

Effectiveness of replacing catalytic converters in LPG-fueled vehicles

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Effectiveness of replacing catalytic converters in LPG-fueled vehicles in Hong Kong

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Abstract

Many taxis and public buses are powered by liquefied petroleum gas (LPG) in Hong Kong. With more vehicles using LPG, they have become the major contributor to ambient volatile organic compounds (VOCs) in Hong Kong. An intervention program aimed to reduce the emissions of VOCs and nitrogen oxides (NO_x) from LPG-fueled vehicles was implemented by the Hong Kong Government in September 2013. Long-term real-time measurements indicated that the program was remarkably effective in reducing LPG-related VOCs, NO_x and nitric oxide (NO) in the atmosphere. Receptor modeling results further revealed that propane, propene, *i*-butane, *n*-butane and NO in LPG-fueled vehicle exhaust emissions decreased by 37.3 ± 0.4 , 50.2 ± 0.3 , 32.9 ± 0.4 , 41.1 ± 0.4 and $75.9 \pm 0.3\%$, respectively, during the implementation of the program. In contrast, despite the reduction of VOCs and NO_x , the O_3 production following the program increased by $0.25 \pm 0.04 \text{ ppbv h}^{-1}$ (4.8%). Moreover, the production rate of HO_x decreased due to the reduction of VOCs, whereas NO reduction resulted in a more significant decrease of the HO_x in destruction compared to the decrease in production, and an increase of hydroxyl (OH) and hydroperoxyl (HO_2). Analysis of O_3 -VOCs- NO_x sensitivity in ambient air indicated VOC-limited regimes in the O_3 formation before and during the program. Moreover, a maximum reduction percentage of NO_x (i.e., 29.4%) and the lowest reduction ratio of VOCs / NO_x (i.e., ~3 : 1) in LPG-fueled vehicle emissions were determined to give a zero O_3 increment. The findings are of great help to future formulation and implementation of control strategies on vehicle emissions in Hong Kong.

1 Introduction

Vehicular exhaust is a major source of air pollutants such as particulate matters (PM), volatile organic compounds (VOCs) and trace gases including carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2) and nitrogen oxides (NO_x) (Xie et al., 2003;

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Barletta et al., 2002; Ruellan and Cachier, 2001). Apart from primary pollutants, secondary pollutants formed from vehicular exhausts, i.e., ozone (O₃) and secondary organic aerosols (SOA) are of high concern due to their detrimental effects on atmospheric environment and human health (Ciccone et al., 1998).

Fuel substitution is a universal and effective method to constrain vehicular emissions. As clean energy, liquefied petroleum gas (LPG) has been widely used either alone or combined with petrol and diesel (Lau et al., 2011; Lai et al., 2009; Gamas et al., 1999), for the benefit of emission reduction of CO₂, fine PMs and VOCs (Chikhi et al., 2014; Myung et al., 2012). However, one must bear in mind that maintenance status, conversion method, composition and driving speed all influence the emissions of air pollutants (Schifter et al., 2000; Gamas et al., 1999). Therefore, regular on-site measurements are necessary to monitor the emission profiles and rates. Although LPG is a relatively clean fuel, the leakage of LPG-related VOCs (i.e., propane, propene, and *n*- and *i*-butanes) from evaporation and incomplete combustion cannot be neglected. For example, source apportionment analysis indicated that LPG accounted for a considerable percentage of ambient VOCs in Guangzhou (8–16%) (Liu et al., 2008) and Hong Kong (32.6 ± 5.8%) (Ou et al., 2015). Furthermore, the LPG-related VOCs can contribute to O₃ formation and cause photochemical smog. Blake and Rowland (1995) emphasized the importance of LPG leakage in OH reactivity and O₃ formation in urban Mexico. Farmer et al. (2011) reported that the increase of LPG-related VOCs led to O₃ increments even though the total VOCs (TVOCs) was reduced, as the peroxy radicals (RO₂) generating from VOCs with low vapor pressure had a higher branching ratio leading to NO₂ formation from NO, rather than reserving nitrogen in the form of organic nitrates. On the other hand, NO emitted from LPG combustion may titrate O₃. Therefore, it still remains undecided whether the LPG usage is contributive or destructive to O₃ formation, especially in Hong Kong.

Hong Kong has experienced rapid development during the past decades, and increasingly suffers from crowded traffic and population, with nearly 0.7 million vehicles running on the total road length of 2.1 × 10³ km and 7.2 million people living on the

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territory of $1.1 \times 10^3 \text{ km}^2$. The road usage rate in Hong Kong is among the highest in the world, transporting approximately 1.2 million passengers per day. As such, traffic emissions significantly influence the air quality in Hong Kong. To improve the air quality, the Hong Kong Environmental Protection Department (HKEPD) launched a series of programs including a stepwise LPG replacement program for taxis and light buses from 1997. By the end of 2010, > 99 % of the registered taxis (i.e., 17 950 vehicles) and 51 % of the registered public and private light buses (i.e., 3280 vehicles) were powered by LPG (HKCSD, 2010). Due to the usage of LPG as vehicle fuel, the ambient VOC profile in Hong Kong changed substantially with the most abundant species switching from toluene to propane and *n/i*-butanes (Ou et al., 2015; Guo et al., 2007; Ho et al., 2004). In addition, studies consistently confirmed an increased contribution of LPG-fueled vehicle emissions to ambient VOC levels, which was 11 % at an urban site in 2001 (Guo et al., 2004), 15 % at a suburban site during 2002–2003 (Guo et al., 2007), $26.9 \pm 0.6 \%$ and $40.8 \pm 0.8 \%$ at an urban site during 2002–2003 and 2006–2007, respectively (Lau et al., 2010). Moreover, O_3 has been experiencing an increasing trend in Hong Kong since last two decades (Wang et al., 2009; Guo et al., 2009). As O_3 formation was generally VOC-limited in Hong Kong (Cheng et al., 2010; Zhang et al., 2007), the contribution of LPG-fueled vehicle emissions to O_3 was not negligible, in view of the dominance of propane and *n/i*-butanes in ambient air and the high contribution of LPG-fueled vehicle emissions to VOCs. As such, an intervention program aimed to reduce VOCs and NO_x emitted by LPG-fueled vehicles was initialized in September 2013. This subsidy program promoted the replacement of catalytic converters in LPG-fueled vehicles, and $\sim 75 \%$ of LPG-fueled vehicles were replaced with new catalytic converters by the end of May 2015. Although laboratory studies identified high removal efficiency of the new catalytic converter on VOCs and NO_x (i.e., 99 % removal of propane and *n/i*-butanes in the taxis, and 91–93 % removal in the public light buses), the impact of the program on roadside air quality, which is more complex, required investigation.

In this study, the effectiveness of the intervention program was evaluated on the reduction of LPG-related VOCs and NO_x , the O_3 production, and the photochemical

reactivity driving the O₃ formation. Furthermore, the sensitivity of O₃ variation (i.e., the difference of net O₃ production by LPG before and during the program) relative to the reduction percentage of LPG-related VOCs and NO_x was studied, and subsequently a maximum NO_x reduction percentage and a reasonable reduction ratio of VOCs / NO_x were proposed for the best O₃ reduction.

2 Methodology

2.1 Site description

Hong Kong, located on the coast of South China Sea (SCS), constitutes the great Pearl River Delta (PRD) together with Macao and nine mainland cities in Guangdong Province (i.e., Guangzhou, Shenzhen, Zhuhai, Foshan, Dongguan, Zhongshan, Huizhou, Jiangmen and Zhaoqing). Hong Kong has a typical coastal hilly terrain with large water area (~ 60 %) and vegetation coverage (~ 70 %) of land area. Marine subtropical monsoon climate dominates, and the prevailing winds are north and northeast in winter, east in spring and autumn, and south and southwest in summer.

This study involves three roadside sites (i.e., Mong Kok (MK, 22.32° N, 114.17° E), Causeway Bay (CWB, 22.28° N, 114.19° E) and Central (22.28° N, 114.16° E)), a general site (i.e., Tap Mun (TM, 22.47° N, 114.36° E)), and a background site (i.e., Hok Tsui (HT, 22.22° N, 114.25° E)). MK, CWB and Central are in mixed residential/commercial areas with heavy traffic and surrounded by dense tall buildings. TM is a rural site surrounded by country parks, and is upwind of Hong Kong in autumn/winter seasons. HT is a remote site at the tip of southeast Hong Kong, serving as a background site due to the sparse anthropogenic interference. Among the 6 sites, MK, CWB, Central and TM are the Air Quality Monitoring Stations deployed by Hong Kong Environmental Protection Department (HKEPD) (more details are provided at <http://www.aqhi.gov.hk/en/monitoring-network/air-quality-monitoring-stations9c57.html/stationid=81>). HT is a research site set up by Hong Kong Polytechnic University, and has been extensively used

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for air quality studies (Wang et al., 2009; Ho et al., 2006; Lee et al., 2002). Figure 1 shows the geographical location of the sampling sites.

2.2 Continuous measurements

2.2.1 Trace gases

Five trace gases (i.e., CO, SO₂, NO, NO₂ and O₃) were continuously measured at all the sites from 2011 to 2014. The analyzers were deployed in the air quality monitoring stations with a height of 3.0 m (MK and CWB), 4.5 m (Central), 11.0 m (TM) and 20.0 m (HT) above the ground level. Air samples were drawn through a perfluoroalkoxy (PFA) Teflon tube with outside diameter (OD) of 12.7 mm and inside diameter (ID) of 9.6 mm.

The inlet of the tube was approximately 0.5 m above the rooftop of the monitoring station, and the outlet was connected to a PFA manifold with a bypass pump drawing air into the analyzers at a rate of 5 L min⁻¹. Details about the analyzers are provided elsewhere (HKEPD, 2014; So and Wang, 2003).

Briefly, CO was analyzed using the method of non-dispersive infra-red absorption with gas filter correlation (TECO 48C/API 300); SO₂ was detected with UV fluorescence analyzers (TECO 43A/API 100E/TECO 43I); NO-NO₂-NO_x were measured by chemiluminescence technique (API 200A); and O₃ was monitored with the UV absorption method (API 400/API 400A). The detection limits for CO, SO₂, NO, NO₂ and O₃ were 50.0, 1.0, 0.5, 0.5 and 2.0 ppbv, respectively.

2.2.2 VOCs

Thirty C₂-C₁₀ non-methane hydrocarbons (NMHCs) including eleven alkanes, ten alkenes and nine aromatics were continuously measured at MK and HT from 2011 to 2014. The VOC samples were collected and analyzed every 30 min with an online analytical system (Syntech Spectra GC 955, Series 600/800, the Netherlands). The

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data were averaged into hourly values. The detection limits varied by VOC species in the range of 0.002–0.787 ppbv.

2.2.3 Quality assurance and control (QA/QC)

To guarantee the quality of the data acquired from the online monitoring systems, the instruments and QA/QC procedures for trace gases measurements were identical to those in the US air quality monitoring program (<http://epic.epd.gov.hk/ca/uid/airdata>). The measurements have been accredited by the Hong Kong Laboratory Accreditation Scheme (HOKLAS). All the instruments were regularly calibrated, tested and audited by standards with known traceability for trace gases measurements. According to HOKLAS criteria, a quality system was established to control the accuracy and precision within the limits of ± 15 and ± 20 %, respectively (HKEPD, 2014). For VOC analysis, a built-in computerized program, including auto-linearization, auto-calibration and calibration with span gas, was adopted to control the quality. The accuracy and precision of VOC measurements were 1.0–10.0 % and 2.5–20.0 %, respectively. Moreover, the online-measurements of VOCs were compared regularly to the canister samples analyzed by University of California at Irvine (UCI), and good agreements were identified (i.e., $R^2 = 0.95$ and 0.85 , slope = 1.14 and 0.97 for propane and butanes, respectively).

2.3 Theoretical calculation and model description

2.3.1 Primary emissions of VOCs and NO_x

The measured VOCs and trace gases include the background values, primary emissions and secondary formation (applicable to O_3 and NO_2). To obtain actual primary emissions of LPG-related VOCs and NO_x at the roadside sites, the values of background and secondary formation (if applicable) in this study were excluded using the Eqs. (1)–(5) (Takekawa et al., 2013):

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$$[VOC]_{\text{prim.}} = [VOC]_{\text{obs.}} - [VOC]_{\text{bg.}} \quad (1)$$

$$[NO_2]_{\text{sec.}} = [O_3]_{\text{bg.}} - [O_3]_{\text{obs.}} \quad (2)$$

$$[NO_2]_{\text{prim.}} = [NO_2]_{\text{obs.}} - [NO_2]_{\text{sec.}} - [NO_2]_{\text{bg.}} \quad (3)$$

$$[NO_x]_{\text{prim.}} = [NO_x]_{\text{obs.}} - [NO_x]_{\text{bg.}} \quad (4)$$

$$5 \quad [NO]_{\text{prim.}} = [NO_x]_{\text{prim.}} - [NO_2]_{\text{prim.}} \quad (5)$$

where $[xx]_{\text{obs.}}$, $[xx]_{\text{prim.}}$, $[xx]_{\text{sec.}}$ and $[xx]_{\text{bg.}}$ represent the observed, primary, secondary and background values, respectively. In this study, the hourly measured VOCs at HT were considered as the background levels for VOCs. For O_3 and NO_x , the 8 h averages at TM were treated as background values because (1) O_3 and NO_x are highly reactive, and the use of 8 h averages would minimize the impact of abrupt changes, (2) TM is located at the upwind location of Hong Kong, and is a rural coastal site, (3) 8 h averages of O_3 and NO_x showed good correlations ($R^2 = 0.75$ and 0.57 for O_3 and NO_x , respectively) between TM and HT, and not all the data were available at HT during the entire study period.

15 2.3.2 Impact of regional and super-regional air masses

Since MK was the only roadside site having VOCs and trace gases data, this study mainly focused on the data analysis of this site. As a roadside site, MK was expected to be strongly influenced by the fresh vehicular emissions. VOC ratios can indicate the relative ages of air masses and regional transport of air pollutants. For example, the ratios of VOCs with higher reactivity to those with lower reactivity (e.g. toluene / benzene and xylenes / ethylbenzene) imply more fresh air with higher values, which have been extensively used in previous studies (Guo et al., 2007; Ho et al., 2004). Therefore, ratios of toluene / benzene and xylenes / ethylbenzene were calculated here to roughly estimate the age of air masses at MK. Table 1 summarizes the ratios at MK (roadside site), Tung Chung (TC) and Yuen Long (YL) (both general am-

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bient sites), and HT (background site) in Hong Kong from October 2012 to May 2014. It is noteworthy that ambient VOCs at all the four sites were simultaneously measured. The ratios of toluene / benzene and xylenes / ethylbenzene at MK were significantly higher than those at the other three sites ($p < 0.05$), indicating that MK was more influenced by fresh emissions. More evidently, the ratios of toluene / benzene and xylenes / ethylbenzene at MK increased significantly after the background values were deducted, and were both much higher than those at the other sites ($p < 0.05$). The results suggested that air masses at MK were dominated by fresh emissions.

However, regional and super-regional transport cannot be completely eliminated only with the VOC ratios, and the influence of regional/super-regional air should be further examined when studying the emissions of local LPG-fueled vehicles. Using the propane / CO ratio method proposed by Guo et al. (2006), i.e., the ratio range of 5.0–300 pptv ppbv⁻¹ for air masses in Hong Kong, the influence of regional/super-regional air masses on local air was evaluated. Figure 2 shows the ratios of propane / CO at MK from 2011–2014. The propane / CO ratios of ~ 96 % air masses were between 5.0 and 300 pptv ppbv⁻¹. Further inspection of the values of LPG-related VOCs and NO_x with ratios of 5.0–300 showed insignificant differences ($p > 0.1$) from those with ratios beyond 5–300, suggesting that the air masses at MK were seldom influenced by regional/super-regional air. Moreover, over 95 % wind speeds were lower than 2.0 m s⁻¹ (i.e., calm or light air according to the Beaufort Wind Scale) (<http://www.spc.noaa.gov/faq/tornado/beaufort.html>), and the values of LPG-related VOCs and NO_x in all air masses were not different from those in the air masses with wind speeds lower than 2.0 m s⁻¹ ($p > 0.1$), confirming minor impact of regional/super-regional pollution on air at MK. Indeed, the prevailing wind direction was from the east, where local urban areas located.

2.3.3 PMF model

Positive matrix factorization (PMF) is a receptor model for source apportionment and has been extensively used in many fields (i.e., PM, VOCs and sediment) (Brown et al.,

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2007; Lee et al., 1999). Based on the principle of mass balance, it decomposes the matrix of measurement (**X**) into the matrices of factor contributions (**G**) and factor profiles (**F**) in p sources, as shown in Eq. (6) (Paatero, 1997; Paatero and Tapper, 1994):

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (6)$$

5 where x_{ij} is the measured concentration of j species in i sample, g_{ik} represents the contribution of k_{th} source to i sample, f_{kj} indicates the fraction of j species in k_{th} source, and e_{ij} is the residual for j species in i sample.

The matrices of **G** and **F** are obtained in the case of the minimum of objective function Q , as shown in Eq. (7):

$$10 \quad Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad (7)$$

where m and n represent the number of species and samples, respectively, and u_{ij} is the uncertainty of j species in i sample. Q (robust) is automatically calculated by excluding the points not fit by the model, and the run with lowest Q (robust) value is selected as the optimum solution by the model.

15 2.3.4 PBM-MCM model

The photochemical box model incorporating the master chemical mechanism (PBM-MCM) is a computing model based on the chemical reactions of observed species. It has been introduced and successfully applied in many previous studies in reproducing the observed values, describing the production and destruction mechanisms, and simulating the photochemical reactivity (Ling et al., 2014; Lam et al., 2013; Cheng

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et al., 2010). Briefly, the observations of VOCs, trace gases and meteorological parameters are input to construct and constrain the model, which consists of 5900 reactions and 16 500 species in the latest version (MCM 3.2). However, it is noteworthy that the heterogeneous reactions are not included, and the model does not consider physical processes (i.e., horizontal and vertical transport).

In this study, CO, SO₂, NO, NO₂, O₃, twenty-seven VOCs and two meteorological parameters (i.e., temperature and relative humidity) were used to construct and constrain the model. Hourly data were used as input (i.e. 24 h day⁻¹) and the outputs were from 07:00 to 19:00 LT by each hour. To better describe the photochemical reactions in Hong Kong, the model was modified, i.e., the photolysis rates were calibrated using the photon fluxes from the Tropospheric Ultraviolet and Visible Radiation (TUV-v5) Model (Madronich and Flocke, 1997) according to the location of Hong Kong and the modeling period, and the height of mixing layer was set as 300–1400 m. The concentrations of some species in the aloft (i.e., free troposphere), which may influence the mixing ratios of air pollutants in the lower troposphere with the development of boundary layer, were set according to the real conditions in Hong Kong (Lam et al., 2013). The base case and constrained cases were established to calculate the LPG contributions to O₃, OH, HO₂ and their formation/destruction rates, which can be extracted from the model output. Briefly, for the base run, the input was the measurement data with background values being deducted. For the constrained runs, the concentrations of species (i.e., VOCs, NO_x and VOCs + NO_x, respectively) in the LPG source were further deducted. As such, the differences of the output between the base run and the three constrained runs were the LPG contributions by each group of species (i.e., VOCs, NO_x and VOCs + NO_x, respectively) in LPG exhaust. The production and destruction pathways of HO_x (HO_x = OH + HO₂ + RO₂) considered in this study are listed in Table 2. Since the regional/super-regional influence was excluded and the backgrounds were deducted, the O₃ production in the base run was a calculation of purely local production of O₃.

2.3.5 Relative incremental reactivity (RIR)

RIR, initially proposed by Carter and Atkinson (1989), has been extensively used to describe the relationship between O₃ and its precursors, i.e., VOCs, NO_x and CO. Although the observation-based models incorporating carbon bond mechanisms were often utilized to simulate the O₃ production rate (Ling et al., 2011; Zhang et al., 2007; Martien et al., 2003), a more explicit PBM-MCM model was applied in this study. The RIR and RIR-weighted concentrations were calculated using Eqs. (8) and (9) (Ling et al., 2011):

$$\text{RIR}^S(X) = \frac{[P_{\text{O}_3-\text{NO}}^S(X) - P_{\text{O}_3-\text{NO}}^S(X - \Delta X)] / P_{\text{O}_3-\text{NO}}^S(X)}{\Delta S(X) / S(X)} \quad (8)$$

$$\text{RIR} - \text{weighted concentration} = \text{RIR}(X) \times \text{concentration} \quad (9)$$

where, $P_{\text{O}_3-\text{NO}}^S(X)$ and $P_{\text{O}_3-\text{NO}}^S(X - \Delta X)$ represent the original O₃ production rate, and that in the scenario, with the a hypothetical change (ΔX) (10% in this study) in source/species X , respectively, both of which considered O₃ titration by NO. $\Delta S(X)$ is the change in the concentration of X ($S(X)$). The “concentration” refers to the observed or PMF-extracted concentration of source/species X .

3 Results and discussion

3.1 Variations of LPG-related VOCs and NO_x during the intervention program

3.1.1 Concentrations of primary LPG-related VOCs and NO_x

Table 3 shows the mixing ratios of LPG-related VOCs and NO_x in primary emissions before (i.e., October 2012–September 2013) and during (i.e., October 2013–May 2014) the intervention program, with 95% confidence intervals. It should be noted that (1)

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September 2013 was defined as “before” period, because only 0.2% LPG-fueled vehicles replaced the catalytic converters in this month, (2) the “during” period only extended to May 2014, since 99.2% replacement had been completed and data were not available after May 2014; and (3) values of backgrounds and secondary formation (if applicable) were both deducted from the observations. The mixing ratios of LPG-related VOCs and NO_x significantly decreased ($p < 0.05$) from before to during the program, implying the possible effectiveness of the program.

To further understand the effectiveness of the program, the monthly reductions of LPG-related VOCs after the commencement of the converter replacement were calculated and compared with those before the program (Fig. 3). Since the program was initiated in October 2013, the averages of VOC species in September in each year were taken as the baselines for the calculation of monthly reduction. Briefly, the monthly reductions of LPG-related VOCs were the differences between their averages in September and those in the other months. Hence, positive and negative values indicate reductions and increments of the corresponding species, respectively. It was found that the monthly averages of LPG-related VOCs consistently decreased from September 2013 to May 2014 except for *n*-butane in October 2013 when the program was just initiated. Compared to those before the program (i.e. September 2013), the mixing ratios of propane, *i*-butane and *n*-butane decreased 3.2 ± 0.2 , 2.8 ± 0.2 and 4.9 ± 0.2 ppbv by May 2014, respectively, when 99.2% of catalytic converters participating in the program had been exchanged. Furthermore, the monthly reductions correlated well with the cumulative converter replacements ($R^2 = 0.92$, 0.93 and 0.89 for propane, *i*-butane and *n*-butane, respectively). In contrast, no consistent reduction was observed from September 2012 to May 2013 for LPG-related VOCs suggesting the effectiveness of the program on the reduction of LPG-related VOCs. On the other hand, although the average mixing ratios of NO_x decreased significantly during the program as shown in Table 2, no consistent reductions were found for their monthly averages. This might be due to the fact that NO_x emitted from LPG-fueled vehicles was minor compared to

gasoline- and diesel-fueled vehicles (~ 4.0% from emission inventory, and 3.0–9.7% from source apportionment. See Sect. 3.2.2).

3.1.2 Temporal variations of primary LPG-related VOCs and NO_x

Figure 4 presents the temporal variations of propane and *n*/*i*-butanes at MK from June 2013 to May 2014 covering the periods of both before (i.e., June 2013–September 2013) and during the intervention program (i.e., October 2013–May 2014). It was found that the LPG-related VOCs experienced a significant ($p < 0.05$) reduction throughout the year. The daily changing rates of LPG-related VOCs in two periods, i.e., September–December and January–May, in different years at MK are shown in Table 4. It is noteworthy that the two periods were selected based on data availability each year, and the minimized influence of meteorological parameters in the same month of different years. The LPG-related VOCs decreased from September to December in 2011 and 2013, but there was no significant difference in 2012. In general, the levels of VOCs in the atmosphere are associated with source emissions, photochemical reactions and regional transport. As the regional influence was excluded in this study, source emissions and photochemical reactions became the main factors determining the ambient concentrations of VOCs. The decreasing and unchanged trends in 2011 and 2012 respectively might be related to the integrated influence of reduced photochemical degradation (which increases ambient VOC levels) and temperature decrease (which reduces evaporative emissions of VOCs) from September to December. It is noticeable that the LPG-related VOCs had the highest decreasing rates in September–December 2013, compared to those in previous years. The higher decreasing rates of LPG-related VOCs in September–December 2013 implied the possible effectiveness of the interventional program on VOCs reduction. For the period of January–May, the LPG-related VOCs increased in January–May 2013, except for propane which did not show significant change from January to May. However, significant decreasing trends ($p < 0.05$) were observed for propane and *n*/*i*-butanes during the same period in 2014, which was likely owing to the continuous replacement

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of catalytic converters on LPG-fueled vehicles. By comparison, the reduction rates of LPG-related VOCs in January–May 2014 were all lower than those in September–December 2013. This was mainly attributable to the fact that a large portion (i.e. ~ 69 %) of the converter replacements were completed by the end of December 2013, and the replaced converters were much fewer (i.e. ~ 31 %) in January–May 2014.

Figure 5 shows the temporal variations of primary NO_x , NO, NO_2 and secondary NO_2 at MK from June 2013 to May 2014. The primary NO_x and NO mixing ratios decreased significantly ($p < 0.05$), implying the possible effectiveness of the intervention program on NO / NO_x reduction. However, the secondary NO_2 levels increased, while there was no significant change ($p > 0.05$) for primary NO_2 . To explore the reasons of NO- NO_2 - NO_x variations, the changing rates of primary NO_x , NO, NO_2 and secondary NO_2 during the same period (i.e., June in the previous year to May in the following year) in different years were compared. Table 5 shows the statistics of changing rates of NO_x -NO- NO_2 at the roadside sites (i.e., MK, CWB and Central) from June 2011 to May 2014. Taking MK as an example, the primary NO_x and NO decreased much faster (i.e., 91 and 94 pptv day⁻¹, respectively) from June 2013 to May 2014 than those during the same period in 2011–2012 and 2012–2013, suggesting the effectiveness of the program in reducing NO_x and NO. Compared to the decreasing rate in June 2012–May 2013 (i.e., 13 pptv day⁻¹), no significant change ($p > 0.05$) was observed for primary NO_2 from June 2013 to May 2014. However, it cannot be concluded that the program caused the increase of primary NO_2 , in view of the same insignificant variation in June 2011–May 2012 and the fact that LPG-fueled vehicles emit negligible NO_2 (see Sect. 3.2.2). In contrast, secondary NO_2 significantly increased (with a rate of 13 pptv day⁻¹) from June 2013 to May 2014, which was also observed in June 2011–May 2012 (i.e., increasing rate of 20 pptv day⁻¹). Since secondary NO_2 is formed by NO reacting with O_3 , inspection of the O_3 production would provide more comprehensive interpretation on the secondary NO_2 increment during the program. Similar variations were observed at CWB and Central, where primary NO_x and NO showed

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significant decreasing trends, whereas the variations of primary and secondary NO₂ were insignificant ($p > 0.05$).

In summary, the LPG-related VOCs were significantly lowered during the program with monthly reductions of 3.2 ± 0.2 , 2.8 ± 0.2 and 4.9 ± 0.2 ppbv for propane, *i*-butane and *n*-butane by the end of this study, respectively. Continuous decreasing trends were observed for LPG-related VOCs, and the reduction rates were almost unprecedented, e.g. 39 pptv day^{-1} for *n*-butane. Furthermore, the mixing ratios of NO and NO_x decreased as well during the program. The reduction rates of NO and NO_x during June 2013–May 2014 at the three roadside sites were much higher than those in previous years. Overall, the field measurement data indicated that the program was effective in reducing emissions of LPG-related VOCs and NO_x.

3.2 Variations of LPG contributions to VOCs and NO_x

3.2.1 Source identification

To investigate the change of the contributions of LPG-fueled vehicles to VOCs and NO_x, the online data of 15 VOCs and 3 trace gases at MK before (i.e., 8753 samples during October 2012–September 2013) and during the intervention program (i.e., 5833 samples during October 2013–May 2014) were separately applied to PMF for source apportionments. Figure 6a and b shows the source profiles of the four factors that best reproduced the concentrations of the input species before and during the intervention program, respectively. The source profiles before and during the program were fairly similar. The first factor is distinguished by *n*/*i*-pentanes, benzene, CO, NO₂ and NO. These species are typical tracers of gasoline evaporation and exhaust (Guo et al., 2011; Ho et al., 2009). Therefore, factor 1 represented the source of gasoline vehicles. Factor 2 was closely associated with LPG usage, with the dominance of propane, *n*/*i*-butanes and propene, the major components and combustion product of LPG (Lau et al., 2010; Blake and Rowland, 1995). Factor 3 had high loadings of ethane, ethyne and benzene, which are common indicators of diesel combustion and/or aged

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air masses (Guo et al., 2011; Liu et al., 2008). However, the level of CO, which has a relatively long atmospheric lifetime, was low in this factor. Hence, factor 3 was likely diesel vehicles. Inconsistent with the fact that NO_x and CO are generally abundant in diesel vehicular exhaust, both were low in this factor. This discrepancy might be related to the control strategies to diesel vehicle emissions in Hong Kong. A long-term program replacing better model for diesel commercial vehicles (DCV) has been implemented in Hong Kong since 2007, and the Euro 5 vehicle emission standard was implemented from June 2012, which tightens NO_x emission from DCV by $\sim 40\%$. Furthermore, selective catalytic reduction devices (SCR) were retrofitted on Euro 2 and Euro 3 DCV to upgrade their emission performance to the level of Euro 5 DCV (more details about the DCV emission control strategies in Hong Kong can be found at http://www.epd.gov.hk/epd/english/environmentinhk/air/prob_solutions/air_problems.html). In this context, Ho et al. (2013) reported that the lowest and second lowest CO emissions were from goods vehicle (0.70 ± 0.01 ppmv) and double-decked bus (1.10 ± 0.01 ppmv) at roadsides in Hong Kong, respectively. In addition, it was found that the emission factor of NO_x from diesel vehicles in Hong Kong (31.1 ± 4.7 g kg-fuel $^{-1}$) was much lower than that in many cities in mainland China and overseas (Ning et al., 2012). Therefore, it is not unreasonable that NO_x and CO are low in diesel vehicle exhausts. However, continuous field measurements and laboratory experiments should be conducted to provide more solid evidence. The last factor explained most of the TEX compounds (toluene/ethylbenzene/xylenes), the tracers of solvent usage (Guo et al., 2007; Borbon et al., 2002). Therefore, factor 4 was identified as solvent usage.

3.2.2 LPG contribution

Table 6 shows the concentrations of species assigned in LPG before and during the intervention program, respectively. LPG usage made considerable contributions to VOCs before ($65.7 \pm 0.3\%$) and during ($53.4 \pm 0.2\%$) the program at MK, higher than that quantified at other sites in Hong Kong, i.e., suburban TC ($32.6 \pm 5.8\%$) (Ou et al., 2015), urban TW ($21 \pm 2\%$) (Ling and Guo, 2014) and suburban YL (15%) (Guo et al.,

ancies (SD $\approx \pm 50\%$) were observed in October 2012, February 2013, October 2013, March 2014 and May 2014, which might be because the model did not consider the physical processes, i.e., the horizontal and vertical transport, neither the influence of aerosol particles which would reduce the photolysis rates of VOCs. Nevertheless, it is difficult to consider all these factors in a chemical box model.

To quantitatively evaluate the performance of the model, the index of agreement (IOA) was introduced to test the agreement between the simulated and observed O_3 . Ranging from 0 to 1, higher values of IOA indicate better agreement between the simulation and observation. The IOA was calculated using Eq. (10) (Huang et al., 2005):

$$IOA = 1 - \frac{\sum_{i=1}^n (O_i - S_i)^2}{\sum_{i=1}^n (|O_i - \bar{O}| + |S_i - \bar{O}|)^2} \quad (10)$$

where O_i and S_i are the hourly observed and simulated values, and \bar{O} represents the average of observations. In this study, the IOA reached 0.67, and the accuracy of the simulation was $7.4 \pm 4.1\%$, suggesting good performance of the model in simulating O_3 formation.

3.3.2 Net O_3 production by LPG

Figure 8 shows the O_3 production by VOCs and NO_x in the LPG source. Generally, VOCs and NO_x made positive and negative contributions to O_3 with average values of 0.10 and -0.36 ppbv, respectively. The negative contribution of NO_x was associated with the titration of O_3 by NO. This is consistent with the fact that O_3 formation is generally limited by VOCs rather than NO_x in Hong Kong, which is more significant at the roadside site. From before to during the intervention program, the O_3 production by VOCs slightly decreased from 0.11 to 0.10 ppbv h^{-1} , with an average decreasing rate of -2.9×10^{-5} ppbv day^{-1} . However, this reduction had no statistical significance

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($p > 0.05$) by the end of this study. On the other hand, the O_3 titrated by NO_x decreased significantly ($p < 0.05$) from 0.50 to 0.22 ppbv h⁻¹, with an average decreasing rate of 1.7×10^{-3} ppbv day⁻¹ from before to during the program. When the combined effect of

It was found that LPG emission was generally O_3 destructive at the roadside MK site, and the O_3 destruction decreased from 0.35 to 0.10 ppbv h⁻¹ due to the intervention program, causing an O_3 increase of 0.25 ppbv h⁻¹ (i.e., 4.8 % of the O_3 average at MK). It is noteworthy that the increase was not a sudden change in reality, but was caused by the segmentation of source apportionment (i.e., October 2012–September 2013 and October 2013–May 2014). Indeed, the measurement data also revealed an increasing O_3 trend from October 2012 to May 2014, with a rate of 3.3 pptv day⁻¹ ($p < 0.05$), higher than the O_3 increase caused by LPG. This discrepancy might be related to the O_3 production by other sources and/or other mechanisms not considered in the above simulations, e.g., alkyl nitrate ($RONO_2$) chemistry.

3.4 Photochemical reactivity

3.4.1 The OH and HO_2 budget

As the “detergent” of atmosphere, OH and HO_2 initiate the oxidation of most pollutants including VOCs and NO, leading to the formation of O_3 . Thus, photochemical O_3 production is closely related to the budget of OH and HO_2 . Figure 10 presents the average diurnal profiles of OH and HO_2 in the whole air (i.e., ambient air that is not partitioned into sources) and LPG source. Typical bell-shaped diurnal patterns were observed for OH and HO_2 with the peaks at noon or in the afternoon. However, there was a trough for LPG-related OH in the morning due to high NO in the morning. More discussions are given below in Sect. 3.4.2.

The average simulated concentrations of OH and HO_2 were $9.6 \pm 0.2 \times 10^4$ and $7.9 \pm 0.2 \times 10^4$ molecules cm⁻³ in the atmosphere of the MK site, respectively, much

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lower than those modeled at an urban site in Hong Kong ($2.3\text{--}3.6 \times 10^6$ molecules cm^{-3} for OH and $3.4\text{--}4.4 \times 10^8$ molecules cm^{-3} for HO_2) (Ling et al., 2014), and those measured at a VOC-rich site in PRD (15×10^6 and 18×10^8 molecules cm^{-3} for OH and HO_2 , respectively) (Lu et al., 2012; Lou et al., 2010). The large discrepancy could be caused by the differences in sampling site, sampling period and evaluation method. Firstly, MK was a roadside site with high exposure to vehicle emissions, which significantly consumed OH and HO_2 . Secondly, the study period in this study was the entire year, rather than the O_3 episodes in Ling et al. (2014) and summer in Lu et al. (2012) and Lou et al. (2010). Lastly, the background values were deducted in this study, causing lower OH and HO_2 due to the constrained production pathways (i.e., photolysis of O_3 and formaldehyde). On the other hand, the OH and HO_2 generated by LPG only accounted for $6.3 \pm 0.1\%$ and $13.9 \pm 0.1\%$ of the total OH and HO_2 in the whole air with average concentrations of $(2.4 \pm 0.1) \times 10^3$ and $(12.9 \pm 0.4) \times 10^3$ molecules cm^{-3} , respectively. From before to during the intervention program, the LPG-related OH and HO_2 increased significantly ($p < 0.05$), with a maximum increase of 1.4×10^4 molecules cm^{-3} for OH and 4.0×10^4 molecules cm^{-3} for HO_2 . This might help explain why O_3 increased (4.8%) during the intervention program.

3.4.2 Production and destruction pathways of OH and HO_2

The budget of OH and HO_2 was determined by the production and destruction pathways of HO_x . Figure 11 shows the pathways generating and consuming HO_x in the LPG source before and during the intervention program. Photolysis of formaldehyde (HCHO) and other oxygenated VOCs (OVOCs), and ozonolysis of alkenes were found to be the main sources of HO_x , while the combination of OH with NO_2 and NO was the major sink. It is noteworthy that O_3 photolysis generally makes a positive contribution to HO_x , and constitutes most HO_x in the global scale (Penkett et al., 1997; Armerding et al., 1995; Logan et al., 1981). However, the combined effect of LPG-related VOCs and NO_x was identified to be O_3 destructive, implying that HO_x generated from O_3

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5 photolysis was consumed by LPG emissions. Therefore, the net HO_x production by O₃ photolysis in the LPG source was negative. Moreover, it is well recognized that HONO photolysis significantly contributes to HO_x in the troposphere (Kleffmann et al., 2005; Alicke et al., 2003; Platt et al., 1980). Nevertheless, the model only considered

 10 the reaction of OH with NO for HONO production, without the sources of NO₂ participating in heterogeneous reactions, photolysis of gas-phase nitric acid (HNO₃) and primary emission. That is, only photo-stationary state concentration in the photochemical equilibrium of HONO was considered. Although there was no significant difference ($\rho > 0.1$) between the formation and photolysis rate of HONO, the model simulation

 15 indicated that the formation rate was slightly higher from 05:00–14:00 and lower from 14:00–17:00, causing the destruction and production of HO_x through HONO chemistry in the early and late stages of a day, respectively, consistent with the diurnal variation of NO levels which decreased from morning to afternoon. As shown in Fig. 10, there was a trough for OH in the LPG source in early morning (i.e., 05:00–09:00), which was likely caused by the higher HONO formation than photolysis rate in the morning, and the largest differences between the formation rate and photolysis rate of HONO at 07:00–08:00 (i.e., 5.9×10^4 and 2.4×10^4 molecules cm⁻³ s⁻¹ before and during the program, respectively).

20 Table 7 summarizes the HO_x production and destruction rates of major pathways at MK before and during the intervention program. The total destruction rate (before: $18.1 \pm 0.2 \times 10^5$ molecules cm⁻³ s⁻¹; during: $13.7 \pm 0.1 \times 10^5$ molecules cm⁻³ s⁻¹) was higher than the production rate (before: $10.6 \pm 0.2 \times 10^5$ molecules cm⁻³ s⁻¹; during: $7.6 \pm 0.1 \times 10^5$ molecules cm⁻³ s⁻¹), suggesting that overall HO_x was consumed by the LPG source. This is consistent with the fact that LPG made a negative contribution to

 25 O₃ production. In addition, from before to during the intervention program, both the production and destruction rates of HO_x decreased. However, more significant decrease ($4.4 \pm 0.3 \times 10^5$ molecules cm⁻³ s⁻¹) was observed in destruction rate of HO_x than in production rate ($3.0 \pm 0.3 \times 10^5$ molecules cm⁻³ s⁻¹), which led to the increase of HO_x during the program and resulted in a slight increase of O₃. Given that NO₂ in the LPG

source was generated from NO oxidation, the decrease of the HO_x destruction rate during the program was mainly caused by the decrease of NO in the LPG source.

3.5 Improvement of the intervention program

3.5.1 O₃-VOCs-NO_x sensitivity in the whole air

O₃-VOCs-NO_x sensitivity can reflect the O₃ variation relative to the change of VOCs and NO_x, from which VOC-limited regimes and NO_x-limited regimes in O₃ formation can be indicated. Figure 12a and b show the O₃-VOCs-NO_x sensitivity in the air at MK between 40–100 % and 0.5–40 % of the observed average NO_x, respectively. The ranges were selected according to the O₃ levels and behaviors responding to the variations of VOCs and NO_x (details were given below). This sensitivity diagram was obtained with the aid of the PBM-MCM model, and based on the average primary emission profiles in the atmosphere before the intervention program. The primary emissions were calculated using the method described in Sect. 2.2.4. The abscissa and longitudinal coordinates represent the percentages of NO_x and VOCs relative to the real average values measured at MK (i.e., 100 % NO_x = 252.8 ppbv; 100 % VOCs = 44.6 ppbv). In other words, they reflect the reduction percentages. For example, 80 % NO_x or VOCs means NO_x or VOCs was cut by 20 %. O₃ production was simulated in 220 cases (i.e., 10 VOCs × 22 NO_x), and the maximum O₃ production in each case was extracted.

It was found that within the cutting range of 0–60 % of NO_x (Fig. 12a), O₃ production increased with the increase of VOCs and the decrease of NO_x, indicating a VOC-limited regime in O₃ formation. The black curve, perpendicular to the isopleths of O₃, demonstrated the most sensitive response of O₃ to VOCs and NO_x. Namely, O₃ reduction could be achieved most efficiently towards the abscissa. Using the absolute value of RIR (i.e., |RIR|) as a measure of the O₃-VOCs-NO_x sensitivity, it increased with the reduction of VOCs and NO_x. For example, |RIR| for VOCs and NO_x increased from 0.14 and 0.33 in the scenario of 90 % VOCs and 90 % NO_x, to 0.36 and 1.04 in the scenario of 50 % VOCs and 50 % NO_x, respectively. From before to during the inter-

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vention program, VOCs and NO_x decreased 15.5 and 14.4%, respectively (i.e., from point A to B), causing a slight O₃ increment as described in Sect. 3.3.2. The green and red curves in the lower right corner of Fig. 12a show the O₃ production as a function of VOCs cut before (NO_x = 100%) and during (NO_x = 85.6%) the program, respectively. With the reduction of VOCs, O₃ decreased linearly in the high VOC region (i.e., VOCs higher than 60 and 30% before and during the program, respectively). Since O₃-VOCs-NO_x sensitivity increased during the program, O₃ decreased by 0.10 and 0.14 ppbv with 10% cut of VOCs before and during the program, respectively, which means that O₃ reduction could be achieved more efficiently by further cutting VOCs during the program. However, O₃ stayed stable in the low VOC region (i.e., VOCs lower than 60 and 30% before and during the program, respectively), which might represent the background O₃ with the photochemical production being completely titrated by NO.

With the continuous reduction of NO_x, it was expected that the O₃-VOCs-NO_x sensitivity might change substantially due to the dual role of NO_x in O₃ formation and titration. Figure 12b shows the O₃-VOCs-NO_x sensitivity in the cutting range of 60–99.5% of NO_x. It is noticeable that in the cutting range of ~60–90% of NO_x, O₃ increased with the increase of VOCs and decrease of NO_x, similar to that in the cutting range of 0–60% of NO_x. However, a transition area appeared when NO_x was further cut, where O₃ stayed relatively stable with NO_x variations, and decreased with VOC reductions. This transition area changed from ~6.5–10% (i.e., VOCs = 100%) to ~3.5–6.5% of NO_x (i.e., VOCs = 10%). The appearance of the transition area implied that the titration of O₃ by NO_x reached the minimum level, and further cutting of NO_x might actually cause O₃ reduction. As expected, O₃ decreased with the reduction of NO_x when NO_x was reduced to lower than ~3.75–6.5% (i.e., ~3.75% and ~6.5% for 10 and 100% VOCs, respectively), and responded weakly to VOC variations. This means that O₃ formation switched to a NO_x-limited regime. It should be emphasized that this is the first attempt on the study of O₃-VOCs-NO_x sensitivity at roadsides in Hong Kong, which could be a reference for the formulation and implementation of future air pollution control strategies in Hong Kong.

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3.5.2 O₃-VOCs-NO_x sensitivity in LPG

Figure 13 shows the sensitivity of O₃ variation (i.e., the difference of net O₃ production by LPG before and during the program) relative to the VOCs and NO_x cut in LPG-fueled vehicle emissions from 0 to 100 % with an interval of 20 %. It was found that O₃ uniformly increased with the increase of NO_x cut and that decrease of VOCs cut. To ensure that O₃ would not increase during the program, the reduction of VOCs and NO_x should be within the highlighted area. That is, the highest cutting percentage of NO_x should be less than 29.4 % (i.e., point A). Furthermore, when the cutting percentage of VOCs increased from 20 to 100 %, the maximum cutting percentage of NO_x for zero O₃ increment was between 4.6 and 29.4 %, and the cutting ratio of VOCs / NO_x decreased from 4.3 to 3.4, suggesting that the cutting ratio of VOCs / NO_x should be > 3.4 in order to maintain zero O₃ increment.

Indeed, NO₂ experienced an overall increase from 1999 to 2013 at the roadsides in Hong Kong (HKEPD, 2014). According to this study, secondary NO₂ might be more responsible for the increase. Considering nil-emission of NO₂ (Sect. 3.2.2) and low emission of NO from LPG usage (i.e., 4.0 and 6.4 % based on the emission inventory and source apportionment, respectively), an alternative scheme was proposed. Namely, reasonable cutting ratio of VOCs / NO_x was used to fulfill zero O₃ increase when VOC and NO_x were cut. Although the O₃ production increase was minor (i.e., 0.25 ppbv h⁻¹ or 4.8 %) in this study, this scheme could be applicable in future programs. Moreover, since the reactivity and concentration of VOCs influenced their O₃ formation potential, the relative incremental reactivity (RIR) and RIR-weighted concentration of LPG-related VOCs were calculated. Table 8 shows the RIR and RIR-weighted concentration of propane, propene and *n/i*-butanes. Propene had the highest RIR (i.e., 0.47), suggesting the highest sensitivity of O₃ production to propene. However, *n*-butane in LPG was found to have the highest RIR-weighted concentration (4.87 μg m⁻³), indicating that cutting *n*-butane in LPG source was optimal for O₃ pollution control.

4 Conclusions

In this study, an intervention program, initialized in September 2013 and aimed to reduce emissions of VOCs and NO_x from LPG-fueled vehicles in Hong Kong, was evaluated. The results indicated that LPG-related VOCs and NO_x decreased significantly during the program, when higher reduction rates were observed for LPG-related VOCs and NO_x compared to those in previous years. Source apportionment revealed that propane, *n/i*-butanes and NO in LPG-fueled vehicle emissions were significantly lower during than before the program. It was therefore concluded that the program was remarkably effective in reducing VOCs and NO_x. To evaluate the program more comprehensively, the variation of O₃ production was simulated with the PBM-MCM model. It was found that LPG-fueled vehicular emission was generally O₃ destructive at the roadside MK site, and the O₃ destruction decreased from 0.35 to 0.10 ppbv due to the intervention program, causing an O₃ production increase of 0.25 ppbv h⁻¹ (4.8%). Although the HO_x production rate decreased due to the VOC reduction in LPG-fueled vehicle emissions, the constraint on NO emission led to a more significant decrease in the HO_x destruction rate than in the production rate, which caused a slight increment of OH and HO₂ during the program, in line with the fact that O₃ increased slightly during the implementation of the program. To improve the program for future application, an O₃-VOCs-NO_x sensitivity analysis was conducted for ambient air that is not partitioned to sources, and the LPG-fueled vehicle emission source. The NO_x-limited regime in O₃ formation was only found when NO_x was reduced to less than 5%. Furthermore, the maximum NO cutting percentage of 29.4% and the lowest cutting ratio of VOCs / NO_x (i.e., 3.4) were determined to maintain zero O₃ increment.

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Table 1. Ratios of toluene / benzene and xylenes / ethylbenzene at MK and other sites in Hong Kong from October 2012 to May 2014 (unit: ppbv ppbv⁻¹).

	Toluene / benzene	Xylenes / ethylbenzene
MK (roadside site)	4.1 ± 0.04	3.0 ± 0.02
MK* (roadside site)	11.3 ± 0.9	5.7 ± 0.2
TC (general site)	0.7 ± 0.1	–
YL (general site)	3.7 ± 0.04	2.4 ± 0.02
HT (background site)	2.5 ± 0.1	1.8 ± 0.03

MK* refers to VOCs at MK with the background values being removed.

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Table 2. Production and destruction pathways of HO_x considered in this study.

Production	Destruction
$\text{HCHO} + h\nu$	$\text{OH} + \text{NO}_2$
$\text{O}_3 + \text{alkenes}$	$\text{OH} + \text{NO}$
Other OVOCs + $h\nu$	$\text{O}_3 + h\nu$
	$\text{HO}_2 + \text{HO}_2$
	$\text{OH} + \text{HO}_2$
	$\text{HO}_2 + \text{RO}_2$

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[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)**Table 3.** Mixing ratios of LPG-related VOCs and NO_x before and during the program (unit: ppbv).

Species	Before	During
Propane	8.5 ± 0.1	5.8 ± 0.1
<i>i</i> -Butane	6.6 ± 0.1	4.7 ± 0.1
<i>n</i> -Butane	13.2 ± 0.2	8.4 ± 0.1
NO	201.7 ± 2.1	172.0 ± 2.7
NO ₂	25.9 ± 0.3	23.8 ± 0.4
NO _x	229.4 ± 2.3	197.7 ± 3.0

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Table 4. Changing rates of propane and *n*/*i*-butanes in September–December and January–May in different years (ppbv day⁻¹).

Time period		Sep–Dec			Jan–May	
Site	Species	2011	2012	2013	2013	2014
MK	Propane	-0.015	-0.004*	-0.017	0.004*	-0.014
	<i>i</i> -butane	-0.010	-0.008*	-0.021	0.012	-0.005
	<i>n</i> -butane	-0.023	-0.009*	-0.039	0.016	-0.028

* The changing rate insignificant ($p > 0.05$); the bold numbers are changing rates during the implementation of the program.

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Table 5. Changing rates of primary NO_x , NO , NO_2 and secondary NO_2 (ppbv day⁻¹).

Site	Species	Jun 2011–May 2012	Jun 2012–May 2013	Jun 2013–May 2014
MK	$[\text{NO}_x]_{\text{prim}}$	-0.004	0.040*	-0.091
	$[\text{NO}]_{\text{prim}}$	0.004*	0.053	-0.094
	$[\text{NO}_2]_{\text{prim}}$	0.008*	-0.013	0.003*
	$[\text{NO}_2]_{\text{sec}}$	0.020	-0.002*	0.013
CWB	$[\text{NO}_x]_{\text{prim}}$	-0.055*	0.089*	-0.121
	$[\text{NO}]_{\text{prim}}$	-0.048*	0.081*	-0.127
	$[\text{NO}_2]_{\text{prim}}$	-0.010*	0.004*	0.006*
	$[\text{NO}_2]_{\text{sec}}$	0.014	-0.001*	0.006*
Central	$[\text{NO}_x]_{\text{prim}}$	-0.041*	0.180	-0.187
	$[\text{NO}]_{\text{prim}}$	-0.045*	0.161	-0.188
	$[\text{NO}_2]_{\text{prim}}$	0.005*	0.018	0.002*
	$[\text{NO}_2]_{\text{sec}}$	0.011*	-0.004*	-0.001*

* The changing rate is insignificant ($p > 0.05$); the bold numbers are changing rates during the implementation of the program.

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Table 7. Production and destruction rates of main HO_x pathways at MK.

Pathways	HO _x production/destruction rates/ molecules cm ⁻³ s ⁻¹ (× 10 ⁵)	
	Before	During
HCHO + <i>hν</i>	6.31 ± 0.08	4.29 ± 0.04
O ₃ + alkenes	3.22 ± 0.04	2.68 ± 0.03
Other OVOCs + <i>hν</i>	1.02 ± 0.02	0.58 ± 0.01
O ₃ + <i>hν</i> *	-2.69 ± 0.03	-0.51 ± 0.01
OH + NO*	-2.82 ± 0.04	-1.21 ± 0.02
OH + NO ₂ *	-12.58 ± 0.11	-11.95 ± 0.10

* Negative values indicate HO_x destruction.

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**Table 8.** RIR and RIR-weighted concentrations of LPG-related VOCs.

	RIR (%/%)	RIR-weighted concentration ($\mu\text{g m}^{-3}$)
Propane	0.10	1.21
Propene	0.47	1.02
<i>i</i> -butane	0.20	2.43
<i>n</i> -butane	0.20	4.87

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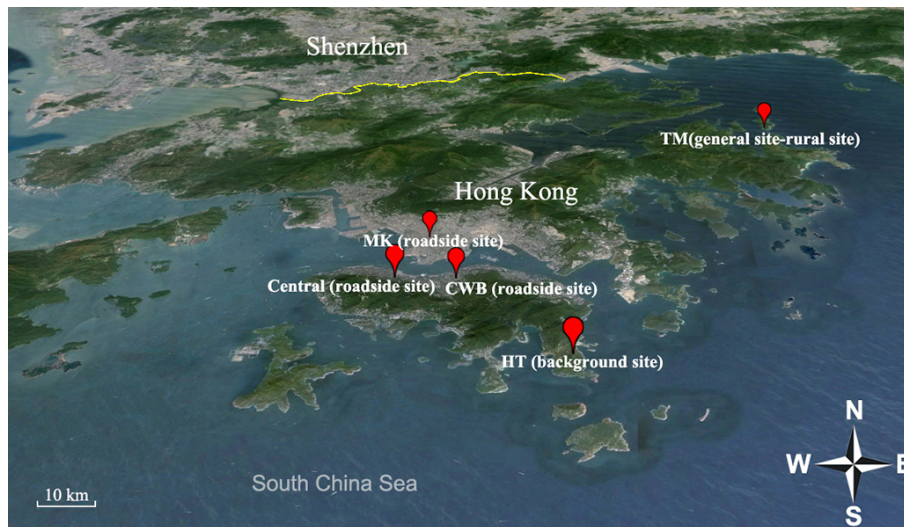


Figure 1. Geographical location of the sampling sites. The yellow line represents the border between Hong Kong and mainland China.

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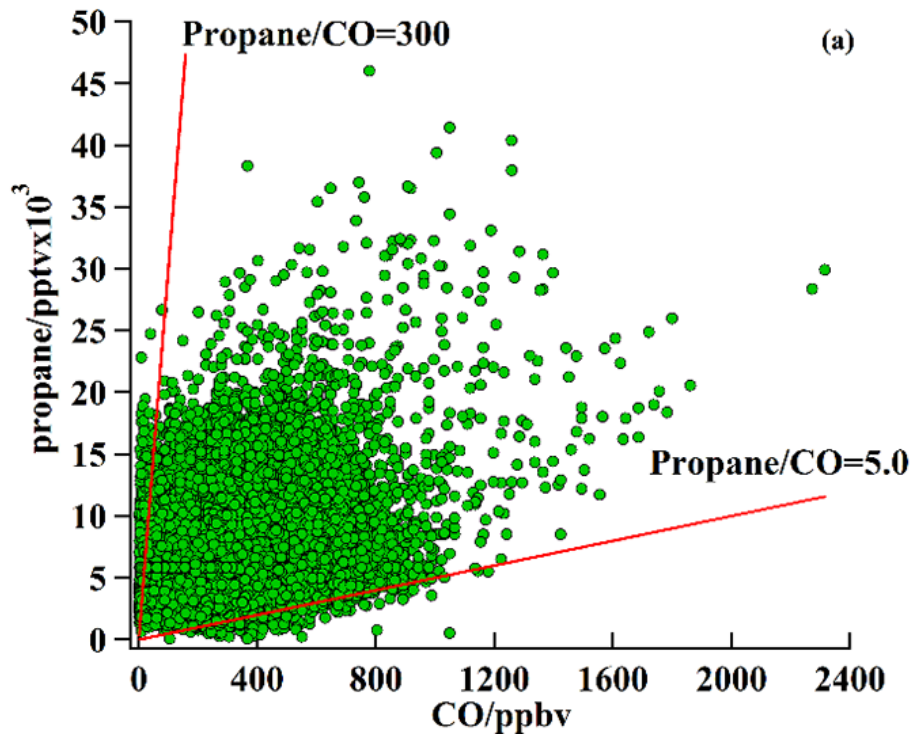


Figure 2. Hourly ratio of propane/CO at MK during 2011–2014.

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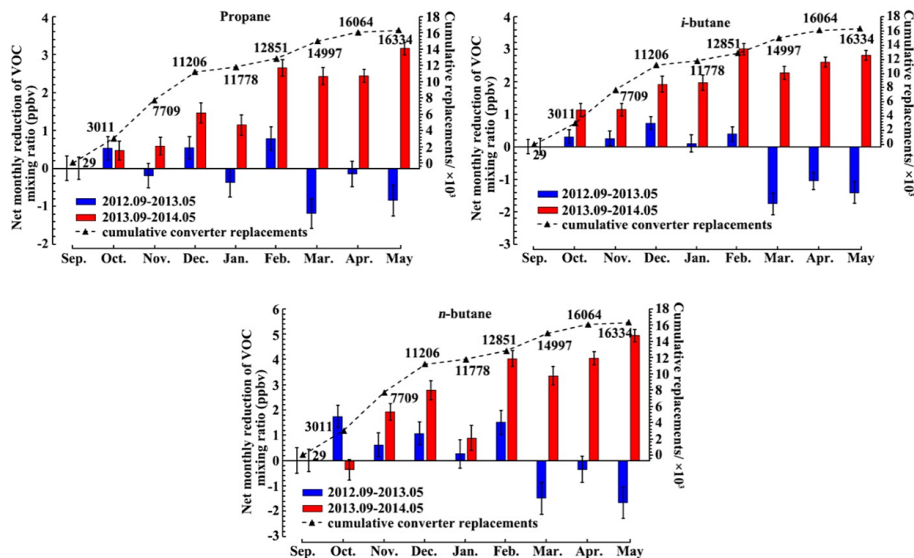


Figure 3. Monthly reductions of LPG-related VOCs at MK before (blue bar) and during (red bar) the program (the average value of VOC species in September is the baseline. The values along the dot line were the cumulative numbers of converters replaced. The bars above and below the x axis refer to the reduction and increase of VOC mixing ratio, respectively).

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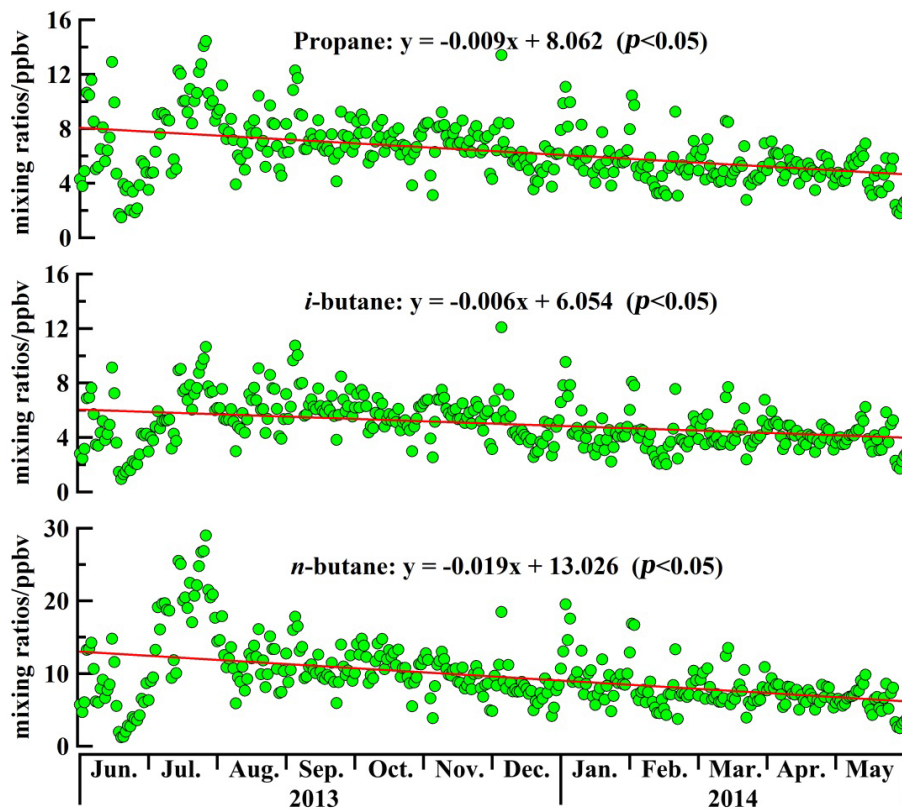


Figure 4. Temporal variations of propane and *n*/*i*-butanes at MK from June 2013 to May 2014.

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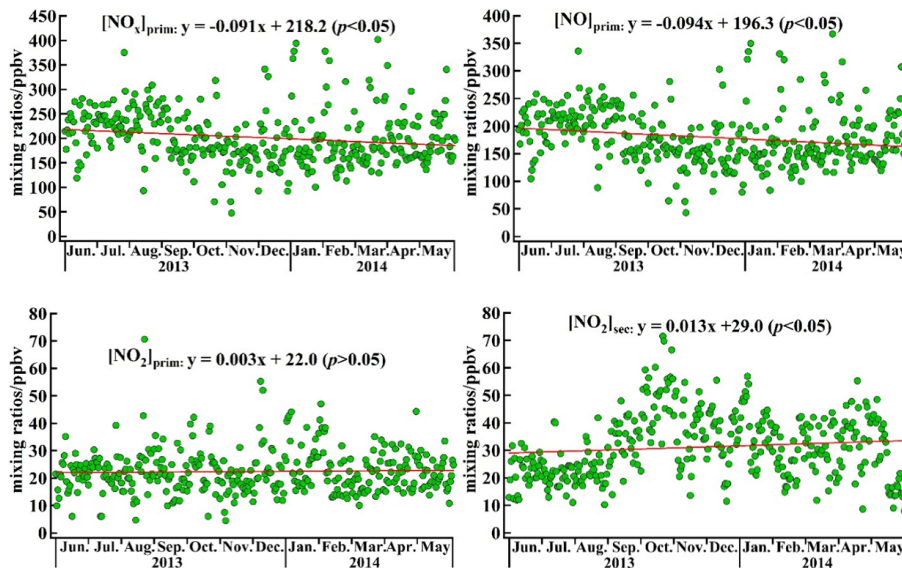


Figure 5. Temporal variations of primary NO_x , NO, NO_2 and secondary NO_2 at MK from June 2013 to May 2014.

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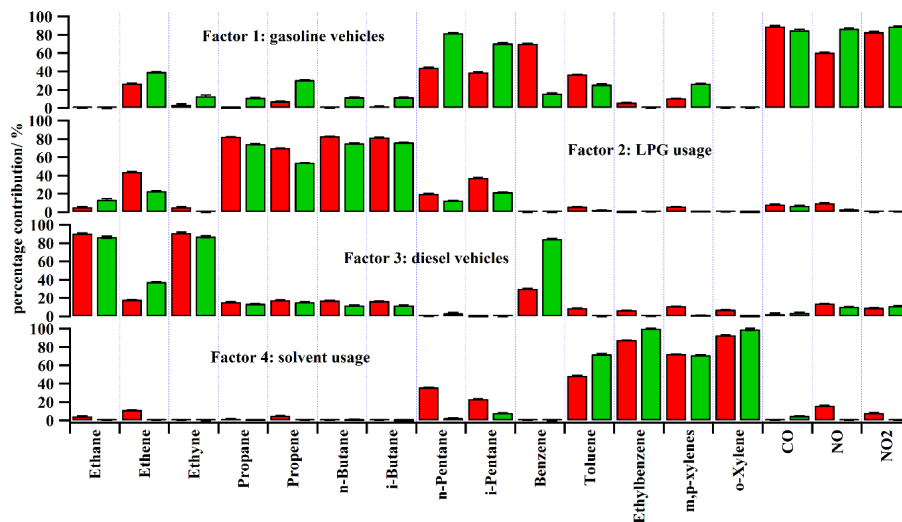


Figure 6. Source profiles resolved by PMF. Red and green bars represent the percentage contributions before and during the intervention program, respectively. The standard errors are estimated with the bootstrap in the model.

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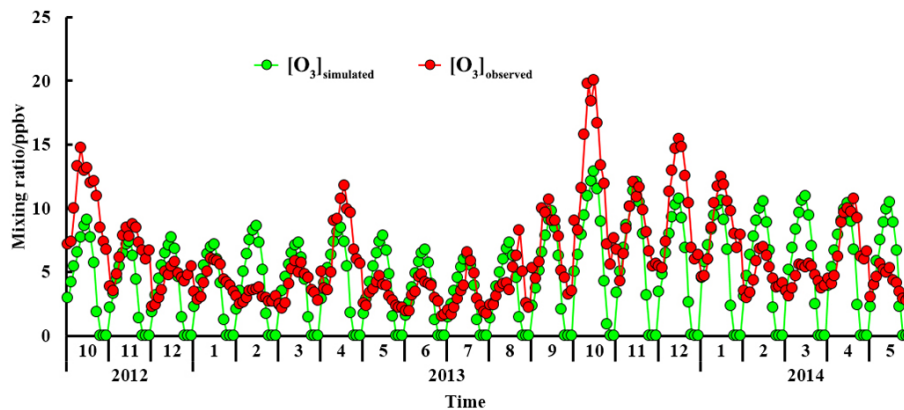


Figure 7. Simulated and observed O₃ at daytime hours (07:00–19:00 LT) at MK.

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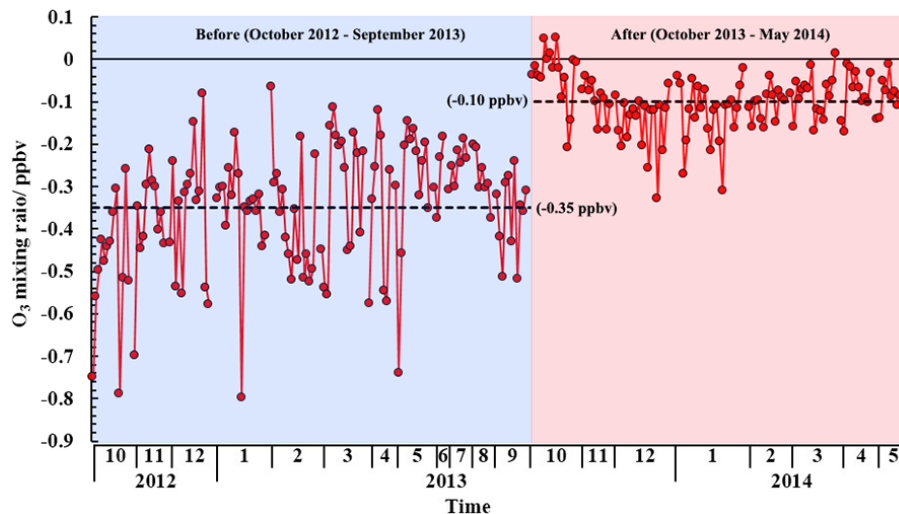


Figure 9. O_3 production by LPG at MK from October 2012 to May 2014. The blue and red highlighted areas represent the period before and during the intervention program with average values (dashed lines), respectively.

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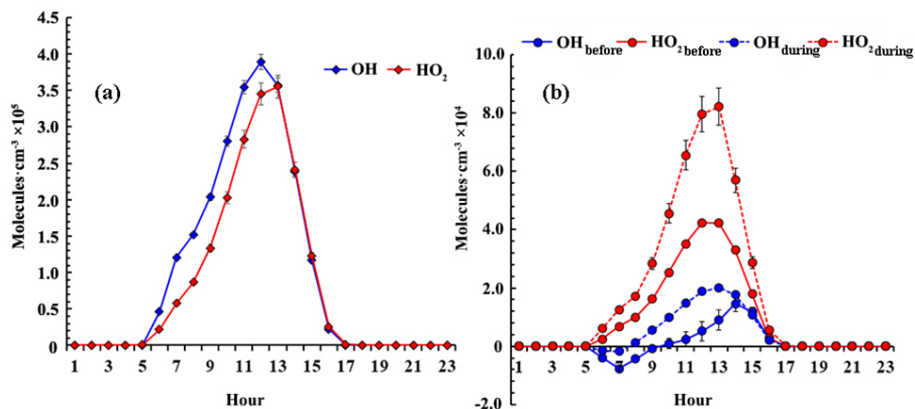


Figure 10. Diurnal profiles of OH and HO₂ in (a) the whole air and (b) LPG source.

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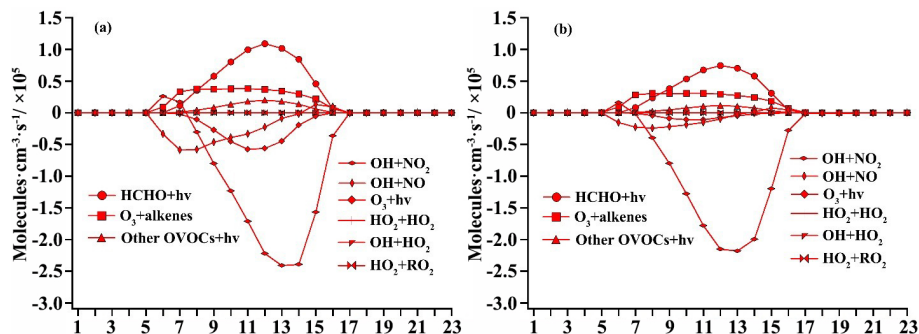


Figure 11. Production and destruction pathways of HO_x in LPG source at MK (a) before, and (b) during the program.

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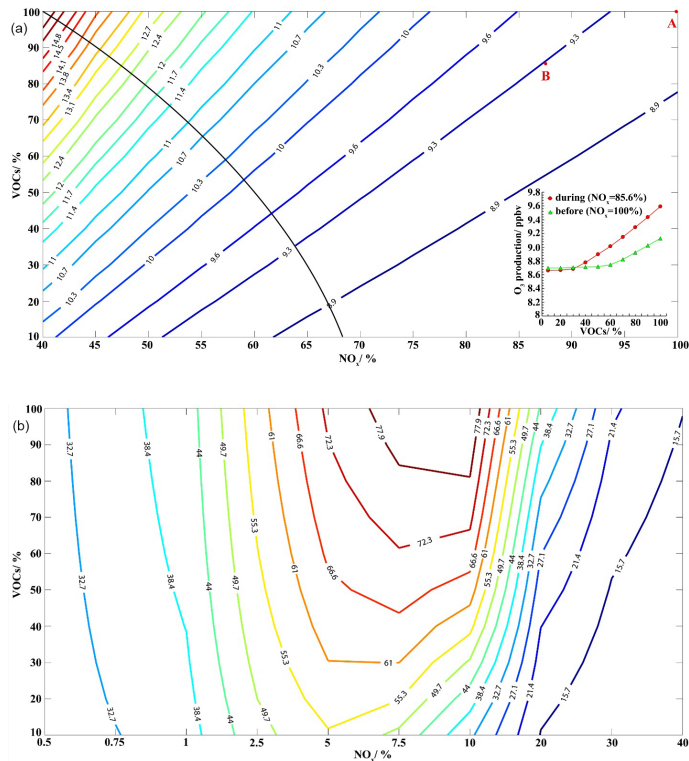


Figure 12. (a) O₃-VOCs-NO_x sensitivity within the cutting range of 0–60 % of NO_x. The black curve demonstrates the most sensitive response of O₃ to VOCs and NO_x. Points A and B represent the O₃-VOCs-NO_x relationship before and during the program, respectively. The green and red curves in the small legend show the O₃ production as a function of VOC cuts before and during the program, respectively. **(b)** O₃-VOCs-NO_x sensitivity within the cutting range of 60–99.5 % of NO_x.

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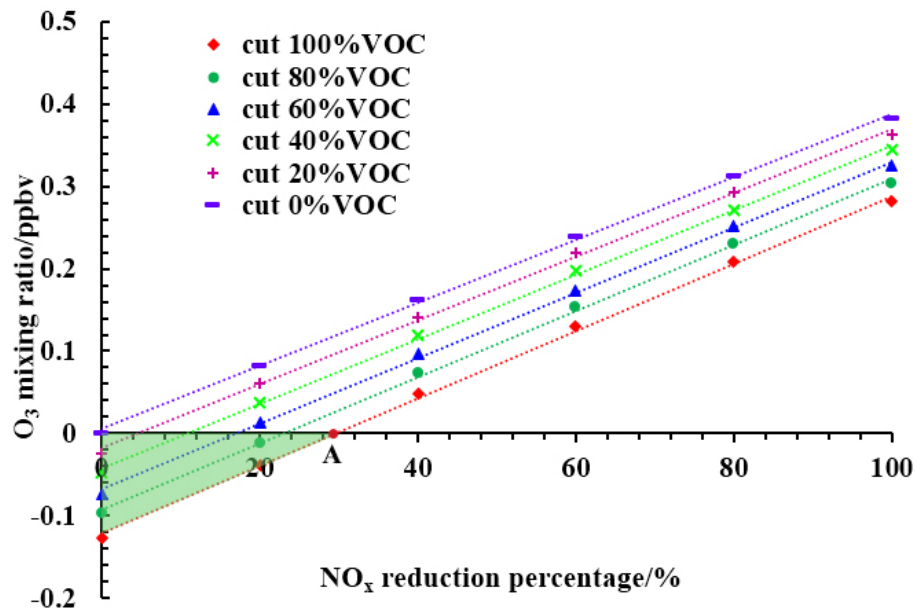


Figure 13. Variation of O₃ mixing ratio as a function of VOCs and NO_x reduction in LPG.