



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

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ABSTRACT

Automobile exhaust emissions represent the main source of atmospheric volatile organic compound (VOC) pollution in urban areas of China. To accurately determine recent emission characteristics of vehicles during urban road conditions, an optimized tunnel experiment was conducted in Longchuan Tunnel, Hefei, in 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 $41.39 \pm 12.81 \text{ mg km}^{-1} \text{ veh}^{-1}$. Benzene homologues contributed the second largest proportion, and alkenes accounted for the smallest fraction. Dimethylbutane exhibited the highest average emission factor ($13.3 \pm 3.19 \text{ mg km}^{-1} \text{ veh}^{-1}$), followed by toluene ($7.06 \pm 3.14 \text{ mg km}^{-1} \text{ veh}^{-1}$) and then 2-methylpentane ($6.44 \pm 2.10 \text{ mg km}^{-1} \text{ veh}^{-1}$). The emission factors of the VOCs in Longchuan Tunnel were consistent with those from other studies in recent years but were considerably lower than those measured in tunnels in 2004. Based on the average emission factors of VOCs for light-duty and heavy-duty vehicles (81 ± 27 and $99 \pm 42 \text{ mg km}^{-1} \text{ veh}^{-1}$, respectively), the predicted vehicle population, and vehicle-kilometers-traveled data, the emissions of VOCs were predicted for 2017–2026. The results show that if no control measures are taken, the total VOC emission volume and emission intensity will increase from $2510 \pm 850 \text{ tons yr}^{-1}$ to $3270 \pm 1120 \text{ tons yr}^{-1}$ and from $1859 \pm 630 \text{ kg km}^{-2}$ to $2422 \pm 830 \text{ kg km}^{-2}$, respectively, between 2017 and 2026.

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 NO_x, in vehicle exhaust (Wang *et al.*, 2001; Pan *et al.*, 2007; Ban-Weiss *et al.*, 2008; Deng *et al.*, 2015; 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

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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 $\mu\text{g m}^{-3}$ (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 analyze 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-kilometers-traveled (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 m². It is a two-way, two-lane tunnel, with no open vents, and is little affected by wind because it is relatively long.

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

The optimal sampling site for providing data for use in calculating EFs was determined using a preliminary experiment examining the spatial characteristics of VOCs within the tunnel. The sampling was conducted during March 6–10, 2017, and five sampling sites were established (#1, #2, #3, #4, and #5; Fig. 1), as described in the supplementary information (SI). As a result, the main distribution characteristics of the VOCs in the tunnel showed a higher concentration in the middle of the tunnel than at each end (Figs. S1–S2). Therefore, the middle interval of the tunnel (between Site #2 and Site #3) was selected as the optimal interval for determination of EFs.

To determine a reasonable sampling time to reflect the relationship of VOCs with traffic volume in one day, a temporal distribution experiment using instantaneous

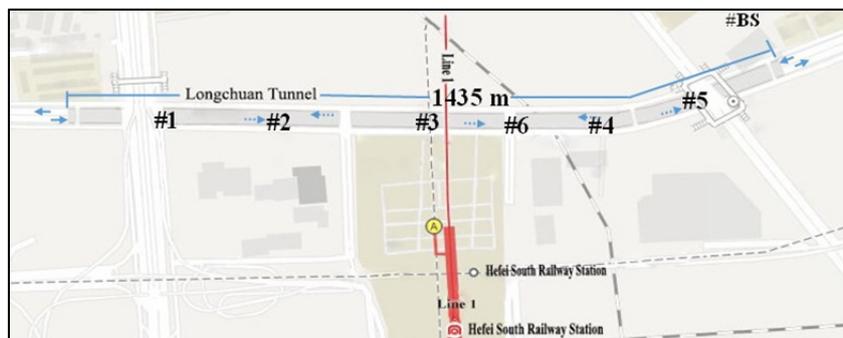


Fig. 1. Sampling sites and road layout of the tunnel experiment. The spatial distribution test was conducted at Sites #1, #2, #3, #4, and #5; the temporal distribution test was conducted at Sites #4 and #6; and the full experiment was conducted at Sites #2, #3, #4, and #6. BS indicates the background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

sampling was conducted during March 20–26, 2017. The sampling period between 06:00 and 21:00 and two sampling sites (825 m from the entrance (#6) and 950 m from the entrance (#4)) were established as described in the SI. The results showed that the change in the total amount of VOCs at the two points was essentially the same as that of the traffic volume, and both reached peak values at 08:00–10:00 in the morning and 16:00–19:00 in the afternoon (Figs. S3–S4). Therefore, the sampling time points of 06:00, 08:00, 09:00, 10:00, 12:00, 13:00, 14:00, 16:00, 18:00, 19:00, 20:00, and 21:00 could reasonably reflect the variation in VOCs with traffic volume during the day for the full experiment.

In the full experiment, the sampling period for the emission characteristics and EFs of VOCs from vehicle exhaust in Hefei was between May 29, 2017, and June 4, 2017. Based on the results from the spatial distribution and temporal distribution experiments, sites were set at 450 m (Site #2), 700 m (Site #3), 825 m (Site #6), and 950 m (Site #4) from the entrance of the tunnel (Fig. 1). Among these, the entrance point (Site #2) and the middle point (Site #3) were used for calculation of the EFs, while Site #6 and Site #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, temperature and traffic volume at the time of sampling (Table S1) were measured for calculation of EFs. The sampling periods were 06:00–07:00, 08:00–09:00, 09:00–10:00, 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 analyzed using a 7100 Preconcentrator (Entech Instruments Inc., USA) combined with a 7890A Gas Chromatograph/5975C 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

Prior to sampling, the SUMMA canister was cleaned using a canister cleaning system (3100D, Entech Instruments Inc., USA) in the laboratory more than five times, then repeatedly flushed with high-purity nitrogen gas to remove interfering substances. After cleaning, the SUMMA canister was evacuated for 24 h, after which a leak check was performed with a pressure gauge to ensure that the seal

was intact.

Photochemical Assessment Monitoring Stations (PAMS) standard mixtures (Spectra Gases Inc., USA) of the 51 VOCs were used for the calibration. These target compounds were quantified using an external standard method with a calibration range of 0.1–10 μg L⁻¹ and the coefficients of determination (R^2) of the calibration curve were higher than 0.999. To control background contamination caused during the sampling, transportation, and analysis process, field blanks were prepared during sampling and sample analysis. To accomplish this, high-purity nitrogen was injected into a cleaned and evacuated sampling canister that was brought to the sampling site. After the field blank underwent the same processes as the sample (including field exposure, transportation, storage, and laboratory analysis), the concentration of the field blank sample was determined. To control the interference introduced by reagents and other factors in the laboratory during the analysis process, high-purity nitrogen was injected into the cleaned sample canister and used as a laboratory blank to be analyzed together with the reagent sample. At least two each of the blank samples and laboratory blank samples were measured for each batch of samples, and all 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 analyzed 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), $C_{in,i}$ 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 (m²), 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 vehicles were analyzed using

multiple regression analysis (Wang *et al.*, 2001; Zhang *et al.*, 2018a):

$$E = \sum_i^2 e_i \times m_i + b, \quad (2)$$

where E is the average EF ($\text{mg km}^{-1} \text{veh}^{-1}$), m_i is the proportion of the number of type i vehicles in the tunnel during the experimental period to the total number of vehicles, e_i is the comprehensive EF of type i vehicles ($\text{mg km}^{-1} \text{veh}^{-1}$), and b is a constant term for a multiple regression equation.

Prediction of VOC Emissions for 2017–2026

A prediction model was constructed using the grey model (GM) to predict the vehicle population in Hefei for the next ten years. The GM (1,1) model was constructed using the 2007–2016 vehicle population data sequence (provided by the Hefei Vehicle Management Department), and the vehicle population for 2017–2026 was obtained through the prediction model. Subsequently, this predicted value was added to the sequence of known data, and the first data point in the original data sequence was removed to achieve the purpose of equal dimensionality of the data sequence. The GM (1,1) model was re-established, and the vehicle population for the next year was forecast. This process continued, the value of another year was predicted, and the first data point was removed until the entire prediction was completed. The dynamic GM (1,1) model with equidimensional grey number filling was established as follows:

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

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

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

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 ($\alpha = -0.0293$ and $\beta = 123.8$) 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:

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

$$k = 1, 2, \dots, n$$

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

Among the 36 VOCs, alkanes were the main components of VOCs from vehicle exhaust in Longchuan Tunnel, accounting for about 52% of total VOCs, followed by benzene homologues, and then alkenes, which accounted for the smallest proportion (only 16%). These results were similar to the composition characteristics of VOCs in Zhujiang Tunnel (Guangzhou) (Zhang *et al.*, 2018b). In addition, alkanes were major contributors to VOCs in Fugui Mountain Tunnel (Nanjing) (Zhang *et al.*, 2018a), Shingmun Tunnel (Hong Kong) (Ho *et al.*, 2009), and Hsuehshan

Table 1. Concentrations of individual VOCs in the Longchuan Tunnel (Mean \pm SD, $\mu\text{g L}^{-1}$).

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

Tunnel (Taipei and Yilan) (Liu *et al.*, 2014). The high concentrations of alkanes in the atmosphere are mainly derived from small gasoline vehicles equipped with a system for catalytic purification of exhaust gas (Stemmler *et al.*, 2005). As the quality of gasoline products and emission standards have increased in recent years, the proportion of alkenes in vehicle exhaust has been reduced (Zhang *et al.*, 2018b).

Among the alkanes, the branched alkanes 2-methylbutane, 2,3-dimethylbutane, and 2-methylpentane made large contributions, accounting for 16.14%, 8.77%, and 7.19% of total 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 10 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,

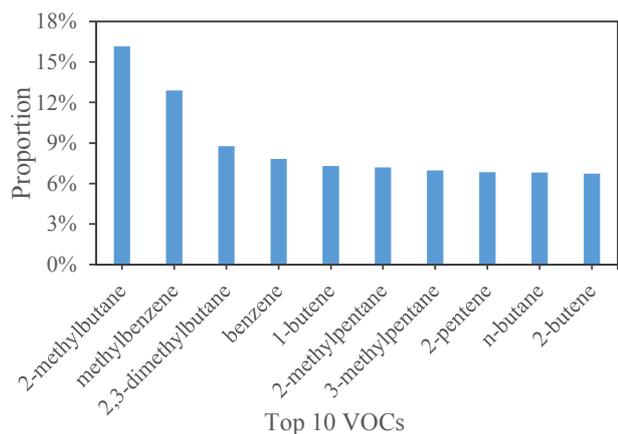


Fig. 2. Composition of top 10 VOCs from vehicle exhaust in Longchuan Tunnel.

with average concentrations of 1.46 ± 0.74 and $1.22 \pm 0.33 \mu\text{g L}^{-1}$, respectively (Fig. 2). The high abundance of 2-methylbutane and toluene indicated that gasoline-fueled 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

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

Analysis of the samples collected at Site #6 and Site #4 at different times revealed that the concentrations of various

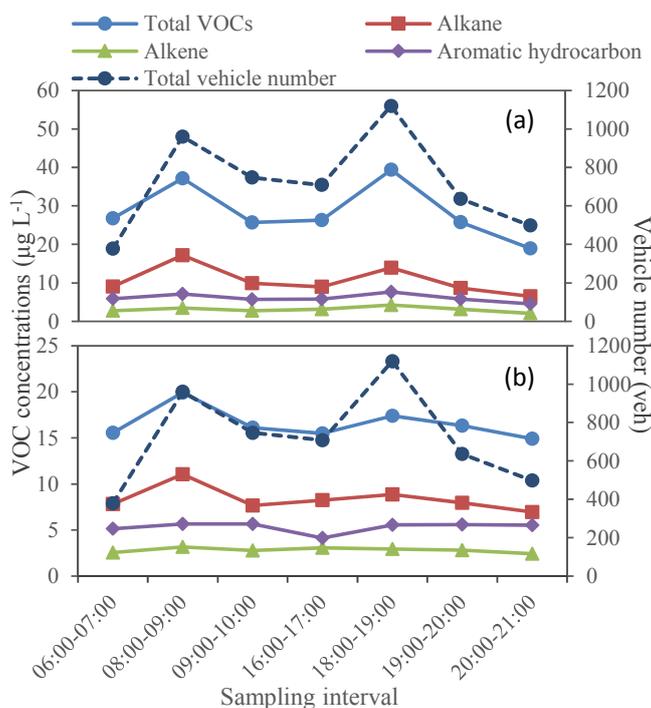


Fig. 3. Variations in selected VOCs and traffic flow during the sampling period (the concentrations in Fig. 3(a) were taken from Site #6; the concentrations in Fig. 3(b) were taken from Site #4).

VOCs at #6 exhibited a higher degree of correlation with the traffic volume than those at #4 (the correlation coefficient r was around 0.70 at #6 and around 0.50 at #4, except for aromatic hydrocarbon, which had an r of 0.06). Moreover, the concentrations of total VOCs and alkanes at Site #6 was approximately double that at Site #4, and the concentrations of alkenes and aromatic compounds at the two sampling sites were similar (Fig. 3). This was largely because #6 was near the middle of the tunnel and less affected by the dilution effect caused by the air inflow from outside the tunnel. The trend of diurnal variation of VOC substances was consistent with traffic volume (Fig. 3), and high-level concentrations mainly occurred during the peak hours of commuting (08:00–09:00; 18:00–19:00). The total concentration of alkanes was substantially higher than that of other 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 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 Site #2 (at the tunnel entrance) and Site #3 (in the middle) 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 $1.98 \pm 0.65 \text{ mg km}^{-1} \text{ veh}^{-1}$, respectively. The highest EF was for alkanes at $41.39 \pm 12.81 \text{ mg km}^{-1} \text{ veh}^{-1}$, accounting for 58% of the total VOCs, followed by benzene homologues ($21.72 \pm 8.24 \text{ mg km}^{-1} \text{ veh}^{-1}$), accounting for 30% of the total VOCs, while alkenes exhibited the lowest EF ($8.42 \pm 2.72 \text{ mg km}^{-1} \text{ veh}^{-1}$), accounting for 12% of the total VOCs. Among the 36 target substances, dimethylbutane showed the highest EF ($13.3 \pm 3.19 \text{ mg km}^{-1} \text{ veh}^{-1}$), followed by toluene ($7.06 \pm 3.14 \text{ mg km}^{-1} \text{ veh}^{-1}$) and 2-methylpentane ($6.44 \pm 2.10 \text{ mg km}^{-1} \text{ veh}^{-1}$) (Table 2).

A comparison of the results of EFs from our study with those of other tunnel studies is presented in Table 2. The EFs of various types of VOCs in Longchuan Tunnel were similar to those of the Fugui Mountain Tunnel (Zhang *et al.*, 2018a), while the EFs of the same 27 VOCs detected in the above two tunnels were 43.4 and 44.8 $\text{mg km}^{-1} \text{ veh}^{-1}$, respectively (Table 2). In the results of the Zhujiang Tunnel experiment (Zhang *et al.*, 2018b), the EFs of other VOCs were close to or only slightly higher than those of the Longchuan Tunnel experiments, except for those of isobutane and *n*-butane, which were significantly higher

(Table 2). However, the EFs for Longchuan Tunnel, Fugui Mountain Tunnel, and Zhujiang Tunnel, which were all measured within the last three years, were significantly lower than those calculated in the 2004 Zhujiang Tunnel experiment (Table 2). This is mainly because the fuel quality has improved continuously in recent years and the exhaust emission standards for vehicles in China have become more stringent, causing the concentration of VOCs in exhaust gas to decline.

Comprehensive EFs of Vehicles

The VOCs emitted by vehicles are affected by vehicle type. A linear regression model was used to calculate the EFs of various types of vehicles based on the EFs of each sample and the proportion of vehicles. Vehicles were classified into light-duty vehicles and heavy-duty vehicles, and their EFs were 81 ± 27 and $99 \pm 42 \text{ mg km}^{-1} \text{ veh}^{-1}$, respectively. The EFs were lower than those from Fugui Mountain Tunnel within the same sampling month (June) in 2015 (161 ± 65 and $358 \pm 125 \text{ mg km}^{-1} \text{ veh}^{-1}$, respectively) (Zhang *et al.*, 2018a). This is because only 51 types of VOCs were quantitatively analyzed for Longchuan Tunnel, while 97 types of VOCs were quantitatively analyzed for Fugui Mountain Tunnel.

Estimated VOC Emissions from Vehicle Exhaust for the Next Ten Years

The simulation results of the vehicle population were verified by four test methods and the results showed that the average residual ($\varepsilon = 1.26\% < 20\%$), the average absolute value of stepwise ratio deviation ($\bar{\rho} = 0.077 < 0.10$), the degree of correlation ($r = 0.62 \geq 0.60$), the posterior variance ratio ($C = 0.072$), and the probability ($P = 0.8$) met the validation requirements (the validation calculation is shown in the SI). Therefore, the established GM (1,1) prediction model for the vehicle population in Hefei was relatively consistent with the actual data.

The vehicle population of Hefei for 2017–2026 was predicted with the GM (1, 1) prediction model (Fig. 4). The average VKT values for light-duty and heavy-duty vehicles in Hefei were 23,000 and 33,600 km in 2017, respectively, which was consistent with the survey for Anhui Province using GPS records in 2015, which showed a VKT of 22,209 km for light-duty vehicles (Liu *et al.*, 2017). In addition, the emission intensity of VOCs of $1859 \pm 630 \text{ kg km}^{-2}$ in Hefei in 2017 was within the range of 500–2000 kg km^{-2} observed for all of Anhui Province in 2015, but lower than those observed in Beijing, Tianjin, and Shanghai, for which values ranged from 4500 to 9000 kg km^{-2} (Liu *et al.*, 2017). Therefore, the VKT survey and estimation of VOC emissions may be considered relatively accurate and reliable. The EFs and VKT were assumed to be invariable in future decades. The calculated emission of VOCs from vehicle exhaust will increase annually as the number of vehicles increases. If no control measures are taken, the target VOC emissions will increase from $2,510 \pm 850 \text{ tons yr}^{-1}$ in 2017 to $3,270 \pm 1120 \text{ tons yr}^{-1}$ in 2026 and the emission intensity will increase from 1859 ± 630 to $2422 \pm 830 \text{ kg km}^{-2} \text{ yr}^{-1}$ (Fig. 4). Although much

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

Groups	Compounds	Longchuan tunnel Hefei ^a (2017) ^b	Fu Gui Mountain tunnel Nanjing (2015)	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-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 <i>et al.</i> , 2018a	Fu <i>et al.</i> , 2005	Zhang <i>et al.</i> , 2018b	

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

stricter emission standards and policies are in place in developed regions in China, reducing the emission intensity is not easy. The vehicle number and VKT are the dominant factors responsible for the increase in VOC emissions; therefore, the most effective strategies for VOC emission control are to reduce vehicle number and VKT by improving public transport.

CONCLUSIONS

Among the 36 VOCs detected in the vehicle exhaust in Hefei, alkanes (primarily branched alkanes) formed the largest contribution, followed by benzene homologues and then alkenes. The diurnal variation in the VOCs was relatively consistent with traffic volume, with the highest

concentration mainly occurring during the peak commuting period. A comparison with the results from the 2004 Zhujiang Tunnel experiment revealed lower EFs of various VOC species in Longchuan Tunnel, indicating that the improvement in fuel quality and more rigorous emission standards have reduced VOC emissions.

A comparison of the emission intensity of VOCs in Hefei with the average values in Anhui Province (Liu *et al.*, 2017) indicated that the estimation method reliably predicts VOCs from vehicle exhaust. These VOC emissions will increase to $3270 \pm 1120 \text{ tons yr}^{-1}$ in 2026, assuming that the EFs and VKT do not vary. The VKT might change with improvements in fuel quality and public transport during the next ten years. Therefore, the impact of variations in the VKT on prediction should be investigated in future

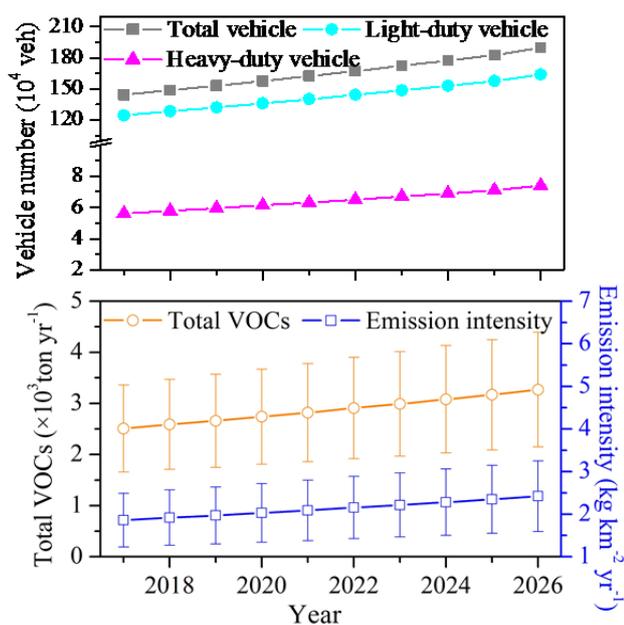


Fig. 4. Predicted vehicle population, estimated emission, and emission intensity of vehicle exhaust VOCs from 2017 to 2026 in Hefei.

studies. Finally, because the model has been shown to be an accurate predictor of VOC emissions in Hefei, it may be useful for predicting VOC emissions in other regions of China.

ACKNOWLEDGEMENTS

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

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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Received for review, July 5, 2018

Revised, September 29, 2018

Accepted, October 2, 2018