1   **Continuous effectiveness of replacing catalytic converters on liquified petroleum gas-**
2   **fueled vehicles in Hong Kong**

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11   **Abstract**

12   To mitigate the concentrations of air pollutants in the atmosphere, an intervention program of
13   replacing the converters of liquefied petroleum gas (LPG) fueled vehicles was implemented by
14   the Hong Kong government between October 2013 and April 2014. Data of ambient volatile
15   organic compounds (VOCs) and other trace gases continuously monitored from September
16   2012 to April 2017 at a roadside site were used to evaluate the continuous effectiveness of the
17   replaced catalytic converters on the reduction of air pollutants. The measurement data showed
18   that LPG-related VOCs (propane and n/i-butanes) and several trace gases (CO, NO and NO_2)
19   decreased significantly from before to after the program ($p < 0.01$). To further assess the
20   efficiency of the program, five periods covering before the program, during the program, 1st
21   year after the program, 2nd year after the program and 3rd year after the program were
22   categorized. The values of propane and n/i-butanes decreased from Period-1 (before the
23   program) to Period-2 (during the program), and from Period-2 to Periods 3-5 (after the program)
24   ($p < 0.01$). In addition, the reduction rates of propane and n/i-butanes remained high and
25   constant in Periods 3-5, suggesting that either had the vehicle owners themselves routinely
26   replaced the converters at suitable interval afterwards, or were their vehicles caught by a remote
27   sensing program checking excessive emissions. Source apportionment analysis indicated that
28   LPG-fueled vehicular emissions were the top contributor to ambient VOCs in the roadside
29   environment while the VOCs emitted from LPG-fueled vehicles indeed decreased at a rate of
30   4.21 ± 2.38 ppbv/year (average $\pm$ 95% confidence interval) from Period-1 to Period-5 ($p <$
31   0.01). Furthermore, the photochemical box model simulations revealed that the net negative

32 contribution of VOCs and NO_x emitted from LPG-fueled vehicles to O_3 production
33 strengthened at a rate of 1.9×10^{-2} pptv/day from Period-1 to Period-5 ($p < 0.01$). The findings
34 proved the continuous effectiveness of the intervention program, and are of help to future
35 control strategies in Hong Kong.

36 **Keyword**: Continuous effectiveness; catalytic converter; LPG-fueled vehicle; VOCs; O_3

37 1 Introduction

38 During the past decades, many cities in the world including Hong Kong have been suffering
39 from severe ozone (O_3) pollution (Jacob, 1999; NARSTO, 2000; So and Wang, 2003; Lam et
40 al., 2005; Wang et al., 2017, 2018). It is essential to mitigate O_3 pollution due to its adverse
41 effects on the environment and human health (Sillman, 1999; Seinfeld and Pandis, 2006).
42 Being key O_3 precursors, volatile organic compounds (VOCs) and nitrogen oxides (NO_x) are
43 important chemicals contributing to high O_3 production in Hong Kong and the adjacent Pearl
44 River Delta (PRD) region (Zhang et al., 2007; Shao et al., 2009; Guo et al., 2007, 2013; Wang
45 et al., 2017). Previous studies revealed that O_3 formation is sensitive to VOCs in urban areas
46 of this region (Cheng et al., 2010; Ling et al., 2011), and subsequently it is a foreseeably
47 effective way to control O_3 pollution through constraining the VOCs concentrations in the
48 atmosphere (Ling et al., 2011). Hence, understanding the characteristics of VOCs and
49 quantifying their source apportionments are fundamental for the formulation and
50 implementation of O_3 control strategies.

51 To improve air quality, the Hong Kong government has implemented a series of control
52 measures in the past decades, mainly focusing on the reduction of air pollutants from emission
53 sources such as motor vehicles and solvent usage (HKEPD, 2007, 2014). With the execution
54 of these control measures, VOCs emissions from some sources have been under control (Ling
55 and Guo, 2014; Huang et al., 2015; Lyu et al., 2017). For example, Huang et al. (2015) found
56 that VOCs emitted from diesel and gasoline vehicles decreased by at least 37% in 2011
57 compared to those in 2003 at the same roadside site in Hong Kong. Lyu et al. (2017) reported
58 that VOCs emitted from diesel exhaust and solvent usage decreased whereas the gasoline and
59 liquefied petroleum gas (LPG) vehicle emissions elevated from 2005 to 2013. Indeed, due to
60 the widespread LPG use in public transport since 2001, VOCs emissions from LPG-fueled
61 vehicles and their contributions to O_3 production gradually increased in the last decade (Guo
62 et al., 2011; Ho et al., 2013; Ou et al., 2015; Lyu et al., 2016a, 2017). Specifically, LPG usage

even accounted for 30% of the ambient non-methane hydrocarbons (NMHCs) in suburban Hong Kong (Ou et al., 2015). With the aid of the positive matrix factorization (PMF) model, Lyu et al. (2016) revealed that LPG fuel consumption was the largest source of VOCs at a roadside site during October 2012-September 2013, accounting for 50% of the total VOCs in Hong Kong.

To specifically reduce air pollutant emissions from LPG-fueled vehicles in Hong Kong, an intervention program of replacing the catalytic converters on LPG-fueled vehicles was undertaken from October 2013 to April 2014 (HKEPD, 2014). In this program, a total of about 17,000 taxis and light buses took part in (Environment Bureau, 2017). To assess the immediate effectiveness of this program on pollutant emissions from LPG-fueled vehicles, Lyu et al. (2016a) compared the data at a roadside site before the program (June – September 2013) with that after the program (October 2013 – May 2014), and claimed that VOCs and nitrogen oxides (NO_x) emitted from LPG-fueled vehicles significantly reduced, notwithstanding very minor increase of O_3 production (Lyu et al., 2016a). Despite instant usefulness, it was reported that the catalyzing capacity of the converters would gradually fade away with the time of use (Heck and Farrauto, 2001; Sharma, et al., 2014). Since the mileages of many LPG-fueled vehicles are very high (e.g. several hundred kilometers per day for many taxis), the catalytic converters need to be replaced approximately every 18 months (Simpson et al., 2015). Hence, it is necessary to evaluate the continuous effectiveness of the intervention program on the reduction of air pollutant emissions from LPG-fueled vehicles.

The main objective of this study was to assess the continuous effectiveness of replacing catalytic converters on LPG-fueled vehicles in Hong Kong. To achieve it, the evolution of air quality at a roadside station in Hong Kong was studied between 2012 and 2017, a long period covering the three stages of before, during and after the implementation of the replacement program. The long term trends of LPG tracers were examined, and a detailed comparison was conducted among different stages of this program. Furthermore, a PMF model and a photochemical box model incorporating Master Chemical Mechanism (PBM-MCM) were applied to understand the changes of the contribution of LPG-fueled vehicles to ambient VOCs and the ground-level O_3 production caused by the replacement program.

2 Methodology

2.1 Sampling site

Continuous measurements of target air pollutants were conducted at an urban roadside location in Hong Kong, namely Mong Kok (MK) site. MK site (22.32°N, 114.17°E, 3 m a.g.l.) is one of the three urban roadside monitoring stations (MK, Causeway Bay and Central) set up by the Hong Kong Environmental Protection Department (HKEPD). The site is located at the junction of Nathan Road and Lai Chi Kok Road, Mong Kok, Kowloon (Figure1), which is surrounded by residential and commercial building blocks with heavy daily traffic (Lee et al., 2002). As an urban roadside station, MK site is less influenced by regional air masses and the main local sources are traffic emissions (Lee et al., 2002; Cui et al., 2016).

Figure 1. Location of (a) the sampling site and (b) the surrounding environment

2.2 Measurements of target air pollutants
2.2.1 Trace gases

Trace gases including SO_2, CO, O_3, NO and NO_2 were continuously monitored at MK from September 2012 to April 2017. CO was analyzed using the method of non-dispersive infrared absorption with gas filter correlation; SO_2 was detected with UV fluorescence analyzers; NO–NO_2–NO_x was measured by chemiluminescence technique; An UV photometric analyzer was used to monitor O_3 mixing ratio. The detection limits for CO, SO_2, NO, NO_2 and O_3 were 50.0, 1.0, 0.5, 0.5 and 2.0 ppbv, respectively. All the instruments were regularly calibrated and tested with the instruments and quality control and assurance (QC/QA) procedures identical to those in the US air quality monitoring program (Ou, et al., 2015; Lyu et al., 2016a; Wang et al., 2017).

2.2.2 Volatile Organic Compounds (VOCs)

Non-methane hydrocarbons (NMHCs) were measured by an online analyzer (Syntech Spectras GC 955, Series 600/800, Netherlands). The instrument is an integrated separating and analytical system consisting of two sampling systems and two columns for separation of the C_2-C_5 hydrocarbons and the C_6-C_{10} hydrocarbons, respectively (HKPU, 2012). The target species included 30 VOCs (10 alkanes, 10 alkenes, 1 alkyne and 9 aromatics). Ambient air samples were collected and analyzed every 30-minute continuously. The 30-minute concentrations were averaged into hourly values for further analysis (Ou, et al., 2015; Lyu et al., 2016a; Wang et al., 2017).

2.3. Quality assurance and quality control (QA/QC)

Strict QA/QC procedures were followed to assure the data quality. Built-in computerized programs of QC system, e.g., auto-linearization and auto-calibration were developed for the analyzer. Weekly calibrations were conducted by injecting certified calibration gas (National Physical Laboratory span gas). Additionally, independent comparisons with canister samples analyzed by UC-Irvine were carried out. Overall, the detection limits of the target NMHCs ranged from 2 to 787 pptv. The accuracy of the measurements was about 1-10% and the measurement precision was about 2.5-20%. More details about the QA/QC protocols can be found in the previous studies (Xue et al., 2014; Ou et al., 2015; Lyu et al., 2016a).

2.4 Theoretical calculation

The ratios of VOCs with different photochemical reactivity against hydroxyl radical (OH) are calculated as a measure of photochemical age (Guo et al., 2007). As *m,p*-xylene and toluene are more reactive than ethylbenzene and benzene, respectively, higher ratios of *m,p*-xylene/ethylbenzene and toluene/benzene indicate the relatively fresher air masses (Guo et al., 2004, 2007). During the study period, the average ratios of *m,p*-xylene/ethylbenzene and toluene/benzene were 2.27 ± 0.11 (average $\pm$ 95% confidence interval) and 4.17 ± 0.32 ppbv/ppbv, respectively. Compared to the values (1.3–1.8) in urban/rural areas in Hong Kong (Guo et al., 2007), the ratio of *m,p*-xylene/ethylbenzene in this study was higher, but comparable to the level (2.61 ± 0.30) measured in a tunnel in Hong Kong (Ho et al., 2009) where freshly vehicular emissions dominated. For the ratio of toluene/benzene (4.17 ± 0.32), it was much higher than that in aged air masses (~ 0.3) in Hong Kong (Lau et al., 2010), and comparable to the typical value from vehicular exhaust (~ 2) (Scheff and Wadden, 1993).

148   Hence, the air masses at MK site were generally fresh and predominantly influenced by local

149   vehicular emissions. Thus, characterizing the VOC mixing ratios at MK site would provide

150   reliable information of the influences of the emissions from local sources on air quality.

151   **2.5 Description of models**

152   **2.5.1 Positive matrix factorization (PMF) model**

153   PMF is a mathematical receptor model developed by U.S. Environmental Protection Agency

154   (EPA) that can analyze a wide range of environmental sample data. As the large number of

155   variables in the actual data set obtained, PMF could reduce the variables and combine them

156   into similar source types according to the specific research problems. The source types are

157   identified by comparing them to measured profiles of each source and source contributions are

158   used to determine how much each source contributed to a sample (https://www.epa.gov/ air-

159   research/positive-matrix-factorization-model-environmental-data-analyses). These results are

160   calculated through the function of the PMF model by analysis based on the measured data at

161   the receptor site. The equation of the model is presented by Eq. (1), with two metrics, i.e., factor

162   contributions and factor profiles, included and exported in the PMF results:

163
$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{1}$$

164   where x_{ij} is the jth species concentration measured in the ith sample, g_{ik} is the species

165   contribution of the kth source to the ith sample, f_{kj} is the jth species fraction from the kth source,

166   e_{ij} is the residual for each sample/species, and p is the total number of independent sources

167   (Paatero, 1997, 2000). In this study, the hourly concentrations of VOCs and CO with the

168   proportion of missing values less than 40% were included in the input file. Values lower than

169   the detection limit (DL) were replaced with DL/2. The uncertainties were set

170   as $\sqrt{(10\% \times concentration)^2 + DL^2}$ and 5/6 × DL for the samples with their concentrations

171   higher and lower than the DL, respectively. The model ran 20 times with a random seed, and

172   the optimum solution automatically recommended by the model was accepted. To keep

173   consistency of the source profiles, the data from the entire study period were input into the

174   model as a whole. Note that to reduce the interference of high rates of missing data on the

175   model performance, not all the measured VOCs were included in source apportionment (Wang

176   et al., 2017). After data filtration, the hourly values of 14 VOCs, CO and NO at MK were

177   applied to PMF for source apportionment. The source contributions extracted from the model

178   were separately calculated for each period.

179   **2.5.2 PBM-MCM model**

180   A photochemical box model incorporating the master chemical mechanism (PBM-MCM) was

181   utilized to simulate the local O_3 formation. The PBM-MCM model has been successfully

182   applied in Hong Kong and been verified reliable in simulating O_3 and photochemical processes

183   (Lam et al., 2013; Ling et al., 2014). In this study, the hourly measurements of VOCs, trace

184   gases and meteorological parameters (temperature and relative humidity) at MK were used to

185   construct the model. The daytime (07:00- 19:00) simulations were conducted for the whole

186   study period. Figure S1 shows the diurnal patterns of the simulated and observed O_3 in Periods

187   1-5 at MK. In general, the simulated O_3 fit the observed values well in terms of magnitude and

188   diurnal patterns. The index of agreement (IOA), which indicates the matching degree between

189   the simulated and observed O_3 (Eq. (2)), was used to evaluate the model performance (Huang

190   et al., 2005; Lyu et al., 2016b; Wang et al., 2017).

191
$$IOA = 1 - \frac{\sum_{i=1}^{n}(o_i - s_i)^2}{\sum_{i=1}^{n}(|o_i - \bar{o}| + |s_i - \bar{o}|)^2} \tag{2}$$

192   where o_i and s_i are observed and simulated hourly values, respectively, $\bar{o}$ represents the

193   average observed values, and n is the sample number. The range of IOA is 0-1. The higher the

194   IOA value is, the better agreement between simulated and observed values is (Huang et al.,

195   2005). In this study, the IOA is 0.73 for all the results, suggesting good performance of the

196   model in O_3 simulation.

197   **3. Results and Discussion**

198   **3.1 Temporal variations of trace gases and LPG-related VOCs**

199   To better understand the variations of VOCs and trace gases, the study period was divided into

200   three stages: before (September 2012-September 2013), during (October 2013-April 2014) and

201   after the replacement program (May 2014-April 2017). Due to the widespread usage of LPG

202   as vehicle fuel, the ambient VOC profile in Hong Kong changed substantially and the most

203   abundant species switched from toluene to propane and *n/i*-butanes (Guo et al., 2007; Ou et al.,

204   2015). Besides, the source profiles acquired in previous studies showed that propane and *n/i*

205   butanes were the most dominant components in LPG-fueled vehicular exhausts in Hong Kong

206   (Ho et al., 2009; Guo et al., 2011, 2015; Lyu et al., 2015). Hence, propane and *n/i*-butanes were

207   referred as LPG-related VOCs hereafter. Figure 2 shows the temporal variations of the mixing

208   ratios of total VOCs and LPG-related VOCs from September 2012 to April 2017. The TVOC

209   concentrations decreased with a rate of -6.68 ± 1.40 ppbv/year (*p* < 0.01) at this roadside site

210   in the study period, which is contradictory to an increasing rate of 0.34 ± 0.02 ppbv/year at a
211   suburban site from 2005 to 2013 reported by Lyu et al. (2015), implying some control measures
212   on VOCs might be effective since 2013. For the LPG-related VOCs, it was found that propane,
213   *i*-butane and *n*-butane decreased significantly, with a rate of -1.25 ± 0.27 ppbv/year ($p < 0.01$),
214   -0.98 ± 0.17 ppbv/year ($p < 0.01$) and -2.11 ± 0.42 ppbv/year ($p < 0.01$) respectively, perhaps
215   implying the continued effectiveness of the replacement program even after 36 months. Table
216   1 summarizes the average mixing ratios of trace gases and LPG-related VOCs at MK before,
217   during and after the replacement program. The mixing ratio of propane, *i*-butane and *n*-butane
218   was 5.51 ± 0.55, 3.75 ± 0.26 and 6.21 ± 0.33 ppbv after the program, respectively, significantly
219   lower than that before the program (propane: 9.27 ± 0.76; *i*-butane: 6.85 ± 0.62; *n*-butane: 13.57
220   ± 1.5 ppbv) ($p < 0.01$). Since the regional influence was minor in the roadside environment,
221   changes in source emissions were believed to be the main factor leading to the decreases of
222   LPG-related VOCs (See Section 2.4). In fact, prior to this replacement program (before
223   September 2013), the levels of LPG-related VOCs (propane and *n/i*-butanes) were even
224   enhanced significantly at the same MK site since 2003 (Huang et al, 2016; Lyu et al., 2016a),
225   while their values were remarkably reduced during the replacement of the catalytic converters
226   on LPG-fueled vehicles (Lyu et al., 2016a), reflecting the immediate usefulness of this control
227   policy. The continued reduction of the LPG-related VOCs after 3-year replacement of the
228   converters in this study revealed the sustained effectiveness of the program. In addition to LPG-
229   related VOCs, the mixing ratios of primary pollutants, i.e., CO, NO_2, NO and SO_2, all decreased
230   from before to after the program ($p < 0.01$). However, the levels of secondary O_3 increased
231   from 5.5 ± 1.5 ppbv before the program to 9.4 ± 2.0 ppbv during the program and 8.8 ± 1.1
232   ppbv after the program. Figure S2 in the Supplementary Material shows the temporal variations
233   of CO, SO_2, NO, NO_2 and O_3 at MK from September 2012 to April 2017. Consistent with the
234   variations at different stages in Table 1, CO, NO_2, NO and SO_2 showed decreasing trends with
235   a rate of -47.5 ± 26.1, -1.9 ± 0.5, -28.3 ± 3.9 and -6.0 ± 1.5 ppbv/year, respectively.
236   Nevertheless, these decreases should not be fully counted by LPG-fueled vehicles as they
237   accounted for a small fraction of on-road vehicles (HKEPD, 2014). Indeed, apart from this
238   replacement program, Hong Kong government also launched other three control programs
239   including 1) "Reducing the emissions from diesel commercial vehicle (DCV)" started in March
240   2014; namely, all DCVs in Hong Kong must comply with the Euro IV emission standard by
241   the end of 2019 (HKEPD, 2013); 2) "Retrofitting selective catalytic reduction (SCR) devices
242   on Euro II and III franchised buses" started in May 2014; and "Franchised bus low emission

243   zones" started on 31 December 2015

244   (https://www.epd.gov.hk/epd/english/environmentinhk/air/prob_solutions/cleaning_air_atroa

245   d.html). Thus, the decreases of CO, SO_2, NO and NO_2 particularly after March 2014 were likely

246   the integrated impacts of these programs. Reversely, the O_3 levels increased with a rate of 1.18

247    $\pm$ 0.61 ppbv/year ($p < 0.01$) in the study period. This is not surprising because NO titration

248   effect was weakened with the decrease of NO mixing ratio from 170.3 ± 11.0 ppbv before the

249   program to 135.7 ± 12.2 ppbv during the program, and then to 92.1 ± 10.5 ppbv after the

250   program, resulting in the enhancement of O_3 levels at the roadside site. The results implied the

251   continuous effectiveness of the intervention program on LPG-related VOCs reduction and

252   possible combined impact on trace gases of both LPG and the other three programs. In

253   particular, the converters on LPG-fueled vehicles replaced between October 2013 and April

254   2014 seemed still effective after more than three years.
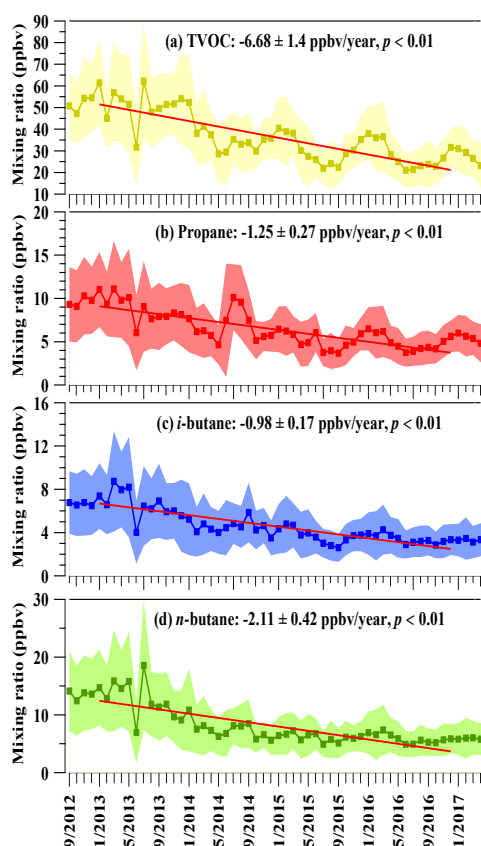
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256   **Figure 2.** Temporal variations of total VOCs and LPG-related VOCs from September 2012 to

257   April 2017. The shaded area indicates the standard deviation of the data.

258 **Table 1.** Mixing ratios of trace gases and LPG-related VOCs (ppbv) at MK (average ± 95%
259 confidence intervals)

|	Before	During	After
CO	912.3±59.2	944.5±105.1	771.1±44.4
SO$_2$	10.5±1.5	12.9±2.3	6.5±0.8
NO$_2$	62.2±5.3	65.2±6.5	47.1±2.3
NO	170.3±11.0	135.7±12.2	92.1±10.5
O$_3$	5.5±1.5	9.4±2.0	8.8±1.1
propane	9.27±0.76	7.18±0.80	5.51±0.55
***i*-butane**	6.85±0.62	5.13±0.56	3.75±0.26
***n*-butane**	13.57±1.5	9.2±1.26	6.21±0.33
TVOC	53.04±4.1	48.97±5.7	32.46±2.0

260

3.2 LPG-related VOCs in the same months of different years

3.2.1 LPG-related VOCs in the atmosphere at various stages

263 To better evaluate the replacement program, the influence of the weather conditions on the
264 changes of trace gases and VOCs needs to be minimized. To do so, the mixing ratios of trace
265 gases and VOCs in the same months of different years were used for comparison, because the
266 inter-annual differences of meteorological conditions were relatively minor for the same
267 months (Lyu et al., 2015). Since the replacement program was from October 2013 to April
268 2014, we categorized the study period into five time spans: Period-1: October 2012 - April
269 2013 (before); Period-2: October 2013 - April 2014 (during); Period-3: October 2014 - April

270   2015 (first-year after); Period-4: October 2015 - April 2016 (second-year after); and Period-5:

271   October 2016 - April 2017 (third-year after the program).

272   Figure 3 shows the box plot of the mixing ratios of LPG-related VOCs in different time spans.

273   Clearly, the values of propane and *n/i*-butanes decreased from Period-1 (propane: 10.1 ± 0.58

274   ppbv; *i*-butane: 7.21 ± 0.64 ppbv; *n*-butane: 13.97 ± 0.88 ppbv) to Period-2 (7.18 ± 0.80 ppbv;

275   5.13 ± 0.56 ppbv; 9.20 ± 1.26 ppbv, respectively), and from Period-2 to Periods 3-5 ($p < 0.01$),

276   while propane and *n*-butane showed insignificant changes for Periods 3-5 ($p > 0.05$). The

277   unchanged levels of LPG-related VOCs from Period-3 to Period-5 suggested the immediate

278   and sustained usefulness of this replacement program.

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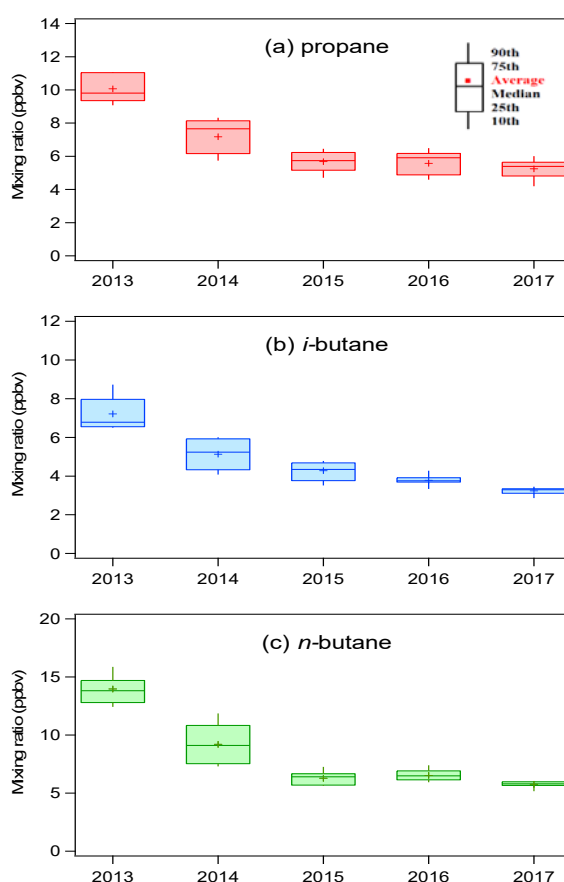
280   **Figure 3.** Box plot of the mixing ratios of LPG-related VOCs in different periods.

281   **3.2.2 Net reduction of LPG-related VOCs**

282   To further look into the utility of the replacement program, the net reduction of LPG-related

283   VOCs in different periods of the replacement program was calculated and compared (Figure

284   4). The monthly averages of LPG-related VOCs in Period-1 were used as the baselines for the

285   calculation of the net reductions. Namely, for each species, its [net reduction] = [monthly
286   average]$_{before}$ – [monthly average]$_{after}$. Hence, positive and negative values indicated reductions
287   and increments of the corresponding species, respectively.

288   Obviously, the values of the three species in Periods 2-5 were positive, indicating the net
289   reduction of LPG-related VOCs during (Period-2) and after the program (Periods 3-5), relative
290   to those before the program. The net reductions of propane, *i*-butane and *n*-butane in Period 2
291   were 2.9 ± 1.0 ppbv, 2.1 ± 1.0 ppbv and 4.8 ± 1.8 ppbv, respectively. It was also found that the
292   reduction amount of the three species was lower in the first several months (October –
293   December) due to the fact that the converter replacement was done step by step and there were
294   fewer number of LPG-fueled vehicles replaced in October-December 2013 (Lyu et al., 2016a).
295   The results are the same as our previous study in which we found that the LPG intervention
296   program was immediately effective on VOC reductions during the replacement of the
297   converters (Lyu et al., 2016a). Most interestingly, the reduction rates of propane and *n/i*-
298   butanes remained high and constant after the program (i.e., Periods 3-5), suggesting that the
299   LPG replacement program was still in effect even after three years. This indicated that either
300   had the vehicle owners themselves routinely replaced the converters at suitable interval
301   afterwards, or might their vehicles been caught by a remote sensing program checking
302   excessive emissions.

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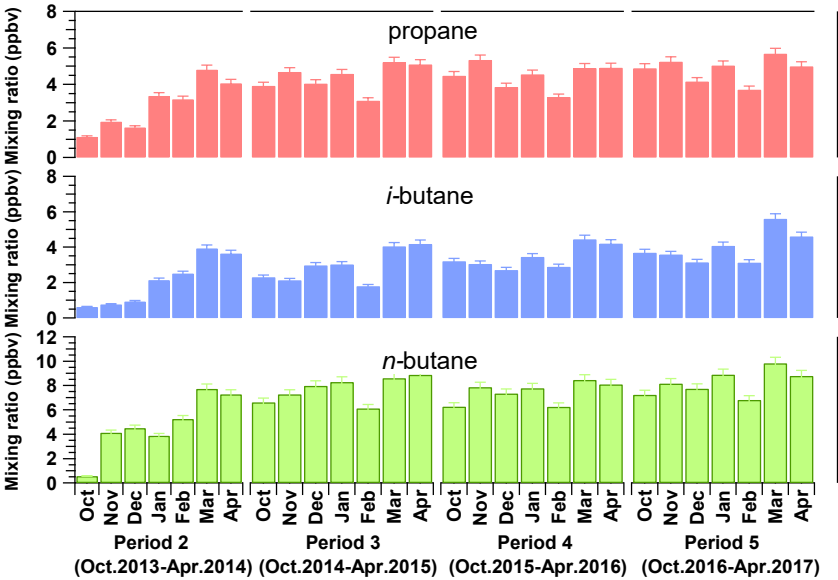
304   **Figure 4.** Net reduction of LPG-related VOCs in different periods of the intervention program.

305

### 3.3. Temporal variations of source contributions to LPG-related VOCs

307 As propane and *n/i*-butanes observed in the atmosphere may not exclusively originate from
308 LPG-fueled vehicular emissions, source apportionment is necessary to know the contributions
309 of different sectors to them, and the variations of LPG-fueled vehicle source contributions to
310 propane and *n/i*-butanes with time. In this way, the actual effect of the replacement program
311 can be obtained. Hence, the contributions of the identified emission sources to VOCs and trace
312 gases (CO and NO) in the five different periods were compared.

313 After the PMF running, four sources including gasoline vehicular exhaust, solvent usage, diesel
314 vehicular exhaust and LPG-fueled vehicles were identified (see Figure 5). Source 1 was
315 characterized by high percentages of C_2 species (ethane, ethene and ethyne), *n/i*-pentanes,
316 benzene and toluene, and a considerable percentage of CO and NO, indicating vehicular
317 emissions, likely from gasoline-fueled vehicles as *n/i*-pentane, benzene and toluene are good
318 tracers of gasoline exhaust in Hong Kong (Tsai et al., 2006; Ho et al., 2009; Guo et al., 2011).

319 Source 2 was dominated by high percentages of toluene, ethylbenzene and xylenes (*m,p*-
320 xylenes and *o*-xylene), with the proportions higher than those in other VOC source profiles.
321 With a certain amount of these species and low contributions of C_2 hydrocarbons, CO and NO,
322 the source was defined as solvent usage rather than vehicular emissions. These species could
323 emit from paints, inks, sealant, varnish and thinner for architecture and decoration (Borbon et
324 al., 2002; Liu et al., 2008; Ling and Guo, 2014).

325 Source 3 was distinguished by high emissions of C_2 hydrocarbons particularly ethane and
326 ethene, and NO. Compared to source 1, this factor made much lower contributions to *n/i*-
327 pentanes, eliminating the possibility of gasoline exhaust. In addition, a certain amount of CO
328 confirmed this source as diesel exhaust.

329 Source 4 was dominated by high percentages of propane and *n/i*-butanes, which are typical
330 tracers of LPG exhaust (Blake and Rowland, 1995; Liu et al., 2008). In addition, ethene,
331 propene and CO showed high levels in the source profile, indicating that this source was related
332 to combustion. Indeed, previous roadside and exhaust samples demonstrated that LPG-fueled
333 vehicles emit significant amount of ethene and propene (Tang et al., 2007; Ling and Guo, 2014).
334 Compared to sources 1 and 3, there were very minor emissions of benzene, toluene and
335 ethylbenzene, which was a feature of LPG-fueled vehicular exhaust.

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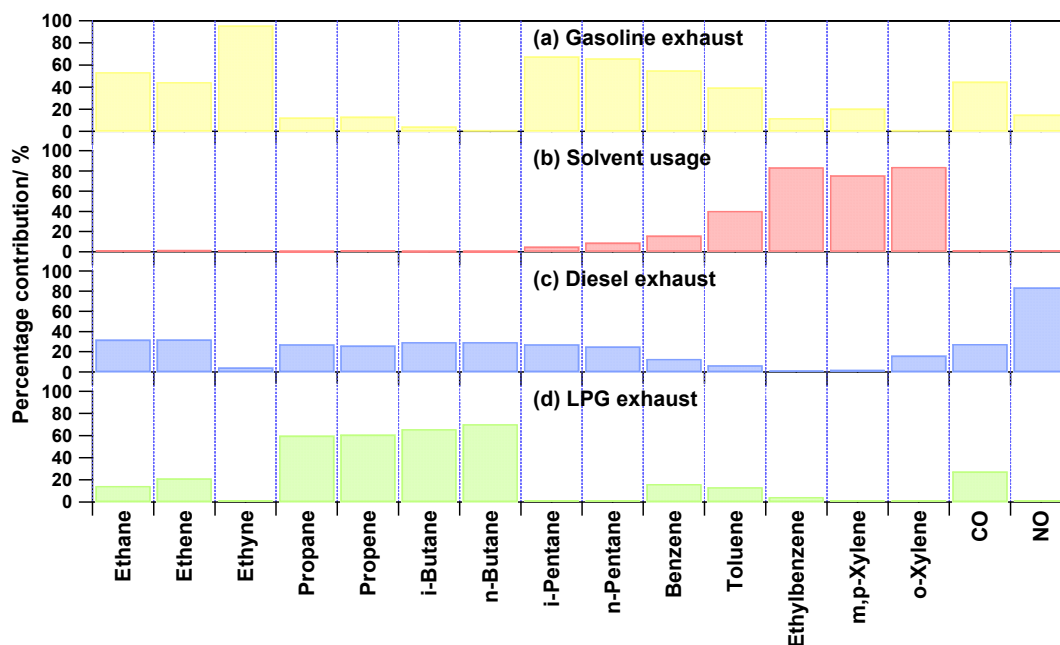
Figure 5. Average source profiles of VOCs and CO extracted from the PMF modeling at MK

Table S1 in the Supplementary Material shows the average mass concentration of each source and its percentage contribution to the total VOCs. The LPG-fueled vehicular emission was the most predominant contributor to VOCs in the roadside environment, with the average mass concentration of 17.96 ± 0.16 μg/m^3, followed by diesel exhaust (9.07 ± 0.11 μg/m^3) and gasoline exhaust (8.60 ± 0.08 μg/m^3). The contribution of solvent usage was the lowest with mass concentration of 1.05 ± 0.02 μg/m^3. The results of source apportionment reflected the urgent necessity of controlling LPG-fueled vehicular emissions, in line with Lyu et al (2016a) who found that LPG exhaust accounted for $39.1 \pm 0.1\%$ - $51.5 \pm 0.1\%$ of VOCs measured at MK.

Figure 6 shows the PMF-resolved temporal trends of VOCs emitted from each individual source from Period-1 to Period-5. The VOCs emitted from LPG-fueled vehicles decreased from Period-1 (before) to Period-2 (during) then to Periods 3-5 (1 to 3 years after the LPG program) ($p < 0.01$), with a rate of 4.21 ± 2.38 ppbv/year. In fact, the reduction of VOC emissions from LPG-fueled vehicles was previously identified by Lyu et al. (2016a). Here, the steady decline of LPG emitted VOCs after the replacement program likely indicated the continuous effectiveness of the LPG program on VOC control. The VOCs from diesel vehicular exhaust decreased at a rate of -3.93 ± 1.34 ppbv/year ($p<0.01$), indicating that the DCV program was in force, consistent with the results of Lyu et al. (2017). Different from the findings of Lyu et al. (2017), VOCs from solvent usage did not show significant change during the study period

14

356 ($p > 0.1$), likely due to the fact that the MK site was a roadside site mainly affected by vehicular

357 emissions (84 - 92%), and it was not appropriate to study the annual trend of solvent usage at

358 this roadside site. In addition, the VOCs originated from gasoline vehicular exhaust also had

359 no significant change at this roadside site throughout the study period, perhaps related to the

360 stable number of gasoline-fueled vehicles running at this roadside site between 2012 and 2017

361 in Hong Kong (HKATC, 2016).

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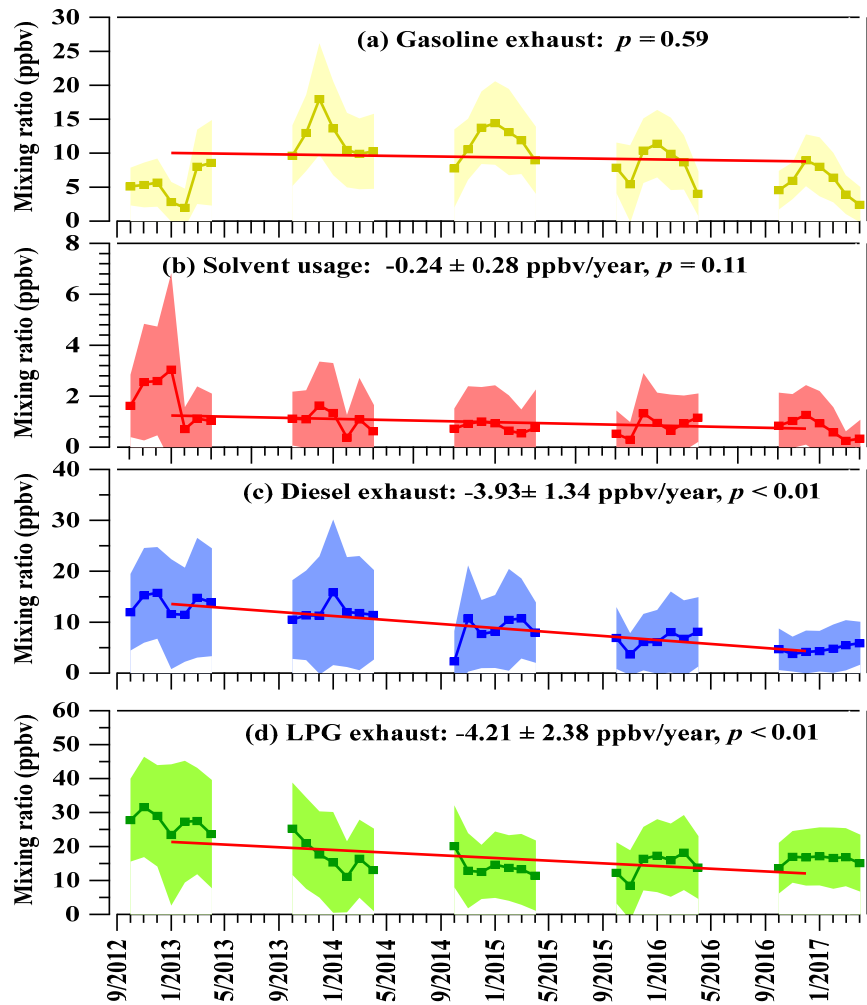
363 **Figure 6.** PMF-resolved temporal trends of VOCs emitted from each individual source from

364 Period-1 to Period-5. The shaded area indicates the standard deviation of the data.

3.4 Influence of the replacement program on ozone production

366 As VOCs and NO_x are key precursors of tropospheric O_3, it is of interest to investigate how the

367 reductions of VOCs and NO_x in LPG exhaust affected the O_3 production at the roadside site

368 (MK). Firstly, O_3 was simulated by the PBM-MCM model (section 2.5.2) with the observed

369   concentrations of air pollutants as input, referred to as the base scenario. Then, a constrained

370   scenario was constructed, in which VOCs and NO_x emitted from LPG-fueled vehicles were

371   excluded from the model input according to the source apportionment (section 3.3). The

372   removal of VOCs and NO_x were conducted separately or together. When only the VOCs in

373   LPG exhaust were removed from the input of the constrained scenario, the difference of the

374   simulated O_3 between the base and constrained scenario represented the contribution of LPG-

375   related VOCs to O_3 production. Similarly, the contributions of LPG-related NO_x and the entire

376   LPG exhaust inclusive of VOCs and NO_x to O_3 were also simulated, which are shown in Figure

377   7.

378   Overall, LPG exhaust made minor contributions to O_3 at MK, ranging from -4 ± 0.7 pptv to -

379   6.7 ± 0.7 pptv (~ 2.4% - ~ 3.1% of the observed O_3). The overall negative contribution of the

380   LPG exhaust to O_3 was explained by the greater O_3 depletion due to the titration by LPG

381   emitted NO than the O_3 production by LPG emitted VOCs. From Period-1 to Period-5, the

382   daily average O_3 production by LPG-related VOCs increased significantly at a rate of 3.7×10^{-2}

383   pptv/day ($p < 0.01$). At the same time, the O_3 depletion by LPG emitted NO also increased

384   significantly at a rate 6.1×10^{-2} pptv/day ($p < 0.01$). As a result, the net negative contribution of

385   the LPG exhaust to O_3 production varied from -4 ± 0.7 pptv in Period-1 to -6.7 ± 0.7 pptv in

386   Period-5, at a rate of 1.9×10^{-2} pptv/day ($p < 0.01$).

387   It is noteworthy that VOCs and NO emitted from LPG-fueled vehicles decreased from period-

388   1 to period-5 ($p < 0.01$), inconsistent with the enhanced positive contribution of LPG emitted

389   VOCs and negative contribution of LPG emitted NO to O_3 production. We found that the

390   observed O_3 increased significantly at MK from 2012 to 2017, with an average rate of 1.18 ±

391   0.61 ppbv/year. This increase was likely caused by other reasons, but not by the variation of

392   LPG exhaust which generally made minor negative contributions to O_3 production. It was

393   reasonable that the increase of O_3 enhanced the oxidative capacity of the atmosphere and hence

394   the oxidation efficiency of VOCs at MK. This explained why the decreased LPG-emitted

395   VOCs made increased contribution to O_3 production from period-1 to period-5. Similarly, the

396   increase of O_3 also accounted for the increased O_3 depletion by LPG emitted NO, though in

397   reality LPG-related NO decreased due to the replacement program. This implied that the

398   effectiveness of some O_3 control measures might be masked or even reversed due to the

399   uncontrolled increase of O_3 caused by other factors.
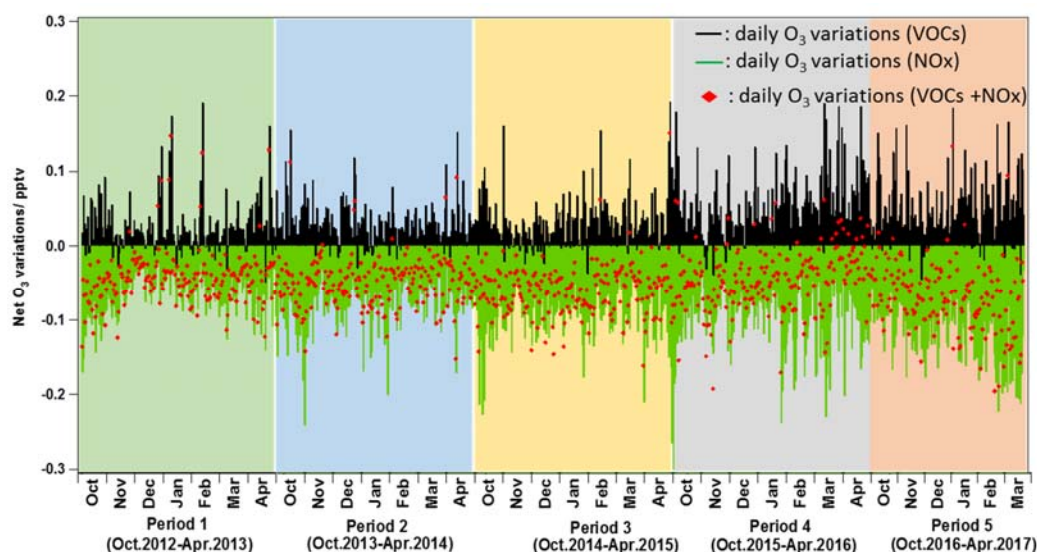
Figure 7. Net O_3 variations caused by VOCs, NO_x and VOCs + NO_x emitted from LPG-fueled vehicles. The shaded area indicates the Periods 1-5 separately.

4 Conclusions

Between October 2013 and April 2014, ~75% of the old converters on LPG-fueled vehicles were replaced to improve air quality in Hong Kong. While our previous study indicated the immediate effectiveness of this program, whether it still played a role in air quality improvement was unknown to us. In this study, online trace gases and VOCs collected at MK from September 2012 to April 2017 were examined to assess the continuous effectiveness of replacing catalytic converters on LPG-fueled vehicles. The LPG-related VOCs, particularly propane and n/i-butanes, decreased significantly in the study period, implying effective control of VOC emissions. The reduction rates of propane and n/i-butanes remained high and constant after the program (i.e., Periods 3-5), suggesting that the vehicle owners routinely replaced the converters at suitable interval afterwards, or their vehicles might be caught by a remote sensing program checking excessive emissions. Furthermore, source apportionment analysis indicated that LPG-fueled vehicular emissions were the most predominant contributor to ambient VOCs. Fortunately, VOCs emitted from LPG-fueled vehicles decreased from 2012 to 2017, which was likely benefited from the continuous effectiveness of the intervention program on VOC control. Though the O_3 depletion by LPG exhaust increased from Period-1 to Period-5, the observed O_3 increased at MK ($p < 0.01$), due to the fact that LPG only made minor negative contribution to O_3 production which however might be enhanced by some other factors. During the study

17

period, measures have been taken to restrict emissions from diesel and gasoline fueled vehicles in Hong Kong, such as phase III of the DCV program, retrofitting of SCR and establishment of low emission zones. These control measures might also contribute to the decrease of LPG-related VOCs. However, it could be anticipated that the reductions of VOC emissions from LPG-fueled vehicles played more important role, as propane and n/i-butanes were mostly emitted from LPG-fueled vehicles according to the source apportionment. Therefore, this study implied the continuous effectiveness of the LPG replacement program and would help policy-makers formulate future control strategies on vehicle emissions in Hong Kong. The impacts of the continuous emission reductions from LPG-fueled vehicles on air quality in entire Hong Kong (spanning from the urban to rural areas) and even in the greater PRD are to be evaluated.

Acknowledgements

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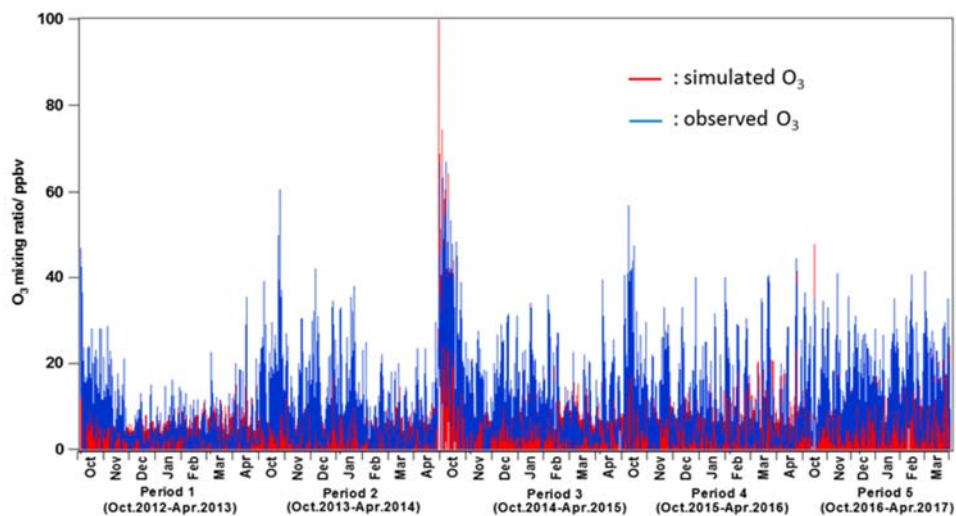
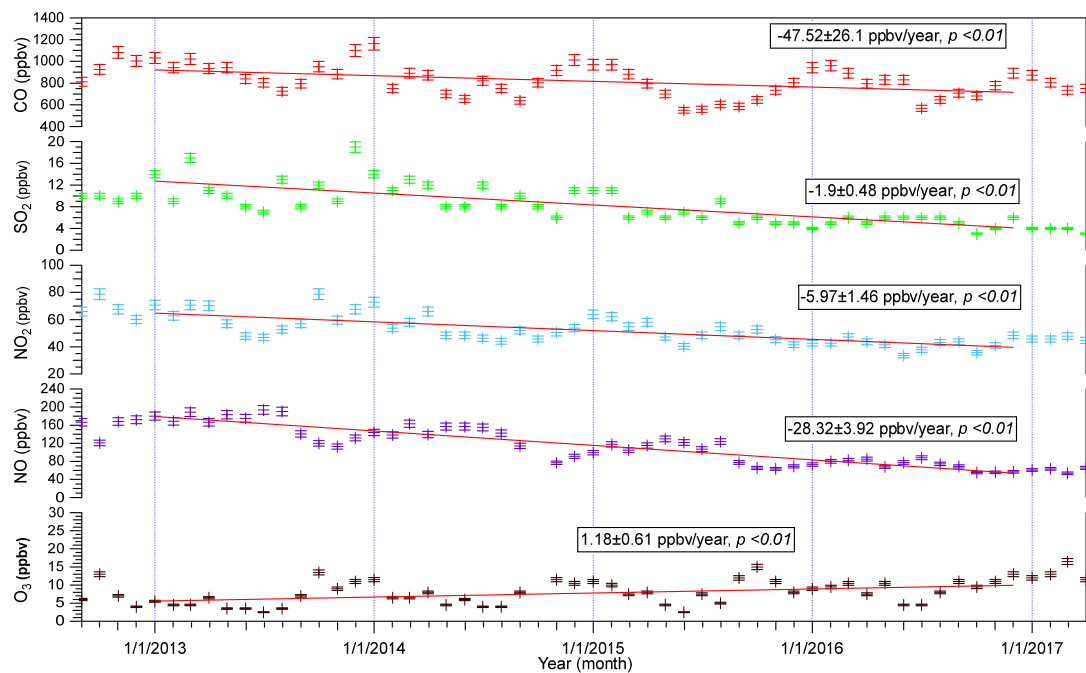574   Atmos. Chem. Phys. 7, 557-573.

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583   **Supplementary Materials**

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585   **Figure S1:** Variations of hourly simulated and observed O_3 during daytime hours (07:00–19:00)

586   at MK.

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589   **Figure S2:** Variations of monthly average trace gases at MK from September 2012 to April

590   2017