1 Exploration of PM_{2.5} sources on the regional scale in the

2 Pearl River Delta based on ME-2 modeling

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4 Xiao-Feng Huang¹, Bei-Bing Zou¹, Ling-Yan He¹, Min Hu², André S. H. Prévôt³, Yuan-Hang
5 Zhang²

¹Key Laboratory for Urban Habitat Environmental Science and Technology, School of
Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen, 518055,
China.

⁹ ²State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of
 ¹⁰ Environmental Sciences and Engineering, Peking University, Beijing, 100871, China.

³Paul Scherrer Institute (PSI), 5232 Villigen-PSI, Switzerland.

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13 Abstract:

14 The Pearl River Delta (PRD) of China, which has a population of more than 58 million people, is 15 one of the largest agglomerations of cities in the world and had severe PM_{2.5} pollution at the 16 beginning of this century. Due to the implementation of strong pollution control in recent decades, 17 $PM_{2.5}$ in the PRD has continuously decreased to relatively lower levels in China. To 18 comprehensively understand the current PM_{2.5} sources in the PRD to support future air pollution control strategy in similar regions, we performed regional-scale PM_{2.5} field observations coupled 19 20 with a state-of-the-art source apportionment model at six sites in four seasons in 2015. The regional annual average PM_{2.5} concentration based on the 4-month sampling was determined to be 21 22 $37 \,\mu g/m^3$, which is still more than three times the WHO standard, with organic matter (36.9%) and 23 $SO_4^{2^{-}}$ (23.6%) as the most abundant species. A novel multilinear engine (ME-2) model was firstly 24 applied to a comprehensive PM_{2.5} chemical dataset to perform source apportionment with 25 predetermined constraints, producing more environmentally meaningful results compared to those obtained using traditional positive matrix factorization (PMF) modeling. The regional annual 26 average PM_{2.5} source structure in PRD was retrieved to be secondary sulfate (21%), vehicle 27 28 emissions (14%), industrial emissions (13%), secondary nitrate (11%), biomass burning (11%), 29 secondary organic aerosol (SOA, 7%), coal burning (6%), fugitive dust (5%), ship emissions (3%) 30 and aged sea salt (2%). Analyzing the spatial distribution of PM_{2.5} sources under different weather conditions clearly identified the central PRD area as the key emission area for SO₂, NOx, coal 31 32 burning, biomass burning, industrial emissions and vehicle emissions. It was further estimated that 33 under the polluted northerly air flow in winter, local emissions in the central PRD area accounted for approximately 45% of the total PM_{2.5}, with secondary nitrate and biomass burning being most 34 35 abundant; in contrast, the regional transport from outside the PRD accounted for more than half of 36 PM_{2.5}, with secondary sulfate representing the most abundant transported species.

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

Correspondence to: L.-Y. He (hely@pku.edu.cn).

39 1 Introduction

40 With China's rapid economic growth and urbanization, air pollution has become a serious problem in recent decades. Due to its smaller size, fine particulate matter (PM_{2.5}) can carry toxic 41 chemicals into human lungs and bronchi, causing respiratory diseases and cardiovascular diseases 42 43 that can harm human health (Sarnat et al., 2008; Burnett et al., 2014). In particular, long-term 44 exposure to high concentrations of fine particulate matter can also lead to premature death (Lelieveld et al., 2015). The Chinese government has attached great importance to improving air 45 quality and issued the "Air Pollution Prevention and Control Action Plan" in September 2013, 46 47 clearly requiring the concentrations levels of fine particulate matter in a few key regions, including the Pearl River Delta (PRD), to drop by 2017 from 15 to 25% of their values in 2012. 48 49 The Pearl River Delta is one of the fastest-growing regions in China and the largest urban agglomeration in the world; it includes the cities of Guangzhou, Shenzhen, Zhuhai, Dongguan, 50 51 Foshan, Huizhou, Zhongshan, Zhaoqing and Jiangmen, and contains more than 58 million people. 52 The PM_{2.5} concentration in this region reached a high level of 58 μ g/m³ in 2007 (Nanfang Daily, 2016); however, the air quality has significantly improved due to the implementation of strict air 53 pollution control measures, which occurred here earlier than in other regions in China. The annual 54 55 average concentration of PM_{2.5} in the PRD dropped to 34 µg/m³ in 2015 (Ministry of 56 Environmental Protection, 2016).

57 In recent years, the receptor model method (commonly, positive matrix factorization) in the PRD was applied to perform the source apportionment of PM2.5, which was carried out in several 58 major cities, including Guangzhou (Gao et al., 2013; Liu et al., 2014; Wang et al., 2016), 59 60 Shenzhen (Huang et al., 2014b), Dongguan (Wang et al., 2015; Zou et al., 2017) and Foshan (Tan 61 et al., 2016). However, the above source apportionment studies only focused on part of $PM_{2.5}$ (e.g., organic matter) or single city in PRD (e.g., Shenzhen and Dongguan), lacking the extensive 62 representation of the PRD region in terms of simultaneous sampling in multiple cities. Since the 63 lifetime of PM2.5 in the surface layer of the atmosphere is days to weeks and the cities in PRD are 64 65 closely linked, the transport of $PM_{2.5}$ between cities should be specifically noteworthy (Hagler et al., 2006). On the other hand, although the positive matrix factorization (PMF) model has been 66 67 successfully applied to source apportionment in the PRD, the apportionment with PMF has high 68 rotational ambiguity and can output non-meaningful or mixed factors. Under such conditions, the 69 multilinear engine (ME-2) model can guide the rotation toward a more objective optimal solution by utilizing a priori information (i.e., predetermined factor profiles). In recent years, ME-2, 70 71 initiated and controlled via the Source Finder (SoFi) written by the Paul Scherrer Institute, was 72 successfully developed to apportion the sources of organic aerosols (Canonaco et al., 2013). The 73 novel ME-2 model has become a widely used and successful source analysis technique (e.g. 74 Crippa et al., 2014; Fröhlich et al., 2015; Visser et al., 2015; Elser et al., 2016; Reyes-Villegas et 75 al., 2016). The key challenges in running ME-2 are the construction of the appropriate constraint source profiles and the determination of factor numbers, and PMF could serve as the first step 76 77 when using ME-2 for the determination of the priori information needed.

Accurately understanding the regional characteristics of $PM_{2.5}$ sources in the PRD can certainly guide the regional joint prevention and control of $PM_{2.5}$ in this region and provide useful references for future air pollution control strategies in China. Thus, in this study, the $PM_{2.5}$ mass and chemical compositions were measured during four seasons in 2015 at six sites in the PRD, which basically represent the pollution level of the PRD on a regional scale rather than on a city scale. For the first time, the novel ME-2 model via the SoFi was applied to a comprehensive
chemical dataset (including EC, OM, inorganic ions and metal elements) to identify the sources of
bulk PM_{2.5} in the regional scale of PRD; then, the spatial locations of the sources were
systematically explored using the analysis of weather conditions.

87 2 Experimental methodology

88 2.1 Sampling and chemical analysis

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

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

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

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

Samples were collected every other day during a one-month long period for each season in
2015, and Table 2 contains the detailed sampling information to refer to. Each sampling period
lasted for 24 h at each site. The sampling sites of University Town (UT) and Dapeng (DP) used
Thermo 2300 PM_{2.5} samplers (Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA, with

101 a flowrate of 16.7 L/min for two channels and a flowrate of 10.0 L/min for the other two channels), 102 while those in Modiesha (MDS), Heshan (HS), Qi-Ao Island (QA) and Doumen (DM) used TH-16A PM_{2.5} samplers (Tianhong Corp., Wu Han, China, with a flow rate of 16.7 L/min for four 103 104 channels). Prior to the sampling campaigns, the six samplers used sampled in parallel three times, 105 and each time lasted for 12 h. The standard deviation of the $PM_{2.5}$ mass concentrations obtained by the six samplers in each parallel sampling was within 5%. The all sample boxes were then 106 107 sealed by Parafilm, stored in an ice-packed cooler during transportation, and stored under 108 freezing temperatures before analysis. A total of 362 valid samples (15-16 samples at each 109 site for each season) were collected in this study. In addition, to track the possible 110 contamination caused by the sampling treatment, a field blank sample was collected at each site for each season. The $PM_{2.5}$ mass can be obtained based on the difference in the weight of the 111 112 Teflon filter before and after sampling in a cleanroom at conditions of 20°C and 50% relative 113 humidity, according to the Quality Assurance and Quality Control procedures of the National 114 Environmental Protection Standard (NEPS, MEE, 2013b). The Teflon filters were analyzed for 115 their major ion contents (SO₄², NO₃⁻, NH₄⁺ and Cl⁻) via an ion chromatography system (ICS-2500, Dionex; Sunnyvale, California, USA), following the guidelines of NEPS (MEE, 2016a, 116 117 b). The metal element contents (23 species) were analyzed via an inductively coupled plasma mass spectrometer (ICP-MS, auroraM90; Bruker, Germany), also following the guidelines of 118 119 NEPS (MEE, 2013a). The Quartz filters were analyzed for organic carbon (OC) and elemental 120 carbon (EC) contents using an OC/EC analyzer (2001A, Desert Research Institute, Reno, Nevada, USA), following the IMPROVE protocol (Chow et al., 1993). The overall organic mass (OM) was 121 estimated as $1.8 \times OC$. In previous aerosol mass spectrometer (AMS) measurement for PM₁, the 122 123 OM/OC ratio was measured to be 1.6 for urban atmosphere (He et al., 2011) and 1.8 for rural 124 atmosphere (Huang et al., 2011). We adopted a uniform OM/OC ratio of 1.8 in this study 125 because it is assumed that the mass difference between PM1 and PM2.5 may mostly contain aged regional aerosol with higher OM/OC. 126

127 2.2 Meteorological conditions and weather classification

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

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Table 2. General meteorological conditions during the observation period in the PRD.

	Mean	Temp.	Rainfall	Mean RH	Mean wind	Predominant
	(°C)		(mm)	(%)	speed (m/s)	wind direction
Winter (Jan.10-Feb.9)	17		35	63%	2.1	ENE
Spring (Apr.2-Apr.30)	23		61	72%	1.8	SSW
Summer (Jul.1-Jul.29)	29		244	74%	2.1	SW

Fall (Oct.11-Nov.10)	25	92	68%	1.7	NNE
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Changes in meteorological conditions with the seasons have significant influences on the air 135 136 quality in the PRD (Hagler et al., 2006). The same type of weather is often repeated. Physick et al. 137 (2001) classified the weather over the region surrounding Hong Kong into seven categories based on surface pressure patterns, i.e., as northerly (winter monsoon), northeasterly (winter monsoon), 138 easterly or southeasterly, trough, southerly or southwesterly (summer monsoon), cyclonic 1 and 139 cyclonic 2 weather types. The PRD region, including Hong Kong, has nearly the similar weather 140 patterns and similar meteorological conditions. In this study, the daily weather types during the 141 142 observation period (excluding rainy days) were also classified into seven categories based on surface pressure patterns. However, according to the surface horizontal wind vectors, the PRD was 143 mostly impacted by two types of airflow, i.e., southerly flow and northerly flow. Southerly flow, 144 including the southeasterly and southerly or southwesterly (summer monsoon) weather types, was 145 relatively clean and originated from the ocean (e.g., Fig. S2 and Fig. S4). Northerly flow, 146 147 including the northerly (winter monsoon) and northeasterly (winter monsoon) weather types, was 148 relatively polluted and originated from the north mainland (e.g., Fig. S3 and Fig. S5). Southerly 149 flow and northerly flow appeared with the highest frequency in the PRD (i.e., above 80%), followed by cyclone (10%), easterly (2%) and trough (2%). In this study, southerly flow days 150 $(PM_{2.5} \le 17 \ \mu g/m^3)$, see Table 3) were selected to better reflect the local source regions in the PRD, 151 and northerly flow days (PM_{2.5} \ge 75 µg/m³, see Table 3) were selected to better understand the 152 pollution accumulation process and regional transport characteristics of pollutants in the PRD. The 153 154 sampling days for southerly flow and northerly flow are listed in Table 3.

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Table 3. Sampling days categorized as southerly flow and northerly flow days.

Souther	ly flow	Wind speed (m/s)	$PM_{2.5}(\mu g/m^3)$	Northerly flow	Wind speed (m/s)	$PM_{2.5}(\mu\text{g/m}^3)$
2015.07	7.01	2.6	16	2015.01.18	2.3	78
2015.07	7.03	3.6	17	2015.01.20	1.5	82
2015.07	7.15	1.9	17	2015.02.03	2	75
2015.07	7.23	2.6	12	2015.02.07	1.7	101
2015.07	7.25	2	13	2015.02.09	2.2	75
2015.07	7.29	1.3	12			

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157 2.3 Input data matrices for source apportionment modeling

PMF is a multivariate factor analysis tool widely used for aerosol source apportionment. The PMF algorithm groups the measured matrix **X** (Eq. (1)) into two non-negative constant matrices **G** (factor time series) and **F** (factor profiles), and **E** denotes the model residuals (Paatero and Tapper, 161 1994). The entries in **G** and **F** are fitted using a least-squares algorithm that iteratively minimizes the object function Q in Eq. (2), where e_{ij} are the elements of the residual matrix **E**, and u_{ij} are the errors/uncertainties of the measured species x_{ij} .

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$$\mathbf{X} = \mathbf{G} \cdot \mathbf{F} + \mathbf{E}$$
(1)
$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij}/u_{ij})^{2}$$
(2)

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The multilinear engine (ME-2) was later developed by Paatero (1999) based on the PMF
algorithm. In contrast to an unconstrained PMF analysis, ME-2 can utilize the constraints (i.e.,
predetermined factor profiles) provided by the user to enhance the control of rotation for a more

objective solution. One or more factor profiles can be expediently input into ME-2, and the output
profiles are allowed to vary from the input profiles to some extent. When using ME-2 modeling,
the "mixed factors" can usually be better resolved.

In this study, both PMF and ME-2 models were run for the datasets observed in the PRD. We 172 173 first need to determine the species input into the models. Species that may lead to high species 174 residuals or lower R²values between measured and model-predicted or non-meaning factors were 175 not included, such as those that fulfilled the following criteria: (1) species that were below detection in more than 40% of samples; (2) species that yielded R² values of less than 0.4 in 176 177 inter-species correlation analysis; and (3) species that had little implication for pollution sources and lower concentrations. Therefore, 18 species were input into the models; these species 178 accounted for 99.6% of the total measured species and included OM, EC, SO42⁻, NO3⁻, NH4⁺, Cl⁻, 179 K, Ca, Na, Mg, Al, Zn, Fe, Cd, V, Ni, Ti and Pb. 180

181 The application of PMF or ME-2 also depends on the estimated realistic uncertainty (u_{ij}) of the individual data point of an input matrix, which determines the Q value in Eq. (2). Therefore, 182 the estimation of uncertainty is an important component of the application of these models. There 183 184 are many sources of uncertainty, including sampling, handling, transport, storage, preparation, and 185 testing (Leiva et al., 2012). In this study, the sources of uncertainty that contributed little to the 186 total uncertainty could be neglected, such as replacing filters, sample transport and sample storage 187 under the strict Quality Assurance and Quality Control. Therefore, we first considered the uncertainties introduced by sampling and analysis processes, such as sampling volume, 188 repeatability analysis and ion extraction. The species uncertainties u_{ij} are estimated using Eq. (5), 189 where \bar{u}_c is the error fraction of the species, which is estimated using the relative combined error 190 191 formula Eq. (6) (BIPM et al., 2008).

$$u_{ij} = \bar{u}_c \times x_{ij} \tag{5}$$

$$\bar{u}_c = \sqrt{\bar{u}_f^2 + \bar{u}_r^2 + \bar{u}_e^2} \tag{6}$$

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194 where \bar{u}_f is the relative error of the sampling volume; \bar{u}_r is the relative error of the repeatability

195 analysis of the standard species; and \bar{u}_e is the relative error of the ion extraction of multiple samples. When the concentration of the species is below the detection limit (DL), the 196 concentration values were replaced by 1/2 of DL, and the corresponding uncertainties were set at 197 5/6 of DL. Missing values were replaced by the geometric mean of the species with corresponding 198 uncertainties of 4 times their geometric mean (Polissar et al., 1998). The uncertainties of SO₄²⁻, 199 NH_4^+ and all metal elements, which have scaled residuals larger than ± 3 due to the small 200 201 analytical uncertainties, need to be increased to reduce their weights in the solution (Norris et al., 2014). In addition, the uncertainties of EC caused by pyrolyzed carbon (PC), the uncertainties of 202 203 OM, NO₃⁻ and Cl⁻ due to semi-volatility under high ambient temperatures should also be taken into account (Cao et al., 2018). In this study, more reasonable source profiles can be obtained 204 205 when further increasing the estimated uncertainties (\bar{u}_c) of all species by a factor of 2.

206 2.4 Constraint setup in ME-2 modeling

207 In this study, the USEPA PMF v5.0 was applied with the concentration matrix and 208 uncertainties matrix described above to identify the PM_{2.5} sources. After examining a range of factor numbers from 3 to 12, the nine-factor solution output by the PMF base run ($Q_{true}/Q_{exp}=2.5$) 209 was found to be the optimal solution, with the scaled residuals approximately symmetrically 210 211 distributed between -3 and +3 (Fig. S6) and the most interpretable factor profiles (Fig. S7). The 212 model-input total mass of the 18 species and the model-reconstructed total mass of all the factors 213 showed a high correlation (R²=0.97, slope=1.01) (Fig. S8). The factor of biomass burning was not extracted in the eight-factor solution, while the factor of fugitive dust was separated into two 214 215 non-meaningful factors when more factors were set to run PMF. For the nine-factor solution of secondary sulfate-rich, secondary nitrate-rich, aged sea salt, fugitive dust, biomass burning, 216 217 vehicle emissions, coal burning, industrial emissions and ship emissions, the source judgment 218 based on tracers for each factor was identical to that of the ME-2 results detailed in Section 3.2. 219 However, in Fig. S7, some factors seemed to be mixed by some unexpected components and were thus overestimated. For example, the secondary sulfate-rich and secondary nitrate-rich factors of 220 221 PMF had certain species from primary particulates, such as EC, Zn, Al, K and Fe, among which 222 EC had obvious percentage explained variation (EV) values, i.e., the percent of a species apportioned to the factor, of 18.7% and 9.7%, respectively; the EV value of OM in the sea salt 223 224 factor (which was theoretically negligible) had a high value of 6.4%, and OM accounted for 37% 225 of the total mass of this factor; the EV value of SO_4^2 in the fugitive dust factor (which was theoretically negligible) had a high value of 8.6%, and the SO₄ z concentration accounted for 26% 226 227 of the total mass of this factor.

SoFi is a user-friendly interface developed by PSI for initiating and controlling ME-2 228 (Canonaco et al., 2013), and it can conveniently constrain multiple factor profiles. Although 229 230 USEPA PMF v5.0 can also use some priori information (such as ratio of elements in factor) to 231 control the rotation after the base run, it is not able to use multiple constrained factor profiles to 232 control the rotation (Norris et al., 2014). Therefore, SoFi is a more convenient and powerful tool to establish various constrained factors for source apportionment modeling. Using the same 233 234 species concentration matrix and uncertainties matrix, we ran the ME-2 model via SoFi for 9-12 235 factors with the four factors constrained as described above, as shown in Table 4. The following 236 considerations were used. Secondary sulfate and secondary nitrate factors should theoretically not 237 contain species from primary particulates, but they may contain secondary organic matter related 238 to the secondary conversion process of SO_2 and NOx (He et al., 2011; Yuan et al., 2006b; Huang 239 et al., 2014b). Therefore, the contributions of the species from primary particulates were 240 constrained to zero in the input secondary aerosol factors, while others were not constrained. In addition, the factors of sea salt and fugitive dust in primary aerosols could be understood based on 241 242 the abundance of species in seawater and the upper crust (Mason, 1982; Taylor and Mclennan, 243 1995). As seen in Table S1, the abundances of Cl⁻, Na⁺, SO₄⁺, Mg⁺, Ca⁺ and K⁺ in sea salt were relatively high, as were the abundances of Al, Fe, Ca, Na, K, Mg and Ti in fugitive dust. Therefore, 244 245 these high-abundance species were not constrained in the sea salt and fugitive dust factors, while 246 the other species (with abundances of less than 0.1% in the particulates) were constrained to zero (Table 4). In addition, HNO₃ might react with sea salt to displace Cl⁻ (Huang et al., 2006); thus, 247 NO₃⁻ was also not constrained in the sea salt factor. 248

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Table 4. The constraints of factor species for ME-2 modeling.

Factors	OM	EC	Cl	NO3-	SO ₄ ²	$\mathrm{NH_4}^+$	Ca	Ti	v	Ni	Zn	Cd	Pb	Na	Mg	Al	Κ	Fe
Secondary sulfate	-	0	0	0	_	_	0	0	0	0	0	0	0	0	0	0	0	0
Secondary nitrate	_	0	0	_	0	_	0	0	0	0	0	0	0	0	0	0	0	0
Sea salt	0	0	-	_	-	0	_	0	0	0	0	0	0	_	-	0	_	0
Fugitive dust	0	0	0	0	0	0	_	_	0	0	0	0	0	_	_	_	_	_

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251 **3 Results and discussion**

252 **3.1 Tempo-spatial variations of PM_{2.5} in the PRD**

253 The 4-month average $PM_{2.5}$ concentration for all six sites in the PRD was 37 µg/m³, which was 254 slightly higher than the Grade II national standards for air quality (with an annual mean of 35 μ g/m³). The chemical compositions of PM_{2.5} in the PRD are shown in Fig. 2. OM had the highest 255 contribution of 36.9%, suggesting severe organic pollution in the PRD. Other important 256 257 components included SO₄² (23.6%), NH₄⁺ (10.9%), NO₃⁻ (9.3%), EC (6.6%) and Cl⁻ (0.9%). 258 The major metallic components included K (1.5%), Na (1.1%), Fe (0.7%), Al (0.6%), and Ca 259 (0.6%), and trace elements accounted for 1.0%. Fig. 3a shows the spatial distribution of the PM_{2.5} 260 and chemical components between six sites. The PM_{2.5} pollution level in the PRD was distinctly 261 higher in the northwestern hinterland (HS and MDS) and lower in the southern coastal areas (DM 262 and DP). The DP background site had little local emission and was hardly influenced by the emissions from the PRD under both southerly flow and northerly flow. Thus, its air pollution 263 264 reflects the large-scale regional air pollution. The average $PM_{2.5}$ concentration at DP was as high 265 as 28 μ g/m³, indicating that the PRD had a large amount of air pollution transported from outside this region. At the background DP site, the fractions of Cl^- and NO_3^- in $PM_{2.5}$ were the lowest of 266 267 the six sites, i.e., 0.3% and 3.9%, respectively, suggesting that they had dominantly local sources in the PRD. The highest concentration level of PM_{2.5} was observed at HS (suburban), which was 268 influenced by the pollution transport of Foshan (industrial city) and Guangzhou (metropolis) under 269 270 the northeastern wind, which is the most frequent wind in the PRD. The back trajectories of the air 271 masses (Fig. S1) show that the northern monsoon prevails in winter and the southern monsoon 272 prevails in summer in the PRD. Under the winter monsoon, the air masses mostly came from the 273 inland and carried higher concentrations of air pollutants. However, under the summer monsoon, the air masses largely originated from the South China Sea and were clean. In addition, the 274 frequent rainfall and higher planetary boundary layer (PBL) in summer in the PRD also favored 275 276 the dispersion and removal of air pollutants (Huang et al., 2014b). Fig. 3b shows that the 277 normalized seasonal variations of the major components in PM2.5 in the PRD were evidently 278 higher in winter and lower in summer, which is consistent with the seasonal variations of monsoon 279 and other meteorological factors as mentioned above.

280 Table 5 summarizes some previous studies that used similar filter-sampling and analytical methods to allow for a better comparison with this study. In 2002-2003, Hagler et al. 281 282 (2006) also conducted observations and analysis of $PM_{2.5}$ in the PRD and Hong Kong region, 283 nearly 12 years before this study, as shown in Table 5. Compared with Hagler's results, the PM_{2.5} 284 concentrations in this study decreased by 42% in Guangzhou (MDS) and 21% in Shenzhen (UT), 285 especially OC, EC and SO₄², which decreased significantly by 20%–47%, indicating that the 286 measures taken to desulfurize coal-fired power plants, improve the fuel standards of motor vehicles and phase-out older and more polluting vehicles have played important roles in 287 improving the air quality in the PRD region (People's Government of Guangdong Province, 2012). 288

Compared with the PM_{2.5} concentrations reported by other cities in China in recent years, the 289 PM_{2.5} concentrations in urban Guangzhou and Shenzhen in this study were 39%-63% lower than 290 those in Beijing (Huang et al., 2017) in northern China, Shanghai (Ming et al., 2017) in eastern 291 292 China, and Chengdu (Wang et al., 2018) in western China. However, the PM_{2.5} concentrations in 293 urban Guangzhou and Shenzhen observed in this study were clearly higher than those in famous 294 mega-cities in developed countries, such as Paris (Bressi et al., 2013), London (Rodr guez et al., 2007), and Los Angeles (Hasheminassab et al., 2014), while they were similar to those of Santiago 295 (Villalobos et al., 2015) and Chuncheon (Cho et al., 2016). It should be highlighted that the higher 296 concentration of SO_4^{z} in the urban atmosphere of the PRD is one of the major reasons leading to 297 298 the higher degree of PM2.5 pollution in the PRD compared to those in developed cities.





Fig. 2. Chemical compositions of 4-month average PM_{2.5} in the PRD region.





Fig. 3. The spatial distributions (a) and seasonal variations (b) of the PM_{2.5} chemical compositions in the PRD. Sizes of the pie charts indicate the concentrations of PM_{2.5} at the six sites, with the detailed numbers (unit: μ g/m³) in brackets.

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Table 5. The comparison of the major chemical compositions of $PM_{2.5}$ in typical cities (unit: $\mu g/m$ 3).

Cities	Periods	PM _{2.5}	OC	EC	SO ₄ ²	NO_3^-	$\mathrm{NH_4}^+$	References
Zhuhai (DM)	2015.1-2015.11	35	6.4	2.3	8.1	4.4	3.6	This study
Zhuhai (QA)		37	7.2	2.2	9.9	3.5	4.4	
Jiangmen (HS)		47	9.0	2.8	9.8	5.6	5.0	
Guangzhou (MDS)		41	9.3	2.7	9.2	3.7	4.6	
Shenzhen (UT)		37	7.8	3.0	8.0	2.6	3.7	
Shenzhen (DP)		28	6.2	1.8	8.0	1.1	3.3	
Hong Kong (Urban)	2002.10-2003.6	34.3	6.6	1.9	9.3	1.0	2.5	Hagler et al., 2006
Shenzhen (Urban)		47.1	11.1	3.9	10.0	2.3	3.2	
Guangzhou (Urban)		70.6	17.6	4.4	14.7	4.0	4.5	
Beijing	2014.6-2015.4	99.5	15.5	6.2	14.3	17.9	11.5	Huang et al., 2017
Shanghai	2013.9-2014.8	94.6	9.89	1.63	14.5	18.0	8.13	Ming et al., 2017
Chengdu/Sichuan	2014.10-2015.7	67.0	10.9	3.6	11.2	9.1	7.2	Wang et al., 2018
Paris/France	2009.9-2010.9	14.8	3.0	1.4	2.0	2.9	1.4	Bressi et al., 2013

London/United Kingdom	2003.12-2005.4	31.0	5.6	1.6	2.8	3.5	2.1	Rodr guez et al., 2007
Los Angeles/United States	2002-2013	17.1	2.2	1.3	2.7	4.9	0.1	Hasheminassab et al., 2014
Santiago/Chile	2013.3-2013.10	40	12.1	4.3	1.9	7.1	3.3	Villalobos et al., 2015
Chuncheon/Korea	2013.1-214.12	34.6	9.0	1.6	3.9	2.8	2.0	Cho et al., 2016

307

308 3.2 Source apportionment of PM_{2.5} using ME-2

The solutions of 9-12 factors of the ME-2 were modeled with the four factors constrained in 309 Table 4, using the SoFi tool, an implementation of ME-2 (Canonaco et al., 2013). Again, the 310 311 nine-factor solution provided the most reasonable source profiles, since non-interpretable factors were produced (e.g., a Ti-high factor) when more factors were set to run ME-2. Based on the EV 312 313 and the contributed concentrations of species in each factor shown in Fig. 4, the sources of PM_{2.5} 314 can be judged as follows: (1) the first factor was explained as secondary sulfate-rich, which had large EV values of SO₄ ² and NH₄⁺. (2) The second factor was explained as secondary nitrate-rich, 315 which had significant EV values of NO_3^- and NH_4^+ . (3) The third factor was related to sea salt 316 317 due to the large EV values and concentrations of Na and Mg. However, the low Cl⁻ concentration 318 and high SO_4^{z} concentration implied that SO_4^{z} replaced Cl⁻ during the sea salt aging process. 319 Therefore, this factor was identified as aged sea salt (Yuan et al., 2006a). (4) The fourth factor was 320 identified as fugitive dust due to its significant EV values of Al, Ca, Mg and Fe. In this study, the 321 undetermined mass of O and Si in this factor was compensated using the elemental abundance in dust particles in Table S1 (Taylor and Mclennan, 1995). (5) The fifth factor was identified as 322 323 biomass burning due to its significant characteristic value of K (Yamasoe et al., 2000). (6) The 324 sixth factor had high concentrations and large EV values of OM and EC, as well as a certain range of EV values of Fe and Zn, which were related to tires and the brake wear of motor vehicles (Yuan 325 et al., 2006a; He et al., 2011). Therefore, this factor was identified as vehicle emissions. (7) The 326 seventh factor had a high EV value of Cl⁻ and certain concentrations of OM, EC, SO₄² and NO₃⁻, 327 implying a combustion source. This factor was identified as coal burning, which was a major 328 source of Cl⁻ in the PRD (Wang et al., 2015). (8) The eighth factor had large EV values of Zn, Cd 329 and Pb, and certain concentrations of OM and EC. Zn, Cd and Pb had high enrichment factors 330 331 (Table S2) of 821, 4121 and 663, respectively, and were thus considered to be related to industrial 332 emissions (Wang et al., 2015). (9) The last factor had large EV values of V and Ni. V and Ni were predominantly derived from heavy oil combustion, and they had high enrichment factors (Table 333 S2) of 64 and 89, respectively. Heavy oil was related to ship emissions in the PRD (Chow et al., 334 335 2002; Huang et al., 2014b). Although these nine factors of the ME-2 modeling generally showed 336 high correlations (R²=0.81-0.97) with the corresponding factors of the PMF modeling in terms of time series, it is easy to see that the ME-2 modeling provided a better Q_{true}/Q_{exp} ratio (1.2) than 337 that of the PMF modeling (Qtrue/Qexp=2.5), indicating that the species residuals were decreased in 338 339 the ME-2 modeling, and the EV values of tracers (e.g., SO₄², NO₃⁻, OM, EC, Cl⁻, V, Ni, Pb and 340 Cd) were assigned to factors more intensively. Therefore, it is concluded that the source 341 apportionment results of the ME-2 modeling were more environmentally meaningful and 342 statistically better than those of the PMF modeling.

In this study, secondary organic aerosol (SOA) did not appear as a single factor, even if we run the ME-2 with ten or more factors. SOA can usually be described by low-volatile oxygenated organic aerosol (LV-OOA) and semi-volatile oxygenated organic aerosol (SV-OOA), based on the volatility and oxidation state of organics (Jimenez et al., 2009). In previous studies (e.g., He et al.,

2011; Lanz et al., 2007; Ulbrich et al., 2009), the time series of LV-OOA and SV-OOA were 347 highly correlated with those of sulfate and nitrate, respectively, implying that LV-OOA and 348 sulfate (or SV-OOA and nitrate) cannot be separated easily in cluster analysis, especially when 349 there is no effective tracer of SOA. In this study, the high OM concentration in the secondary 350 351 sulfate-rich factor was considered to represent LV-OOA, while the high OM concentration in the 352 secondary nitrate-rich factor was considered to represent SV-OOA (Yuan et al., 2006b; He et al., 2011). Therefore, it should be acknowledged that mixed secondary factors cannot be solved even 353 using ME-2. However, the contribution time-series of LV-OOA (or SV-OOA) can be extracted 354 355 based on the contribution time-series of the secondary sulfate-rich factor (or the secondary 356 nitrate-rich factor) and the mass percentage of OM in this factor, leaving the remaining mass as 357 the "pure" secondary sulfate (or secondary nitrate). Therefore, a new SOA factor can be reasonably estimated by LV-OOA+SV-OOA. 358







Fig. 4. The factor profiles and explained variations of the ME-2 modeling.

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



368 369

Fig. 5. The 4-month average contributions of PM_{2.5} sources in the PRD.

370 3.3 Tempo-spatial variations of sources in the PRD

371 The spatial distributions of the $PM_{2.5}$ sources between six sites are shown in Fig. 6a. Secondary sulfate represented the largest fraction (31%) of PM_{2.5} at DP, indicating that it was a 372 major air pollutant in the air mass transported to the PRD. Vehicle emissions also contributed 373 374 relatively highly to urban sites (18% in MDS and 17% in UT). Industrial emissions, biomass burning, secondary nitrate, and coal burning contributed larger fractions of PM2.5 at HS, which 375 376 could be attributed to both strong local sources (e.g., the surrounding township factories and 377 farmlands) and regional transport from upwind cities at this site. Fugitive dust, which is primarily related to construction activities, was relatively high at DM (9%). The contributions of ship 378 379 emissions and aged sea salt were the highest at QA due to the site being located on Qi-Ao Island in the Pearl River Estuary, which records the greatest impact from the sea. SOA contributed 380 similar amounts (7%-8%) at all sites. It should be noted that, although QA was a background site 381 without local anthropogenic sources, its PM2.5 level was moderate in the PRD, indicating that QA 382 383 was impacted by severe regional transport from the surrounding cities.

384 Fig. 6b shows the seasonal variations of the major sources of PM_{25} in the PRD. The contributions of most sources were higher in winter and lower in summer, e.g., secondary sulfate, 385 secondary nitrate, fugitive dust, biomass burning, vehicle emissions, coal burning, industrial 386 387 emissions and SOA; these sources were greatly influenced by the seasonal variations of monsoon, 388 rainfall and PBL, as discussed in Section 3.1. For example, although secondary sulfate was proven to be a typical regional pollutant in the PRD (Huang et al., 2014b; Zou et al., 2017), the more 389 polluted continental air mass in the winter monsoon made its concentrations in winter much higher 390 than in summer. The semi-volatile secondary ammonium nitrate was also significantly affected by 391 392 seasonal ambient temperatures. In contrast, the average contributions of aged sea salt and ship emissions for the whole region displayed little seasonal variations, consistent with that the 393 394 emissions were from local surrounding sea areas.

Previous studies of the source apportionment of bulk $PM_{2.5}$ in the PRD have mainly focused on Guangzhou, Dongguan and Shenzhen, as seen in Table 6. It can be seen that in those studies, $PM_{2.5}$ was apportioned to 6–9 sources and that secondary sulfate was the prominent source, although the results of different studies exhibited certain differences due to the use of different models or data inputs. Compared with the study of Huang et al. (2014b) in Shenzhen in 2009, the contributions of secondary sulfate and vehicle emissions in Shenzhen in this study were obviously lower due to power plant desulfurization and motor vehicle oil upgrades in recent years (People's 402 Government of Shenzhen Municipality, 2013). Compared with previous studies in Guangzhou, this study attained more PM2.5 sources, which can more clearly describe the source structure of 403 PM_{2.5} in this region, especially industrial emissions (11%). The PRD region has experienced a 404 405 high degree of industrialization; thus, industrial sources should be a major source, contributing 406 8.1% of PM_{2.5} reported by the Guangzhou Environmental Protection Bureau (2017), similar to our 407 results. Tao et al. (2017) apportioned PM2.5 to 6 sources using PMF in Guangzhou, including some mixed sources. For example, ship emissions in Tao's study may not actually represent a primary 408 409 source due to the significant existence of some secondary inorganics and sea salt in the source profile; thus, they obtained a significantly higher contribution (17%) than that in our study. Ship 410 emissions were unidentified in Huang's study (2014a) in Guangzhou. 411





413 Fig. 6. The spatial distributions (a) and seasonal variations (b) of PM_{2.5} sources in the PRD. Sizes of the pie charts 414 indicate the concentrations of PM_{2.5} at the six sites, with the detailed numbers (unit: μ g/m³) in brackets.

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Table 0. Comparison of the results of source apportionment of F102.5 in the FK	Table 6. Com	parison of the	results of source	e apportionment	of PM2.5 ir	1 the PRD
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Cities	Periods	Model	Results	References
Shenzhen	2015.1—2015.11	ME-2	Secondary sulfate (21%), secondary nitrate (8%) and SOA (7%), vehicle	This study
	(Four seasons)		emissions (17%), industrial emissions (11%), biomass burning (9%), coal	
			burning (3%), fugitive dust (6%), ship emissions (3%) and aged sea salt (1%).	
Shenzhen	2009.1-2009.12	PMF	Secondary sulfate (30.0%), vehicular emission (26.9%), biomass burning (9.8),	Huang et al. (2014b)
	(Four seasons)		secondary nitrate (9.3%), high chloride (3.8%), heavy oil combustion (3.6%),	

Guangzhou	2015.1-2015.11	ME-2	Secondary sulfate (23%), secondary nitrate (11%), SOA (7%), vehicle	This study
	(Four seasons)		emissions (18%), industrial emissions (11%), biomass burning (8%), coal	
			burning (6%), fugitive dust (3%), ship emissions (2%) and aged sea salt (1%).	
Guangzhou	2014.1-2014.12	PMF	Secondary sulfate and biomass burning (38%), ship emissions (17%), coal	Tao et al. (2017)
	(Four seasons)		combustion (15%), traffic emissions (10%), secondary nitrate and chloride	
			(12%), soil dust (7%).	
Guangzhou	2015.1-2015.2	ME-2	Secondary sulfate (20%), secondary nitrate (16%), SOA (8%), vehicle	This study
	(Winter)		emissions (11%), industrial emissions (13%), biomass burning (6%), coal	
			burning (9%), fugitive dust (2%), ship emissions (1%) and aged sea salt (1%).	
Guangzhou	2013.1	ME-2	Secondary inorganic-rich (59.0%), secondary organic-rich (18.1%), traffic	Huang et al. (2014a)
	(Winter)		(8.6%), coal burning (3.4%), biomass burning (6.7%), cooking (0.8%), dust	
			related (3.4%).	
Dongguan	2013.12-2014.11	PMF	Secondary sulfate (20%), secondary nitrate (8%), SOA (10%), vehicle	Zou et al. (2017)
	(Four seasons)		emissions (21%), industrial emissions (7%), biomass burning (11%), coal	
			burning (5%), fugitive dust (8%), ship emissions (6%).	
Dongguan	2010.2-2012.12	PMF	Secondary sulfate (27%), secondary nitrate (19%), industrial emission (15%),	Wang et al. (2015)
	(Four seasons)		biomass burning (9%) and coal combustion (9%); ship emissions/sea salt,	
			vehicle exhaust, plastic burning and dust no more than 7%.	

sea salt (2.6%), dust (2.5%), metallurgical industry (2.1%)

417

418 **3.4** Identification of high-emission areas in the PRD in typical meteorological conditions

419 Fig. 7 shows the contributions of PM_{2.5} sources under southerly flow and northerly flow 420 conditions in the PRD, based on the classification of weather types in Section 2.2. Southerly flow primarily originated from the South China Sea and carried clean ocean air masses to the PRD with 421 overall PM_{2.5} values of 15 µg/m³. As shown in Fig. 7, secondary sulfate (19%), vehicle emissions 422 (15%) and biomass burning (11%) had higher contributions under southerly flow. In contrast, in 423 northerly flow, the level of PM_{2.5} (82 μ g/m³) was 4.5 times higher than that of southerly flow due 424 425 to the transport of polluted air masses southward from the north mainland. Under northerly flow, 426 secondary sulfate (18%) and biomass burning (10%) were still the major sources, but secondary 427 nitrate became the dominant source of PM2.5, accounting for 20% of PM2.5. In addition, industrial emissions also exhibited a relatively high contribution (14%). 428



429

430 Fig. 7. The contributions of PM_{2.5} sources under southerly flow and northerly flow conditions in the PRD.

431 The spatial distributions of the $PM_{2.5}$ sources under southerly flow and northerly flow are 432 shown in Fig. 8. The high-emission areas for different sources identified by the discussion below 433 are marked on the map in Fig. 9. The average concentration levels of aged sea salt were similar in the summer southerly flow and the winter northerly flow, reflecting local release of sea salt. The spatial distribution of aged sea salt among the different sites was a complex result of the site locations relative to the sea and meteorological conditions, e.g., wind and tide. A relatively high level of aged sea salt was observed at the Qi-Ao Island (QA), especially in the northerly flow, which can be attributed to that the QA site was surrounded by the sea and had lower wind speeds in the northerly flow (in Table 3).

440 The influences of ship emissions exhibited large differences between six sites, showing 441 significant local characteristics. In addition, the ship emissions have similar average 442 concentrations in the summer southerly flow and winter northerly flow, also reflecting the 443 emissions of local ports in the PRD region. The concentrations of ship emissions were the highest 444 at DP under southerly flow, mainly due to the impact of vessels in the upwind Yiantian Port, while 445 they were the highest at QA under northerly flow, primarily due to the effects of the upwind 446 Nansha Port, as shown in Fig. 9. Yantian Port and Nansha Port are among the ten largest ports in 447 the world (Hong Kong Marine Department, 2012).

The contributions of fugitive dust also exhibited significant differences between six sites, which are consistent with local construction activities. DM is located in a newly developed zone that has experienced relatively high levels of fugitive dust during southerly flow and northerly flow due to active construction activities. Sample records indicate that the high value of fugitive dust at UT under southerly flow maybe related to its surrounding short-term road construction project, while the high value at QA under northerly flow maybe related to the reconstruction project of the adjacent Nansha Port (Guangzhou Municipal People's Government, 2015).

Motor vehicles are a common source of air pollution in the highly urbanized and 455 456 industrialized PRD region. The average concentration of vehicle emissions during northerly flow 457 was nearly 3-fold that during southerly flow. Under southerly flow, MDS, HS and UT, which are located in the hinterland of the PRD, had much higher levels of vehicle emissions than the other 458 459 three sites; in particular, the highest level at the urban MDS site was caused by the high density of 460 motor vehicles in Guangzhou. Under northerly flow, the highest concentration of vehicle emissions was still at the urban MDS site, while QA also recorded the prominent contribution of 461 462 vehicle emissions, which was probably closely related to the container trucks in the neighboring 463 Nansha Port. It should be noted that the concentration of vehicle emissions at the background DP site exceeded half the regional average value, approaching 4 μ g/m³, thus indicating that vehicle 464 465 emissions had a significant impact on the regional transport of air masses from the north.

466 During southerly air flow, the background DP and QA sites and the urban UT site all 467 recorded similar concentrations of secondary sulfate, suggesting that the secondary sulfate at these sites was dominated by regional transport from the southern ocean with heavy vessel transport and 468 469 had little to do with the urban emissions at UT. Kuang et al. (2015) also found that ship emissions 470 could be a major source of secondary sulfate in the PRD in summer. HS and MDS had significantly higher concentrations than their upwind site, DM, suggesting that the area between 471 MDS and HS could be a high-SO₂-emission area, which is consistent with the fact that this area is 472 473 an intensive industrial area. During northerly air flow in winter, HS and DM had lower concentrations than the four upwind sites, i.e., MDS, QA, UT, and especially DP (the background 474 475 site), indicating that secondary sulfate could mainly be derived from regional transport from 476 outside the PRD in this season. Although the industrial area between HS and MDS could emit 477 significant amounts of SO₂, the lower temperatures and dry air in winter did not appear to favor the quick conversion of SO₂ to secondary sulfate. Since both secondary sulfate and LV-OOA
belong to a mixed factor with fixed proportions, the spatial distribution of secondary sulfate also
reflects the corresponding characteristics of LV-OOA.

481 The spatial distributions of coal burning were significantly different between the six sites 482 during periods of both south wind and north wind, thus showing conspicuous local characteristics. 483 The contribution of coal burning was higher at MDS under southerly flow and higher at HS under 484 northerly flow. Most of the coals in the PRD were consumed by thermal power plants, but there 485 were no coal-fired power plants near the urban MDS and background DP sites. Therefore, it is 486 speculated that the high-emission areas of coal burning sources mainly exist in the region between 487 HS and MDS, as shown in Fig. 9. The distributions of coal-fired power plants in Guangdong 488 (Wang et al. 2017) reveal that some important coal-fired power plants are distributed in this region. 489 Additionally, DM also exhibited relatively obvious contributions of coal burning during southerly 490 flow and northerly flow, which is also consistent with the distribution of coal-fired power plants in 491 the vicinity.

492 The average concentration of secondary nitrate during northerly flow in winter was 40 times greater than that during southerly flow in summer; this occurred not only because of the 493 494 unfavorable conditions of atmospheric diffusion in winter but also due to the high semi-volatility 495 of ammonium nitrate, which cannot stably exist in fine particles in the PRD during hot summer (Huang et al. 2006). Under southerly flow conditions, the concentrations of secondary nitrate 496 497 presented prominent differences between six sites, showing local characteristics. Moreover, the 498 relatively low concentrations at the background DP site during northerly flow also indicated that secondary nitrate mainly originated from the interior of the PRD. The spatial distribution 499 500 characteristics of secondary nitrate were very similar to those of coal burning, with the highest 501 occurring at MDS under southerly flow, the highest occurring at HS under northerly flow and 502 significantly high values occurring at DM under southerly and northerly flow, displaying that the 503 NOx emissions produced by coal burning maybe the main reason for the high nitrate levels in 504 those areas. Since both secondary nitrate and SV-OOA belong to a mixed factor with fixed 505 proportions, the spatial distribution of secondary nitrate also reflects the corresponding 506 characteristics of SV-OOA.

507 Under southerly flow, the influence of industrial emissions differed vastly between six sites, showing obvious local characteristics. Under northerly flow, the average concentration of 508 509 industrial emissions reached 14-fold that of southerly flow, and the high contributions at 510 background DP suggested that regional transport probably dominated the industrial sources of fine 511 particulate matter in the PRD in winter. HS had the highest concentration of industrial emissions during southerly flow and northerly flow conditions, which is consistent with the dense factories 512 513 present in the surrounding area (Hu, 2004; Environmental Protection Agency of Jiangmen City, 514 2017). In addition, the contribution of industrial emissions was relatively high at MDS during southerly flow and relatively high at QA during northerly flow, which supports the inference that a 515 high-emission region of industrial sources was located between MDS and QA, as seen in Fig. 9. 516

517 The impacts of biomass burning exhibited relatively large differences between six sites 518 during both south and north wind conditions, presenting somewhat local characteristics. Suburban 519 HS site had relatively high biomass burning levels during southerly flow and northerly flow, 520 which should be related to the presence of many farmlands in its vicinity and thus the popular 521 events of open burning and residential burning of biomass wastes. The concentrations of biomass burning were relatively high at the urban MDS site during southerly flow and relatively high at the background QA site during northerly flow, implying that there was a high-emission area of biomass burning between MDS and QA, as shown in Fig. 9. Those spatial distribution characteristics of biomass burning were similar to those of industrial emissions in the PRD, suggesting that not only the combustion of residential biomass but also the use of industrial biomass-boilers could make important contributions to PM_{2.5} in the PRD.

As a summary, the central PRD area, i.e., the middle region between MDS, HS and QA (the shaded region in Fig. 9), represents the most important pollutant emissions area in the PRD; these emissions include SO₂, NOx, coal burning, biomass burning, industrial emissions and vehicle emissions, thus leading to high pollution levels in the PRD. Therefore, this area is a key area for pollution control in the PRD. Primary fine particulate matter and SO₂ from ship emissions had significant impacts on PM_{2.5} in the southern coastal area of the PRD during summer southerly flow, and special attention must be paid to them.



535



537 northerly flow.



Fig. 9. The schematic diagram of high-emission areas in the PRD (map from Google Earth). The white shaded area
indicates the key emission area for the multiple sources of SO₂, NOx, coal burning, biomass burning, industrial
emissions and vehicle emissions, and is explained further in the text.

542 **3.5** Distinguishing local and regional PM_{2.5} pollution in the PRD

538

543 The analyses presented in Section 3.4 indicate that the secondary sulfates at the four southern coastal sites (DM, QA, UT and DP) in the PRD were almost entirely derived from the conversion 544 of SO_2 from the emissions of ships in the southern ocean during southerly flow, contributing 545 546 approximately 20% of the average $PM_{2.5}$ (13 µg/m³) at the four sites. Considering that the ship emissions directly contributed approximately 10% of the average $PM_{2.5}$ at the four sites, the total 547 548 ship emissions contributed approximately 30% of PM2.5 in the southern coastal PRD area and 549 acted as the largest source of PM_{2.5}. Under northerly flow conditions, the background DP site, 550 which was barely affected by pollution emissions within the PRD, reflected regional transport from the north air mass outside the PRD, while the background QA site reflected the superposition 551 effect of regional background pollution and the input of the most serious pollution area in the PRD. 552 553 The consistency of the secondary sulfate concentrations at the background QA and DP sites was interpreted to reflect almost the same regional background effect during northerly flow; thus, the 554 differences in the six anthropogenic sources between the two background sites, including 555 secondary nitrate (and SV-OOA), biomass burning, industrial emissions, coal burning, vehicle 556 557 emissions and ship emissions, could be used to trace the internal inputs from the most serious pollution area within the PRD to the downwind area. The internal inputs of six anthropogenic 558 559 sources to the corresponding sources of PM_{2.5} at the background QA site were 66%, 67%, 28%, 560 76%, 59% and 75%, respectively, and the total internal input of 37.7 μ g/m³ accounted for 45% of 561 $PM_{2.5}$ at the background QA site (83 μ g/m³), showing that the local contributions of anthropogenic 562 pollution emissions in the key source area of the PRD were still crucial in winter but lower than the contribution of the regional background. Ignoring natural sources, such as aged sea salt and 563

fugitive dust, under northerly flow, the contributions of other anthropogenic sources to DP were 564 considered to represent regional background pollution (47.5 μ g/m³), and the differences in their 565 corresponding source concentrations between QA and DP were expected to represent the local 566 emissions of source areas in the PRD. Therefore, the source structures in the regional background 567 568 air mass and local emissions of heavy pollution sources area in the PRD are shown in Fig. 10. 569 Secondary sulfate and LV-OOA occupied the vast majority (45.6%) of the regional background air 570 mass from the northern mainland, followed by industrial emissions (17.8%), secondary nitrate and SV-OOA (15.5%). However, the major sources between the sources output by local emissions 571 from the heavy pollution source area of the PRD were secondary nitrate and SV-OOA (37.3%), 572 biomass burning (20.6%), vehicle emissions (14.9%) and coal burning (11.9%). Therefore, 573 574 measures implemented for the effective control of PM2.5 in the PRD should focus on local controls 575 and regional joint prevention and control under winter northerly flow conditions.



576

577 Fig. 10. The PM_{2.5} source structures in regional background air and local contributions of the central PRD area578 under northerly flow.

579

580 4 Conclusions

The PRD is one of the largest agglomeration of cities in the world, and its air quality has largely improved in the past ten years. To reveal the current $PM_{2.5}$ pollution characteristics on a regional scale in the PRD, six sampling sites were selected to conduct four months (one for each season) of sampling and chemical analysis in 2015; then, the source exploration of $PM_{2.5}$ was performed using a novel method. The conclusions are described below.

586 (1) The 4-month average $PM_{2.5}$ concentration for all six sites in the PRD was 37 µg/m³, of which 587 OM, $SO_4^{2^-}$, NH_4^+ , NO_3^- , EC, metal elements and Cl⁻ contributed 36.9%, 23.6%, 10.9%, 9.3%, 588 6.6%, 6.5% and 0.9%, respectively. The tempo-spatial $PM_{2.5}$ variations were generally 589 characterized as being higher in the north inland region and higher in winter.

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

(3) Based on the spatial distribution characteristics of PM_{2.5} sources under typical southerly and
northerly airflow conditions, the central PRD area between MDS, HS and QA is identified as a
key area for source emissions, including SO₂, NOx, coal burning, biomass burning, industrial

emissions and vehicle emissions, and thus deserves more attention when implementing local pollution control in the PRD. In addition, ship emissions should be controlled more strictly during summer due to its contribution of approximately 30% of $PM_{2.5}$ in the southern coastal area of the PRD under southerly air flow.

603 (4) Under typical winter northerly flow, the contributions of anthropogenic pollution emissions in 604 the central PRD area contributed 37.7 μ g/m³ (45% of PM_{2.5}) to the regional background air. 605 Secondary sulfate (36.9%), industrial emissions (17.8%), and secondary nitrate SV-OOA (12.8%) 606 were the major PM_{2.5} sources for the PM_{2.5} transported in the regional background air mass, while 607 secondary nitrate (30.9%), biomass burning (20.6%), vehicle emissions (14.9%) and coal burning

- (11.9%) were the major sources for the PM_{2.5} produced in the central PRD area. Therefore, effective control measures of PM_{2.5} in the PRD in the future should pay more attention to both local controls and regional joint prevention.
- 611

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617 References

- BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, and OIML: Evaluation of measurement data -- Guide
 to the expression of uncertainty in measurement, https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf , 2008.
- Bressi, M., Sciare, J., Ghersi, V., Bonnaire, N., Nicolas, J. B., Petit, J. E., Moukhtar, S., Rosso, A.,
 Mihalopoulos, N., Féron, A.: A one-year comprehensive chemical characterisation of fine aerosol
- 623 (PM_{2.5}) at urban, suburban and rural background sites in the region of Paris (France), Atmos. Chem.

624 Phys., 15, 7825-7844, doi: 10.5194/acp-13-7825-2013, 2013.

- 625 Burnett, R. T., Pope, C. A. I., Ezzati, M., Olives, C., Lim, S. S., Mehta, S., Shin, H. H., Singh, G.,
- Hubbell, B., Brauer, M., Anderson, H. R., Smith, K. R., Balmes, J. R., Bruce, N. G., Kan, H., Laden,
- 627 F., Prüss-Ustün, A., Turner, M. C., Gapstur, S. M., Diver, W. R., and Cohen, A.: An Integrated Risk
- Function for Estimating the Global Burden of Disease Attributable to Ambient Fine Particulate
 Matter Exposure, Environ. Health Persp., 122, A235-A235, doi: 10.1289/ehp.122-A235, 2014.
- Canonaco, F., Crippa, M., Slowik, J. G., Baltensperger, U., and Pr év ôt, A. S. H.: SoFi, an IGOR-based
 interface for the efficient use of the generalized multilinear engine (ME-2) for the source
 apportionment: ME-2 application to aerosol mass spectrometer data, Atmos. Meas. Tech., 6,
 3649-3661, doi: 10.5194/amt-6-3649-2013, 2013.
- Cao, L. M., Huang, X. F., Li, Y. Y., Hu, M., and He, L. Y.: Volatility measurement of atmospheric
 submicron aerosols in an urban atmosphere in southern China, Atmos. Chem. Phys., 18, 1729-1743,
 dio: 10.5194/acp-18-1729-2018, 2018.
- Cho, S. H., Kim, P. R., Han, Y. J., Kim, H. W., and Yi, S. M.: Characteristics of Ionic and
 Carbonaceous Compounds in PM_{2.5} and High Concentration Events in Chuncheon, Korea, J. Korean
 Soc. Atmos. Environ., 32, 435-447, doi: 10.5572/KOSAE.2016.32.4.435, 2016.
- 640 Chow, J. C., and Watson, J. G.: Review of PM_{2.5} and PM₁₀ Apportionment for Fossil Fuel Combustion
- and Other Sources by the Chemical Mass Balance Receptor Model, Energ. Fuel., 16, 222-260, doi:
- 642 10.1021/ef0101715, 2002.

- Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The DRI
 thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S.
- 645 Air quality studies, Atmos. Environ., 27, 1185-1201, dio: 10.1016/0960-1686(93)90245-T, 1993.
- 646 Crippa, M., Canonaco, F., Lanz, V. A., Äij äl ä, M., Allan, J. D., Carbone, S., Capes, G., Ceburnis, D.,
- 647 Dall'Osto, M., Day, D. A., DeCarlo, P. F., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L.,

Hillamo, R., Jimenez, J. L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A. M., Kulmala, M.,

- Laaksonen, A., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N.,
- 650 Pet äjä, T., Poulain, L., Saarikoski, S., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D. R.,
- Baltensperger, U., and Pr év ôt, A. S. H.: Organic aerosol components derived from 25 AMS data sets
 across Europe using a consistent ME-2 based source apportionment approach, Atmos. Chem. Phys.,
 14, 6159-6176, doi: 10.5194/acp-14-6159-2014, 2014.
- Elser, M., Huang, R., Wolf, R., Slowik, J. G., Wang, Q., Canonaco, F., Li, G., Bozzetti, C.,
 Daellenbach, K. R., Huang, Y., Zhang, R., Li, Z., Cao, J., Baltensperger, U., El-Haddad, I., and
 Pr év ôt, A. S. H.: New insights into PM_{2.5} chemical composition and sources in two major cities in
 China during extreme haze events using aerosol mass spectrometry, Atmos. Chem. Phys., 16,
 3207-3225, doi: 10.5194/acp-16-3207-2016, 2016.
- Environmental Protection Agency of Jiangmen City: Key pollution sources basic information in
 Jiangmen, http://hbj.jiangmen.gov.cn/thirdData/hbsjzx/hjjc/fs/201712/t20171218_268676.html,
 2017.
- 662 Fröhlich, R., Crenn, V., Setyan, A., Belis, C. A., Canonaco, F., Favez, O., Riffault, V., Slowik, J. G., Aas, W., Aij ä ä, M., Alastuey, A., Arti ñano, B., Bonnaire, N., Bozzetti, C., Bressi, M., Carbone, C., 663 664 Coz, E., Croteau, P. L., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., 665 Herrmann, H., Javne, J. T., Lunder, C. R., Minguillón, M. C., Močnik, G., O'Dowd, C. D., 666 Ovadnevaite, J., Petralia, E., Poulain, L., Priestman, M., Ripoll, A., Sarda-Estève, R., Wiedensohler, A., Baltensperger, U., Sciare, J., and Prévât, A. S. H.: ACTRIS ACSM intercomparison – Part 2: 667 668 Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located 669 aerosol mass spectrometers, Atmos. Meas. Tech., 8, 2555-2576, doi: 10.5194/amt-8-2555-2015, 670 2015.
- Gao, B., Guo, H., Wang, X., Zhao, X., Ling, Z., Zhang, Z., and Liu, T.: Tracer-based source
 apportionment of polycyclic aromatic hydrocarbons in PM_{2.5} in Guangzhou, southern China, using
 positive matrix factorization (PMF), Environ. Sci. Pollut. R., 20, 2398-2409, doi:
 10.1007/s11356-012-1129-0, 2013.
- Guangzhou Environmental Protection Bureau: The Results of Source apportionment on PM_{2.5} in
 Guangzhou in 2016,
- 677 http://www.gz.gov.cn/gzgov/s5837/201706/1dcb25be6dd14dc6ab6506e0a5383745.shtml, 2017.
- 678Guangzhou Municipal People's Government: Three-year Action Plan for the Construction of679GuangzhouInternationalShippingCenter(2015-2017),620Construction of Construction of Constructio
- 680 http://www.gz.gov.cn/gzgov/s2811/201509/19601daa69c84e439fe2fb8baea448bb.shtml, 2015.
- Hagler, G., Bergin, M., Salmon, L., Yu, J., Wan, E., Zheng, M., Zeng, L., Kiang, C., Zhang, Y., and
 Lau, A.: Source areas and chemical composition of fine particulate matter in the Pearl River Delta
 region of China, Atmos. Environ., 40, 3802-3815, doi: 10.1016/j.atmosenv.2006.02.032, 2006.
- 684 Hasheminassab, S., Daher, N., Ostro, B. D., and Sioutas, C.: Long-term source apportionment of
- ambient fine particulate matter (PM_{2.5}) in the Los Angeles Basin: A focus on emissions reduction
- from vehicular sources, Environ. Pollut., 193, 54-64, doi: 10.1016/j.envpol.2014.06.012, 2014.

- He, L., Huang, X., Xue, L., Hu, M., Lin, Y., Zheng, J., Zhang, R., and Zhang, Y.: Submicron aerosol
 analysis and organic source apportionment in an urban atmosphere in Pearl River Delta of China
 using high-resolution aerosol mass spectrometry, J. Geophys. Res.-Atmos., 116, doi:
 10.1029/2010JD014566, 2011.
- Hong Kong Marine Department: Ranking of container ports of the world,
 https://www.mardep.gov.hk/hk/publication/pdf/portstat_2_y_b5c.pdf, 2012.
- Hu, Z. Y.: Studies on the Discharging and Distribution of Heavy Metal Pollution in the Pearl River
- 694 Delta, Doctoral dissertation, Graduate School of the Chinese Academy of Sciences (Guangzhou
- Institute of Geochemistry), 2004.
- Huang, R., Zhang, Y., Bozzetti, C., Ho, K., Cao, J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S.
 M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G.,
 Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z.,
 Szidat, S., Baltensperger, U., Haddad, I. E., and Prévôt, A. S. H.: High secondary aerosol
 contribution to particulate pollution during haze events in China, Nature, 514, 218-222, doi:
 10.1038/nature13774, 2014a.
- Huang, X.F., He, L. Y., Hu, M., Canagaratna, M. R., Kroll, J. H., Ng, N. L., Zhang, Y. H., Lin, Y.,
 Xue, L., Sun, T. L., Liu, X. G., Shao, M., Jayne, J. T., Worsnop, D. R. Characterization of submicron
 aerosols at a rural site in Pearl River Delta of China using an Aerodyne High-Resolution Aerosol
 Mass Spectrometer. Atmos. Chem. Phys., 11(5), 1865 –1877, 2011.
- Huang, X. F., Hui, Y., Gong, Z. H., Xiang, L., He, L. Y., Zhang, Y. H., and Min, H.: Source apportionment and secondary organic aerosol estimation of PM_{2.5} in an urban atmosphere in China, Sci. China Earth Sci., 57, 1352-1362, doi: 10.1007/s11430-013-4686-2, 2014b.
- Huang, X., Liu, Z., Liu, J., Hu, B., Wen, T., Tang, G., Zhang, J., Wu, F., Ji, D., and Wang, L.:
 Chemical characterization and source identification of PM_{2.5} at multiple sites in the
 Beijing-Tianjin-Hebei region, China, Atmos. Chem. Phys., 17, 12941-12962, doi:
 10.5194/acp-17-12941-2017, 2017.
- Huang, X., Yu, J. Z., He, L., and Yuan, Z.: Water-soluble organic carbon and oxalate in aerosols at a
 coastal urban site in China: Size distribution characteristics, sources, and formation mechanisms, J.
 Geophys. Res.-Atmos., 111, doi: 10.1029/2006JD007408, 2006.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S., Zhang, Q., Kroll, J. H., Decarlo, P.
 F., Allan, J. D., Coe, H., and Ng, N. L.: Evolution of organic aerosols in the atmosphere, Science,
- 718
 326, 1525-1529, doi: 10.1126/science.1180353, 2009.
- Kuang, B. Y., Lin, P., Huang, X. H. H., and Yu, J. Z.: Sources of humic-like substances in the Pearl
 River Delta, China: positive matrix factorization analysis of PM_{2.5} major components and source
 markers, Atmos. Chem. Phys., 15, 1995-2008, doi: 10.5194/acp-15-1995-2015, 2015.
- 722 Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.:
- Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling
 of aerosol mass spectra, Atmos. Chem. Phys., 7, 1503-1522, doi: 10.5194/acp-7-1503-2007, 2007.
- Leiva, M. A., Araya, M. C., Alvarado, A. M., and Seguel, R. J.: Uncertainty estimation of anions and cations measured by ion chromatography in fine urban ambient particles (PM_{2.5}), Accredit. Qual. Assur., 17, 53-63, doi: 10.1007/s00769-011-0844-4, 2012.
- 728 Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., and Pozzer, A.: The contribution of outdoor air
- pollution sources to premature mortality on a global scale, Nature, 525, 367-371, doi:
 10.1038/nature15371, 2015.

- Liu, J., Li, J., Zhang, Y., Liu, D., Ding, P., Shen, C., Shen, K., He, Q., Ding, X., and Wang, X.: Source
 apportionment using radiocarbon and organic tracers for PM_{2.5} carbonaceous aerosols in Guangzhou,
 South China: contrasting local- and regional-scale haze events, Environ. Sci. Technol., 48, 12002,
- doi: 10.1021/es503102w, 2014.
- Mason, B., Principles of Geochemistry, 2nd edition, John Wiley and Sons, 1982.
- Ming, L., Jin, L., Li, J., Fu, P., Yang, W., Liu, D., Zhang, G., Wang, Z., and Li, X.: PM_{2.5} in the
 Yangtze River Delta, China: Chemical compositions, seasonal variations, and regional pollution
 events, Environ. Pollut., 223, 200-212, doi: 10.1016/j.envpol.2017.01.013, 2017.
- Ministry of Ecology and Environment (MEE): Ambient Air-Determination of the water soluble anions
 (F⁻ 、 Cl⁻、 Br⁻、 NO₂⁻、 NO₃⁻、 PO₄⁻、 SO₃⁻ 2、 SO₄⁻ 2) from atmospheric particles-Ion chromatography
- 741 (HJ 799-2016), http://kjs.mep.gov.cn/hjbhbz/bzwb/jcffbz/201605/t20160519_337906.shtml, 2016a.
- Ministry of Ecology and Environment (MEE): Ambient air-Determination of the water soluble
 cations(Li⁺ 、 Na⁺ 、 NH₄⁺ 、 K⁺ 、 Ca^{*} 、 Mg^{*}) from atmospheric particles-Ion chromatography (HJ
 800-2016), http://kjs.mep.gov.cn/hjbhbz/bzwb/jcffbz/201605/t20160519_337907.shtml, 2016b.
- 745Ministry of Ecology and Environment (MEE): Ambient air and stationary source emission -746Determination of metals in ambient particulate matter -747spectrometry748(ICP-MS)749(HJ657-2013),
- 748 http://kjs.mep.gov.cn/hjbhbz/bzwb/jcffbz/201308/t20130820_257714.shtml, 2013a.
- Ministry of Ecology and Environment (MEE): Technical Specifications for gravimetric measurement
 methods for PM_{2.5} in ambient air (HJ 656-2013),
 http://kjs.mep.gov.cn/hjbhbz/bzwb/jcffbz/201308/t20130802_256857.shtml, 2013b.
- Ministry of Environmental Protection: Report on the State of the Environment in China 2015,
 http://www.zhb.gov.cn/hjzl/zghjzkgb/lnzghjzkgb/201606/P020160602333160471955.pdf, 2016.
- Norris, G., and Duvall, R.: EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and user guide,
 https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf , 2014.
- Nanfang Daily: PM_{2.5} level fluctuations down in PRD region in the past decade,
 http://epaper.southcn.com/nfdaily/html/2016-01/03/content_7504954.htm, 2016.
- 758 Paatero, P., and Tapper, U.: Positive matrix factorization: A non - negative factor model with optimal 759 utilization of error estimates of data values, Environmetrics, 5, 111-126, doi: 760 10.1002/env.3170050203, 1994.
- Paatero, P.: The Multilinear Engine—A Table-Driven, Least Squares Program for Solving Multilinear
 Problems, Including the n-Way Parallel Factor Analysis Model, J. Comput. Graph. Stat., 8, 854-888,
 doi: 10.1080/10618600.1999.10474853, 1999.
- People's Government of Guangdong Province: Major Pollutants Emission Reduction implementation
 plan during the 12th Five-year Plan in Guangdong Province,
 http://zwgk.gd.gov.cn/006939748/201212/t20121219_359131.html, 2012.
- People's Government of Shenzhen Municipality: Air quality improvement plan in Shenzhen,
 http://zwgk.gd.gov.cn/007543382/201309/t20130930_407564.html, 2013.
- Physick, W. L., and Goudey, R.: Estimating an annual-average RSP concentration for Hong Kong using days characteristic of the dominant weather patterns, Atmos. Environ., 35, 2697-2705, doi: 10.1016/S1352-2310(00)00413-1, 2001.
- 772 Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., and Sisler, J. F.: Atmospheric aerosol over
- Alaska: 2. Elemental composition and sources, J. Geophys. Res.-Atmos., 103, 19045 19057, 1998.
- 774 Reyes-Villegas, E., Green, D. C., Priestman, M., Canonaco, F., Coe, H., Pr év ôt, A. S. H., and Allan, J.

- D.: Organic Aerosol source apportionment in London 2013 with ME-2: exploring the solution space
 with annual and seasonal analysis, Atmos. Chem. Phys., 16, 15545-15559, doi:
 10.5194/acp-16-15545-2016, 2016.
- Rodr guez, S., Van Dingenen, R., Putaud, J.-P., Dell'Acqua, A., Pey, J., Querol, X., Alastuey, A.,
 Chenery, S., Ho, K.-F., Harrison, R., Tardivo, R., Scarnato, B., and Gemelli, V.: A study on the
 relationship between mass concentrations, chemistry and number size distribution of urban fine
 aerosols in Milan, Barcelona and London, Atmos. Chem. Phys., 7, 2217-2232, doi:
 10.5194/acp-7-2217-2007, 2007.
- 783 Sarnat, J. A., Marmur, A., Klein, M., Kim, E., Russell, A. G., Sarnat, S. E., Mulholland, J. A., Hopke, P.
- K., and Tolbert, P. E.: Fine Particle Sources and Cardiorespiratory Morbidity: An Application of
 Chemical Mass Balance and Factor Analytical Source-Apportionment Methods, Environ. Health
 Persp., 116, 459-66, doi: 10.1289/ehp.10873, 2008.
- Tan, J., Duan, J., Ma, Y., He, K., Cheng, Y., Deng, S., Huang, Y., and Si-Tu, S.: Long-term trends of
 chemical characteristics and sources of fine particle in Foshan City, Pearl River Delta: 2008–2014,
 Sci. Total Environ., 565, 519-528, doi: 10.1016/j.scitotenv.2016.05.059, 2016.
- 790 Tao, J., Zhang, L., Cao, J., Zhong, L., Chen, D., Yang, Y., Chen, D., Chen, L., Zhang, Z., Wu, Y., Xia,
- Y., Ye, S., and Zhang, R.: Source apportionment of PM_{2.5} at urban and suburban areas of the Pearl
 River Delta region, south China With emphasis on ship emissions, Sci. Total Environ., 574,
 1559-1570, doi: 10.1016/j.scitotenv.2016.08.175, 2017.
- Taylor, S. R., and Mclennan, S. M.: The geochemical evolution of the continental crust, Rev. Geophys.,
 33, 293-301, doi: 10.1029/95RG00262, 1995.
- Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos.
 Chem. Phys., 9, 2891-2918, doi: 10.5194/acp-9-2891-2009, 2009.
- Villalobos, A. M., Barraza, F., Jorquera, H., and Schauer, J. J.: Chemical speciation and source apportionment of fine particulate matter in Santiago, Chile, 2013, Sci. Total Environ., 512-513, 133-142, doi: 10.1016/j.scitotenv.2015.01.006, 2015.
- **1**55 142, **u**01. 10.1010/j.seltoteliv.2015.01.000, 2015.
- Visser, S., Slowik, J. G., Furger, M., Zotter, P., Bukowiecki, N., Canonaco, F., Flechsig, U., Appel, K.,
 Green, D. C., Tremper, A. H., Young, D. E., Williams, P. I., Allan, J. D., Coe, H., Williams, L. R.,
- Mohr, C., Xu, L., Ng, N. L., Nemitz, E., Barlow, J. F., Halios, C. H., Fleming, Z. L., Baltensperger,
- 805 U., and Pr év $\hat{\alpha}$, A. S. H.: Advanced source apportionment of size-resolved trace elements at multiple 806 sites in London during winter, Atmos. Chem. Phys., 15, 11291-11309, doi: 807 10.5194/acp-15-11291-2015, 2015.
- Wang, H., Tian, M., Chen, Y., Shi, G., Liu, Y., Yang, F., Zhang, L., Deng, L., Yu, J., and Peng, C.:
 Seasonal characteristics, formation mechanisms and source origins of PM_{2.5} in two megacities in
- 810 Sichuan Basin, China, Atmos. Chem. Phys., 18, 865-881, doi: 10.5194/acp-18-865-2018, 2018.
- Wang, J., Ho, S. S. H., Ma, S., Cao, J., Dai, W., Liu, S., Shen, Z., Huang, R., Wang, G., and Han, Y.:
 Characterization of PM_{2.5} in Guangzhou, China: uses of organic markers for supporting source
 apportionment, Sci. Total Environ., 550, 961-971, doi: 10.1016/j.scitotenv.2016.01.138, 2016.
- Wang, Q. Q., Huang, X. H. H., Zhang, T., Zhang, Q., Feng, Y., Yuan, Z., Wu, D., Lau, A. K. H., and
 Yu, J. Z.: Organic tracer-based source analysis of PM_{2.5} organic and elemental carbon: A case study
 at Dongguan in the Pearl River Delta, China, Atmos. Environ., 118, 164-175, doi:
 10.1016/j.atmosenv.2015.07.033, 2015.
- 818 Wang, Q., Feng, Y., Huang, X. H. H., Griffith, S. M., Zhang, T., Zhang, Q., Wu, D., and Yu, J. Z.: Non

- Polar organic compounds as PM_{2.5} source tracers: Investigation of their sources and degradation in
 the Pearl River Delta, China, J. Geophys. Res.-Atmos., 121, 11862-11879, doi:
 10.1002/2016JD025315, 2017.
- Yamasoe, M. A., Artaxo, P., Miguel, A. H., and Allen, A. G.: Chemical composition of aerosol
 particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and
 trace elements, Atmos. Environ., 34, 1641-1653, doi: 10.1016/S1352-2310(99)00329-5, 2000.
- 825 Yuan, Z., Lau, A., Zhang, H., Yu, J., Louie, P., and Fung, J.: Identification and spatiotemporal
- variations of dominant PM10 sources over Hong Kong, Atmos. Environ., 40, 1803-1815, doi:
- 827 10.1016/j.atmosenv.2005.11.030, 2006a.
- Yuan, Z. B., Yu, J. Z., Lau, A. K. H., Louie, P. K. K., and Fung, J. C. H.: Application of positive matrix factorization in estimating aerosol secondary organic carbon in Hong Kong and its relationship with secondary sulfate, Atmos. Chem. Phys., 6, 25-34, doi: 10.5194/acp-6-25-2006, 2006b.
- 832 Zou, B. B., Huang, X. F., Zhang, B., Dai, J., Zeng, L. W., Feng, N., and He, L. Y.: Source
- apportionment of PM_{2.5} pollution in an industrial city in southern China, Atmos. Pollut. Res., 8,
- 834 1193-1202, doi: 10.1016/j.apr.2017.05.001, 2017.