1	Inter-comparison of O_3 formation and radical chemistry in the past decade at a suburban site in
2	Hong Kong

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10 Abstract

11 Hong Kong, as one of the densely populated metropolises in East Asia, has been suffering from severe photochemical smog in the past decades, though the observed nitrogen oxides 12 13 (NO_x) and total volatile organic compounds (TVOCs) were significantly reduced. This study, based on the observation data in the autumns of 2007, 2013 and 2016, investigated the 14 15 photochemical ozone (O_3) formation and radical chemistry during the three sampling periods in Hong Kong with the aid of a Photochemical Box Model incorporating the Master 16 17 Chemical Mechanism (PBM-MCM). While the simulated locally produced O₃ remained unchanged (p=0.73) from 2007 to 2013, the observed O₃ increased (p<0.05) at a rate of 1.78 18 19 ppbv/yr driven by the rise in regionally transported O_3 (1.77 ± 0.04 ppbv/yr). Both the 20 observed and locally produced O_3 decreased (p < 0.05) from the VOC sampling days in 2013 to those in 2016 at a rate of -5.31 ± 0.07 and -5.52 ± 0.05 ppbv yr⁻¹, respectively. However, a 21 levelling-off (p=0.32) was simulated for the regionally transported O₃ during 2013 – 2016. 22 23 The mitigation of autumn O₃ pollution in this region was further confirmed by the continuous 24 monitoring data, which has never been reported in previous studies. Benefited from the air 25 pollution control measures taken in Hong Kong, the local O₃ production rate decreased

26 remarkably (p < 0.05) from 2007 to 2016, along with the lowering of recycling rate of 27 hydroxyl radical (OH). Specifically, VOCs emitted from the source of liquefied petroleum 28 gas (LPG) usage and gasoline evaporation decreased in this decade at a rate of -2.61±0.03 ppbv yr⁻¹, leading to a reduction of the O₃ production rate from 0.51 ± 0.11 ppbv h⁻¹ in 2007 to 29 0.10 ± 0.02 ppbv h⁻¹ in 2016. In addition, solvent usage made decreasing contributions to both 30 VOCs (rate = -2.29 ± 0.03 ppbv yr⁻¹) and local O₃ production rate (1.22 ± 0.17 and 0.14 ± 0.05 31 32 ppbv h^{-1} in 2007 and 2016, respectively) in the same period. All the rates reported here were 33 for the VOC sampling days in the three sampling campaigns. It is noteworthy that 34 meteorological changes also play important roles in the inter-annual variations of the 35 observed O₃ and the simulated O₃ production rates. Evaluations with more data in longer 36 periods are therefore recommended. The analyses on the decadal changes of the local and 37 regional photochemistry in Hong Kong in this study may be a reference for combating 38 China's national-wide O₃ pollution in near future.

Keywords: Ozone formation; Volatile organic compounds; Radical chemistry; Source
 apportionment; Control measures

41 **1 Introduction**

42 Ground-level ozone (O_3) is one of the most representative air pollutants in photochemical 43 smog, produced through photochemical reactions between volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in presence of sunlight (NRC, 1992; Jacob et al., 1999; 44 45 Guo et al., 2017). It is well documented that O₃ is harmful to human health (Bell et al., 2004), 46 crops (Wang et al., 2005) and natural ecosystems (Ashmore, 2005). Through the last 30 years, 47 extensive efforts have been made by the local and federal governments to alleviate the 48 tropospheric O₃ pollution around the world (NRC, 1992; NARSTO, 2000; Wang et al., 2017a; Wang et al., 2018a). Effectiveness has gradually shown in some countries/regions, such as 49

50 Switzerland, Germany, Ireland and eastern North America (Lefohn et al., 2010; Cui et al., 51 2011; Derwent et al., 2013; Parrish et al., 2014; Lin et al., 2017). In contrast, the O₃ levels in 52 many places are still increasing or not decreasing at the expected rates, particularly in East 53 Asia (Ding et al., 2008; Xu et al., 2008; Parrish et al., 2014; Xue et al., 2014a; Wang et al., 54 2017a).

55 Hong Kong, as one of the densely populated metropolises in East Asia, has been suffering 56 from severe photochemical smog in the past decades, though the locally-emitted NO_x and 57 total VOCs (TVOCs) were significantly reduced (Xue et al., 2014a; Ou et al., 2015; Lyu et al., 58 2016a; Wang et al., 2017a). On one hand, this indicates the non-linear relationship between 59 O_3 and its precursors. On the other hand, in addition to local O_3 formation, the observed O_3 in 60 Hong Kong is also influenced by the regional transport due to the proximity of the highly industrialized Pearl River Delta (PRD) region. Earlier studies revealed that the local O₃ 61 62 production is typically limited by VOCs in urban and some suburban areas in Hong Kong 63 (Zhang et al., 2007; Ling et al., 2014; Wang et al., 2017b). Namely, cutting VOCs emissions 64 will reduce O₃ production, while the reduction of NO_x may cause an O₃ increment (Cheng et 65 al., 2010, 2013; Guo et al., 2011; Wang et al., 2017a). Previous studies also documented that 66 photochemical O₃ formation is dependent upon the ratios between TVOCs and NO_x (Sillman, 67 1999; Guo et al., 2013a; Ling et al., 2013), reactivity of VOC species (Zhang et al., 2007; Liu et al., 2008; Cheng et al., 2010) and the composition of NO_x (*i.e.* relative abundances of NO_2 68 69 and NO) (Richter et al., 2005; Xu et al., 2008; Wang et al., 2018a). Moreover, located in the 70 subtropical region, Hong Kong has relatively high temperature and strong solar radiation, 71 which are favourable for local O₃ formation. For regional transport, studies (Wang et al., 72 2001; Ding et al., 2004; Wang et al., 2017b) indicated that O₃ was generally built up in Hong Kong under the northerly winds, whereas it was often driven down by the sea breeze from 73 74 South China Sea (SCS) and by the southwest monsoon in warm seasons. The contribution of

regional transport to O₃ in Hong Kong even reached 70% under the dominance of tropical 75 76 cyclone (Huang et al., 2005), a typical synoptic condition conducive to severe O₃ pollution in 77 the Northern Hemisphere (So and Wang, 2003; Huang et al., 2005; Lam et al., 2005). To 78 improve the air quality in Hong Kong, a series of control measures aiming at restriction of VOC emissions have been implemented by Hong Kong government since 2007, which 79 80 effectively reduced the concentrations of some VOCs, such as propane and i-/n-butanes 81 emitted from taxis and public light buses fuelled by liquefied petroleum gas (LPG) (Lyu et al., 82 2016b), the aromatics mainly attributable to solvent usage, and the alkenes in association 83 with diesel exhaust (Lyu et al., 2017a). As a result, Xue et al. (2014a) and Wang et al. 84 (2017a) found that the locally produced O₃ decreased. However, the regional and super-85 regional transport of O₃ and its precursors from PRD and eastern China to Hong Kong had 86 offset the decrease of the local O₃ production, resulting in an overall increase of the observed 87 O₃ in Hong Kong from 2005 to 2013. Overall, the previous studies have greatly enhanced our 88 understanding on O₃ pollution in Hong Kong, and details about the studies can be referred to 89 in Table S1.

90 Despite many previous studies (Xue et al., 2014a, 2016; Ou et al., 2015; Lyu et al., 2016a; 91 Wang et al., 2017a; Wang et al., 2018a), the inter-annual variations of the O_3 formation 92 regimes and radical chemistry have yet been fully understood in Hong Kong. Additionally, 93 the online measurement data used in previous long-term O₃ study might hamper the exact 94 understanding of the local O₃ formation mechanisms, due to the unavailability of many 95 reactive VOCs, such as formaldehyde. Besides, the trends of the local production and 96 regional transport of O_3 were only updated to 2013 in previous studies (Xue et al., 2014a; 97 Wang et al., 2017a). In fact, many measures were taken to reduce air pollutants' emissions in 98 the latest years in Hong Kong and PRD. For examples, nearly 75% of the old catalytic 99 converters on LPG-fuelled vehicles were renewed during September 2013 - May 2014. A 100 program to eliminate the pre-Euro IV diesel vehicles or to upgrade their emission standards to 101 Euro IV was initiated in March 2014 and is still ongoing till 2019 at its third phase. In PRD, 102 the second stage of the clean air controlling program was implemented in 2013 - 2015 103 (DGEPD, 2013). In 2014, the Guangdong provincial government has launched an Action 104 Plan for Air Pollution Prevention and Control (MEE PRC, 2014), putting the emphases on the 105 emission control of traffics, coal-fired power plants and industrial sources. Investigations on 106 the post-2013 variations of the local O_3 production in Hong Kong and the regional impacts 107 provide a good opportunity for us to examine the effectiveness of these local and regional 108 measures.

109 The objectives of this study were to re-examine the O_3 trend in the pre-2013 and trace the O_3 110 evolution in the post-2013 in Hong Kong, and to explore the underlying mechanisms for the 111 variations of O₃ formation and radical chemistry. With the aid of a photochemical box model, 112 the locally produced and regionally transported O₃, as well as their variation trends, were 113 determined (see section 2.5). Under the assumption that the local O_3 production in these years 114 was changed due to a series of control measures in Hong Kong, we also aimed to evaluate the 115 actual effectiveness of these control measures. China is suffering from severe O₃ pollution, almost second to none over the world. While O3 began to decrease in most areas of North 116 117 America and Europe, China's O₃ pollution was even aggravated in recent years. A series of 118 air pollution control strategies have been implemented in China, though most of them were 119 not specifically designed for O₃ abatement. Investigations on O₃ trends and the potential 120 causes in Hong Kong would provide a good example of assessing the evolution of O₃ 121 pollution and the effects of artificial interventions in China. In addition, the changes in the regional contribution to O₃ in Hong Kong determined in this study would throw light upon 122 123 the variations of O₃ in China, particularly in South China. It is expected that this study would 124 have some inspiration to the O₃ pollution control in other cities and regions in China.

125 2 Methodolgy

126 **2.1 Sampling site**

127 Hong Kong is located on the southern coast of China with Guangdong province to the north 128 and Pearl River Estuary (PRE) to the northwest. The sampling site (22.29N, 113.94E), Tung 129 Chung (TC), was in a newly-developed suburban area in western Hong Kong, with a 130 population of ~77,400 in 2016 (CSD, 2011, 2018). The urban centre of Hong Kong is ~20 km 131 northeast of TC. Hong Kong is dominated by the subtropical oceanic monsoon climate. 132 During warm seasons, the prevailing winds mainly come from SCS at a relatively low speed 133 (southwest winds). In cold seasons, the east and northeast winds are predominant. Generally, 134 the sampling site receives relatively polluted air masses from mainland China, *i.e.* PRD 135 region, Yangtze River Delta region and even North China between October and March, when 136 high O₃ levels are often observed (Wang et al., 2009). Therefore, the samplings were mainly conducted in October and November in this study, except for 4 out of 45 sampling days in 137 138 September. The sampling site was close to a highway linking to the Hong Kong International 139 Airport (HKIA), and the HKIA was around 3 km to the north of the site. In addition, the local 140 emissions from residential activities may modulate the air quality at this site. It was expected 141 that O₃ at TC would be significantly influenced by NO emitted from the aforementioned 142 sources. As shown in Figure S1, the O₃ titrated by NO (ΔO_3 -1) was equivalent to 29.9±8.8%, 143 $26.7\pm12.7\%$ and $32.5\pm16.6\%$ of the photochemically formed O₃ (Δ O₃-2) in the 2007, 2013 144 and 2016 sampling campaigns, respectively, confirming the importance of NO titration in 145 modulating O_3 at the site. Figure 1 shows the locations of the sampling site (TC) and the 12 146 air quality monitoring stations in PRD, which witnessed the evolution of air quality in PRD 147 over the last decade and is used to demonstrate the variations of regional O_3 in this study. 148 More detailed description of the site can be found in our previous studies (Jiang et al., 2010: 149 Cheng et al., 2010; Ling et al., 2013; Ou et al., 2015).



151 Figure 1. Location of the sampling site (yellow circle) and the surrounding environment. The 152 red line in the right panel shows the border between Hong Kong and Shenzhen, Guangdong. 153 The three regional and nine urban air quality monitoring stations in PRD are symbolized by 154 orange blocks and green circles, respectively.

155 2.2 Continuous measurements of trace gases and collection of VOC/OVOC samples

156 Trace gases (SO₂, CO, NO, NO₂ and O₃) and meteorological conditions were continuously 157 measured at TC site for three autumn periods in 2007, 2013 and 2016 (see Table S2 for the 158 specific sampling periods), including 25 O_3 episode days with the maximum hourly average 159 O₃ exceeding 100 ppbv (Level II of China National Ambient Air Quality Standard) and 185 160 non-episode days. VOC and OVOC samples were selectively collected on 8, 19 and 18 days 161 in 2007, 2013 and 2016, respectively (see Table S2 for the specific sampling dates). The three 162 sampling periods were used as representatives of the autumns in the three years in this study, and the rationality will be discussed in section 3.1. 163

Trace gases were continuously measured at the TC air quality monitoring station operated by the Hong Kong Environmental Protection Department (HKEPD), ~0.8 km to our sampling site. The instruments were the same as those used in the US air quality monitoring program (HKEPD, 2017a). Table S3 summarizes the instruments, analysis techniques, detection limits and the time resolutions for measurements of the trace gases. The high resolution data were

collected and averaged into the hourly averages. All the analysers except O₃ analyser were 169 170 zeroed daily by analysing scrubbed ambient air and calibrated every two weeks by a span gas 171 mixture with a NIST (National Institue of Standards and Technology) traceable standard, 172 while the O_3 analyser was calibrated using a transfer standard (Thermo Environmental Instruments (TEI) 49PS) every two weeks. Details about the quality assurance and control 173 174 procedures can be found in Ling et al. (2016a). The meteorological parameters, including 175 temperature, relative humidity, pressure, wind speed, wind direction, precipitation and solar 176 radiation, were also continuously monitored by a mini weather station (Vantage Pro TM & 177 Vantage Pro 2 Plus TM Weather Stations, Davis Instruments) during the sampling periods. 178 Data were integrated into 30-minute averages by a built-in program in the weather station. 179 The collection and analysis of VOCs and OVOCs were detailed in our previous studies (Guo 180 et al., 2009; Wang et al., 2018b). Briefly, pre-cleaned and evacuated 2 L electropolished 181 stainless-steel canisters were used to collect VOC samples. On O₃ episode days, one-hour 182 sample was collected in each hour during the daytime (07:00-19:00 LT), generating 13 183 samples per day, while 5-7 one-hour samples were collected every other hour on non-O₃ episode days from 07:00 to 19:00 LT in the 2013 and 2016 sampling campaigns. However, 184 185 12 one-hour samples were collected on each VOC sampling day between 07:00 and 18:00 in 186 2007, regardless of O_3 episodes or non-episodes. The O_3 episode days were predicted prior to 187 sampling based on weather forecast and numerical simulation of O_3 . Overall, the O_3 episodes 188 were usually associated with high temperature, strong solar radiation, low humidity, and 189 weak or northerly winds. A total of 414 canister samples, including 96 samples in 2007, 146 190 samples in 2013 and 172 samples in 2016, were collected and analysed during the three 191 sampling periods (Table S2).

In addition to VOC samples, OVOC samples were also collected on the same days as thosefor the collection of VOCs. Dinitrophenylhydrazine (DNPH)-silica cartridges (Waters Sep-

194 Pak DNPH-Silica, Milford, MA) were used to collect the OVOC samples. An ozone scrubber 195 (Sep-Pak; Waters Corporation, Milford, MA) was connected in front of the DNPH cartridge 196 to prevent interference of ozone. The ozone scrubber was replaced every two OVOC samples. 197 For each OVOC sample, air was drawn to pass the O_3 scrubber and the cartridge for 2 hours (2.5 hours in 2007 sampling campaign) at a flow rate of 0.5 L min⁻¹, which was controlled by 198 199 a rotameter. During the sampling periods in 2013 and 2016, 5-7 OVOC samples were 200 collected every two hours from 06:00-20:00 LT on both O₃ episode and non-episode days. In 201 2007, only 2 samples were collected on non- O_3 episode days at 10:30-13:00 and 13:00-15:30, 202 and 4 samples between 08:00 and 18:00 on O₃ episode days. In total, 275 OVOC samples (28 203 in 2007, 124 in 2013 and 124 in 2016) were collected and analysed in the three sampling 204 campaigns (Table S2).

205 2.3 Chemical analysis

206 2.3.1 Analysis of VOCs

207 The concentrations of 48 speciated non-methane hydrocarbons (NMHCs) in the canisters 208 were determined with an Entech Model 7100 Preconcentrator (Entech Instruments Inc., 209 California, USA) coupling with a gas chromatography-mass selective detector (Model 5973N, 210 Agilent Technologies, USA), a flame ionization detector, and an electron capture detector 211 (GC-MSD/FID/ECD). The NMHCs were analysed in Guangzhou Institute of Geochemistry 212 (GIG), Chinese Academy of Sciences for the samples collected in both 2007 and 2013, and in 213 The Hong Kong Polytechnic University (HKPolyU) for the samples collected in 2016. It 214 should be noted that the GC-MSD/FID/ECD system in the latter two institutes was the same 215 as that at UCI, and inter-comparisons were performed regularly among the three institutes, 216 which showed reasonably good agreements (Ling et al., 2014; Wang et al., 2018b; Zeng et al., 217 2018). Detailed information about the analysis procedures and quality assurance and control

can be found in Colman et al. (2001) and Simpson et al. (2010). Table S4 summarizes the
limits of detection (LoDs), precisions and accuracies of the VOC analyses in the three
institutes.

221 The OVOC samples were stored in a refrigerator at $4 \,^{\circ}$ after sampling. For analyses of 222 OVOCs, the cartridges were eluted slowly with 2 ml of acetonitrile into a 2-ml volumetric 223 flask. A high-performance liquid chromatography (HPLC) system (Perkin Elmer Series 2000, 224 MA, USA) coupled with an ultraviolet (UV) detector operating at 360 nm was used for 225 analysis. The instrument was calibrated using standards of 5 gradient concentrations covering 226 the concentrations of interest for different OVOCs in ambient air. Good linear relationships $(R^2 > 0.999)$ between the standard concentrations and responses of the instrument were 227 228 obtained for the 16 analysed OVOC species. The built-in computerized programs of quality 229 control systems such as auto-linearization and auto-calibration were used to guarantee the 230 data quality. Detailed information about the analysis and quality control of OVOC samples 231 was provided in Cheng et al. (2014), Cui et al. (2016) and Ling et al. (2016b). Due to the low 232 detection rate of many OVOCs, this study only focused on formaldehyde, acetaldehyde, 233 acetone and propionaldehyde, which had relatively high concentrations.

234 2.4 Model description

235 **2.4.1 Positive matrix factorization (PMF)**

PMF is a receptor model that has been extensively used for source apportionment of airborne particulate matters and VOCs (Lee et al., 1999; Brown et al., 2007). In this study, US EPA PMF 5.0 model (US EPA, 2017) was applied to identify the sources of O_3 precursors, according to Equation (1) (Paatero, 1997; Ling et al., 2014).

240
$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$
 Equation (1)

where x_{ij} is the measured concentration of *j*th species in *i*th sample, g_{ik} represents the contribution of *k*th source to *i*th sample, f_{kj} denotes the fraction of *j*th species in *k*th source, and e_{ij} is the residual for *j*th species in *i*th sample. *p* stands for the total number of independent sources (Paatero, 2000a, b).

245 The uncertainties of the concentrations applied to PMF were set in the same way as Polissar 246 et al. (1998) and Reff et al. (2007). Values below or equal to the LoD were replaced by half 247 of the LoDs and the uncertainties for these values were set as 5/6 of the corresponding LoDs. For the values greater than LoDs, the uncertainties were calculated as [(Error Fraction \times 248 concentration)² + $(LoD)^2$]^{1/2} where 10% was assigned as the error fraction. Missing values 249 (mainly due to maintenance or malfunction of the instruments) were replaced by the 250 251 geometric mean of the measured values and their accompanying uncertainties were set as four times the geometric mean value. More details about the settings of the uncertainty were 252 253 provided in Norris et al. (2008) and Zhang et al. (2012).

The model was run for 20 times with a random seed, and tests with different number of factors were conducted. The optimum solution was finally determined based on both a good fit to the observed data and the most reasonable and interpretable results according to the knowledge on the sources of O_3 precursors in Hong Kong (Ling et al., 2011, 2014; Ou et al., 2015).

259 2.4.2 Observation-based model (OBM)

A photochemical box model coupled with the Master Chemical Mechanism (PBM-MCM) was used to simulate the photochemical O_3 formation on the VOC sampling days. In this study, MCM v3.2, a near explicit chemical mechanism consisting of 5,900 species and 16,500 reactions which fully describes the homogeneous gas phase reactions in the atmosphere (Jenkin et al., 1997, 2003; Saunders et al., 2003), was used. The observation data 265 of temperature, relative humidity, O₃, SO₂, CO, NO, NO₂ and 52 C₂-C₁₀ VOCs/OVOCs were 266 input into the model. Specifically, the 52 VOCs/OVOCs included 19 alkanes, 16 alkenes, 13 267 aromatics and 4 OVOCs, as shown in Table S5, where the statistics of the mixing ratios of 268 VOCs/OVOCs are also presented. Though previous studies (Guo et al., 2013b; Ling et al., 2016b) indicated that secondary formation dominated the sources of OVOCs in Hong Kong, 269 270 the primary emissions could not be neglected. Therefore, formaldehyde, acetaldehyde, 271 acetone and propionaldehyde with relatively high abundances were constrained to the 272 observed concentrations in the model, while the other OVOCs with low concentrations and 273 low detection rates were simulated by the model. Nitrous acid (HONO) was not monitored in 274 this study. The average diurnal cycle of HONO mixing ratios measured at the same site in 275 autumn in 2011 (Xu et al., 2015) was input into the model to roughly represent its role in O₃ 276 formation and atmospheric radical chemistry. Due to the data limitation, the trends of HONO 277 at TC in the three sampling campaigns were not traceable. However, the measurements at a 278 background site in Hong Kong indicated comparable levels of HONO (p>0.1) between the 279 autumn in 2012 and in 2018 (unpublished data). Therefore, adopting the HONO measured in 280 2011 as the inputs of the simulations in the three sampling campaigns was likely a plausible 281 assumption, despite some uncertainties. The model was also tailored to the real situations in 282 Hong Kong. Specifically, the height of the planetary boundary layer was allowed to vary 283 from 300 m at night to 1400 m at noon. The photolysis rates were calculated according to the 284 measured solar radiations by the Tropospheric Ultraviolet and Visible Radiation model 285 (Madronich and Flocke, 1999; Wang et al., 2017a), with the detailed method described in Lyu et al. (2017b). In addition to the chemical processes, the exchange between the lower 286 287 troposphere and free troposphere, and dry deposition were also considered in the model. The concentrations of air pollutants in the free troposphere were set according to the observations 288 at a mountainous site in Hong Kong (Lam et al., 2013). The dry deposition rates were 289

290 adopted from the previous studies (Saunders et al., 2003; Lam et al., 2013). The other 291 physical processes were not included in the model, which might lead to insufficient 292 description of the transport. However, since the model was constrained to the observations 293 which included the transported air pollutants, the regional transport was partially considered. 294 Besides, the observations at 07:00 on each day were used to initiate each day's modelling, 295 through which the effect of regional transport before the daytime modelling was also 296 considered. We admit that the PBM-MCM cannot perfectly reproduce the real atmospheric 297 processes. However, it performed well in describing the in-situ photochemistry in previous 298 studies (Lam et al., 2013; Ling et al., 2014; Lyu et al., 2017b; Wang et al., 2017a). Actually, 299 the deficiency of PBM-MCM in consideration of the atmospheric dynamics enabled us to 300 assess the contributions of regional transport to O₃ in Hong Kong, based on the differences 301 between the observed and simulated O₃ (Wang et al., 2017a).

302 2.5 Simulation scenarios

303 The PBM-MCM simulates the in-situ O₃ photochemistry based on the observed O₃ precursors. 304 Figure S2 shows the average mixing ratios of some O₃ precursors in different wind sectors. 305 The higher levels of CO, ethyne, ethane, propane and toluene under northwest winds 306 indicated the transport of these species from PRD to Hong Kong. Meanwhile, O₃ might also 307 be transported to Hong Kong. Text S1 discusses the determination of the locally produced 308 and regionally transported O₃, as well as the uncertainties. Furthermore, to evaluate the 309 contributions of VOC sources to the local O₃ production, two scenarios of model simulation 310 were performed, *i.e.*, Scenario A and Scenario B. The scenario A simulated the O₃ 311 photochemistry in the whole air, which was constrained by the observed concentrations of all 312 the O₃ precursors. The model simulations in scenario B (including six assumed sub-scenarios) were constrained by the concentrations of O₃ precursors with those contributed by individual 313 314 sources being subtracted from the observed concentrations. Text S2 elaborates the set-up of

315 these scenarios. The simulated O₃ in scenario A was regarded as the locally produced O₃, as 316 the observed O₃ concentrations were not input to constrain the model. Bearing in mind that 317 the regional effects cannot be completely eliminated in this approach, due to the impacts of 318 regional air on the observed concentrations of O_3 precursors. The differences between the 319 scenario A and scenarios B reflected the contributions of the individual sources to the 320 simulated O₃ production rate. It should be noted that due to the nonlinear relationships between O₃ and its precursors, the subtraction approach only qualitatively rather than 321 322 quantitatively evaluated the contributions of VOC sources to O_3 production.

323 **3 Results and discussion**

324 **3.1 Observation overview**

325 Figure 2 shows the hourly mixing ratios of O₃ observed at TC in the autumns of 2007-2017 326 with the data on VOC sampling days being highlighted in red. It was found that the autumn O₃ increased significantly from 2007 to 2013 (p < 0.01), with a rate of 0.34±0.002 ppbv yr⁻¹. 327 328 This was consistent with Wang et al. (2017a) who reported an overall increase rate of autumn O_3 of 0.67 \pm 0.07 ppbv yr⁻¹ at the same site for the period of 2005-2013. On one hand, the 329 330 discrepancy in O₃ increasing rates might be due to the different statistics used to draw the 331 rates, *i.e.* hourly values in this study and monthly averages in Wang et al. (2017a). On the other hand, the autumn O_3 increased substantially from 23.9 ± 0.97 ppbv in 2005 to 30.2 ± 0.97 332 333 ppbv in 2007, much quicker than the increase between 2007 and 2013. Without the inclusion of the period of 2005-2007 might be another reason of the less O₃ enhancement calculated 334 335 here. In contrast to the increased autumn O₃ during 2007-2013, the autumn O₃ decreased obviously from 2013 to 2017 (p<0.01), at a rate of -2.27 \pm 0.003 ppbv yr⁻¹, indicating a 336 337 fundamental alleviation of O₃ pollution in Hong Kong in the latest 5 years. Overall, a statistically significant decreasing trend (rate = -0.44 ± 0.001 ppbv yr⁻¹) was observed for the 338 339 autumn O_3 at TC through 2007 to 2017 (*p*<0.05). The average O_3 on VOC sampling days in 340 the three sampling campaigns also followed the same pattern, which increased from 341 32.8 ± 2.6 ppbv in 2007 to 36.9 ± 2.3 ppbv in 2013, while decreased to 24.4 ± 1.9 ppbv in 2016. 342 Further, we investigated the number of O_3 episode days in the autumns of the three VOC sampling years (see Figure S3) and identified 15 (16.5% of the autumn days, same below) 343 344 and 16 (17.6%) O₃ episode days in 2007 and 2013, respectively. However, there was only 5 345 (5.5%) O₃ episode days in the autumn of 2016. Similarly, the O₃ episode days accounted for 346 12.5%, 26.3% and 5.6% of the 2007, 2013 and 2016 sampling campaigns, respectively. 347 Therefore, the increase of O_3 from 2007 to 2013 and the decrease in the following years 348 could be represented by O_3 observed in the three sampling periods.



Figure 2. Long-term trends of the observed O_3 at TC from 2007 to 2017. Hourly O_3 values on the VOC sampling days in the autumns of 2007, 2013 and 2016 are marked in red. The hourly variation rates of O_3 are converted to yearly rates in periods of 2007 – 2013 and 2013 -2017.

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Table 1 and Table S6 present the observed O_3 , CO, NO, NO₂, SO₂ and TVOCs, as well as the meteorological conditions averaged on the VOC sampling days in 2007, 2013 and 2016, respectively. From 2007 to 2013, the TVOCs decreased by nearly a half, which was expected to result in the reduction of O_3 in view of the VOC-limited regime of O_3 formation at TC (Cheng et al., 2010; Wang et al., 2017a). However, the increases of CO and the notable 359 decrease of NO in 2013 could enhance the O₃ production. The higher O₃ in 2013 indicated 360 that this effect overrode the reduction of TVOCs in influencing the O_3 production. In 361 particular, the decrease of NO meant the reduced NO titration to O_3 , which has been 362 recognized as a primary reason of O₃ increase in VOC-limited regime (Chou et al., 2006; Wang et al., 2018b). From 2013 to 2016, the decrease of O₃ was accompanied by the 363 364 reductions of TVOCs and NO₂, though CO remained increasing at the same time. NO₂, as a direct source of O₃ through photolysis, plays important role in modulating the O₃ variation. 365 366 Though the causes of NO₂ reduction are unknown to us, it might be one of the critical factors 367 contributing to the decline of O₃ in Hong Kong in recent years. On the contrary, the increase 368 of CO was also confirmed by the continuous monitoring data at TC, with a rate of 33.9±0.7 ppbv yr⁻¹ between 2013 and 2016. In fact, the consistent increasing trend (p<0.05) 369 370 was also observed at the roadside sites in Hong Kong (not shown here). While the causes of 371 CO increase in Hong Kong may be complicated, the increased vehicle emission is a plausible 372 explanation. Studies (Johnson, 2008; Yao et al., 2008) revealed that while the new engine 373 technologies performed well in reducing NO_x emission, they might lead to the increased 374 emission of CO, with the application of lower air-to-fuel ratio and engine temperature.

375 In addition, studies have confirmed that continental anticyclones and tropical cyclones are conducive to severe O₃ pollution in Hong Kong, because these synoptic systems are often 376 377 accompanied with northerly winds, high temperature, strong solar radiation, and relatively 378 high pressure in Hong Kong (Ding et al., 2004; Huang et al., 2005; Jiang et al., 2015). 379 Table S7 summarizes number of O₃ episode days with tropical cyclone, continental 380 anticyclone and low pressure trough in the autumns of 2007, 2013 and 2016. In autumn 2007, 381 8, 8 and 1 O_3 episode day(s) were found to be related to the tropical cyclone, continental anticyclone and low-pressure trough, respectively, with 2 O₃ episode days under the 382 383 combined influence of tropical cyclone and continental anticyclone. There were also 11 and 5 O_3 episode days in association with tropical cyclone and continental anticyclone in autumn 2013, respectively (Wang et al., 2018b). However, 4 out of the 5 episode days found in autumn 2016 were associated with tropical cyclone, with the other one related to lowpressure trough. Therefore, the lower O_3 and less O_3 episode days in 2016 were also benefited from the meteorological conditions.

Table 1. Mixing ratios of the measured trace gases and TVOCs averaged on the selective 45
VOC sampling days in 2007, 2013 and 2016.

	2007		2013		2016	
Unit: ppbv	Mean ±95% C.I.	Max.	Mean ±95% C.I.	Max.	Mean ±95% C.I.	Max.
03	32.8±2.6	137.0	36.9±2.2	121.2	24.4±1.9	124.9
CO	456.3±19.8	847.0	585.0±11.9	1047.9	691.8±9.5	1074.7
NO	17.2±3.2	124.7	10.9±1.3	98.6	11.3±1.4	94.6
NO_2	27.7±2.1	69.6	31.5±1.4	80.8	22.0±1.1	103.2
SO ₂	6.9±0.4	21.8	7.0±0.2	18.0	3.0±0.1	10.7
TVOCs	49.7±4.4	111.1	25.1±1.4	68.0	21.1±1.4	71.9

391

392 **3.2 Model simulation of O**₃

393 3.2.1 Model validation

Figure 3 compares the simulated O_3 in scenario A and the observed O_3 on the VOC sampling days. Overall, both the magnitudes and the temporal patterns of the observed O_3 were reasonably reproduced, though the mean of the simulated O_3 (33.8±1.9 ppbv) was slightly lower than the observed average (37.1±2.0 ppbv). To quantitatively evaluate the model performance, the index of agreement (IOA) was used to examine the goodness of fit between simulated and observed O_3 . Within the range of 0-1, higher IOA represents better agreement between the simulated and observed values (Willmott, 1982). In this study, the overall IOA for the three sampling periods was 0.74, within the range of IOA (0.67-0.89) accepted by the previous studies (Wang et al., 2015; Lyu et al., 2015, 2016a, c; Wang et al., 2017a, 2018a). Good correlations (R^2 =0.61) were also shown between the simulated and observed hourly O₃. Bearing in mind the deficiencies of the box model in describing the atmospheric dynamics, we believed that the modelling results were acceptable, but special attention and explanation to the discrepancies between the simulated and observed O₃ was needed.

407 It was found that the discrepancies were most likely caused by the transport processes, *i.e.*, 408 vertical and horizontal transport, which were not fully represented in the PBM-MCM model 409 (George et al., 2013; Lakey et al., 2015; Wang et al., 2017a). For example, the simulated O_3 410 (maximum: 122.6 ppbv) was much higher than the observed O₃ (maximum: 44.3 ppbv) on 411 November 16, 2007, when the strong southeast winds (wind direction: 90 °-180 °) with the highest wind speed of 5.3 m s⁻¹ prevailed in Hong Kong. The south sector winds from SCS 412 might dilute the locally produced O_3 and the O_3 precursors/intermediates (such as the radicals) 413 414 which were not constrained by the observations. The same circumstances were also observed 415 on October 27, November 17, 2007 and September 11-12, November 20, 2013, with 416 southeast winds dominated (74.4%) during the daytime (Figure 3). For those days with the 417 simulated O₃ lower than the observed O₃, *i.e.* October 3, 22-25, 2013 and November 6, 2016, 418 69.3% of the winds during the daytime came from the north (wind directions: $0-90^{\circ}$ and 419 270 $^{\circ}$ -360 $^{\circ}$, which might transport the air masses laden with O₃ and/or O₃ 420 precursors/intermediates not constrained to the observations from inland PRD to the sampling 421 site. The observed O_3 mixing ratios are plotted against the wind fields in Figure S4. It is 422 obvious that O₃ were higher under the north winds, while lower in the south wind sectors, confirming the effects of dilution and regional transport of the south and north winds on O_3 423 424 pollution in Hong Kong, respectively.



425

Figure 3. Hourly mixing ratio of the simulated and observed O_3 at TC during the VOC sampling periods in 2007, 2013 and 2016. The arrows represent the hourly wind sectors monitored at the sampling site.

429 **3.2.2** Inter-annual variations of the locally produced and regional transported O₃

430 As discussed in section 2.5, the simulated O_3 in scenario A could be regarded as the locally 431 produced O₃. Therefore, the differences between the observed O₃ and O₃ simulated in 432 scenario A were treated as the regionally transported O_3 (Wang et al., 2017a). It is 433 noteworthy that some negative values were generated with this method, corresponding to the 434 dilution of the south winds to the locally produced O₃ as elaborated in section 3.2.1. Figure 4 435 shows the hourly mixing ratios of the observed, local and regional O₃ at TC in daytime hours 436 (07:00-19:00 LT) of the three sampling campaigns. Overall, the observed O₃ was mainly 437 (88.7±2.5%) contributed by the local photochemical production, with regional transport only 438 accounting for 11.3±2.5% of the observed daily maximum O₃. However, regional transport 439 was responsible for as high as $58.0\pm5.4\%$ of the observed daily maximum O₃ in Hong Kong on the O_3 episode days when northerly winds prevailed, indicating the heavy O_3 burden 440 441 superimposed by regional air masses from PRD. From 2007 to 2013, the simulated locally-442 produced O_3 remained statistically unchanged (p>0.1), in contrast to the increase of observed

 O_3 and regional O_3 at rates of 1.78 ±0.05 ppbv yr⁻¹ (*p*<0.05) and 1.77 ±0.04 ppbv yr⁻¹ (*p*<0.05), 443 respectively, the same trends as those reported by Wang et al. (2017a) for the autumn O₃ 444 during 2005-2013. However, the decease of the locally produced O_3 in the same period as 445 446 that simulated by Wang et al. (2017a) was not seen here according to the simulated O_3 in the 447 2007 and 2013 sampling campaigns. This discrepancy was likely caused by the limited 448 samples in this study, no OVOCs considered in Wang et al. (2017a) and/or the inexactly same study periods between the two studies. Instead, we found that the locally produced O_3 449 showed a significant decline at a rate of -5.52 ± 0.05 ppbv yr⁻¹ during 2013-2016 (p<0.05), 450 451 when the regionally transported O_3 did not change (p=0.32), resulting in a downward trend (-452 5.31 \pm 0.07) of the observed O₃. As such, the increase of the observed O₃ from 2007 to 2013 453 was reversed by the decrease between 2013 and 2016, leading to an overall decreasing trend of the observed O₃ during 2007-2016 (rate = -0.57 ± 0.03 ppbv yr⁻¹, p<0.05). 454



455

Figure 4. Hourly values (first panel) and the throughout-campaign statistical results (second to fourth panels) of the observed, simulated (locally-produced) and regional O_3 mixing ratios in daytime hours (07:00 – 19:00 LT) in the three sampling campaigns.

459 The significant alleviation of O₃ pollution in Hong Kong from 2013 to 2016 might be related 460 to the measures taken to control the emissions of O₃ precursors in Hong Kong and in 461 mainland China. The effectiveness of the actions launched by Hong Kong government in O₃ 462 abatement was fully demonstrated in previous studies (Xue et al., 2014a; Lyu et al., 2017a; 463 Wang et al., 2017a), and would be further evaluated in this study (section 3.4). Besides, the 464 emission controls in mainland China might contribute to the decrease of O₃ or at least lessen the regional O₃ burden in this period. For example, the China's NO_x emissions for the first 465 466 time showed a decreasing trend from 2013, benefited from the implementation of the China's 467 Clean Air Action Plan (Zheng et al., 2018). Furthermore, we looked into the monthly average O₃ observed at the 12 air quality monitoring stations across the inland PRD, including three 468 469 regional monitoring stations, *i.e.* Tianhu, Wanqingsha and Jinguowan, and nine urban 470 monitoring stations, *i.e.* Xiapu, Jinjuzui, Donghu, Tangjia, Liyuan, Huijingcheng, Zimaling, 471 Luhu and Chengzhong (https://www.epd.gov.hk/epd/sc_chi/resources_pub 472 /publications/m_report.html). As shown in Figure 5, O_3 at these stations remained relatively 473 stable (p=0.68) during 2006-2013, which however showed a contrastively decreasing trend at a rate of -1.27±0.25 ppbv yr⁻¹ from 2013 to 2016. This corroborated our modelling results 474 475 that the regional contribution to O₃ in Hong Kong ceased increasing or even began to 476 decrease since 2013. While the substantial decrease of NO_x was a plausible reason for the 477 alleviated regional O₃ pollution, meteorological variations might also play roles in 478 modulating O₃ variations in these years (Li et al., 2019). However, analyses on the causes are 479 out of the scope of this study. In addition to the reduced local formation and regional

480 transport of O₃, the more favourable meteorological conditions in 2016 might be another

481 reason of the O_3 decrease, as discussed in section 3.1.



Figure 5. Trends of the observed monthly average O_3 at the 12 air quality monitoring stations in inland PRD.

485 **3.3 Local production and destruction pathways of O₃ and OH radical**

486 **3.3.1 In-situ net O₃ production**

482

Figure 6 shows the average diurnal profiles of the simulated O_3 production and destruction pathways during the three sampling campaigns. Also shown are the average diurnal cycles of the simulated O_3 . The shift of the peaks between the net O_3 production rate and the simulated O_3 was due to the accumulation of the newly generated O_3 over time in the model, which was also true in the real situations. The reactions between NO_2 and O_3 , leading to the formation of NO_3 and N_2O_5 , in addition to dry deposition and aloft exchange, were the main depletions of the simulated O_3 in the late afternoon. Consistent with previous studies (Kanaya et al., 2009; 494 Liu et al., 2012; Xue et al., 2014b), these pathways were not included in the calculation of the net O₃ production rate, because we mainly focused on the photochemical processes in the 495 hours when O₃ was accumulated. It was found that the reaction between HO₂ with NO 496 dominated the O₃ production rates in all the cases, with an average rate of 3.7 ± 0.7 ppbv h⁻¹ 497 (56.5±1.1%, percentage of the total O_3 production rate, same below), 2.5±0.3 ppbv h⁻¹ 498 $(64.3\pm0.8\%)$ and 1.4 ± 0.2 ppbv h⁻¹ $(67.7\pm0.7\%)$ in the 2007, 2013 and 2016 sampling 499 500 campaigns, respectively. In addition, the sum of the reaction rates between RO₂ radicals and NO contributed 3.0 ± 0.6 ppbv h⁻¹ (43.5±1.1%), 1.5 ± 0.2 ppbv h⁻¹ (35.7±0.8%) 501 and 0.7 ± 0.1 ppbv h⁻¹ (32.3\pm0.7%) to the O₃ production rate in 2007, 2013 and 2016, respectively. 502 503 The formation of HNO₃ though the reaction between OH and NO₂ served as the main scavenger pathway of O₃, as NO₂ would be photolyzed and produce O₃ otherwise. On 504 average, O_3 was consumed in this way at a rate of -1.3 ± 0.2 ppbv h⁻¹ (80.7±3.3%, percentage 505 of the total O₃ destruction rate, same below), -1.0 ± 0.1 ppbv h⁻¹ (79.3±1.8%) 506 and -0.6 ± 0.07 ppby h⁻¹ (81.6 $\pm2.0\%$) in 2007, 2013 and 2016, respectively. The photolysis of 507 O_3 was the second contributor to O_3 destruction, with an average contribution of -0.11 ± 0.01 508 ppbv h^{-1} (8.5±0.5%) for the three sampling periods. Besides, the ozonolysis of unsaturated 509 510 VOCs and the reactions between O_3 and radicals (OH and HO₂) were responsible for $3.5 \pm 0.3\%$ 511 and $1.7 \pm 0.2\%$ of the total destruction rate of the locally produced O₃, respectively. Overall, the net local O_3 production rate decreased from 5.2±1.1 ppbv h⁻¹ in 2007, to 512

513 2.7 ± 0.4 ppbv h⁻¹ in 2013, till 1.4 ± 0.3 ppbv h⁻¹ in 2016, corresponding to the decline of the

514 locally produced O_3 through 2007 to 2016 (Section 3.2.2).



516 Figure 6. Average diurnal profiles of the local O_3 production and destruction rates in the 517 sampling campaigns of (a) 2007, (b) 2013 and (c) 2016.

518 **3.3.2 Recycling of OH radical**

515

As one of the most important radicals in the atmosphere, OH initiates the oxidation of VOCs, 519 520 leading to O_3 formation. Figure 7 presents the average diurnal profiles of the simulated OH 521 and the formation and loss pathways dominating the recycling of OH during the three 522 sampling periods, which roughly followed the typical pattern of the intensities of 523 photochemical reactions, *i.e.* higher at noon and lower at the beginning and end of the day. 524 On average, the simulated OH concentration was comparable (p=0.4) between the 2007 sampling campaign $(1.6\pm0.3\times10^6 \text{ molecules cm}^{-3})$ and the 2013 sampling campaign 525 $(1.5\pm0.2\times10^6 \text{ molecules cm}^{-3})$, but it decreased (p<0.05) to $1.0\pm0.2\times10^6 \text{ molecules cm}^{-3}$ in the 526 2016 sampling campaign. 527

As expected, the formation and loss rates of OH were basically balanced in all the cases. OH was mainly formed from the reaction of HO₂+NO, which accounted for $69.8\pm1.1\%$ of the total OH production rate over the three sampling campaigns. The photolysis of HONO ranked the second in supplying OH with the contribution of $22.0\pm1.4\%$. As stated in section 2.4.2, the average diurnal cycle of HONO measured at TC in 2011 was adopted in the simulations. To assess the uncertainties, we also calculated the HONO concentrations according to the 534 measured HONO/NO_x ratios and the NO_x concentrations at TC in the three sampling 535 campaigns (Figure S5). The uncertainties in HONO concentrations and in the contributions of 536 HONO to OH formation and loss rates are discussed in Text S3. The formation of OH from 537 HONO photolysis was most efficient in the early morning, which was explained by the morning peak of HONO concentration, due to the nocturnal heterogeneous formation and the 538 539 vehicle emissions in morning rush hours. Apart from the two dominant pathways, O₃ photolysis (6.3±0.2%), ozonolysis of unsaturated VOCs (1.5±0.2%) and H₂O₂ photolysis 540 541 $(0.2 \pm 0.01\%)$ also made some contributions to the formation of OH, with the highest rates at 542 noon or in the early afternoon when the productions of O_3 and H_2O_2 were the most intensive. 543 To sum up, the total formation rates of OH from the primary sources (photolysis of HONO, 544 O₃ and H₂O₂, and ozonolysis of VOCs) were lower than the recycling rates of OH (HO₂+NO) 545 throughout the day at TC, consistent with the results in Xue et al. (2016) simulated at the 546 same site. The dominant role of HO₂+NO in OH formation at TC (average contribution of 547 69.8±1.1%) might be related to the abundant NO at this site. The same pathway was 548 simulated and accounted for only 42.7±0.2% of the total OH formation rate at an island more than 40 km away from Hong Kong with very low NO concentrations, *i.e.* maximum of 0.56 549 550 ppbv (Wang et al., 2018a).

551 OH was mainly depleted by the reactions with VOCs $(32.3\pm1.2\%)$, NO₂ $(31.9\pm0.9\%)$, CO 552 (19.3±0.6%) and NO (16.5±1.1%). The reaction rates of OH+NO (formation rates of HONO) 553 had the highest values in the morning, approximately in line with the diurnal pattern of the 554 HONO photolysis rates, which however were not completely balanced due to the constraint of HONO to observations in the model. The average net photolysis rates of HONO 555 556 (differences between the HONO photolysis and formation rates) were $0.68\pm0.21\times10^6$, $0.70\pm0.12\times10^{6}$ and $0.87\pm0.12\times10^{6}$ molecules cm⁻³ s⁻¹ in the 2007, 2013 and 2016 sampling 557 558 campaigns, respectively. The losses of OH through the other pathways all exhibited the highest efficiencies at noon or in the early afternoon. It should be noted that the reaction between OH and NO₂ was not only the sink of OH but also a termination reaction in the photochemical system. In comparison, the termination reaction rates were lower than the OH formation rates from the primary sources (photolysis of HONO, O₃ and H₂O₂, and ozonolysis of VOCs) in the morning (7:00 – 10:00 LT), which were reversed in the following hours of the day due to the increases in OH concentrations.

565 Consistent with the variations of the local O₃ production, both the local formation and loss 566 rates of OH decreased through 2007 to 2016 (p<0.05), with much more obvious reductions in 567 the later phase (2013-2016). On one hand, the continuous reduction of VOCs resulted in lower HO₂ and RO₂ concentrations (Figure S6), hence the lower production rate of OH 568 569 through the reaction of HO₂+NO. At the same time, the destruction rates of OH also 570 decreased due to the reductions of OH and the O₃ precursors, except for CO (Figure 7 and Table 1). The decreases of the OH production and destruction rates indicated that the 571 572 propagation of the reaction cycles, namely the recycling of OH, became slower from 2007 to 2016. This also explained why the locally produced O_3 decreased in these ten years, since O_3 573 574 is formed with the consumption and recycling of OH radical.



575

576 Figure 7. Average diurnal cycles of the OH formation and loss rates during the sampling

577 periods in (a) 2007, (b) 2013 and (c) 2016.

578 **3.4 Source contributions to the production of O₃ and radicals**

579 **3.4.1 Source apportionment**

580 To resolve the sources of O₃ precursors, 27 species, including CO, NO, NO₂, 12 alkanes, 4 581 alkenes and 8 aromatics, were applied to PMF for source apportionment. These species were 582 either of high abundances or typical tracers of VOC sources in Hong Kong. Source 583 apportionment was conducted for a total of 414 samples covering the three sampling periods, 584 so that the uncertainty of the source apportionment results could be reduced, compared to 585 separate source apportionments for each of the three sampling periods. Figure 8 shows the 586 average profiles of the six sources resolved by PMF. The modelling errors were estimated 587 with the bootstrap method integrated in PMF (Brown et al., 2015).

588 Factor 1 was assigned as the combination of LPG usage and gasoline evaporation, in view of 589 the high loadings of C_2 - C_5 hydrocarbons. Specifically, propane and *i*-/*n*-butanes are the main 590 components of LPG in Hong Kong, and gasoline evaporation generally contains large 591 quantities of *i*-/*n*-pentanes, in particularly *i*-pentane (Guo et al., 2013a; Lyu et al., 2017a). 592 Factor 2 was characterized by moderate to high percentages of i-/n-pentanes and TEX 593 (toluene, ethylbenzene and xylenes). These species are commonly seen in gasoline exhausts. 594 Therefore, we defined this factor as gasoline exhausts. Both the third and fourth factors 595 indicated solvent-related emissions. While Factor 3 likely represented household solvent 596 usage, due to the dominance of hexane and hexane isomer (3-methylpentane) (Ling and Guo, 597 2014; Ou et al., 2015), Factor 4 was more related to emissions from coatings and paints, in 598 view of the dominance of the aromatics (Ling and Guo, 2014). Factor 5 was distinguished by 599 the high concentrations of ethane, ethene, ethyne and benzene, together with the relatively 600 heavy (C_7-C_{10}) alkanes, which are typical species in diesel exhausts (Schauer et al., 1999; 601 Kashdan et al., 2008; Sahoo et al., 2011). Therefore, this factor was designated as diesel



602 exhausts. The last factor denoted for biogenic emissions (BVOCs), due to the exclusive603 dominance of isoprene (Guenther, 2006).

Figure 8. Average profiles of the O_3 precursors sources at TC in the three sampling campaigns. The uncertainties were estimated with the bootstrap method in PMF.

607 Figure S7 presents the total mixing ratio of VOCs emitted from each individual source 608 extracted from PMF during the three sampling periods in Hong Kong. The VOC emissions 609 from LPG usage and gasoline evaporation decreased significantly (p < 0.05) at a rate of -2.61±0.03 ppbv yr⁻¹ from 2007 to 2016. However, the VOCs in association with gasoline 610 exhausts experienced an increase (rate = 1.32 ± 0.02 ppbv yr⁻¹, p<0.05) in these years, 611 612 indicating that the reduction of VOC emissions from LPG usage and gasoline evaporation 613 was not attributable to the change in emissions of gasoline-fuelled vehicles. Insight into the 614 mixing ratios of propane and i-/n-butanes (LPG tracers) in this source revealed a significant 615 decline from 3.51 ±0.52 ppbv in the 2007 sampling campaign to 1.27 ±0.11 ppbv in the 2016

616 sampling campaign. Therefore, the reduction of VOC emissions from LPG usage was most 617 likely the reason of the decrease of VOCs allocated to the source of LPG usage and gasoline 618 evaporation. In fact, it was confirmed by our previous studies (Lyu et al., 2016b; Yao et al., 619 2019) that the replacement of catalytic converters on LPG-fuelled vehicles during September 620 2013-May 2014 effectively reduced the VOC emissions from LPG-fuelled vehicles in Hong 621 Kong. In addition, the variations in LPG usage in inland PRD, where LPG was extensively 622 used as vehicular and domestic fuels (Liu et al., 2008), might also contribute to the emission 623 reduction of VOCs, in view of the decrease of LPG tracers in this source from 2007 624 (3.51±0.52 ppbv) to 2013 (2.04±0.27 ppbv), when no control was performed against LPG 625 fuelled vehicle emissions in Hong Kong. The VOCs emitted from solvent usage (including 626 the household solvent, coatings and paints) also decreased significantly (p < 0.05) from 2007 627 to 2016, likely benefiting from the actions taken to restrict the VOC contents in solvent 628 products starting from 2007 (phase I) and 2010 (phase II) in Hong Kong (Lyu et al., 2017a). 629 VOCs attributable to diesel exhausts decreased (p < 0.05) from the 2007 (2.6 ± 0.3 ppbv) to 630 2013 sampling campaign (2.0±0.2 ppbv), which however were unchanged between 2013 and 631 2016 (2.2±0.2 ppby). In fact, a subsidy program has been implemented in Hong Kong since 632 2007 to progressively eliminate the pre-Euro IV diesel vehicles or to upgrade their emission 633 standards to Euro IV (HKEPD, 2017b), and the effectiveness of this program in VOC 634 reductions till 2013 was confirmed by Lyu et al. (2017a) with the online measurement data at 635 the same site. However, while the phase III of this program (2014-2019) is still ongoing, the 636 VOCs emitted from diesel vehicles remained stable between the 2013 and 2016 sampling campaigns. This undesirable result might be due to the fact that the actions were mainly 637 638 targeted at the pre-Euro, Euro I and Euro II diesel vehicles before 2013, whereas the phase III 639 of the program initiated in 2014 focused on the Euro III vehicles (HKEPD, 2017b, 2018). Since the former were vehicles with higher emissions, it is not unreasonable that reduction of 640

641 VOCs was more discernible between 2007 and 2013. Further, the effectiveness of the phase 642 III program might be somewhat offset by the wearing-out of the pre-existing vehicles and the 643 increase of diesel vehicle populations (Competition Commission, 2017). Further evaluation 644 with more data in a longer period is recommended. At last, the increase of BVOCs from 2007 to 2013 but comparable levels between 2013 and 2016 seemed to be related to the lower 645 646 (p<0.05) temperature in the 2007 sampling campaign (Figure S8 and Table S6). Besides, the more frequent (62.8%) southeast winds from SCS with higher wind speeds $(2.3\pm0.2 \text{ m s}^{-1})$ 647 might dilute BVOCs emitted from the terrestrial plants in the 2007 sampling campaign. 648

649 **3.4.2 Source contributions to O₃ production**

Figure 9 presents the contributions of VOCs emitted from individual sources to the 650 production and destruction rates of O₃, as well as the simulated contributions to the O₃ 651 mixing ratios. NO_x was not included in these analyses, because of its relatively high 652 653 uncertainties in source apportionment results due to the short lifetimes. Consistent with the 654 O₃ production and destruction in the whole air, the pathway of HO₂+NO dominated over the reactions between RO₂ and NO in O₃ production for all the individual sources. The 655 656 destruction of O₃ was mainly driven by NO₂ reacting with OH. For the net O₃ production rate, VOCs attributable to the coatings and paints made the largest contribution (0.38±0.05 ppbv h⁻ 657 ¹), followed by gasoline exhausts (0.22±0.03ppbv h⁻¹), LPG and gasoline evaporation 658 $(0.21 \pm 0.03 \text{ ppbv h}^{-1})$, BVOCs $(0.19 \pm 0.03 \text{ ppbv h}^{-1})$, household solvent usage $(0.15 \pm 0.04 \text{ ppbv})$ 659 h^{-1}) and diesel exhausts (0.13±0.01ppbv h^{-1}). Despite some peak shifts for the reasons 660 661 illustrated in section 3.3.1, the O₃ mixing ratios elevated by the individual sources followed 662 the same pattern as the net O_3 production rates, with the highest O_3 enhancement (1.92 \pm 0.21) 663 ppbv) by the source of coatings and paints and the lowest increase by household solvent usage (0.86±0.06 ppbv) and diesel exhausts (0.83±0.06 ppbv). The contributions of source-664 665 specific VOCs to O₃ production, particularly the importance of solvent usage in O₃ formation

in Hong Kong, were generally in line with previous studies (Ling and Guo, 2014; Ou et al., 2015). This was actually expected according to the reactivity of major VOCs in each source. For example, the TEX in the source of coatings and paints (Figure 8) have been identified to be of high O_3 formation potentials (Lau et al., 2010; Ling et al., 2011, 2013). However, the PBM-MCM model simulations enabled us to quantitatively evaluate the contributions of VOC sources to O_3 production rates.



Figure 9. Contributions of VOCs in individual sources to the production and destruction rates of O_3 and to the O_3 mixing ratios in the three sampling campaigns.

672

675 From a historical perspective, we found that the contribution of LPG usage and gasoline evaporation to O_3 production significantly decreased (p < 0.05) from 2007 to 2016 sampling 676 campaign (2007: 0.51±0.11 ppbv h⁻¹; 2013: 0.20±0.03 ppbv h⁻¹; 2016: 0.10±0.02 ppbv h⁻¹), 677 which coincided with the variations of VOCs emitted from LPG-fuelled vehicles as discussed 678 679 above. Gasoline exhaust contributed much less (p < 0.05) to the net O₃ production rate in 2007 $(0.02\pm0.01$ ppbv h⁻¹), than those in 2013 $(0.26\pm0.05$ ppbv h⁻¹) and 2016 $(0.27\pm0.07$ ppbv h⁻¹), 680 681 in line with the variations of VOCs emitted from this source. The reductions of VOC emissions from solvents also resulted in the consistent decrease of the net O₃ production rate 682 from 1.22 ± 0.17 ppbv h⁻¹ in the 2007 to 0.14 ± 0.05 ppbv h⁻¹ in the 2016 sampling campaign. 683 684 The O₃ production rates contributed by VOCs in diesel exhausts were reduced from 2007 $(0.21\pm0.05 \text{ ppbv h}^{-1})$ to 2013 $(0.11\pm0.02 \text{ ppbv h}^{-1})$ and remained unchanged thereafter (2016: 685 0.11±0.02 ppbv/h). The O₃ production rate traceable to BVOCs showed a significant increase 686 from 2007 (0.04 \pm 0.02 ppbv h⁻¹) to 2016 (0.22 \pm 0.04 ppbv h⁻¹), since the mixing ratios of 687 688 BVOCs significantly increased (p < 0.05) in these years. It is noteworthy that the changes in 689 meteorological conditions in these three sampling campaigns might also partially account for 690 the variations in the source contributions to O₃ production. For example, the 2013 sampling 691 campaign was characterized by the relatively higher temperature and lowest relative humidity 692 among the three sampling periods, which favoured O₃ formation in 2013 (Table S6). Besides, 693 due to limited samples in this study, we recommend further assessments with more data in 694 longer periods to be carried out in future study.

695 4 Conclusions

696 Photochemical pollution with high and increasing concentrations of O_3 has been an important 697 environmental issue in South China. With the observation data of O_3 and its precursors at a 698 suburban site in Hong Kong, downwind of South China, this study analysed the inter-annual 699 variations of O_3 and its photochemistry, as well as the contributions of VOC sources to the 700 local O₃ production rates in 2007, 2013 and 2016. To our knowledge, this is the first time that 701 a substantial alleviation of O₃ pollution in this region was identified between 2013 and 2016, 702 in contrast to the repeatedly confirmed O₃ increase before 2013. In addition to the changes in 703 meteorological conditions among the three sampling campaigns, the termination of the rise in 704 regionally transported O₃ and the decrease of the local O₃ production rate contributed to the 705 decline of O_3 in the later period. The emission reductions (particularly for NO_x) in mainland 706 China starting from 2013, the year when the China's Clean Air Action Plan was launched, 707 might more or less play a role in ceasing the increase of regional O₃. In Hong Kong, the 708 replacement of catalytic converters and the constraints of VOC contents in solvent products 709 led to the reductions of VOC emissions from LPG-fuelled vehicles and solvent usage, 710 respectively. As a result, the local O₃ production rate and the recycling rate of OH radical 711 decreased substantially from 2013 to 2016. Though the variations in meteorological 712 conditions and the limited sample size might somewhat introduce uncertainties to the 713 conclusions drawn from the present study, it is plausible that the local and regional 714 interventions were effective on the control of O_3 pollution in Hong Kong. Nevertheless, 715 studies with more data in longer periods should be conducted, not only in Hong Kong but 716 also in mainland China where O_3 is still increasing in most of the territories.

717 Author contribution

Hai Guo and Fei Jiang initiated and designed the experiments, and Xufei Liu and Xiaopu Lyu carried them out. Xiaopu Lyu and Yu Wang developed the model code and performed the simulations. Xufei Liu and Xiaopu Lyu prepared the manuscript and Hai Guo finalized the manuscript with contributions from all co-authors.

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