



# Chemical characteristics and source apportionment of fine particulate organic carbon in Hong Kong during high particulate matter episodes in winter 2003

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## ABSTRACT

PM<sub>2.5</sub> samples were collected at six general stations and one roadside station in Hong Kong in two periods of high particulate matter (PM) in 2003 (27 October–4 November and 30 November–13 December). The highest PM<sub>2.5</sub> reached 216  $\mu\text{g m}^{-3}$  during the first high PM period and 113  $\mu\text{g m}^{-3}$  during the second high PM period. Analysis of synoptic weather conditions identified individual sampling days under dominant influence of one of three types of air masses, that is, local, regional and long-range transported (LRT) air masses. Roadside samples were discussed separately due to heavy influences from vehicular emissions. This research examines source apportionment of fine organic carbon (OC) and contribution of secondary organic aerosol on high PM days under different synoptic conditions. Six primary OC (POC) sources (vehicle exhaust, biomass burning, cooking, cigarette smoke, vegetative detritus, and coal combustion) were identified on the basis of characteristic organic tracers. Individual POC source contributions were estimated using chemical mass balance model. In the roadside and the local samples, OC was dominated by the primary sources, accounting for more than 74% of OC. In the samples influenced by regional and LRT air masses, secondary OC (SOC), which was approximated to be the difference between the total measured OC and the apportioned POC, contributed more than 54% of fine OC. SOC was highly correlated with water-soluble organic carbon and sulfate, consistent with its secondary nature.

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## 1. Introduction

Organic carbon (OC) and elemental carbon (EC) constitute a significant fraction of airborne particulate matter

(PM) mass, ranging from ~10% in remote areas to ~40% in urban areas (Jacobson et al., 2000; Seinfeld and Pandis, 1998). At urban and roadside locations in Hong Kong, the carbonaceous materials are the most abundant component of PM<sub>2.5</sub> (particles of less than 2.5  $\mu\text{m}$  in diameter), accounting for 44% and 67%, respectively, on an annual average (Louie et al., 2005a,b). Compared with inorganic components in PM, identities of individual organic compounds and their source contributions, are far less understood mainly

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due to the large number of individual organic compounds and a wide variety of emission sources and multiple secondary formation pathways.

Chemical characterization of sources and ambient PM<sub>2.5</sub> is an essential step to identifying and quantifying major contributing sources to PM<sub>2.5</sub> in the ambient air. Individual organic tracers, combined with chemical mass balance (CMB) model, have long been demonstrated to be able to provide source apportioning of primary organic aerosols (e.g., Hu et al., 2010; Li et al., 2012; Manchester-Neesvig et al., 2003; Schauer and Cass, 2000; Schauer et al., 1996; Zheng et al., 2002, 2006). In this work, a total of 27 ambient PM<sub>2.5</sub> samples were collected at six air quality monitoring stations in Hong Kong in two periods of high PM (Period I: 26 October–4 November 2003 and Period II: 30 November–13 December 2003). The highest PM<sub>2.5</sub> reached 216  $\mu\text{g m}^{-3}$  during the first high PM period and 113  $\mu\text{g m}^{-3}$  during the second high PM period. The objectives of this work are (1) to characterize major components of PM<sub>2.5</sub> during high PM episodes in Hong Kong; (2) to obtain chemical composition of the organic fraction of PM<sub>2.5</sub> and to identify and quantify the major contributing sources of fine OC under different episodic conditions.

## 2. Experimental section

### 2.1. Samples

The 27 samples were collected at six general air quality monitoring stations (AQMSs) and one roadside station in the AQMS network in Hong Kong. Sample collection was carried out by the Hong Kong Environmental Protection Department (HKEPD). Three of the samples were collocated duplicate samples. Fig. S1 (Fig. S# and Table S# denotes materials provided as supporting information) shows the geographical distribution of the six general stations (CW—Central Western, KT—Kwon Tong, SSP—Sham Shui Po, TC—Tung Chung, TW—Tsuen Wan, YL—Yuen Long) and the Mong Kok (MK) roadside station. Among the general AQMSs, CW and SSP are in mixed residential and commercial neighborhoods; KT and TW are in mixed residential, commercial, and industrial neighborhoods; TC and YL are in new town residential areas. The MK roadside station is located in a busy commercial and residential down town area surrounded by tall buildings. Table 1 lists the locations and sampling dates of individual samples. The PM<sub>2.5</sub> samples were collected on quartz fiber filters (20×25 cm) prebaked at 550 °C using high-volume air samplers (GT22001; Andersen Instruments, Smyrna, GA, USA) at a flow rate of 1.13 m<sup>3</sup> min<sup>-1</sup> for 24 h (from midnight to midnight). All the filter samples were stored in a freezer at 4 °C until analysis.

### 2.2. Analysis of EC and OC

EC and OC were determined using a thermal/optical aerosol carbon analyzer (Sunset Laboratories, Forest Grove, Oregon, USA) (Birch and Cary, 1996). A filter punch of 1×1 cm<sup>2</sup> in size was removed from each filter and loaded into the aerosol carbon analyzer. The thermal analysis conditions (i.e., temperature program and the type of atmosphere)

were the same as those established for the NIOSH method 5040 (Wu et al., 2012).

### 2.3. Extraction and analysis of solvent extractable organic compounds

Half of each filter was spiked with tetracosane-D<sub>50</sub>, phenanthrene-D<sub>10</sub>, CD<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>COOH, phthalic acid-D<sub>4</sub> and levoglucosan-<sup>13</sup>C, and then Soxhlet-extracted with a mixture of ~140 mL high purity dichloromethane and ~140 mL high purity methanol. The extract was reduced to ~5 mL using a rotary evaporator and then filtered through glass wool to a test tube and rinsed with dichloromethane. To the extract, 250  $\mu\text{L}$  of high purity acetonitrile was added. Acetonitrile served to replace methanol upon further solvent evaporation to 250  $\mu\text{L}$ . Methanol had to be replaced due to its reaction with silylation reagent N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA), which was used to derivatize -OH and -COOH containing compounds later in the analytical procedure. The samples were then blown down to 200  $\mu\text{L}$  and split into two equal portions of 100  $\mu\text{L}$  and transferred to two vials capped with Teflon-lined lid. One portion was used to analyze non-polar species (e.g., alkanes, polycyclic aromatic hydrocarbons (PAHs), cycloalkanes, hopanes, steranes, and phthalates) using gas chromatography-mass spectrometry (GC-MS). The second portion was silylated by BSTFA and analyzed using GC-MS within 18 h. This portion was used to quantify both acid compounds (i.e., alkanolic acids, alkenoic acids, etc.) and alcohol compounds (i.e., alkanols, levoglucosan, mono-glycerides, cholesterol). The recoveries of a set of 22 selected compounds representing the target compound classes were determined by spiking deuterated standards onto a blank filter. The recoveries ranged from 60% to 99%, demonstrating that our analytical protocol provided acceptable quantitative results.

### 2.4. Extraction and analysis of water-soluble organic carbon and ion species

The total water-soluble organic carbon (WSOC) was determined by measuring the OC content of aerosol water extracts using a TOC analyzer (Yang et al., 2003). A portion of the filter sample was extracted with 10 mL aliquots of UV-oxidized high-purity water in a sonication bath for 30 min. The water extracts were rid of filter debris and suspending insoluble particles using a syringe filter. A 3-mL aliquot of the extract was used for quantification of carbon content with a total organic carbon (TOC) analyzer. The water extracts were also used for analysis of organic anions (formate, acetate, methanesulfonate, oxalate), inorganic anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) and cations (e.g., NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) using an ion chromatography (IC) system (Dionex DX 500). The IC method detail was given by Yang et al. (2004).

The analysis of mono- and dicarboxylic acids,  $\omega$ -oxo-carboxylic acids, mid-chain ketocarboxylic acids, and aldehydes was carried out using a method developed in our lab (Li and Yu, 2005). Briefly, one-fourth of the 20×25 cm quartz filter was mixed with a mixture of BF<sub>3</sub>/BuOH for derivatization. The reaction mixture was washed with water

**Table 1**

Locations, sampling dates, and major characteristics of individual samples.

Sample ID <sup>a</sup>	Site <sup>b</sup>	Date	PM <sub>2.5</sub> mass (μg m <sup>-3</sup> )	OC/EC	Dominating air mass <sup>c</sup>
031027TC	TC	10/27/2003	94.8	1.07	Local
031028TW	TW	10/28/2003	112.5	1.28	Regional
031029KT	KT	10/29/2003	93.5	1.76	Mainly local pollution
031030CW	CW	10/30/2003	77.0	2.21	Mainly local pollution
031030SSP	SSP	10/30/2003	88.9	0.89	Mainly local pollution
031031MK	MK	10/31/2003	93.9	0.63	Roadside
031101YL	YL	11/1/2003	134.5	2.47	Prominent regional influence
031102TC	TC	11/2/2003	215.8	4.78	Prominent regional influence
031103TW	TW	11/3/2003	153.7	2.18	Prominent regional influence
031104KT	KT	11/4/2003	76.4	0.57	Local, lowest OC/EC
031201YL	YL	12/1/2003	144.8	3.21	Regional
031203TW	TW	12/3/2003	67.0	2.37	Local
031205CW	CW	12/5/2003	74.9	2.25	Local
031206MK	MK	12/6/2003	115.6	0.78	Roadside
031207YL	YL	12/7/2003	175.5	2.27	LRT, cold front arriving, aged air mass
031208TC	TC	12/8/2003	109.6	4.14	LRT, cold front arriving, aged air mass
031209TW	TW	12/9/2003	84.0	1.49	Local
031210KT	KT	12/10/2003	82.0	1.01	Local
031210YL	YL	12/10/2003	113.4	2.90	Regional, aged air mass
031210TC	TC	12/10/2003	96.9	3.08	Regional, aged air mass
031211CW	CW	12/11/2003	76.6	3.12	Regional, aged air mass
031212MK	MK	12/12/2003	73.6	1.24	Roadside
031213KT	KT	12/13/2003	74.7	1.39	Local
031213YL	YL	12/13/2003	108.2	1.14	Local

<sup>a</sup> The sample ID is in the format of sampling date in yymmdd followed by the site abbreviation.

<sup>b</sup> Site abbreviations are TC—Tung Chung, TW—Tsuen Wan, KT—Kwun Tong, CW—Central Western, SSP—Sham Shui Po, MK—Mong Kok, and YL—Yuen Long.

<sup>c</sup> Features are identified through a combination of analysis on synoptic weather conditions and observations of various pollutant levels. Details are described in Appendix S1 in the supporting information document.

and the derivatives in the hexane layer were separated from the mixture and injected into GC–MS for analysis.

### 2.5. CMB modeling

CMB model (EPA-CMB 8.2) (<http://www.epa.gov/scram001/tt23.htm>) was used for source apportionment. The concentrations of EC and 20 particle-phase organic tracers serve as inputs to the CMB model (Table S1). More information of choosing tracers and CMB applications has been provided in a number of published studies (e.g., Schauer and Cass, 2000; Schauer et al., 1996; Zheng et al., 2002). Wherever possible, source profiles local to Hong Kong or specific to China were used in the CMB. Chemical composition derived from samples collected in roadway tunnel in Hong Kong (Table S2) was used to represent the source profile from vehicular emissions, without distinguishing diesel engine exhaust from gasoline-powered engine exhaust (Yu and Schauer, 2005). Cooking source profile is from Hong Kong local Daoxiang cooking (Yu et al., unpublished results). The source profile of biomass burning is that from burning cereal straw, which is one of the most abundant biomass burned in China (Zhang et al., 2007). In Zhang et al.'s (2007) study, the source profile of cereal straw burning emissions represents three main kinds of cereal straws (wheat, corn and rice) collected from five grain producing areas (Beijing, Henan, Hebei, Sichuan, and Zhejiang) in China. Coal combustion is from specific Chinese industrial mixed coal boilers (Zhang et al., 2008). The source profiles of vegetative detritus and cigarette smoke are obtained from the United States (Hildemann et al., 1991; Rogge et al., 1993a, 1994). The source profiles are plotted in Fig. S5.

### 3. Results and discussion

Synoptic conditions were first characterized for individual sampling days by examining weather maps and meteorological measurements (e.g., wind speed, wind direction, temperature, and solar radiation) to identify the origin of dominating air mass. Criteria air pollutant concentrations monitored across the AQMS network in Hong Kong were also examined for concentration levels, and spatial and temporal variations to assist the identification of the origin of dominating air mass. On the basis of the synoptic weather conditions and characteristics of common air pollutants (e.g., respirable suspended particulate (RSP), SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, and CO) monitored across the AQMS station, individual sampling days were classified into one of the following three categories according to the dominating air mass types, local, regional and long-range transport (LRT) days. The detailed synoptic weather condition analysis is given in Appendix S1 in the supporting information document. Briefly, on days dominated by local emissions, the prevailing winds were southeasterly, southwesterly or easterly and low to moderate concentrations of SO<sub>2</sub>, O<sub>3</sub>, and RSP were observed across Hong Kong. On days dominated by regional pollution, the prevailing winds were from the north or northeast or northwest, or winds were generally weak, favoring the formation of land–sea breeze circulation. Elevated SO<sub>2</sub>, CO, and O<sub>3</sub> concentrations were observed. Days affected by arrival of cold fronts were significantly impacted by LRT air masses (Li et al., 2012). Samples collected at the roadside station MK were discussed separately because of heavy impact of vehicular emissions on these samples. The classification is listed in Table 1 for each sample.

PM<sub>2.5</sub> in the samples analyzed in this work ranged from 67.0 to 215.8  $\mu\text{g m}^{-3}$ , with a median concentration of 94.3  $\mu\text{g m}^{-3}$ . HKEPD conducted a study of PM<sub>2.5</sub> in Hong Kong with a sampling schedule of one sample every six days and sampling at three sites for 12 months from November 2000 to October 2001 (Louie et al., 2005b). In comparison, the average PM<sub>2.5</sub> level obtained from the HKEPD regular sampling program for the three winter months from October to December was 38.6  $\mu\text{g m}^{-3}$  at a general AQMS (TW) (Louie et al., 2005b). All the 27 samples had PM<sub>2.5</sub> concentration at least 70% higher than the average PM<sub>2.5</sub> level during this period, and the majority of the samples were more than twice higher than the average level. In the extreme case, the highest PM<sub>2.5</sub> concentration (216  $\mu\text{g m}^{-3}$ ) in this set of high PM samples was 5.6 times the average PM<sub>2.5</sub> observed for the three winter months in the HKEPD one year study. Sampling days discussed in this work can therefore be regarded as high PM<sub>2.5</sub> days.

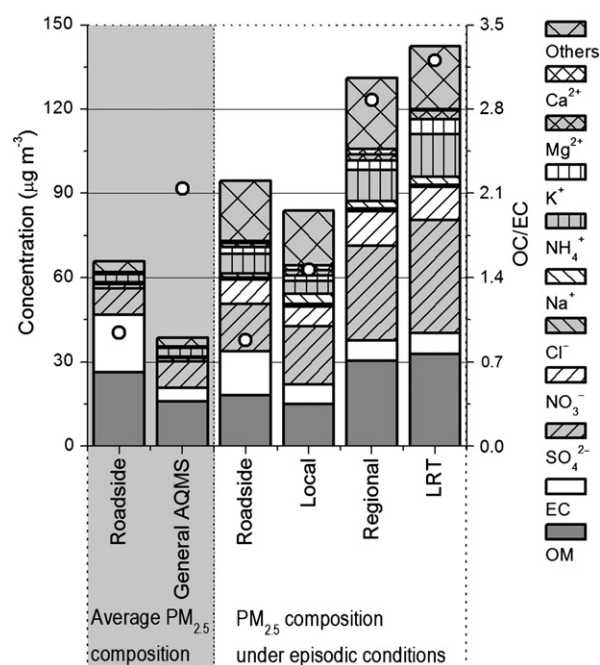
### 3.1. PM<sub>2.5</sub> mass concentration and general chemical composition

The average PM<sub>2.5</sub> mass concentrations reached 94.4  $\mu\text{g m}^{-3}$  in the roadside samples, 83.8  $\mu\text{g m}^{-3}$  in the local episodic samples, 131  $\mu\text{g m}^{-3}$  in the regional episodic samples, and 143  $\mu\text{g m}^{-3}$  in the LRT episodic samples. PM<sub>2.5</sub> concentrations in individual episodic samples are given in Table 1 while concentrations of the major constituents and organic compounds are given in Table S3 in the supporting document. Fig. 1 compares the concentrations of PM<sub>2.5</sub> and major constituents in different groups of high PM samples. The average PM<sub>2.5</sub> and the major constituents in the three winter months from October to December at a general AQMS (TW) and at the same roadside

station (MK) are also shown in Fig. 1 for comparison. In another study by Bergin et al. (2004), the average PM<sub>2.5</sub> concentration in a general AQMS (CW) was measured to be 35.7  $\mu\text{g m}^{-3}$ , similar to the level found in the HKEPD one year study. Among the different groups of episodic samples, the average PM<sub>2.5</sub> mass concentrations of regional and LRT episodic samples (131 and 143  $\mu\text{g m}^{-3}$ , respectively) were much higher than those of roadside and local episodic samples (94 and 84  $\mu\text{g m}^{-3}$ , respectively). The roadside samples had more than twice the EC amount than the other types of samples, reflecting the heavy influence of vehicular emissions.

The dominant components in these PM episodic samples were organic matter (OM) and sulfate (Fig. 1). OM accounted for 18–23% and sulfate accounted for 18–28% of PM<sub>2.5</sub>. EC, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were the next abundant major components, accounting for 5–17%, 8–9%, and 5–11% of PM<sub>2.5</sub>, respectively. Lesser constituents (<5% of PM<sub>2.5</sub>) were Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>. There was still a significant fraction of mass (16–23%) not accounted for by the measured species. In comparison with the average chemical composition measured for the months of October, November and December in the HKEPD one year study (i.e., the baseline chemical composition), the additional PM<sub>2.5</sub> mass in the roadside and local episodic samples were mainly attributed by increase in sulfate, nitrate, and ammonium mass (Fig. 1). In addition to these three secondary inorganic species, OM also contributed significantly to the elevation of PM<sub>2.5</sub> concentration in the regional and LRT episodic samples. In reference to the baseline chemical composition, the increase in the sum of the three secondary inorganic PM components during the episodic days was 130–480%, significantly higher than the 20–30% increase in EC concentrations observed in the local, regional, and LRT episodic samples. EC is known from a number of previous studies to be predominately associated with local vehicular emissions (e.g., Yu et al., 2004; Lin et al., 2010).

The elevated OM concentrations in the regional and LRT episodic samples were also linked with elevation in OC/EC ratios, indicating that OM increases were mainly due to SOA contributions (Fig. 1). The average concentrations of OC and EC were 13 and 15.7  $\mu\text{g m}^{-3}$  in the roadside samples, 9.3 and 7.1  $\mu\text{g m}^{-3}$  in the local samples, 19 and 7.1  $\mu\text{g m}^{-3}$  in the regional samples, and 21 and 7.3  $\mu\text{g m}^{-3}$  in the LRT samples. The average OC/EC ratios were 0.88, 1.47, 2.88, and 3.20 in roadside, local, regional, and LRT groups, respectively. MK station had the lowest OC/EC ratio (0.88), confirming the significant impact of vehicular emissions on PM<sub>2.5</sub> at this location. Obviously, OC was elevated in the regional and LRT samples and the OC/EC ratios (2.9 and 3.2) were also much higher, consistent with the characteristics of more aged air masses. The highest value (4.8) occurred at TC station on 2 November, coinciding with arrival of the Melor storm, which brought pollutants emitted from the highly industrialized PRD area during these days. The second highest value (4.1) occurred at TC station on 8 December, coinciding with arrival of a cold front, during which strong northerly wind brought aged air mass to Hong Kong. In the local episodic samples, the OC/EC ratio was relatively low (1.47), reflecting that PM<sub>2.5</sub> particles were dominated by more fresh primary particles from local emission sources. Among them, sample 031104KT had even lower OC/EC ratio than MK station. The most possible reason is that this sample was significantly affected



**Fig. 1.** Major constituents and their concentrations ( $\mu\text{g m}^{-3}$ ) in PM<sub>2.5</sub> under different synoptic conditions. (OM = 1.6 × OC for general stations considering these samples dominated by urban aerosols, while OM = 1.4 × OC for roadside samples considering they are dominated by fresh emission (Turpin and Lim, 2001). "Others" is the residue mass unaccounted by the measured constituents.)



by ship emissions which have even higher emission factor of EC (1.9) (Lee and Kan, 2000) than diesel exhaust (1.47). Yu et al. (2004) reported that KT station, north to the container port, had relative high concentration of EC due to ship emissions.

### 3.2. Organic compounds in $PM_{2.5}$

A total of about 180 organic species were identified and quantified (Table S3). They are in the compound classes of *n*-alkanes, branched alkanes, hopanes, PAHs, alkanolic acids, alkanols, dicarboxylic acids, keto-carboxylic acids, mono-carboxylates, dicarbonyls, and a few miscellaneous -OH containing compounds (i.e., glycerin, levoglucosan, monopalmitin, monolein, monostearin, cholesterol, and a few other sterols). The concentrations of individual compound classes in different samples are shown in Fig. 2. Mono-carboxylic acids and dicarboxylic acids were the most abundant classes. Their average percentages among total identified organic compounds in roadside, local, regional and LRT episodic samples were 46.8%, 42.4%, 39.3%, and 32.4% for mono-carboxylic acids and 30.8%, 40.4%, 42.5%, and 46.6% for dicarboxylic acids, respectively. The decreasing trend of mono-carboxylic acids from the roadside samples to LRT samples indicates that they were likely dominated by local primary sources. Hexadecanoic acid and octadecanoic acid, the two most abundant mono-carboxylic acids, are known to be abundant in cooking emissions (e.g., He et al., 2004; Rogge et al., 1991). On the other hand, the increasing trend of dicarboxylic acids from the roadside samples to LRT samples indicates that this compound group was possibly dominated by secondary formation sources, which were favored during regional and LRT. Secondary formation of dicarboxylic acids has been reported in a number of studies (e.g., Ervens et al., 2004; Li and Yu, 2010; Yu et al., 2005). *n*-Alkanes, branched alkanes, hopanes, and PAHs account for much lower percentages of total identified organic compounds, and they had similar decreasing trend as mono-carboxylic acids, accounting

for 2.1–5.3%, 0.17–1.22%, 0.11–0.55%, and 0.17–0.56% of total identified compounds, respectively. Keto-carboxylic acids and aldehydes accounted for 3.0–7.1% and 0.9–4.1% of the total identified organic compounds, respectively. They showed a similar increasing trend as dicarboxylic acids did. *n*-Alkanols and miscellaneous -OH compounds accounted for only 0.8–1.1% and 5.5–9.7% of total identified organic compounds, respectively. They did show discernable pattern among the four sample groups. The sum of these compounds accounted for 15%, 19%, 13% and 11% (based on a carbon mass) of OC in the roadside, local, regional and LRT episodic samples, respectively.

#### 3.2.1. Odd number $C_{29}$ – $C_{33}$ alkanes

A dominant presence of odd number  $C_{29}$ – $C_{33}$  alkanes over the even number analogs ( $C_{28}$ ,  $C_{30}$ , and  $C_{32}$ ) is indicative of the presence of vegetative detritus. The abundance ratio of the odd/even *n*-alkane analogs was determined to be 16.5 in source samples of vegetative detritus (Rogge et al., 1993a). This ratio was in the range of 2.1–4.2 in the episodic samples, indicating some contributions by vegetative detritus to the *n*-alkanes. It is noted that the odd–even distribution may be affected to some extent by particles from smoking cigarette (the ratio is about 5.8) (Rogge et al., 1994), which has the similar odd–even *n*-alkane characteristic to those of vegetative detritus. As a result, excessive abundance of odd number *n*-alkanes of  $C_{29}$ – $C_{33}$  compounds is not always due to increase in contribution from vegetative detritus. Fig. 3 shows the total concentrations of  $C_{29}$ – $C_{33}$  *n*-alkanes in the roadside ( $97.9 \text{ ng m}^{-3}$ ), local ( $70.6 \text{ ng m}^{-3}$ ), regional ( $68.4 \text{ ng m}^{-3}$ ), and LRT ( $59 \text{ ng m}^{-3}$ ) episodic samples. Considering that it was unlikely that roadside station was more affected by vegetative detritus than other stations, we attribute the highest concentration observed in the roadside samples to cigarette smoke and fossil fuel combustion.

#### 3.2.2. Branched alkanes

Branched alkanes (i.e., iso- and anteiso-alkanes) are tracers of cigarette smoke or emissions from burning tobacco plants.

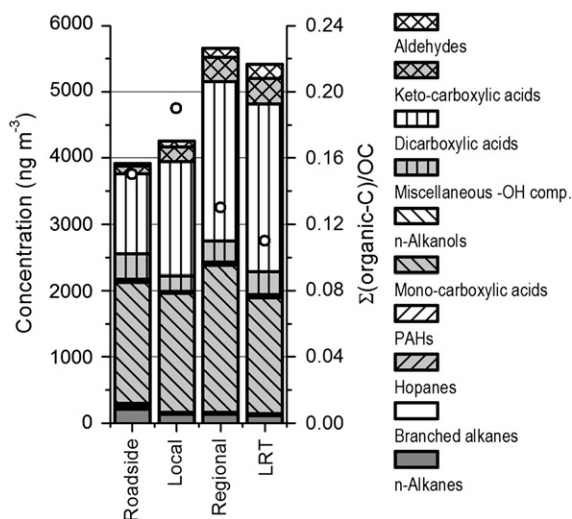


Fig. 2. Concentrations of quantified organic compound classes under different synoptic conditions. Here mono-carboxylic acids = *n*-alkanoic acids + other acids + monocarboxylates.

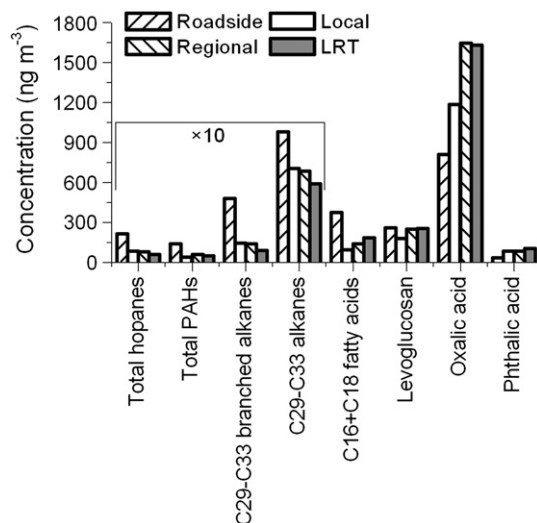


Fig. 3. Comparison of average concentrations of organic tracer classes under different synoptic conditions. Note: the concentrations of hopanes, PAHs, branched alkanes and alkanes are all magnified by 10 times.

A predominance of odd-number iso-alkanes and even-number anteiso-alkanes over *n*-alkanes in range of C<sub>29</sub>–C<sub>33</sub> indicates influence of cigarette smoke. The average values during roadside, local, regional, and LRT episodes were 47.7, 14.3, 14.0, and 9.0 ng m<sup>-3</sup>, respectively (Fig. 3). The roadside samples had the highest level, an anticipated result due to its location in a densely-populated, busy commercial and residential area.

### 3.2.3. Hopanes

Hopanes are constituents of fossil fuels. They are found in diesel fuels and present in lubricating oil used for both diesel-powered and gasoline-powered motor vehicles. Their presence in the atmosphere is a result of vehicular emissions and coal combustion (Cass, 1998; Schauer et al., 1996). Yu et al. (2011) have showed, through examining a larger data set of hopanes and other relevant measurements, that vehicular emissions dominated the ambient concentrations of hopanes in Hong Kong. The total concentrations of hopanes were 21.5, 8.3, 8.0, and 6.1 ng m<sup>-3</sup> during roadside, local, regional, and LRT episodes, respectively (Fig. 3). The roadside samples had the highest concentrations, consistent with the expected heavy influence from vehicular emissions. The regional and local episodic samples had similar values of hopanes while the LRT episodic samples had lower hopane concentrations, most likely a result of more atmospheric degradation during LRT (Yu et al., 2011).

### 3.2.4. PAHs

PAHs are emitted from virtually all combustion processes using carbonaceous fuels. The total concentrations of PAHs were 13.9, 4.1, 5.8, and 5.0 ng m<sup>-3</sup> during roadside, local, regional, and LRT episodes, respectively (Fig. 3). The highest PAH concentrations also occurred in the roadside samples, again indicating vehicular emissions to be a significant combustion source at this site. Different from the branched alkanes and hopanes, PAH concentrations were higher in the regional and LRT episodic samples than those in the local episodic samples. This suggests that there were significant PAH sources other than vehicular emissions outside Hong Kong in the PRD and in the northern China. Coal combustion and biomass burning were likely the significant sources in the regional and LRT episodes (Yu et al., 2011; Li et al., 2012).

### 3.2.5. C<sub>16</sub> and C<sub>18</sub> fatty acids and cholesterol

Among the identified primary sources for C<sub>16</sub> and C<sub>18</sub> fatty acids, cooking has the highest emission factor. Seed oil cooking especially emits a large quantity of C<sub>16</sub> fatty acid (i.e., C<sub>16</sub> fatty acid contributes to avg. ~18% of fine OC) (Chow et al., 2007; Schauer et al., 2002a). Both the highest abundance of the total fatty acids and the highest contribution of C<sub>16</sub> and C<sub>18</sub> fatty acids were observed in the roadside samples. These results were consistent with the characteristics of this site (i.e., in a densely populated commercial district with many restaurants). The highest concentration of oleic acid in the roadside samples (an average of 100 ng m<sup>-3</sup> versus 27–37 ng m<sup>-3</sup> in the other groups of episodic samples) further confirmed the significant contribution from cooking, because oleic acid is a major constituent of aerosols from seed oil cooking (~27% of fine OC) (Chow et al., 2007; Schauer et al., 2002a). We note that fatty acids have also non-cooking sources, such as road

dust, biomass burning, and vehicle exhaust; however, among the possible sources, cooking has the highest emission factors of C<sub>16</sub> and C<sub>18</sub> fatty acids (Schauer and Cass, 2000).

The average concentrations of cholesterol in the roadside, local, regional, and LRT episodic samples were 6.9, 3.1, 3.3, and 3.6 ng m<sup>-3</sup>, respectively. Meat cooking in urban area is an important source for cholesterol in ambient aerosols (Schauer et al., 1999a). This is reflected in that the highest concentration of cholesterol was observed in the roadside episodic samples.

### 3.2.6. Levoglucosan

Levoglucosan is a major constituent of the fine particle emissions from pyrolysis of cellulose during biomass burning and has been widely accepted as a tracer for biomass burning (e.g., Nolte et al., 2001; Simoneit et al., 1999; Yue and Fraser, 2004). The average concentrations of levoglucosan in the roadside, local, regional, and LRT episodic samples were 257, 179, 247, and 252 ng m<sup>-3</sup>, respectively (Fig. 3). The level of levoglucosan in these episodic samples was comparable to those measured in the winter samples in the study by Zheng et al. (2006). The higher levels in the regional and LRT episodic samples than those in the local samples indicate that biomass burning was mainly outside Hong Kong from the PRD and northern China. The highest value of levoglucosan (395 ng m<sup>-3</sup>) coincided with the highest concentration of potassium (7.2 μg m<sup>-3</sup>) on 7 December during the LRT episode. We note that the roadside samples had higher concentrations of levoglucosan than the local episodic samples. Zheng et al. (2006) also reported higher concentrations of levoglucosan at MK than at a general AQMS (TW) in their study and suggested that charcoal combustion in hotpot cooking, barbecues at restaurants, snack bars, and households was the likely source for elevated levoglucosan concentration at MK. However, charcoal, largely pure carbon, is not expected to produce levoglucosan any more during thermal process. Instead, we suggest that grilling cellulose-containing vegetables (e.g., peppers, corns, and mushrooms) could be the source for levoglucosan. However, this remains a speculation and further investigation is needed to verify emissions of levoglucosan from grilling vegetables.

### 3.2.7. Oxalate and phthalic acid

Oxalate and phthalic acids are regarded as secondary organic aerosol tracers (Li and Yu, 2010; Schauer et al., 2002b; Yu et al., 2005). Oxalate was the most abundant species among all the identified organic compounds, with the average concentrations at 812, 1186, 1645, and 1633 ng m<sup>-3</sup> in the roadside, local, regional, and LRT episodic samples, respectively (Fig. 3). The average concentrations of phthalic acid were much lower, with 36, 84, 86, and 105 ng m<sup>-3</sup> in the roadside, local, regional, and LRT episodic samples, respectively. Different from above mentioned organic tracer compounds, oxalate and phthalic acid showed an increasing trend from roadside to local, regional, and LRT episodic conditions, consistent with a secondary origin.

## 3.3. Source apportionment of PM<sub>2.5</sub> organic carbon

Six primary sources were identified on the basis of organic tracers, including vehicle exhaust, cooking, biomass burning, cigarette smoke, vegetative detritus, and coal combustion. The

**Table 2**  
Source contributions to fine organic carbon ( $\mu\text{g C m}^{-3}$ ).

Sample ID	Vehicle exhaust	Biomass burning	Cooking	Cigarette smoke	Vegetative detritus	Coal combustion	Other OC <sup>a</sup>	Measured OC	%Mass <sup>b</sup>	R <sup>2</sup>	$\chi^2$	DF <sup>c</sup>
<i>Roadside station</i>												
031031MK	9.45 ± 1.46(87.8) <sup>d</sup>	3.03 ± 0.88(28.1)	2.24 ± 0.58(20.8)	1.66 ± 0.3(15.4)	0.02 ± 0.23(0.2)	0.51 ± 0.37(4.7)	−6.15 ± 0(−57.2)	10.76 ± 1.08	157.16	0.97	0.47	15
031206MK	10.21 ± 1.66(69.1)	3.43 ± 1(23.2)	3.72 ± 0.89(25.2)	1.79 ± 0.32(12.1)	0.07 ± 0.25(0.5)	0.85 ± 0.43(5.8)	−5.31 ± 0(−35.9)	14.77 ± 1.48	135.94	0.97	0.41	15
031212MK	5.8 ± 0.98(43)	2.34 ± 0.68(17.3)	3.35 ± 0.76(24.9)	0.99 ± 0.15(7.4)	0 ± 0(0)	0.61 ± 0.26(4.5)	0.39 ± 0(2.9)	13.48 ± 1.35	97.11	0.97	0.47	16
Avg.	8.49 ± 1.37(66.6)	2.93 ± 0.86(22.9)	3.11 ± 0.74(23.6)	1.48 ± 0.26(11.6)	0.03 ± 0.16(0.2)	0.66 ± 0.35(5)	−3.69(−30.1)	13 ± 1.3	130.07	0.97	0.45	
<i>Local episode</i>												
031027TC	2.19 ± 0.28(27)	1.16 ± 0.33(14.4)	0.36 ± 0.1(4.4)	0.14 ± 0.04(1.7)	0.47 ± 0.1(5.8)	0 ± 0(0)	3.79 ± 0(46.7)	8.11 ± 0.81	53.31	0.84	2.14	16
031029KT	2.83 ± 0.37(28)	1.79 ± 0.52(17.7)	0.37 ± 0.12(3.6)	0.3 ± 0.06(3)	0.83 ± 0.17(8.2)	0 ± 0(0)	4.01 ± 0(39.6)	10.13 ± 1.01	60.39	0.95	0.68	16
031104KT	2.28 ± 0.28(44.6)	1.17 ± 0.35(22.9)	0.11 ± 0.06(2.2)	0.26 ± 0.05(5.2)	0.37 ± 0.09(7.2)	0 ± 0(0)	0.92 ± 0(17.9)	5.11 ± 0.51	82.09	0.80	2.94	16
031210KT	4.67 ± 0.55(49)	1.63 ± 0.48(17.1)	0.13 ± 0.11(1.3)	0.81 ± 0.15(8.5)	0.58 ± 0.18(6.1)	0 ± 0(0)	1.73 ± 0(18.1)	9.54 ± 0.95	81.88	0.93	1.00	16
031213KT	3.83 ± 0.45(41.4)	1.62 ± 0.48(17.5)	0.09 ± 0.1(1)	0.72 ± 0.13(7.8)	0.5 ± 0.16(5.4)	0 ± 0(0)	2.49 ± 0(26.9)	9.26 ± 0.93	73.09	0.94	0.77	16
031030CW	1.87 ± 0.44(25.3)	2.46 ± 0.71(33.4)	0.88 ± 0.25(11.9)	0.55 ± 0.1(7.4)	0.77 ± 0.18(10.5)	0.47 ± 0.15(6.4)	0.38 ± 0(5.1)	7.38 ± 0.74	94.91	0.96	0.62	15
031205CW	2.38 ± 0.49(20.8)	2.16 ± 0.62(18.9)	1.41 ± 0.35(12.4)	0.55 ± 0.1(4.8)	0.67 ± 0.16(5.8)	0.42 ± 0.15(3.7)	3.84 ± 0(33.6)	11.44 ± 1.14	66.42	0.96	0.56	15
031030SPP	2.71 ± 0.37(40.4)	1.61 ± 0.46(24.1)	1.25 ± 0.31(18.7)	0.79 ± 0.14(11.9)	0.35 ± 0.13(5.2)	0 ± 0(0)	−0.02 ± 0(−0.2)	6.7 ± 0.67	100.24	0.89	1.48	16
031203TW	2.29 ± 0.41(22)	2.58 ± 0.73(24.8)	0.85 ± 0.23(8.1)	0.31 ± 0.06(3)	0.17 ± 0.08(1.7)	0.25 ± 0.11(2.4)	3.97 ± 0(38.1)	10.41 ± 1.04	61.90	0.95	0.76	15
031209TW	3.95 ± 0.66(32.9)	3.32 ± 0.95(27.6)	0.55 ± 0.21(4.6)	0.41 ± 0.09(3.4)	0.32 ± 0.12(2.7)	0.3 ± 0.17(2.5)	3.16 ± 0(26.3)	12.01 ± 1.2	73.68	0.92	1.31	15
031213YL	3.45 ± 0.41(27.7)	3.52 ± 0.95(28.3)	0.65 ± 0.21(5.2)	0.33 ± 0.08(2.7)	0.13 ± 0.09(1)	0 ± 0(0)	4.38 ± 0(35.2)	12.46 ± 1.25	64.85	0.88	1.71	16
Avg.	2.95 ± 0.43(32.6)	2.09 ± 0.6(22.4)	0.6 ± 0.19(6.7)	0.47 ± 0.09(5.4)	0.47 ± 0.13(5.4)	0.13 ± 0.05(1.4)	2.6(26.1)	9.32 ± 0.93	73.89	0.91	1.27	
<i>Regional episode</i>												
031028TW	3.08 ± 0.72(21.4)	2.43 ± 0.68(16.9)	0.41 ± 0.2(2.8)	0.69 ± 0.13(4.8)	0.09 ± 0.12(0.6)	1.22 ± 0.23(8.5)	6.45 ± 0(44.9)	14.36 ± 1.44	55.10	0.88	2.08	15
031103TW	5.01 ± 0.86(22.2)	2.62 ± 0.74(11.6)	0.71 ± 0.23(3.1)	0.53 ± 0.11(2.4)	0.18 ± 0.12(0.8)	0.61 ± 0.23(2.7)	12.91 ± 0(57.2)	22.56 ± 2.26	42.79	0.92	1.25	15
031101YL	3.39 ± 0.42(18.6)	3.79 ± 1.1(20.8)	0.45 ± 0.2(2.5)	0.49 ± 0.1(2.7)	0.36 ± 0.13(2)	0 ± 0(0)	9.73 ± 0(53.5)	18.21 ± 1.82	46.55	0.93	1.01	16
031201YL	3.2 ± 0.41(14.4)	4.38 ± 1.18(19.7)	1.63 ± 0.42(7.3)	0.45 ± 0.1(2)	0.26 ± 0.11(1.2)	0 ± 0(0)	12.34 ± 0(55.4)	22.26 ± 2.23	44.57	0.94	0.88	16
031210YL	2.88 ± 0.48(15.6)	4.27 ± 1.14(23.1)	1.22 ± 0.34(6.6)	0.39 ± 0.09(2.1)	0.14 ± 0.09(0.8)	0.01 ± 0.12(0.1)	9.6 ± 0(51.8)	18.52 ± 1.85	48.17	0.95	0.81	15
031102TC	2.6 ± 0.36(8.4)	2.01 ± 0.58(6.5)	1.81 ± 0.41(5.9)	0.31 ± 0.07(1)	0.82 ± 0.17(2.6)	0 ± 0(0)	23.41 ± 0(75.6)	30.96 ± 3.1	24.38	0.90	1.30	16
031210TC	2.06 ± 0.27(13.1)	1.45 ± 0.41(9.2)	0.91 ± 0.21(5.8)	0.16 ± 0.04(1)	0.52 ± 0.11(3.3)	0 ± 0(0)	10.57 ± 0(67.4)	15.68 ± 1.57	32.59	0.88	1.51	16
031211CW	1.84 ± 0.48(19.3)	2.65 ± 0.76(27.8)	0.92 ± 0.27(9.6)	0.6 ± 0.11(6.2)	0.76 ± 0.18(8)	0.66 ± 0.17(7)	2.12 ± 0(22.2)	9.55 ± 0.96	77.81	0.97	0.42	15
Avg.	3.01 ± 0.5(16.6)	2.95 ± 0.82(16.9)	1.01 ± 0.29(5.5)	0.45 ± 0.09(2.8)	0.39 ± 0.13(2.4)	0.31 ± 0.09(2.3)	10.89(53.5)	19.01 ± 1.9	46.49	0.92	1.16	
<i>LRT episode</i>												
031207YL	4.63 ± 0.56(19.6)	5.12 ± 1.36(21.6)	1.82 ± 0.46(7.7)	0.5 ± 0.11(2.1)	0.23 ± 0.13(1)	0 ± 0(0)	11.4 ± 0(48.1)	23.7 ± 2.37	51.92	0.93	1.00	16
031208TC	1.52 ± 0.21(8.8)	1.31 ± 0.37(7.5)	1.29 ± 0.28(7.4)	0.13 ± 0.03(0.7)	0.45 ± 0.09(2.6)	0 ± 0(0)	12.66 ± 0(73)	17.35 ± 1.74	27.04	0.87	1.60	16
Avg.	3.08 ± 0.39(14.2)	3.21 ± 0.87(14.6)	1.55 ± 0.37(7.6)	0.31 ± 0.07(1.4)	0.34 ± 0.11(1.8)	0 ± 0(0)	12.03(60.5)	20.53 ± 2.05	39.48	0.90	1.30	

<sup>a</sup> Other OC is the difference between measured OC and calculated primary OC.

<sup>b</sup> %Mass means the sum percentage of estimated primary source contributions in total measured fine OC.

<sup>c</sup> DF means degrees of freedom.

<sup>d</sup> The value in parentheses is the contribution percentage of each source to fine OC.

results of CMB source apportionment analysis are given in Table 2. Fig. 4 shows the bar charts of source distributions for the different sample groups.  $R^2$  and  $\chi^2$ , parameters used to evaluate the CMB solutions, are in the range of 0.80–0.97 and 0.41–2.94, respectively. The tracer concentrations calculated by the CMB model and the measured ones are in good agreement. Three example comparisons are shown in Fig. S6.

The CMB results indicated that vehicle exhaust and biomass burning were the most important primary sources of fine OC in Hong Kong. Vehicle exhaust accounted for 3.0–8.5  $\mu\text{g Cm}^{-3}$  (Table 2). The highest contribution occurred at the roadside station (67% of fine OC), in line with its site characteristics and the lowest OC/EC ratios. Vehicular emissions accounted for 33% of fine OC in the local episodic samples, while decreased to 17% in the regional samples and 14% in the LRT episodic samples. This result is consistent with the source apportionment work by Zheng et al. (2006). Zheng et al. reported that the annual mean combined contributions of diesel and gasoline exhausts to fine OC in Hong Kong ranged from 14 to 27%. Biomass burning accounted for 2.1–3.2  $\mu\text{g Cm}^{-3}$  (15–23% of fine OC) (Table 2). Biomass burning mainly occurred outside Hong Kong. As a result, contribution of this source is expected to be relatively uniform across Hong Kong territory. However, MK had a relatively higher average contribution from biomass burning. As discussed earlier, possible local sources at MK could be the grilling of cellulose-containing vegetables.

Cooking was also a significant OC contributor, accounting for 0.6–3.1  $\mu\text{g Cm}^{-3}$ . The highest cooking contribution occurred in the roadside samples (24% of fine OC). In the local, regional, and LRT episodic samples, cooking contributions were much lower, in the range of 6–8% of fine OC.

Cigarette smoke, vegetative detritus, and coal combustion were smaller OC contributors, contributing 0.31–1.48  $\mu\text{g Cm}^{-3}$ , 0.03–0.47  $\mu\text{g Cm}^{-3}$ , and 0–0.66  $\mu\text{g Cm}^{-3}$ , respectively. The highest contribution of cigarette smoke occurred in the roadside samples (1.48  $\mu\text{g Cm}^{-3}$ ), consistent with its densely populated site characteristics. A high contribution of cigarette smoke (1.23  $\mu\text{g Cm}^{-3}$ ) in winter was also reported by Zheng et al.

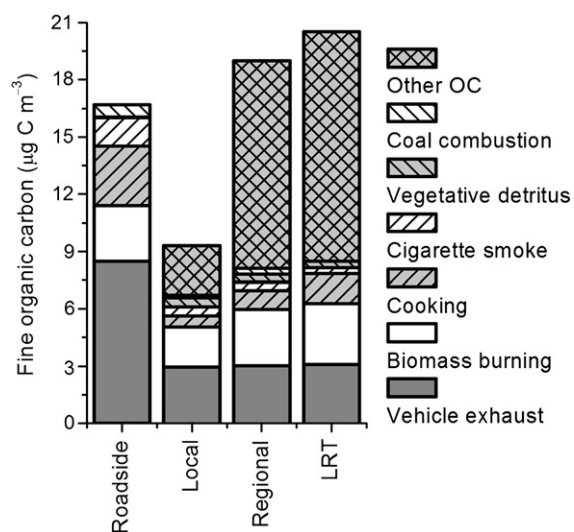


Fig. 4. Source contributions to fine organic carbon under different synoptic conditions.

(2006). This CMB model-derived result may be the upper limit contribution of cigarette smoke, considering that some missing sources might also emit branched alkanes. The lowest contribution of vegetative detritus was observed in the roadside samples (0.03  $\mu\text{g Cm}^{-3}$ ). During local, regional, and LRT episodes, no significant variations in contributions from cigarette smoke and vegetative detritus were observed, with values in the range of 0.31–0.47  $\mu\text{g Cm}^{-3}$  and 0.34–0.47  $\mu\text{g Cm}^{-3}$ , respectively. It is noted that the contributions the CMB model estimated from coal combustion in the MK roadside samples were considerably higher than other groups of samples. We suspect that the unexpectedly higher coal combustion contribution at MK was a result of limitation of CMB modeling in relying on PAHs to apportion contributions from gasoline exhaust and coal combustion. An inspection on the uncertainty indicates that the estimated contributions of coal combustion were associated with large uncertainties.

Suspended soil dust and ship emissions were not included in the base case CMB modeling. On four of the sampling dates during 28 October–9 December 2003, Teflon membrane filters were also collected and analyzed for elements using X-ray fluorescence (XRF) (Table S4). The XRF analysis provided concentrations of unique inorganic tracers, i.e., Al and Si for suspended soil dust and V for ship emissions. For these four sampling days, the source apportionment analysis results using CMB model were carried out with and without consideration of the two sources. The contributions of suspended soil and ship emission in OC were in the range of 0.52–1.28  $\mu\text{g Cm}^{-3}$  (avg. 0.80  $\mu\text{g Cm}^{-3}$ ) and 0.04–0.49  $\mu\text{g Cm}^{-3}$  (avg. 0.16  $\mu\text{g Cm}^{-3}$ ), respectively. The percentages of contribution to OC by suspended soil and ship emissions were in the range of 4.3–12% and 0.4–2.2%, respectively. The results (Table S5) indicate that there is almost no difference in source contributions apportioned for other sources with and without consideration of these two sources.

Other OC, which is taken to be the difference between the measured OC and the apportioned primary OC by the CMB model, may include contributions of unidentified primary OC sources (e.g., suspended soil, marine sources), potential artifacts in sampling, and SOA. The dominant portion of “other OC” was expected to be secondary OC. The values of “other OC” were –3.7, 2.6, 10.9, and 12.0  $\mu\text{g Cm}^{-3}$  in the roadside, local, regional, and LRT episodic samples, respectively (Table 2). There are two negative values of “other OC” at MK station. This could be due to uncertainties in the source profiles or cooking or biomass burning contribution being overestimated at the roadside site. Obviously, “other OC” dominated the measured OC in the regional and LRT episodic samples, accounting for 53.5% and 60.5% of fine OC, respectively. In comparison, primary sources dominated the measured OC in the roadside and the local samples, which contributed more than 74% of OC. “Other OC” was found to correlate with WSOC ( $R^2=0.75$ ,  $n=21$ ) (Fig. 5). It is also noted that much higher concentrations of WSOC and “other OC” occurred during regional and LRT episodes. In comparison, CMB source apportionment for samples collected following a regular schedule, therefore representing averaging condition, estimated that “other OC” only accounts for 14–33% of measured OC (Bergin et al., 2004; Zheng et al., 2006). It is clear that during regional and LRT high PM episodes examined in this study, much higher “other OC” contributions have been encountered. In another



words, secondary OC was a significant contributor to elevated  $PM_{2.5}$  OC on these high PM days.

Our recent studies have indicated that the majority of WSOC is likely secondary in origin (Yang et al., 2004, 2005; Yu, 2002). An additional observation is that WSOC is also well correlated with sulfate ( $R^2=0.84$ ,  $n=21$ ) (Fig. 5), further strengthening the proposition of WSOC being mainly secondary. Similar observations of well-correlated WSOC and sulfate were also seen in  $PM_{2.5}$  in Nanjing, China (Yang et al., 2005). The similar levels of WSOC and other OC, in conjunction with their correlation, seem to suggest that “other OC” was mainly associated SOA. This suggestion was consistent with characteristics associated with more aged air masses.

### 3.4. Sensitivity test

Omission of unknown important sources and lack of local source profiles may affect the CMB results significantly. China and HKEPD have in recent years made efforts to close this gap. Sensitivity tests were carried out to explore the effects on source apportionment results with the application of local source profiles. The source profiles described in earlier section are taken as the base case (Fig. S5). For the sensitivity test of a certain source, all the other source profiles in the base case remain unchanged.

#### 3.4.1. Cooking

There exist many different cooking source profiles. The ambient samples have similar  $C_{18}/C_{16}$  ratios to those of many cooking source profiles (Fig. S7A). In comparison, non-cooking sources have much lower  $C_{16}$  and  $C_{18}$  fatty acids emission factors and also different  $C_{18}/C_{16}$  ratios from those in ambient samples (Fig. S7B). These observations indicate that  $C_{16}$  and  $C_{18}$  fatty acids in the atmosphere mainly come from cooking sources.

We compare the CMB results between the base case and other cooking source profiles in three groups. The first group is Hong Kong local and Chinese-style cooking, including KFC, theater, Hunan, Guangdong cooking (Fig. S8A). The second group includes the combined source profiles of Hong Kong local/Chinese-style cooking (He et al., 2004; Yu et al.,

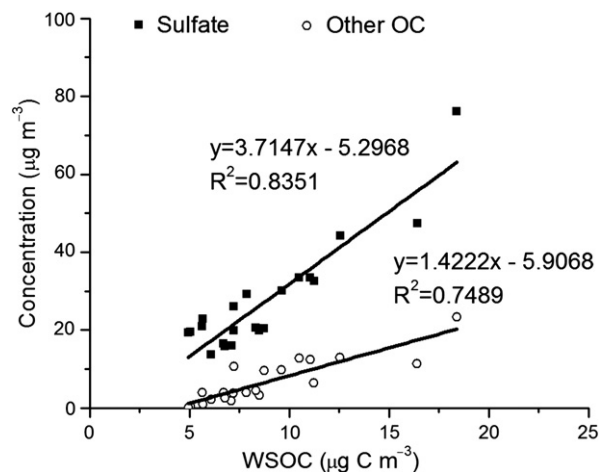


Fig. 5. Relationships between WSOC and other OC, sulfate (the three roadside samples were excluded).

unpublished results) and other ones from the United States (Rogge, et al., 1991; Schauer et al., 1999a, 2002a) (Fig. S8B). The third one includes the combined source profiles from the U.S. (Fig. S8C). In all three groups, the estimated contributions of all the other kinds of cooking are within the 1:2 and 2:1 lines. The contribution ratios between the test cases and base case are in the range of 0.34–1.46, suggesting that Hong Kong local cooking source profiles are not significantly different from those in the United States.

#### 3.4.2. Vehicle exhaust

A total of 10 combinations of diesel and gasoline exhaust available in the literature (Chow et al., 2007; Lough and Schauer, 2007; Rogge et al., 1993b; Schauer et al., 1999b, 2002c) were compared with the Hong Kong local tunnel profile base case. From Fig. S9A, we can see that most of the CMB results using vehicle exhaust profiles from the U.S. show higher contributions by vehicle exhaust. The ratios between the test cases and the base case are in the range of 0.59–5.03. Generally higher marker-to-OC ratios would lead to lower contributions. The higher EC/OC ratio in the Hong Kong tunnel profile (1.47) than all the other diesel exhausts (1.01–1.26) can partly explain this difference (Fig. S10). The other reason is that most source profiles from the U.S. were obtained more than ten years ago. The averaged diesel and gasoline exhaust obtained from the updated study of Lough and Schauer (2007) yields results similar to those in the base case in this study.

The estimated contributions of vehicle exhaust in the study by Zheng et al. (2006) at MK and TW station during winter were 13.98 and 5.37  $\mu\text{g C m}^{-3}$ , which were 1.64 and 1.48 times than those obtained in this study. The differences can be explained by the different EC emission factors in OC used in the two studies.

#### 3.4.3. Biomass burning

Pine, oak, eucalypt, combined wood combustion (Schauer et al., 2001; Zheng et al., 2002) from the U.S. and five kinds of biomass burning from South Asia (including coconut leaves, rice straw, cow dung, biomass briquettes, and Jackfruit branches) (Sheesley et al., 2003) were compared with the cereal straw burning profile obtained in China (Zhang et al., 2007). Fig. S9B illustrates that much lower biomass burning contributions were obtained with most tested source profiles. The estimated contributions of rice straw from South Asia and combined wood from the southern United States are almost within the 1:2 and 2:1 lines. The sensitivity test results indicate the importance of having biomass burning source profiles representative of sources influencing Hong Kong.

#### 3.4.4. Coal combustion

The CMB model was run using various industrial and residential coal combustion source profiles presented by Zhang et al. (2008) and Zheng et al. (2006). The results are compared with the base case in Fig. S9C. Coal combustion contribution in the base case falls between those using profiles for individual industrial and residential conditions. Considering there is not much domestic coal burning due to the general warm climate in the PRD area, we believe that industrial mixed coal combustion (base case) is reasonable to represent the coal combustion condition in PRD. The estimated

contributions were lower with the residential coal combustion source profiles, which was an expected result of higher marker-to-OC ratio (Fig. S10) due to its low combustion efficiency in residential coal combustion.

#### 4. Conclusions

PM<sub>2.5</sub> samples collected in two periods of high PM in 2003 were categorized into four groups on the basis of dominating aerosol source origins, which were identified through interpreting synoptic weather conditions and characteristics of common air pollutants. The four groups were roadside samples, local, regional and LRT episodic samples. The roadside samples had much higher concentrations of EC, total *n*-alkanes, branched alkanes, hopanes, PAHs, fatty acids, and cholesterol, while the lowest OC/EC ratio. The regional and LRT episodic samples had much higher levels of PM<sub>2.5</sub>, OC, and OC/EC ratio. There were no significant differences in total *n*-alkanes, branched alkanes, hopanes, PAHs, fatty acids, cholesterol, and levoglucosan among the local, regional, and LRT episodic samples. Using CMB model, we have estimated the contributions of six major primary OC sources, including vehicle exhaust, biomass burning, cooking, cigarette smoke, vegetative detritus, and coal combustion. Among the identified primary sources, vehicle exhaust and biomass burning were the most important aerosol sources. Vehicular exhaust accounted for larger than 14% of fine OC. The highest contribution to OC by vehicles (avg. 67%) was at the roadside station, in line with its site characteristics. Biomass burning accounted for 15–23% of fine OC. Cooking, cigarette smoke, vegetative detritus, and coal combustion were less significant sources. Other OC, defined to be the difference between the measured OC and the apportioned primary OC by CMB, could be taken to approximate secondary OC. Other OC was found to be a dominate fraction of OC (> 54%) in the regional and LRT episodic samples, indicating the significant contribution of SOA.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.atmosres.2012.08.005>.

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