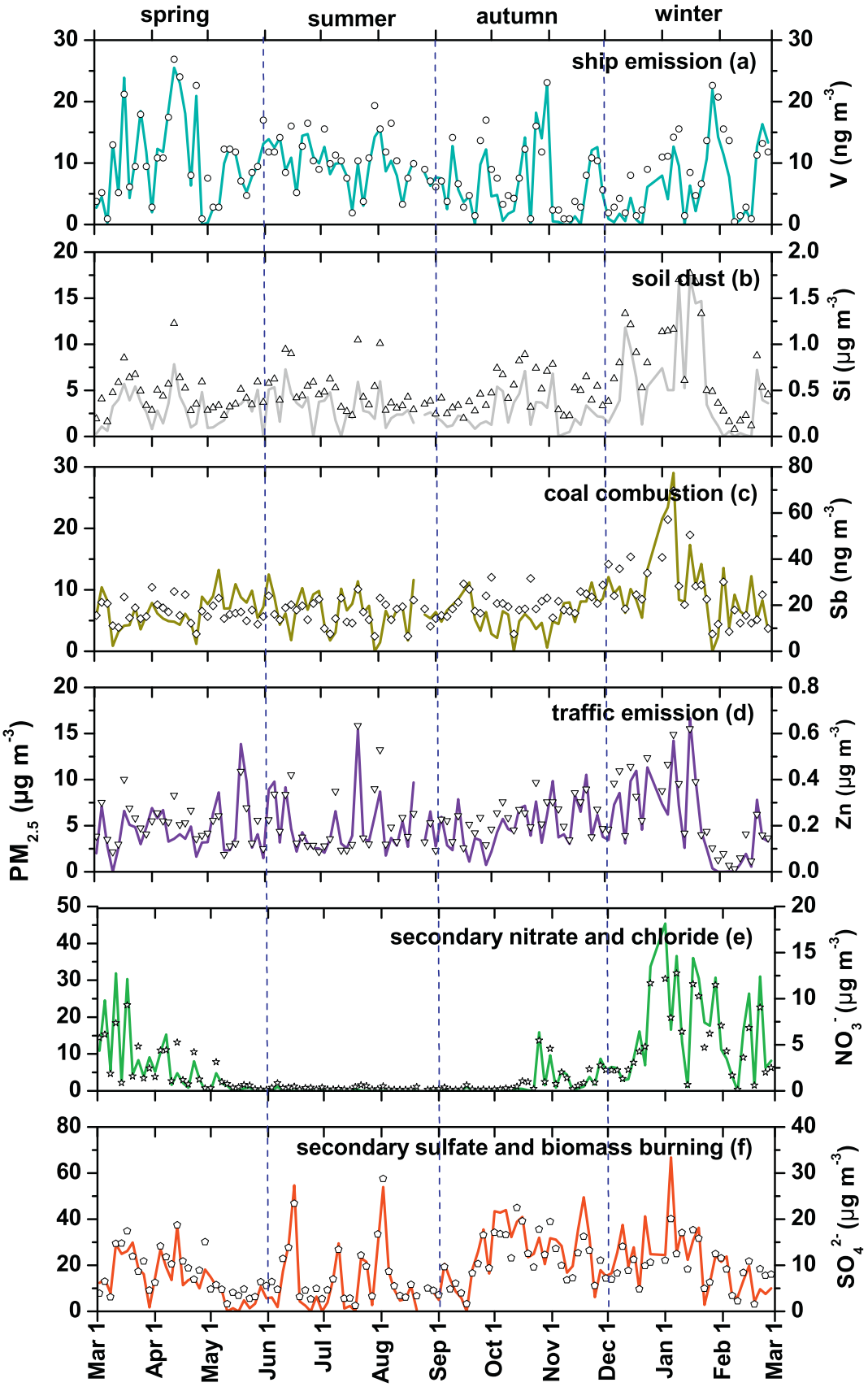

Fig. 4. Time series of daily contributions from each identified source (continuous line and left y-axis) and from specific chemical species (dots and right y-axis) in urban Guangzhou.

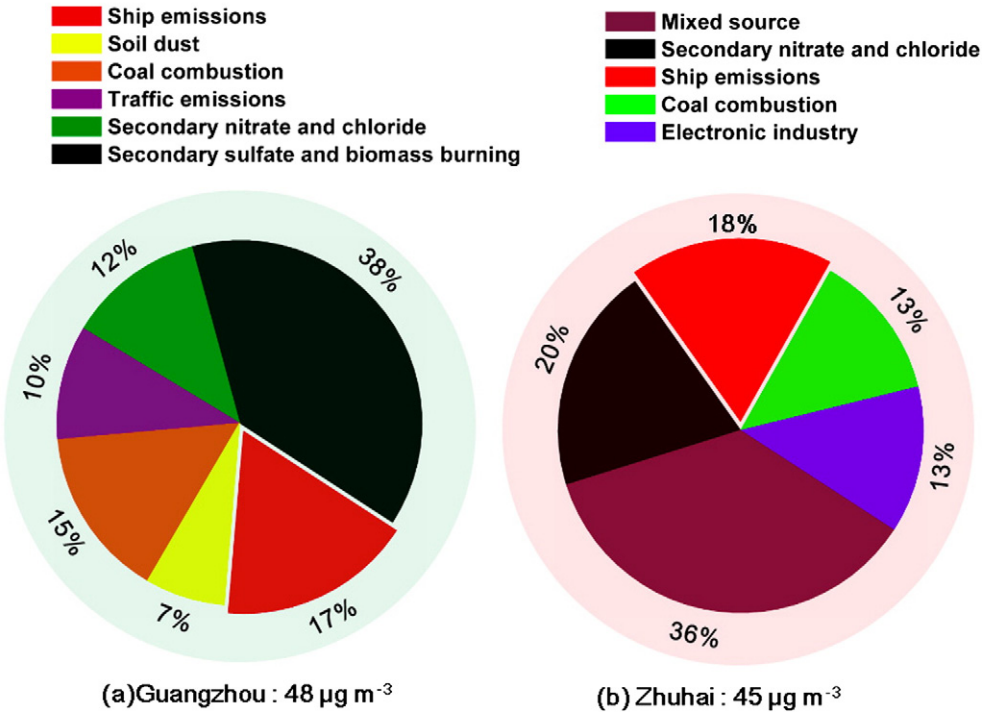

Fig. 5. Contributions of the identified sources for $PM_{2.5}$ in urban Guangzhou and suburban Zhuhai.

Guangzhou. A good correlation ($R^2 = 0.84$) was found between Si and soil dust.

The third source is coal combustion, characterized by high Sb and Ba concentrations. This factor accounted for 15% of the $PM_{2.5}$ mass concentration. Moreover, moderate OC and EC levels were also observed in this source factor. Coal combustion and nonferrous metal smelting accounted for 62% and 27%, respectively, of Sb emissions in China (Tian et al., 2012). Coal combustion was also an important source of carbonaceous aerosols in south China. A good correlation ($R^2 = 0.60$) was found between Sb and coal combustion dust.

The fourth source is traffic emissions, characterized by high Cu, Zn, Cr, Mn, and EC. This source factor accounted for 10% of the $PM_{2.5}$ mass concentration. Seasonal variations of the contributions of this source factor to $PM_{2.5}$ were small, ranging from 4.5 to 5.0 μg m^{-3}, but a sharp decrease was observed during the Spring Festival holiday period (30 Jan–7 Feb). EC was the dominant chemical component from this source factor, accounting for ~45% of $PM_{2.5}$ mass attributed to this factor. EC identified in this source factor accounted for 32% of the overall observed EC, much higher than those identified in other source factors. Note that high levels of trace elements including Zn, Cu, Mn and Pb have also been verified as the dominant chemical components from on-road vehicles in Zhujiang tunnel in Guangzhou (He et al., 2008). As for Cr emissions in China, coal combustion, oil combustion, and iron and steel industry contributed 47%, 27%, and 14%, respectively (Cheng et al., 2014). The number of vehicles reached 2.5 million in 2014 in Guangzhou (http://data.gzstats.gov.cn/). Thus, Cr was categorized into traffic emission source factor in urban Guangzhou due to the large amount of oil combustion by vehicles in this city. Moreover, the good correlation between OC and EC in the present study also suggested the factor traffic emission was the dominant source of carbonaceous aerosols in Guangzhou. A good correlation ($R^2 = 0.75$) was found between Zn and traffic emissions.

The fifth source is relevant to secondary nitrate and chloride, identified by high NO_3^- and Cl^- concentrations. This source factor accounted for 12% of the $PM_{2.5}$ mass concentration on annual average, but with large seasonal variations with the highest percentage contribution (27%) in winter and the lowest in summer (<1%). This is because both NO_3^- and Cl^- are unstable in high temperature conditions. Certain amounts of OC, EC and NH_4^+ concentrations were also observed in this factor. Note that coal power plant industry in PRD consumes a large amount of coal and coal combustion emits both NO_x (the gaseous precursor of NO_3^-) and Cl^-, which partially explains why this source factor is characterized by these two ions.

The sixth source is mixed source of secondary sulfate and biomass burning, identified by high NH_4^+, SO_4^{2-}, OC and K^+ concentrations. This source factor accounted for 38% of the $PM_{2.5}$ mass concentration annually, with higher contributions in autumn (54%) than in other seasons (30–34%). K^+ was regarded as a reliable tracer for biomass burning in PRD and a good correlation between K^+ and levoglucosan was found in PRD (Zhang et al., 2015b). Ozone concentration in autumn was much higher than in other seasons in PRD, which suggested higher ozone favor sulfate formation.

Five main sources were identified in suburban Zhuhai, including (1) mixed source, (2) secondary nitrate and chloride, (3) ship emissions, (4) coal combustion, and (5) electronic industry. The profiles of these sources are shown in Fig. 6 and Fig. 7 and their contributions are shown in Fig. 5(b) and they are discussed in detail below.

The first source is mixed source of secondary sulfate, biomass burning, traffic emission and soil dust, identified by high SO_4^{2-}, NH_4^+, K^+, OC, EC, Cu, Zn, and crustal elements (Si, Ca, Ti and Fe) concentrations. This factor was likely caused by regional transport of pollutants, which raised difficulties in assigning the chemical components to their respective original sources. This source factor accounted for 36% of the $PM_{2.5}$ mass concentration annually, with higher seasonal contributions in autumn (51%) and winter (38%) than in spring (16%) and summer (22%). The seasonal variations were mainly caused by different air mass origins since the prevailing wind direction was from south in wet season (spring and summer) and from north in dry season (autumn and winter) (Fig. 2), suggesting regional transport being a large contribution to $PM_{2.5}$ mass in suburban Zhuhai, especially in dry season.

The second source is secondary nitrate and chloride, characterized by high NO_3^- and Cl^-, as discussed for the urban site above. This source

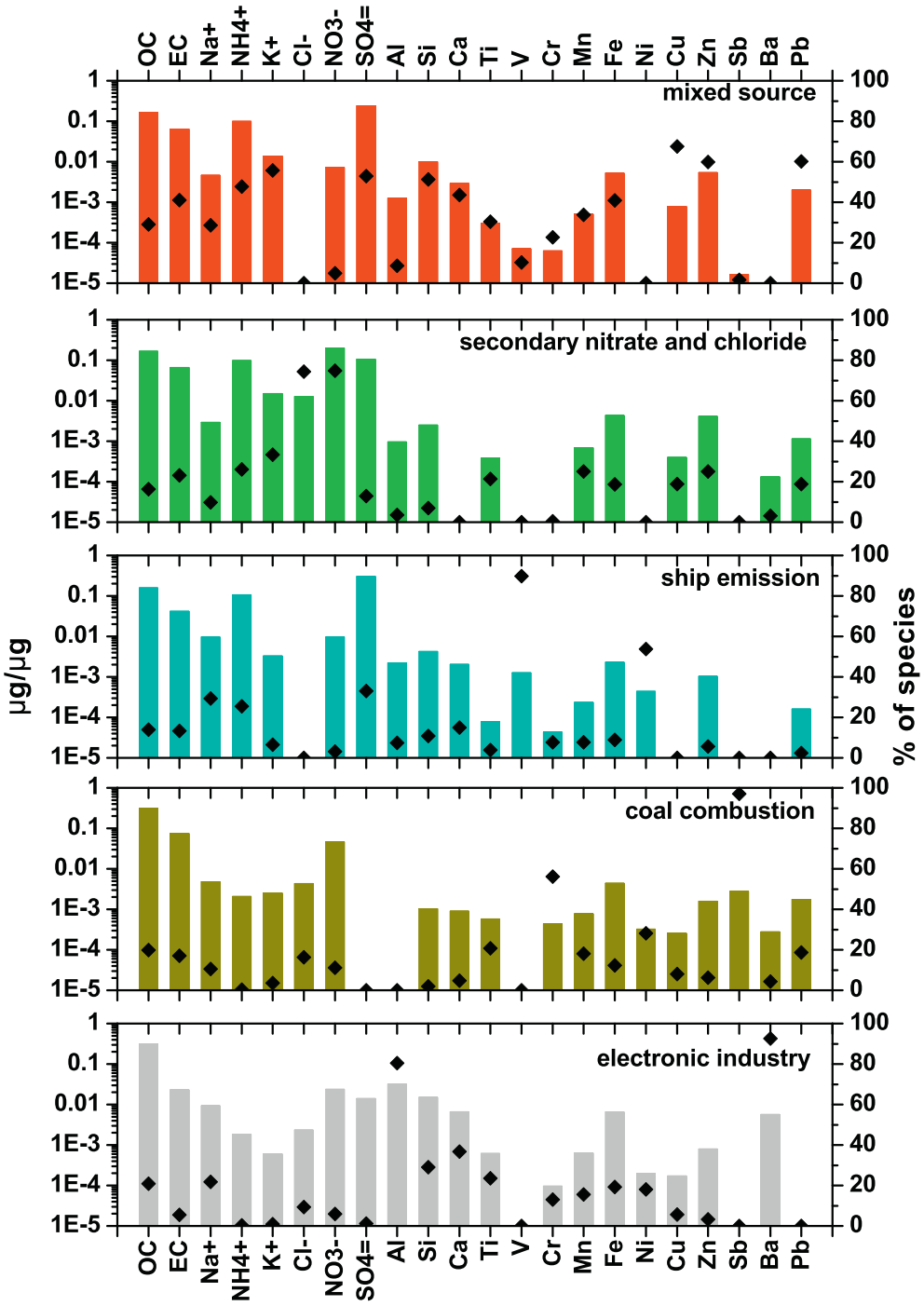

Fig. 6. Five source profiles (bars and left y-axis) and percentage contributions (dots and right y-axis) of each chemical component resolved from PMF model analysis in suburban Zhuhai.

factor accounted for 20% of the $PM_{2.5}$ mass concentration annually with the highest seasonal contribution in winter (34%), similar to what was found in urban Guangzhou.

The third source is ship emissions, characterized by high Ni and V concentrations, as also discussed above for the urban site. This source factor accounted for 18% of the $PM_{2.5}$ mass concentration annually. As mentioned above, Ni and V mass concentrations in Zhuhai were slightly higher than those in Guangzhou due to shorter distances between the Zhuhai site and the South China Sea or harbors. The much higher V mass concentration in spring (22 ng m^{-3}) than in other seasons (5–10 ng m^{-3}) was caused by the east-direction prevailing winds, from where sits a series of busy harbors (e.g. Shenzhen and Hong Kong) (Fig. 2). A good correlation with R^2 of 0.88 was found between the temporal variations of ship emission and V concentration.

The fourth source is coal combustion, characterized by high Sb and Cr concentrations, slightly differed from those for the urban site above (high Sb and Ba). This source factor accounted for 13% of the $PM_{2.5}$ mass concentration. Sb was a typical tracer element for coal combustion in China. As also discussed above for Guangzhou, the emission of Cr mainly came from coal combustion, oil combustion, and iron and steel industry in China (Cheng et al., 2014). However, the number of vehicles was 0.3 million in 2014 in Zhuhai (http://www.stats-zh.gov.cn/), which was much lower than that in Guangzhou. Thus, Cr was categorized as a tracer element for coal combustion in Zhuhai. A good correlation with R^2

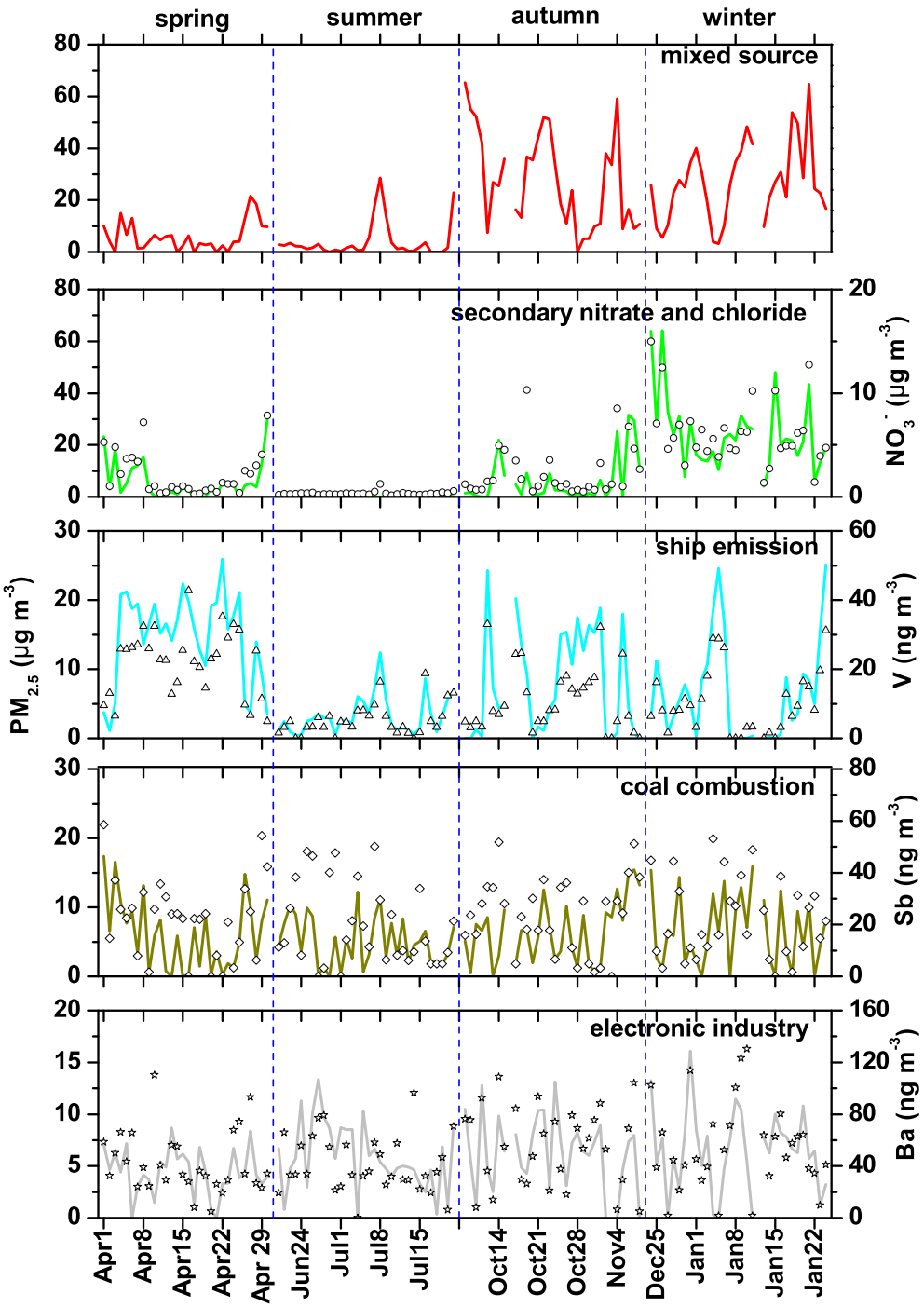

Fig. 7. Time series of daily contributions from each identified source (continuous line and left y-axis) and from specific chemical species (dots and right y-axis) in suburban Zhuhai.

of 0.47 was found between the temporal variations of coal combustion and Sb concentrations.

The fifth source is electronic industry, characterized by high Al and Ba. This source factor contributed 13% to the $PM_{2.5}$ mass concentration. Although Al and Ba were mainly emitted from crust and coal combustion, respectively, they were also widely used in electronic industry. For example, the aluminum substrate was widely used in circuit board, and barium sulfate was important auxiliary material for solder mask and electronic component marking ink. Besides barium sulfate, most of the other auxiliary materials were organic materials. High OC and low EC concentrations were observed in this source factor due to the use of organic materials in the production processes. To our knowledge, this is the first time this source factor was identified in China. Further investigations are needed to verify these findings. A moderate good correlation with R^2 of 0.40 was obtained between the time series of this source contribution and the observed Ba concentration.

3.4. Implications of the source apportionment analysis results

Ship emissions were identified for the first time as an important source for $PM_{2.5}$ in the PRD region, and this source factor has been ignored by local officials in making emission control policies. More research is needed in quantifying the impact of this source factor to pollution levels in various environments of this and other similar

regions in China for proving scientific evidence in making related emission control policies.

The sources related to coal combustion, including coal combustion dust and secondary inorganic aerosols, accounted for 65% of annual $PM_{2.5}$ in urban Guangzhou due to the continued slight increase in coal consumption in PRD. Further control measures for coal combustion are still needed in this region. PMF results for the suburban site in Zhuhai suggested that the mixed source factor from regional transport was the dominant source of $PM_{2.5}$ in autumn and winter, when the prevailing wind was from the north. However, $PM_{2.5}$ mass in Guangzhou was slightly lower than that in suburban Zhuhai in these two seasons, although Guangzhou is located north of Zhuhai. Thus, sources in between the two cities such as those in Zhongshan, Shenzhen, Dongguan and Foshan cities should be the important source regions for Zhuhai in autumn and winter (dry season). Similarly, these in-between sources would be important source regions for Guangzhou in spring and summer (wet season) when the prevailing wind is from the opposite direction. These findings demonstrated the importance of intraregional pollutant transport in affecting air quality in these cities, besides the contributions from interregional transport. A joint pollution prevention and control program in the whole PRD region is needed for reducing the impact of pollutants region transport on $PM_{2.5}$ level in individual cities.

4. Conclusions

Although $PM_{2.5}$ pollution was alleviated in recent years in PRD, the annual average $PM_{2.5}$ concentrations in urban Guangzhou and suburban Zhuhai were still about 30% higher than the NAAQS for annual $PM_{2.5}$ standard. Regional transport of air pollutants is a common phenomenon in this region, and played a major role in causing the very different seasonal-average $PM_{2.5}$ concentration between the two sites, despite their similar annual average levels. Intraregional pollutant transport is as important as interregional transport in affecting air quality in these cities. Although the concentrations of the dominant chemical components of $PM_{2.5}$ were lower at these two PRD sites than at in inland Chinese cities, the concentrations of tracer elements (Ni and V) of ship emissions were evidently higher.

Six and five source factors were identified for $PM_{2.5}$ in Guangzhou and Zhuhai, respectively, through PMF model analysis. Ship emissions were identified as a main source factor at both sites. Moreover, a special source - electronic industry, was also identified and accounted for 13% of $PM_{2.5}$ mass concentration at the Zhuhai suburban site. None of these two newly identified source factors was among the control measure list of the local Environmental Protection Bureau. A joint venture from Marine Safety Administration, Environmental Protection Bureau, local governments of different cities, and various industries should be established in controlling ship emissions as well as emissions from other major sources for further reducing $PM_{2.5}$ level in this region.

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