

Sources of excess urban carbonaceous aerosol in the Pearl River Delta Region, China

Mei Zheng^a, Fu Wang^a, G.S.W. Hagler^b, Ximei Hou^a, Michael Bergin^{a,c}, Yuan Cheng^a, L.G. Salmon^d, James J. Schauer^e, Peter K.K. Louie^f, Limin Zeng^g, Yuanhang Zhang^{g,*}

^aSchool of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA

^bUS EPA, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC 27711, USA

^cSchool of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^dEnvironmental Quality Laboratory, California Institute of Technology, Pasadena, CA 91125, USA

^eCivil and Environmental Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

^fEnvironmental Protection Department, Hong Kong Special Administrative Region of the People's Republic of China, PR China

^gCollege of Environmental Sciences and Engineering, Peking University, Beijing, PR China

ARTICLE INFO

Article history:

Received 25 April 2010

Received in revised form

2 September 2010

Accepted 18 September 2010

Keywords:

Organic carbon

Source apportionment

Molecular markers

Chemical mass balance

The Pearl River Delta

ABSTRACT

Carbonaceous aerosol is one of the important constituents of fine particulate matter (PM_{2.5}) in southern China, including the Pearl River Delta (PRD) region and Hong Kong (HK). During the study period (October and December of 2002, and March and June of 2003), the monthly average organic carbon (OC) ranged from 3.52 to 7.87 $\mu\text{g m}^{-3}$ in Hong Kong and 4.14–20.19 $\mu\text{g m}^{-3}$ in the PRD from simultaneous measurements at three sites in HK and four sites in the PRD. Compared to the PRD, the spatial distribution of carbonaceous aerosol in Hong Kong was relatively homogeneous. Sources contributing to excess OC in the PRD were examined, which is the difference between OC concentrations measured at the PRD sites to the average level in Hong Kong. Eight primary sources contributing to excess OC were identified with chemical mass balance modeling in a combination with molecular markers analyzed by gas chromatography/mass spectrometry. Excess OC at Guangzhou, the capital city of Guangdong province, was consistently high, ranging from 9.77 to 13.6 $\mu\text{g m}^{-3}$. Four primary sources including gasoline engine exhaust, diesel engine exhaust, biomass burning, and coal combustion accounted for more than 50% of excess OC in the PRD, especially in December (up to 76%). Mobile source emissions alone can contribute about 30% of excess OC. The unexplained or other excess OC was the highest at the rural site, but in general less than 20% at other sites. The coal combustion source contribution was unique in that it exhibited relatively homogeneous spatial distribution, indicating it was still an important source of carbonaceous aerosol in the PRD (17% of excess OC) during the study period. This analysis revealed that primary emissions are important sources of excess OC in the PRD and there is a need to reduce the emissions of mobile sources, biomass burning, and coal combustion in order to improve air quality in southern China.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The Pearl River Delta (PRD) in China refers to the regions or cities alongside the Pearl River Estuary where the Pearl River flows into the South China Sea. Nine cities in Guangdong Province, including Guangzhou and Shenzhen, are also often referred to as the PRD, which has become one of the leading economic areas in China. With a total area covering less than 0.5% of China and a population of about 4% of the Chinese total, the PRD accounts for

19% of the total GDP in China (Zhang et al., 2008a). This is a highly urbanized region including three large population cities: Guangzhou (~10 million), Hong Kong (~7 million) and Shenzhen (~4 million) (Wang et al., 2003). With such rapid increase in both economy and population, it is not surprising that the air quality in the PRD has deteriorated rapidly.

The PRD along with two other major city clusters in China (Beijing-Tianjin and Yangtze River Delta) have suffered from high concentrations of PM_{2.5} and ozone (Zhang et al., 2008a). Numerous studies have shown that these pollutants can cause adverse impacts on human health, visibility, climate change, and even crop production (Chameides and Bergin, 2002; Deng et al., 2008; Pope et al., 2002). In Guangzhou, the largest city in the PRD, only a few

* Corresponding author. Tel.: +86 10 62756592; fax: +86 10 62751927.

E-mail address: yhzhang@pku.edu.cn (Y.H. Zhang).

days per year exhibited low visibility (<10 km) between 1954 and 1972. After 1980 visibility degraded quickly (up to 150 days per year) and fine particulate matter (PM), especially those <1 μm in radius, contributed to 70% of the visibility reduction (Deng et al., 2008) and up to 93% in episodic days (Cheng et al., 2008). In Guangzhou, a clear and positive correlation was found between aerosol extinction coefficient and mortality associated with lung cancer (Tie et al., 2009). For $\text{PM}_{2.5}$ pollution, there were few studies in the PRD before 2000, while it became a major concern in recent years (Wang et al., 2005; Zhang et al., 2008b).

The PRD region is under the influence of the Asian Monsoon with the prevailing wind as southwesterly in summer and north-easterly in winter, resulting in inevitable cross-boundary pollution. For example, Lau et al. (2007) reported that regional air masses from upwind Guangdong impacted Hong Kong 36% of the time in a year (132 days) while 53% of the time local air masses dominated. The assessment of the number of days or the extent of regional impact, to some extent, depends on the approaches applied. Compared to Hong Kong, the Pearl River Delta Economic Zone contributed significantly to the emissions in this region based on an emission inventory approach (95% of PM_{10} , 88% of VOC, 87% of SO_2 , and 80% of NO_x) (CH2M HILL, 2002). Organic matter is one of the most important constituents of $\text{PM}_{2.5}$ in this region, accounting for 24–35% of $\text{PM}_{2.5}$ mass (Hagler et al., 2006). This is not surprising considering the rapid economic growth in this region and the significant consumption of fossil fuel and biofuel. In order to develop effective control strategies for $\text{PM}_{2.5}$, it is critical to understand what sources contribute to the excess part of carbonaceous aerosol over Hong Kong since the PRD contributed more than 90% of PM emissions in this region. It has been well recognized that without speciation analysis, it is difficult to conclude what sources cause high OC concentrations in ambient aerosol. A recent special issue published various findings of an air quality study in the PRD (Zhang et al., 2008a), although the contributions of specific sources to particulate OC concentrations are not fully addressed.

Therefore, in this study, the major goal is to better understand source contributions to excess OC in the PRD, defined by the difference between the levels in the PRD and the average in Hong Kong. The method using molecular markers in a chemical mass balance model (CMB-MM) allows quantifying source impacts from individual sources to OC. Among the compounds that can be identified by gas chromatography/mass spectrometry (GC/MS) are important markers to pinpoint the major source types of OC including cholesterol in meat charbroiling smoke, hopanes and steranes from lubricating oil in motor vehicles, levoglucosan from cellulose breakdown in biomass smoke, pincene in coal combustion smoke etc. (Cass, 1998).

Most previous $\text{PM}_{2.5}$ -related studies have focused on major ions, EC and OC, whereas speciated data for organic carbon are very limited. A few previous studies aimed to assess the composition of organic matter in $\text{PM}_{2.5}$ in Hong Kong (Sin et al., 2005) or in size-segregated aerosols in Guangzhou (Bi et al., 2005) and Hong Kong (Zheng et al., 2000, 2008), but none was a regional-wide study, covering both Hong Kong and the PRD. This is the first effort to carry out simultaneous regional sampling for detailed molecular marker measurements in $\text{PM}_{2.5}$ in the PRD region and to conduct source apportionment of carbonaceous aerosol from regional sites with the same technique (CMB-MM), thus data from various sites can be directly compared. In addition, we measured a great number of organic compounds, providing rich information on the organic aerosol composition and the related sources in the PRD region.

Simultaneous $\text{PM}_{2.5}$ sampling was conducted at 7 sites in this region (4 in the PRD and 3 in Hong Kong) during four months of one year (October, December 2002; March, June 2003). Hagler et al. (2006, 2007) reported values for bulk carbonaceous fractions,

ionic, and elemental data from these $\text{PM}_{2.5}$ samples, while this study focuses on $\text{PM}_{2.5}$ organic speciation (up to 100 compounds) in order to better understand the sources of excess OC found at the sites in the PRD over Hong Kong. The overall objective of this work is to supply critical source apportionment data to be used for developing effective control strategies for carbonaceous aerosol and mitigating the adverse effects of air pollution in the PRD.

2. Methodology

2.1. Sampling

The details of the field sampling have been discussed elsewhere (Hagler et al., 2006). For every sixth day in each of the four months, $\text{PM}_{2.5}$ samples were collected over a 24 h period. $\text{PM}_{2.5}$ particles were collected on filter media installed in four parallel channels through a cyclone-based size selection with quartz fiber filter in one of the channels for organic speciation analysis. The flow rate was 16.7 L min^{-1} . Samples were collected simultaneously from three sites of Tap Mun (TM), Tung Chung (TC), and Central and Western (CW) in Hong Kong and four sites of Zhongshan (ZS), Shenzhen (SZ), Conghua (CH), and Guangzhou (GZ) in the PRD, of which TM and CH were background sites (indicated as “B” in Fig. 1), TC and ZS were receptor sites (“R”), and the rest were urban sites (“U”). Fig. 1 illustrates the locations of sampling sites.

The TM site, on top of a police station in Tap Mun Island, northeast of Hong Kong Island, is a background site with minimal anthropogenic local emissions. The TC site, on top of a medical clinic on Lantau Island, west of Hong Kong Island, is a site with residential high rises, schools, and airport nearby. The CW site, on top of a police station in north side of Hong Kong Island, is located in an urban area with dense residential and industry high rises surrounding. The SZ site, on top of the PKU/HKUST/Shenzhen University Building, is located north of Hong Kong. The site is in the university campus, surrounded by multi-story residential and nearby industrial buildings. The ZS site is located southwest of Guangzhou with the sampler placed on top of the air monitoring building at Zhongshan park, a public park in an urban area. The GZ site is located on top of the Guangzhou EPB building, representing an urban area with industrial and residential buildings nearby. The CH site is in a rural area and located on top of Jinhua hotel, Conghua, northeast of Guangzhou.

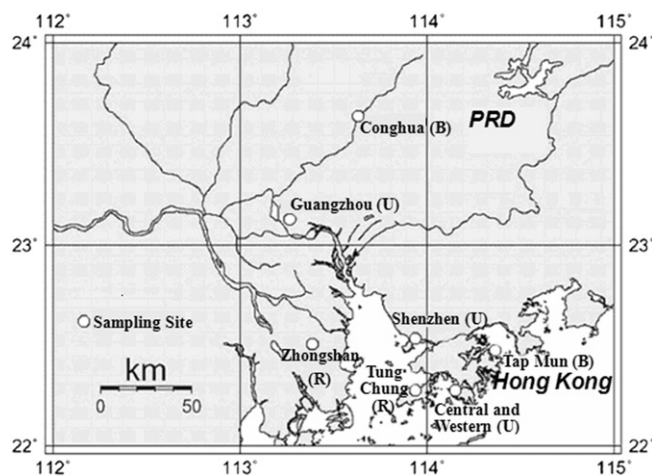


Fig. 1. Sampling sites in the current study including four sites in the PRD (Conghua, Guangzhou, Zhongshan, and Shenzhen) and three sites in Hong Kong (Tap Mun, Tung Chung, and Central and Western). The letter in parentheses indicates the type of the site with B, R, and U as background site, receptor site, and urban site, respectively.

Samples on the prebaked quartz fiber filters of the same month at each site were combined as a monthly composite prior to organic speciation analysis. The winter, spring, summer, and fall samples in the following text represent filters obtained from the following months: December 2002, March 2003, June 2003, and October 2002.

2.2. Chemical analysis

The experimental procedure has been well described elsewhere (Zheng et al., 2002). Briefly, a mixture of 16 deuterated internal standards (IS) was spiked in each sample before extraction. The amount of the internal standard mixture spiked into a composite sample was proportional to the amount of the OC content in the sample. Each sample was ultrasonically extracted, 15 min for each extraction, by using hexane (twice) and a mixture of benzene and isopropanol (2:1) (three times). The extract was filtered, combined, and reduced to about 5 mL by a rotary evaporator, and then further blown down to 250 μL by ultrapure N_2 . The final extract was split into two fractions, one of which was derivatized by diazomethane in order to convert the organic acids to their methyl ester analogues before GC/MS analysis.

The target organic species in the derivatized extracts were identified and quantified by GC/MS on a Hewlett–Packard 6890 GC equipped with a Hewlett–Packard 5973 Network mass selective detector using a 30 mL \times 0.25 mm i.d. \times 0.25 μm film thickness HP-5 MS capillary column. The GC/MS operating conditions were as follows: isothermal hold at 65 $^\circ\text{C}$ for 2 min, temperature ramp of 10 $^\circ\text{C min}^{-1}$ to 300 $^\circ\text{C}$, and isothermal hold at 300 $^\circ\text{C}$ for 22 min. The interface temperature of GC/MS is 300 $^\circ\text{C}$. Other operation conditions included helium as carrier gas with a flow rate of 1.0 mL min^{-1} , 1 μL splitless injection, scan range 50–500 amu, and electron ionization mode with 70 eV. A set of quantification standards (PMSTD#1–#6) containing more than one hundred standard compounds was created by mixing quantification standards with the deuterated internal standard mixture. Each target compound in the present study was quantified by reference to a deuterated internal standard having chemical characteristics and retention time similar to the target compound. For those target compounds which were not found in the quantification standards, identification was achieved by using secondary standards such as candle wax and source samples.

2.3. Receptor modeling

The chemical mass balance modeling approach using molecular markers as fitting species or CMB-MM have been proved as an efficient tool to apportion sources of organic carbon in various regions (Schauer et al., 1996; Schauer and Cass, 2000; Zheng et al., 2002, 2005, 2006). Species included in the model are nine *n*-alkanes (with the carbon number between 25 and 33), seven hopanes and steranes, three resin acids, six polycyclic aromatic hydrocarbons (PAHs), two unsaturated fatty acids, other key tracers including picene, levoglucosan, cholesterol, and additional constituents such as EC and road dust tracers (Al and Si). EC and OC were measured using the established NIOSH protocol (Birch and Cary, 1996) whereas Al and Si were determined using X-ray fluorescence (XRF) analysis (Watson et al., 1996). Markers applied in CMB represent a variety of sources including biomass burning, gasoline and diesel combustion, coal combustion, meat cooking, cigarette smoke, vegetative detritus, and road dust. Source contributions of eight sources to OC were identified. Source profiles were the same as those applied in a previous study in Hong Kong (Zheng et al., 2006). Given these profiles have not been directly measured in the PRD region, the application of most profiles from the tests

performed in North America served as the best estimate of source contribution to OC. A sensitivity test using different biomass burning source profiles by Sheesley et al. (2007) showed that the standard deviation of CMB results for biomass burning was about 30%. A comparison between positive matrix factorization (PMF) and CMB-MM results for PM_{2.5} in Beijing showed good agreement when the source profiles for diesel and gasoline exhaust were from the source tests in the U.S., which are also the same as those used in the current study (Song et al., 2006).

The coal source profile applied in this study represented emissions from burning Datong coal in China (Zheng et al., 2005). Burning process is the single most important factor in determining how much OC is emitted to the atmosphere and what constitutes the coal profile (Zhang et al., 2008). The study by Zhang et al. (2008) also shows that emissions of particulate OC from large power plants are negligible while the emissions of OC from coal combustion are primarily from incomplete and low temperature burning processes. Therefore, the coal profile applied in this study could represent the major source of coal combustion-derived OC in the atmosphere. CMB analysis was computed using CMB8.0 software.

3. Results and discussion

3.1. Excess OC and EC in the PRD

Summer season samples for organic speciation were collected in June when southerly winds (from the South China Sea) prevailed. However, during the other three seasons, samples were primarily influenced by northerly, northeasterly and mixed flows (Hagler et al., 2006). Averaged OC and EC concentrations and EC/OC ratios at sites in Hong Kong and the PRD are shown in Table 1.

The OC/EC ratio in both areas exhibited a distinctly higher value in rural areas (6.1 in TM and 6.5 in CH) with the highest ratio in spring and the lowest in winter (Table 1). The average OC/EC ratio at ZS was 4.2, followed by Guangzhou (4.1), CW (3.5), TC (3.2) and SZ (3.0). No distinct seasonal variation was seen for the OC/EC ratio at urban sites such as SZ and TC. The lowest ratio at SZ was due to its high EC concentration (averaged as 3.85 $\mu\text{g m}^{-3}$), which was greater than the urban site in Hong Kong (1.91 $\mu\text{g m}^{-3}$ at CW). Many heavy-duty trucks traveled across the border in SZ, and their emissions especially EC could impact the local air quality and adversely affect health of local population.

Compared to the levels in the PRD, the spatial distributions of OC and EC were relatively homogeneous in Hong Kong. The difference among sites in Hong Kong was minor as can be seen from the same annual mean OC ($\sim 6 \mu\text{g m}^{-3}$) and EC ($\sim 2 \mu\text{g m}^{-3}$) concentration at CW and TC, only slightly higher ($\sim 1 \mu\text{g m}^{-3}$) than the levels at its rural site TM. Even the seasonal average values of OC and EC concentrations among the three sites in Hong Kong during March, October and December were very close (Table 1). In June, a lower level can be seen for both OC and EC, but the spatial variations within Hong Kong were still relatively minor. Unlike Hong Kong, the sites in the PRD exhibit much larger spatial variation. For example, OC during October at the four sites in the PRD varied from 8.85 to 20.2 $\mu\text{g m}^{-3}$, compared to only 5.74–7.54 $\mu\text{g m}^{-3}$ in Hong Kong. This demonstrates that, relative to carbonaceous aerosols in the PRD, those in Hong Kong were homogeneously distributed. Thus, in the following discussions, we will focus on the difference between OC in the PRD and the average value in Hong Kong. Guangzhou was by far the highest of the PRD sites with an annual mean PM concentration as high as 70.6 \pm 30.2 $\mu\text{g m}^{-3}$ and organic matter (OC \times 1.4) as 24.6 \pm 11.6 $\mu\text{g m}^{-3}$. Even excluding the Guangzhou site, the values in the PRD were still elevated (Hagler et al., 2006).

Based on the ratios in Table 2, it can be seen that concentrations of OC and EC in the PRD were about two- or three-fold higher than

Table 1
Average concentrations of OC and EC ($\mu\text{g m}^{-3}$) and OC/EC ratios at three sites in Hong Kong and four sites in PRD.

	Hong Kong				PRD				
	TM ^a	TC	CW	HK Average \pm STD	CH ^a	ZS	SZ	GZ	PRD Average \pm STD
OC									
March	4.79	6.88	7.48	6.38 \pm 1.15	12.08	11.30	12.15	16.99	13.13 \pm 2.25
June	3.52	4.06	4.69	4.09 \pm 0.48	8.11	4.14	6.64	13.86	8.19 \pm 3.57
October	5.74	7.54	6.44	6.57 \pm 0.74	8.85	11.65	12.36	20.19	13.26 \pm 4.21
December	5.53	6.75	7.87	6.72 \pm 0.95	7.81	15.15	11.51	19.28	13.44 \pm 4.26
Annual Mean	4.90	6.31	6.62		9.21	10.56	10.67	17.58	
EC									
March	0.69	2.14	1.85	1.56 \pm 0.63	1.51	2.48	3.96	4.49	3.11 \pm 1.18
June	0.60	1.23	1.35	1.06 \pm 0.33	1.16	1.40	2.47	3.05	2.02 \pm 0.77
October	0.89	2.02	2.00	1.64 \pm 0.53	1.51	2.10	4.06	4.64	3.08 \pm 1.31
December	1.11	2.56	2.43	2.04 \pm 0.65	1.48	3.95	4.91	5.30	3.91 \pm 1.49
Annual Mean	0.82	1.99	1.91		1.42	2.48	3.85	4.37	
OC/EC Ratio									
March	6.9	3.2	4.0	4.73 \pm 1.60	8.0	4.6	3.1	3.8	4.85 \pm 1.89
June	5.9	3.3	3.5	4.23 \pm 1.19	7.0	3.0	2.7	4.5	4.30 \pm 1.70
October	6.5	3.7	3.2	4.47 \pm 1.43	5.9	5.5	3.0	4.4	4.70 \pm 1.11
December	5.0	2.6	3.2	3.61 \pm 0.99	5.3	3.8	2.3	3.6	3.77 \pm 1.04
Annual Mean	6.1	3.2	3.5		6.5	4.2	2.8	4.1	

^a Rural sites.

those measured in Hong Kong. However, sulfate levels between the PRD and Hong Kong, a known secondarily formed component in PM, were comparable as shown in Table 2. EC at CH, the rural site in the PRD, was sometimes even lower than the average level in Hong Kong, but its excess OC ranged from 1.09 $\mu\text{g m}^{-3}$ in winter to 5.70 $\mu\text{g m}^{-3}$ in spring. EC can easily reflect the difference between urban and rural emissions based on the fact that it is mainly from combustion-related primary emissions of fossil fuel and biomass burning while secondary organic aerosol could be a major component of OC.

Excess EC ranged from negligible at CH to 3.3 $\mu\text{g m}^{-3}$ at Guangzhou, which exhibited a distinct spatial pattern. Excess EC at two urban sites (SZ and GZ) did not vary significantly from season to season, ranging from 2.0 $\mu\text{g m}^{-3}$ in summer to 3.3 $\mu\text{g m}^{-3}$ in winter at GZ, and 1.4 $\mu\text{g m}^{-3}$ in summer to 2.9 $\mu\text{g m}^{-3}$ in winter at SZ.

Excess OC was obviously much higher than excess EC and its sources and composition were more complicated as well. Excess OC, contrary to excess EC, did not always show the lowest excess level at CH. During summer, the lowest excess level was found at ZS, when most of the time ZS was the upwind site of Guangzhou. The highest excess OC levels were found at Guangzhou during all

seasons, ranging from 9.8 to 13.6 $\mu\text{g m}^{-3}$. These high excess OC and EC levels clearly indicated that GZ was an important and consistent source area of carbonaceous PM, impacting regional air quality. OC excess at SZ varied from 2.6 $\mu\text{g m}^{-3}$ in summer to 5.8 $\mu\text{g m}^{-3}$ in spring and fall. Compared to CH and ZS, GZ and SZ exhibited much less seasonal variations of excess carbonaceous aerosols, suggesting they have local sources of excess OC.

Wind direction plays a role when investigating the seasonal variation of OC excess. Since Hong Kong is influenced by Asian monsoon, with prevailing wind as SW in summer and NE in winter, thus CH becomes downwind site of Guangzhou in summer and switches to upwind site of Guangzhou in winter. The influence of Guangzhou on its downwind site was clearly seen by the increase of carbonaceous materials. For example, CH, a rural site, exhibited an excess OC as high as 4 $\mu\text{g m}^{-3}$ in summer while at the same time excess OC at the urban site ZS was only 0.06 $\mu\text{g m}^{-3}$ because at this season ZS became the upwind site. However, in winter, as the downwind site, OC and EC excess at ZS was increased dramatically, up to 8.4 $\mu\text{g m}^{-3}$ and 1.9 $\mu\text{g m}^{-3}$, respectively. SZ was less sensitive to such influence compared to ZS as reflected by nearly the same levels of OC and EC in each season except for a slightly lower level in summer, suggesting the excess in SZ was mostly due to the local sources.

Table 2
Ratios of EC and OC at each PRD site to the average in Hong Kong and their excess concentration at the PRD sites ($\mu\text{g m}^{-3}$).

	CH/HK Avg	ZS/HK Avg	SZ/HK Avg	GZ/HK Avg	CH excess ^a	ZS excess	SZ excess	GZ excess
OC								
Spring	1.9	1.8	1.9	2.7	5.70 \pm 1.12	4.92 \pm 1.04	5.77 \pm 1.20	10.61 \pm 2.25
Summer	2.0	1.0	1.6	3.4	4.02 \pm 0.99	0.06 \pm 0.02	2.55 \pm 0.64	9.77 \pm 2.03
Fall	1.3	1.8	1.9	3.1	2.28 \pm 0.51	5.08 \pm 1.05	5.79 \pm 1.30	13.60 \pm 2.82
Winter	1.2	2.3	1.7	2.9	1.09 \pm 0.25	8.43 \pm 1.73	4.80 \pm 1.20	12.56 \pm 2.59
EC								
Spring	1.0	1.6	2.5	2.9	na ^b	0.92 \pm 0.22	2.40 \pm 0.48	2.93 \pm 0.54
Summer	1.1	1.3	2.3	2.9	0.10 \pm 0.04	0.34 \pm 0.11	1.41 \pm 0.35	1.99 \pm 0.41
Fall	0.9	1.3	2.5	2.8	na	0.47 \pm 0.10	2.42 \pm 0.46	3.00 \pm 0.52
Winter	0.7	1.9	2.4	2.6	na	1.91 \pm 0.35	2.88 \pm 0.73	3.26 \pm 0.56
Sulfate								
Spring	1.4	1.3	1.0	1.6	4.37 \pm 0.66	2.92 \pm 0.37	0.35 \pm 0.003	6.08 \pm 0.50
Summer	1.3	1.1	1.0	1.8	2.48 \pm 0.44	1.09 \pm 0.24	0.31 \pm 0.05	6.39 \pm 1.02
Fall	1.2	1.4	1.1	1.8	1.70 \pm 0.26	3.63 \pm 0.61	0.68 \pm 0.07	6.07 \pm 0.83
Winter	0.7	1.3	1.2	1.3	na	3.34 \pm 0.55	1.66 \pm 0.20	3.62 \pm 0.54

^a Excess concentration is the difference between the concentration at each PRD site to the average concentration in Hong Kong.^b Excess species not available (negative numbers).

3.2. Source apportionment of excess OC

To answer the question of what sources constituted the urban excess OC at each site and season, a receptor modeling approach was taken for OC source apportionment. Averaged organic compound concentrations in Hong Kong and the PRD during each season are shown in Table S1. With CMB-MM, eight sources contributing to OC were determined (see Fig. 2). Table 3 gives the annual average source impacts of OC while Table S2 presents OC source apportionment results of each season. These tables also included the statistical diagnostic results of CMB output including R^2 (target: 0.8–1), chi square (χ^2 , target: 0–4), degrees of freedom (DF, target: >5). Other indices all met the diagnostic criteria including no cluster sources, t test above 2, and calculated to measured ratio for fitting species between 0.5 and 2. Excess OC for each of the eight source categories at each site in the PRD was computed by comparing source impacts at each PRD site to the average level in Hong Kong for each specific source (see Table 4 and Fig. 3).

On a monthly basis, the most two or three important sources contributing to excess OC at each specific site in the PRD were examined. In March, the rural site CH exhibited surprisingly high excess OC, dominated by biomass burning ($2.75 \mu\text{g m}^{-3}$) and followed by meat cooking and coal combustion. Biomass burning was active during spring at CH, which was much higher than other sites (e.g., only $0.25 \mu\text{g m}^{-3}$ at SZ), and even slightly higher than Guangzhou. On the contrary, coal combustion source in spring exhibited the least spatial variation, ranging from $1.0 \mu\text{g m}^{-3}$ at CH to $1.5 \mu\text{g m}^{-3}$ at GZ, indicating the influence of coal combustion was on a regional scale. It is not surprising to find the highest vegetative source contribution at the rural CH site ($0.38 \mu\text{g m}^{-3}$). While meat cooking contributed about $0.40 \mu\text{g m}^{-3}$ to OC at all sites in March, a higher level was found at CH, whereas this source was not significant in October and December. The CH site was located at the top of a 3-story hotel building with some residential buildings around and surrounded by some hills. There was potential local source impact under occasions when strong meat cooking emissions occurred along with stagnant air with no mixing. During March, the two most important sources of excess OC were coal combustion and biomass burning at ZS, diesel engine exhaust and coal combustion at SZ, and biomass burning and gasoline exhaust

at GZ. Mobile source impact was significantly higher at SZ and GZ, with SZ influenced more by diesel engine exhaust (69% of mobile source) while GZ mostly by gasoline engine exhaust (58% of mobile source).

In June, excess OC ranged from $0.06 \mu\text{g m}^{-3}$ at ZS to $9.8 \mu\text{g m}^{-3}$ at GZ. Due to the prevailing wind direction as SW, wind blew from Hong Kong to the PRD. In such a case, ZS served as an upwind site of GZ while CH was downwind site of GZ. The excess OC level was only $0.06 \mu\text{g m}^{-3}$ at the urban site ZS compared to a much higher level ($4.0 \mu\text{g m}^{-3}$) at the downwind site (the rural site CH). Thus, the influence on the downwind site can be clearly seen. It is interesting to note other OC as the dominant source of excess OC, which is computed as the difference between the measured OC and the summed OC from the eight primary sources. Thus, other OC was primarily composed of secondary organic carbon. Other excess OC at CH was slightly higher than GZ, while not found at the upwind sites (SZ and ZS) at all. Other sources of excess OC at CH included biomass burning, meat cooking, and coal combustion, which were all major sources found at GZ, its upwind site. Although mobile source was an important source at GZ, its influence on the downwind site CH was not obvious. Similar to spring, excess OC from coal combustion was a source that distributed more homogeneously among sites.

In October, excess OC ranged from $2.3 \mu\text{g m}^{-3}$ at CH to $13.6 \mu\text{g m}^{-3}$ at GZ. Fall is a season when the prevailing wind switched from SW to NE. Under the influence of NE winter monsoon, CH served as the upwind site, while ZS became a downwind site of Guangzhou. The impact of wind direction on aerosol characteristics can be seen from the difference in excess OC levels between CH and ZS in June and October. Starting from October, excess OC at ZS was higher than CH. At GZ, other OC contributed to nearly one third of the excess OC, and the other sources of excess OC included biomass burning, gasoline exhaust, and coal combustion. Other OC at GZ showed the highest level in October ($4.50 \mu\text{g m}^{-3}$), followed by March, June, and December. This is probably due to a combination of the increasing emission of precursors for secondary OC plus plenty of solar radiation, leading to a favorable condition for secondary organic aerosol formation. In December, on the contrary, other excess OC was only $0.31 \mu\text{g m}^{-3}$, probably due to colder temperature, lower solar radiation, and enhanced primary emissions during this period. The major sources

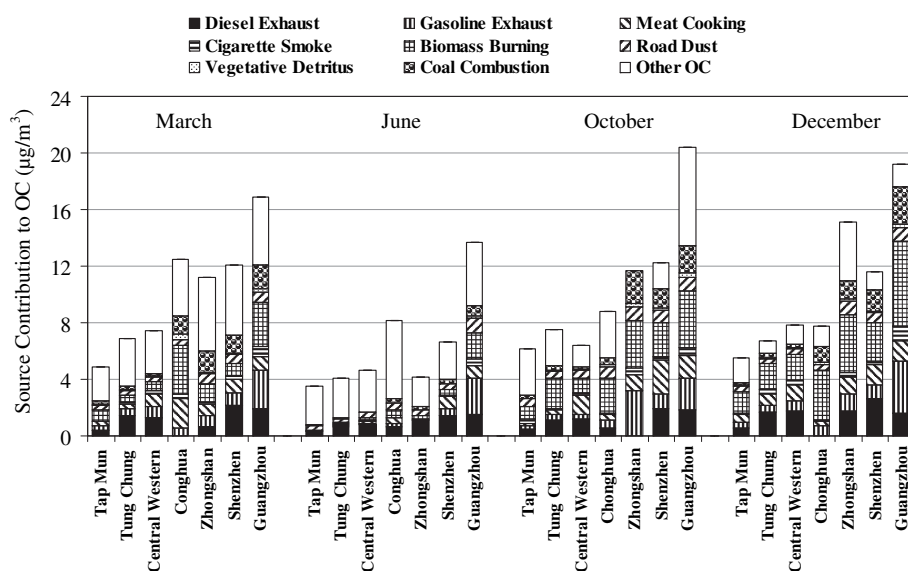


Fig. 2. Source contributions to OC at four PRD sites and three Hong Kong sites.

Table 3
Annual Average Source Contribution to OC ($\mu\text{g m}^{-3}$) in the PRD (CH, ZS, SZ, and GZ) and Hong Kong (TM, TC, and CW).

Site	Diesel Exhaust	Gasoline Exhaust	Meat Cooking	Cigarette Smoke	Biomass Burning	Road Dust	Vegetative Detritus	Coal Combustion	Other OC	Measured Organic Carbon	R ²	χ^2	% Mass	DF
Tap Mun (TM)	0.42 ± 0.12	0.26 ± 0.07	0.32 ± 0.13	0.16 ± 0.05	0.8 ± 0.23	0.41 ± 0.02	0.06 ± 0.02	0.15 ± 0.02	2.32	4.90 ± 0.99	0.96	2.4	48	16
Tung Chung(TC)	1.24 ± 0.19	0.35 ± 0.07	0.38 ± 0.16	0.14 ± 0.03	1.18 ± 0.33	0.33 ± 0.02	0.07 ± 0.02	0.23 ± 0.03	2.38	6.29 ± 1.52	0.96	2.2	59	20
Central Western(CW)	1.27 ± 0.22	0.49 ± 0.09	0.87 ± 0.29	0.19 ± 0.04	0.95 ± 0.27	0.38 ± 0.02	0.07 ± 0.02	0.15 ± 0.03	2.23	6.60 ± 1.42	0.97	1.8	64	21
Chonghua(CH)	0.61 ± 0.17	0.51 ± 0.11	0.81 ± 0.30	0.12 ± 0.02	2.47 ± 0.70	0.53 ± 0.03	0.21 ± 0.04	0.79 ± 0.09	3.27	9.32 ± 2.20	0.97	2.4	61	18
Zhongshan(ZS)	1.16 ± 0.24	1.74 ± 0.22	0.82 ± 0.22	0.24 ± 0.05	2.24 ± 0.66	0.75 ± 0.03	0.13 ± 0.04	1.32 ± 0.14	2.11	10.56 ± 4.61	0.98	2.0	69	18
Shenzhen(SZ)	2.06 ± 0.34	0.83 ± 0.14	1.40 ± 0.34	0.22 ± 0.04	1.61 ± 0.46	0.63 ± 0.03	0.09 ± 0.03	1.10 ± 0.12	2.75	10.70 ± 2.72	0.98	1.7	73	22
Guangzhou(GZ)	1.70 ± 0.37	2.83 ± 0.33	1.21 ± 0.47	0.72 ± 0.13	3.74 ± 1.10	0.91 ± 0.04	0.21 ± 0.07	1.77 ± 0.21	4.51	17.61 ± 2.93	0.97	2.7	74	22

Table 4
Source Contributions ($\mu\text{g m}^{-3}$) to excess OC at four sites in the PRD.

Source	CH	ZS	SZ	GZ	CH	ZS	SZ	GZ	CH	ZS	SZ	GZ	CH	ZS	SZ	GZ		
Category	March				June				October				December					
Diesel Exhaust			1.11 ± 0.18	0.90 ± 0.18	0.08 ± 0.02	0.51 ± 0.06	0.90 ± 0.13	0.91 ± 0.17					1.01 ± 0.18	0.88 ± 0.18		0.37 ± 0.07	1.30 ± 0.23	0.21 ± 0.06
Gasoline Exhaust	0.05 ± 0.01	0.22 ± 0.03	0.39 ± 0.06	2.16 ± 0.26	0.07 ± 0.02		0.31 ± 0.06	2.50 ± 0.29	0.21 ± 0.04	2.86 ± 0.31	0.68 ± 0.11	1.95 ± 0.24	0.23 ± 0.04	0.77 ± 0.11	0.46 ± 0.08	3.23 ± 0.37		
Meat Cooking	1.57 ± 0.48	0.36 ± 0.10	0.40 ± 0.10	0.47 ± 0.27	0.31 ± 0.14	0.01 ± 0.002	0.79 ± 0.22	0.75 ± 0.20		0.54 ± 0.13	1.81 ± 0.43	0.97 ± 0.46		0.35 ± 0.10	0.56 ± 0.13	0.61 ± 0.14		
Cigarette Smoke	0.16 ± 0.03	0.02 ± 0.003	0.11 ± 0.02	0.56 ± 0.09	0.02 ± 0.003		0.07 ± 0.01	0.47 ± 0.08		0.31 ± 0.07	0.05 ± 0.01	0.42 ± 0.08		0.04 ± 0.01	0.05 ± 0.01	0.82 ± 0.15		
Biomass Burning	2.75 ± 0.80	0.60 ± 0.17	0.25 ± 0.07	2.51 ± 0.74	0.40 ± 0.12	0.10 ± 0.03	0.31 ± 0.09	1.73 ± 0.51	1.09 ± 0.31	2.00 ± 0.62	1.04 ± 0.30	2.62 ± 0.76	1.70 ± 0.47	2.33 ± 0.66	0.92 ± 0.26	4.20 ± 1.23		
Road Dust	0.10 ± 0.01	0.36 ± 0.01	0.30 ± 0.01	0.37 ± 0.02	0.15 ± 0.01	0.05 ± 0.001	0.04 ± 0.002	0.73 ± 0.02	0.30 ± 0.01	0.45 ± 0.02	0.34 ± 0.01	0.43 ± 0.02	0.07 ± 0.003	0.64 ± 0.02	0.37 ± 0.02	0.63 ± 0.03		
Vegetative Detritus	0.38 ± 0.07	0.07 ± 0.02	0.05 ± 0.01	0.16 ± 0.05	0.03 ± 0.01	0.01 ± 0.003		0.07 ± 0.04	0.10 ± 0.02	0.12 ± 0.04	0.06 ± 0.02	0.22 ± 0.06	0.07 ± 0.01	0.07 ± 0.02	0.03 ± 0.01	0.14 ± 0.06		
Coal Combustion	1.00 ± 0.11	1.25 ± 0.14	1.00 ± 0.11	1.50 ± 0.17	0.26 ± 0.03	0.22 ± 0.03	0.28 ± 0.04	0.75 ± 0.10	0.25 ± 0.03	2.09 ± 0.20	1.18 ± 0.13	1.71 ± 0.20	0.92 ± 0.09	1.00 ± 0.12	1.23 ± 0.13	2.37 ± 0.27		
Other OC	1.10 ± 0.40	2.29 ± 0.41	2.08 ± 0.40	1.85 ± 0.65	2.67 ± 0.34			1.65 ± 0.44	0.86 ± 0.25			4.50 ± 1.29	0.10 ± 0.08	2.85 ± 1.11	0.01 ± 0.01	0.31 ± 0.44		

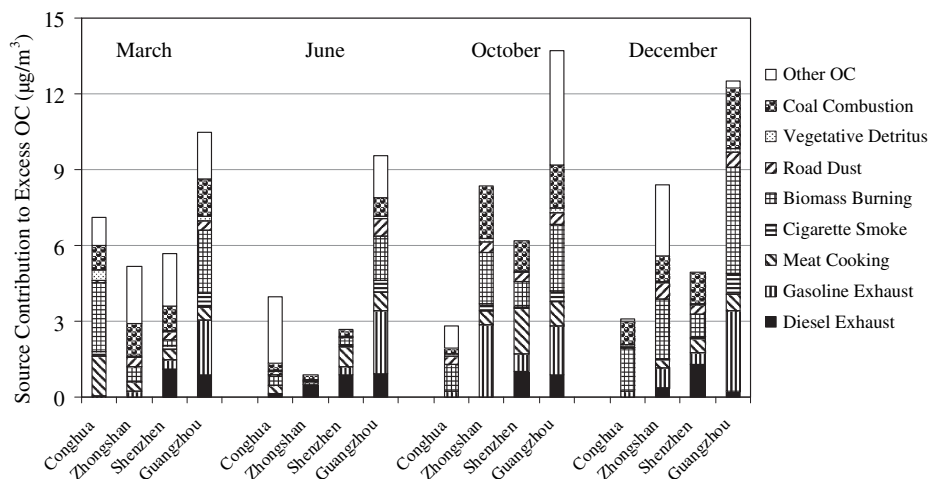


Fig. 3. Source contributions to excess OC at four PRD sites.

contributing to excess OC at the downwind site ZS were very similar to GZ and exhibited similar levels (around $2 \mu\text{g m}^{-3}$ for each of three sources, including gasoline exhaust, biomass burning, and coal combustion). During October, excess coal combustion at CH was lower than other three urban sites, but it ranged from 1 to $2 \mu\text{g m}^{-3}$ at other three sites.

In December, excess OC ranged from $1.1 \mu\text{g m}^{-3}$ at CH to $12.6 \mu\text{g m}^{-3}$ at GZ, similar to what was observed in October. ZS, the downwind site, again received very high excess OC ($8.4 \mu\text{g m}^{-3}$). The major sources contributing to excess OC at GZ in winter were exactly the same as those in fall, but the source impacts were higher in December. The difference was seen in other OC, which was higher in October at GZ. This indicates that excess OC at GZ in December was dominated by the primary sources, and primary source emissions were enhanced during winter. Mobile sources were important at GZ and SZ, but similar to other seasons, GZ was heavily influenced by gasoline exhaust. Biomass burning was an important source contributing to excess OC during December. Both mobile sources and biomass burning exhibited more spatial variations than coal combustion.

Cigarette smoke, road dust, and vegetative detritus were consistently found as the minor sources compared other sources. It is not surprising to find the highest cigarette smoke excess OC at GZ during all seasons as it is the largest city in the PRD. Road dust excess OC was about the same at different sites, but a slightly lower impact was found at the rural site. Vegetative detritus excess OC was generally less than $0.4 \mu\text{g m}^{-3}$.

The major sources contributing to excess OC at GZ included gasoline exhaust, biomass burning, coal combustion, and diesel engine exhaust. The sum of the four sources accounted for 68%, 62%, 52%, and 80% of excess OC in March, June, October, and December, respectively. These four sources during the study period were consistently the dominant sources of excess OC at GZ in each season. This study shows that vehicle exhaust was very important source of excess OC at GZ and SZ, accounting for 21–45% of excess OC. However, during the study period, excess OC at GZ was characterized by high gasoline exhaust (22% of excess OC, compared to only 7% from diesel engine exhaust), while excess OC at SZ was dominated by diesel engine exhaust (24% of excess OC compared to only 10% from gasoline exhaust).

In December, the identified eight primary sources in this study explained nearly all excess OC at GZ, about 80% of excess OC in March and June, and two thirds of excess OC in October. The unexplained OC, or other OC, was the highest at CH, the rural site

(29%). In December, as one of the downwind site of Guangzhou emissions, ZS experienced the highest other OC in winter (34%, compared to less than 5% at other sites). At SZ, a heavily populated city right next to Hong Kong, diesel engine exhaust, coal combustion and meat cooking sources contributed to about 44% of excess OC in March, 73% in June, 65% in October, and 63% in December.

4. Conclusions

Carbonaceous aerosol in $\text{PM}_{2.5}$ was found to be more homogeneously distributed in Hong Kong compared to its adjacent PRD, which is known to have much higher pollutant levels and has thus been a major pollution source in this region. Therefore, our study investigated what sources constituted the excess OC at four sites in the PRD as well as the spatial and seasonal variations of these excess OC. The highest excess OC was constantly found at Guangzhou. The results from receptor modeling revealed that gasoline engine exhaust, biomass burning, coal combustion, and diesel engine exhaust were major components of excess OC at Guangzhou, accounting for more than 50% of excess OC. The CMB-MM results also revealed that mobile sources (gasoline and diesel engine exhaust) accounted for $\sim 30\%$ of excess OC at SZ and GZ, but the split between gasoline exhaust and diesel engine exhaust at these two sites is very different (gasoline exhaust contributing 22% to excess OC at GZ and diesel engine exhaust contributing 24% of excess OC at SZ).

The other two sites in the PRD include a rural site CH and an urban site ZS. The results from this study clearly showed how meteorology could impact the air quality when one of the two sites served as a downwind site. As the downwind site of Guangzhou, its excess OC obviously increased, e.g., as high as $4.0 \mu\text{g m}^{-3}$ of excess OC at CH in June and $8.4 \mu\text{g m}^{-3}$ at ZS in December. Coal combustion remained as an important source of fine excess OC with relatively homogeneous distribution in the PRD. The results from this study revealed that it was primary emissions that contributed to the majority of excess OC in the PRD.

The unexplained or other excess OC was less than 5% in December except for ZS, suggesting that the eight primary sources in this study can well explain the excess OC in winter. In October, the other excess OC at GZ was estimated as $4.5 \mu\text{g m}^{-3}$, probably due to a combination of enhanced emissions of gaseous precursors and the presence of abundant sunshine in this subtropical region. Further research can reveal more information when individual secondary organic tracers are investigated.

Acknowledgments

This research was sponsored by Hong Kong Jockey Club Charities Trust, Castle Peak Power Co. Ltd., the Environmental Protection Department of the Hong Kong Special Administrative Region, the Shell Hong Kong Ltd., through Civic Exchange. We thank Christine Loh, the founder of Civic Exchange, and C.S. Kiang for coordinating the project, Dr. Tao Wang of Hong Kong Polytechnic University for the project assistance throughout this study, and Tao Liu of the Guangzhou Environmental Monitoring Center, Jianjun Chen of the Conghua Environmental Monitoring Center, and Wendong Yang of the Zhongshan Environmental Monitoring Center for their assistance in sampling coordination. We thank two anonymous referees for their valuable comments and constructive suggestions to the manuscript. While one of the coauthors, G. Hagler, is currently identified as an U.S. Environmental Protection Agency (USEPA) employee, the data were collected while she was a doctoral student at the Georgia Institute of Technology. This article has been subjected to the USEPA and HKEPD technical and administrative review process and approved for publication. The content of this paper does not necessarily reflect the views or policies of any governments, including USEPA, the Governments of Guangdong and the Hong Kong Special Administrative Region, nor does any mention of trade names or commercial products constitute an endorsement or recommendation of their use.

Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2010.09.041.

References

- Bi, X., Sheng, G., Peng, P., Chen, Y., Fu, J., 2005. Size distribution of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in urban and rural atmospheres of Guangzhou, China. *Atmospheric Environment* 39, 477–487.
- Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology* 25, 221–241.
- Cass, G.R., 1998. Organic molecular tracers for particulate air pollution sources. *Trends in Analytical Chemistry* 17, 356–366.
- CH2M HILL (China) Limited, 2002. Study of Air Quality in the Pearl River Delta Region available at HKEPD website. http://www.epd.gov.hk/epd/english/environmentinhk/air/study/rpts/study_pearl.html.
- Chameides, W.L., Bergin, M.H., 2002. Soot takes center stage. *Science* 297, 2214–2215.
- Cheng, Y.F., Wiedensohler, A., Eichler, H., Su, H., Gnauk, T., Brüggemann, E., Herrmann, H., Heintzenberg, J., Slanina, J., Tuch, T., Hu, M., Zhang, Y.H., 2008. Aerosol optical properties and related chemical apportionment at Xinken in Pearl River Delta of China. *Atmospheric Environment* 42, 6351–6372.
- Deng, X., Tie, X., Wu, D., Zhou, X., Bi, X., Tan, H., Li, F., Jiang, C., 2008. Long-term trend of visibility and its characterizations in the Pearl River Delta (PRD) region, China. *Atmospheric Environment* 42, 1424–1435.
- Hagler, G.S.W., Bergin, M.H., Salmon, L.G., Yu, J.Z., Wan, E.C.H., Zheng, M., Zeng, L.M., Kiang, C.S., Zhang, Y.H., Lau, A.K.H., Schauer, J.J., 2006. Sources areas and chemical composition of fine particulate matter in the Pearl River Delta region of China. *Atmospheric Environment* 40, 3802–3815.
- Hagler, G.S.W., Bergin, M.H., Salmon, L.G., Yu, J.Z., Wan, E.C.H., Zheng, M., Zeng, L.M., Kiang, C.S., Zhang, Y.H., Schauer, J.J., 2007. Local and regional anthropogenic influence on PM_{2.5} elements in Hong Kong. *Atmospheric Environment* 41, 5994–6004.
- Lau, A., Lo, A., Gray, J., Yuan, Z., Loh, C., 2007. Relative Significance of Local vs. Regional Sources: Hong Kong Technical report to Civic Exchange, Hong Kong.
- Pope III, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thurston, G.D., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *Journal of the American Medical Association* 287, 1132–1141.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30, 3837–3855.
- Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental Science and Technology* 34, 1821–1832.
- Sheesley, R., Schauer, J.J., Zheng, M., Wang, B., 2007. Sensitivity of molecular marker-based CMB models to biomass burning source profiles. *Atmospheric Environment* 41, 9050–9063.
- Sin, D.W.M., Fung, W.H., Choi, Y.Y., Lam, C.H., Louie, P.K.K., Chow, J.C., Watson, J.G., 2005. Seasonal and spatial variation of solvent extractable organic compounds in fine suspended particulate matter in Hong Kong. *Journal of Air & Waste Management Association* 55, 291–301.
- Song, Y., Zhang, Y., Xie, S., Zeng, L., Zheng, M., Salmon, L.G., Shao, M., Slanina, S., 2006. Source apportionment of PM_{2.5} in Beijing by positive matrix factorization. *Atmospheric Environment* 40, 1526–1537.
- Tie, X., Wu, D., Brasseur, G., 2009. Lung cancer mortality and exposure to atmospheric aerosol particles in Guangzhou, China. *Atmospheric Environment* 43, 2375–2377.
- Wang, T., Poon, C.N., Kwok, Y.H., Li, Y.S., 2003. Characterizing the temporal variability and emission patterns of pollution plumes in the Pearl River Delta of China. *Atmospheric Environment* 37, 3539–3550.
- Wang, X.M., Carmichael, G., Chen, D., Tang, Y., Wang, T., 2005. Impacts of different emission sources on air quality during March 2001 in the Pearl River Delta, PRD region. *Atmospheric Environment* 39, 5227–5241.
- Watson, J.G., Chow, J.C., Frazier, C.A., 1996. X-ray Fluorescence Analysis of Ambient Air Samples, in *Elemental Analysis of Airborne Particles*. Gordon and Breach, Newark, pp. 1–31.
- Zhang, Y.H., Hu, M., Zhong, L.J., Wiedensohler, A., Liu, S.C., Andreae, M.O., Wang, W., Fan, S.J., 2008a. Regional integrated experiments on air quality over Pearl River Delta 2004 (PRIDE-PRD2004): overview. *Atmospheric Environment* 42, 6157–6173.
- Zhang, Y.H., Su, H., Zhong, L.J., Cheng, Y.F., Zeng, L.M., Wang, X.S., Xiang, Y.R., Wang, J.L., Gao, D.F., Shao, M., Fan, S.J., Liu, S.C., 2008b. Regional ozone pollution and observation-based approach for analyzing ozone–precursor relationship during the PRIDE-PRD2004 campaign. *Atmospheric Environment* 42, 6203–6218.
- Zhang, Y.X., Schauer, J.J., Zhang, Y.H., Shao, M., Wie, Y.J., Liu, Y., Zeng, L.M., 2008. Characteristics of particulate carbon emissions from real world Chinese coal combustion. *Environmental Science and Technology* 42, 5068–5073.
- Zheng, M., Fang, M., Wang, F., To, K.L., 2000. Characterization of the solvent extractable organic compounds in PM_{2.5} aerosols. *Atmospheric Environment* 34, 2691–2702.
- Zheng, M., Cass, G.R., Schauer, J.J., Edgerton, E.S., 2002. Source apportionment of fine particle air pollutants in the Southeastern United States using solvent-extractable organic compounds as tracers. *Environmental Science and Technology* 36, 2361–2371.
- Zheng, M., Salmon, L.G., Schauer, J.J., Zeng, L., Kiang, C.S., Zhang, Y., Cass, G.R., 2005. Seasonal trends in PM_{2.5} source contributions in Beijing, China. *Atmospheric Environment* 39, 3967–3976.
- Zheng, M., Hagler, G.S.W., Ke, L., Bergin, M.H., Wang, F., Louie, P.K.K., Salmon, L., Sin, D.W.M., Yu, J., Schauer, J.J., 2006. Composition and sources of carbonaceous aerosols at three contrasting sites in Hong Kong. *Journal of Geophysical Research-Atmospheres* 111, D20313. doi:10.1029/2006JD007074.
- Zheng, M., Kester, D.R., Wang, F., Shi, X., Guo, Z., 2008. Size distributions of organic and inorganic species in Hong Kong aerosols during the wet and dry seasons. *Journal of Geophysical Research-Atmospheres* 113, D16303. doi:10.1029/2007JD009494.