Emission Characteristics of VOCs from On-road Vehicles in an Urban Tunnel in Eastern China and Predictions for 2017–2026

Chengxun Deng[1], Yujuan Jin[1], Min Zhang[2*], Xiaowei Liu[3], Zhimin Yu[1*]

[1]*Department of Biological and Environmental Engineering, Hefei University, Hefei City, 230022, China*

[2]*Anhui Environmental Monitoring Center Station, Hefei City, 230071, China*

[3]*School of Resources and Environmental Engineering, Hefei University of Technology, Hefei City, 230009, China*

Abstract

Automobile exhaust emissions represent the main source of atmospheric volatile organic compound (VOC) pollution in urban areas of China. To accurately obtain recent emission characteristics of vehicles under urban road conditions, an optimized tunnel experiment was conducted in Longchuan Tunnel, Hefei, eastern China. Based on preliminary experiments examining the spatial and temporal characteristics of VOCs within the tunnel, a sampling scheme was designed to quantitatively analyze 51 VOCs. Among the 36 detected VOCs, about 52% were alkanes (mainly branched alkanes), with a total average emission factor of 41.39 ± 12.81 mg km^{-1} veh^{-1}. The compounds with the second highest proportion were benzene homologues, while alkenes accounted for the smallest proportion. Dimethylbutane exhibited the highest average emission factor (13.3 ± 3.19 mg km^{-1} veh^{-1}), followed by toluene (7.06 ± 3.14 mg km^{-1} veh^{-1}) and then 2-methylpentane (6.44 ± 2.10 mg km^{-1} veh^{-1}). The emission factors of VOCs in Longchuan Tunnel were consistent with those of other studies in recent years, but were considerably lower than those of tunnels measured in 2004. Based on the average emission factors of VOCs for light-duty and heavy-duty vehicles (81 ± 27 and 99 ± 42 mg km^{-1} veh^{-1}, respectively), the predicted vehicle population and vehicle-kilometers-traveled data, the emissions of VOCs were predicted for 2017–2026. The results showed that if no control measures are taken, the total VOC emission volume and emission intensity will increase from 2510 ± 850 tons yr^{-1} to 3270 ± 1120 tons yr^{-1} and from 1859 ± 630 kg km^{-2} to 2422 ± 830 kg km^{-2}, respectively, between 2017 and 2026.

* Corresponding author. Tel: 0-86-0551-62158447

E-*mail address*: yuzhimin@hfuu.edu.cn

Keywords: Volatile organic compounds; Tunnel study; Emission factor; Emission intensity; Grey model

INTRODUCTION

Volatile organic compounds (VOCs) can be divided into those originated from anthropogenic sources and those from natural sources. The two primary anthropogenic emission sources with the largest impact on the global atmosphere are vehicle transportation and industrial sources. As industrial enterprises have gradually moved out of urban areas and the vehicle population in cities has rapidly increased, automobile exhaust emissions have increased to comprise almost half of VOCs entering the atmosphere via pollution in urban areas (Che *et al.*, 2011; Han *et al.*, 2015). VOCs exceeding specific concentration thresholds can irritate the eyes and respiratory tracts of humans and animals, damage human organs, induce deformities, and cause cancer and other serious diseases (USEPA, 1998). In addition, as precursors to the generation of ozone and secondary aerosols (Wang *et al.*, 2013), VOCs are one of the major pollutants responsible for smog.

At present, tunnel experiments are the main method used to study pollutant emissions from urban vehicle exhaust in the real world. These experiments are generally not affected by environmental conditions, can quantify the emissions from a large number of vehicle samples at the same time, and can reflect the emission characteristics of pollutants from vehicles under actual driving conditions (Chiang *et al.*, 2007). Tunnel experiments have been used to study emission characteristics and emission factors (EFs) of trace gases, such as non-methane

hydrocarbons, particulate matter, CO, and NOx, in vehicle exhaust (Ban-Weiss *et al.*, 2008; Deng *et al.*, 2015; Pan *et al.*, 2007; Wang *et al.*, 2001; Zhang *et al.*, 2015). In the last decade, Wang *et al.* (2001) and Fu *et al.* (2005) studied the emission characteristics of VOCs in vehicle exhaust in China. As exhaust emission standards for vehicles in China have become more stringent and fuel quality standards have been raised, the emission characteristics and EFs obtained in previous studies have failed to accurately reflect the current state of emissions. In the past decade, the size of cities in China has increased, with eastern China becoming the fastest-growing region in terms of the scale of urbanization. Accordingly, air quality in eastern China has continuously deteriorated and fine particulate matter ($PM_{2.5}$) concentrations now exceed 35 μg m^{-3} (World Health Organization Air Quality Interim Target). Specifically, $PM_{2.5}$ levels increased from 23.08% to 29.89% from 1998 to 2012 (Luo *et al.*, 2017), which has also resulted in haze becoming an issue. Determination of the emission characteristics and EFs of various types of VOCs in exhaust gas provides a reference for air pollution prevention and control and the updating of VOC emission standards. Moreover, such data are of great importance for the protection of the health of citizens and improvement of the quality of the atmospheric environment.

In recent years, researchers have conducted further studies regarding the emission characteristics and EFs of different types of VOCs from vehicle exhaust in southern and eastern China (Zhang *et al.*, 2018a; Zhang *et al.*, 2018b). In this study, Hefei, which is the capital of

Anhui Province and has undergone an increase in vehicle population of more than 60% in the past five years, was used as an example. An optimized tunnel experiment considering the spatial and temporal characteristics of VOCs was used to qualitatively analyse the types of VOCs emitted from automobile exhaust. Specifically, the emission characteristics of 51 VOCs were quantitatively investigated, and the concentration level and time distribution characteristics of the 36 VOCs that were detected in the atmosphere were determined. Based on mass balance and multiple regression analysis, the average EFs and the comprehensive EFs of various types of VOCs in vehicle exhaust were calculated. In combination with the vehicle population and vehicle-kilometres-travelled (VKT) data in Hefei, the total emission of VOCs from vehicle exhaust in the next ten years was predicted.

METHODOLOGY

Selection of Sampling Sites and Sample Collection

The sampling site for the tunnel experiment was the urban tunnel at Longchuan Road, Hefei (Fig. 1). The tunnel, which is the only road to Hefei South Railway Station, has a high traffic volume and a speed limit of 60 km h^{-1}. The tunnel has a total length of 1,435 m, an internal width of 12 m, a height of 4.5 m, and an effective sectional area of 54 m^2. It is a two-way, two-lane tunnel, with no open vents, and is little affected by wind because it is relatively long.

93 The sampling method was a combination of instantaneous sampling and 1 h sampling. A 6 L
94 Summa canister (Entech, USA) was placed about 1.5 m above the ground at pre-set sampling
95 sites. Instantaneous sampling was used in the preliminary experiment to determine the
96 appropriate sampling time. Instantaneous sampling applied the pressure difference between the
97 inside and outside of the Summa canister to draw the air into the canister, which was filled within
98 about 5 min. For the 1 h sampling, a flow restrictor was connected in advance to the Summa
99 canister, the valves of the steel canister and the sampling head were opened, and the sampling
100 was completed at a constant flow rate over 1 h. A camera was used to continuously record the
101 traffic volume during the sampling period, after which the data were classified and counted. The
102 vehicles were divided into two categories: light vehicles (private cars, taxis, light trucks, and mini
103 buses) and heavy vehicles (heavy-duty trucks and coach buses). Although motorcycles may
104 contribute substantially to VOCs in the atmosphere (Tsai et al., 2017), they were not included in
105 this study category because Hefei has restricted motorcycle use since July 1, 2014.

106 The optimal sampling site for providing data for use in calculating EFs was determined using a
107 preliminary experiment examining the spatial characteristics of VOCs within the tunnel. The
108 sampling was conducted during 6–10 March, 2017 and five sampling sites were established (#1,
109 #2, #3, #4, and #5) (Fig. 1), as described in the supplementary information (SI). As a result, the
110 main distribution characteristics of the VOCs in the tunnel showed a higher concentration in the

111 middle of the tunnel than at each end (Figs. S1 and S2). Therefore, the middle interval of the
112 tunnel (between point #2 and point #3) was selected as the optimal interval for determination of
113 EFs.

114 To determine a reasonable sampling time to reflect the relationship of VOCs with traffic
115 volume in one day, a temporal distribution experiment using instantaneous sampling was
116 conducted during 20–26 March, 2017. The sampling period between 6:00 and 21:00 and two
117 sampling sites (825 m from the entrance (#6) and 950 m from the entrance (#4)) were established
118 as described in the SI. The results showed that the change in the total amount of VOCs at the two
119 points was essentially the same as that of the traffic volume, and both reached peak values at
120 8:00–10:00 in the morning and 16:00–19:00 in the afternoon (Figs. S3 and S4). Therefore, the
121 sampling time points of6:00, 8:00, 9:00, 10:00, 12:00, 13:00, 14:00, 16:00, 18:00, 19:00, 20:00,
122 and 21:00 could reasonably reflect the variation in VOCs with traffic volume during the day for
123 the full experiment.

124 In the full experiment, the sampling period for the emission characteristics and EFs of VOCs
125 from vehicle exhaust in Hefei was between 29 May, 2017 and 4 June, 2017. Based on the results
126 from the spatial distribution and temporal distribution experiments, sites were set at 450 m (site
127 #2), 700 m (site #3), 825 m (site #6), and 950 m (site #4) from the entrance of the tunnel (Fig. 1).
128 Among these, the entrance point (site #2) and the middle point (site #3) were used for calculation

of the EFs, while point #6 and point #4 were used for determination of the temporal distribution characteristics of VOCs. One background point was set outside the tunnel to exclude the interference of other sources. Additionally, meteorological parameters such as wind speed and temperature and traffic volume at the time of sampling (Table S1) were measured for calculation of EFs. The sampling periods were 6:00–7:00, 8:00–9:00, 9:00–10:00, 16:00–17:00, 18:00–19:00, 19:00–20:00, and 20:00–21:00, and the 1 h average value was used.

Analysis of VOCs

Fifty-one VOCs were analysed using a 7100 preconcentrator (Entech Instruments Inc., USA) combined with a 7890A gas chromatograph/597C mass spectrometer (GC-MS, Agilent, USA). A polysiloxane capillary column (DB-624, 60 m × 0.25 mm, 1.4 μm film, Agilent, USA) was used for separation of target compounds, which was conducted under the following conditions: injector temperature, 140°C; injection volume, 1 μL; column temperature, 35°C for 5 min, then increased to 150°C at 5°C min^{-1} (held for 7 min), then maintained at 200°C for 4 min. During analysis, helium (99.99% purity) was applied as the carrier gas at a constant flow rate of 1.0 mL min^{-1}. The MS was operated using selected ion monitoring mode and the ion source was electron ionization at 230°C (70 eV). The detailed identification parameters and cryogenic concentration steps are given in Table S3.

Quality Control and Quality Assurance

149 Prior to sampling, the Summa canister was cleaned using a canister cleaning system (ENTECH
150 3100D) in the laboratory more than five times, then repeatedly flushed with high-purity nitrogen
151 gas to remove interfering substances. After cleaning, the Summa canister was evacuated for 24 h,
152 after which a leak check was performed with a pressure gauge to ensure that the seal was intact.
153 Photochemical Assessment Monitoring Stations (PAMS) standard mixtures (Spectra Gases Inc.,
154 USA) of the 51 VOCs were used for the calibration. These target compounds were quantified
155 using an external standard method with a calibration range of 0.1–10 μg L^{-1} and the coefficients
156 of determination (R^2) of the calibration curve were higher than 0.999. To control background
157 contamination caused during the sampling, transportation, and analysis process, field blanks were
158 prepared during sampling and sample analysis. To accomplish this, high-purity nitrogen was
159 injected into a cleaned and evacuated sampling canister that was brought to the sampling site.
160 After the field blank underwent the same processes as the sample (including field exposure,
161 transportation, storage, and laboratory analysis), the concentration of the field blank sample was
162 determined. To control the interference introduced by reagents and other factors in the laboratory
163 during the analysis process, high-purity nitrogen was injected into the cleaned sample canister
164 and used as a laboratory blank to be analysed together with the reagent sample. At least 2 each
165 blank samples and laboratory blank samples were measured for each batch of samples, and all
166 target compounds were either not detected or below the method detection limit in all blank

samples. In addition, a background sampling site was set in an open area far from the tunnel to measure the background value of VOCs in the atmosphere. To ensure the stability of the experimental analysis process, one duplicated sample was analysed for every ten samples, and the relative deviation of the target in the parallel sample was less than 15%.

EF Calculation

Based on the principle of mass balance, the Pierson method (Pierson and Brachaczek, 1983; Pierson *et al.*, 1996) was used to calculate the EF of each VOC pollutant in vehicle exhaust:

$$E_i = \frac{(C_{out,i} - C_{in.i}) \times v \times t \times A}{N \times L}, \quad (1)$$

where E is the average EF (mg km^{-1} veh^{-1}) of VOC i emitted by vehicles in the experimental tunnel, $C_{out,i}$ is the concentration of VOC i at the exit of the experimental tunnel (mg m^{-3}), C_{in} is the concentration of VOC i at the entrance of the experimental tunnel (mg m^{-3}), v is the average wind speed in the tunnel during the sampling period (m s^{-1}), t is the sampling interval (1 h), A is the cross-sectional area of the tunnel (m^2), N is the number of vehicles passing through the tunnel during the sampling period, and L is the distance between two sampling sites.

The average EF of a VOC pollutant reflects the pollutant emission levels of all vehicles passing through the tunnel at different sampling times. To reflect the impact of different vehicle types in this region on VOC EFs, vehicles were classified into light vehicles and heavy vehicles according to the actual conditions of vehicles in Hefei. Comprehensive EFs for the two types of

188 vehicles were analysed using multiple regression analysis (Wang *et al.*, 2001; Zhang *et al.*,
189 2018a):
190
191 $$E = \sum_{i}^{2} e_i \times m_i + b\,, \quad (2)$$
192
193 where E is the average EF (mg km^{-1} veh^{-1}), m_i is the proportion of the number of type *i* vehicles
194 in the tunnel during the experimental period to the total number of vehicles, e_i is the
195 comprehensive EF of type *i* vehicles (mg km^{-1} veh^{-1}), and *b* is a constant term for a multiple
196 regression equation.
197
198 ***Prediction of VOC Emissions for 2017–2026***
199 A prediction model was constructed using the grey model (GM) to predict the vehicle
200 population in Hefei for the next ten years. The GM (1,1) model was constructed using the 2007–
201 2016 vehicle population data sequence (provided by the Hefei Vehicle Management Department),
202 and the vehicle population for 2017–2026 was obtained through the prediction model.
203 Subsequently, this predicted value was added to the sequence of known data, and the first data
204 point in the original data sequence was removed to achieve the purpose of equal dimensionality
205 of the data sequence. The GM (1,1) model was re-established, and the vehicle population for the
206 next year was forecast. This process continued, the value of another year was predicted, and the
207 first data point was removed until the entire prediction was completed. The dynamic GM (1,1)
208 model with equidimensional grey number filling was established as follows:

$$\hat{x}^{(1)}(k) = (x^{(0)}(1) - \frac{\beta}{\alpha})e^{-\alpha(k-1)} + \frac{\beta}{\alpha}, k = 1, 2, \ldots, n. \quad (3)$$

Consequently, the vehicle population of year k+1 could be predicted:

$$\hat{x}^{(0)}(k+1) = \hat{x}^{(1)}(k+1) - \hat{x}^{(1)}(k), k = 1, 2, \ldots, n. \quad (4)$$

The reliability of the model was verified using the residual test, stepwise ratio deviation test, degree of correlation test, and the posterior variance test. A smaller average residual in the residual test indicated a higher accuracy of the model (generally $\varepsilon < 20\%$). In the test of stepwise ratio deviation, an average absolute value of the stepwise deviation ratio $\rho < 0.2$ was considered to indicate that the general requirements were met, while a $\rho < 0.1$ was considered to indicate that the high requirements were met. When the degree of correlation r was ≥ 0.6, the prediction accuracy of the model was satisfactory. In the posterior variance test, a smaller posterior variance ratio (C) value and a higher probability (P) of small error indicated a higher model accuracy and the simulation result was considered ideal if $C \leq 0.35$ and $P \geq 0.7$.

The values of parameters α and β were obtained (α = –0.0293 and β = 123.8) using the sequence of 2012–2016 vehicle population in Hefei $x^{(0)}$ = (31.8, 40.0, 50.0, 55.3, 83.0). The detailed calculation process is shown in the SI. The values of α and β were substituted into Eq. (3) to yield the prediction model of the Hefei vehicle population:

$$\hat{x}^{(1)}(k) = (97.61 + 4226.05)e^{0.0293(k-1)} - 4226.05, k = 1, 2, \ldots, n \quad (5)$$

After the model was restored, the predicted value was given as follows:

$$\hat{x}^{(0)}(1) = 97.61$$

Then

$$\hat{x}^{(0)}(k+1) = 4323.66e^{0.0293k} - 4323.66e^{0.0293(k-1)} \quad (6)$$

The forecasted sequence of the vehicle population for 2007–2011 was

$$\hat{x}^{(0)} = (97.61, 128.55, 132.37, 136.32, 140.37)$$

It was assumed that the road conditions of Hefei and gasoline quality in the next ten years will be the same as those of today and no purchase restriction or access restrictions will be implemented. Thus, the emissions of VOCs from vehicles in Hefei in the next ten years were obtained by multiplying the predicted population of various types of vehicles in Hefei from 2017 to 2026 with the EFs of different types of vehicles and the annual VKT data obtained from the questionnaire (n = 100).

RESULTS AND DISCUSSION

Concentrations and Composition Profiles of VOCs

According to qualitative analysis of all valid samples using the NIST (National Institute of Standards and Technology) mass spectral library, a total of 67 compounds were detected (including alkanes, benzene homologues, alkenes, halogenated hydrocarbons, and oxygenated VOCs) (Table S4). Quantitative analysis was performed to determine the presence of 51 VOCs, among which 13 were not detected or exhibited a low detection rate. Therefore, 36 compounds with a high detection rate were used for the subsequent calculation of EFs. The 36 target

255 compounds included 19 alkanes, 6 alkenes, and 11 benzene homologues. The means and standard
256 deviations of these compounds at the five sampling sites are shown in Table 1. The average total
257 concentrations of the 36 VOCs at #2, #3, #6, #4, and the background point were 15.18 ± 2.27,
258 17.83 ± 5.56, 19.47 ± 6.64, 16.38 ± 3.26, and 11.95 ± 1.91 μg L^{-1}, respectively.

259 Among the 36 VOCs, alkanes were the main components of VOCs from vehicle exhaust in
260 Longchuan Tunnel, accounting for about 52% of total VOCs, followed by benzene homologues,
261 and then alkenes, which accounted for the smallest proportion (only 16%). These results were
262 similar to the composition characteristics of VOCs in Zhujiang Tunnel (Guangzhou) (Zhang *et al.*,
263 2018b). In addition, alkanes were major contributors to VOCs in Fugui Mountain Tunnel
264 (Nanjing) (Zhang *et al.*, 2018a), Shingmun Tunnel (Hongkong) (Ho *et al.*, 2009) and Hsuehshan
265 Tunnel (Taipei and Yilan) (Liu *et al.*, 2014). The high concentrations of alkanes in the
266 atmosphere are mainly derived from small gasoline vehicles equipped with a system for catalytic
267 purification of exhaust gas (Stemmler *et al.*, 2005). As the quality of gasoline products and
268 emission standards have increased in recent years, the proportion of alkenes in vehicle exhaust
269 has been reduced (Zhang *et al.*, 2018b)

270 Among the alkanes, the branched alkanes 2-methylbutane, 2,3-dimethylbutane, and 2-
271 methylpentane made large contributions, accounting for 16.14%, 8.77%, and 7.19% of total
272 VOCs, respectively (Fig. S5). This was consistent with the large proportion of branched alkanes

found in Chung-Bor Tunnel (Chen *et al.*, 2003) and Hsuehshan Tunnel (Liu *et al.*, 2014). However, the results for Zhujiang Tunnel in 2014 showed a relatively low proportion of branched alkanes (Zhang *et al.*, 2018b), which was mainly because a relatively large number of liquefied petroleum gas (LPG) vehicles pass through Zhujiang Tunnel, while a high number of gasoline vehicles pass through Longchuan Tunnel. The largest contributor of benzene homologues was toluene, accounting for 41.15% of total VOCs, followed by benzene, o-xylene, and ethylbenzene, which accounted for 24.92%, 20.54%, and 19.83%, respectively (Fig. S6). These findings were similar to those of a previous study that showed benzene, toluene, and xylenes being the dominant species in a dynamometer test (Alves et al. 2015). Among the alkenes, 1-butene accounted for the largest proportion of total VOCs (23.33%), followed by 2-pentene (21.85%) and 2-butene (21.44%) (Fig. S7).

The ten compounds with the highest concentrations of the 36 VOCs were 2-methylbutane, toluene, 3-dimethylbutane, benzene, 1-butene, 2-methylpentane, 3-methylpentane, 2-pentene, n-butane, and 2-butene. Among these, 2-methylbutane and toluene were the main components, accounting for 8.40% and 6.71% of total VOCs, respectively, with average concentrations of 1.46 ± 0.74 and 1.22 ± 0.33 μg L^{-1}, respectively (Fig. 2). The high abundance of 2-methylbutane and toluene indicated that gasoline-fuelled vehicles were the main contributor of VOCs in Longchuan Tunnel, which was similar to the results observed in a study conducted in Hong Kong (Ho *et al.*,

2013). The above results showed some differences from the composition of VOCs in Fugui Mountain Tunnel and Shingmun Tunnel. Specifically, in Fugui Mountain Tunnel, ethane, propane, ethylene, and propylene were the most abundant VOCs (Zhang *et al.*, 2018a). However, ethene, ethyne, n-butane, toluene, and propane were the most abundant VOCs in Shingmun Tunnel (Hong Kong) (Ho *et al.*, 2009).

In summary, alkanes were the main components of the 36 detected VOCs, which was comparable to those in Fugui Mountain Tunnel (Zhang *et al.*, 2018a), Shingmun Tunnel (Ho *et al.*, 2009), and Hsuehshan Tunnel (Liu *et al.*, 2014). In the current study, branched alkanes made the largest contribution to the total detected VOCs. However, the results from Zhujiang Tunnel showed a relatively low proportion of branched alkanes (Zhang *et al.*, 2018b). In addition, the top 10 VOCs with high concentrations varied between tunnel studies. Therefore, the differences in vehicle composition, fuel quality, and emission standards during testing can cause changes in the composition of VOCs in the atmosphere of different periods and regions. Accordingly, additional studies investigating the recent concentrations and compositions of VOCs in the atmosphere should be conducted so that the pollution emission standards of VOCs can be updated to achieve the goal of improving the quality of the atmospheric environment.

Diurnal Variations in Traffic Volume and VOCs Concentrations

309 The traffic volume through Longchuan Tunnel during the sampling period ranged from 378 to
310 1,471 veh h^{-1} (Fig. 3). The vehicles were classified as heavy or light vehicles according to
311 differences in emission characteristics. Vehicle counting showed that the main type was light
312 duty vehicles, which accounted for more than 90% of the total vehicles (Table S2). The traffic
313 volume exhibited apparent differences during the day, with the peak period mainly being
314 concentrated in two rush hours, 08:00–09:00 and 18:00–19:00.

315 Analysis of the samples collected at point #6 and point #4 at different times revealed that the
316 concentrations of various VOCs at sampling site #6 exhibited a higher degree of correlation with
317 the traffic volume than those at point #4 (the correlation coefficient *r* was around 0.70 at point #6
318 and around 0.50 at the point #4, except for aromatic hydrocarbon, which had a *r* of 0.06).
319 Moreover, the concentrations of total VOCs and alkanes at point #6 was approximately double
320 that at point #4, and the concentrations of alkenes and aromatic compounds at the two sampling
321 sites were similar (Fig. 3). This was largely because point #6 was near the middle of the tunnel
322 and less affected by the dilution effect caused by the air inflow from the outside the tunnel. The
323 trend of diurnal variation of VOC substances was consistent with traffic volume (Fig. 3), and
324 high-level concentrations mainly occurred during the peak hours of commuting (08:00–09:00;
325 18:00–19:00). The total concentration of alkanes was substantially higher than that of other
326 VOCs and they were the major contributor to urban atmospheric VOCs. Therefore, the temporal

distribution characteristics of VOCs in Longchuan Tunnel were apparently affected by the diurnal variations in traffic volume, especially by the light duty vehicles. Further, VOCs at sampling site #6 with a high correlation with the traffic volume indicated that the choice of the middle of the tunnel as the sampling site for EF calculation is reasonable. In addition, the variation in VOCs with traffic volume also verified the reasonable choice of sampling periods during the full experiment.

EFs of VOCs

EFs of Individual VOCs

According to the findings of the spatial and temporal distribution experiments (shown in the SI), the data collected from tunnel entrance point #2 and middle point #3 were used to calculate the EFs of VOCs. The sampling sites in this study were distributed similarly to a study of the emission characteristics of VOCs in Chung-Liao Tunnel, Taiwan (Chiang *et al.*, 2007). In the current study, the average EFs of the 36 total VOCs and the individual VOCs were 71.45 ± 23.41 and 1.98 ± 0.65 mg km^{-1} veh^{-1}, respectively. The highest EF was for alkanes at 41.39 ± 12.81 mg km^{-1} veh^{-1}, accounting for 58% of the total VOCs, followed by benzene homologues (21.72 ± 8.24 mg km^{-1} veh^{-1}), accounting for 30% of the total VOCs, while alkenes exhibited the lowest EF (8.42 ± 2.72 mg km^{-1} veh^{-1}), accounting for 12% of the total VOCs. Among the 36 target

346 substances, dimethylbutane showed the highest EF (13.3 ± 3.19 mg km^{-1} veh^{-1}), followed by
347 toluene (7.06 ± 3.14 mg km^{-1} veh^{-1}) and 2-methylpentane (6.44 ± 2.10 mg km^{-1} veh^{-1}) (Table 2).

348 A comparison of the results of EFs from our study with those of other tunnel studies is
349 presented in Table 2. The EFs of various types of VOCs in Longchuan Tunnel were similar to
350 those of the Fugui Mountain Tunnel (Zhang *et al.*, 2018a), while the EFs of the same 27 VOCs
351 detected in the above two tunnels were 43.4 and 44.8 mg km^{-1} veh^{-1}, respectively (Table 2). In
352 the results of the Zhujiang Tunnel experiment (Zhang *et al.*, 2018b), the EFs of other VOCs were
353 close to or only slightly higher than those of the Longchuan Tunnel experiments, except for those
354 of iso-butane and n-butane, which were significantly higher (Table 2). However, the EFs for
355 Longchuan Tunnel, Fugui Mountain Tunnel, and Zhujiang Tunnel, which were all measured
356 within the last three years, were significantly lower than those calculated in the 2004 Zhujiang
357 Tunnel experiment (Table 2). This is mainly because the fuel quality has improved continuously
358 in recent years and the exhaust emission standards for vehicles in China have become more
359 stringent, causing the concentration of VOCs in exhaust gases to decline.

360

361 *Comprehensive EFs of Vehicles*

362 The VOCs emitted by vehicles are affected by vehicle type. A linear regression model was
363 used to calculate the EFs of various types of vehicles based on the EFs of each sample and the
364 proportion of vehicles. Vehicles were classified into light-duty vehicles and heavy vehicles, and

365 their EFs were 81 ± 27 and 99 ± 42 mg km^{-1} veh^{-1}, respectively. The EFs were lower than those
366 from Fugui Mountain Tunnel within the same sampling month (June) in 2015 (161 ± 65 and 358
367 ± 125 mg km^{-1} veh^{-1}, respectively) (Zhang *et al.*, 2018a). This is because only 51 types of VOCs
368 were quantitatively analysed for Longchuan Tunnel, while 97 types of VOCs were quantitatively
369 analysed for Fugui Mountain Tunnel.
370
371 *Estimated VOC Emissions from Vehicle Exhaust for the Next Ten Years*
372 The simulation results of the vehicle population were verified by four test methods and the
373 results showed that the average residual (ε = 1.26% < 20%), the average absolute value of
374 stepwise ratio deviation ($\overline{\rho}$ = 0.077 < 0.10), the degree of correlation (r = 0.62 ≥ 0.60), the
375 posterior variance ratio (C = 0.072), and the probability (P = 0.8) met the validation requirements
376 (the validation calculation is shown in the SI). Therefore, the established GM (1,1) prediction
377 model for the vehicle population in Hefei was relatively consistent with the actual data.
378 The vehicle population of Hefei for 2017–2026 was predicted with the GM (1, 1) prediction
379 model (Fig. 4). The average VKT values for light-duty and heavy-duty vehicles in Hefei were
380 23,000 and 33,600 km in 2017, respectively, which was consistent with the survey for Anhui
381 Province using GPS records in 2015, which showed a VKT of 22,209 km for light-duty vehicles
382 (Liu *et al.*, 2017). In addition, the emission intensity of VOCs of 1859 ± 630 kg km^{-2} in Hefei in
383 2017 was within the range of 500–2000 kg km^{-2} observed for all of Anhui Province in 2015, but

384 lower than those observed in Beijing, Tianjin, and Shanghai, for which values ranged from 4500
385 to 9000 kg km^{-2} (Liu *et al.*, 2017). Therefore, the VKT survey and estimation of VOC emissions
386 may be considered relatively accurate and reliable. The EFs and VKT were assumed to be
387 invariable in future decades. The calculated emission of VOCs from vehicle exhaust will increase
388 annually as the number of vehicles increases. If no control measures are taken, the target VOC
389 emissions will increase from 2,510 ± 850 tons yr^{-1} in 2017 to 3,270 ± 1120 tons yr^{-1} in 2026 and
390 the emission intensity will increase from 1859 ± 630 to 2422 ± 830 kg km^{-2} yr^{-1} (Fig. 4).
391 Although much stricter emission standards and policies are in place in developed regions in
392 China, reducing the emission intensity is not easy. The vehicle number and VKT are the
393 dominant factors responsible for the increase in VOC emissions; therefore, the most effective
394 strategies for VOC emission control are to reduce vehicle number and VKT by improving public
395 transport.
396
397 **CONCLUSIONS**
398
399 Among the 36 VOCs detected in the exhaust of vehicles in Hefei, alkanes (primarily branched
400 alkanes) made the most important contribution, followed by benzene homologues, and then
401 alkenes. The diurnal variation in VOCs was relatively consistent with traffic volume, with the
402 highest concentration mainly occurring during the peak commuting period. Comparison with the

403 results from the 2004 Zhujiang Tunnel experiment revealed lower EFs of various VOC species in
404 Longchuan Tunnel, indicating that improvement of fuel quality and more rigorous emission
405 standards have reduced VOC emissions.

406 Comparisons of the emission intensity of VOCs in Hefei with the average values of Anhui
407 Province (Liu *et al.*, 2017) indicated that the estimation method is reliable for the prediction of
408 VOCs from vehicle exhaust. The predicted emissions of VOCs from vehicle exhaust will increase
409 to 3,270 ± 1120 tons yr^{-1} in 2026 assuming that the EFs and VKT do not vary. Although the
410 uncertainty associated with the EFs was considered, the VKT might change with improvements
411 to fuel quality and public transport in the next ten years. Therefore, the impact of variations in
412 VKT on prediction should be investigated in future studies. Finally, because the model has been
413 shown to be able to predict VOC emissions in Hefei, it may be useful for predicting VOC
414 emissions in other regions in China.

415

416 **ACKNOWLEDGEMENTS**

417

418 The authors gratefully acknowledge the financial support from the Anhui Provincial
419 Department of Natural Science Major Research Projects (KJ2017ZD46) and Anhui Province's
420 2018 Annual Key Research and Development Plan Project (1804a09020096).

421

REFERENCES

Alves, C.A., Lopes D.J., Calvo A.I., Evtyugina M., Rocha S. and Nunes T. (2015). Emissions from Light-Duty Diesel and Gasoline in-use Vehicles Measured on Chassis Dynamometer Test Cycles. *Aerosol Air Qual. Res.* 15(1): 99-116.

Ban-Weiss, G.A., McLaughlin, J.P., Harley, R.A., Kean, A.J., Grosjean, E. and Grosjean, D. (2008). Carbonyl and nitrogen dioxide emissions from gasoline-and diesel-powered motor vehicles. *Environ. Sci. Technol.* 42: 3944-3950.

Che, W., Zheng, J., Wang, S., Zhong, L. and Lau, A. (2011). Assessment of motor vehicle emission control policies using Model-3/CMAQ model for the Pearl River Delta region, China. *Atmos. Environ.* 45: 1740-1751.

Chen, K., Lai, C. and Ho, Y. (2003). Source profiles and ozone formation potentials of volatile organic compounds in three traffic tunnels in Kaohsiung, Taiwan. *J. Air Waste Manag. Assoc.* 53: 102-112.

Chiang, H.L., Hwu, C.S., Chen, S.Y., Wu, M.C., Ma, S.Y. and Huang, Y.S. (2007). Emission factors and characteristics of criteria pollutants and volatile organic compounds (VOCs) in a freeway tunnel study. *Sci. Total Environ.* 381: 200-211.

Deng, Y., Chen, C., Li, Q., Hu, Q., Yuan, H., Li, J. and Li, Y. (2015). Measurements of real-world vehicle CO and NOx fleet average emissions in urban tunnels of two cities in China. *Atmos. Environ.* 122: 417-426.

441 Fu, L., Shao, M., Liu, Y., Liu, Y., Lu, S. and Tang, D. (2005). Tunnel experimental study on the
442 emission factors of volatile organic compounds (VOCs) from vehicles. *Acta Scientiae*
443 *Circumstantiae* 25: 879-885.
444 Han, M., Lu, X., Zhao, C., Ran, L. and Han, S. (2015). Characterization and source
445 apportionment of volatile organic compounds in urban and suburban Tianjin, China. *Adv.*
446 *Atmos. Sci.* 32: 439-444.
447 Ho, K.F., Ho, S.S.H., Lee, S.C., Louie, P.K.K., Cao, J. and Deng, W. (2013). Volatile organic
448 compounds in roadside environment of Hong Kong. *Aerosol Air Qual. Res*. 13: 1331-
449 1347.
450 Ho, K.F., Lee, S.C., Ho, W.K., Blake, D.R., Cheng, Y., Li, Y.S., Ho, S.S.H., Fung, K., Louie,
451 P.K.K. and Park, D. (2009). Vehicular emission of volatile organic compounds (VOCs)
452 from a tunnel study in Hong Kong. *Atmos. Chem. Phys.* 9: 7491-7504.
453 Liu, W.-T., Chen, S.-P., Chang, C.-C., Ou-Yang, C.-F., Liao, W.-C., Su, Y.-C., Wu, Y.-C., Wang,
454 C.-H. and Wang, J.-L. (2014). Assessment of carbon monoxide (CO) adjusted non-
455 methane hydrocarbon (NMHC) emissions of a motor fleet–A long tunnel study. *Atmos.*
456 *Environ.* 89: 403-414.

457 Luo, J., Du, P., Samat, A., Xia, J., Che, M. and Xue, Z. (2017). Spatiotemporal pattern of PM 2.5
458 concentrations in mainland China and analysis of its influencing factors using
459 geographically weighted regression. *Sci. Rep.* 7: 40607.
460 Pant, P., Shi Z., Pope F.D. and Harrison R.M. (2017). Characterization of Traffic-Related
461 Particulate Matter Emissions in a Road Tunnel in Birmingham, UK: Trace Metals and
462 Organic Molecular Markers. *Aerosol Air Qual. Res.* 17(1): 117-130.
463 Pierson, W.R. and Brachaczek, W.W. (1983). Emissions of ammonia and amines from vehicles
464 on the road. *Environ. Sci. Technol.* 17: 757-760.
465 Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinska, B., Bishop, G.A.,
466 Stedman, D.H., Zweidinger, R.B. and Ray, W.D. (1996). Real-world automotive
467 emissions—summary of studies in the Fort McHenry and Tuscarora mountain tunnels.
468 *Atmos. Environ.* 30: 2233-2256.
469 Stemmler, K., Bugmann, S., Buchmann, B., Reimann, S. and Staehelin, J. (2005). Large decrease
470 of VOC emissions of Switzerland's car fleet during the past decade: results from a
471 highway tunnel study. *Atmos. Environ.* 39: 1009-1018.
472 Tsai, J.H., Yao Y.C., Huang P.H. and Chiang H.L. (2017). Criteria Pollutants and Volatile
473 Organic Compounds Emitted from Motorcycle Exhaust under Various Regulation Phases.
474 *Aerosol Air Qual. Res.* 17(5): 1214-1223.

475 U.S. EPA. (1998). Carcinogenic Effects of Benzene: An Update (Draft Report). U.S.
476 Environmental Protection Agency, Office of Research and Development, National Center
477 for Environmental Assessment, Washington Office, Washington, DC, EPA/600/P-
478 97/001F.
479 Wang, B., Zhang, Y., Wu, Z. and Chen, H. (2001). Tunnel test for motor vehicle emission factors
480 in Guangzhou. *Research of Environmental Sciences* 14: 13-16.
481 Wang, S., Wu, D., Wang, X.M., Fung, J.C.H. and Yu, J.Z. (2013). Relative contributions of
482 secondary organic aerosol formation from toluene, xylenes, isoprene, and monoterpenes
483 in Hong Kong and Guangzhou in the Pearl River Delta, China: an emission‐based box
484 modeling study. *Journal of Geophysical Research: Atmospheres* 118: 507-519.
485 Zhang, Q., Wu, L., Fang, X., Liu, M., Zhang, J., Shao, M., Lu, S. and Mao, H. (2018a). Emission
486 factors of volatile organic compounds (VOCs) based on the detailed vehicle classification
487 in a tunnel study. *Sci. Total Environ.* 624: 878-886.
488 Zhang, Y., Wang, X., Li, G., Yang, W., Huang, Z., Zhang, Z., Huang, X., Deng, W., Liu, T. and
489 Huang, Z. (2015). Emission factors of fine particles, carbonaceous aerosols and traces
490 gases from road vehicles: recent tests in an urban tunnel in the Pearl River Delta, China.
491 *Atmos. Environ.* 122: 876-884.

492 Zhang, Y., Yang, W., Simpson, I., Huang, X., Yu, J., Huang, Z., Wang, Z., Zhang, Z., Liu, D. and
493 Huang, Z. (2018b). Decadal changes in emissions of volatile organic compounds (VOCs)
494 from on-road vehicles with intensified automobile pollution control: Case study in a busy
495 urban tunnel in south China. *Environ. Pollut.* 233: 806-819.
496
497

Table Captions

Table 1. Concentrations of individual VOCs in the Longchuan Tunnel (Mean ± SD, μg L^{-1}).

Table 2. Emission factors of individual VOCs from the Longchuan Tunnel and other studies (mg km^{-1} veh^{-1}).

504 **Table 1.** Concentrations of individual VOCs in the Longchuan Tunnel (Mean ± SD, μg L^{-1}).

Group	Compounds	VOCs concentrations (N=7)				
		Sampling site 2	Sampling site 3	Sampling site 6	Sampling site 4	Background site
Alkane	iso-butane	0.45 ± 0.13	0.49 ± 0.15	0.51 ± 0.23	0.36 ± 0.22	0.36 ± 0.16
	n-butane	0.63 ± 0.17	0.72 ± 0.39	0.58 ± 0.54	0.54 ± 0.33	0.33 ± 0.22
	2-methylbutane	0.91 ± 0.29	1.80 ± 1.12	1.87 ± 1.11	1.28 ± 0.43	0.20 ± 0.19
	n-pentane	0.39 ± 0.11	0.55 ± 0.32	0.78 ± 0.55	0.48 ± 0.12	0.20 ± 0.01
	2,2-dimethylbutane	0.27 ± 0.01	0.28 ± 0.02	0.29 ± 0.02	0.28 ± 0.02	0.26 ± 0.00
	2,3-dimethylbutane	0.70 ± 0.26	0.72 ± 0.43	1.03 ± 0.65	0.74 ± 0.35	0.50 ± 0.15
	2-methylpentane	0.48 ± 0.16	0.70 ± 0.42	0.85 ± 0.67	0.58 ± 0.31	0.38 ± 0.15
	cyclopentane	0.18 ± 0.01	0.19 ± 0.03	0.25 ± 0.15	0.19 ± 0.02	0.16 ± 0.02
	3-methylpentane	0.58 ± 0.04	0.64 ± 0.12	0.69 ± 0.12	0.62 ± 0.04	0.52 ± 0.01
	n-hexane	0.35 ± 0.03	0.40 ± 0.10	0.53 ± 0.23	0.38 ± 0.02	0.31 ± 0.03
	methylcyclopentane	0.55 ± 0.04	0.58 ± 0.07	0.63 ± 0.09	0.57 ± 0.02	0.51 ± 0.01
	2-methylhexane	0.30 ± 0.02	0.32 ± 0.04	0.36 ± 0.08	0.31 ± 0.01	0.27 ± 0.01
	3-methylhexane	0.31 ± 0.02	0.33 ± 0.04	0.37 ± 0.08	0.32 ± 0.01	0.28 ± 0.01
	2,2,3,3-tetramethylbutane	0.24 ± 0.02	0.26 ± 0.05	0.27 ± 0.03	0.25 ± 0.02	0.22 ± 0.00
	n-heptane	0.23 ± 0.01	0.25 ± 0.04	0.28 ± 0.07	0.24 ± 0.01	0.22 ± 0.01
	methylcyclohexane	0.53 ± 0.01	0.54 ± 0.03	0.57 ± 0.04	0.54 ± 0.01	0.52 ± 0.01
	2,3,4-trimethylpentane	0.33 ± 0.01	0.34 ± 0.02	0.34 ± 0.01	0.33 ± 0.01	0.32 ± 0.00
	2-methylheptane	0.20 ± 0.01	0.20 ± 0.02	0.21 ± 0.01	0.21 ± 0.01	0.19 ± 0.00
	octane	0.18 ± 0.01	0.18 ± 0.01	0.19 ± 0.01	0.18 ± 0.01	0.17 ± 0.01
Alkene	1-butene	0.53 ± 0.12	0.70 ± 0.21	0.78 ± 0.26	0.64 ± 0.10	0.36 ± 0.11
	2-butene	0.53 ± 0.12	0.70 ± 0.23	0.64 ± 0.13	0.57 ± 0.09	0.42 ± 0.02
	1-pentene	0.17 ± 0.01	0.18 ± 0.03	0.18 ± 0.02	0.25 ± 0.20	0.17 ± 0.05
	2-pentene	0.31 ± 0.04	0.35 ± 0.08	0.37 ± 0.06	0.35 ± 0.04	0.28 ± 0.00
	isoprene	0.45 ± 0.13	0.49 ± 0.15	0.51 ± 0.23	0.36 ± 0.22	0.36 ± 0.16
	1-hexene	0.31 ± 0.01	0.35 ± 0.06	0.34 ± 0.03	0.33 ± 0.01	0.35 ± 0.06
Aromatics	benzene	0.58 ± 0.07	0.71 ± 0.27	0.88 ± 0.35	0.67 ± 0.09	0.37 ± 0.11
	toluene	1.04 ± 0.20	1.24 ± 0.62	1.36 ± 0.35	1.23 ± 0.15	0.57 ± 0.16
	ethylbenzene	0.55 ± 0.04	0.55 ± 0.07	0.59 ± 0.08	0.56 ± 0.07	0.50 ± 0.03
	n-propylbenzene	0.47 ± 0.00	0.47 ± 0.01	0.48 ± 0.01	0.47 ± 0.01	0.45 ± 0.02
	styrene	0.45 ± 0.01	0.45 ± 0.02	0.47 ± 0.04	0.45 ± 0.01	0.43 ± 0.01
	p-xylene	0.28 ± 0.04	0.34 ± 0.14	0.38 ± 0.08	0.32 ± 0.08	0.20 ± 0.02
	o-xylene	0.55 ± 0.04	0.58 ± 0.08	0.60 ± 0.06	0.61 ± 0.09	0.50 ± 0.01
	1,2,3-trimethylbenzene	0.27 ± 0.01	0.28 ± 0.02	0.33 ± 0.12	0.28 ± 0.02	0.27 ± 0.03
	1,3,5-trimethylbenzene	0.32 ± 0.03	0.37 ± 0.11	0.38 ± 0.07	0.35 ± 0.06	0.29 ± 0.01
	1-ethyl-3-methylbenzene	0.28 ± 0.02	0.30 ± 0.04	0.31 ± 0.04	0.29 ± 0.03	0.26 ± 0.00
	1-ethyl-4-methylbenzene	0.28 ± 0.01	0.29 ± 0.02	0.29 ± 0.02	0.29 ± 0.01	0.27 ± 0.00

505

506 **Table 2.** Emission factors of individual VOCs from the Longchuan Tunnel and other studies (mg
507 km^{-1} veh^{-1}).

Groups	Compounds	Longchuan tunnel Hefei (2017)[b]	Fu Gui Mountain tunnel Nanjing (2015)[a]	Zhujiang tunnel Guangzhou (2004)	Zhujiang tunnel Guangzhou (2014)
Alkane	iso-butane	1.10 ± 0.40	4.09 ± 1.64	5.10 ± 2.40	31.0 ± 3.00
	n-butane	2.49 ± 1.51	4.34 ± 0.13	10.3 ± 5.10	53.0 ± 6.00
	2-methylbutane	13.3 ± 3.19	–	–	–
	n-pentane	2.61 ± 1.34	4.89 ± 3.59	14.1 ± 2.30	7.00 ± 1.00
	2,2-dimethylbutane	0.42 ± 0.07	0.36 ± 0.23	1.10 ± 0.20	0.80 ± 0.10
	2,3-dimethylbutane	4.95 ± 2.17	5.63 ± 2.71	4.00 ± 0.70	1.50 ± 0.20
	2-methylpentane	6.44 ± 2.10	4.60 ± 2.69	20.5 ± 3.40	5.70 ± 0.80
	cyclopentane	0.33 ± 0.08	0.33 ± 0.14	4.20 ± 1.40	0.80 ± 0.10
	3-methylpentane	1.77 ± 0.32	2.03 ± 1.10	13.2 ± 2.20	3.60 ± 0.50
	n-hexane	1.40 ± 0.38	1.70 ± 1.35	8.10 ± 1.50	2.30 ± 0.50
	methylcyclopentane	1.10 ± 0.22	1.18 ± 0.60	–	0.60 ± 0.10
	2-methylhexane	0.84 ± 0.15	1.12 ± 0.56	7.30 ± 1.20	0.60 ± 0.10
	3-methylhexane	0.87 ± 0.15	1.21 ± 0.61	7.40 ± 1.10	2.50 ± 0.30
	2,2,3,3-tetramethylbutane	0.88 ± 0.18	–	–	–
	n-heptane	0.65 ± 0.26	0.85 ± 0.42	4.70 ± 0.70	1.90 ± 0.20
	methylcyclohexane	0.88 ± 0.09	0.45 ± 0.25	7.00 ± 1.10	1.10 ± 0.10
	2,3,4-trimethylpentane	0.60 ± 0.10	0.16 ± 0.08	–	0.60 ± 0.10
	2-methylheptane	0.36 ± 0.07	0.79 ± 0.32	3.50 ± 0.60	0.90 ± 0.10
	octane	0.37 ± 0.04	0.59 ± 0.29	3.20 ± 0.80	0.80 ± 0.10
Alkene	1-butene	2.62 ± 1.35	0.79 ± 0.13	17.7 ± 6.30	2.80 ± 0.30
	2-butene	2.07 ± 0.61	1.23 ± 0.21	9.50 ± 2.10	3.20 ± 0.50
	1-pentene	0.36 ± 0.02	0.23 ± 0.01	4.60 ± 0.70	0.80 ± 0.10
	2-pentene	1.52 ± 0.28	1.29 ± 0.56	–	2.30 ± 0.40
	isoprene	1.35 ± 0.35	–	2.70 ± 1.00	–
	1-hexene	0.49 ± 0.11	0.30 ± 0.14	4.50 ± 1.00	0.50 ± 0.10
Aromatics	benzene	3.59 ± 1.50	3.68 ± 1.40	18.7 ± 2.60	4.60 ± 0.50
	toluene	7.06 ± 3.14	–	31.7 ± 5.50	–
	ethylbenzene	1.32 ± 0.42	1.32 ± 0.83	8.60 ± 3.00	2.90 ± 0.40
	n-propylbenzene	0.72 ± 0.24	0.33 ± 0.11	1.80 ± 0.30	1.60 ± 0.20
	styrene	0.74 ± 0.12	0.44 ± 0.19	1.80 ± 0.50	1.10 ± 0.40
	p-xylene	2.21 ± 0.89	–	25.3 ± 5.40	–
	o-xylene	1.68 ± 0.45	–	8.90 ± 1.40	–
	1,2,3-trimethylbenzene	0.71 ± 0.17	0.55 ± 0.18	2.70 ± 0.80	4.30 ± 0.50
	1,3,5-trimethylbenzene	2.04 ± 0.81	0.35 ± 0.10	3.01 ± 0.80	3.60 ± 0.40
	1-ethyl-3-methylbenzene	1.04 ± 0.30	–	–	–
	1-ethyl-4-methylbenzene	0.60 ± 0.19	–	–	–
References		This study	Zhang et al.,	Fu et al., 2005	Zhang et al.,

	2018a	2018b

Superscript a and b indicate the sampling site and test time, respectively.

Figure Captions

Fig. 1. Sampling sites and road layout of the tunnel experiment. The spatial distribution test was conducted at sites #1, #2, #3, #4, and #5; the temporal distribution test was conducted at sites #4 and #6; and the full experiment was conducted at sites #2, #3, #4, and #6. BS indicates the background sampling site.

Fig. 2. Composition of top 10 VOCs from vehicle exhausts in Longchuan Tunnel.

Fig. 3. Variations in selected VOCs and traffic flow during the sampling period (the concentrations in Fig. 3(a) were taken from sampling site #6; the concentrations in Fig. 3(b) were taken from sampling site #4).

Fig. 4. Predicted vehicle number, estimated emission, and emission intensity of vehicle exhaust VOCs from 2017 to 2026 in Hefei.

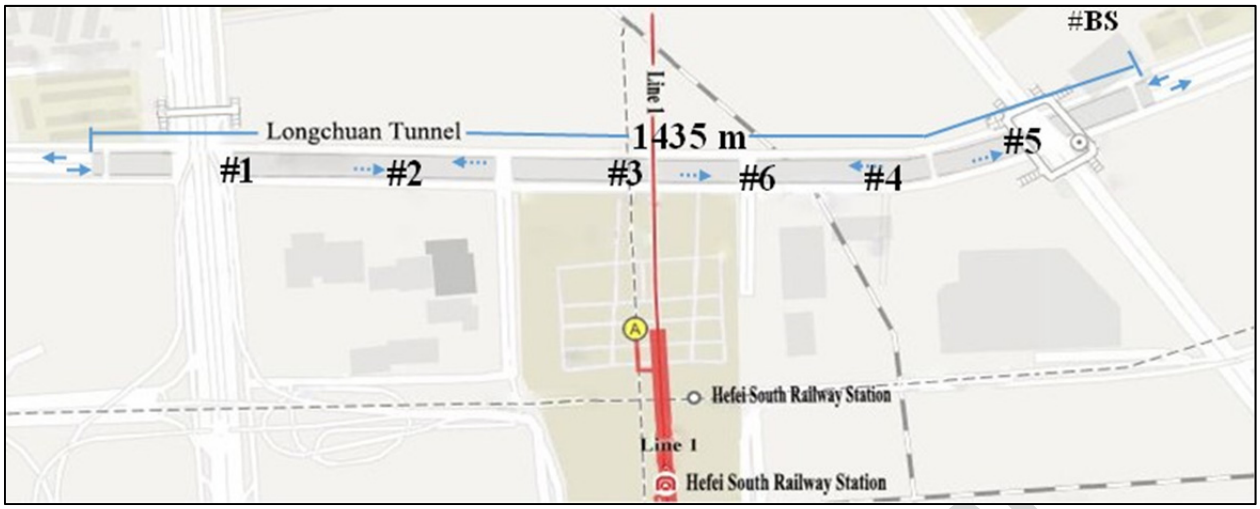
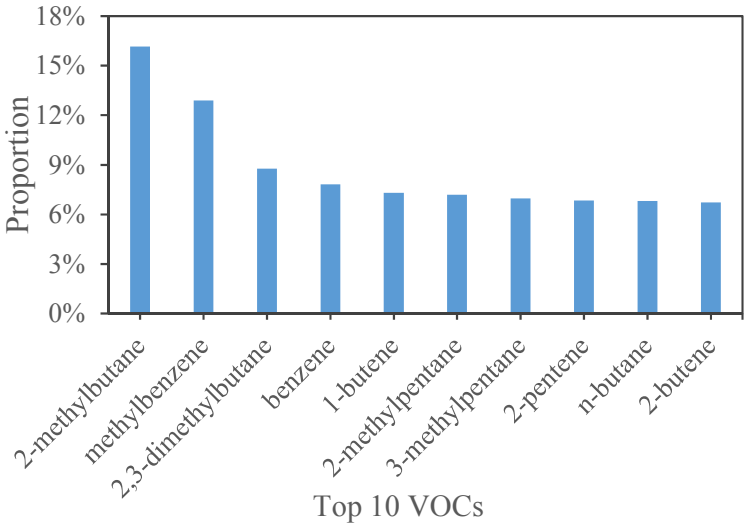


Fig. 1. Sampling sites and road layout of the tunnel experiment. The spatial distribution test was conducted at sites #1, #2, #3, #4, and #5; the temporal distribution test was conducted at sites #4 and #6; and the full experiment was conducted at sites #2, #3, #4, and #6. BS indicates the background sampling site.

530

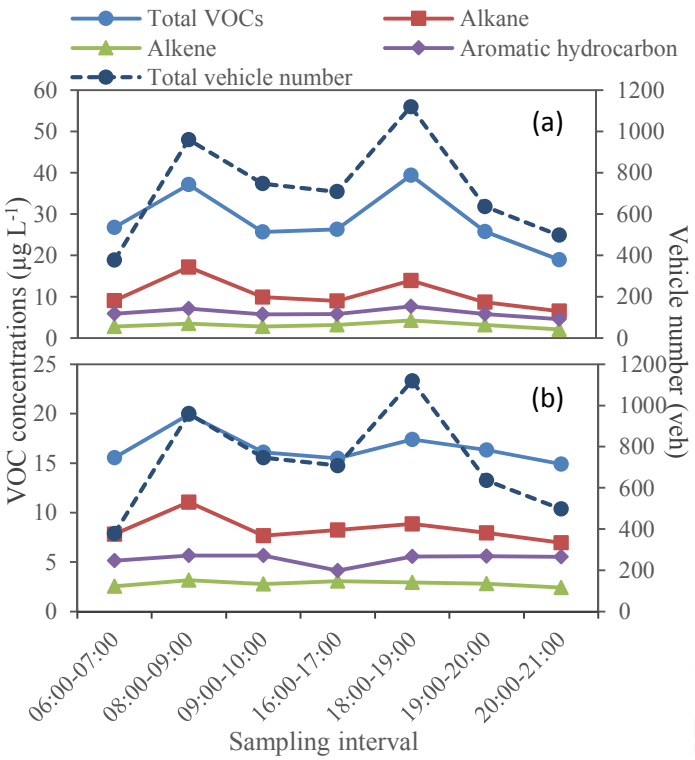


531

532 **Fig. 2.** Composition of top 10 VOCs from vehicle exhausts in Longchuan Tunnel.

533

534



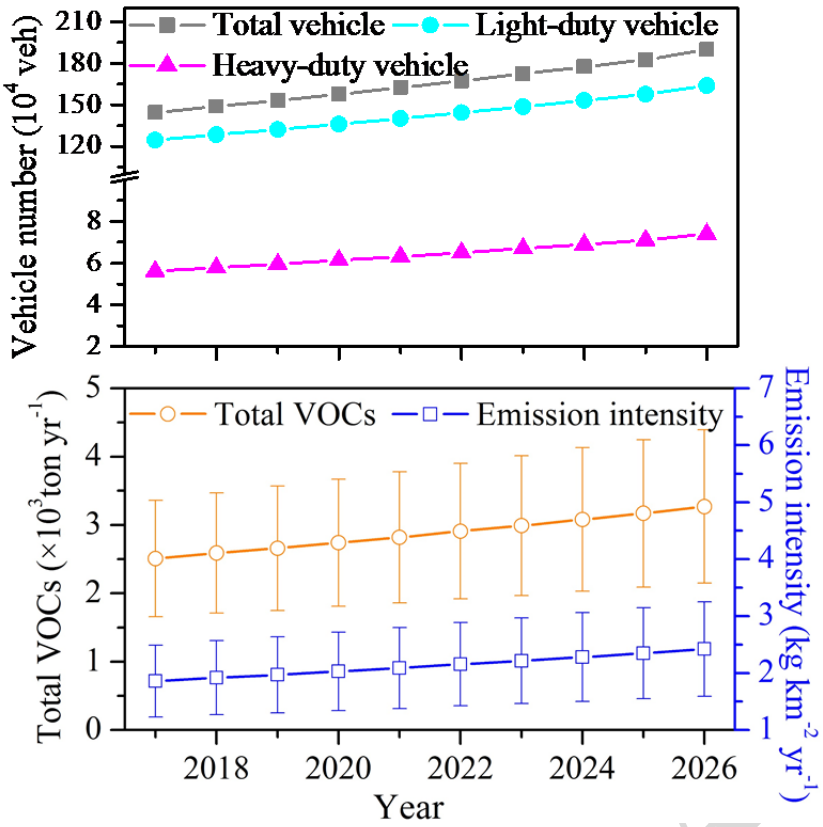
535

536 **Fig. 3.** Variations in selected VOCs and traffic flow during sampling period (the concentrations

537 in Fig. 3(a) were taken from sampling site 6; the concentrations in Fig. 3(b) were taken from

538 sampling site #4).

539



540

541 **Fig. 4.** Predicted vehicle number, estimated emission, and emission intensity of vehicle exhaust

542 VOCs from 2017 to 2026 in Hefei.

543