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Volatile Organic Compounds in Roadside Environment of Hong Kong

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ABSTRACT

Vehicular exhaust emissions are one of major sources of anthropogenic volatile organic compounds (VOCs) in urban areas of Pearl River Delta Region (PRDR). Six types of vehicle emission (VE)-dominated samples were collected at representative locations in Hong Kong in the winter of 2003. A total of 111 VOC species were quantified in the samples collected. *n*-Butane (31%) was the most abundant species in liquefied petroleum gas (LPG)-fueled VE-dominated samples, followed by propane (26%) and *i*-butane (25%). Toluene was the most abundant species in gasoline-fueled VE-dominated samples (16%), comprising about half of the quantified aromatic content. While ethene and ethyne have the greatest abundance in all diesel-fueled VE-dominated VOCs profiles (except at Tuen Mun Bus Depot). VOCs were also quantified at three roadside locations in Hong Kong. And ethene was the most abundant VOCs at roadside locations which accounted for 9.5 to 29% of the total quantified VOCs, except at Hong Kong Polytechnic University roadside monitoring station (PUX). Moreover, several VOCs were clearly in abundances in the roadside samples, namely toluene, ethyne, propane, *i*-butane, *n*-butane and *i*-pentane. Generally, strong and fair correlations were determined from the marker species of fuel vapor (i.e., LPG, gasoline, and diesel), which show significant fuel evaporation from vehicles in roadside environment of Hong Kong. Maximum incremental reactivity (MIR) was also calculated to evaluate the contributions of individual VOCs to ozone (O_3) formation potential. The largest contributors to O_3 production at Mong Kok roadside station (MKX) and Lok Ma Chau roadside station (LMX) were toluene (17 and 15% of the measured VOC reactivity, respectively), ethene (14 and 17% of the measured VOC reactivity, respectively), and propene (7 and 8% of the measured VOC reactivity, respectively), indicating the important roles of alkenes and aromatics in the ambient O_3 formation.

Keywords: VOCs; Roadside; Diesel; Gasoline; LPG; Vehicular emissions; Chemical profiles.

INTRODUCTION

Volatile organic compounds (VOCs) are an important group of organic compounds in atmospheric chemistry. They can be either emitted into or formed in the atmosphere. Primary emission VOC sources include both natural (e.g., biomass burning) and anthropogenic (e.g., vehicular exhaust, cooking emission, incense burning, and cigarette smoke). Many VOCs have adverse health effects and play important roles in stratospheric ozone (O_3) depletion, the formation of toxic secondary organic aerosols, the formation of tropospheric ozone, and the escalation of global warming (Luis *et al.*, 2003; Han and Naeher, 2006; Ran *et al.*, 2009; Choi *et al.*, 2011). Therefore, understanding source profiles of VOCs from vehicles (which is one of the major VOC sources in the urban areas) is critical to identify effective strategies for reducing VOC levels in the urban atmosphere. As one of the fastest growth regions in China, Pearl River Delta Region (PRDR) is experiencing severe air pollution due to rapid urbanization and increased use of motorized vehicles. Vehicular emissions (VE) are one of major sources of anthropogenic VOCs in the urban areas throughout the PRDR. Fuel reformation, use of lubricating oils, exhaust aftertreatment, and engine operation can highly vary the

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compositions and volatilities of the pollutants emitted into the atmosphere (Ålander *et al.*, 2004). Guo *et al.* (2006) concluded from receptor model analysis that VE is a dominant VOCs source in Hong Kong, accounted for 39% of total emission, while it also accounted for 32% of total VOC emission in the PRDR.

Hong Kong is a densely populated city. According to the Hong Kong Transportation Department, there were 532,872 licensed vehicles in December 2004 (Hong Kong Transport Department, 2004). Several ambient studies have recently been completed indicating VE are the most important source for VOCs in Hong Kong (Ho and Lee, 2002; Lee *et al.*, 2002; Guo *et al.*, 2004). Liquefied petroleum gas (LPG), gasoline, and diesel are the main fuels used by vehicles in Hong Kong. In 2004, gasoline fueled vehicles accounted for 70.4% of the total licensed vehicles, while diesel and LPG fueled vehicles accounted for 24.5% and 3.5%, respectively (Hong Kong Transport Department, 2004). Vehicular performance affects fuel consumption and emissions in part because it would affect the combustion efficiency and evaporative emissions from the fuel system. In 2000, the Hong Kong Government implemented a subsidy program to switch diesel taxis to LPG taxis in order to reduce the impact of smoke, NO_x and VOC emissions on the street level air pollution in Hong Kong (Hong Kong Environmental Protection Department, 2001). Nearly all (99.8%) of the 18,000 taxis in Hong Kong were LPG powered in 2003. In PRDR, most previous studies (e.g., Lee *et al.*, 2002; Ho *et al.*, 2004; Chan *et al.*, 2006; Guo *et al.*, 2007) reported the urban/rural levels of VOCs. To our best knowledge, there are only limited measurement-based VOC emission profiles available in Hong Kong (Tsai *et al.*, 2006; Ho *et al.*, 2009; Guo *et al.*, 2011; Ho *et al.*, 2012). In previous studies, we have determined the emission factors of VOCs at a roadway tunnel in Hong Kong (Ho *et al.* 2007, 2009). Influences from VE to the local ambient VOCs in roadside environments had not been thoroughly investigated. In this study, each type of VE-dominated samples was collected in the atmosphere in a location (e.g., taxi stations and bus depots) where is mainly contributed by a particular emission from vehicles fueled with liquefied petroleum gas (LPG), gasoline, or diesel. The VOC concentrations and profiles of the source dominated samples were compared. Samples were also collected at three representative roadside sites. The VOC markers for LPG, gasoline, or diesel can be used as indicators for source identification in the roadside environments. The in-depth understanding of source contributions provides important information for management of Hong Kong air quality.

EXPERIMENTAL SECTION

Sampling Sites

Sample collection can be divided into two different categories including (I) VE-dominated and (II) roadside samples (Fig. 1 and Table1).

(I) VE-dominated samples: In order to obtain the comprehensive chemical source profiles for different type of VE-dominated emissions in Hong Kong, ground-based roadside sampling at six traffic intersections and highway on/off ramps was conducted. The most important use of vehicle emission dominated profiles is for the source marker identification for the different types of vehicular exhaust. The six sampling sites are described as below: 1) The Hong Kong Polytechnic University (HKPU) car park station (PCX) is situated at ground floor of the HKPU, Hung Hom. The sampling equipment was placed at the entrance of the car park. It was chosen to represent the gasoline-fueled light-duty passenger car emissions. 2) Wan Chai liquefied petroleum gas (LPG) refilling station (TAS) is located at Wan Shing Street, Wan Chai. The sampling equipment was placed at the roadside near the LPG refilling station. It was chosen to represent the LPG taxi emission. 3) Shau Kei Wan minibus station (MBS) is situated at Mong Lung Street, Shau Kei Wan. The sampling equipment was placed next to the minibus station. It was chosen to represent the minibus diesel emission. 4) Cheung Sha Wan Whole Food Market station (GVX) is located at the Yen Chow Street West, Cheung Sha Wan. The sampling equipment was placed at the entrance of the whole food market. It was chosen to represent the light- and heavy-duty vehicle diesel emission. 5) The Peak station (SBS) is situated at the Peak car park, near the Peak Road. The sampling equipment was placed at the roadside of the car park. It was chosen to represent the single-decked bus diesel emission. 6) Tuen Mun Bus Depot station (DBS) is located at the Ho Tin Street, Tuen Mun. The sampling equipment was placed at the roadside of the bus depot. It was chosen to represent the double-decked bus diesel emission.

(II) Roadside samples (collected in the summer and winter of 2003): 1) The Mong Kok Environmental Protection Department (HKEPD) roadside air quality monitoring station (MKX) is located at the junction of the heavily traffic Lai Chi Kok and Nathan Roads. 2) HKPU roadside monitoring station (PUX) is located 1 m adjacent to Hong Chong Road, which leads to the Cross Harbor Tunnel. It can represent street-level emissions from nearby vehicle exhaust and road dust. It is aimed to get slow traffic emission exhausts when vehicles are idling and under slow traffic/for cross-boundary vehicles. 3) Lok Ma Chau roadside monitoring station (LMX) is located at the entrance of the boundary-crossing point that vehicles come from Mainland China to Hong Kong.

Engine and Fuel Types

There were a large number of pre-Euro diesel-fueled buses and heavy duty vehicles on the road in Hong Kong. In 2003, the pre-Euro fleet contributed > 40% of the total number of heavy duty vehicles and > 10% of the buses. And Euro II fleet also had a contribution of > 24% for heavy duty vehicles and > 30% for the buses. In this study, classification of the diesel-fueled engine type by the European emission standard was not done owing to too many vehicles passing the monitoring stations in a short period. For the same reason, classification of gasoline vehicles by either models or years was not applicable as well. Therefore the inter-variations of engines for each fueled type were not taken into account. Euro III unleaded

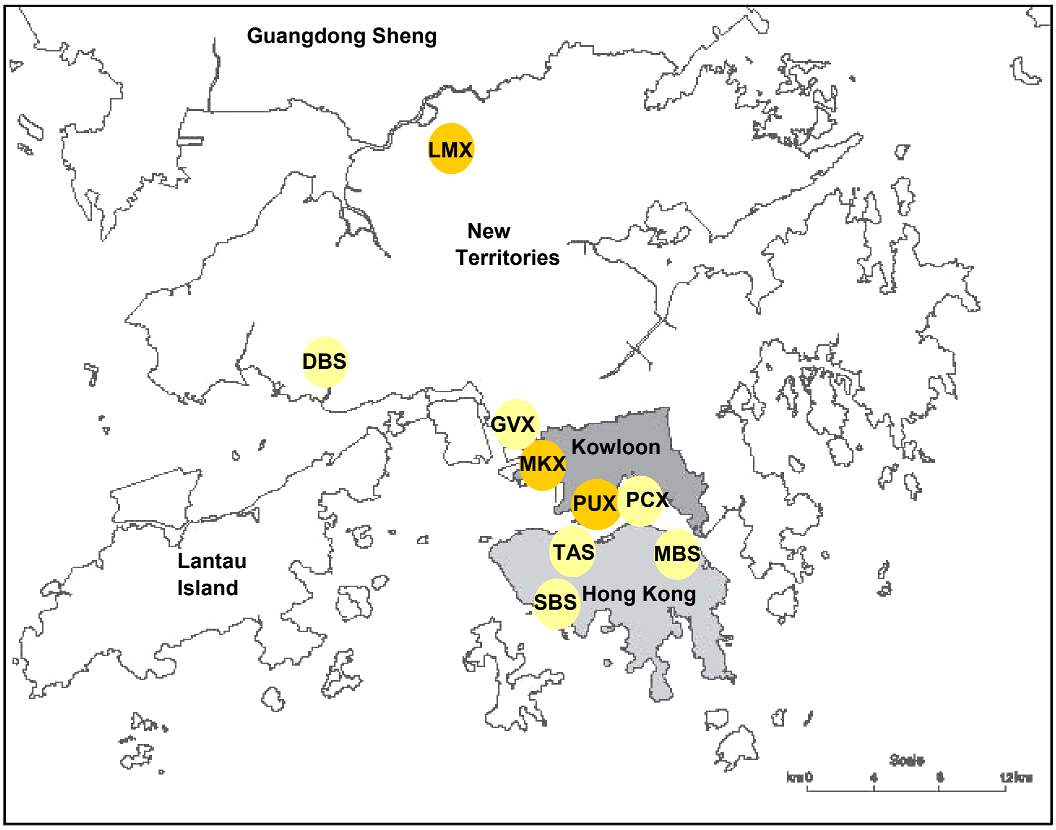

Fig. 1. The map showing the sampling locations in this study. Location acronyms are shown in Table 1.

Table 1. Brief summary of the sampling locations of vehicle emission dominated samples.

Abbreviation	Locations	Dominated Vehicle Type	Fuel Used
PCX	PolyU Car Park	Private Car	Gasoline
TAS	Wan Chai LPG Refilling Station	Taxi	LPG
GVX	Cheung Sha Wan Food Market	Light and Heavy Good Vehicles	Diesel
MBS	Shau Kei Wan Minibus Station	Minibus	Diesel
DBS	Tuen Mun KMB Bus Depot	Double-decked Bus	Diesel
SBS	Victoria Peak Car Park	Single-decked Bus	Diesel

petrol was the major fuel used in Hong Kong in 2003. It should be noted that a few heavy duty vehicles might refill petrol in Mainland of China during their journeys for goods transportation to Hong Kong. Its fuel specification might be thus varied from the Euro III standard.

Sample Collection

A total of 51 VE-dominated and roadside samples were collected in Hong Kong between 8:00 and 19:00 in summer (23 May–9 July) and winter (9 December–28 December) of 2003. At least three samples were collected for each type of VE-dominated samples while twelve samples were collected in each roadside station. Ambient volatile organic canister samplers (AVOCS) (Andersen Instruments Inc. Series 97–300, Smyrna, GA, USA) were used to collect whole air roadside samples into pre-cleaned and pre-evacuated 2-L stainless steel canisters at a flow rate of 20 to 25 mL/min for 3 h in winter and 2 h in summer, respectively. The canisters were pressurized when sampling. The sampler was fixed on the ground level with an inlet at a height of ~1.5 m. The flow rates were checked in the field before and after each run using a calibrated flow meter. After sampling, the filled canisters were shipped to the laboratory of the University of California, Irvine for chemical analysis within two weeks of being collected.

Sample Analyses

All canisters were shipped to the laboratory at the University of California, Irvine (UCI) and analyzed for carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and non-methane hydrocarbon (NMHCs). CO and CO_2 analyses were carried out using a hydrogen gas methanizer upstream of a HP 5890 gas chromatography (GC) equipped with a flame ionization detector (FID) and an 3m molecular sieve column. CH_4 was also analyzed using an HP 5890 GC equipped with an FID. The samples were injected into an 1/8” stainless steel 0.9 m column packed with 80/100 mesh Spherocarb.

The analytical system used to analyze NMHCs (i.e., saturated, unsaturated, aromatic, and halogenated hydrocarbons) involved the cryogenic pre-concentration of 1520 ± 1 cm^3 (STP) of air sample in a stainless steel tube filled with glass beads (1/8” diameter) and immersed in liquid nitrogen (–196°C). A mass flow controller with a maximum allowed flow of 500 mL/min controlled the trapping process. The trace gases were revolatilized using a hot water bath and then reproducibly split into five streams directed to different column-detector combinations.

Three different kinds of detectors, including quadrupole mass spectrometry detectors (MSD; for unambiguous compound identification and selected ion monitoring), FID (sensitive to hydrocarbons), and electron capture detectors (ECD; sensitive to halogenated hydrocarbon), were employed. The first column-detector combination (abbreviated as ‘‘DB5ms/MSD’’) was a DB-5ms column (J&W; 60 m × 0.25 mm i.d. × 0.5 µm film thickness) output to the HP 5973 MSD. The second combination (‘‘DB1/FID’’) was a DB-1 column (J&W; 60 m × 0.32 mm i.d. × 1 µm film thickness) output to the FID. The third combination (‘‘PLOT-DB1/FID’’) was a PLOT column (J&W GS-Alumina; 30 m × 0.53 mm i.d. × 1.5 µm film thickness) connected in series to a DB-1 column (J&W; 5 m × 0.53 mm i.d. × 1.5 µm film thickness) and output to the FID. The fourth combination (‘‘Restek1701/ECD’’) was a RESTEK 1701 column (60 m × 0.25 mm i.d. ×0.50 µm film thickness) which was output to the ECD. The fifth combination (‘‘DB5-Restek1701/ECD’’) was a DB-5 (J& W; 30 m × 0.25 mm i.d. × 1 µm film thickness) column connected in series to a RESTEK 1701 column (5 m, 0.25 mm i.d. × 0.5 µm film thickness) and output to the ECD. The DB5ms/MS, DB1/FID, PLOT-DB1/FID, Restek1701/ ECD, and DB5-Restek1701/ECD combinations received 10.1, 15.1, 60.8, 7.2, and 6.8% of the sample flow, respectively. Additional analytical details are given by Colman *et al.* (2001). The measurement precision, detection limits and accuracy vary by compound and are quantified for each species in Colman *et al.* (2001). Briefly, the detection limit is 5 ppbv for CO, 0.01–10 pptv for halogenated hydrocarbons, and 3 pptv for other NMHCs (CH_4 is always above its detection limit). The accuracy of our measurements is 5% for CO, 1% for CH_4, 2–20% for halogenated hydrocarbons, and 5% for other NMHCs. The measurement precision is 2 ppbv for CO, 2 ppbv for CH_4, 1–5% for halogenated hydrocarbons, and ranges from 0.5–5% for other NMHCs.

Photochemical Reactivity

It is well known that VOCs are significant precursors of O_3 formation (Chameides *et al.*, 1992). Individual compound has different characteristic photochemical reactivity. In order to calculate the O_3-forming potential of the VE, the speciated emission factors for each vehicle type were multiplied by the maximum incremental reactivity (MIR) scale developed by Carter (1994). The MIR are in units of grams of O_3 per gram of organic compound and therefore are simply multiplied by the emission factors (grams of organic compound per vehicle-km driven), to yield reactivity-adjusted emission rates in units of O_3 per vehicle-km.

RESULTS AND DISCUSSION

Vehicular Emission-Dominated Samples

Although some of the sources of VOCs in Hong Kong originate from fuel combustion, no comprehensive chemical source profiles for individual type of VE have been performed. There is limited information on source or source-dominated emissions in Hong Kong. Mobile source emissions are among the most difficult to measure with respect to chemical composition. This difficulty arises from: 1) different mobile source types; 2) inadequate characterization of the high emitters within motor vehicle fleet; 3) a large number of individual emitters within each vehicle category; 4) fuel use characteristics and emission control technology that change from year to year; 5) undefined operating conditions; 6) several emission points on each vehicle i.e. tailpipe and fuel evaporation; and 7) a mixture of primary particles, semi-volatile compounds, and secondary particle precursors (Watson *et al.*, 1990). Source-dominated profiles for motor vehicle emissions were constructed from ground-based roadside sampling at various traffic intersections and highway on/off ramps where the sampled air was dominated by emissions from different type vehicle exhaust. The most important use of source-dominated profiles in this section is for the source marker identification for the six different types of vehicular exhaust which is very useful in source apportionment using receptor models.

In this study, a total of 111 species were quantified in the samples collected. These include CH_4, CO, CO_2, carbonyl sulfide (OCS), carbon disulfide (CS_2), methyl tertiary butyl ether (MTBE), 40 C_2–C_{10} saturated hydrocarbons, 32 C_2–C_{10} unsaturated hydrocarbons, 21 C_6–C_{10} aromatic hydrocarbons and 12 halogenated hydrocarbons. Table 2 shows the VOC concentrations collected from different VE-dominated locations in Hong Kong. It is critical to point out that the ambient levels and contributions of VOCs were possibly varied by other local anthropogenic emission sources, regional transportation of pollutants, and photochemical reactions of organic compounds in the atmospheres. For these reasons, the samplings were carried out at rush hours in order to obtain the most representative samples.

The highest total quantified VOC concentration (except CH_4, CO and CO_2), 682 ppbv, was found in the gasoline-fueled light-duty passenger car (PCX) sample. The LPG-fueled taxis dominated samples were collected in TAS which had a mean concentration of 526 ppbv. The mean total concentrations were 140 and 76 ppbv, respectively, at the diesel-fueled minibus (MBS) and double-desk buses (DBS) stations. The total quantified VOC concentrations was 58 ppbv on average at the diesel-fueled single-desk buses station (SBS) while a lower value of 37 ppbv was found in the diesel-fueled goods samples (GVX).

Fig. 2 shows the variations of different groups of VOCs at the source-dominated roadside environment. Saturated hydrocarbons are the most abundant (> 85%) group in LPG-fueled dominated samples because the major compositions of LPG in Hong Kong are butane and propane. Therefore, the emissions from LPG-fueled dominated sample are mainly

Table 2. VOC and other gaseous pollutant concentrations in different types of vehicular-emission-dominated samples.

	Concentration, pptv (±standard deviation) (b.d. = below detection limit)					
	Light & Heavy Good Vehicle - GVX	Minibus - MBS	Double-deck big bus - DBS	Single-deck big bus - SBS	Private car - PCX	Taxi - TAS
CH_4 (ppmv)	1.9 ± 0.096	2.0 ± 0.10	2.0 ± 0.099	2.0 ± 0.10	2.0 ± 0.10	2.0 ± 0.10
CO (ppbv)	710 ± 71	4600 ± 460	1100 ± 110	1200 ± 120	15000 ± 1500	1700 ± 170
CO_2 (ppmv)	400 ± 20	420 ± 21	420 ± 21	420 ± 21	530 ± 27	410 ± 21
OCS	740 ± 150	750 ± 150	940 ± 190	830 ± 170	760 ± 150	820 ± 160
CS_2	100 ± 23	84 ± 20	250 ± 51	110 ± 24	100 ± 22	68 ± 17
MTBE	93 ± 6.8	2400 ± 120	700 ± 36	100 ± 7.1	14000 ± 710	340 ± 18
alkane						
Ethane	2800 ± 56	4100 ± 81	3300 ± 66	3800 ± 75	11000 ± 210	9700 ± 190
Propane	2100 ± 43	2400 ± 49	5400 ± 110	5500 ± 110	4800 ± 96	140000 ± 2800
i-Butane	990 ± 20	1200 ± 25	4700 ± 94	3000 ± 61	5400 ± 110	130000 ± 2600
n-Butane	1800 ± 36	2100 ± 43	7700 ± 150	4600 ± 92	19000 ± 380	160000 ± 3300
2,2-Dimethylbutane	100 ± 5.4	340 ± 8.4	86 ± 5.3	47 ± 5.1	270 ± 7.3	61 ± 5.1
2,3-Dimethylbutane	110 ± 5.5	430 ± 9.9	140 ± 5.7	80 ± 5.2	3200 ± 64	120 ± 5.5
2,2,3-Trimethylbutane	10 ± 5.0	19 ± 5.0	16 ± 5.0	8.0 ± 5.0	170 ± 6.1	12 ± 5.0
i-Pentane	1200 ± 25	5100 ± 100	3800 ± 77	1400 ± 28	48000 ± 970	2600 ± 52
n-Pentane	640 ± 14	1600 ± 32	2200 ± 44	640 ± 14	19000 ± 370	700 ± 15
2-Methylpentane	940 ± 20	3300 ± 67	920 ± 19	680 ± 14	15000 ± 300	790 ± 17
3-Methylpentane	700 ± 15	2100 ± 43	720 ± 15	540 ± 12	10000 ± 200	650 ± 14
3-Ethylpentane	47 ± 5.1	100 ± 5.4	140 ± 5.8	30 ± 5.0	860 ± 18	39 ± 5.1
2,2-Dimethylpentane	31 ± 5.0	69 ± 5.2	48 ± 5.1	22 ± 5.0	470 ± 11	41 ± 5.1
2,3-Dimethylpentane	40 ± 5.1	67 ± 5.2	120 ± 5.5	26 ± 5.0	530 ± 12	38 ± 5.1
2,4-Dimethylpentane	80 ± 5.2	170 ± 6.0	92 ± 5.3	58 ± 5.1	1800 ± 36	75 ± 5.2
3,3-Dimethylpentane	45 ± 5.1	110 ± 5.4	160 ± 5.9	37 ± 5.1	750 ± 16	68 ± 5.2
2,2,4-Trimethylpentane	130 ± 5.6	330 ± 8.3	130 ± 5.6	130 ± 5.6	11000 ± 220	310 ± 8.0
2,3,4-Trimethylpentane	30 ± 5.0	76 ± 5.2	39 ± 5.1	37 ± 5.1	3200 ± 64	54 ± 5.1
n-Hexane	1100 ± 22	1900 ± 37	1000 ± 21	810 ± 17	10000 ± 200	840 ± 17
2-Methylhexane	500 ± 11	910 ± 19	1400 ± 28	320 ± 8.1	5600 ± 110	440 ± 10
3-Methylhexane	480 ± 11	890 ± 18	1600 ± 33	330 ± 8.3	5500 ± 110	490 ± 11
2,5-Dimethylhexane	68 ± 5.2	300 ± 7.7	180 ± 6.2	66 ± 5.2	4900 ± 98	100 ± 5.4
2,4-Dimethylhexane	71 ± 5.2	330 ± 8.2	200 ± 6.4	75 ± 5.2	4800 ± 95	110 ± 5.5
2,3-Dimethylhexane	19 ± 5.0	170 ± 6.0	76 ± 5.2	24 ± 5.0	2900 ± 57	49 ± 5.1
n-Heptane	620 ± 13	720 ± 15	1600 ± 32	460 ± 11	5200 ± 100	530 ± 12
2-Methylheptane	50 ± 5.1	320 ± 8.2	210 ± 6.5	65 ± 5.2	1900 ± 37	110 ± 5.4
3-Methylheptane	60 ± 5.1	370 ± 8.9	260 ± 7.2	81 ± 5.3	1600 ± 33	120 ± 5.6
4-Methylheptane	12 ± 5.0	74 ± 5.2	50 ± 5.1	14 ± 5.0	320 ± 8.2	23 ± 5.0
2,4-Dimethylheptane	14 ± 5.0	75 ± 5.2	51 ± 5.1	16 ± 5.0	320 ± 8.2	63 ± 5.2
2,5-Dimethylheptane	4.5 ± 5.0	63 ± 5.2	36 ± 5.1	10 ± 5.0	260 ± 7.2	21 ± 5.0
2,6-Dimethylheptane	11 ± 5.0	76 ± 5.2	130 ± 5.7	37 ± 5.1	220 ± 6.7	130 ± 5.6
3,3-Dimethylheptane	b.d.	57 ± 5.1	31 ± 5.0	10 ± 5.0	210 ± 6.5	21 ± 5.0
4,4-Dimethylheptane	b.d	12 ± 5.0	25 ± 5.0	7.0 ± 5.0	32 ± 5.0	26 ± 5.0
n-Octane	77 ± 5.2	380 ± 9.2	500 ± 11	150 ± 5.8	2200 ± 45	250 ± 7.0
n-Nonane	40 ± 5.1	180 ± 6.1	550 ± 12	140 ± 5.7	710 ± 15	500 ± 11
n-Decane	26 ± 5.0	170 ± 6.0	450 ± 10	120 ± 5.6	300 ± 7.8	430 ± 10
cycloalkane						
Cylopentane	280 ± 7.5	1500 ± 30	650 ± 14	270 ± 7.3	4900 ± 99	340 ± 8.5
Methylcyclopentane	370 ± 8.9	940 ± 19	440 ± 10	250 ± 7.0	6100 ± 120	270 ± 7.3
Methylcyclohexane	430 ± 9.9	440 ± 10	1200 ± 25	190 ± 6.3	3400 ± 68	210 ± 6.5
Cyclohexane	570 ± 12	350 ± 8.6	480 ± 11	220 ± 6.7	2300 ± 46	260 ± 7.2
alkene						
Ethene	5700 ± 170	24000 ± 730	5000 ± 150	9100 ± 270	57000 ± 1700	9700 ± 290
Propene	1200 ± 35	6000 ± 180	1300 ± 41	2200 ± 66	21000 ± 630	4900 ± 150
i-Butene	300 ± 10	3100 ± 93	720 ± 22	650 ± 20	15000 ± 450	14000 ± 410
cis-2-Butene	72 ± 5.4	330 ± 11	320 ± 11	120 ± 6.1	6300 ± 190	4200 ± 120

	Concentration, pptv (±standard deviation) (b.d. = below detection limit)					
	Light & Heavy Good Vehicle - GVX	Minibus - MBS	Double-deck big bus - DBS	Single-deck big bus - SBS	Private car - PCX	Taxi - TAS
trans-2-Butene	93 ± 5.7	430 ± 14	400 ± 13	190 ± 7.7	7500 ± 230	8800 ± 260
1-Butene	290 ± 10	1100 ± 34	440 ± 14	450 ± 15	4800 ± 150	7000 ± 210
1,3-Butadiene	150 ± 6.7	980 ± 30	120 ± 6.2	240 ± 8.8	3500 ± 110	1200 ± 37
2-Methyl-1-butene	45 ± 5.2	400 ± 13	170 ± 7.2	71 ± 5.4	5200 ± 160	83 ± 5.6
2-Methyl-2-butene	70 ± 5.4	800 ± 24	280 ± 9.7	110 ± 6.1	14000 ± 430	150 ± 6.6
3-Methyl-1-butene	37 ± 5.1	190 ± 7.5	73 ± 5.5	44 ± 5.2	2200 ± 65	86 ± 5.6
cis-2-Pentene	62 ± 5.3	420 ± 13	190 ± 7.6	99 ± 5.8	6300 ± 190	94 ± 5.7
trans-2-Pentene	77 ± 5.5	550 ± 17	270 ± 9.5	95 ± 5.8	8700 ± 260	180 ± 7.4
1-Pentene	65 ± 5.4	620 ± 19	250 ± 8.9	140 ± 6.5	2700 ± 81	88 ± 5.6
2-Methyl-1-pentene	100 ± 5.8	1000 ± 31	250 ± 8.9	150 ± 6.6	9300 ± 280	120 ± 6.1
3-Methyl-1-pentene	31 ± 5.1	110 ± 5.9	42 ± 5.2	40 ± 5.1	640 ± 20	19 ± 5.0
4-Methyl-1-pentene	21 ± 5.0	170 ± 7.2	60 ± 5.3	51 ± 5.2	1400 ± 44	37 ± 5.1
2-Methyl-2-pentene	31 ± 5.1	420 ± 14	75 ± 5.5	37 ± 5.1	4800 ± 150	41 ± 5.1
cis-3-Methyl-2-pentene	23 ± 5.0	360 ± 12	65 ± 5.4	33 ± 5.1	4800 ± 150	37 ± 5.1
trans-3-Methyl-2-pentene	16 ± 5.0	240 ± 8.7	40 ± 5.1	20 ± 5.0	2900 ± 87	21 ± 5.0
1-Hexene	48 ± 5.2	550 ± 17	120 ± 6.1	59 ± 5.3	6700 ± 200	63 ± 5.3
cis-2-Hexene	14 ± 5.0	160 ± 6.9	34 ± 5.1	17 ± 5.0	1800 ± 55	18 ± 5.0
trans-2-Hexene	26 ± 5.1	280 ± 9.8	66 ± 5.4	36 ± 5.1	3200 ± 96	34 ± 5.1
cis-3-Hexene	16 ± 5.0	27 ± 5.1	27 ± 5.1	12 ± 5.0	470 ± 15	14 ± 5.0
trans-3-Hexene	10 ± 5.0	120 ± 6.1	27 ± 5.1	12 ± 5.0	1300 ± 41	15 ± 5.0
limonene	b.d.	12 ± 5.0	95 ± 5.8	20 ± 5.0	39 ± 5.1	24 ± 5.0
alpha-Pinene	3.5 ± 5.0	13 ± 5.0	210 ± 8.1	8.0 ± 5.0	140 ± 6.5	8.0 ± 5.0
beta-Pinene	b.d.	b.d.	15 ± 5.0	3.0 ± 5.0	15 ± 5.0	b.d.
Isoprene	66 ± 5.4	400 ± 13	120 ± 6.2	130 ± 6.3	2400 ± 71	77 ± 5.5
alkyne						
Ethyne	3900 ± 79	30000 ± 610	4400 ± 88	6100 ± 120	45000 ± 910	6200 ± 120
Propyne	97 ± 5.4	650 ± 14	110 ± 5.5	180 ± 6.1	2000 ± 40	170 ± 6.0
2-Butyne	b.d.	8.0 ± 5.0	b.d.	b.d.	88 ± 5.3	b.d.
1-Butyne	4.5 ± 5.0	11 ± 5.0	7.0 ± 5.0	4.0 ± 5.0	82 ± 5.3	b.d.
aromatic hydrocarbon						
Benzene	1000 ± 31	3400 ± 100	1400 ± 41	1400 ± 42	20000 ± 590	1300 ± 40
Ethylbenzene	180 ± 6.2	1100 ± 32	930 ± 28	580 ± 18	9100 ± 270	1200 ± 35
1,4-Diethylbenzene	b.d.	360 ± 11	23 ± 3.1	6.0 ± 3.0	690 ± 21	120 ± 4.6
1,3-Diethylbenzene	b.d.	110 ± 4.4	51 ± 3.4	12 ± 3.0	280 ± 8.9	40 ± 3.2
1,2-Diethylbenzene	b.d.	27 ± 3.1	32 ± 3.1	8.0 ± 3.0	63 ± 3.5	27 ± 3.1
1,2,3-Trimethylbenzene	42 ± 3.2	1200 ± 35	520 ± 16	140 ± 5.0	3500 ± 110	440 ± 13
1,2,4-Trimethylbenzene	120 ± 4.7	3500 ± 100	1200 ± 35	360 ± 11	9700 ± 290	1100 ± 32
1,3,5-Trimethylbenzene	42 ± 3.3	730 ± 22	170 ± 5.9	76 ± 3.8	2000 ± 61	200 ± 6.6
Isopropylbenzene	7.0 ± 3.0	110 ± 4.5	40 ± 3.2	24 ± 3.1	470 ± 14	39 ± 3.2
n-Propylbenzene	24 ± 3.1	400 ± 12	180 ± 6.2	75 ± 3.8	1100 ± 34	190 ± 6.4
Isobutylbenzene	b.d.	26 ± 3.1	10 ± 3.0	3.0 ± 3.0	40 ± 3.2	16 ± 3.0
sec-Butylbenzene	b.d.	28 ± 3.1	45 ± 3.3	9.0 ± 3.0	64 ± 3.6	30 ± 3.1
n-Butylbenzene	b.d.	60 ± 3.5	47 ± 3.3	10 ± 3.0	96 ± 4.2	34 ± 3.2
Toluene	3400 ± 100	9000 ± 270	6600 ± 200	5500 ± 160	110000 ± 3200	7500 ± 230
2-Ethyltoluene	26 ± 3.1	940 ± 28	300 ± 9.5	110 ± 4.4	3100 ± 93	330 ± 10
3-Ethyltoluene	51 ± 3.4	1400 ± 41	320 ± 10	140 ± 5.1	5100 ± 150	330 ± 10
4-Ethyltoluene	24 ± 3.1	430 ± 13	150 ± 5.4	50 ± 3.4	1900 ± 58	130 ± 5.0
Isopropyltoluene	b.d.	10 ± 3.0	17 ± 3.0	4.0 ± 3.0	19 ± 3.1	11 ± 3.0
o-Xylene	150 ± 5.3	1900 ± 56	780 ± 24	410 ± 13	11000 ± 320	780 ± 24
m-Xylene	240 ± 7.8	2200 ± 67	1300 ± 40	740 ± 22	20000 ± 590	1300 ± 39
p-Xylene	100 ± 4.3	890 ± 27	540 ± 16	340 ± 11	8600 ± 260	590 ± 18
halogenated hydrocarbon						
CH_3Cl	930 ± 140	730 ± 110	820 ± 120	940 ± 140	760 ± 110	880 ± 130
CH_2Cl_2	180 ± 27	200 ± 30	1000 ± 150	420 ± 62	220 ± 32	710 ± 110

	Concentration, pptv (±standard deviation) (b.d. = below detection limit)					
	Light & Heavy Good Vehicle - GVX	Minibus - MBS	Double-deck big bus - DBS	Single-deck big bus - SBS	Private car - PCX	Taxi - TAS
$CHCl_3$	43 ± 6.5	61 ± 9.1	110 ± 17	63 ± 9.4	130 ± 19	68 ± 10
CCl_4	100 ± 15	100 ± 15	100 ± 15	110 ± 17	98 ± 15	110 ± 16
CH_3Br	13 ± 2.0	16 ± 2.3	140 ± 21	67 ± 10	14 ± 2.1	13 ± 2.0
CH_2Br_2	1.5 ± 0.24	2.4 ± 0.37	1.4 ± 0.23	1.3 ± 0.22	1.5 ± 0.25	1.8 ± 0.28
$CHBr_3$	3.0 ± 0.46	30 ± 4.5	17 ± 2.5	3.4 ± 0.52	7.4 ± 1.1	6.5 ± 0.98
CH_3CCl_3	31 ± 4.6	33 ± 4.9	76 ± 11	36 ± 5.4	140 ± 21	44 ± 6.7
1,2-DCE	13 ± 2.0	25 ± 3.8	33 ± 4.9	46 ± 6.9	54 ± 8.2	35 ± 5.3
C_2HCl_3	51 ± 7.7	57 ± 8.6	130 ± 20	500 ± 75	41 ± 6.2	260 ± 39
C_2Cl_4	75 ± 11	230 ± 35	1200 ± 180	380 ± 57	430 ± 64	290 ± 43
H-1211	7.1 ± 1.1	6.8 ± 1.0	11 ± 1.7	10 ± 1.5	8.2 ± 1.2	19 ± 2.8

low molecular weight VOC species. In gasoline-fueled dominated samples, unsaturated hydrocarbons are the most abundant (36%), followed by unsaturated hydrocarbons (32%) and aromatic hydrocarbons (30%). The relatively high aromatic fraction in gasoline enhances its combustion performance but generally at the expense of an increase in the NO_x emissions (Wang *et al.*, 2001). And in diesel-fueled dominated samples (except minibus), saturated hydrocarbons are the most abundant, followed by unsaturated hydrocarbons and aromatic. Moreover, the abundance of halogenated hydrocarbons in diesel-fueled dominated samples are relatively higher than LPG-fueled and gasoline-fueled dominated samples.

VOC molar composition profiles in the different types of VE-dominated samples are shown in Fig. 3. It shows that *n*-butane (31%) constituted the largest fraction of measured VOCs in TAS sample, followed by propane (26%) and *i*-butane (25%). These three species are the major constituents of LPG in Hong Kong (Tsai *et al.*, 2006).

Toluene was the most abundant aromatic in PCX samples (16%), comprising about half of the quantified aromatic content. Toluene is a commonly used gasoline additive and the amount of toluene added varies with different oil companies. The second most abundance VOC specie is ethene (8.4%), followed by pentane (7.1%) and ethyne (6.6%) in PCX sample. Toluene and *i*-pentane were the two main constituents of gasoline and they were used as tracers for estimating gasoline evaporative losses (Tsai *et al.*, 2006). However, in PCX samples, the abundance of MTBE is significantly higher (2.1%). MTBE is a gasoline additive, used as an oxygenate and to raise the octane number. According to previous studies, evaporative loss of unburned fuel is an important emission source from automobiles (Na *et al.*, 2004). Generally speaking, ethene, and ethyne have the greatest abundance in all the other diesel-fueled dominated VOCs profiles (except DBS samples). They are the major sources for incomplete combustion. And in DBS sample, *n*-butane and toluene are the most abundance VOC species. They are the major sources for fuel evaporation. As diesel is a mixture of hydrocarbons with higher density, viscosity and sulfur content than gasoline or LPG, the abundances of OCS and CS2 (sulfur emission) in SBS, DBS and GVX samples (mainly diesel-fueled emission samples) are higher than in LPG-fueled and gasoline-fueled dominated samples. Anthropogenic sources of OCS arise from the combustion of biomass and fossil fuel. Emission of OCS from diesel-fueled vehicles is one of such example.

VOC Concentrations in Roadsides

Table 3 shows the VOC concentrations collected in the atmosphere at different roadside locations in Hong Kong. The vehicle numbers and their fuel types were counted during sampling events in order to evaluate their effects on the ambient concentrations. The statistical counting precision were < 1%. On average, the mean concentrations of total quantified VOCs (sum of all of species except for CH_4, CO_2, and CO) at Mong Kok (MKX), The Hong Kong Polytechnic University (PUX), Lok Ma Chau (LMX), were 74.9 ± 12.1 ppbv, 238 ± 117 ppbv, 58.5 ± 63.8 ppbv respectively. The concentration of total quantified VOCs at PUX was the highest, especially in summer, as the site is at the tunnel exit in downtown area. Traffic flow record shows an average of > 5,000 of different classes of LPG-, gasoline-, and diesel-fueled vehicles accessing the site during the sampling events (LPG: 21%; gasoline: 41%; and diesel: 38%). Moreover, there is a traffic light near the sampling location at PUX, emissions resulting from vehicle idling increased. In addition, the high concentration of C_6 to C_9 saturated hydrocarbons observed at PUX perhaps may be due to the evaporation of fuels from fuel tanks of gasoline-fueled vehicles or other special VOCs sources near the sampling site. Except the unknown saturated hydrocarbons emission, toluene has the greatest abundance in all the VOC profiles, this suggests that roadside areas are significantly influenced by the gasoline-fueled VE. The lowest (0.98 ppbv) and the highest (36.1 ppbv) mean concentrations of toluene were also observed at LMX (with high standard deviation), it means the emission of toluene in LMX was not stable during the sampling period. The site is the main transportation gate for goods between Hong Kong and China. More than 80% of the vehicles passing through the site were diesel-fueled light and heavy goods vehicles during the sampling events. Although toluene is the most abundance specie of gasoline evaporation but significant amount of toluene can be observed in diesel fuel also (Tsai *et al.*, 2006). This indicated the importance

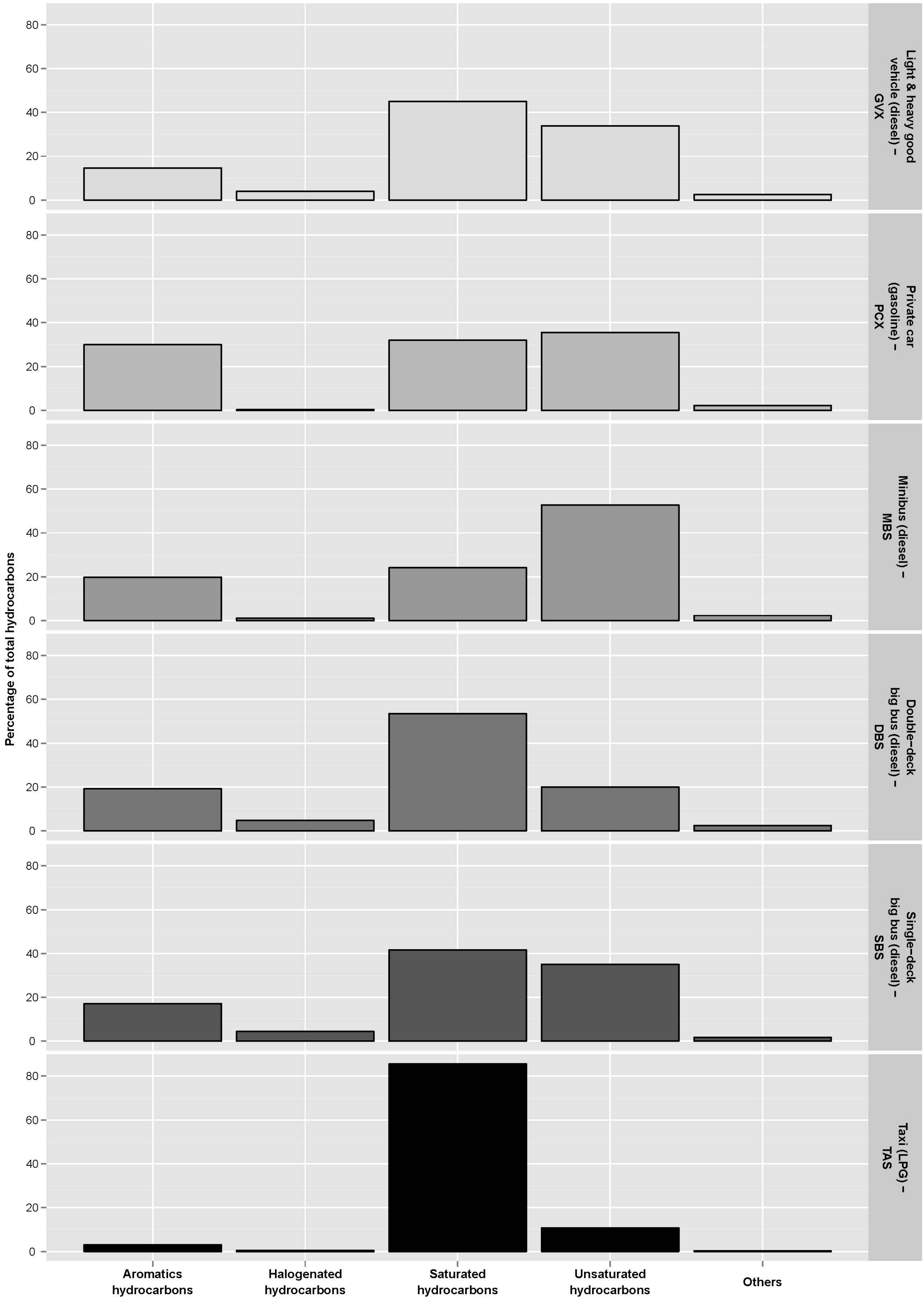

Fig. 2. The abundance of five groups of VOCs for the source-dominated samples.

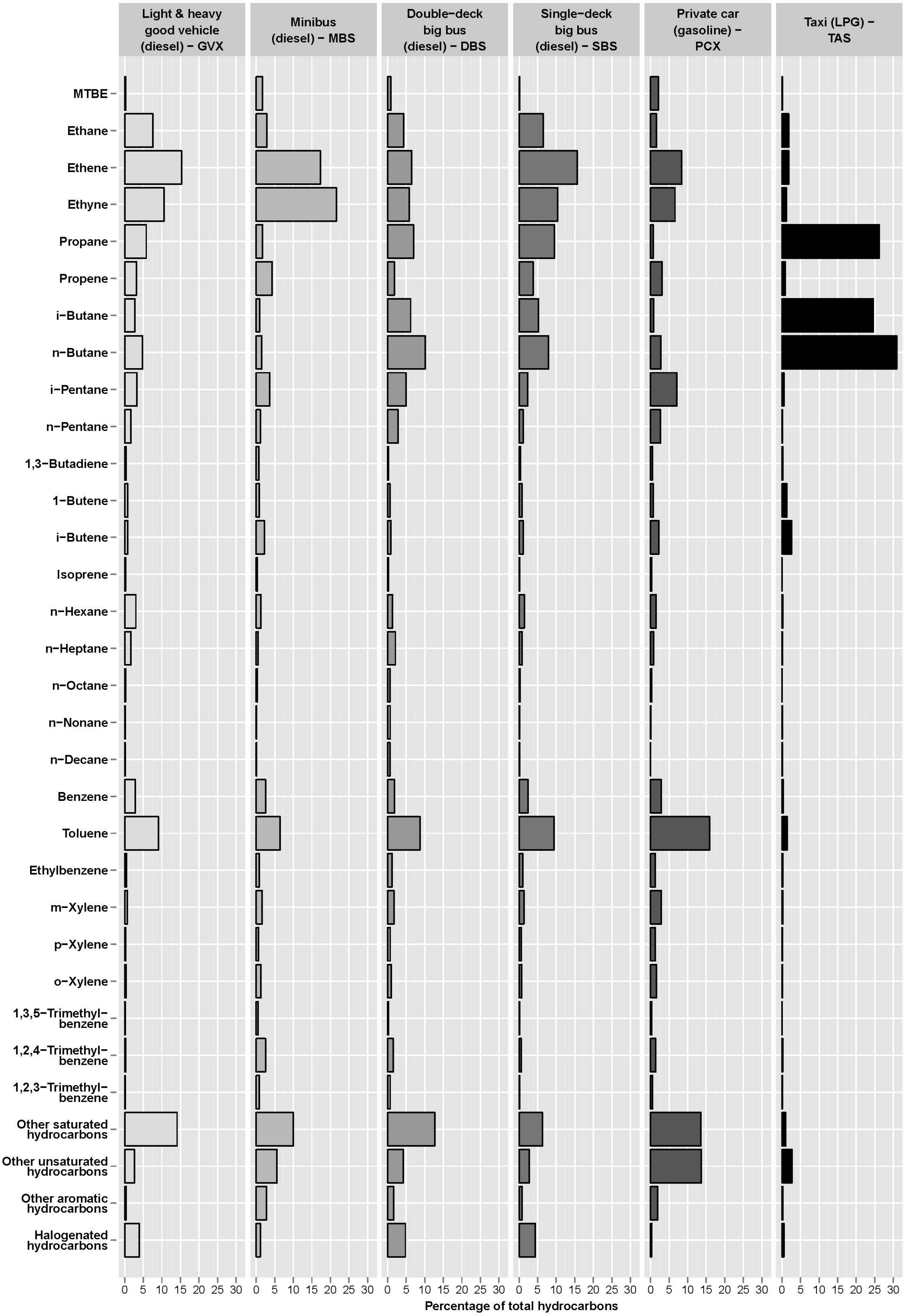

Fig. 3. Average VOC molar composition profiles for the vehicular emission dominated samples.

Table 3. VOC and other gaseous pollutant concentrations in three roadside locations in Hong Kong.

	Concentration, pptv (± standard deviation)		
	MKX	PUX	LMX
CH_4 (ppmv)	2.0 ± 0.11	2.0 ± 0.14	2.1 ± 0.69
CO (ppbv)	1600 ± 220	1800 ± 470	800 ± 550
CO_2 (ppmv)	460 ± 27	450 ± 24	430 ± 33
OCS	740 ± 160	930 ± 580	740 ± 130
CS_2	58 ± 50	760 ± 1800	110 ± 110
MTBE	370 ± 130	650 ± 180	310 ± 360
alkane			
Ethane	3600 ± 820	3600 ± 1200	1400 ± 1400
Propane	6600 ± 1400	11000 ± 3000	4100 ± 7800
i-Butane	4700 ± 840	8300 ± 3700	2300 ± 2500
n-Butane	7100 ± 1400	10000 ± 2100	4100 ± 5100
2,2-Dimethylbutane	95 ± 20	270 ± 170	65 ± 89
2,3-Dimethylbutane	160 ± 42	1400 ± 1900	140 ± 210
2,2,3-Trimethylbutane	11 ± 3.9	130 ± 60	11 ± 24
i-Pentane	3000 ± 630	5000 ± 1300	1900 ± 1300
n-Pentane	920 ± 150	1800 ± 770	800 ± 900
2-Methylpentane	960 ± 220	12000 ± 16000	890 ± 1500
3-Methylpentane	680 ± 160	9300 ± 12000	690 ± 1100
3-Ethylpentane	39 ± 17	2000 ± 1000	39 ± 94
2,2-Dimethylpentane	32 ± 15	430 ± 250	40 ± 93
2,3-Dimethylpentane	71 ± 59	4200 ± 4200	67 ± 81
2,4-Dimethylpentane	88 ± 26	1300 ± 770	68 ± 130
3,3-Dimethylpentane	47 ± 26	1300 ± 650	80 ± 180
2,2,4-Trimethylpentane	360 ± 130	1100 ± 420	68 ± 35
2,3,4-Trimethylpentane	100 ± 33	340 ± 130	17 ± 7.1
n-Hexane	930 ± 310	24000 ± 29000	770 ± 1400
2-Methylhexane	410 ± 160	15000 ± 7900	440 ± 950
3-Methylhexane	440 ± 170	16000 ± 8900	490 ± 1000
2,5-Dimethylhexane	140 ± 46	1300 ± 760	70 ± 120
2,4-Dimethylhexane	150 ± 48	1500 ± 980	82 ± 140
2,3-Dimethylhexane	72 ± 23	520 ± 390	31 ± 44
n-Heptane	550 ± 230	19000 ± 12000	510 ± 1000
2-Methylheptane	100 ± 34	1100 ± 860	97 ± 140
3-Methylheptane	100 ± 28	630 ± 430	88 ± 130
4-Methylheptane	17 ± 8.2	110 ± 71	19 ± 32
2,4-Dimethylheptane	34 ± 15	230 ± 180	43 ± 30
2,5-Dimethylheptane	18 ± 6.5	130 ± 84	20 ± 20
2,6-Dimethylheptane	58 ± 34	160 ± 61	50 ± 72
3,3-Dimethylheptane	14 ± 8.3	48 ± 39	9.8 ± 20
4,4-Dimethylheptane	15 ± 6.3	140 ± 200	15 ± 12
n-Octane	220 ± 74	1900 ± 1100	220 ± 250
n-Nonane	270 ± 130	3000 ± 2100	340 ± 270
n-Decane	250 ± 120	600 ± 340	350 ± 210
cycloalkane			
Cylopentane	470 ± 110	2900 ± 3500	470 ± 640
Methylcyclopentane	350 ± 110	6300 ± 6000	300 ± 500
Methylcyclohexane	300 ± 110	8600 ± 4200	250 ± 400
Cyclohexane	310 ± 120	11000 ± 9500	220 ± 380
alkene			
Ethene	8900 ± 1300	8900 ± 1900	10000 ± 5800
Propene	2300 ± 370	2900 ± 720	2300 ± 1100
i-Butene	1000 ± 220	1700 ± 560	630 ± 260
cis-2-Butene	290 ± 80	510 ± 170	270 ± 140
trans-2-Butene	400 ± 99	790 ± 300	320 ± 170
1-Butene	550 ± 84	760 ± 260	650 ± 230

	Concentration, pptv (± standard deviation)		
	MKX	PUX	LMX
1,3-Butadiene	330 ± 78	380 ± 100	500 ± 210
2-Methyl-1-butene	190 ± 57	330 ± 81	180 ± 91
2-Methyl-2-butene	420 ± 130	760 ± 160	280 ± 160
3-Methyl-1-butene	80 ± 21	120 ± 31	85 ± 35
cis-2-Pentene	200 ± 61	330 ± 68	150 ± 81
trans-2-Pentene	290 ± 81	500 ± 110	210 ± 110
1-Pentene	290 ± 180	360 ± 190	700 ± 290
2-Methyl-1-pentene	190 ± 120	270 ± 240	110 ± 220
3-Methyl-1-pentene	37 ± 12	48 ± 17	37 ± 29
4-Methyl-1-pentene	56 ± 21	76 ± 39	56 ± 60
2-Methyl-2-pentene	110 ± 35	230 ± 66	69 ± 53
cis-3-Methyl-2-pentene	97 ± 29	200 ± 51	55 ± 45
trans-3-Methyl-2-pentene	63 ± 20	130 ± 35	36 ± 29
1-Hexene	110 ± 55	190 ± 150	96 ± 74
cis-2-Hexene	40 ± 12	77 ± 19	31 ± 26
trans-2-Hexene	73 ± 21	140 ± 38	52 ± 42
cis-3-Hexene	18 ± 6.4	26 ± 8.6	12 ± 7.0
trans-3-Hexene	32 ± 11	77 ± 23	27 ± 20
limonene	41 ± 24	33 ± 17	14 ± 27
alpha-Pinene	17 ± 6.8	32 ± 24	47 ± 92
beta-Pinene	4.2 ± 2.4	5.8 ± 4.5	7.4 ± 11
Isoprene	250 ± 65	450 ± 150	430 ± 240
alkyne			
Ethyne	7700 ± 900	6400 ± 1500	4500 ± 4400
Propyne	160 ± 22	180 ± 41	150 ± 97
2-Butyne	0.92 ± 1.4	1.3 ± 1.8	3.4 ± 2.5
1-Butyne	5.3 ± 2.8	5.9 ± 4.2	7.0 ± 6.2
aromatic hydrocarbon			
Benzene	1400 ± 390	1600 ± 400	1300 ± 1700
Ethylbenzene	690 ± 230	770 ± 190	680 ± 1200
1,4-Diethylbenzene	33 ± 46	90 ± 93	77 ± 68
1,3-Diethylbenzene	28 ± 14	46 ± 28	46 ± 41
1,2-Diethylbenzene	18 ± 9.7	22 ± 16	32 ± 22
1,2,3-Trimethylbenzene	300 ± 140	470 ± 160	350 ± 460
1,2,4-Trimethylbenzene	770 ± 280	1300 ± 590	720 ± 920
1,3,5-Trimethylbenzene	150 ± 39	300 ± 100	120 ± 70
Isopropylbenzene	32 ± 5.8	85 ± 38	25 ± 24
n-Propylbenzene	140 ± 41	280 ± 96	150 ± 83
Isobutylbenzene	7.5 ± 4.6	11 ± 6.9	13 ± 11
sec-Butylbenzene	21 ± 9.9	24 ± 15	29 ± 27
n-Butylbenzene	24 ± 14	32 ± 20	43 ± 32
Toluene	7300 ± 2500	9900 ± 3300	5900 ± 12000
2-Ethyltoluene	220 ± 75	380 ± 120	190 ± 220
3-Ethyltoluene	280 ± 69	510 ± 180	170 ± 140
4-Ethyltoluene	120 ± 27	260 ± 97	80 ± 71
Isopropyltoluene	11 ± 14	15 ± 22	19 ± 31
o-Xylene	600 ± 160	850 ± 220	530 ± 730
m-Xylene	1000 ± 280	1500 ± 370	810 ± 1400
p-Xylene	440 ± 120	590 ± 160	370 ± 620
halogenated hydrocarbon			
CH_3Cl	800 ± 200	780 ± 130	750 ± 230
CH_2Cl_2	530 ± 410	500 ± 310	530 ± 1100
$CHCl_3$	89 ± 16	260 ± 160	37 ± 30
CCl_4	100 ± 4.2	100 ± 6.8	110 ± 29
CH_3Br	15 ± 2.1	16 ± 2.7	40 ± 30
CH_2Br_2	1.5 ± 0.24	1.5 ± 0.45	1.0 ± 0.33

	Concentration, pptv (± standard deviation)		
	MKX	PUX	LMX
$CHBr_3$	6.8 ± 2.0	6.2 ± 2.2	3.5 ± 3.2
CH_3CCl_3	50 ± 13	180 ± 170	35 ± 15
1,2-DCE	31 ± 19	21 ± 17	16 ± 27
C_2HCl_3	73 ± 120	68 ± 100	310 ± 790
C_2Cl_4	320 ± 150	310 ± 170	230 ± 510
H-1211	37 ± 91	8.7 ± 4.4	14 ± 16

of running evaporative loss from the fuels in the roadside environment. Among the VOCs analyzed, the concentration of ethene (10 ppbv) was the most abundant specie in LMX, followed by toluene (5.9 ppbv) and ethyne (4.5 ppbv).

High concentrations of LPG tracers (n-butane, i-butane and propane) were also observed in roadside environment. This suggests that the downtown area is significantly influenced by the LPG-fueled VE. Statistic shows that the amounts and contributions of LPG-fueled taxi accessing PUX were higher than MKX, therefore, higher levels of LPG tracers were found in PUX than in MKX. Moreover, high concentrations of ethene and ethyne were observed. They are typical tracers for combustion, and thus VE was the likely source of these two compounds (Barrefors and Petersson, 1996; Stoeckenius *et al.*, 2006). Fig. 4 shows the abundance of four groups of VOCs at each roadside sampling location. Saturated hydrocarbons are the most abundant group, followed by unsaturated hydrocarbons, and aromatic hydrocarbons in PUX and MKX. Moreover, the VOC profiles at roadside locations are shown in Fig. 5. Ethene was the most abundant VOCs which accounted for 9.5 to 29% of the total quantified VOCs, except in PUX (due to the unknown saturated hydrocarbons emission). Moreover, it is clear that there are several VOCs that were abundant in the roadside samples, namely toluene, ethyne, propane, *i*-butane, *n*-butane and *i*-pentane. Our findings were consistent with the compositions reported by Tsai *et al.* (2006) and Ho *et al.* (2009). The result also promises an important input of fuel from gasoline-fueled and LPG-fueled vehicles to the roadside areas. As diesel samples consisted mainly of heavy C_8–C_{10} alkanes, these compounds have low vapor pressures and thus do not readily evaporate into the atmosphere, suggesting that evaporative loss from diesel to the roadside atmosphere was insignificant (Tsai *et al.*, 2006).

VOC Ratios

A high ratio of a more reactive VOC to a less reactive VOC (photochemical lifetimes or reactivities) against hydroxyl radical (OH) indicates relatively little photochemical processing of the air mass and major impact from primary emissions. On the other hand, a lower ratio is reflective of more aged VOC mixes and thus presumably that the VOCs were emitted from more distant sources (Guo *et al.*, 2007).

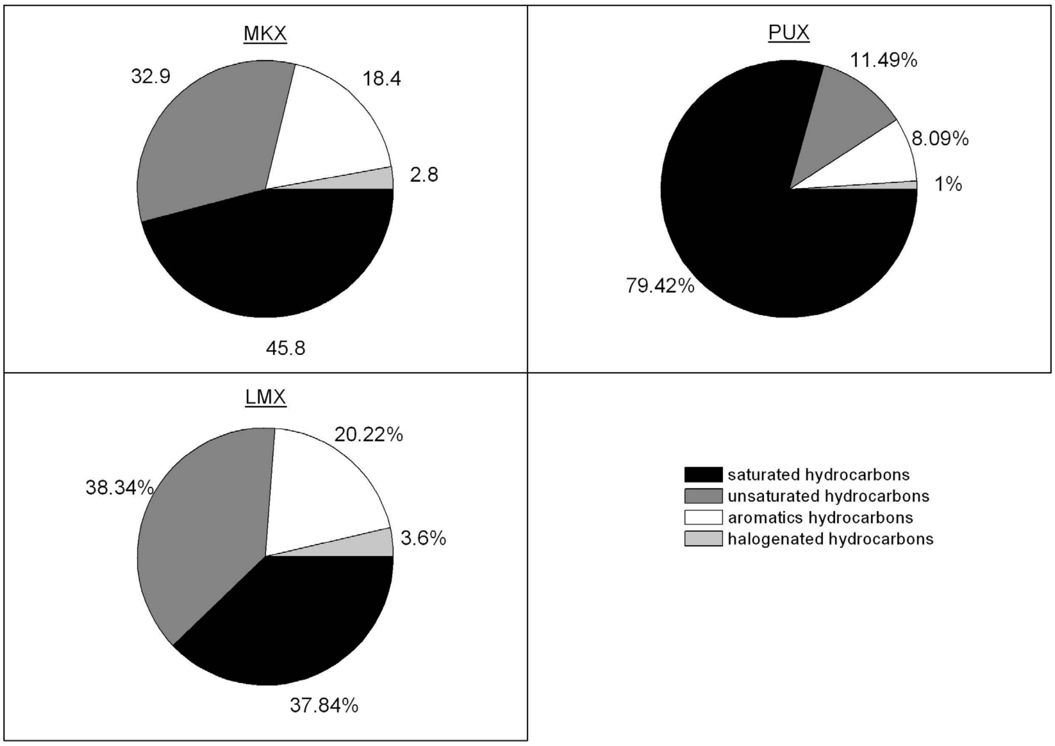

Fig. 4. The abundance of five groups of VOCs for the roadside samples.

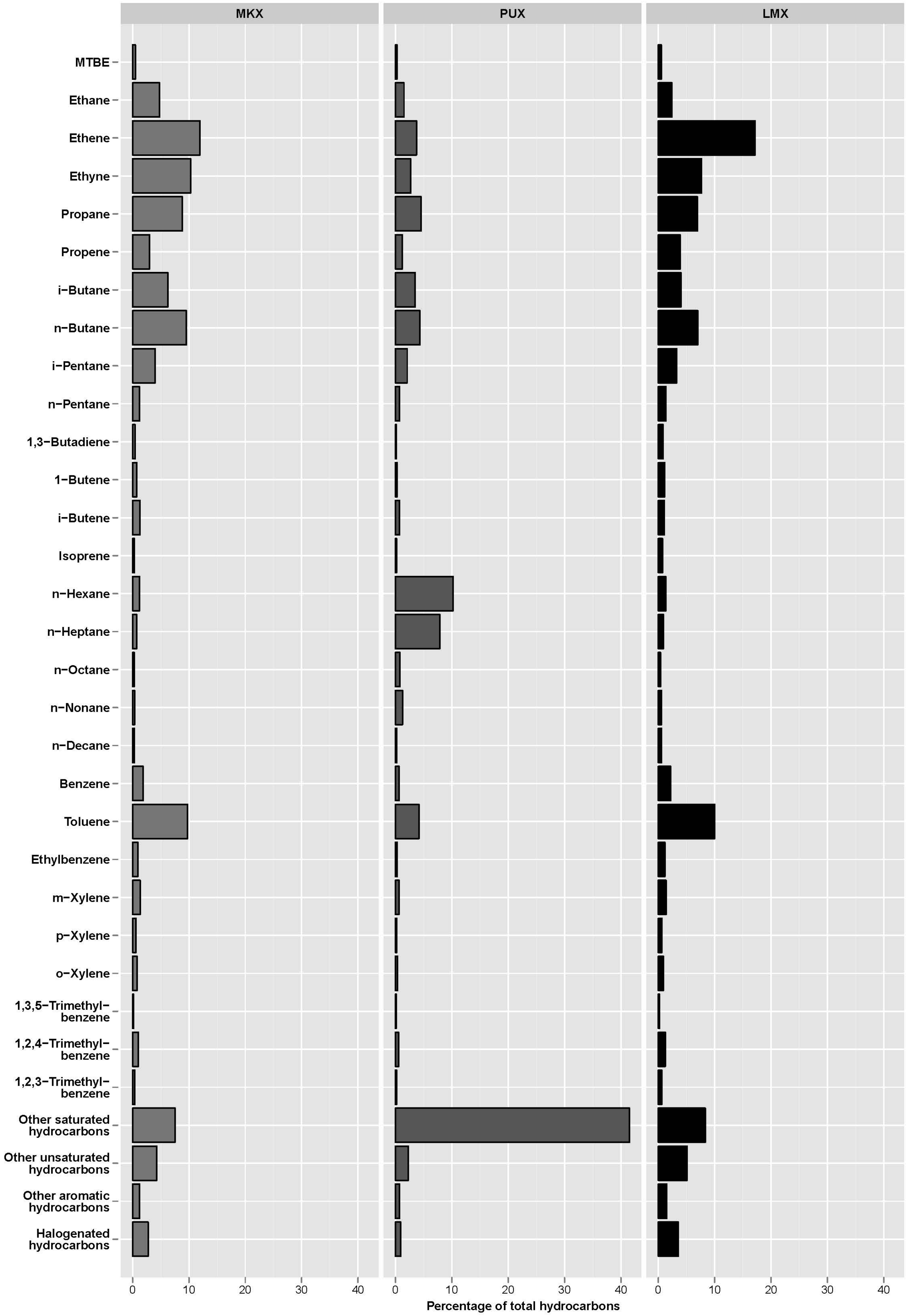

Fig. 5. Average VOC molar composition profiles for the roadside samples.

Comparisons of the ratios can be used to estimate the relative ages of air parcels. In this study, the ratio of *m*,*p*-xylene/ethylbenzene were used for comparison (Nelson and Quigley, 1983; Smyth *et al.*, 1999; So and Wang, 2004). The average value of *m*,*p*-xylene/ethylbenzene in tunnel (2.61 ± 0.30) (Ho *et al.*, 2009) are close to/or slightly higher than the ratios measured at the roadside sampling location at MKX, PUX, LMX (2.16 ± 0.32, 2.74 ± 0.22, 2.02 ± 0.55) and higher than other urban/rural sites in Hong Kong (range from 1.3–1.8) (Guo *et al.*, 2007). Ethene and ethyne are typical tracers for combustion, and thus vehicle exhaust was the likely source of these two gases (Barrefors and Petersson, 1996; Stoeckenius *et al.*, 2006). Tsai *et al.* (2006) concluded that the ethyne/ethene ratio for Hong Kong was 0.53 ± 0.03. And the studies conducted in highways tunnels throughout the U.S. indicate that the ratio range from 0.59–1.0 (Harley *et al.*, 2002). The average ethyne/ethene ratio in this study ranged from 0.32 to 1.04 which is close to the previous studies. These indicated that the three sites have more influence from VE.

The major sources of toluene and benzene in urban areas are VE and solvent use. Toluene has a shorter life time (~3 days) than benzene (~12 days). The average toluene/benzene (T/B) ratios were 22.1 ± 12.7 in the gasoline used in Hong Kong (Tsai *et al.*, 2006). The T/B ratios in gasoline were higher than the ratios found at a roadside microenvironment in Hong Kong (ranged from 1.4 to 9.6; an average of 5.2 ± 2.2). Different source-dominated samples have different T/B ratios (range from 2.8 to 6.0), and the variations should depend on the fuel use characteristics, emission control technology and fuel evaporation. And the differences were mainly due to the variations of toluene emission. More studies should be done in order to have a clear picture for these source characteristics.

Correlation of VOCs

The correlations among CO and VOCs for all roadside samples were evaluated by correlation analysis. CO is generally emitted from incomplete combustion of fossil fuel. Determining the relationship between CO and VOCs can provide useful information on their sources and emission signatures (Wang *et al.*, 2002, 2003; Guo *et al.*, 2007). Among the VOCs measured, ethane was best correlated with CO (R = 0.94), follow by propane and *i*-butene (R = 0.83) as well as ethyne (R = 0.81) confirming a common source origin in roadside environment of Hong Kong. Generally, good and fair correlations were observed between most of the combustion emitted VOCs and CO, except halogenated hydrocarbons, isoprene and pinenes which are emitted from different sources. Isoprene is mainly emitted from biogenic sources (e.g., vegetables) although a few studies report the contribution of isoprene from VE (e.g., Borbon *et al.*, 2001; Barletta *et al.*, 2002). Here, the poor correlation between isoprene and CO suggests that VE of isoprene is not significant. Moreover, biogenic isoprene emissions from the vegetation near the sampling locations may have significant impact to the result. Moreover, strong and fair correlations were determined from marker species of fuel vapor (LPG, gasoline, and diesel). As observed in previous section, propane, *n*-butane and *i*-butane are the major constituents of LPG-fueled vehicles, strong correlations were found (R = 0.81–0.94) among the species which indicated that unburned LPG was emitted to the roadside atmosphere. *n*-pentane, *i*-pentane, toluene, *m*-xylene, *p*-xylene, *o*-xylene are the most abundant VOCs from the exhaust of gasoline-fueled vehicle and the evaporative loss from gasoline vapor (Ho *et al.*, 2009). Fair and strong correlations (R = 0.64–0.92) of these species indicated the importance of emissions from gasoline-fueled vehicles. Moreover, good correlations (R = 0.69–0.80) were observed among diesel-fueled species (*n*-octane, *n*-nonane and *n*-decane), which is match with the results of Tsai *et al.* (2006).

Reactivity with Respect to Ozone Formation

It is well known that VOCs are significant precursors of O_3 formation. Individual VOCs have different photochemical reactivities. To assess the relative importance of VOCs from roadside environment in Hong Kong, we have applied the MIR to evaluate the contributions of individual VOCs (except OCS, H-1211, $CHBr_3$, and isobutylbenzene, as no MIR values are available for those species) to O_3 production (Carter, 2010). The product of the concentration and the MIR coefficient, where MIR is the amount (g) of O_3 formed per gram of VOC, indicates how much the individual VOCs may contribute to O_3 formation in the air mass (Grosjean *et al.*, 1998). Although the calculations of O_3 formation in this study are not very accurate, it provides rough ideas about individual VOCs on their photochemical reactivity.

The top ten reactivities with respect to O_3 formation of three roadside environments are presented in Table 4. The contributions of these ten VOCs were 51 to 64% of those of total measured VOC reactivity. The largest contributors to O_3 production in MKX and LMX were toluene (17 and 15% of the measured VOC reactivity, respectively), ethene (14 and 17% of the measured VOC reactivity, respectively), and propene (7 and 8% of the measured VOC reactivity, respectively), indicating the importance of alkenes and aromatics in the production of O_3. However, in PUX, the largest contributors to O_3 production were toluene (9% of the measured VOC), 3-methylhexane (6% of the measured VOC) and *n*-hexane (6% of the measured VOC). Toluene, 3-methylhexane and *n*-hexane were mainly from sources such as gasoline evaporation and use of solvents. Therefore, other than VE, fuel evaporation (which depends on temperature) also makes contributions to the O_3 production in roadside environment of Hong Kong.

CONCLUSIONS

In order to study the chemical concentrations and profiles of the source dominated samples, six types of VE-dominated samples were collected at representative locations in Hong Kong. A total of 111 VOCs were analyzed and reported. The dominant species for LPG-fueled dominated samples were *n*-butane, followed by propane (26%) and *i*-butane (25%). Toluene (16%), *i*-ethene (8.4%), pentane (7.1%) and ethyne (6.6%) were the dominant species for gasoline-

Table 4. Top 10 VOCs for ozone-forming potential at the three roadside locations.

LMC VOCs	μg-O_3/m^3	%ΔO_3^{a}	MK VOCs	μg-O_3/m^3	%ΔO_3^{a}	PU VOCs	μg-O_3/m^3	%ΔO_3^{a}
Ethene	103.65	17.322	Ethene	92.188	13.921	Ethene	91.513	5.438
Propene	45.39	7.585	Propene	45.410	6.857	n-Hexane	106.111	6.306
1-Butene	14.47	2.418	n-Butane	19.485	2.942	n-Heptane	81.657	4.852
1,3-Butadiene	14.02	2.342	i-Butene	14.349	2.167	Methylcyclohexane	58.772	3.493
1-Pentene	14.40	2.406	2-Methyl-2-butene	16.878	2.549	2-Methylpentane	62.549	3.717
Toluene	88.14	14.730	Toluene	109.927	16.600	3-Methylpentane	58.772	3.493
m-Xylene	34.18	5.712	m-Xylene	42.836	6.469	2-Methylhexane	71.602	4.255
o-Xylene	17.42	2.912	o-Xylene	19.950	3.013	3-Methylhexane	106.545	6.331
1,2,4-Trimethylbenzene	31.53	5.269	1,2,4-Trimethylbenzene	33.612	5.076	Toluene	148.965	8.852
1,2,3-Trimethylbenzene	20.60	3.442	1,2,3-Trimethylbenzene	17.733	2.678	m-Xylene	63.145	3.752

[a] Percent of total O_3 formed by carbonyls.

fueled dominated samples while ethene and ethyne were the most dominant species for diesel-fueled dominated samples (except in DBS samples). Moreover, the abundances of OCS and CS2 (sulfur emission) in diesel-fueled dominated samples are higher than in LPG-fueled and gasoline-fueled dominated samples because of higher sulfur content in diesel than gasoline and LPG. Except the unidentified sources for saturated hydrocarbons at PUX, toluene has the highest abundance in all the roadside sites, suggesting that roadside areas are significantly influenced by the gasoline-fueled VE in Hong Kong. This gas acts as a tracer of gasoline evaporation and its high abundances indicates the importance of running evaporative loss from gasoline-fueled vehicles in the roadside environment. The strong and fair correlations were determined from the marker species of fuel vapor (i.e., LPG, gasoline, and diesel), which show significant fuel evaporation from vehicles. The O_3 formation potential (OFP) of individual VOCs for VE were assessed. The largest contributors to O_3 production in roadside environments were toluene, ethane, propene, methylhexane and *n*-hexane, indicating vehicular fuel evaporation also has contributions to the O_3 production in roadside environment of Hong Kong. The in-depth understanding of source contributions provides important information for management of Hong Kong air quality.

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