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

Yu Huanga, b, Zhen Hao Lingc, Shun Cheng Led, Steven Sai Hang Ho e, Jun Ji Caoa, b, Donald R. Blakef, Yan Chengg, Sen Chao Lah, Kin Fai Hoi, Yuan Gaod, Long Cuid, Peter K.K. Louie j

a Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an, 710075, China
b State Key Lab of Loess and Quaternary Geology (SKLLQG), Institute of Earth Environment, Chinese Academy of Sciences, Xi’an, 710075, China
c School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou, 510275, China
d Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong
e Division of Atmospheric Sciences, Desert Research Institute, Reno, NV, United States
f Department of Chemistry, University of California, Irvine, USA
g Department of Environmental Science and Technology, School of Human Settlements and Civil Engineering, Xi’an Jiaotong University, No. 28 Xianning West Road, Xi’an, Shaanxi, 710049, China
h College of Environment and Energy, South China University of Technology, Higher Education Mega Centre, Guangzhou, 510006, China
i School of Public Health and Primary Care, The Chinese University of Hong Kong, Hong Kong
j Hong Kong Environmental Protection Department, Hong Kong

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.

ARTICLE INFO

Article history:
Received 3 February 2015
Received in revised form 20 May 2015
Accepted 11 September 2015
Available online 21 September 2015

Keywords:
Vehicular emission
Volatile organic compounds
Roadside environment
Liquefied petroleum gas
Source apportionments

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 (CH₄), 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-O₃ m⁻³, which was 47% lower than the value of 567.3 µg-O₃ 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
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 (O3) 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 km² 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 emission has attracted more and more public attention. As estimated by the Hong Kong Environmental Protection Department (HK EPA), 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 C1–C8 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 ± 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 subsequent 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., 1998), 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 have 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 O3 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 ± 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
ground level. The filled canisters were properly shipped to the laboratory in the University of California, Irvine (UCI) for analysis of CO, methane (CH₄), 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 CH₄ and then analyzing with a gas chromatography (GC) with a flame ionization detector (FID). The mixing ratios of CH₄ 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 (CH₄ is always above its detection limit). The accuracy of our measurements is 5% for CO, 1% for CH₄, 2–20% for halogenated hydrocarbons and 5% for other NMHCs. The measurement precision is 2% for CO, 2% for CH₄, 1–5% for halogenated hydrocarbons, and ranges from 0.5 to 5% for other NMHCs. The simultaneous measurements data of selected trace gases (O₃, CO, and nitrogen oxides (NO₂/NOₓ)) and PM₂.₅/PM₁₀ were supplied by HKPDE. O₃ was monitored with UV photometric instruments (API 400, San Diego, CA), and NO₂/NOₓ was measured by chemiluminescence instruments (API 200A, San Diego, CA). The mixing ratios of CH₄ and VOCs were determined using a gas chromatography (GC) with an electron capture detector (ECD). 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 (CH₄ is always above its detection limit). The accuracy of our measurements is 5% for CO, 1% for CH₄, 2–20% for halogenated hydrocarbons and 5% for other NMHCs. The measurement precision is 2% for CO, 2% for CH₄, 1–5% for halogenated hydrocarbons, and ranges from 0.5 to 5% for other NMHCs. The simultaneous measurements data of selected trace gases (O₃, CO, and nitrogen oxides (NO₂/NOₓ)) and PM₂.₅/PM₁₀ were supplied by HKPDE. O₃ was monitored with UV photometric instruments (API 400, San Diego, CA), and NO₂/NOₓ was measured by chemiluminescence instruments (API 200A, San Diego, CA). The detection limits are 1 ppbv for O₃, and 0.5 ppbv for NO₂/NOₓ. The concentration of PM₁₀ and PM₂.₅ were determined by the 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)):

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

where $X_{ij}$ is the measured concentration of the $ith$ species in the $jth$ sample, $C_{ip}$ is the concentration of the $ith$ 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 $jth$ 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 $n - p(n + m)$, 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 model3.
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 statistical differences in the total mixing ratios between the two sea-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 statistical differences in the total mixing ratios between the two seasons.

Table 1 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, ethylene, 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 ppbv, 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 ppbv, 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 ppbv 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 C₈-C₁₀ alkanes have low vapor pressures and thus do not readily evaporate into the atmosphere. Besides, the typical combustion VOCs products such as ethene, propane, 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 ppbv in 2011, respectively.

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 PM₂.₅, PM₁₀, and

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Summer</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (hPa)</td>
<td>1007.6</td>
<td>1016.6</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>27.9</td>
<td>19.1</td>
</tr>
<tr>
<td>RH (%)</td>
<td>78.1</td>
<td>79.8</td>
</tr>
<tr>
<td>Cloud (%)</td>
<td>63.2</td>
<td>78.7</td>
</tr>
<tr>
<td>Rainfall (mm)</td>
<td>9.5</td>
<td>16.1</td>
</tr>
<tr>
<td>Reduced visibility (h)</td>
<td>4.1</td>
<td>3.6</td>
</tr>
<tr>
<td>Sunshine hours (h)</td>
<td>6.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Solar radiation (MJ m⁻²)</td>
<td>18.1</td>
<td>9.3</td>
</tr>
<tr>
<td>Wind direction</td>
<td>141.8</td>
<td>46.0</td>
</tr>
<tr>
<td>Wind speed (km h⁻¹)</td>
<td>15.1</td>
<td>27.0</td>
</tr>
</tbody>
</table>
other trace gases (e.g., O₃, CO, and NOₓ) 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 CH₄ 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 et al., 2002b).
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, O₃, PM₂.₅ and PM₁₀ 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 CH₃Cl 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
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 C2–C7 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 C2–C3 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 n-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 n-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, ethene, ethyne, benzene, with certain...
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. Reversely, 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 (OPF) for individual VOC was thus assessed. The product of the VOC mass concentration and its maximum incremental reactivity (OFP), where OFP 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\(_{\text{sum}}\)) 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\(_{\text{sum}}\) can be ascribed by the decrease of total VOCs mass concentration, especially for toluene. Toluene was the largest contributor (19.5%) to the OFP\(_{\text{sum}}\) in 2003 but its OFP was reduced by >60% in 2011/2012. Its contribution to the OFP\(_{\text{sum}}\) 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.

### Acknowledgments

This study was sponsored by the “Sampling and Testing of Volatile Organic Compounds and Oxygenated Volatile Organic Compounds at Mong Kok, Tsuen Wan and the Hong Kong University of Science and Technology” (Ref. 10-05751) projected from the HKEPD., the Research Grant (1-ZV9R) of the Hong Kong Polytechnic University, Research Grants Council of Hong Kong (PolyU 152083/14E), and is also partially supported by National Natural Science Foundation of China (41401567).

The authors are grateful to the HKEPD for provision of the data sets and permission for publication. The content of this paper does not necessarily reflect the views and policies of the HK SAR Government, nor does the mention of trade names or commercial products constitute endorsement or recommendation of use.
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.

References


Xue, Y., Berkowitz, C.M., 2006. The use of positive matrix factorization with...
conditional probability functions in air quality studies: an application to hydrocarbon emissions in Houston, Texas. Atmos. Environ. 40, 3070–3091.