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Characterization of volatile organic compounds at a roadside environment in Hong Kong: An investigation of influences after air pollution control strategies

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HIGHLIGHTS

- A series of control strategies has been implemented by HKSAR in recent years.
- Characteristics of VOCs were compared at roadside between 2003 and 2011/2012.
- Besides alkanes, the mixing ratios of other VOCs decreased by >50% since 2003.
- LPG fuel consumption becomes the largest contributor to the pollution.
- The sum of OFP for the target VOCs was reduced by 47% compared to that in 2003.

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ABSTRACT

Vehicular emission is one of the important anthropogenic pollution sources for volatile organic compounds (VOCs). Four characterization campaigns were conducted at a representative urban roadside environment in Hong Kong between May 2011 and February 2012. Carbon monoxide (CO) and VOCs including methane (CH_4), non-methane hydrocarbons (NMHCs), halocarbons, and alkyl nitrates were quantified. Both mixing ratios and compositions of the target VOCs show ignorable seasonal variations. Except CO, liquefied petroleum gas (LPG) tracers of propane, *i*-butane and *n*-butane are the three most abundant VOCs, which increased significantly as compared with the data measured at the same location in 2003. Meanwhile, the mixing ratios of diesel- and gasoline tracers such as ethyne, alkenes, aromatics, halogenated, and nitrated hydrocarbons decreased by at least of 37%. The application of advanced multivariate receptor modeling technique of positive matrix factorization (PMF) evidenced that the LPG fuel consumption is the largest pollution source, accounting for 60 ± 5% of the total quantified VOCs at the roadside location. The sum of ozone formation potential (OFP) for the target VOCs was 300.9 μg-O^3 m^{-3}, which was 47% lower than the value of 567.3 μg-O^3 m^{-3} measured in 2003. The utilization of LPG as fuel in public transport (i.e., taxis and mini-buses) contributed 51% of the sum of OFP, significantly higher than the contributions from gasoline- (16%) and diesel-fueled (12%) engine emissions. Our results demonstrated the effectiveness of the switch from diesel to LPG-fueled engine for taxis and mini-buses implemented by the Hong Kong Special Administrative Region (HKSAR) Government between the recent

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ten years, in additional to the execution of substitution to LPG-fueled engine and restrictions of the vehicular emissions in compliance with the updated European emission standards.

1. Introduction

Volatile organic compounds (VOCs) in the atmosphere are emitted from both biogenic (mainly from vegetation) and anthropogenic sources (e.g., vehicular and fossil-fueled power plant emission and solvent usage) (Apel et al., 2010; Atkinson, 2000; Atkinson and Arey, 2003). VOCs are important precursors to the formation of ground-level ozone (O_3) and secondary organic aerosols (SOA), and can also pose adverse health effects on human (Ho et al., 2013; Louie et al., 2013). Many studies have demonstrated that vehicular emission is one of the major sources of anthropogenic VOCs in urban areas (Cai and Xie, 2009; Niedojadlo et al., 2007; Song et al., 2007; Vega et al., 2000; Watson et al., 2001). Vega et al. reported that vehicular exhaust contributed 58.7% to non-methane hydrocarbons (NMHC) in Mexico City's atmosphere (Vega et al., 2000).

Hong Kong is one of the most densely populated cities in the world, with over 7.0 million people and more than 707,000 registered vehicles in an area of 1104 km^2 by the end of 2011 (Hong Kong Transport Department, 2012). Over the past years, urban and street-level air pollution pertaining to vehicular emission has attracted more and more public attention. As estimated by the Hong Kong Environmental Protection Department (HKEPD), local road transport contributed to 23% of the total VOCs emissions in 2011, with a number of 7567 tonnes VOCs emitted into the airs (Hong Kong Environmental Protection Department, 2011). Lau et al. (2010) found that vehicle- and marine vessel-related sources accounted for 31–48% of the ambient VOCs in Hong Kong in 2002–2003, while the contributions increased to 40–54% in 2006–2007. Guo et al. (2007) also investigated the C_1–C_8 VOCs at four urban and rural areas in Hong Kong from September 2002 to August 2003, and their results demonstrated that vehicular emissions contributed significantly to ambient VOCs levels in urban areas (65 $\pm$ 36%). Therefore, vehicular emission is confirmed as one of the key VOCs emission sources in Hong Kong. It is critical to determine the VOC emission characteristics from vehicles in order to further assess the associated human exposure risk and to understand their effects on subsequence photochemical reactions.

Methods adopted to quantify VOCs from vehicular emissions primarily include laboratory-based single-vehicle dynamometer tests (Guo et al., 2011b; Tsai et al., 2003), tunnel studies (Ho et al., 2007, 2009a; Hsu et al., 2001; Legreid et al., 2007; Lonneman et al., 1986), on-board mobile monitoring (Lau et al., 2011), and monitoring in roadside environment (Chan et al., 2002; Guo et al., 2011b; Ho et al., 2002; Ho et al., 2006; Kawashima et al., 2006; Tsai et al., 2006; Wang et al., 2002b). In the dynamometer tests, the VOCs emissions from vehicles were determined under different driving cycles which were set in advance (Guo et al., 2011b; Tsai et al., 2003). However, this method cannot accurately reflect a vehicle's emission under real-world traffic conditions. In contrast to dynamometer tests, the tunnel studies can directly determine vehicular emission profiles, and the monitoring is normally conducted under complicated on-road conditions with emissions from vehicle tailpipes and fuel evaporations (Ho et al., 2009a, b). The result from tunnel study is thus more representative and accurate to estimate the contributions of vehicle fleets to the total air pollutants in local urban areas. Ho et al. determined the emission factors for a number of 110 VOCs species in a tunnel in Hong Kong, of which the total measured VOC emission factors ranged from 67 mg veh^{-1} km^{-1} to 148 mg veh^{-1} km^{-1} (Ho et al., 2009a). However, there are several assumptions and limitations for roadway tunnel measurements, including approval by the administrative authorities for field monitoring, no cold start emissions from vehicles, bias in fleet distributions, resistance caused by tunnel walls, and speed limits established in the tunnels (Ho et al., 2009a; Kawashima et al., 2006). On-board measurement of vehicular emissions facilitates the examination of a vehicle's emission under real-world conditions. For example, Lau et al. measured the instantaneous carbon monoxide (CO), nitrogen monoxide (NO), and VOCs emissions from LPG-fueled taxis in Hong Kong using a sophisticated portable emission measurement system (Lau et al., 2011). Even though the method can accurately measure the instantaneous emission factors on-route under different operation modes (stop, start, creeping, cruising, idling and speed changes), only two vehicles can be examined per day only and the monitoring equipment procedures are complex and expensive.

In this study, we have conducted a one-year intensive VOCs monitoring program at a representative urban roadside environment in Hong Kong from May 2011 to February 2012. VOCs were collected in canister and speciated offline to investigate their mixing ratios and compositions. The results has been compared with a previous study at the same site in 2003, to demonstrate the effectiveness of VOCs control strategies implemented by the Hong Kong Special Administrative Region (HKSAR) Government between the years. The O_3 formation potential for each VOCs emission source was identified in further.

2. Methodology

2.1. Sampling site

Four characterization campaigns were conducted at an urban roadside location, namely Mong Kok Air Quality Monitoring Station (MKAQMS), in May 2011, August 2011, November 2011 and February 2012, respectively. The station is surrounded by residential and commercial building blocks with heavy daily traffic (shown in Fig. 1) (Lee et al., 2002), which is one of the three roadside monitoring stations established by the HKEPD. Based on the local geography, MKAQMS is the most representative roadside environment in Hong Kong. During the sampling period, any activity potentially generating additional pollutants (e.g., constructions sites) was prohibited near the sampling locations.

2.2. Measurement of VOCs and other trace gases

Twenty-four hour (0:00–23:59) integrated VOCs samples were collected into pre-treated and evacuated 2-L electro-polished stainless steel canisters by an ATEC automated sampler (Model 2200, Malibu, CA) once every three days during the periods of four campaigns. The final pressure of the sampled canister was 29 $\pm$ 1 psi. A Teflon PFA filter holder contains a 47 mm Teflon filter to remove particulates from the air stream prior to entering the flow lines. The sampling inlet was approximate 3 m above the

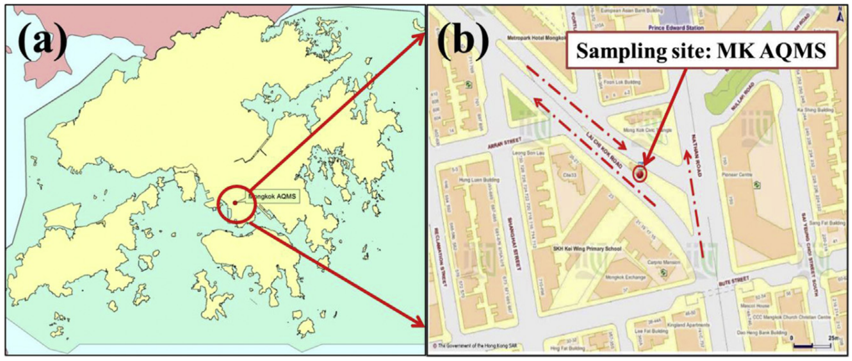

Fig. 1. Location of the sampling site, Mong Kok Air Quality Monitoring Station (MKAQMS) (a), and the surrounding environment (b).

ground level. The filled canisters were properly shipped to the laboratory in the University of California, Irvine (UCI) for analysis of CO, methane (CH_4), NMHCs, halocarbons, and alkyl nitrates within two weeks after the samples were collected. The stability of the target compounds was demonstrated by preparing a purified air filled canister injected with a known amount of certified gas mixture. The recovery of each of the target compounds was close to 100%, demonstrating the targeted VOCs are stable during the shipping and storage processes. CO was quantified from the canister samples by firstly reducing CO to CH_4 and then analyzing with a gas chromatography (GC) with a flame ionization detector (FID). The mixing ratios of CH_4 and VOCs were determined using a combination of GC with FID and mass spectrometric detection (MSD). The measurement detection limit, accuracy, and precision varied by compounds and were shown in the publications by Colman et al.(Barletta et al., 2002; 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% for CO, 2% for CH_4, 1–5% for halogenated hydrocarbons, and ranges from 0.5 to 5% for other NMHCs. The simultaneous measurements data of selected trace gases (O_3, CO, and nitrogen oxides (NO_2/NO_x)) and $PM_{2.5}/PM_{10}$ were supplied by HKEPD. O_3 was monitored with UV photometric analyzers (API 400, San Diego, CA), and NO_2/NO_x was measured by chemiluminescence instruments (API 200A, San Diego, CA). The detection limits are 1 ppbv for O_3, and 0.5 ppbv for NO_2/NO_x. The concentration of PM_{10} and $PM_{2.5}$ were determined by the tapered element oscillating microbalance (TEOM) continuous PM monitors (R&P TEOM Series 1400a-AB-PM_{10} and R&P TEOM Series 1400a-AB-$PM_{2.5}$, Thermo Scientific TEOM 1405-DF, Franklin, MA). The TEOM uses a tapered element oscillating microbalance that converts changes in frequency of a particulate-matter-impacted vibrating glass tube to mass loading and concentration on a continuous near-real-time basis (Meyer et al., 2000). All the instruments were regularly calibrated, tested, and audited using standards with known traceability (Hong Kong Environmental Protection Department, 2011).

2.3. Positive matrix factorization (PMF) receptor model

Positive matrix factorization (PMF) is an advanced multivariate receptor modeling technique, which calculates site-specific source profiles together with time variations of these sources based on correlations imbedded in ambient data. PMF has been successfully applied to VOCs data as reported in previous studies (Anderson et al., 2001; Guo et al., 2011a; Jorquera and Rappenglück, 2004; Latella et al., 2005; Lau et al., 2010; Ling et al., 2011; Sauvage et al., 2009; Xie and Berkowitz, 2006; Yuan et al., 2009). The model EPA PMF 3.0 was adopted for the VOCs source apportionment in this study. PMF was based on a mass balance equation to estimate the source profiles and their contributions (Eq. (1)):

$$X_{ij} = \sum_{p=1}^{p} C_{ip} S_{jp} + E_{ij} \tag{1}$$

where X_{ij} is the measured concentration of the *i*th species in the *j*th sample, C_{ip} is the concentration of the *i*th species in the material emitted by *p*th source, and S_{jp} is the airborne mass contribution of material from the *p*th source contributing to the *j*th sample. E_{ij} represents random errors in the measurement of C_{ip} and S_{jp} or the unaccounted sources. PMF solves the general receptor modeling problem using constrained non-negative source compositions and contributions, weighted and least-squares (Cheng et al., 2011; Paatero and Tapper, 1994; Yau et al., 2013). The non-negativity constraint is natural and more realistic in receptor modeling of environmental data. Also, a point-by-point weighting scheme, for error estimates for each data value, allows the inclusion of uncertain data in the analysis by giving them low weights.

For this study, measured VOC concentration values (concentration file) and their uncertainties (equation-based uncertainty file) were used as input data. For the choice of chemical species, species with more than 50% of samples below method detection limit (MDL) were screened out. Otherwise, values below the detection limit were replaced by half of the MDL. As described in the United States Environmental Protection Agency (U.S.EPA) user guide, the species were categorized as “Strong”, “Weak”, and “Bad” based on the signal-to-noise ratio (S/N ratio) and % of data above MDL (Paatero and Hopke, 2003). In this study, 19 species, which were typical tracers of different sources and were widely used in the source apportionments of VOCs in Hong Kong were selected for this receptor modeling (Lau et al., 2010; Guo et al., 2011a; Ling and Guo, 2014). The number of factors to be chosen depends on the understanding of the sources affecting the air shed, number of samples, sampling frequency, and species characteristics. For a good fit, theoretical Q values, goodness-of-fit parameters, should be approximately equal to the number of degree of freedom or approximately equal to the number of data points in the data array. The theoretical Q was estimated as nm-p(n + m), where n is the number of species, m is the number of samples, and p is the number of factors fitted by the model. Solutions in which Q (true) [including all points] is greater than Q (robust) [excluding outliers] by 1.5 times were avoided to prevent the disproportionate influence of peak events on the model.3.

3. Results and discussion

3.1. VOC characteristics in the roadside environment

The climate in Hong Kong is sub-tropical, and the time length of spring and autumn are comparatively shorter than those of summer and winter. According to the observatory's data, the months of November to February are classified as winter while summer includes the months from May to August (Ho et al., 2004). In this study, the months selected for the sampling campaigns can representatively cover the two seasons, and thus their seasonal variations and characteristics of VOCs can be investigated in the roadside microenvironments. The meteorological parameters were recorded during sampling days, as shown in Table 1. The daily average temperature was 27.9 °C during summer and was 19.1 °C in winter, respectively. The difference of temperature between summer and winter was about 10 °C. The average summer solar radiation per day (18.1 MJ m^{-2}) was about two times of that in winter (9.3 MJ m^{-2}) and the bright sunshine hours (6.6 h) were higher than that of winter (4.6 h) as well.

The averages of total target VOCs mixing ratios were 51.8 ± 4.9 (mean ± 95% confidence interval (C.I.)) and 52.3 ± 3.4 ppbv at the MKAQMS in summer and winter, respectively. There were no statistical differences in the total mixing ratios between the two seasons. This can be ascribed to stable vehicle fleets passing through the roads near the site all year around and minor variations in dilution or dispersion of the pollutants, even though meteorological conditions (e.g., wind speed and direction) are different during the sampling periods (Table 1). In addition, the mixing ratios of the individual VOCs were statistically the same according to Student's *t* test, with a 95% confidence level for the samples collected in the same season. This proves that the sampling strategy in this study can allow precise collection of representatives for all concerned seasons. In comparison, the mixing ratios and compositions of each sub-group of VOCs appeared little seasonal variations. In the summer, the alkanes were the most dominant species which contributed 62.2% to the total target VOCs mixing ratios, followed by the alkenes (13.8%), the aromatics (12.7%), the alkyne (7.5%), the halocarbons (3.7%) and the alkyl nitrates (0.1%). While in winter, the contributions of each sub-group exhibited the same sequence with those in summer; namely, the alkanes had the largest fraction (62.9%), followed by the alkenes (13.2%), the aromatics (10.8%), the alkyne (9.1%), the halocarbons (3.8%) and the alkyl nitrates (0.2%). Hence, the seasonal variations were ignorable in the roadside environment and the annual average mixing ratio for each target VOCs was presented afterwards.

Table 2 summarizes the average, minimum and maximum mixing ratios of target VOCs with the 95% C.I. measured at MKAQMS in 2011. A previous study had been conducted in the same sampling location with identical analytical approaches in 2003 (Ho et al., 2013), and the data has been included and compared in Table 1 as well. The total mixing ratio of the alkenes was 7051 pptv in 2011, which is decreased by more than 50% as compared with that in 2003 (14,345 pptv). The mixing ratios of the aromatics, ethyne, the halogenated and the nitrated hydrocarbons were also reduced in half in 2011, while the alkanes were kept constant levels between the two years. It should be noted that the data comparison is potentially ambitious because only daytime samples (3 h in winter and 2 h in summer) were collected in 2011 instead of 24-h integrated values obtained in this study (Ho et al., 2013). However, it can partially reflect the effectiveness of a series of air pollution control strategies to reduce the roadside air pollution implemented by the HKSAR Government, including incentive programmes to encourage public transport vehicle (i.e., taxis and light bus) owners for replacing diesel-fueled engines by liquefied petroleum gas (LPG)-fueled or electric ones and to restrict the vehicular emissions in compliance with the updated European emission standards (Hong Kong Transport Department, 2004; Hong Kong Environmental Protection Department, 2011.).

High levels of LPG tracers (i.e., propane, *i*-butane and *n*-butane) were observed in the roadside environment with the mixing ratios of 8136 ± 505, 6678 ± 473, and 11,421 ± 833 pptv, respectively. As reported by Tsai et al., the LPG consumed in Hong Kong was mainly constituted of the alkanes, of which propane, *i*-butane, and *n*-butane contributed 26.0%, 22.4%, and 46.4%, respectively (Tsai et al., 2006). The sum of the LPG tracers showed the greatest abundances and accounted for 50.3% of the total quantified VOCs in 2011, which increased significantly as compared with the data measured in 2003. This suggests that the roadside area was greatly influenced by the direct evaporation loss of the LPG fuels. At the year-end of 2011, there were 2848 licensed LPG public light buses in Hong Kong as compared with only a number of 637 in the year-end of 2003. Almost all (99.8%) of the licensed 18,000 taxis and 80% of the newly registered public light buses were equipped with LPG-fueled engines in 2011. The pollutants emitted from motor vehicles are often trapped between very tall buildings and accumulated along streets in Hong Kong. Taxis and public light buses are the two most common types of vehicles which run for long hours and generate high total vehicle trip mileage (Hong Kong Transport Department, 2012). Our data supports the influences from LPG fueled vehicles increased sharply after the execution of engine substitution program.

Toluene and *i*-pentane are the two major components of gasoline and their mixing ratios are 2744 ± 250 and 1093 ± 73 pptv, respectively, in 2011, which were 37% lower than those in 2003. However, it is essential to point out that the ratios of *i*-pentane/toluene were consistent between the two years, indicating that the direct gasoline evaporation was still the source for these two pollutants. *n*-Octane and *n*-nonane are the two diesel fuel tracers and their mixing ratios were 86 ± 5 and 98 ± 7 pptv in 2011, which were >60% lower than those in 2003. Even though the reduction was also significant, the amounts of direct evaporative loss from diesel fuel were much less as compared with that from LPG and gasoline. Heavy C_8–C_{10} alkanes have low vapor pressures and thus do not readily evaporate into the atmosphere. Besides, the typical combustion VOCs products such as ethene, propene, and ethyne, were predominant species in roadside airs (Ho et al., 2013; Tsai et al., 2006), with the average mixing ratios of 4077 ± 226, 1569 ± 87, and 4343 ± 233 pptv in 2011, respectively.

Table 1
Meteorological parameters during the sampling periods.

	Summer	Winter
Pressure (hPa)	1007.6	1016.6
Temperature (°C)	27.9	19.1
RH (%)	78.1	79.8
Cloud (%)	63.2	78.7
Rainfall (mm)	9.5	16.1
Reduced visibility (h)	4.1	3.6
Sunshine hours (h)	6.6	4.6
Solar radiation (MJ m^{-2})	18.1	9.3
Wind direction	141.8	46.0
Wind speed (km h^{-1})	15.1	27.0

3.2. Temporal variations of VOCs at the MKAQMS

Fig. 2 shows the temporal variations of the VOCs at MKAQMS in the month of May in 2011, while the trends of the other three sampling campaigns were displayed in Fig. S1a–c (please refer to the supporting information). The time series of $PM_{2.5}$, PM_{10}, and

Table 2
The minimum detection limit (MDL) and mixing ratios of VOCs measured at MKAQMS in 2003 (Ho et al., 2012) and 2011 (this study).

Group	Species	MDL	2011 (n = 41)				2003 (n = 15)			
			Average	95% C.I.	Min	Max	Average	95% C.I.	Min	Max
Alkanes	CH_4 (ppmv)	0.01	2.01	0.03	1.81	2.23	2.01	0.06	1.93	2.34
	CO (ppbv)	1	843	44	411	1137	1631	131	1340	1989
	Ethane	3	2682	319	819	5515	3598	498	2261	5148
	Propane	3	8136	505	4962	11,685	6626	865	4547	9680
	i-Butane	3	6678	473	3905	9480	4691	506	3420	6479
	n-Butane	3	11,421	833	6492	18,005	7143	836	4582	9589
	i-Pentane	3	1093	73	585	2226	2993	379	2247	4040
	n-Pentane	3	601	47	295	1398	923	90	726	1173
	n-Hexane	3	309	42	95	1343	934	188	398	1412
	n-Heptane	3	253	18	95	636	549	138	198	947
	n-Octane	3	86	5	44	184	217	45	119	389
	n-Nonane	3	98	7	47	238	269	77	132	582
	n-Decane	3	80	18	0	262	247	73	112	472
	2,3-Dimethylbutane	3	80	8	35	202	155	25	85	201
	2-Methylpentane	3	304	38	110	1145	958	133	592	1226
	3-Methylpentane	3	201	31	73	753	680	99	450	973
	2-Methylhexane	3	210	20	77	501	409	98	195	770
	3-Methylhexane	3	234	17	114	676	441	100	226	794
	2,2,4-Trimethylpentane	3	203	17	92	424	360	76	156	520
	Sub-total		32,670				31,192			
Alkenes	Ethene	3	4077	226	2398	5674	8944	771	6668	11,161
	Propene	3	1569	87	883	2121	2267	221	1765	2984
	1-Butene	3	214	11	115	325	549	51	420	724
	i-Butene	3	539	36	295	742	996	131	743	1504
	trans-2-Butene	3	92	5	41	161	405	60	299	579
	cis-2-Butene	3	69	4	32	115	290	48	211	435
	1,3-Butadiene	3	112	8	49	168	328	47	206	468
	1-Pentene	3	61	3	33	97	292	110	114	757
	Isoprene	3	255	30	113	471	252	39	99	376
	alpha Pinene	5	50	4	17	108	17	4	10	30
	beta Pinene	5	14	3	0	37	4	1	0	9
	Sub-total		7051				14,345			
Alkyne	Ethyne	3	4343	233	1562	7097	7708	545	6465	9518
Aromatics	Benzene	3	906	91	294	1721	1408	238	833	2305
	Toluene	3	2744	250	1441	8035	7304	1489	3760	12,599
	Ethylbenzene	3	519	66	166	2305	687	138	389	1154
	p-Xylene	3	438	61	100	1828	440	73	267	666
	m-Xylene	3	346	49	110	1159	1013	169	650	1525
	o-Xylene	3	256	28	88	977	602	94	372	906
	i-Propylbenzene	3	30	3	11	88	32	3	24	40
	n-Propylbenzene	3	53	8	20	140	139	25	97	234
	3-Ethyltoluene	3	159	22	59	378	280	42	192	405
	4-Ethyltoluene	3	95	17	28	266	119	16	79	156
	2-Ethyltoluene	3	72	11	26	199	223	45	116	342
	1,3,5-Trimethylbenzene	3	82	13	32	235	150	23	104	217
	1,2,4-Trimethylbenzene	3	294	62	85	1032	772	169	370	1246
	1,2,3-Trimethylbenzene	3	115	39	16	616	302	82	126	592
	Sub-total		6110				13,471			
Halocarbons	$CHCl_3$	0.1	79	6	37	115	89	10	58	113
	CH_2Cl_2	0.1	791	112	220	2673	534	246	200	1593
	C_2HCl_3	0.1	59	21	6	275	73	70	14	447
	C_2Cl_4	0.1	81	14	25	215	320	90	89	576
	CH_3Cl	10	934	76	551	1607	804	119	626	1198
	Sub-total		1945				1820			
Alkyl nitrates	$MeONO_2$	0.1	6	0	4	14	4	0	3	5
	$EtONO_2$	0.1	6	0	2	12	5	1	3	7
	i-$PrONO_2$	0.1	17	2	3	33	15	3	8	27
	n-$PrONO_2$	0.1	2	0	1	7	2	0	1	3
	2-$BuONO_2$	0.1	25	4	2	55	16	4	4	33
	Sub-total		56				41			

Note: Unit is parts per trillion by volume (pptv) for all VOCs except CH_4 (ppmv) and CO (ppbv); C. I., confidence interval.

other trace gases (e.g., O_3, CO, and NO_x) are also plotted in Fig. 2 and Fig. S1a–c, which were integrated from the hourly measurement data. It can be seen that the total VOC mixing ratios (sum of quantified VOCs except for CH_4 and CO) in May ranged from 35.5 ppbv (on May 12) to 60.2 ppbv (on May 15). Its temporal trend was consistent with that of CO, which is also true for the other three sampling campaigns. CO is emitted from incomplete combustion of fossil fuels in urban areas (Ho et al., 2013; Wang et al., 2002a; Zhang

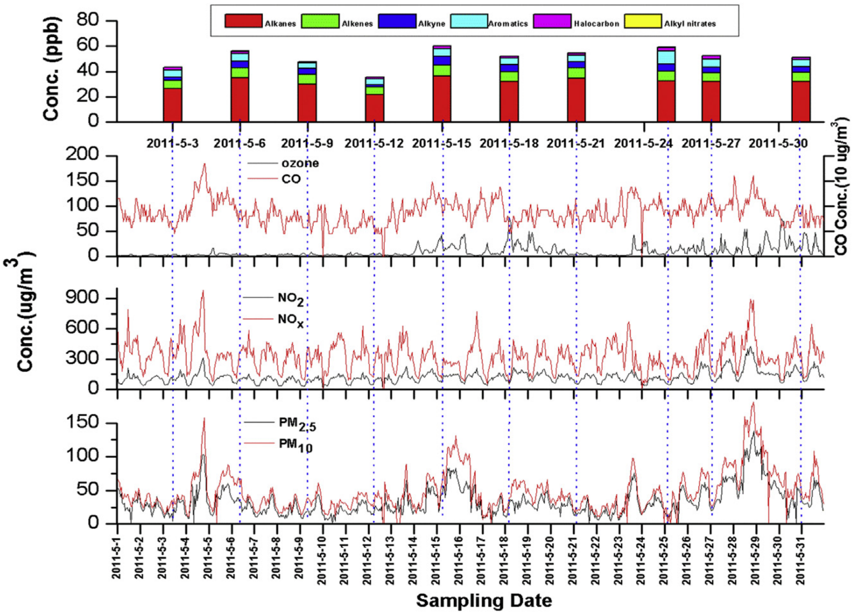

Fig. 2. Time series of VOCs, trace gases and $PM_{2.5}/PM_{10}$ at MKAQMS in May 2011.

et al., 2012). The trends suggest that the VOCs at the roadside environment were mainly contributed from the fuel combustion sources. It is noted that on the peak day, namely 15 May 2011, high mixing ratios of both CO, O_3, $PM_{2.5}$ and PM_{10} occurred at the same time. The formation of secondary pollutants such as SOA is favored with the presence of these precursors of high concentrations, which not only cause air pollution issues but also impose potential health risks on human.

3.3. Atmospheric processing of VOCs impacting the roadside microenvironment

To identify the nature of VOCs impacting the roadside microenvironment, we examined the ratios of VOCs with different photochemical reactivities against hydroxyl radical (•OH) as a measure of "photochemical age". If the ratio of a more reactive VOC to a less reactive VOC is high, it indicates relatively little photochemical processing of the air mass and the greater impact from primary emissions. On the other hand, a lower ratio reflects the more aged VOC mixes which are transported from more distant pollution sources (Guo et al., 2007). The ratio of *m*,*p*-xylene/ethylbenzene is 1.70 ± 0.55 in this study, which is consistent with the ratio of 1.3–1.8 in urban/rural sites in Hong Kong as reported by Guo and coworkers (Guo et al., 2007). It is reasonable that a higher average ratio of *m*,*p*-xylene/ethylbenzene (2.61 ± 0.30) was measured in a local tunnel study (Ho et al., 2009a). Ethene and ethyne are typical tracers of combustion sources. The ratio of ethyne to ethene was 1.05 ± 0.20 in this study. In comparison, its ratio ranged from 0.32 to 1.04 at the same sampling site in 2003 (Ho et al., 2013). Tsai et al. (2006) concluded that the ethyne/ethene ratio in Hong Kong was 0.53 ± 0.03 (Tsai et al., 2006). Our ratio suggests a greater influence from fresh primary emission to the roadside microenvironment. The average ratio of toluene to benzene is 3.32 ± 1.31. The major sources of the two aromatics in urban include vehicular emission and solvent use. Toluene has a shorter life time (~3 days) than benzene (~12 days). Different source-dominated samples show a particular ratio of toluene/benzene (range from 2.8 to 6.0), and the variations are subjected to the characteristics of fuel utilization, emission control technology and fuel evaporation. These results also evidenced that the roadside has been dominantly polluted by primary vehicular emission.

3.4. Comparison of roadside VOCs results with other studies

Table 3 illustrates the comparison of key VOCs levels at the MKAQMS with those measured in other roadside studies. In general, the absolute mixing ratios of VOCs can be affected by the geographical condition, meteorological factors, vehicular fleets and compositions of fuels used. Compared with the data obtained at MKAQMS in 2003 (Ho et al., 2013), most mixing ratios of VOCs decreased by 50% or even more except the LPG components (i.e., propane, *i*/*n*-butane). The LPG fuel evaporation increased significantly at roadside environments, which are consistent with the results found in the Hong Kong tunnel study after the execution of engine substitution program (Ho et al., 2009a). The gasoline evaporation markers of *n*-pentane, *i*-pentane and hexane reduced significantly, and comparable to those measured in London, England (von Schneidemesser et al., 2010) but much lower than Guangzhou, China (Tang et al., 2008). Aromatics such as benzene, toluene, ethylbenzene, *m* + *p*-xylene, and *o*-xylene were also reduced significantly from 2003, especially for toluene, of which the mixing ratio dropped from 7300 to 2730 pptv in 2010. However the values were still much higher than those measured in the London roadside environment (von Schneidemesser et al., 2010). The mixing ratio of CH_3Cl slightly increased compared with that in 2003. The HKSAR Government has implemented a series of control measures to recover petrol vapor released during petrol unloading and refueling at petrol stations, and to tighten vehicular emissions standards in line with the European Union standards. The VOC Regulation, effective from 1 April 2007 under the Air Pollution Control Ordinance in Hong Kong, controls the VOC content in 51 types of architectural paints/coatings, seven types of printing inks and six broad categories of consumer products; and requires emission reduction devices to be installed on certain printing machines. The regulation was amended in October 2009 to extend the control to other products with high VOC content, including adhesives, sealants, vehicle refinishing paints/coatings, and marine vessel and pleasure craft paints/coatings, starting from 1 January

Table 3
Measured VOC mixing ratios at urban roadside environments.

VOC species	Study area	Hong Kong	Hong Kong	Hong Kong	Guangzhou, China	London, UK
	Study period	2010–2011	2003	2003 (Tunnel study)	2005	2008
	Reference	This work	Ho et al., 2013	Ho et al., 2009	Tang et al., 2008	von Schneidemesser et al., 2010
CO (ppbv)		847	1600	4100	–	530
Ethane		2712	3600	5500	3630	7100
Propane		8138	6600	8200	29,850	2700
n-Butane		11,398	7100	8500	10,710	2000
i-Butane		6676	4700	5300	5720	1200
n-Pentane		599	920	1400	1630	540
i-Pentane		1088	3000	3200	3730	1600
n-Hexane		306	930	980	660	150
Ethene		4085	8900	25,000	12,670	2400
Propene		1567	2300	6900	2910	720
Isoprene		254	250	56	–	–
Ethyne		4369	7700	10,000	10,200	1300
Benzene		907	1400	3500	2070	320
Toluene		2730	7300	8700	4010	1000
Ethylbenzene		514	690	820	910	140
m + *p*-Xylene		776	1440	2160	1920	790
o-Xylene		254	600	940	630	200
CH_3Cl		938	800	790	–	–

Notes: All the units of VOCs are in pptv unless otherwise stated.

2010 in phases. All of these revolutions are the critical factors for the changes of key VOCs profiles at the MKAQMS.

3.5. Source profiles and apportionments of VOCs at MKAQMS

Table 4 presents the PMF extracted source profiles for the air samples collected at MKAQMS. To identify the potential emissions for NMHCs at the roadside environment, different species were selected as tracers of particular pollution source. CO and C_2–C_7 VOCs are probably emitted from the combustion sources (i.e., vehicular emissions). In addition to vehicular exhaust, aromatics (e.g., benzene, toluene, ethylbenzene and xylenes) can be produced by solvent usage. Furthermore, propane and *n*/*i*-butane are tracers for LPG fuel consumption. In the present study, five sources were identified at the roadside sampling site, including LPG fuel consumption, gasoline fueled exhaust, gasoline evaporation, diesel fueled exhaust, and solvent usage.

Factor 1 was characterized by high mixing ratios of propane and *n*/*i*-butanes, with significant amounts of CO, ethene, ethyne and propene. Propane and *n*/*i*-butanes are typical tracers for LPG, while the other three VOCs could be emitted from the fuel combustion processes (Guo et al., 2011a; Ho et al., 2009a; Ling et al., 2011; Liu et al., 2008). It has been reported that C_2–C_3 species, especially ethene and propene contributed significantly to LPG vehicular emissions (Tang et al., 2007, 2008). Therefore, this factor was defined to be LPG fuel consumption.

Compared with Factor 1, it shows relatively lower mixing ratios of CO, ethene, ethyne and propene, while elevated levels of *i*-pentane, *n*-heptane, toluene and *m,o,p*-xylenes were found in Factor 2. This suggests that this source was probably derived from gasoline-fueled vehicles because *i*-pentane, *n*-heptane, toluene and *m,o,p*-xylenes are good tracers for gasoline exhaust (Ho et al., 2009a; Liu et al., 2008).

Factor 3 was characterized by high mixing ratios of *n*/*i*-pentanes, *n*-hexane and 2,3-methylpentane (*i*-hexane), which are representative VOCs emitted from gasoline-related emissions in Hong Kong (Ho et al., 2009a; Tsai et al., 2006). However, it was found that the mixing ratios of other combustion and/or vehicular tracers (i.e., ethane, ethene, benzene and CO) were extremely low, while high *n*/*i*-pentanes and 2,3-methylpentane levels were seen. Therefore, this source is regarded as gasoline evaporation.

High mixing ratios of CO, ethane, ethyne, benzene, with certain

Table 4
PMF extracted source profiles for VOCs collected at Mong Kok (unit: μg/m^3).

VOC species	LPG usage	Gasoline exhaust	Gasoline evaporation	Diesel exhaust	Solvent usage
CO	338.61	154.74	0.00	467.67	0.00
Ethane	0.00	0.00	0.00	3.29	0.00
Ethene	2.64	0.76	0.00	1.23	0.00
Ethyne	1.36	0.33	0.00	2.73	0.00
Propane	11.31	0.00	0.00	2.35	0.86
Propene	1.97	0.51	0.00	0.14	0.06
i-Butane	13.17	0.80	1.20	0.49	0.00
n-Butane	24.69	0.00	0.00	0.00	1.97
i-Pentane	0.77	1.01	1.26	0.00	0.00
n-Pentane	0.46	0.00	1.18	0.04	0.00
2,3-Methylpentane	0.15	0.06	1.15	0.01	0.20
n-Hexane	0.00	0.00	0.80	0.00	0.13
n-Heptane	0.00	0.95	0.00	0.00	0.00
Benzene	0.00	0.00	0.05	1.93	0.68
Toluene	1.32	3.75	0.00	1.49	2.71
Ethylbenzene	0.00	0.00	0.00	0.52	1.33
m,p,o-Xylene	0.94	0.44	0.00	0.00	2.49

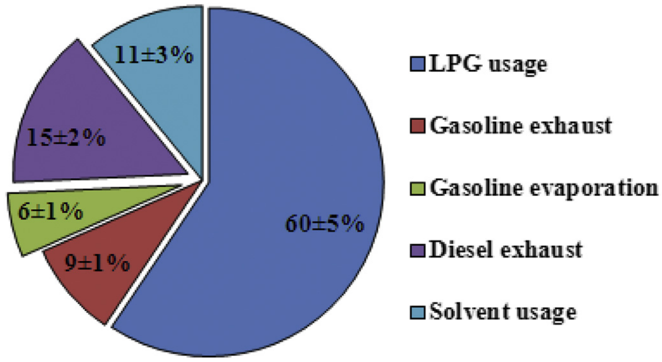

Fig. 3. Average source contributions of each factor to total VOCs at MKAQMS, Hong Kong (mean ± standard error).

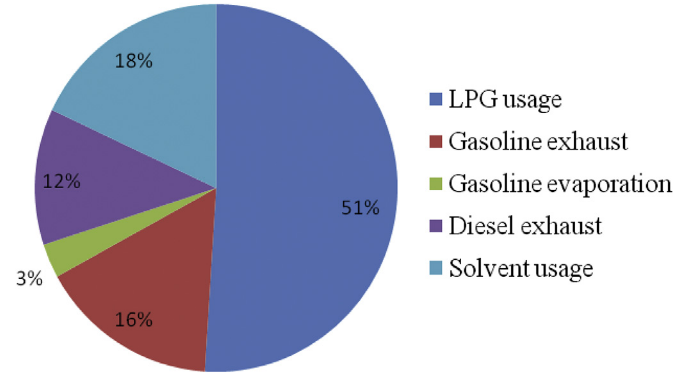

Fig. 4. Contributions to OFPs from different VOCs emission sources based on PMF results.

amounts of ethene, propane and ethylbenzene were found in Factor 4. These VOCs are all associated with diesel-fueled vehicular emissions because high levels of ethane, ethyne and benzene were typically observed especially when the vehicular speed was over 50 km h^{-1} (Ho et al., 2009a; Ling and Guo, 2014; Ling et al., 2011).

Factor 5 was dominated by toluene, ethylbenzene and xylenes, which totally accounted for about 65% of the source profile. In addition to vehicular emissions, these species could be emitted from the use of paints, inks, sealant, varnish and thinner for architecture and decoration (Borbon et al., 2002; Liu et al., 2008; Seila et al., 2001). As poor correlations were found between these aromatic species and combustion tracers (i.e., CO, ethene, ethane and ethyne), this factor was identified as solvent usage.

Fig. 3 shows that LPG fuel consumption is the largest pollution contributor, accounting for 60 ± 5% of the total quantified VOCs at MKAQMS. This is explainable because LPG is applied as a major clean fuel for most taxis and public and private light buses (Lau et al., 2010; Ling and Guo, 2014). Diesel-fueled exhaust is the second largest contributor, accounting for 15 ± 2% of VOCs. Solvent usage, gasoline-fueled exhaust, and gasoline evaporation accounted for 11 ± 3%, 9 ± 1%, and 6 ± 1%, respectively. Our results are totally different from the emission inventory surveyed by HKEPD which road transport contributed for only 23% of the total VOCs production in Hong Kong (HKEPD, 2012). Non-combustion source (60%) such as consumer products, paints and printing is the largest contributor. The differences are certainly reasonable as our source apportionment was conducted in the roadside environment instead of taking account for all local emissions. Reversibly, it does further demonstrate that the impacts from other sources to our samples were ignorable.

3.6. Contribution of OFPs by VOCs from different emission sources

Many VOCs are significant precursors of O_3 formation, but each performs with different reaction rates and mechanisms (Atkinson and Arey, 2003; Barletta et al., 2005). The ozone formation potential (OFP) for individual VOC was thus assessed. The product of the VOC mass concentration and its maximum incremental reactivity (MIR), where MIR is in units of grams of O_3 formed per gram of VOC, indicates how much the individual VOC may contribute to O_3 formation in the air mass (Carter, 1994). The sum of OFP (OFP_{sum}) for the total target VOCs in this study was 300.9 μg-O^3 m^{-3}, which was 47% lower than the value of 567.3 μg-O^3 m^{-3} measured in 2003. The large reduction of OFP_{sum} can be ascribed by the decrease of total VOCs mass concentration, especially for toluene. Toluene was the largest contributor (19.5%) to the OFP_{sum} in 2003 but its OFP was reduced by >60% in 2011/2012. Its contribution to the OFP_{sum} dropped to 10%. Even though the calculation only gives an estimation of potential O_3 formation value, it reflects individual VOC on their photochemical reactivity.

Fig. 4 illustrated the contributions of OFP by different pollution sources from the PMF data analysis. The most significant contributor was LPG fuel consumption, accounting for 51% of the total OFP, followed by solvent usage (18%), gasoline-fueled exhaust (16%), diesel-fueled exhaust (12%), and gasoline evaporation (3%). The sequence of the contributions to OFP by each emission source is slightly different with that in Fig. 3, indicating that the reactivity of VOCs is a key factor to be considered during the implementation of VOC control strategies.

4. Conclusion

The VOCs characterization has been done at MKAQMS in Hong Kong in 2011. High mixing ratios of the LPG tracers were measured in the roadside environment. These compounds accounted for 50.3% of the total quantified VOCs, which increased significantly as compared with the data obtained in 2003. In addition to the reductions of mixing ratios and compositions of the gasoline and diesel fuel tracers, our results prove that the influences from LPG-fueled vehicles became more critical after the execution of engine substitution program. The ratios of individual VOC demonstrated that primary vehicular emission is the most dominated pollution source with relatively little photochemical processing at the roadside environment. Even though LPG is defined as a “cleaner” fuel than gasoline and diesel, the reactivity of their tracers towards other oxidants must be considered for further establishment of VOCs control strategies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.09.036.

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