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Figure The Characteristics and Sources of Roadside VOCs in Hong Kong: Effect of the LPG Catalytic Converter Replacement Programme

Long Cui [a,b,c,d], Hai Wei Li [e], Yu Huang [a,b,c,d], Zhou Zhang [f,g], Shun Cheng Lee [h], Donald Ray Blake [i], Xin Ming Wang [f,g], Kin Fai Ho [j], Jun Ji Cao [a,b,c,d]

[a] Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an 710061, China

[b] State Key Lab of Loess and Quaternary Geology (SKLLQG), Institute of Earth Environment, Chinese Academy of Sciences, Xi’an 710061, China

[c] Shaanxi Key Laboratory of Atmospheric and Haze-fog Pollution Prevention, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an 710061, China

[d] CAS Center for Excellence in Quaternary Science and Global Change, Xi’an 710061, China

[e] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (CIC-AEET), School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing, 210044, China

[f] State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

*Graphical Abstract

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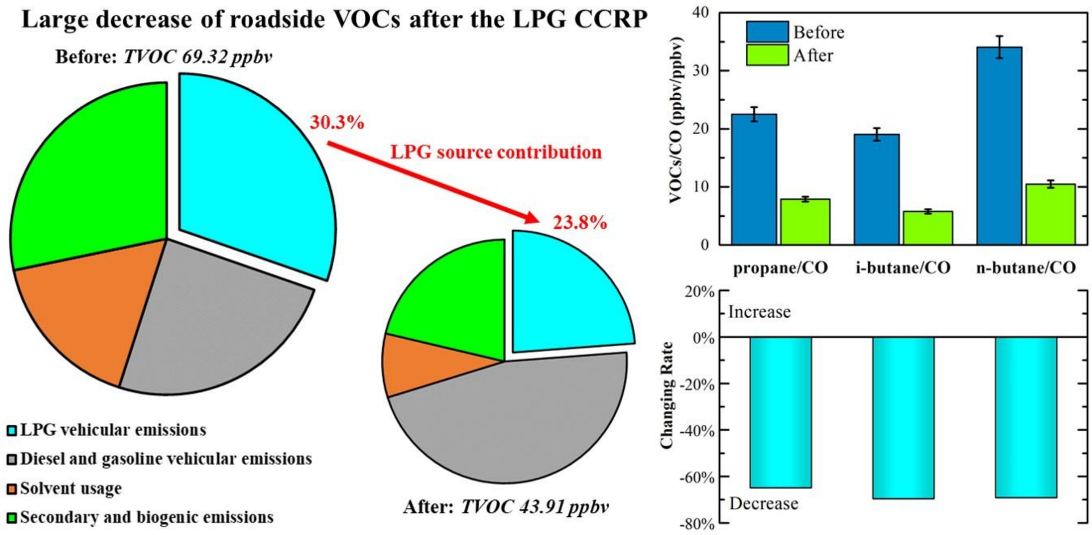

**Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)

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- Emission ratios were applied to explore the contributions of primary and secondary/biogenic sources for roadside VOCs
- LPG vehicular emissions was the dominant source of roadside VOCs and its contribution has decreased after the air pollution control programme

[g] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

[h] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China.

[i] Department of Chemistry, University of California, Irvine, CA, USA

[j] The Jockey Club School of Public Health and Primary Care, The Chinese University of Hong Kong, Shatin, Hong Kong, China

Corresponding authors: Yu Huang (huangyu@ieecas.cn) and Shungcheng Lee (ceslee@polyu.edu.hk)

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Abstract

In order to improve local air quality of Hong Kong, more than 99% taxies and public light buses were changed from diesel to liquefied petroleum gas (LPG) fuel type in the early 2000s. In addition to the catalytic converters wear and tear, it is necessary to control air pollutants emitted from LPG vehicles. Therefore, an LPG catalytic converter replacement programme (CCRP) was fulfilled from October 2013 to April 2014 by the Hong Kong government. Roadside volatile compounds (VOCs) were measured by on-line measurement techniques before and after the programme to evaluate the effectiveness of the LPG CCRP. The mixing ratios of total measured VOCs were found decreased from 69.3 ± 12.6 ppbv to 43.9 ± 6.5 ppbv after the LPG CCRP with the decreasing percentage of 36.7%. In addition, the total mixing ratio of LPG tracers, namely propane, i-butane, and n-butane, accounted for 49% of total measured VOCs before the LPG CCRP and the weighting percentage decreased to 34% after the programme. Moreover, the source apportionment of roadside VOCs also reflects the large decreasing trend of LPG vehicular emissions after the air pollution control measure. Due to the application of PTR-MS on measuring real-time VOCs and oxygenated volatile compounds (OVOCs) in this study, the emission ratios of individual OVOCs were investigated and being utilized to differentiate primary and secondary/biogenic sources of roadside OVOCs in Hong Kong. The findings demonstrate the effectiveness of the intervention programme, and are helpful to further implementation of air pollution control strategies in Hong Kong.

Keywords:

VOCs; PTR-MS; Emission Ratio; Secondary source; LPG emission.

1 Introduction

Hong Kong has been suffering from ozone (O_3) pollution with an increasing O_3 trend through the past decades like many other cities worldwide (Ding et al., 2013; Liu et al., 2019; Wang et al., 2003; Zhang et al., 2007). Since O_3 pollution has both adverse effects on civil environment and human health (Bell et al., 2004; Lippmann, 1993; Sillman, 1999), it is necessary to mitigate O_3 pollution. Volatile organic compounds (VOCs) have been found to be the key factor leading to severe O_3 pollution in Hong Kong and the Pearl River Delta (PRD) region in China. Many previous studies have found that O_3 formation is VOCs-sensitive in urban areas of this region (Cheng et al., 2010; He et al., 2019; Ling and Guo, 2014; Wang et al., 2017a; Zhang et al., 2007). Therefore, in order to formulate and develop effective O_3 pollution controlling strategies, a better understanding on the characteristics and sources of VOCs in urban areas is required through different air pollution controlling stages.

VOCs are important precursors of O_3 and secondary organic aerosol (SOA), and have adverse health impact on human beings (Lelieveld et al., 2015; Sillman, 2002; von Schneidemesser et al., 2010). Ambient VOCs can be emitted from multiple sources, including anthropogenic and biogenic emissions (Kansal, 2009; Watson et al., 2001). Vehicular emissions are the major anthropogenic source in urban areas, especially for roadside environment in Hong Kong (Chan et al., 2002; Huang et al., 2015; Lee et al., 2002; Ling et al., 2011). It has been found that on-road vehicles contributed about 40% of ambient VOCs from 2002 to 2003 in Hong Kong. Later, vehicular emissions were found accounted up to 54% of ambient VOCs from 2006 to 2007 in Hong Kong (Lau et al., 2010). A multi-year study on source apportionment of ambient VOCs has been conducted from 2005 to 2013 in Hong Kong. It was found that gasoline evaporation and liquified petroleum gas (LPG) usage, together with vehicle exhaust accounted for

30~60% of ambient VOCs in urban areas of Hong Kong (Ou et al., 2015a). For roadside environment, vehicular emissions contributed the most (up to 89%) to ambient VOCs because of the high vehicle density in Hong Kong (Huang et al., 2015). Based on the statistics of Hong Kong Transport Department, there are more than 794,366 licensed vehicles in an area of 1,104 km^2 by the end of 2019. Hong Kong government has undertaken a series of air pollution control measures to improve local air quality through the past decades (Lau et al., 2015). In order to mitigate vehicular emissions, a series of control strategies have been implemented in Hong Kong since early 2000s (Cui et al., 2018; Lyu et al., 2017). Therefore, total VOC emission factor has been decreased from 107 mg veh^{-1} km^{-1} in 2003 to 58 mg veh^{-1} km^{-1} in 2015. Moreover, nearly 99% taxis and public light buses have been switched from diesel to LPG fuel type from 2000 to 2003, and the most abundant VOCs species in ambient air changed from toluene to propane, i-butane and n-butane during this period (Cui et al., 2018). It was found that ozone formation potential (OFP) of LPG vehicular emissions comprised more than 51% of total measured VOCs at a roadside station in 2011 (Huang et al., 2015). Hong Kong government has conducted an LPG catalytic converter replacement programme (CCRP) to replace the worn-out catalytic converters for taxies and public light buses since October 2013, and more than 80% LPG vehicles have fulfilled the replacement by the end of April 2014 (Lyu et al., 2016). Hence, it is necessary to evaluate the effectiveness of the LPG CCRP on VOCs reduction through investigating roadside VOCs.

Oxygenated volatile organic compounds (OVOCs) are important portion of VOCs, and they can be formed through primary anthropogenic emissions such as vehicular emissions, secondary source through photochemical production, and direct biogenic emissions (Karl et al., 2018; Mo et al., 2016; Ou et al., 2015b). Due to the lack of on-line measurement techniques for OVOCs before, it is hard to differentiate primary and secondary sources of ambient OVOCs in Hong Kong (Cui et al., 2016). Proton transfer reaction mass spectrometry (PTR-MS), a newly developed on-line measurement technique for OVOCs and VOCs, was firstly applied to measure roadside OVOCs and VOCs in this study. Therefore, primary and secondary sources of roadside OVOCs can be separated by using Linear regression fit (LRF) and positive matrix factorization (PMF) methods (Millet et al., 2005; Yuan et al., 2012).

In this study, roadside VOCs were continuously measured by on-line measurement techniques at a roadside air quality monitoring station in Hong Kong. The variations of roadside VOCs were investigated before and after the LPG CCRP. Emission ratios of OVOCs were calculated and utilized to differentiate primary and secondary sources for individual OVOCs species. Multiple sources of roadside VOCs and OVOCs were identified to evaluate the effectiveness of the LPG CCRP which has been launched in Hong Kong from October 2013 to April 2014.

2 Methodology

2.1 Sampling site

Mong Kok Air Quality Monitoring Station (MKAQMS), which is an urban roadside station set up by the Hong Kong Environmental Protection Department (HKEPD), was selected as the field sampling site in this study (Chan et al., 2002; Cui et al., 2016; Yao et al., 2019). MKAQMS (22.32^{o}N, 114.17^{o}E) is located in a commercial and residential area with high vehicle density, because it is at the junction of two main roads, namely Lai Chi Kok Road, and Nathan Road in Mong Kok, Kowloon (Figure S1). Local anthropogenic emissions are the major sources of air pollutants at this site, and the influence of regional air masses is negligible (Cheung et al., 2014; Guo et al., 2011; Guo et al., 2013a). Real-time measurement of CO is continuously monitored by HKEPD, and non-dispersive infrared absorption method is used to measure CO concentration at MKAQMS (Ling et al., 2016; Louie et al., 2013; Ou et al., 2015a; Wang et al., 2017b). The instrument is regularly checked and calibrated according to the quality control and quality assurance (QA/QC) procedure established by HKEPD.

2.2 Measurement of VOCs

VOCs and OVOCs were continuously measured by PTR-MS (PTR-QMS 500, IONICON Analytik GmbH, Innsbruck, Austria) during 1st to 31st May 2013 and 1st to 31st May 2014 at MKAQMS in this study. Detailed information of PTR-MS can be found elsewhere (de Gouw et al., 2003; de Gouw et al., 2006; Lindinger et al., 1998). H_3O^+ was selected as the reagent ion for PTR-MS, the drift tube was operated at 2.2 mbar pressure and the electric field was maintained at 600 V difference. In order to minimize wall loss, the inlet system and drift tube were maintained at 60 ^{o}C during the whole sampling period. The E/N (electric field strength / air density inside drift tube) value in the drift tube was kept at 136 Td. The residence time of sampling air passing through the inlet 1/8" Teflon tube was less than 2 s. Sampling inlet was 2 m above the ground and the sampling flow rate was about 75 mL/min. Ionimed mix-VOC gas standard (IONICON Analytik GmbH, Innsbruck, Austria) was used for PTR-MS calibration in this study. One-point calibration was conducted every 24 hours, and full calibration (gas standard was diluted by four different ratios) was performed every 6 days. Temperature and humidity influence on formaldehyde measurement was modified through multiple factor adjustment method raised by our group (Cui et al., 2016). The accuracy and the measurement precision of the PTR-MS was 3~20% and 1.6~10.0%, respectively.

An on-line GC-FID analyzer (Syntech Spectras GC 955, Series 600/800, the Netherlands) was used to continuously measure non-methane hydrocarbons (NMHCs) during whole sampling period. The analyzer was operated by HKEPD following strict QA/QC procedure as described in detail elsewhere (Cui et al., 2016; Xue et al., 2014). Two sampling systems and two columns were integrated together for the separation of C_2-C_5 hydrocarbons and C_6-C_{10} hydrocarbons. In total, 27 VOCs species were monitored by the on-line GC-FID analyzer with the time resolution of 30 minutes. And hourly averaged VOCs mixing ratios were used for data analysis. The accuracy and precision of the measurements were 5~20% and 1.2~10.1%, respectively.

2.3 Positive matrix factorization (PMF) receptor model

USEPA PMF 5.0 model, a mathematical receptor model developed by U.S. Environmental Protection Agency (EPA), was utilized to perform source apportionment of roadside VOCs at MKAQMS in this study. Detailed information of this model can be found elsewhere (Paatero, 1997; Paatero and Tapper, 1994). In brief, the concentration of individual VOC could be proportional to its emission amounts from different sources in the certain atmospheric volume (Song et al., 2007). Different source types could be identified by comparing with measured source profiles. Data set can be represented as a data matrix of factor contributions and factor profiles in the PMF results:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (1)$$

where x_{ij} is the j species concentration measured in the i sample, g_{ik} is the species contribution of the k source to the i sample, f_{kj} is the j species fraction from the k source, e_{ij} is the residual for each sample/species, and p is the total number of independent sources (Paatero, 2000). Hourly mixing ratios of VOCs and CO were used in the input file. The uncertainties for each sample/species were set as $(DL^2 + Precision^2)^{1/2}$ and DL ×5/6 for the samples/species with their concentration higher and lower than the DL, respectively. In order to reduce the interference of high rates of missing data for some species, hourly mixing ratios of 26 VOCs species and CO during the sampling period were selected to conduct the source apportionment by PMF model in this study. The PMF model has been run by 20 times with a random seed, and base models encompassing 3 to 6 factors were derived. These models were then compared, so as to find the optimal solution. The optimum solution was finally determined based on both a good fit to the observed data and the most reasonable and interpretable results according to the knowledge on the sources of ambient VOCs in

Hong Kong. Good correlations were found between the observed and predicted VOC concentrations (r^2 = 0.83 ~ 0.95) when four factors were derived, and the Q (robust)/Q (true) ratio was 0.85, which was less than 1.5 for the result to be accepted.

3 Results and discussion

3.1 Mixing ratios and compositions of roadside VOC characteristics

Average CO concentration and mixing ratios of different VOC species before/after the LPG CCRP were listed in Table 1. Since the total vehicle loading at the sampling site was steady, the decreased of CO from 1.07 ± 0.23 ppm before the LPG CCRP to 0.65 ± 0.14 ppm by 39.3% was due to the control of primary combustion source, namely vehicular emission in this study. On the other hand, the mixing ratio of total measured VOCs was 69.3 ± 12.6 ppbv before the LPG CCRP, and decreased to 43.9 ± 6.5 ppbv after the LPG CCRP with the decreasing percentage of 36.7%. Alkanes comprised the most of total measured VOCs both before (54.9%) and after (46.5%) the LPG CCRP. OVOCs was the second dominant group (22.7% before the LPG CCRP and 25.1% after the LPG CCRP), followed by alkenes (before: 12.2%; after: 12.8%), aromatics (before: 5.4%; after: 7.2%), alkyne (before: 4.2%; after: 8.0%) and others (before: 0.6%; after: 0.6%). As the three most abundant VOC species, propane, i-butane, and n-butane, which are the tracers of LPG vehicular emissions (Chen et al., 2001; Liu et al., 2008), comprised 49.0% of total VOCs before the LPG CCRP. Moreover, previous study at the same sampling site found that the sum concentration of propane, i-butane and n-butane comprised about 50% of total measured VOCs in 2011 (Huang et al., 2015). Due to the large decrease of propane (54.6%), i-butane (51.7%), and n-butane (59.4%) after the LPG CCRP, weighting percentage of alkanes to total VOCs decreased from 54.9% to 46.5%. For OVOCs, even though its weighting percentage to total VOCs changed from 22.7% to 25.1%, total OVOC mixing ratio decreased by 30.0% after the LPG CCRP. Formaldehyde as the most abundant OVOC species, its mixing ratio decreased the most after the LPG CCRP by 55.5%. Other OVOC species also showed decreasing trend with the changing rate ranged from 11.1% to 28.3%.

The number of on-road vehicles at AMKAQMS has been recorded by camera and manually counted for 16 days totally in May and August 2013, February and August in 2014 by HKEPD. Traffic volume and the diurnal variation pattern of different fuel types for on-road vehicles at MKAQMS was given in Figure 1. It was found that LPG vehicle was the dominant vehicle type during the period of 1:00 a.m. ~ 4:00 a.m. LT. The average total VOCs mixing ratio decreased by 43.9% from 82.4 ± 16.2 ppbv to 43.7 ± 6.7 ppbv after the LPG CCRP (as shown in Table S1). The decreasing percentage of total VOCs during nighttime was higher than that during whole day, especially for LPG tracers and OVOCs, which could be resulted from negligible photochemistry reaction and accumulation of primary anthropogenic emissions during nighttime (Figure 2). Moreover, the decreasing percentage of propane, i-butane, and n-butane were 58.2%, 53.9%, and 62.2%, respectively during nighttime when total LPG vehicle loading was the highest during 1:00 a.m. ~ 4:00 a.m. LT. Based on a repeated tunnel study in Hong Kong, it was found that the LPG vehicle emission factors of propane, i-butane, and n-butane decreased by 77.8%, 57.8%, and 60.5%, respectively (Cui et al., 2018). The large reduction of propane, i-butane, and n-butane emission factors from LPG vehicle was consistent with their decreasing trends in roadside environment from this study.

3. 2 Diurnal variation of individual VOCs

Diurnal variations of several individual VOCs and CO were illustrated in Figure 3. Apart from morning traffic peak and afternoon traffic peak, CO concentrations showed a midnight peak around 1:00 a.m. to 2:00 a.m., due to the lower boundary layer and high LPG vehicle loading at midnight. and the sum weight percentage of LPG tracers comprised more than 50% of total VOCs. Therefore, midnight peaks for propane, i-butane, and n-butane can be found from 1:00 a.m. to 3:00 a.m.. Because of the effectiveness of LPG vehicular emission control measure, midnight peaks of propane, i-butane, and n-butane decreased from 18.3 ppbv, 14.9 ppbv, 28.2 ppbv, respectively, to 7.5 ppbv, 6.8 ppbv, 10.6 ppbv, respectively, after the LPG CCRP. Otherwise, diurnal cycle of benzene only showed two traffic peaks in the morning and afternoon without the midnight peak since diesel and gasoline vehicular emissions were its major sources (Ho et al., 2009; Liu et al., 2008). Mixing ratios of formaldehyde and acetaldehyde increased to their maximum level around 10 a.m. and then showed decreasing trends through the day, their diurnal variation patterns reflected the importance of secondary formation for these reactive OVOC species (Corrêa et al., 2003; Taatjes et al., 2012). Diurnal cycle of isoprene mixing ratio followed the solar radiation cycle as expected since biogenic emission is its major source (Mayrhofer et al., 2005; Rinne et al., 2002). Meanwhile, MVK and MACR, which are the photooxidation products of isoprene had a single afternoon peak due to photochemical reactions from isoprene (Biesenthal and Shepson, 1997; Cheung et al., 2014; Ling et al., 2019).

3.3 Photochemical reactivity of VOCs

Photochemical reactivity of VOCs can be analyzed by both maximum incremental reactivity (MIR) method and propene-equivalent (Prop-Equiv) concentration (Carter, 1995; Chameides et al., 1992; So and Wang, 2004; Venecek et al., 2018). Detailed information of the above two methods were given in supplementary material. As shown in Figure 4, total ozone formation potential (OFP) of VOCs decreased from 209.4 ppbv O_3/ppbv to 132.7 ppbv O_3/ppbv by 36.6%, and total Prop-Equiv concentration of VOCs decreased from 70.3 ppbC to 48.3 ppbC by 31.2%. Alkenes comprised the most of total OFP both before (34.4%) and after (36.3%) the LPG CRRP, followed by OVOCs (before: 28.8%; after: 28.8%), alkanes (before: 20.8%; after: 15.4%), aromatics (before: 15.6%; after: 18.6%), and alkyne (before: 0.4%; after: 0.7%) as shown in Figure 4b. For Prop-Equiv concentration, alkenes contributed the most among different VOC groups (before: 58.2%; after: 62.1%), followed by alkanes (before: 16.2%; after: 11.2%), OVOCs (before: 13.5%; after: 13.9%), aromatics (before: 11.8%; after: 12.3%), and alkyne (before: 0.3%; after: 0.5%) as shown in Figure 4d. OFP and the weight percentage of individual VOCs before and after the LPG CCRP were given in Table S2. TOP 10 species contributed more than 80% of total OFP both before and after the LPG CCRP. Formaldehyde contributed the most (12.7%) of total OFP for OVOCs before the LPG CCRP and decreased to only 8.9% after the LPG CCRP. OFP of n-butane decreased from 21.5 ppbv O_3/ppbv to 8.7 ppbv O_3/ppbv with its ranking changed from TOP 3 to TOP 9. Similarly, Prop-Equiv concentration of TOP 10 species also contributed more than 80% both before and after the LPG CCRP (as given in Table S3). Moreover, Prop-Equiv concentration of n-butane decreased by 59.4% with its ranking changed from TOP 4 to TOP 8 after the LPG CCRP.

3.4 Primary and secondary/biogenic sources of individual VOCs

Linear regression fit (LRF) method was utilized in this study to determine emission ratios of individual VOCs. Since nighttime chemistry process is negligible for most VOCs, the VOCs data obtained during 1:00 a.m. to 4 a.m. can be used for the LRF method (Brito et al., 2015). As one of products from incomplete combustion source, CO was usually used as the long-lived anthropogenic marker (de Gouw et al., 2008). Thus, the slope of individual VOCs to CO during nighttime can be selected as their emission ratios (von Schneidemesser et al., 2010; Warneke et al., 2007). The temporal filter used in this study was suitable as shown in Figure 5 and Figure S2. Furthermore, primary and secondary/biogenic source of individual VOCs could be determined by their emission ratios through following equations (Millet et al., 2005).

$$\tau_a = \tau_{pri} + \tau_{sec/bio} + \tau_b \qquad (a)$$

$$\tau_{pri} = ER \times \tau_{co} \qquad (b)$$

Where τ_a is the mixing ratio of specie *i* in ambient air, τ_{pri} is the mixing ratio of specie *i* from primary source, $\tau_{sec/bio}$ is the mixing ratio of specie *i* from secondary/biogenic source, τ_b the background mixing ratio of specie *i* is defined as the 0.1 quantile of measured mixing ratio (Goldan et al., 1995), ER stands for the emission ratio of specie *i*, and τ_{co} is the mixing ratio of ambient CO.

Emission ratio of formaldehyde was 4.92 ppbv/ppmv before the LPG CCRP, and decreased to 1.41 ppbv/ppmv after the LPG CCRP. A previous study conducted in Huston at the Moody Tower site found the average emission ratio of formaldehyde to CO was about 3.0 ppbv/ppmv through early morning traffic peak periods (Parrish et al., 2012), which is in the same range as in this study. For other OVOC species, their emission ratios shown decreasing trend after the LPG CCRP, which could reflect the effectiveness of air pollution control measure. However, the emission ratio of acetone increased from 2.83 ppbv/ppmv to 3.21 ppbv/ppmv, since the emissions from anthropogenic emissions such as solvent usage could affect the results (Guo et al., 2013b), but its range was consistent with the emission ratio in London (3.18 ppbv/ppmv) (Valach et al., 2014). The emission ratio of isoprene was steady around 0.74 ~ 0.77 ppbv/ppmv, which is slightly lower than that found in São Paulo (1.17 ppbv/ppmv) and London (1.13 ppbv/ppmv) (Brito et al., 2015; Valach et al., 2014), but higher than that reported in Los Angeles (0.30 ppbv/ppmv) and Mexico City (0.08 ppbv/ppmv) (Bon et al., 2011; Borbon et al., 2013).

The ratios of propane, i-butane, n-butane to CO were used in this study to evaluated the changing source contributions from LPG vehicular emissions (as shown in Figure 6). The average emission ratio of propane decreased from 22.5 to 7.9 after LPG CCRP with the decreasing percentage by 65.0%. And the emission ratios of i-butane and n-butane decreased by 69.4% and 69.2%, respectively. Moreover, the changing rate of the emission ratios of LPG tracers, namely propane, i-butane, and n-butane were consistent with their changing rate of LPG vehicular emission factors through previous tunnel study in Hong Kong (Cui et al., 2018). Therefore, the large decrease of emission ratios of propane, i-butane, and n-butane in this study could reflect the effective reduction of on-road LPG emissions after the LPG CCRP in Hong Kong.

The diurnal cycles of individual OVOCs and biogenic VOCs (BVOCs) from primary and secondary/biogenic emissions before and after the LPG CCRP were plotted in Figure 7 and Figure S3. In general, the portion of methanol, acetone, and monoterpenes from primary source contributed more than 60% and 70%, respectively, before and after the LPG CCRP. For formaldehyde, acetaldehyde, isoprene, and MVK+MACR, secondary/biogenic component were more significant than other species, which could reflect the importance of secondary/biogenic emissions for these species. Moreover, secondary/biogenic peaks of most selected OVOCs and BVOCs occurred in the afternoon due to photochemistry reaction process, and early morning peaks for their primary component (Yuan et al., 2012).

3.5 Source apportionments of roadside VOCs

Four sources, namely diesel and gasoline vehicular emissions, LPG vehicular emissions, solvent usage, and secondary and biogenic emissions, were identified for roadside VOCs by using PMF method before and after the LPG CCRP (as shown in

Figure 8). Factor 1 was considered to be diesel and gasoline vehicular emissions because it was dominated by C_2-C_5 alkanes/alkene , large amount of CO, benzene, and toluene, which are typical markers from diesel-related and gasoline-related source (Liu et al., 2008; Schmitz et al., 2000). Since propane, i-butane, and n-butane these three LPG tracers contributed the most in Factor 2, it was identified as LPG vehicular emissions (Chen et al., 2001). Factor 3 contributed the largest portion to ethylbenzene, m, p-xylene, and o-xylene, thus, it was regarded as solvent usage (Ou et al., 2015a; Seila et al., 2001). Isoprene and OVOCs were dominant species in Factor 4, since biogenic emission is the major source of isoprene (Rinne et al., 2002), and most OVOCs were mainly formed through secondary formation (Li et al., 2015; Taatjes et al., 2012; Yuan et al., 2012), this factor could be considered as secondary and biogenic emissions.

LPG vehicular emissions was the dominant source for total VOCs mixing ratio both before and after the LPG CCRP (Figure 9). However total VOCs emitted from LPG vehicular emissions decreased from 30.5 ppbv to 13.8 ppbv by about 55% after the LPG CCRP. Meanwhile, the contribution of LPG vehicular emissions to total VOCs decreased from 45% to 38% (Figure S4). The contributions of diesel and gasoline vehicular emissions, solvent usage, secondary and biogenic emissions increased to 35%, 11%, and 17%, respectively, due to the large decreasing portion of LPG vehicular emissions. However, the absolute mixing ratios of VOCs from diesel and gasoline vehicular emissions, solvent usage, secondary and biogenic emissions all decreased with the changing percentage of 22%, 59%, and 50%, respectively.

Vehicle-related source, in sum, contributed 69% and 46%, respectively, before and after the LPG CCRP. Secondary and biogenic emissions cannot be negligible in roadside environment since they contributed around 17% of total VOCs both before and after the LPG CCRP.

Secondary/biogenic source contributions to individual OVOCs and BVOCs by LRF and PMF method before and after the LPG CCRP were compared in Figure 10. It could be found that these two different methods agree well with each other with the difference less than 20%. The ratio of m,p-xylenes to ethylbenzene, which was commonly used to indicate the photochemical age (de Gouw et al., 2005), was 1.35 ± 0.02 and 1.75 ± 0.03, respectively, before and after the LPG CCRP in this study, and these ratios were in the normal range from 1.3 to 1.8 in urban areas of Hong Kong (Guo et al., 2007; Ho et al., 2004). Therefore, the contributions of secondary/biogenic source for most OVOCs decreased after the LPG CCRP through both LRF and PMF method resulted from less secondary formation could demonstrate the reduction of VOCs from primary sources.

3.6 OFP of roadside VOCs from different sources

Because of the large decrease of VOC mixing ratios, total OFP of VOCs decreased from 193.3 ppbv O_3/ppbv to 108.5 ppbv O_3/ppbv after the LPG CCRP. Based on the VOC mixing ratios obtained from source apportionment, OFP of roadside VOCs from different sources could be calculated, and their contributions were illustrated in Figure 11. LPG vehicular emissions were found to be the dominant source of total OFP accounting for 30% before the LPG CCRP. While this percentage decreased to 24% after the LPG CCRP. Diesel and gasoline vehicular emissions, however, changed to be the dominant source of total OFP accounting for 14% after the LPG CCRP, but its absolute OFP decreased from 58.0 ppbv O_3/ppbv to 50.4 ppbv O_3/ppbv. Moreover, the contributions of solvent usage and secondary/biogenic emissions both decreased by 30~50%. Therefore, the implementation of on-road LPG vehicular emission control measure improved the reduction of local ozone formation potential of roadside VOCs.

4 Conclusions

A programme to replace worn-out catalytic converters for nearly all LPG-fueled taxis and public light bused has been implemented between October 2013 and April 2014 to reduce vehicular emissions in Hong Kong. In this study, PTR-MS was firstly introduced to continuously monitor roadside VOCs and OVOCs in Hong Kong, coupling with on-line GC-FID measurement technique, the effectiveness of this programme was evaluated through investigating roadside VOCs before and after the LPG CCRP. The decreasing percentage of the mixing ratio of total measured VOCs was 40.6% after the implementation of the LPG CCR, and the total weighting percentage of LPG tracers decreased from 49% to 34%. Emission ratios of individual VOCs were estimated through LRF method, the reduction of emission ratios of individual VOCs, especially for propane, i-butane, and n-butane, reflect the effectiveness of this air pollution control programme on improving roadside air quality of Hong Kong. LPG vehicular emissions was the dominant source which comprised about 44.7% of total VOCs at the roadside monitoring station, and its weighting percentage reduced to only 37.8% with the absolute VOCs mixing ratio from LPG vehicular emissions decreased from 30.5 ppbv to 13.8 ppbv by about 55% after the LPG CCRP. The ozone formation potentials of each emission source were also investigated, and large decrease of total OFP and the portion of LPG vehicular emissions were also found in this study. In the sight of VOCs, the air pollution control measure conducted by the Hong Kong government could effectively reduce on-road vehicle emissions and improve roadside air quality.

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Table 1. The mixing ratios (in ppbv) of CO and VOCs measured at MKAQMS before and after the LPG CCRP

Group	Species	Before the LPG CCRP				After the LPG CCRP			
		Average	S.D.	Max	Min	Average	S.D.	Max	Min
	CO	978.47	169.55	1650.20	675.76	703.48	169.77	1554.52	336.79
Alkanes	Ethane[a]	1.90	0.49	3.89	1.02	4.00	1.29	9.03	0.55
	Propane[a]	10.23	5.84	40.03	2.89	4.64	2.28	17.38	1.02
	i-Butane[a]	8.32	5.07	35.02	2.09	4.02	1.99	18.23	1.10
	n-Butane[a]	15.44	8.97	63.01	4.23	6.27	3.29	27.28	1.44
	i-Pentane[a]	1.10	0.68	4.83	0.00	0.78	0.56	8.28	0.11
	n-Pentane[a]	0.52	0.32	2.06	0.00	0.32	0.30	5.74	0.00
	i-hexane[a]	0.10	0.22	1.74	0.00	0.15	0.26	1.56	0.00
	n-Hexane[a]	0.24	0.30	3.40	0.00	0.07	0.22	2.26	0.00
	i-Octane[a]	0.11	0.10	0.81	0.00	0.11	0.11	0.79	0.00
	n-Heptane[a]	0.10	0.14	1.18	0.00	0.02	0.09	0.90	0.00
	n-Octane[a]	0.01	0.04	0.31	0.00	0.00	0.02	0.25	0.00
	Sub-Total	*38.08*	*11.89*			*20.40*	*4.71*		
Alkenes	Ethene[a]	4.35	1.15	8.76	2.07	3.17	1.58	7.31	0.00
	Propene[a]	2.01	0.73	4.50	0.65	0.97	0.37	2.64	0.28
	trans-2-Butene[a]	0.01	0.04	0.27	0.00	0.32	0.15	1.21	0.00
	1-Butene[a]	0.38	0.17	1.19	0.00	0.01	0.03	0.16	0.00
	cis-2-Butene[a]	0.10	0.07	0.40	0.00	0.04	0.05	0.43	0.00
	1,3-Butadiene[a]	0.13	0.06	0.36	0.00	0.07	0.05	0.39	0.00
	trans-2-Pentene[a]	0.08	0.09	0.66	0.00	0.03	0.07	0.84	0.00
	1-Pentene[a]	0.17	0.17	1.29	0.00	0.03	0.08	1.29	0.00
	Isoprene[b]	0.88	0.35	2.08	0.27	0.63	0.25	1.61	0.19
	Monoterpenes[b]	0.39	0.15	0.97	0.14	0.34	0.15	1.58	0.11

	Sub-Total	*8.49*	*1.44*			*5.61*	*1.66*		
Alkyne	Ethyne[a]	2.89	2.01	21.70	0.00	3.49	3.28	26.11	0.00
Aromatics	Benzene[b]	0.33	0.18	1.15	0.03	0.28	0.16	0.91	0.04
	Toluene[b]	1.64	0.91	5.78	0.21	1.73	1.05	6.19	0.24
	C_2-Benzenes[b]	1.19	0.69	4.45	0.17	0.65	0.40	3.73	0.12
	1,3,5-Trimethylbenzene[a]	0.00	0.01	0.07	0.00	0.00	0.02	0.22	0.00
	1,2,4-Trimethylbenzene[a]	0.08	0.07	0.40	0.00	0.05	0.08	0.51	0.00
	1,2,3-Trimethylbenzene[a]	0.00	0.01	0.11	0.00	0.00	0.01	0.26	0.00
	Chlorobenzene[b]	0.12	0.08	0.38	0.00	0.14	0.06	0.36	0.05
	Dichlorobenzene[b]	0.29	0.11	0.74	0.10	0.21	0.10	0.88	0.02
	Trichlorobenzene[b]	0.07	0.09	0.94	0.02	0.09	0.03	0.34	0.00
	Sub-Total	*3.72*	*1.17*			*3.15*	*1.15*		
OVOCs	Formaldehyde[b]	4.49	2.29	12.62	0.17	2.00	1.21	8.13	0.24
	Methanol[b]	4.38	1.54	10.48	1.30	3.31	1.47	22.35	1.29
	Acetaldehyde[b]	1.99	1.03	5.92	0.00	1.74	0.82	5.70	0.42
	Acrolein[b]	1.67	0.74	4.29	0.08	1.20	0.52	3.54	0.38
	Acetone[b]	2.45	0.94	5.79	0.92	2.18	0.89	6.88	0.90
	MVK&MACR[b]	0.29	0.14	0.77	0.05	0.21	0.10	0.57	0.05
	MEK[b]	0.46	0.25	1.33	0.08	0.37	0.19	1.27	0.11
	Sub-Total	*15.73*	*3.19*			*11.00*	*2.32*		
Other	Acetonitrile[b]	0.42	0.09	0.75	0.21	0.25	0.06	0.63	0.10
	Total	**69.32**	**12.61**			**43.91**	**6.51**		

[a] Measured by on-line GC-FID. [b] Measured by PTR-MS.

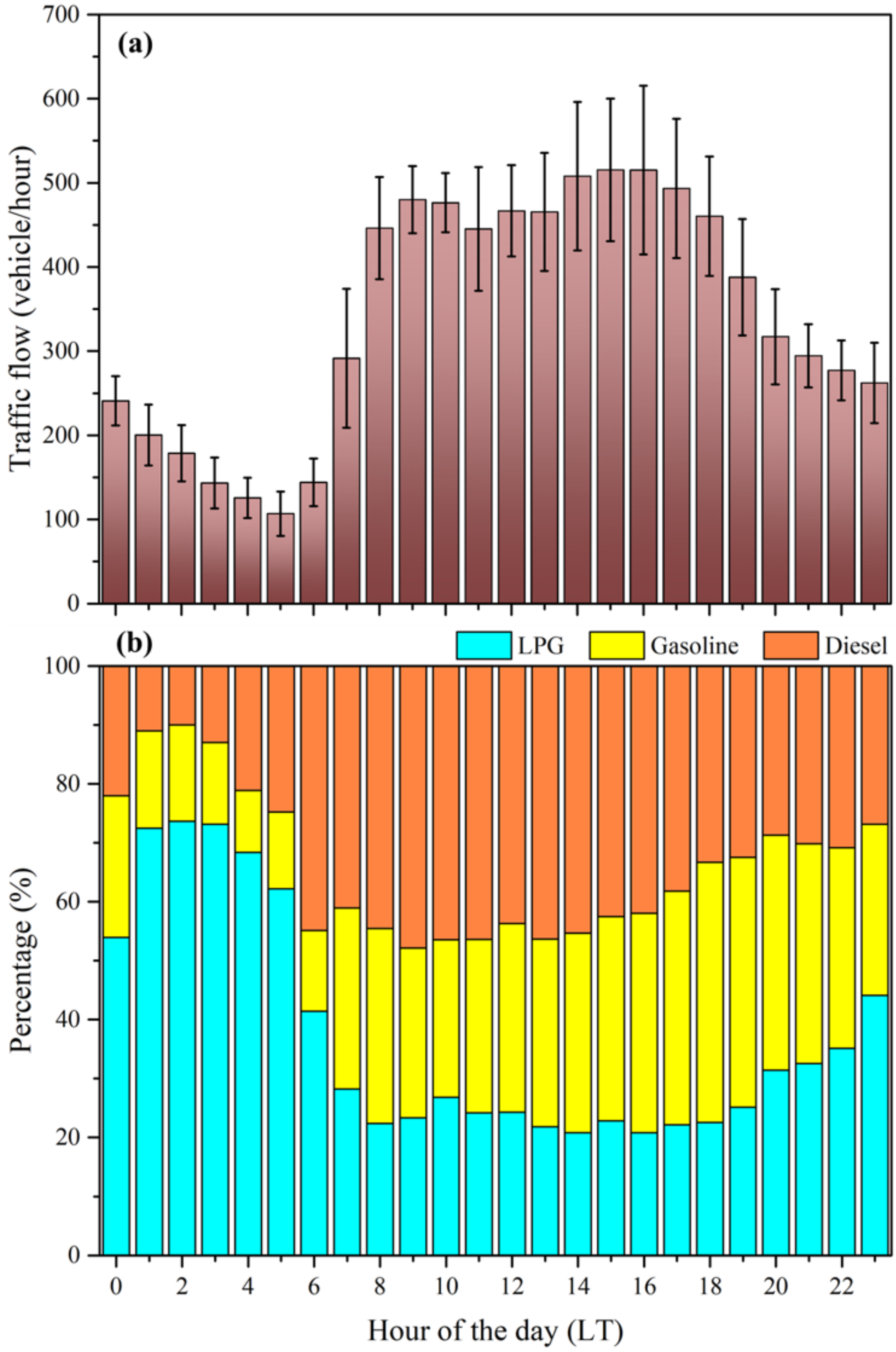

Figure 1. (a) Traffic flow and (b) weighting percentage of different vehicle types at MKAQMS in Hong Kong

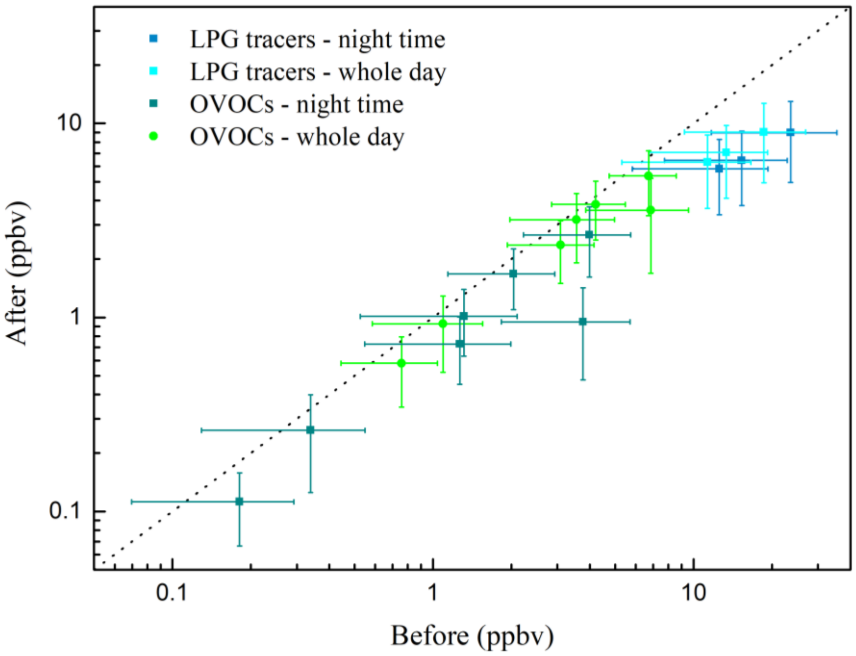

Figure 2. Mixing ratios of LPG tracers and individual OVOCs at MKAQMS before and after the LPG CCRP. Nighttime is during 1:00 a.m. ~ 4:00 a.m.. Dashed line is the 1:1 line for reference.

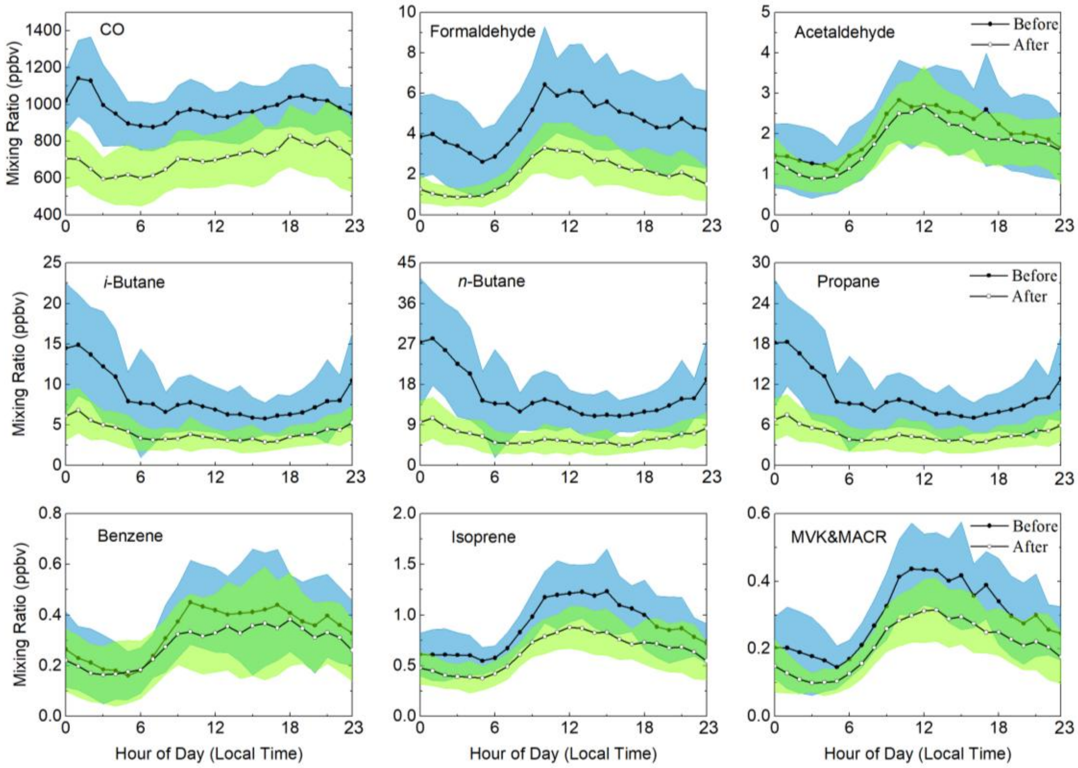

Figure 3. Diurnal variation of individual VOC species at MKAQMS before and after the LPG CCRP.

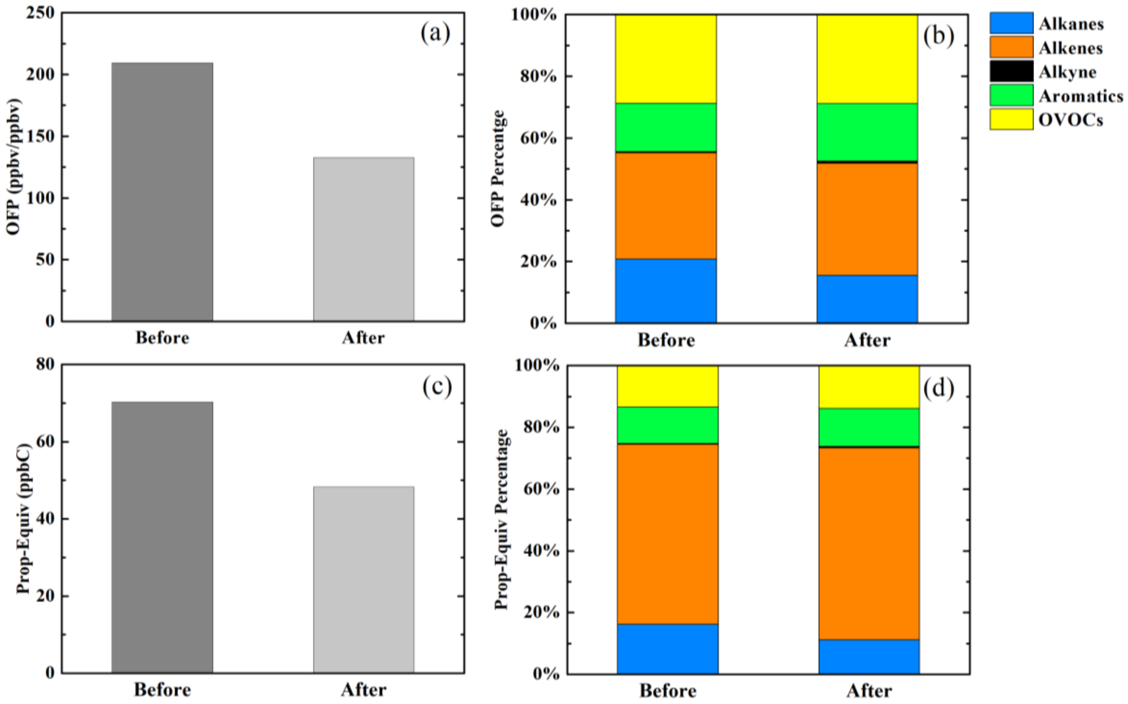

Figure 4. Ozone formation potential (OFP) and propene-equivalent (Prop-Equiv) concentration of roadside VOCs at MKAQMS before and after the LPG CCRP.

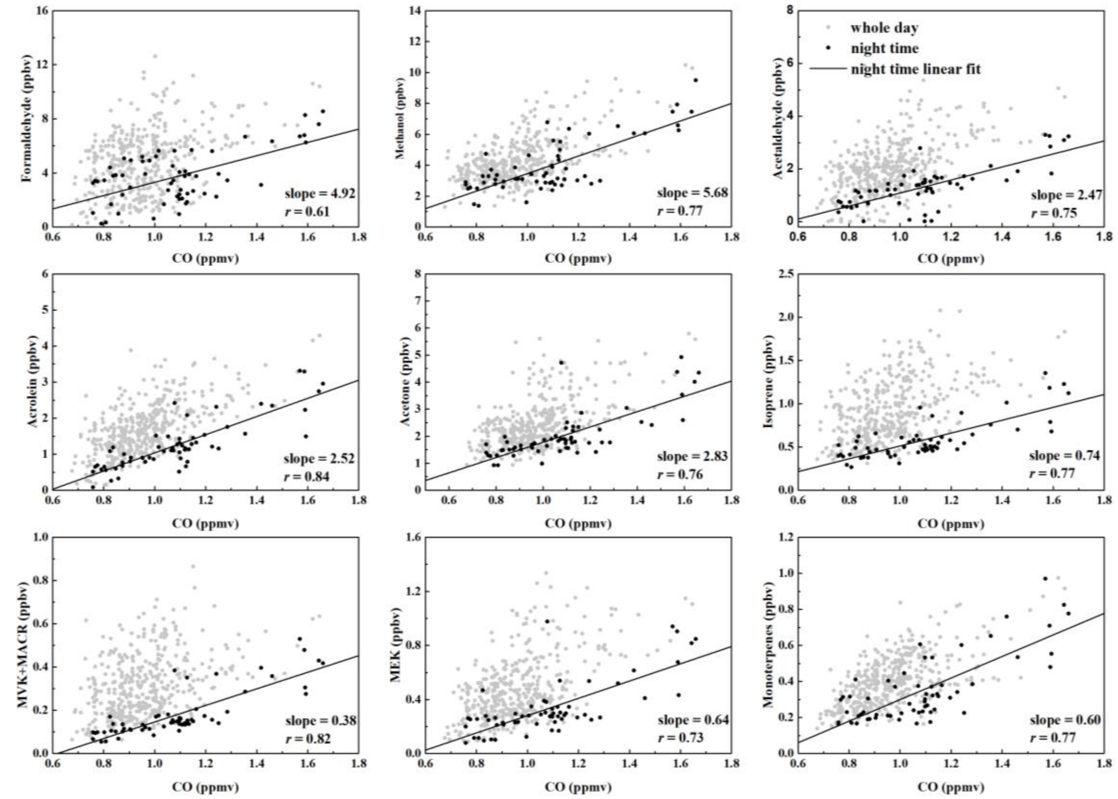

Figure 5. Scatterpolts of individual VOCs during nighttime (black dots) and whole day (grey dots) at MKAQMS before the LPG CCRP.

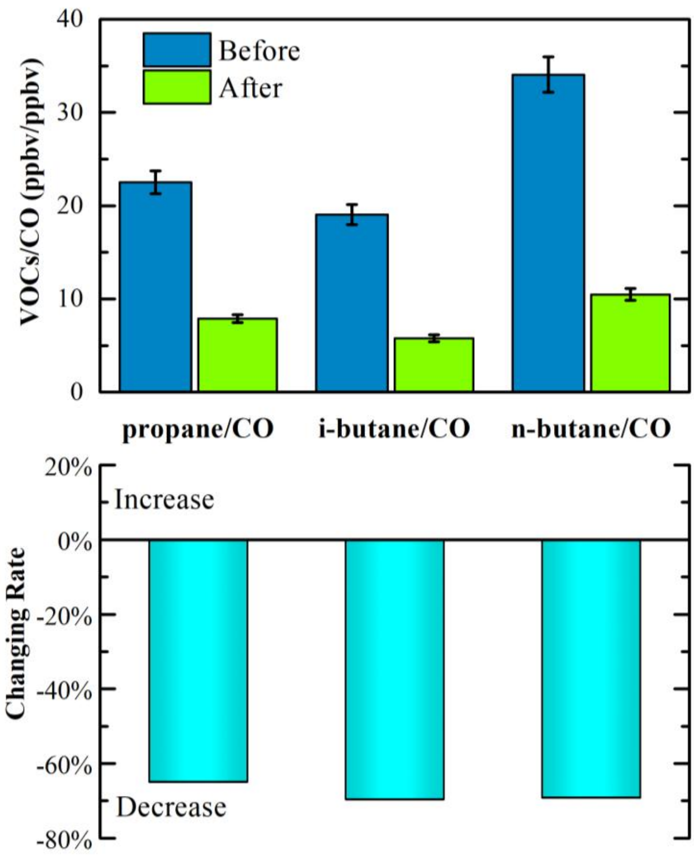

Figure 6. The ratios of LPG tracers (propane, i-butane, and n-butane) to CO and their changing rates at MKAQMS before and after the LPG CCRP.

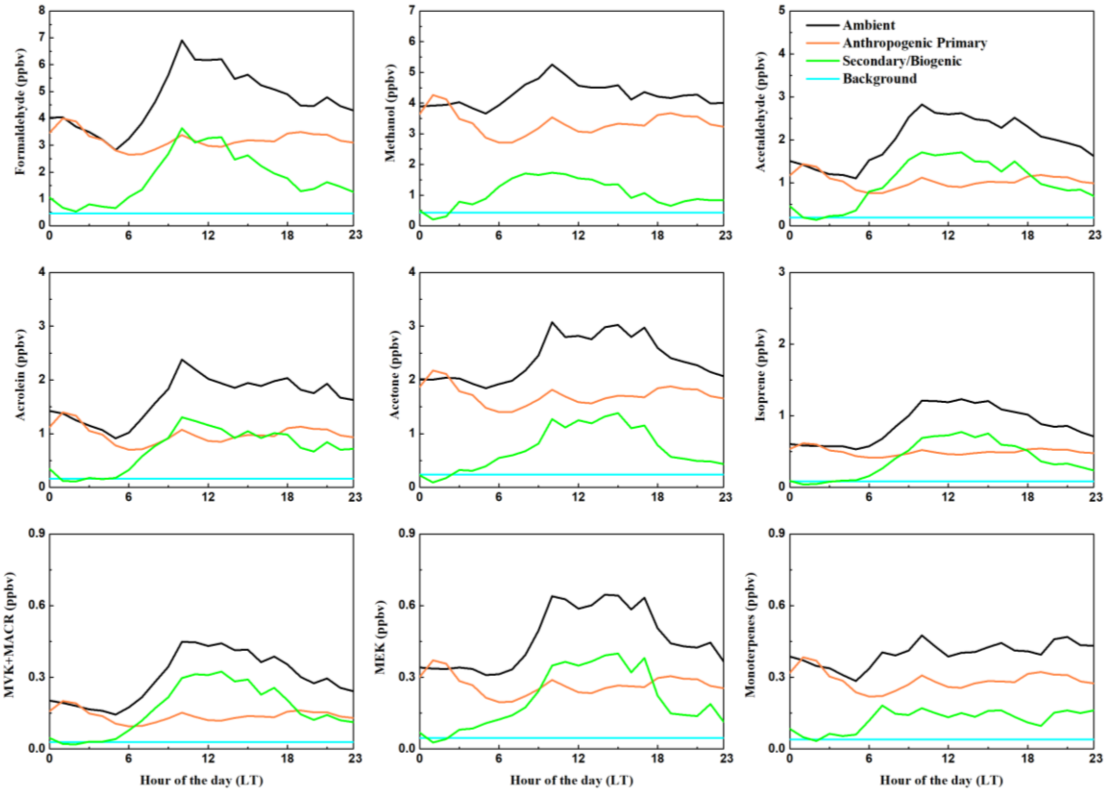

Figure 7. Diurnal mixing ratio of individual VOCs before the LPG CCRP. Black line is the ambient mixing ratio, orange line is the mixing ratio from anthropogenic source, freen line is the mixing ratio from secondary/biogenic source, blue line is the background mixing ratio.

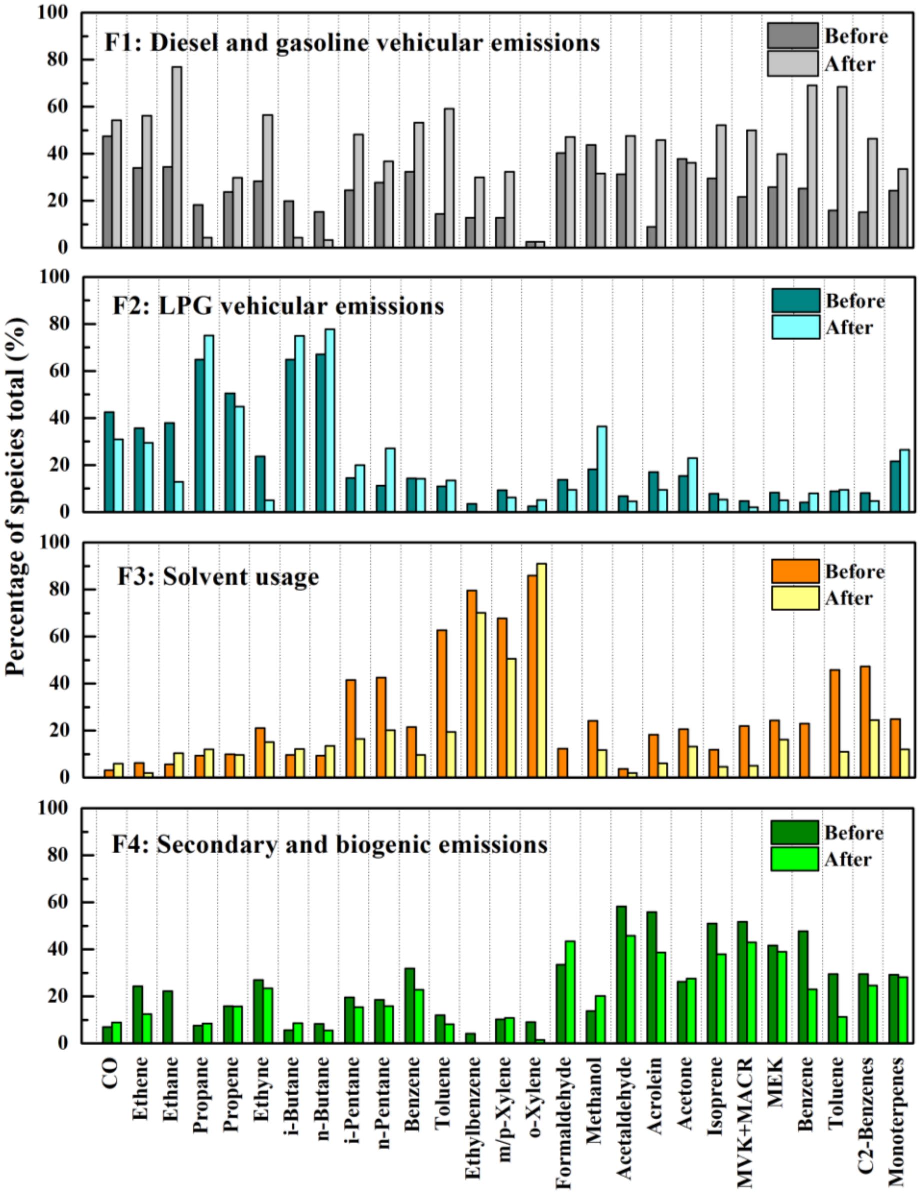

Figure 8. Factor profiles (% of species) for roadside VOCs at MKAQMS before and after the LPG CCRP.

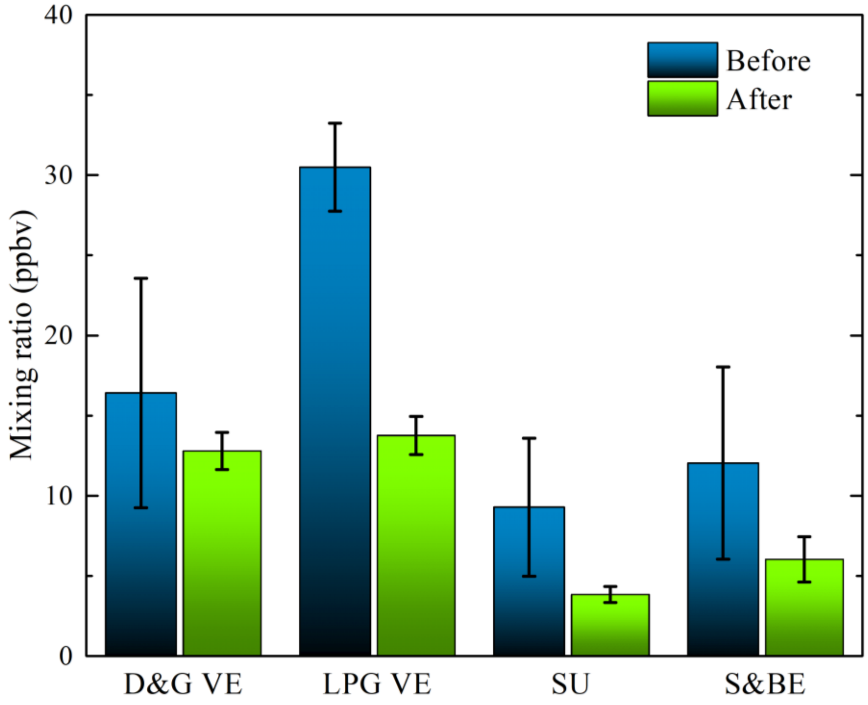

Figure 9. Mixing ratios of roadside VOCs from different sources at MKAQMS before and after the LPG CCRP. D&G VE: diesel and gasoline vehicular emissions; LPG VE: LPG vehicular emissions; SU: solvent usage; S&BE: secondary and biogenic emissions.

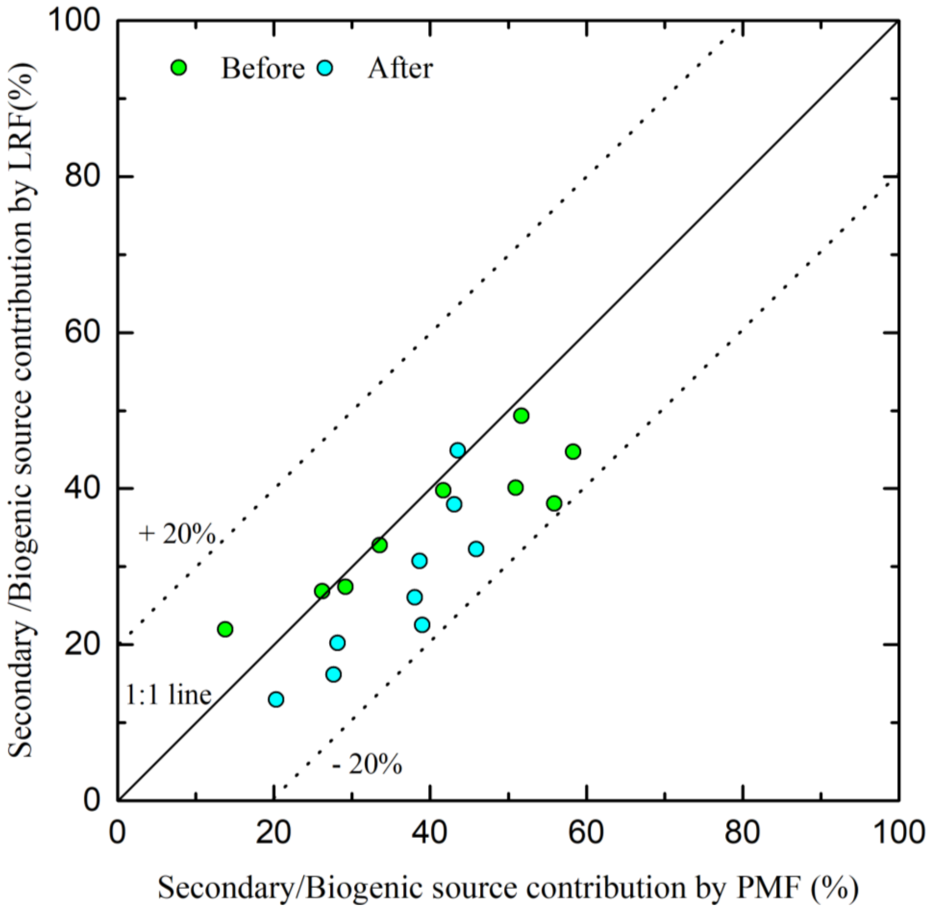

Figure 10. Secondary/biogenic source contributions to individual OVOCs and BVOCs by LRF and PMF method before (green dots) and after (blue dots) the LPG CCRP. For reference, solid line and dashed lines are the 1:1 and ±20% lines, respectively.

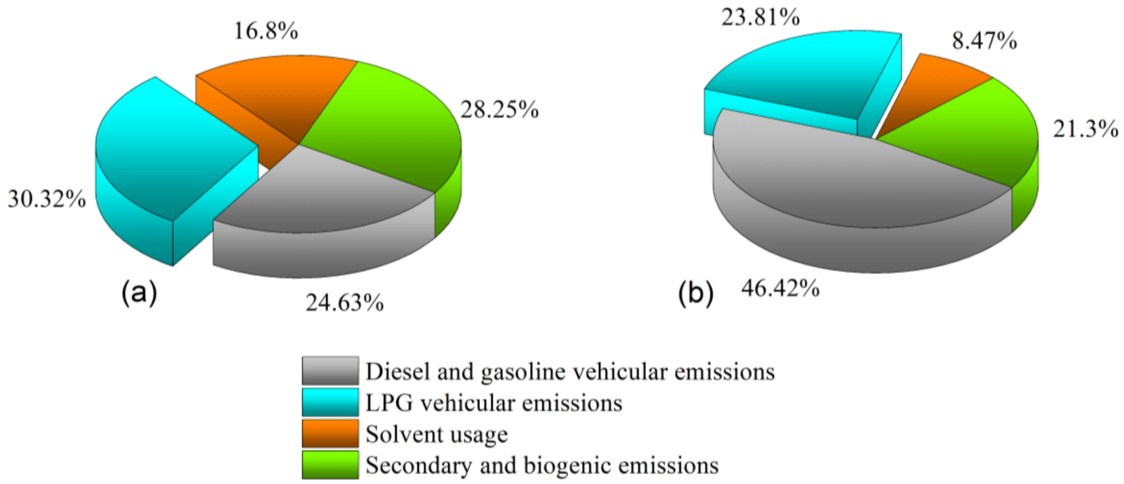

Figure 11. OFP of roadside VOCs from different sources at MKAQMS (a) before and (b) after the LPG CCRP based on PMF results.

Conflict of interest statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of the manuscript entitled “The Characteristics and Sources of Roadside VOCs in Hong Kong: Effect of the LPG Catalytic Converter Replacement Programme”.

Credit Author Statement

Long Cui: Data curation; Formal analysis; Methodology; Writing - original draft. Hai Wei Li: Software; Writing - review & editing. Yu Huang: Funding acquisition; Investigation; Writing – editing. Zhou Zhang: Validation; Visualization. Shun Cheng Lee: Project administration; Funding acquisition; Supervision. Donald Ray Blake: Methodology; Writing – review. Xin Ming Wang: Software, Validation. Kin Fai Ho: validation; Visualization. Jun Ji Cao: Visualization; Writing – editing.

***Declaration of Interest Statement**

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: