



Composition and sources of carbonaceous aerosols at three contrasting sites in Hong Kong

Mei Zheng,¹ Gayle S. W. Hagler,² Lin Ke,^{1,3} Michael H. Bergin,^{1,4} Fu Wang,¹ Peter K. K. Louie,⁵ Lynn Salmon,⁶ Della W. M. Sin,⁷ Jian Zhen Yu,⁸ and James J. Schauer⁹

Received 13 January 2006; revised 30 April 2006; accepted 9 June 2006; published 31 October 2006.

[1] A significant fraction of the fine particulate matter in Hong Kong is made up of organic carbon. In order to quantitatively assess the contributions of various sources to carbonaceous aerosol in Hong Kong, a chemical mass balance (CMB) receptor model in combination with organic tracers was employed. Organic tracers including *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs), steranes, hopanes, resin acids, cholesterol, levoglucosan, and picene in PM_{2.5} collected from three air monitoring sites located at roadside, urban, and rural areas in Hong Kong are quantified using gas chromatography-mass spectrometry (GC/MS) in the present study. Analyses of some overlapping species from two separate laboratories will be compared for the first time. Spatial and seasonal source contributions to organic carbon (OC) in PM_{2.5} from up to nine air pollution sources are assessed, including diesel engine exhaust, gasoline engine exhaust, meat cooking, cigarette smoke, biomass burning, road dust, vegetative detritus, coal combustion, and natural gas combustion. Diesel engine exhaust dominated fine organic carbon in Hong Kong ($57 \pm 13\%$ at urban sites and $25 \pm 2\%$ at the rural site). Other sources that play an important role are meat cooking and biomass burning, which can account for as much as 14% of fine organic carbon. The primary sources identified by this technique explained 49%, 79%, and 94% of the measured fine organic carbon mass concentration at the rural, the urban, and the roadside sites, respectively. The unexplained fine OC is likely due to secondary organic aerosol formation.

Citation: Zheng, M., G. S. W. Hagler, L. Ke, M. H. Bergin, F. Wang, P. K. K. Louie, L. Salmon, D. W. M. Sin, J. Z. Yu, and J. J. Schauer (2006), Composition and sources of carbonaceous aerosols at three contrasting sites in Hong Kong, *J. Geophys. Res.*, *111*, D20313, doi:10.1029/2006JD007074.

1. Introduction

[2] The rapid economic growth in the past few decades in Hong Kong and the Pearl River Delta (PRD) has resulted in high levels of fine particulate matter (PM). Epidemiological

studies have shown that fine particulates are more related to adverse health effects than total suspended particulate matter [Lall *et al.*, 2004]. In urban areas, fine particulate pollution poses a health risk to the local population and contributes to the formation of smog [Cohen, 2000; Schauer *et al.*, 2002a]. In Hong Kong, this problem is more severe in winter. The Hong Kong Environmental Protection Department (HKEPD) has implemented a regular monitoring program for total suspended particulates (TSP) and respirable suspended particulates (RSP) since the mid 1980s. In Hong Kong, the long-term and the episodic PM levels have exceeded the air quality standards developed in the United States [Louie *et al.*, 2005]. Carbonaceous aerosol, which includes both organic carbon and elemental carbon (EC), is the major component of fine particulate matter in Hong Kong, accounting for $\sim 70\%$ of the PM_{2.5} (particles with an aerodynamic diameter less than or equal to 2.5 μm) mass concentration at a roadside site, $\sim 50\%$ at urban sites, and $\sim 30\%$ at rural sites [Louie *et al.*, 2005]. However, a comprehensive characterization of fine organic aerosol as well as its major sources is still lacking.

[3] There are some efforts of aerosol source apportionment in Hong Kong, including the application of principle

¹School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.

²School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA.

³Now at Department of Biological Sciences, California State University, Los Angeles, California, USA.

⁴Also at School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA.

⁵Hong Kong Environmental Protection Department, Wan Chai, Hong Kong Special Administrative Region.

⁶Environmental Quality Laboratory, California Institute of Technology, Pasadena, California, USA.

⁷Government Laboratory, Kowloon, Hong Kong Special Administrative Region.

⁸Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong Special Administrative Region.

⁹Environmental Chemistry and Technology Program, University of Wisconsin, Madison, Wisconsin, USA.

component analysis to TSP data by *Fung and Wong* [1995] and positive matrix factorization analysis for PM₁₀ (particles with an aerodynamic diameter equal to or less than 10 μm) by *Lee et al.* [1999]. To the best of our knowledge, source apportionment of organic carbon in PM_{2.5} has not yet been done in Hong Kong.

[4] Organic carbon is one of the major components in PM_{2.5} in the atmosphere, accounting for 10–70% of the total dry fine particulate mass in urban areas [*Cao et al.*, 2004; *Turpin et al.*, 2000; *Yang et al.*, 2005]. However, compared to the inorganic species, identification and quantification of organic carbon as well as its major sources are far from well understood because OC is a complex mixture of hundreds of organic compounds emitted from a variety of sources. In general, $\sim 20\%$ of the fine organic carbon in aerosol is solvent extractable and GC-resolvable, including alkanes, fatty acids, polycyclic aromatic hydrocarbons, alkanols, and other polar compounds [*Sin et al.*, 2005; *Zheng et al.*, 2000].

[5] The recent application of organic molecular markers to CMB has proven to be a valuable tool in determining the contribution of specific sources to organic carbon and fine particulate matter in the atmosphere [*Schauer et al.*, 1996; *Watson and Chow*, 2001; *Zheng et al.*, 2002]. In CMB modeling, the ambient concentration of each tracer compound in the model is reconstructed from the best fit linear combination of source emission profiles, and the contributions of major sources are estimated.

[6] In 2000–2001, a 12-month ad hoc project was therefore launched in Hong Kong aiming to better understand the chemical composition as well as the sources of carbonaceous aerosol in PM_{2.5}. As part of this project, the present study has two objectives which include (1) investigating the seasonal and spatial variations of the organic tracers in the fine particulate matter and (2) identifying the major sources of carbonaceous aerosol in Hong Kong. The results from this study provide important information of aerosol sources which is necessary for effective air quality management strategies.

[7] PM_{2.5} samples from the same three sampling sites during the same study period were also analyzed for solvent extractable and GC-resolvable organic compounds by the Government Laboratory of Hong Kong Special Administrative Region (HKSAR) [*Sin et al.*, 2005]. A direct comparison of organic compound analysis was made between two laboratories. To our best knowledge, this is the first comparison of organic compound analysis in ambient aerosol samples.

2. Methods

2.1. Sampling

[8] Samples were obtained every sixth day from three sites in Hong Kong including Hok Tsui (HT), Tsuen Wan (TW), and Mong Kok (MK) (see Figure 1). Each 24 hours a PM_{2.5} sample was collected on a quartz fiber filter from November 2000 to October 2001 using R&P Partisol samplers with a 2.5 μm inlet and a flow rate of 16.7 L min⁻¹. The MK site, about 2 m above the ground, is a roadside site located in a mixed commercial and residential area. The TW site, which is located on the rooftop of a government building (about 15–18 m above the ground),

represents an area of mixed residential and commercial activities. The rural HT site is located at the southern tip of Hong Kong Island, and experiences the least impact of anthropogenic activities among the three sites.

[9] The PM_{2.5} samples at each site were combined into seasonal composites before solvent extraction. The number of filters in each composite sample is shown in Table 1. The starting and ending dates for each season match those for the analysis of the organic compound analysis by the Government Laboratory of HKSAR, allowing the direct comparison of results. The winter, spring, summer, and fall seasons represent the PM_{2.5} filters collected from the following periods respectively: 11 December 2000 to 13 March 2001, 17 March 2001 to 16 May 2001, 19 May 2001 to 20 September 2001, and 21 September 2001 to 31 October 2001.

2.2. Chemical Analysis

[10] OC and EC data were provided by the Government Laboratory of HKSAR. The measurements were done using the NIOSH thermal evolution technique as described by *Birch and Cary* [1996]. The fraction of water soluble organic compounds (WSOC) was obtained by water extraction of filter samples. The water extracts were used to determine the total WSOC concentration and quantify the individual components of WSOC. The experimental procedure of organic speciation analysis has been well described in the previous publication [*Zheng et al.*, 2002], and is briefly described here. Deuterated internal standards as well as six sets of standard mixtures (PMSTD#1–#6) were used for identification and quantification of organic compounds in ambient samples. The deuterated standards were spiked in each sample before extraction, including benzaldehyde-*d*₆, dodecane-*d*₂₆, decanoic acid-*d*₁₉, phthalic acid-3,4,5,6-*d*₄, acenaphthene-*d*₁₀, levoglucosan-¹³C₆, hexadecane-*d*₃₄, eicosane-*d*₄₂, heptadecanoic acid-*d*₃₃, 4,4'-dimethoxybenzophenone-*d*₈, chrysene-*d*₁₂, octacosane-*d*₅₈, $\alpha\alpha\alpha$ -20*R*-cholestane-*d*₄, cholesterol-2,2,3,4,4,6-*d*₆, dibenz(ah)anthracene-*d*₁₄, and hexatriacontane-*d*₇₄. The amount of the internal standard mix spiked into each composite sample is proportional to the amount of the organic carbon that presents in the sample, with about 250 microliters of the internal standard mix spiked per milligram of OC.

[11] Each sample was ultrasonically extracted using hexane (twice), and a mixture of benzene and isopropanol (2:1) (three times) for 15 min for each extraction. The extract was filtered and reduced to about 5 mL by a rotary evaporator. It was further blown down using the ultrapure N₂. The extract was split into two fractions, with one fraction derivatized by diazomethane to convert the organic acids to their methyl ester analogues. After derivatization, the extract was ready for the GC/MS analysis.

[12] A Hewlett-Packard GC/MSD (6890 GC and 5973MSD) equipped with a 30 m i.d. \times 0.25 mm i.d. \times 0.25 μm film thickness HP 5 MS capillary column was used. The operation conditions were: isothermal hold at 65°C for 2 min, temperature ramp of 10°C min⁻¹ to 300°C, isothermal hold at 300°C for 22 min, GC/MS interface temperature of 300°C. The flow of the carrier gas (ultrapure He) was 1 mL min⁻¹. The injection volume was 1 μL for each sample. The scan range was 50–500 amu, and

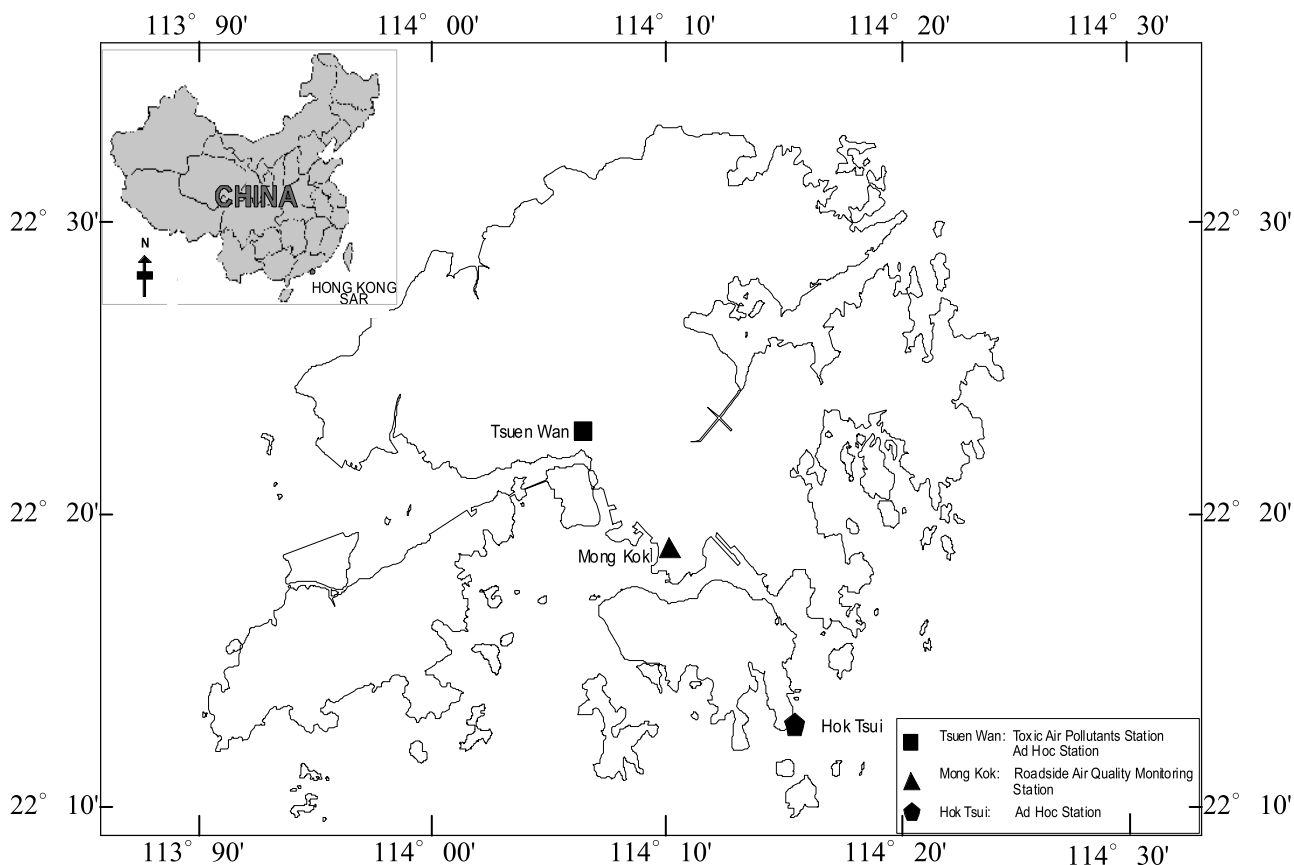


Figure 1. Sampling locations in the present study including the rural site (Hok Tsui), the urban site (Tsuen Wan), and the roadside site (Mong Kok).

the sample was analyzed under electron ionization mode (70 eV).

[13] Identification of the target compounds in the extracts was confirmed by comparing with the retention time and mass spectrum of the same compound in six sets of standard mixtures (PMSTD). For those compounds that could not be found in PMSTD, the identification was made using a commercially available standard such as picene and two secondary standards (a wood smoke secondary standard and a candle wax secondary standard) as well as the National Institute of Standards and Technology Mass Spectral Database. Quantification of the target compounds was calculated using the relative response factor (RRF) of each compound to a corresponding deuterated internal standard that has similar retention time and chemical structure. All solvents (hexane, dichloromethane, methanol, isopropanol) are Optima Grade (Fisher Scientific Inc.). Benzene from E&M Scientific Ominisolv was distilled prior to use.

[14] The solvent-extractable organic compound (SEOC) analysis by the Government Laboratory of HKSAR has been detailed by *Sin et al.* [2005]. In brief, internal standards including hexadecane- d_{34} , eicosane- d_{42} , tetracosane- d_{50} , triacontane- d_{62} , acenaphthalene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12} were spiked to the samples before extraction. The solvent system used for extracting SEOC from aerosol samples ultrasonically includes (1) 30 mL of hexane for 30 min, (2) 20 mL of 2:1 v/v mixture of toluene and isopropanol for 15 min, and (3) 10 mL of 2:1 v/v

mixture of toluene and isopropanol. The extracts were combined, filtered with Whatman 42 filter paper, concentrated, and added with 0.5 mL of the 14% boron trifluoride in methanol to etherify fatty acids at 85 °C for 30 min. Distilled DI water was added to quench the reaction and the organics were extracted by 2 mL dichloromethane for three times. The extracts were evaporated under nitrogen, reconstituted with 10 mL of hexane, and reconcentrated to 1 mL under nitrogen. Then the extracts were subjected to column chromatography to separate each extract into four fractions (aliphatic hydrocarbon, PAHs, methyl esters of fatty acids, and alcohols). The alcohols were further derivatized by adding 20 μ L of 1% trimethylchlorosilane at 70 °C for 30 min. For identification of SEOC, each fraction was then injected to a Thermo Finnigan GCQ GC/MS using an ion trap mass spectrometer with a DB-5 capillary column. For quantification, GC-flame ion detection analysis with a HP-5 capillary column was used for aliphatic hydrocarbon and methyl esters of fatty acids, while a Trace 2000 GC and a Voyager mass spectrometer with a DB-5 MS capillary column, operated under the selected ion mode, was used for PAHs and alcohols.

2.3. CMB Modeling

[15] Hong Kong PM_{2.5} samples were subjected to the organic tracer-based CMB analysis developed by *Schauer et al.* [1996]. The CMB7.0 model was applied to estimate the contributions of major sources to the measured organic

Table 1. Atmospheric Concentrations of Organic Tracers (ng m^{-3}), EC, and OC ($\mu\text{g m}^{-3}$) in PM_{2.5}^a

Compound	Hok Tsui (HT)				Tsuen Wan (TW)				Mong Kok (MK)			
	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter
Pentacosane	0.42	nd	0.43	2.61	3.67	2.84	1.30	7.09	6.87	6.95	4.23	12.9
Hexacosane	0.58	0.28	0.45	2.34	3.03	2.85	1.29	5.46	4.31	4.75	2.66	7.87
Heptacosane	0.76	0.28	0.79	2.23	3.20	2.75	2.10	5.68	4.69	4.23	4.03	8.05
Octacosane	0.59	0.35	0.61	1.56	1.75	1.68	1.25	3.04	1.87	1.93	1.84	2.48
Nonacosane	0.79	1.61	1.10	2.52	2.68	3.15	2.14	4.83	3.91	3.40	3.91	7.37
Triacontane	0.37	0.25	0.44	0.99	1.10	1.15	0.97	2.25	1.63	1.31	1.73	2.40
Hentriacontane	0.73	0.47	1.08	2.48	2.90	2.88	2.91	6.44	7.32	5.82	6.86	10.3
Dotriacontane	0.30	0.19	0.36	0.80	0.85	0.97	0.90	2.03	1.79	1.51	1.70	2.90
Tritriacontane	0.30	0.20	0.53	1.10	1.29	1.27	1.52	2.90	3.37	2.63	3.39	5.21
17 α (H)-21 β (H)-29-norhopane	0.08	0.04	0.02	0.15	0.75	0.60	0.24	1.13	2.61	2.78	2.66	3.94
17 α (H)-21 β (H)-hopane	0.09	0.06	0.04	0.26	0.78	0.71	0.32	1.23	2.28	2.45	2.25	3.40
22,29,30-trisnorhopane	nd	nd	nd	nd	0.07	0.10	nd	0.23	0.68	0.66	0.67	1.28
20S,R-5 α (H),14 β (H), 17 β (H)-cholestanes	nd	nd	nd	nd	0.17	0.09	nd	0.23	0.58	0.49	0.43	0.99
20R-5 α (H),14 α (H), 17 α (H)-cholestane	0.11	0.18	0.27	0.20	0.62	0.59	0.47	0.48	1.07	1.19	0.60	1.18
20S,R-5 α (H),14 β (H), 17 β (H)-ergostanes	nd	nd	nd	nd	0.14	0.06	nd	0.26	0.53	0.48	0.51	0.78
20S,R-5 α (H),14 β (H), 17 β (H)-sitostanes	nd	nd	nd	nd	0.42	0.37	0.08	0.56	1.42	1.50	1.40	1.97
Levoglucosan	14.6	3.40	29.8	154	69.8	77.0	8.56	172	53.0	72.2	271	458
Cholesterol	0.12	nd	nd	nd	1.12	nd	nd	0.28	4.33	1.31	nd	1.98
Benzo(b)fluoranthene	0.083	0.027	0.087	0.30	0.41	0.42	0.24	1.06	1.24	2.04	2.08	0.50
Benzo(k)fluoranthene	0.11	0.030	0.095	0.38	0.49	0.40	0.24	1.18	1.09	4.34	1.94	0.68
Benzo(a)pyrene	0.036	0.010	0.067	0.18	0.27	0.31	0.16	0.78	0.78	0.98	0.98	0.38
Indeno(cd)fluoranthene	0.033	0.015	0.041	0.14	0.14	0.10	0.091	0.42	0.24	nd	nd	0.082
Indeno(cd)pyrene	0.11	0.043	0.12	0.38	0.36	0.24	0.26	1.19	0.35	nd	0.58	0.16
Benzo(ghi)perylene	0.11	0.056	0.13	0.38	0.55	0.41	0.30	1.46	0.60	nd	1.49	0.29
Picene	nd	nd	nd	0.062	nd	nd	nd	0.13	nd	nd	nd	nd
iso-Nonacosane	nd	nd	0.01	0.10	nd	nd	0.16	0.32	nd	nd	0.34	1.12
anteiso-triacontane	nd	nd	0.01	0.07	0.69	0.53	0.24	0.76	1.57	1.88	0.78	2.01
iso-hentriacontane	nd	nd	0.01	0.05	0.76	0.75	0.45	1.10	2.53	2.39	1.31	4.08
Elemental carbon (EC)	1.32	0.72	1.44	1.85	5.76	6.09	5.04	6.54	17.8	21.4	19.4	20.1
Organic carbon (OC)	2.75	1.84	3.72	4.97	6.08	5.47	7.02	9.82	13.9	13.3	13.3	18.7
EC to OC ratio	0.48	0.39	0.39	0.37	0.42	0.46	0.38	0.67	1.29	1.61	1.46	1.07
Number of filters	10	21	6	21	9	22	6	20	10	22	6	20

^and, not detected.

carbon concentrations at the three monitoring sites during each season [Watson *et al.*, 1990]. The organic tracer concentrations, along with the concentrations of Al, Si, and EC supplied by HKEPD serve as inputs to the CMB model.

[16] Key input parameters to the CMB model include source profiles of diesel engine exhaust, gasoline engine exhaust, vegetative detritus, biomass burning, cigarette smoke, road dust, meat cooking, and natural gas combustion that were obtained from previous studies in North America and applied to this study [Hildemann *et al.*, 1991; Rogge *et al.*, 1993a, 1993b; Schauer, 1998; Schauer *et al.*, 1999a, 1999b, 2002b; Zheng *et al.*, 2002; McDonald *et al.*, 2003]. The meat cooking source profile was reconstructed by combining the cholesterol data from the chicken under-char source test by McDonald *et al.* [2003] with the other organic compound data from the source test by Schauer *et al.* [1999a]. The coal source profile was obtained from the analysis of fine particulate matter emitted from burning Datong coal in China [Zheng *et al.*, 2005]. Given that these source profiles have not been directly measured in Hong Kong, the model inputs serve as best estimates of the actual emission profiles based on available data. Tracer species are limited to a few tracers per source and they are expected to be more specific to sources than locations. A

sensitivity test is performed and discussed in the following text to evaluate the impact of source profiles on CMB results.

3. Results and Discussion

[17] Organic tracer concentrations provide semiquantitative insight on the sources of carbonaceous aerosol since the tracers are highly specific for distinct sources. The tracer compounds including *n*-alkanes, PAHs, steranes, hopanes, resin acids, cholesterol, levoglucosan, and picene were identified and quantified in the PM_{2.5} samples collected from the three HKEPD monitoring sites of MK, TW, and HT. Concentrations of major organic tracers are listed in Table 1. Table S1¹ presents concentrations of other measured organic compounds.

3.1. Intercomparison Between Two Laboratories

[18] Two different methods for the analysis of *n*-alkanes and PAHs were employed separately by the Government Laboratory of HKSAR and our research group, represented by GIT in Figure 2. Analyses of these overlapping species

¹Auxiliary materials are available at <ftp://ftp.agu.org/apend/jd/2006jd007074>.

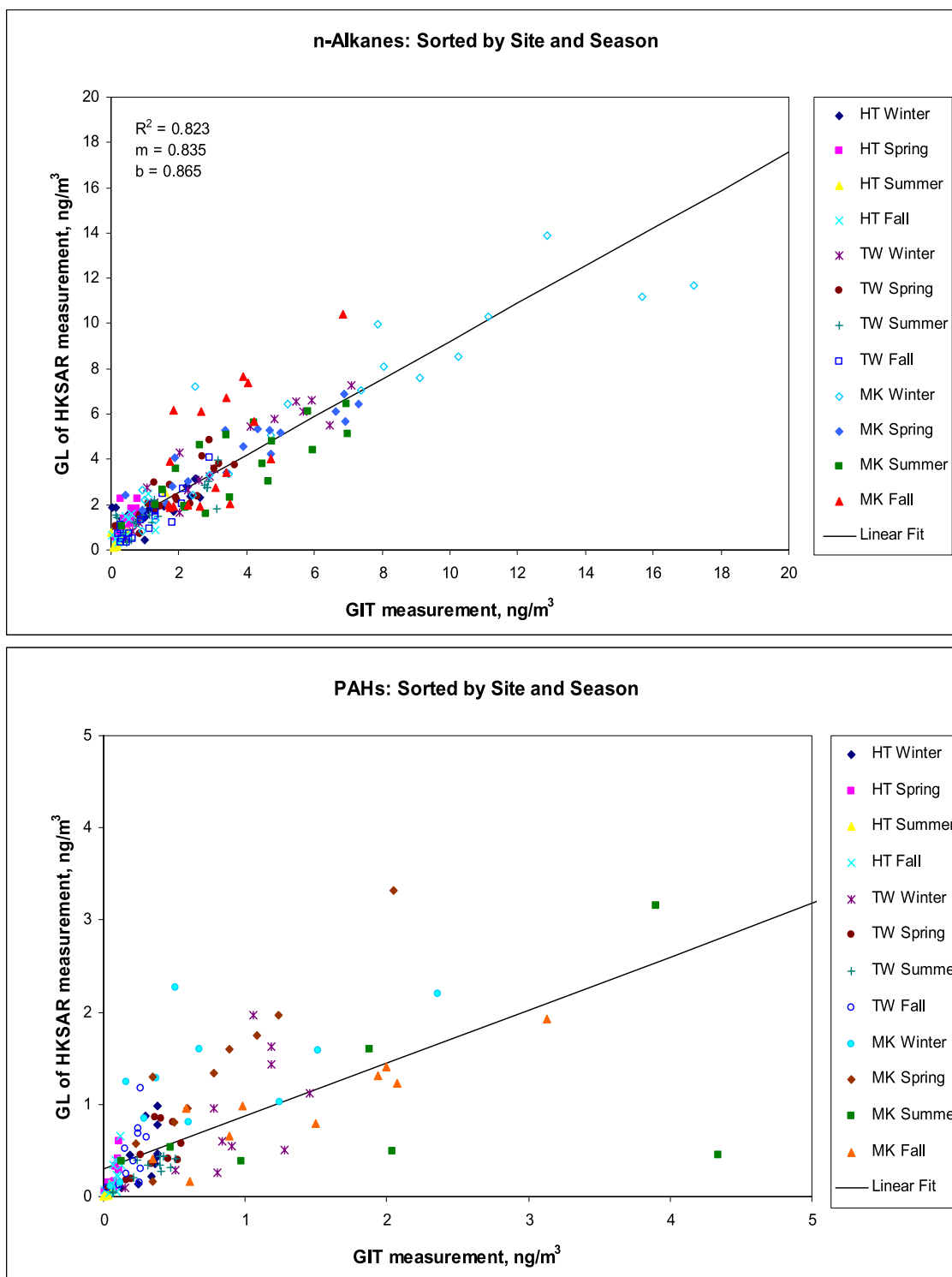


Figure 2. Comparison of the concentrations of *n*-alkanes and PAHs measured by two different laboratories (GIT, Georgia Institute of Technology; GL of HKSAR, Government Laboratory of the Hong Kong Special Administrative Region). The R^2 , slope (m) and intercept (b) are shown.

in ambient aerosol samples from two separate laboratories are compared for the first time. The method used in this study and the method applied in the Government Laboratory of HKSAR will be designated as “the tracer analysis” and “the SEOC analysis,” respectively, in the following discussions. The uncertainty of the organic tracer analysis at

GIT has been determined by the Standard Reference Material for Urban Dust (SRM1649a) and authentic standard mixtures (PMSTD). The tracer analysis shows that the recoveries of authentic standards are in the range of 83–143%, while recoveries of nine PAHs in SRM1649a range

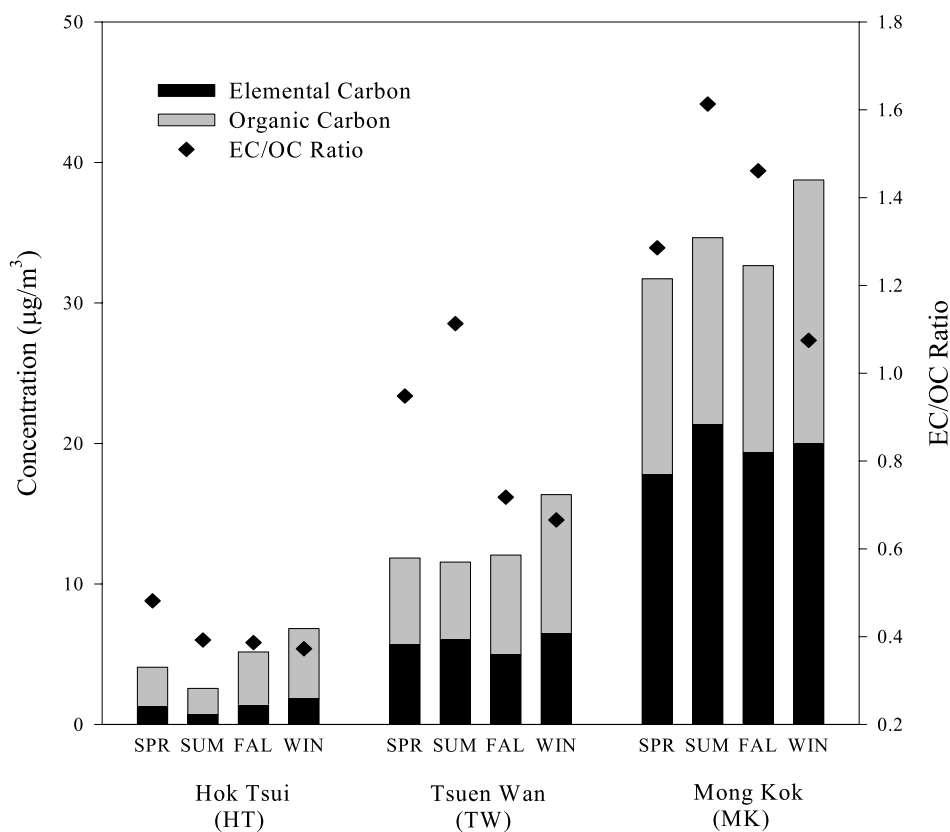


Figure 3. Seasonal and spatial distributions of elemental carbon (EC) and organic carbon measured (OC) as well as ratios of EC to OC at three sites in Hong Kong: HT, Hok Tsui; TW, Tsuen Wan; MK, Mong Kok; SPR, spring; SUM, summer; FAL, fall; WIN, winter.

from 70 to 144%. The uncertainty of organic species is compound specific and less than 20% in general.

[19] Some alkanes and PAHs were analyzed by both the tracer analysis and SEOC analysis. A regression analysis was conducted with the concentrations of *n*-alkanes and PAHs and the slopes, intercepts, as well as the R^2 values are shown in Figure 2. The comparison shows a better agreement for *n*-alkanes than PAHs, with both R^2 and slope values of around 0.8 for *n*-alkanes. PAH concentrations are lower than alkanes in general and a lower R^2 (0.452) and slope (0.576) were obtained. Many factors may contribute to the difference in organic compound concentrations reported from two individual laboratories, including the selection of internal standards, filter extraction procedures, and the instrumental conditions.

3.2. Organic Tracers in PM_{2.5}

[20] The seasonal and spatial distributions of OC and EC as well as EC to OC ratios are shown in Figure 3. In general, the highest concentrations of fine particulate organic carbon were observed at each site during the winter. During the winter, the combination of less precipitation, the more northerly flow from the land, and the lower mixing heights associated with cooler surface temperature results in higher concentrations across Hong Kong [Hagler *et al.*, 2006; Louie *et al.*, 2005].

[21] Different emission sources can be characterized by their EC/OC ratios as can be seen from the source profiles

used in the present study. The EC combined with OC provides important information for diesel engine exhaust, which has higher EC/OC ratios (1.24) than most of the other sources including gasoline exhaust with (0.45) and without (0.12) a catalyzed converter, coal combustion (0.3), wood combustion (0.06–0.25), road dust (0.08), vegetative detritus (0.03), and meat cooking (0). Fuel oil is an exception with a EC/OC ratio (6) higher than diesel engine exhaust. The EC concentration alone is able to implicate the importance of diesel exhaust to the total organics in PM only when the contribution from other EC sources (e.g., fuel oil and coal combustion) is insignificant. Much more EC was measured at MK, followed by TW and HT. Spatial variations of EC/OC ratios are obvious between monitoring sites. The EC/OC ratios range from 1.1 to 1.6 for MK, and are below 0.7 for TW and HT. Higher EC/OC ratios at the roadside MK site indicate that EC sources at MK may be significantly impacted primarily by diesel exhaust. It is reasonable to assume that MK is not significantly impacted by emissions from fuel oil and coal combustion due to the close proximity of the MK monitoring site to a main road. The consistently high EC concentration at the MK site demonstrates the dominance of diesel exhaust in PM emissions from mobile source at this site. Although high EC/OC ratios have been measured for cold-start gasoline powered vehicles in cold environments, this is not expected to be important at the roadside site in Hong Kong since it is located in the subtropics. EC exhibited less seasonal varia-

tions compared to OC, thus the lower EC to OC ratios in winter are most likely due to the higher OC concentrations measured in colder season.

[22] In the present study, the total concentrations of *n*-alkanes (C_{17} – C_{36}) for HT, TW and MK ranged from 4.3–23.6, 20.4–58.6 and 53.6–125.6 ng m^{-3} , respectively. The seasonal as well as the spatial variations were significant. At all three monitoring sites, *n*-alkanes were only found in significantly higher concentrations in the winter season as compared with the other seasons. MK had much higher *n*-alkane concentrations than TW, followed by the remote HT site. The carbon preference index (CPI) can be used to determine the distribution of biogenic and anthropogenic sources for *n*-alkanes in fine particles [Simoneit, 1986]. The CPI of *n*-alkanes is defined as the sum of the concentrations of the odd carbon number alkanes divided by the sum of the concentrations of the even carbon number alkanes. Vegetative detritus, emitted to the atmosphere from the abrasion of protrusions on plant leaves, contains more odd carbon number alkanes than even carbon number alkanes, which results in a higher CPI (>1). Moreover, it should be noted that smoke from low-temperature biomass combustion fire is enriched in odd-carbon isomers, which could also result in high CPIs. Anthropogenic emissions (e.g., petroleum residues) have no evidence of carbon preference and thus its CPI is close to 1. Urban sites, with large contributions from anthropogenic emissions, generally have CPIs ranging between 1.1 and 2.0, while rural areas with more biogenic influence generally have CPIs above 2.0 [Simoneit, 1989; Zheng *et al.*, 2000]. The CPIs of *n*-alkanes in the present study ranged from 1.25 to 1.73, similar to the value (ranging from 1.26 to 1.50) reported by the Government Laboratory of HKSAR [Sin *et al.*, 2005]. The similar low CPI values were also found by Zheng *et al.* [2000], who suggested that most *n*-alkanes in Hong Kong are from petroleum residue.

[23] Hopanes and steranes (H+S) are found in diesel fuel, and present in lubricating oil used by both diesel-powered and gasoline-powered motor vehicles [Cass, 1998]. They can be used as molecular tracers for the fine particulate matter emitted from motor vehicles [Schauer *et al.*, 1996]. Figure 4 shows the seasonal and spatial distribution of H+S. Very high concentrations of H+S were found at MK (13.6–20.7 ng m^{-3}), followed by TW (1.51–6.31 ng m^{-3}) and HT (0.36–0.42 ng m^{-3}). Generally, more H+S was observed in winter while the difference was minor for the spring, summer, and fall seasons except for the TW Fall sample.

[24] The ratios of H+S to fine organic carbon were calculated and shown in Figure 4. Since H+S is predominately from motor vehicles, the ratios implicate the relative importance of automobile emissions to OC. The highest average ratio was found at the MK site (1.1e-3), while the lowest average ratio was at the HT site (1e-4). This clearly showed that the impact from primary emissions of automobiles was more important at the roadside MK site. The seasonal variation of ratios of H+S to fine organic carbon at the MK site was insignificant, suggesting that the contribution of automobile emissions to fine OC near the MK site remains relatively constant for all seasons though fine organic carbon concentrations are the highest in winter and lower during the other seasons.

[25] In addition, the ratio of H+S to elemental carbon is also a helpful indicator to evaluate the importance of diesel vs. gasoline exhaust contributions. Source tests revealed that diesel-powered vehicles and gasoline-powered vehicles emit H+S and EC in different ratios. Diesel-powered vehicles are important sources of both EC and H+S, while gasoline-powered vehicles are important sources of H+S but minor contributors to EC. Therefore emissions from different types of engine (i.e., diesel and gasoline) would have diagnostic H+S to EC ratios, with the H+S/EC ratios being 4.6e-4 and 0.15 for the diesel- and gasoline-powered vehicle exhausts, respectively [Schauer *et al.*, 1999b, 2002b]. A higher H+S/EC ratio indicates a greater contribution from gasoline exhaust, assuming that diesel and gasoline exhaust are the only major sources of H+S. In the present study, the average H+S to EC ratios were 8e-4 at MK (7e-4–1e-3), 6.5e-4 at TW (3e-4–1e-3), and 3.5e-4 at HT (3e-4–5e-4) (Figure 4). These ratios are close to that of diesel engine exhaust, suggesting that diesel exhaust is indeed an important source of fine primary OC in Hong Kong.

[26] Levoglucosan is a major constituent of fine particle emissions from cellulose during biomass burning and has been widely accepted as a major tracer for biomass burning [Simoneit *et al.*, 1999]. The distribution of levoglucosan is shown in Figure 5. The levels of levoglucosan were the highest in winter (154–458 ng m^{-3}), compared to spring (15–70 ng m^{-3}), summer (3–77 ng m^{-3}) and fall (9–271 ng m^{-3}), indicating the highest impact of biomass burning during winter. Potassium also peaked in winter and exhibited a positive correlation with levoglucosan (correlation coefficient as 0.6614). This correlation coefficient is relatively low, which is probably due to the wide range of values of levoglucosan in aerosol samples in Hong Kong (3.40–458 ng m^{-3}). Levoglucosan concentrations also varied from site to site. The highest values of levoglucosan were measured at MK (53–458 ng m^{-3} , 215 ng m^{-3} on average), while samples collected from TW and HT had less levoglucosan, with the annual average for TW and HT as 81 and 51 ng m^{-3} , respectively. Unlike the U.S., there is no large-scale prescribed burning or active wood burning activities in homes during winter in Hong Kong. It is more likely that the significant increase of levoglucosan concentrations in winter measured at all three sites is due to transport from the surrounding regions of HKSAR. However, it is important to note that the combustion of charcoal for making food (e.g., hotpot cooking) and barbecues is popular in HK, especially at the densely populated MK site during winter. Unfortunately, the source profile for charcoal combustion is still not available. However, it is quite possible that the activities related to charcoal combustion at restaurants, snack bars, and even households at MK during winter contributes to the extremely high level of levoglucosan found in the MK fall and winter samples.

[27] Cholesterol is an excellent marker for the fine particulate matter released from meat cooking. In the present study, cholesterol was only detectable in 6 of the 12 seasonal samples. The presence of cholesterol in particle emissions was mainly found in spring and winter. Cholesterol was not found in all samples collected from the summer and fall seasons except the MK summer sample. Slightly higher concentrations of cholesterol were found at MK (not detectable to 4.33 ng m^{-3}), followed by TW (not

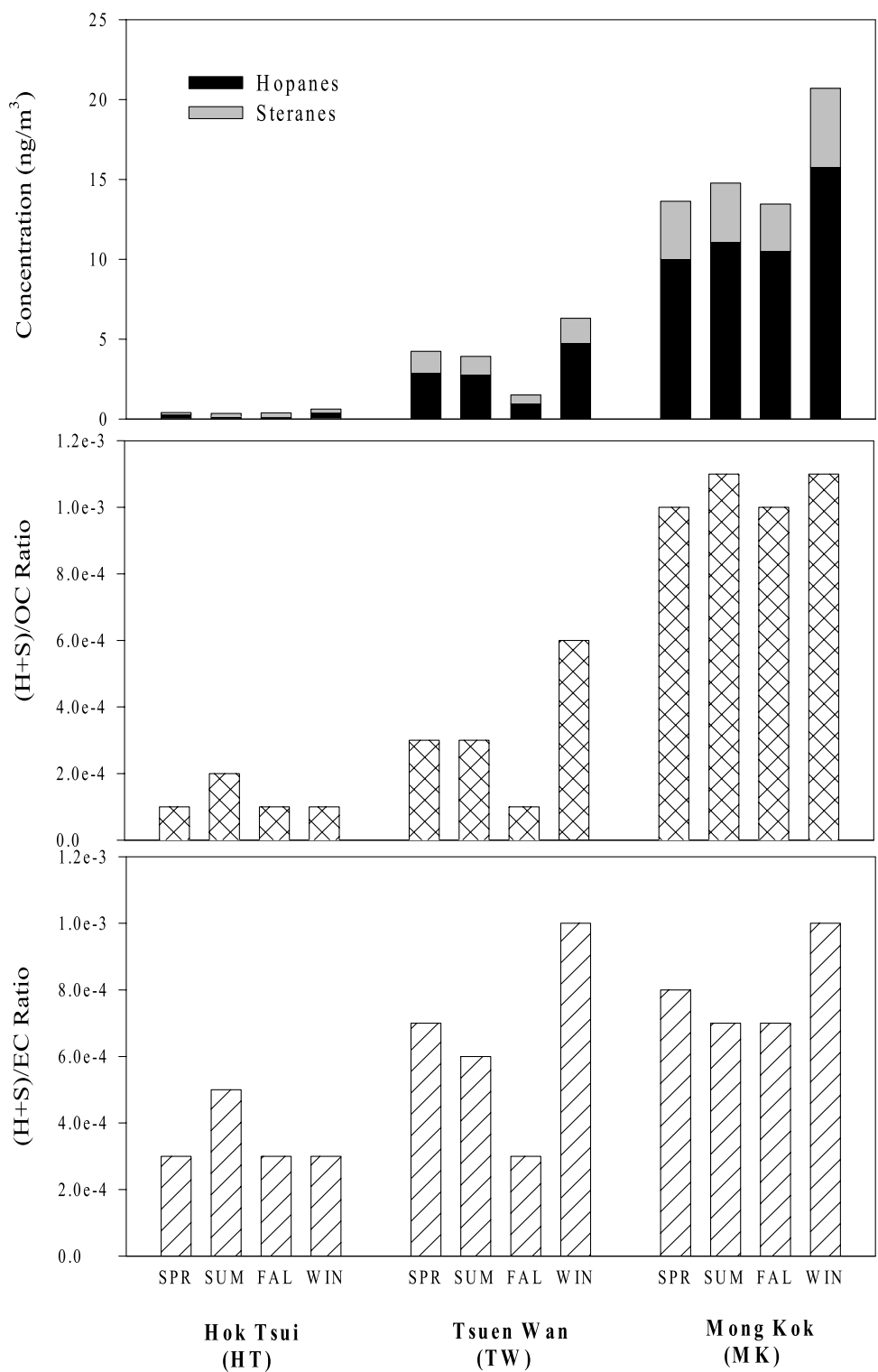


Figure 4. Seasonal and spatial distributions of hopanes and steranes (H+S), ratio of H+S to organic carbon (OC), and ratio of H+S to elemental carbon (EC) at three sites.

detectable to 1.12 ng m^{-3}) and HT (not detectable to 0.12 ng m^{-3}). This suggests that meat cooking is more active at the MK site than at the other two sites, which is not surprising given that MK is located in a mixed and densely populated residential and commercial area.

[28] PAHs are the products of incomplete combustion from various sources, such as fossil fuel combustion and biomass burning. The seasonal and spatial variations of total PAHs are shown in Figure 6. The concentrations of total PAHs varied significantly by seasons and sites. The highest

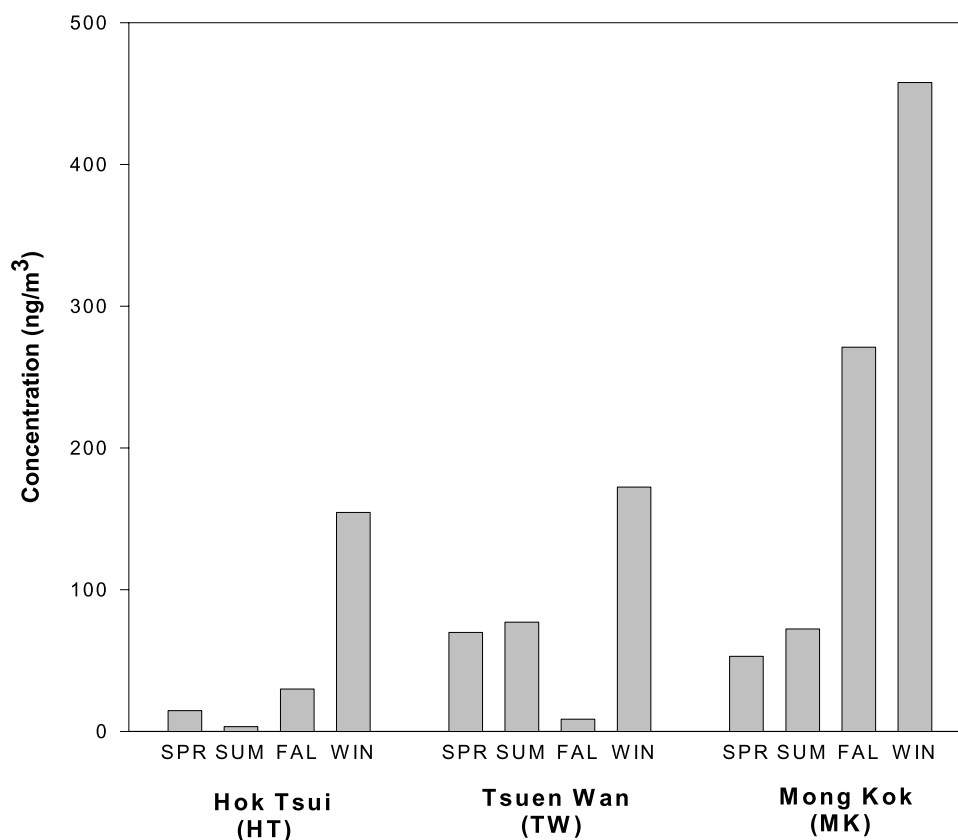


Figure 5. Seasonal and spatial distribution of levoglucosan measured at three sites in Hong Kong.

concentrations were found in winter for HT and TW, but in fall for MK. The annual average PAH concentrations for HT, TW and MK were 1.6, 6.0 and 12.8 ng m⁻³, respectively. PAH concentrations at MK were less variable than the other two sites. This suggests that diesel- and gasoline-powered vehicles, which are major sources of PAHs, continuously impacted the MK site.

[29] Important sources for PAHs include automobile emissions, coal combustion, biomass burning, and natural gas combustion. Picene is a tracer of coal burning [Oros and Simoneit, 2000]. Picene was detected in only 2 of the 12 samples, which were the winter samples from HT and TW. However, picene was detected in nearly all PM_{2.5} samples from five sites during four seasons in Beijing [Zheng *et al.*, 2005]. The level of picene stayed undetectable at MK in all seasons. This finding further supported that EC at MK was mainly from vehicular emissions. Picene was found at HT and TW but not at MK in winter indicating emissions of coal combustion do not exhibit significant impact on the roadside site. Figure 5 shows that levoglucosan concentration increased significantly only during winter, indicating that contribution from biomass burning became more important during winter. However, at MK the PAH concentrations remained high especially during summer and fall. This suggests that PAHs measured at MK are mainly from local mobile source emissions. Compared to other seasons, the higher levels of PAHs found in winter at TW and HT sites might be partially due to the increase of biomass burning and coal combustion in winter.

[30] An interesting finding was that PAH distributions were different among the three sites. The grouped PAHs according to their molecular weight were normalized by the total PAHs (Figure 7). Higher proportions of the low molecular weight PAHs (with molecular weight of 202–228) were found at MK as compared to HT and TW. MK is a roadside site which is only 2 m above the ground while TW is about 15–18 m above the ground and HT is a remote rural station. As a result, PAHs from fresh and local emissions dominate total PAHs at MK. Broman *et al.* [1991] suggested that some gas-phase PAHs are more susceptible than others to degradation via gas-phase reactions with the OH radical, so the semivolatile low molecular weight PAH components may be reduced when the distance from the source increases. Atkinson and Arey [1994] also found the short atmospheric lifetimes of 3–5 hours for fluoranthene and pyrene when reacted with OH radical. MK was found to have lower proportions of coronene and PAHs with molecular weight of 276, which is opposite to the HT and TW sites. Besides the factor of fresh vs. aged aerosols, the difference of the distribution pattern in Figure 7 might be also due to the different sources of PAHs at MK and at HT and TW. The previous work by Rogge *et al.* [1993c] showed that some high molecular weight PAHs such as benzo(ghi)perylene and coronene are mainly emitted from automobiles without a catalytic convertor. The presence of coronene at HT and TW but not at MK (except the winter sample) as well as the greater proportions of the high molecular weight PAHs (MW = 276) at HT and TW indicate that there may be more emissions from noncatalyst powered

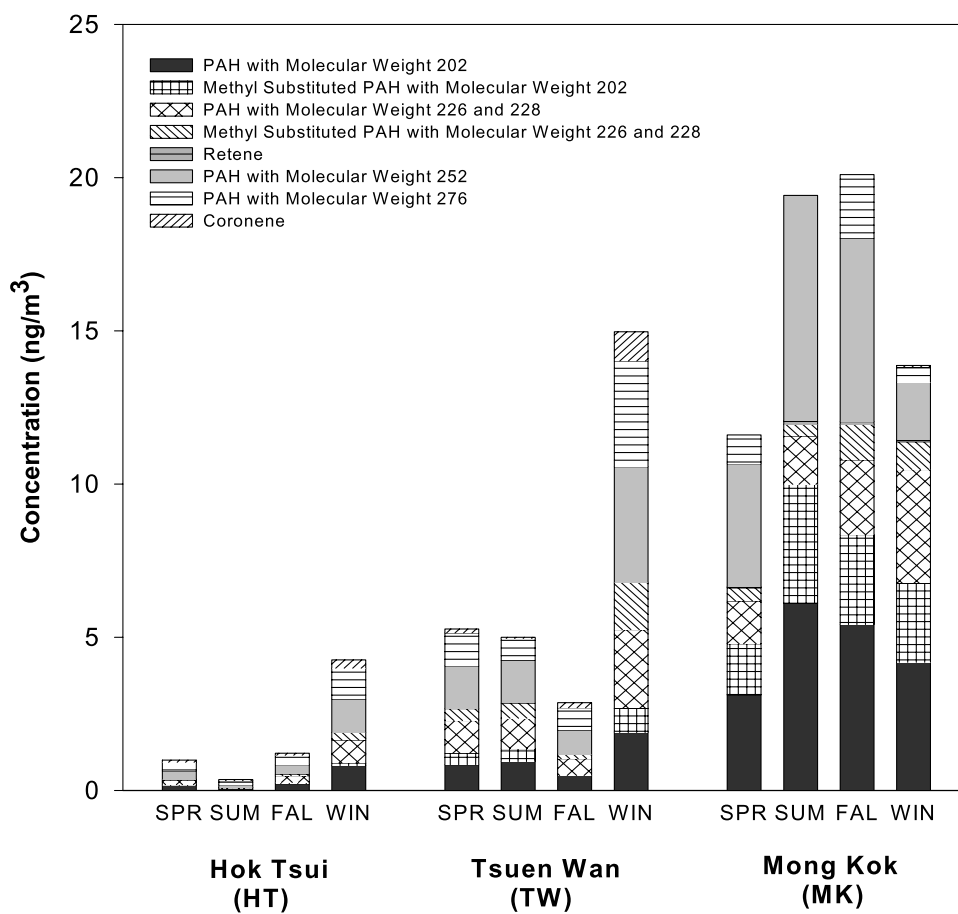


Figure 6. Seasonal and spatial distributions of PAHs measured at three sites in Hong Kong.

vehicles at HT and TW as compared to MK. The percentages of some methyl substituted PAHs (the PAHs with molecular weight 202) to the total PAHs were also found to be higher at MK than at HT and TW (Figure 7). It has been reported that crude oils and many refined petroleum products have a higher ratio of methyl substituted PAHs to unsubstituted PAHs than the ratio found in engine exhaust emissions due to thermal dealkylation within the engine [Tancell *et al.*, 1995]. However, Jensen and Hites [1983] reported that decreasing the exhaust gas temperature (decreased engine load) would increase the total emission rate for alkyl-PAHs. The present study indicates that the higher emissions of methyl-PAHs at MK may be due to an increase in traffic congestion (longer time periods of decreased engine load) as compared to TW and HK.

3.3. PM_{2.5} Organic Carbon Apportionment

[31] The results of the CMB source apportionment are given in Figure 8 and Table 2, which are statistically significant with the average R^2 , χ^2 , and degree of freedom as 0.93, 2.40, and 16, respectively. The percent explained mass ranged from 34 to 111%. The R^2 , χ^2 , and degrees of freedom were derived from the characteristics of the fitting species and the comparison of measured value to the modeled value for each fitting species in the model. Up to nine sources including diesel exhaust, gasoline exhaust, meat cooking, cigarette smoke, biomass burning, road dust, vegetative detritus, coal combustion, and natural

gas combustion were included in this study. *Iso*-nonacosane, *anteiso*-triacontane, and *iso*-hentriacontane are used as the major tracers for cigarette smoke. Since *iso*-nonacosane, *anteiso*-triacontane, and *iso*-hentriacontane can also be from vegetative detritus, the estimate of cigarette smoke in the present study could be influenced by this additional source. Therefore cigarette smoke in Table 2 can be viewed as an upper limit estimate.

[32] The highest concentrations of organic carbon were observed at MK as previously discussed. This is not surprising given that the location is influenced directly by mobile source emissions. The CMB results showed that the dominant source of fine organic carbon at MK was diesel exhaust, which was estimated to account for 60% of the fine particulate organic carbon concentration. Gasoline exhaust was estimated to account for about 8% of measured fine OC at MK. As discussed earlier, the measured H+S to EC ratio also indicates the significant contribution by diesel vehicles at this roadside site. Other sources are estimated to play an important role including meat cooking and biomass burning, which could account for as much as 26% of the fine OC. The average absolute difference between the primary fine particulate organic carbon concentrations estimated by the CMB model and the measured OC was only 4% at MK. This suggests that OC at this site was mainly primary in origin.

[33] In contrast to MK, HT experienced the lowest OC concentrations among all sampling sites. The CMB model

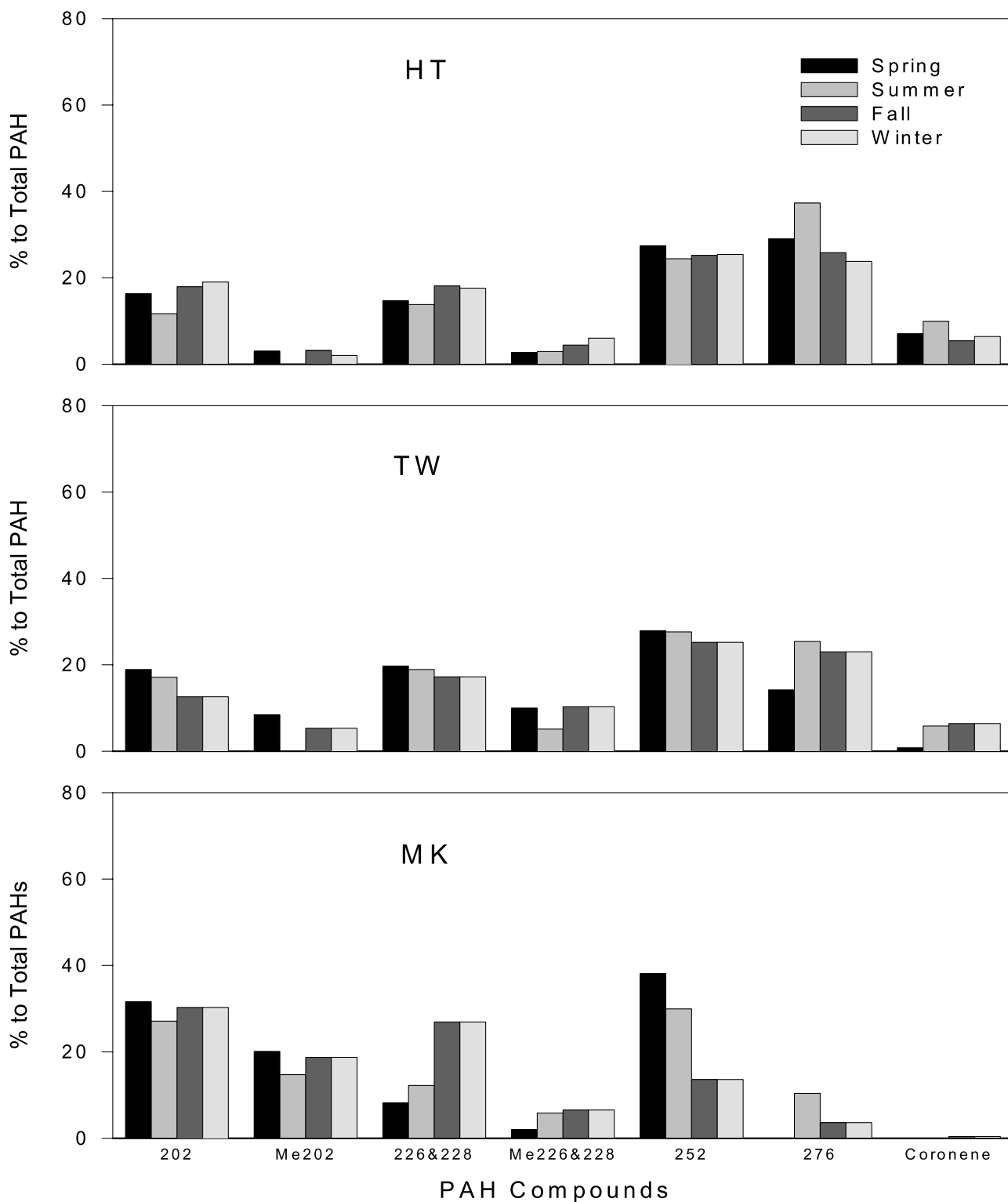


Figure 7. Seasonal and spatial distributions of PAH composition measured at three sites. 202, PAH with molecular weight (MW) 202; Me202, methyl substituted PAH with MW202; 226&228, PAH with MW226 and 228; Me226&228, methyl substituted PAH with MW226 and 228; 252, PAH with MW252; 276, PAH with MW276.

estimated that diesel exhaust accounted for about 25% of the organic carbon at Hok Tsui throughout the year. An interesting finding was that the CMB model only accounted for 34–64% of the fine organic carbon mass concentrations

at this rural site. The remainder, classified as “Other OC” in Figure 8, could be attributed to uncertainties in the CMB model and more likely the existence of particulate

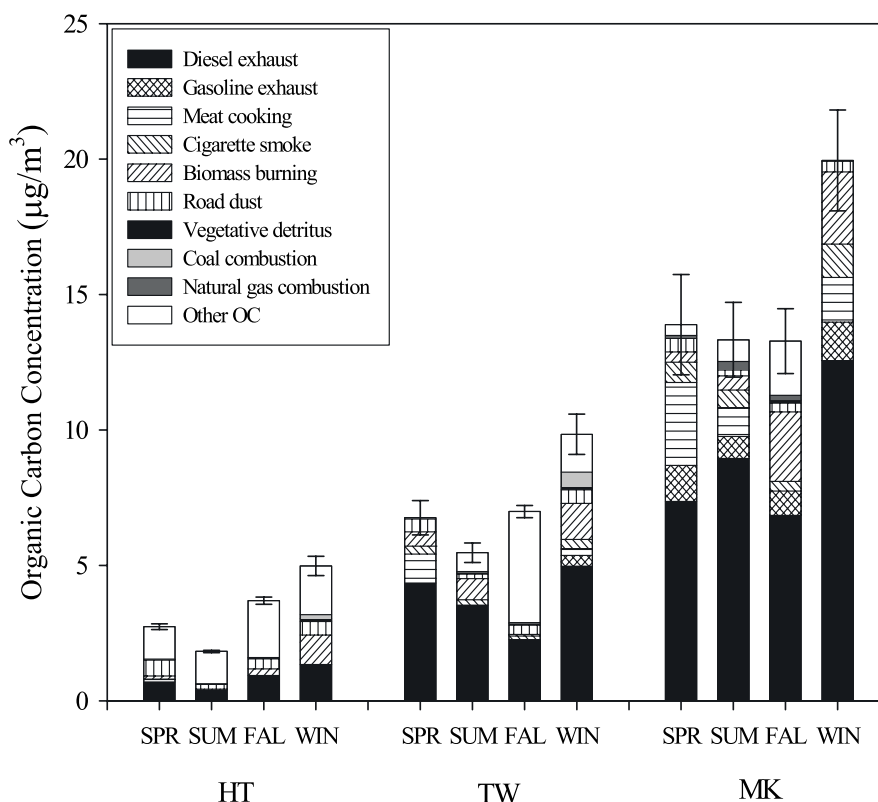


Figure 8. Source contributions to organic carbon in PM_{2.5}. The CMB7.0 model was used to estimate contributions of major sources, and the modeled OC was compared to the measured OC concentrations. The error bar represents the error of modeled OC, which is propagated from the error of each identified source category.

organic carbon formed through secondary formation in the atmosphere.

[34] Fine particulate organic carbon concentrations in Tsuen Wan, a relatively populated urban site in Hong Kong, were also significantly influenced by diesel exhaust. About 55% of the fine OC at this site was estimated to be from diesel engine exhaust. Gasoline engine exhaust was estimated to account for <5% of primary OC at Tsuen Wan.

[35] The results suggest that organic carbon concentrations at all sites were significantly impacted by diesel engine exhaust, with a relatively small contribution from gasoline exhaust. On the basis of the emission inventory, *Barron and Steinbrecher* [1999] estimated that 98% of respirable suspended particulates in Hong Kong were from diesel vehicles while only 2% were from petrol vehicles though 70% of motor vehicles in Hong Kong were powered by gasoline. This corresponds well to our findings that diesel emission is indeed a very important component of measured fine organic carbon and fine particulate matter in the atmosphere. However, this study also shows that distinct spatial distributions of diesel exhaust exist with the highest level at the roadside site and the lowest level at the rural site. The lack of uniformity of organic carbon concentrations from diesel exhaust at the MK, TW and HT sites for a given season also suggests that local Hong Kong diesel emissions dominate the diesel component of OC.

[36] The road dust source at HT exhibited similar levels compared to the values at TW and MK, ranging from 0.18 to 0.59 $\mu\text{g m}^{-3}$. At all three sites, similar seasonal patterns of the road dust source can be seen with the lowest levels in summer and increased levels during spring and winter. Since the lowest OC content was measured at the rural HT site, the road dust is relatively more important to OC at HT than those at the other sites. It is very likely that the Hong Kong sites, particularly HT, are also impacted by wind blown dust from longer-range transport. Certainly this can be true during the spring when dust storms commonly occur in arid regions of China. It has been reported by *Fang et al.* [1999] that Asian dust can be transported to Hong Kong under appropriate meteorological conditions. Therefore our estimates here should be taken as an upper limit of road dust contribution to fine OC.

[37] Other sources such as meat cooking, cigarette smoke, and natural gas combustion exhibited similar spatial variations as diesel and gasoline engine exhaust with the highest level found at the densely populated MK site and the lowest level at the rural HT site.

[38] The relatively higher levels of unidentified OC or “Other OC” at the TW and HT sites suggest that the secondary formation of organic compounds may play an important role in fine OC in Hong Kong. The results of the WSOC analyses indicate that the ratio of WSOC to OC at MK, TW, and HT range from 14–26%, 30–45%, and 49–

Table 2. Source Contributions to Organic Carbon in PM_{2.5} ($\mu\text{g m}^{-3}$)^a

Site	Season	Diesel Exhaust	Gasoline Exhaust	Meat Cooking ^b	Cigarette Smoke ^c	Biomass Burning ^b	Road Dust ^b	Vegetative Detritus	Coal Combustion	Natural Gas Combustion	Other OC	Measured OC	R ²	χ^2	% Mass	Degree of Freedom
HT	spring	0.70 ± 0.08		0.10 ± 0.05		0.12 ± 0.03	0.59 ± 0.04	0.02 ± 0.004		0.009 ± 0.002	1.2	2.7 ± 0.2	0.97	1.57	56	10
HT	summer	0.40 ± 0.04				0.03 ± 0.01	0.18 ± 0.01	0.01 ± 0.003		0.003 ± 0.001	1.2	1.8 ± 0.1	0.97	1.93	34	8
HT	fall	0.94 ± 0.11				0.24 ± 0.07	0.37 ± 0.02	0.04 ± 0.007		0.008 ± 0.002	2.1	3.7 ± 0.2	0.97	1.95	43	9
HT	winter	1.33 ± 0.15			0.01 ± 0.005	1.09 ± 0.32	0.50 ± 0.04	0.10 ± 0.02	0.15 ± 0.02		1.8	5.0 ± 0.3	0.91	3.13	64	16
TW	spring	4.35 ± 0.35		1.07 ± 0.50	0.29 ± 0.04	0.53 ± 0.15	0.47 ± 0.04			0.05 ± 0.01		6.1 ± 0.4	0.95	1.45	111	17
TW	summer	3.53 ± 0.30			0.20 ± 0.04	0.78 ± 0.19	0.17 ± 0.02	0.05 ± 0.02		0.04 ± 0.01	0.7	5.5 ± 0.3	0.91	2.87	87	17
TW	fall	2.26 ± 0.22			0.13 ± 0.02	0.06 ± 0.02	0.34 ± 0.02	0.07 ± 0.02		0.027 ± 0.006	4.1	7.0 ± 0.4	0.94	2.45	41	14
TW	winter	4.97 ± 0.59			0.34 ± 0.06	1.33 ± 0.38	0.50 ± 0.05	0.12 ± 0.04	0.53 ± 0.07		1.4	9.8 ± 0.6	0.95	1.61	86	21
MK	spring	7.36 ± 1.02		0.25 ± 0.13	0.75 ± 0.09	0.38 ± 0.11	0.50 ± 0.05			0.11 ± 0.03	0.4	13.9 ± 0.8	0.91	2.82	97	20
MK	summer	8.95 ± 1.21		3.06 ± 1.51	0.65 ± 0.08	0.53 ± 0.16	0.21 ± 0.04			0.32 ± 0.07	0.8	13.3 ± 0.8	0.9	3.28	95	18
MK	fall	6.85 ± 0.98		1.06 ± 0.52	0.36 ± 0.06	2.57 ± 0.62	0.32 ± 0.04	0.11 ± 0.04		0.18 ± 0.04	2.0	13.3 ± 0.8	0.91	3.29	85	18
MK	winter	12.56 ± 1.42		1.65 ± 0.81	1.23 ± 0.14	2.67 ± 0.77	0.39 ± 0.06			0.03 ± 0.02		18.7 ± 1.1	0.91	2.4	107	22

^aThe CMB7.0 model was used to estimate contributions of major sources and the modeled OC was compared to the measured OC concentrations.

^bThe sensitivity test results of source contribution estimates from meat cooking, biomass burning, and road dust to source profiles are shown in Table 3.

^cCigarette smoke here is an upper limit estimate (see section 3.3 for details).

64%, respectively. Generally, the roadside site has the least amount of water soluble organic compounds, with the highest amount at the remote site. This qualitatively agrees with the relationship of unidentified or other organic carbon across the sites, with highest levels at HT and the lowest at MK. However, the TW fall sample was an exception which has an unusually high proportion of unidentified carbon as shown in the CMB results (Figure 8). The OC concentration in the TW fall sample was comparable with the other seasons (Figure 3) though the measured concentrations of several organic tracer compounds such as hopanes and steranes, levoglucosan and PAHs were much lower than those of other seasons. The large amount of unidentified carbon in OC as well as extremely low concentrations of organic tracers in TW fall sample is still unclear. Since secondary organic compounds are likely more water soluble than directly emitted organic compounds due to the oxidation processes that create these compounds, the assumption that the “Other OC” is secondary in nature does appear valid.

3.4. Sensitivity Test

[39] Because the local PM_{2.5} profiles specific for Hong Kong sources are not yet available, the CMB analyses were performed with the existing source profiles tested in the United States and Datong, China. The source profiles chosen can be regarded as the most representative of the region on the basis of the available data. However, it is important to understand the sensitivity of CMB results to the source input data. In the present study, biomass burning, meat cooking and road dust were selected for the sensitivity test since multiple source profiles are available for these sources. Because of the lack of information for some chemical tracers in the published source profiles, only the most key tracers (levoglucosan, cholesterol, and Al and Si for biomass burning, meat cooking and road dust, respectively) instead of the entire source profiles were replaced. Table 3 lists the sensitivity test results at the MK site.

[40] For biomass burning, a total of nine different wood species were used in the sensitivity test. The contribution estimates of biomass burning with nine individual source inputs at MK were 0.14–0.87, 0.20–0.68, 0.89–3.22, and 1.46–5.49 $\mu\text{g m}^{-3}$ during the spring, summer, fall, and winter, respectively. The estimates with the source profile we selected in this study for biomass burning were close to the average contributions of the nine wood species. The percentage of the difference as compared to the CMB output from the biomass burning profile employed in this study ranged from –63 to 130%.

[41] To test the sensitivity for meat cooking source, the contribution estimates from the three cholesterol-replaced source profiles (hamburger auto-char, hamburger under-char, and steak under-char) at MK were 7.23–11.5, 2.58–5.51, and 3.95–8.67 $\mu\text{g m}^{-3}$ for the spring, summer and winter season, respectively (No cholesterol was detected in the MK fall sample). The relative differences compared to the selected source profile (chicken under-char) were between 136 and 425%. Pork is perhaps the most common meat for cooking in Hong Kong. However, its source profile is not available. Thus the source profile of chicken under-char was applied in the present study. For road dust, the source profiles reported by *Ho et al.* [2003] were applied.

Table 3. Sensitivity of Source Apportionment Results to Source Profiles

Source Categories and Profiles	Tracers ^a	Source Contribution to Fine OC, $\mu\text{g}/\text{m}^3$				Relative Differences, % ^b				References
		MK Spring	MK Summer	MK Fall	MK Winter	MK Spring	MK Summer	MK Fall	MK Winter	
Biomass burning										
Biomass burning ^c	Levogluconan	0.38	0.53	2.57	2.67	28	28	25	72	Zheng <i>et al.</i> [2002]
White oak	Levogluconan	0.49	0.68	3.22	4.60	3	-47	-27	9	Fine <i>et al.</i> [2004]
Sugar maple	Levogluconan	0.39	0.28	1.88	2.91	-47	-47	-49	-21	Fine <i>et al.</i> [2004]
Black oak	Levogluconan	0.20	0.28	1.32	2.11	130	19	55	106	Fine <i>et al.</i> [2004]
American beech	Levogluconan	0.87	0.63	3.99	5.49	-63	-63	-65	-45	Fine <i>et al.</i> [2004]
Black cherry	Levogluconan	0.14	0.20	0.89	1.46	-34	-34	-35	-2	Fine <i>et al.</i> [2004]
Quaking aspen	Levogluconan	0.25	0.35	1.67	2.62	-12	-12	-12	27	Fine <i>et al.</i> [2004]
White spruce	Levogluconan	0.33	0.47	2.25	3.39	-55	-54	-56	-32	Fine <i>et al.</i> [2004]
Douglas fir	Levogluconan	0.17	0.24	1.12	1.82					
Meat cooking										
Meat cooking ^c	Cholesterol	3.06	1.06		1.65	256	183		190	McDonald <i>et al.</i> [2003], Schauer <i>et al.</i> [1999a]
Hamburger auto-char	Cholesterol	10.89	3.00		4.79	136	143		139	McDonald <i>et al.</i> [2003]
Hamburger under-char	Cholesterol	7.23	2.58		3.95	275	420		425	McDonald <i>et al.</i> [2003]
Steak under-char	Cholesterol	11.48	5.51		8.67					McDonald <i>et al.</i> [2003]
Road dust										
Road dust ^c	Al, Si	0.50	0.21	0.32	0.43	-80	-79	-77	-79	Schauer [1998]
Country soil	Al, Si	0.10	0.05	0.07	0.09	-58	-58	-54	-57	Ho <i>et al.</i> [2003]
Urban soil	Al, Si	0.21	0.09	0.15	0.19	8	10	19	10	Ho <i>et al.</i> [2003]
Paved road dust	Al, Si	0.54	0.23	0.38	0.47	-60	-62	-57	-61	Ho <i>et al.</i> [2003]
Cement	Al, Si	0.20	0.08	0.14	0.17	-95	-95	-94	-95	Ho <i>et al.</i> [2003]
Aggregate	Al, Si	0.03	0.01	0.02	0.02					Ho <i>et al.</i> [2003]

^aKey tracers.^bThe relative differences (%) were calculated by $(C - C_0)/C_0 * 100$, where C_0 denotes the source contribution estimated with the source profile used in the present study; C denotes the source contribution estimated with another source profile of the same source category.^cSource profiles used in the present study.

The results clearly show that the CMB results of road dust are not sensitive to the source profiles. The relative differences are minor, ranging from 8 to 19%.

4. Conclusions

[42] Similar to EC and OC, the organic tracers exhibited a distinct spatial pattern with the highest levels of hopanes and steranes, PAHs, levoglucosan, and cholesterol measured at the roadside MK site, indicating the strong impact of mobile source and residential activities at this site. The CMB analysis identified diesel exhaust, gasoline exhaust, biomass burning, and meat cooking as the major sources of fine organic carbon in Hong Kong. The contributions from cigarette smoke, road dust, coal combustion, and vegetative detritus to fine OC were minor with the average contribution from each source less than 8%. The absolute dominance of diesel exhaust in fine OC found at both the urban and rural sites was a distinguished characteristic of Hong Kong fine aerosol. However, the highest impact was observed at the roadside site throughout the year, followed by the urban site, and the rural site. In winter, higher OC at all sites was primarily due to the higher diesel exhaust and wood burning source contributions. This corresponded well to the higher concentrations of hopanes, steranes, and levoglucosan measured in PM_{2.5} in Hong Kong.

[43] The lack of uniformity of diesel related organic carbon concentrations across the sampling sites for each season suggested that local sources (i.e., sources within Hong Kong) were most likely responsible for the diesel contribution to particulate matter. More than 85% of fine OC at the roadside MK site was explained by the primary emissions, indicating that fresh and local emissions dominate at this site. At Hok Tsui and Tsuen Wan, the unidentified organic carbon can account for on average 51% and 19% of the OC mass, respectively. In combination with the relatively high concentrations of water soluble organic compounds at HT, it suggested that secondary formation of organic particulate matter could have an important influence on fine OC concentrations measured in rural sites in Hong Kong.

[44] The source profiles which can best describe the local source emission characteristics were employed to estimate the source contributions to fine OC in Hong Kong. However, a sensitivity test was employed to assess how sensitive the CMB outputs of biomass burning, meat cooking, and road dust are to various source profiles available in the literature. In general, meat cooking source was the most sensitive source category, followed by biomass burning source. Only minor differences, with the relative difference ranging from 8 to 19%, can be seen for road dust source when different road dust source profiles were applied in CMB. A comparison of organic compound analysis results with actual PM_{2.5} samples between two laboratories showed a better agreement for alkanes than PAHs, which normally exhibit a lower concentration in aerosol.

[45] **Acknowledgments.** The authors are thankful for the assistance from graduate students Karari Hanks, Bo Wang, and Bo Yan and undergraduate student Justin T. Friel for sample preparation and data analysis. This 12-month project was initiated and funded by the Government of the Hong Kong Special Administrative Region. This study would not have

been possible without the initiation and coordination by the late Glen R. Cass.

References

- Atkinson, R., and J. Arey (1994), Atmospheric chemistry of gas-phase polycyclic aromatic-hydrocarbons—formation of atmospheric mutagens, *Environ. Health Perspect.*, *102*, 117–126.
- Barron, W., and N. Steinbrecher (Eds.) (1999), *Heading Towards Sustainability? Practical Indicators of Environmental Sustainability for Hong Kong*, Univ. of Hong Kong, Hong Kong.
- Birch, M. E., and R. A. Cary (1996), Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, *Aerosol Sci. Technol.*, *25*, 221–241.
- Broman, D., C. Näf, and Y. Zebühr (1991), Long-term high and low-volume air sampling of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons along a transect from urban to remote areas on the Swedish Baltic Coast, *Environ. Sci. Technol.*, *25*, 1841–1850.
- Cao, J. J., S. C. Kee, K. F. Ho, S. C. Zou, K. Fung, Y. Li, J. G. Watson, and J. C. Chow (2004), Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China, *Atmos. Environ.*, *38*, 4447–4456.
- Cass, G. R. (1998), Organic molecular tracers for particulate air pollution sources, *Trends Anal. Chem.*, *17*, 356–366.
- Cohen, A. J. (2000), Outdoor air pollution and lung cancer, *Environ. Health Perspect.*, *108*, 743–750.
- Fang, M., M. Zheng, F. Wang, K. S. Chim, and S. C. Kot (1999), The long-range transport of aerosols from northern China to Hong Kong—A multi-technique study, *Atmos. Environ.*, *33*, 1803–1817.
- Fine, P. M., G. R. Cass, and B. R. T. Simoneit (2004), Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the midwestern and western United States, *Environ. Eng. Sci.*, *21*, 387–409.
- Fung, Y. S., and L. W. Y. Wong (1995), Apportionment of air pollution sources by receptor modeling in Hong Kong, *Atmos. Environ.*, *29*, 2041–2048.
- Hagler, G. S. W., et al. (2006), Source areas and chemical composition of fine particulate matter in the Pearl River Delta region of China, *Atmos. Environ.*, *40*, 3802–3815.
- Hildemann, L. M., G. R. Markowski, and G. R. Cass (1991), Chemical composition of emissions from urban sources of fine organic aerosol, *Environ. Sci. Technol.*, *25*, 744–759.
- Ho, K. F., S. C. Lee, J. C. Chow, and J. R. Watson (2003), Characterization of PM₁₀ and PM_{2.5} source profiles for fugitive dust in Hong Kong, *Atmos. Environ.*, *37*, 1023–1032.
- Jensen, T. E., and R. A. Hites (1983), Aromatic diesel emissions as a function of engine conditions, *Anal. Chem.*, *55*, 594–599.
- Lall, R., M. Kendall, K. Ito, and G. D. Thurston (2004), Estimation of historical annual PM_{2.5} exposures for health effects assessment, *Atmos. Environ.*, *38*, 5217–5226.
- Lee, E., C. K. Chan, and P. Paatero (1999), Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong, *Atmos. Environ.*, *33*, 3201–3212.
- Louie, P. K. K., J. G. Watson, J. C. Chow, A. Chen, D. W. M. Sin, and A. K. H. Lau (2005), Seasonal characteristics and regional transport of PM_{2.5} in Hong Kong, *Atmos. Environ.*, *39*, 1695–1710.
- McDonald, J. D., B. Zielinska, E. M. Fujita, J. C. Sagebiel, J. C. Chow, and J. G. Watson (2003), Emissions from charbroiling and grilling of chicken and beef, *J. Air Waste Manage. Assoc.*, *53*, 185–194.
- Oros, D. R., and B. R. T. Simoneit (2000), Identification and emission rates of molecular tracers in coal smoke particulate matter, *Fuel*, *79*, 515–536.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1993a), Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants, *Environ. Sci. Technol.*, *27*, 2700–2711.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass (1993b), Sources of fine organic aerosol. 5. Natural gas home appliances, *Environ. Sci. Technol.*, *27*, 2736–2744.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1993c), Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks, *Environ. Sci. Technol.*, *27*, 636–651.
- Schauer, J. J. (1998), Source contributions to atmospheric organic compound concentrations: Emissions measurement and model predictions, Ph.D. dissertation, Calif. Inst. of Technol., Pasadena.
- Schauer, J. J., W. F. Rogge, L. M. Hildemann, M. A. Mazurek, and B. R. T. Simoneit (1996), Source apportionment of airborne particulate matter using organic compounds as tracers, *Atmos. Environ.*, *30*, 3837–3855.
- Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (1999a), Measurement of emissions from air pollution sources. 1. C-1 through

- C-29 organic compounds from meat charbroiling, *Environ. Sci. Technol.*, **33**, 1566–1577.
- Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (1999b), Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks, *Environ. Sci. Technol.*, **33**, 1578–1587.
- Schauer, J. J., M. P. Fraser, G. R. Cass, and B. R. T. Simoneit (2002a), Source reconciliation of atmospheric gas-phase and particle-phase pollutants during a severe photochemical smog episode, *Environ. Sci. Technol.*, **36**, 3806–3814.
- Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (2002b), Measurement of emissions from air pollution sources. 5. C-1–C-32 organic compounds from gasoline-powered motor vehicles, *Environ. Sci. Technol.*, **36**, 1169–1180.
- Simoneit, B. R. T. (1986), Characterization of organic constituents in aerosols in relation to their origin and transport: A review, *Int. J. Environ. Anal. Chem.*, **23**, 207–237.
- Simoneit, B. R. T. (1989), Organic matter of the troposphere—V. Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations, *J. Atmos. Chem.*, **8**, 251–275.
- Simoneit, B. R. T., J. J. Schauer, C. G. Nolte, D. R. Oros, V. O. Elias, M. P. Fraser, W. F. Rogge, and G. R. Cass (1999), Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, *Atmos. Environ.*, **33**, 173–182.
- Sin, D. W. M., W. H. Fung, Y. Y. Choi, C. H. Lam, P. K. K. Louie, J. C. Chow, and J. G. Watson (2005), Seasonal and spatial variation of solvent extractable organic compounds in fine suspended particulate matter in Hong Kong, *J. Air Waste Manage. Assoc.*, **55**, 291–301.
- Tancell, P. J., M. M. Rhead, R. D. Remberton, and J. Braven (1995), Survival of polycyclic aromatic-hydrocarbons during diesel combustion, *Environ. Sci. Technol.*, **29**, 2871–2876.
- Turpin, B. J., P. Saxena, and E. Andrews (2000), Measuring and simulating particulate organics in the atmosphere: Problems and prospects, *Atmos. Environ.*, **34**, 2983–3013.
- Watson, J. G., and J. C. Chow (2001), Source characterization of major emission sources in the Imperial and Mexicali Valleys along the US/Mexico border, *Sci. Total Environ.*, **276**, 33–47.
- Watson, J. G., N. F. Robinson, J. C. Chow, R. C. Henry, B. M. Kim, T. G. Pace, E. I. Meyer, and Q. Nguyen (1990), The USEPA/DRI chemical mass balance receptor model, CMB 7.0, *Environ. Software*, **5**, 38–49.
- Yang, H., J. Z. Yu, S. S. H. Ho, J. Xu, W. Wu, C. H. Wan, X. Wang, X. Wang, and L. Wang (2005), The chemical composition of inorganic and carbonaceous materials in PM_{2.5} in Nanjing, China, *Atmos. Environ.*, **39**, 3735–3749.
- Zheng, M., M. Fang, F. Wang, and K. L. To (2000), Characterization of the solvent extractable organic compounds in PM_{2.5} aerosols in Hong Kong, *Atmos. Environ.*, **34**, 2691–2702.
- Zheng, M., G. R. Cass, J. J. Schauer, and E. S. Edgerton (2002), Source apportionment of PM_{2.5} in the Southeastern United States using solvent-extractable organic compounds as tracers, *Environ. Sci. Technol.*, **36**, 2361–2371.
- Zheng, M., L. G. Salmon, J. J. Schauer, L. Zeng, Y. Zhang, C. S. Kiang, and G. R. Cass (2005), Seasonal trends in PM_{2.5} source contributions in Beijing, China, *Atmos. Environ.*, **39**, 3967–3976.
-
- M. H. Bergin, F. Wang, and M. Zheng, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA. (mzheng@cas.gatech.edu)
- G. S. W. Hagler, School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.
- L. Ke, Department of Biological Sciences, California State University, Los Angeles, CA 90032, USA.
- P. K. K. Louie, Hong Kong Environmental Protection Department, 47/F, Revenue Tower, 5 Gloucester Road, Wan Chai, Hong Kong Special Administrative Region.
- L. Salmon, Environmental Quality Laboratory, California Institute of Technology, Pasadena, CA 91125, USA.
- J. J. Schauer, Environmental Chemistry and Technology Program, University of Wisconsin, Madison, WI 53706, USA.
- D. W. M. Sin, Government Laboratory, 7/F., Homantin Government Offices, 88 Chung Hau Street, Homantin, Kowloon, Hong Kong Special Administrative Region.
- J. Z. Yu, Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong Special Administrative Region.