Environmental Pollution 233 (2018) 806–819

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Decadal changes in emissions of volatile organic compounds (VOCs) from on-road vehicles with intensified automobile pollution control: Case study in a busy urban tunnel in south China☆

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ARTICLE INFO

Article history:
Received 8 March 2017
Received in revised form
23 October 2017
Accepted 28 October 2017
Available online 13 November 2017

Keywords:
Emission factors
Volatile organic compounds
Vehicle exhaust
Ozone
Secondary organic aerosols

ABSTRACT

In the efforts at controlling automobile emissions, it is important to know in what extent air pollutants from on-road vehicles could be truly reduced. In 2014 we conducted tests in a heavily trafficked tunnel in south China to characterize emissions of volatile organic compounds (VOC) from on-road vehicle fleet and compared our results with those obtained in the same tunnel in 2004. Alkanes, aromatics, and alkenes had average emission factors (EFs) of 338, 63, and 42 mg km^{-1} in 2014 against that of 194, 129, and 160 mg km^{-1} in 2004, respectively. In 2014, LPG-related propane, n-butane and i-butane were the top three non-methane hydrocarbons (NMHCs) with EFs of 184 ± 21, 53 ± 6 and 31 ± 3 mg km^{-1}; the gasoline evaporation marker i-pentane had an average EF of 17 ± 3 mg km^{-1}; ethylene and propene were the top two alkenes with average EFs of 16 ± 1 and 9.7 ± 0.9 mg km^{-1}, respectively; isoprene had no direct emission from vehicles; toluene showed the highest EF of 11 ± 2 mg km^{-1} among the aromatics; and acetylene had an average EF of 7 ± 1 mg km^{-1}. While EFs of total NMHCs decreased only 9% from 493 ± 120 mg km^{-1} in 2004 to 449 ± 40 mg km^{-1} in 2014, their total ozone formation potential (OFP) decreased by 57% from 2.50 × 10^3 mg km^{-1} in 2004 to 1.10 × 10^3 mg km^{-1} in 2014, and their total secondary organic aerosol formation potential (SOAFP) decreased by 50% from 50 mg km^{-1} in 2004 to 25 mg km^{-1} in 2014. The large drop in ozone and SOA formation potentials could be explained by reduced emissions of reactive alkenes and aromatics, due largely to fuel transition from gasoline/diesel to LPG for taxis/buses and upgraded vehicle emission standards.

1. Introduction

Volatile organic compounds (VOCs) are precursors of tropospheric ozone and secondary organic aerosols (SOA) (Carter, 1994; Finlayson-Pitts and Pitts, 1999; Atkinson and Arey, 2003). They are emitted from both biogenic and anthropogenic sources

☆ This paper has been recommended for acceptance by Charles Wong.

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https://doi.org/10.1016/j.envpol.2017.10.133
0269-7491/

(Seinfeld et al., 1998), with global biogenic emissions accounting for 10 times the amount of anthropogenic emissions (Guenther et al., 1995). However, anthropogenic VOC emissions can predominate on a global level, especially in densely populated urban areas or highly industrialized regions (Atkinson and Arey, 2003). Vehicle exhaust, an important anthropogenic source of ambient VOCs worldwide (Streets et al., 2003), contributes substantially to air pollution in China due to the increasing number of automobiles over the past three decades. The number of civilian vehicles in China has increased by approximately 20% per year, from 1.8 million in 1980 to 126.7 million in 2013 (China Statistical Yearbook, 2014). Recent emission inventories suggest that vehicle exhaust makes up approximately 36% of the anthropogenic VOCs in China (Zhang et al., 2009). In the Pearl River Delta (PRD) region of the South China, bottom-up estimates suggest that motor vehicles contribute to 40–57% of VOCs from anthropogenic emission sources (Zhang et al., 2009; Zheng et al., 2009b; Che et al., 2011; Lu et al., 2013). Similarly, field measurements in the PRD region have also demonstrated that vehicle exhaust may constitute 20–53% of anthropogenic VOCs (Guo et al., 2007a; Liu et al., 2008b; Zhang et al., 2012, 2013; Ling et al., 2011) and 24–40% of the ozone formation potentials (OFPs) (Zheng et al., 2009a; Cheng et al., 2010; Zhang et al., 2012).

To combat air pollution from vehicle exhaust, which is surging along with vehicle numbers, China has strengthened its emission standards for vehicles in the past decade. Standards have been upgraded from China I (equals to Euro I) in 2001, to China IV in 2010, and, finally, to China V in 2015. The rapidly changing vehicle fleet composition and emission standards make it difficult to estimate motor vehicle VOC emissions on regional and national scales. The uncertainties of the bottom-up on-road vehicle VOC emission estimates in the PRD region were up to -50% - +70% (Zheng et al., 2009b). Therefore, updated local emission factors (EFs) for automobiles are urgently needed for better emission estimates.

Vehicular EFs can be determined by many methods, including chassis and engine dynamometer testing under controlled conditions (Nine et al., 1999), on-road measurements (Shorter et al., 2005), remote sensing (Bishop and Stedman, 1996), and tunnel studies (Jamriska et al., 2004; Hueglin et al., 2006). Tunnel studies have the advantage of obtaining absolute emission levels by capturing a snapshot of the on-road vehicle fleet, thus representing real-world operations and conditions (Franco et al., 2013). On-road EF measurements of vehicular emissions have been extensively performed throughout China by using portable emissions measurement systems (PEMS) in locations such as Shanghai (Chen et al., 2007), Beijing (Liu et al., 2009; Huo et al., 2011; Wang et al., 2011; Shen et al., 2014; Yao et al., 2015), Macao (Hu et al., 2012; Wang et al., 2014), and Chongqing (Wang et al., 2012). Remote sensing measurements of EFs were previously conducted in Hangzhou in 2004 and 2005 (Guo et al., 2007b). In those studies total rather than speciated non-methane hydrocarbons (NMHCs) or total VOCs (TVOC) were measured, except that very recently Yao et al. (2015) measured EFs for some speciated VOCs from 18 typical diesel vehicles based on on-road measurements in Beijing.

Although the results from tunnel studies reflect emissions under real-world conditions, only a few tunnel studies have been conducted to characterize vehicular VOC emissions on mainland China. Wang et al. (2001b) and Lu et al. (2010) measured vehicular VOC emissions by sampling from the middle of tunnels in Beijing and Shanghai, respectively. Most EFs from tunnel studies in China come from field campaigns conducted in the Zhujiang Tunnel, the tunnel that is also the subject of the current study. EFs have been reported for fine particulate matter ($PM_{2.5}$) and inorganic traces gases (Wang et al., 2001a; Dai et al., 2015; Liu et al., 2014a), total NMHCs (Wang et al., 2001a), and speciated VOCs (Fu et al., 2005). In the PRD region, EFs for vehicular VOCs were determined from Hong Kong tunnel measurements of the Cross-Harbor Tunnel in 1999 (Ho et al., 2004) and the Shing Mun Tunnel in 2003 (Ho et al., 2009). The last tunnel campaign for vehicular VOC emissions in the PRD region was conducted in 2004 (Fu et al., 2005); therefore, VOC composition profiles and EFs from on-road vehicles should be upgraded to reflect the changing vehicle fleet composition and tightened emission standards. Liquefied petroleum gas (LPG)-driven taxis and buses, were not present in Guangzhou until 2004, but have already contributed substantially to ambient VOCs (Tang et al., 2008; Zhang et al., 2012, 2013).

From June 25th to July 1st, 2014, we measured the EFs of a variety of gaseous and particulate pollutants from on-road vehicles in the Zhujiang Tunnel in the urban area of Guangzhou, China. The EFs of $PM_{2.5}$, organic carbon (OC), elemental carbon (EC) and total VOCs were previously reported by Zhang et al. (2015a), and those of dicarbonyls were detailed by Zhang et al. (2016). The present study focuses on source profiles and EFs of speciated VOCs. Here, we provide the latest emission characterization of vehicular VOCs in the PRD region, which could be used to assess the effectiveness of vehicle emission policies.

2. Experimental methods

2.1. Field work

This study was conducted in 2014 from June 25th to July 1st, in the Zhujiang Tunnel, a busy underwater tunnel that crosses the Pearl River in urban Guangzhou. Trace gases were simultaneously detected with on-line instrumentations. One hour VOC samples were collected in pre-evacuated 2-L electro-polished stainless-steel canisters at a constant flow rate of 66.7 mL min^{-1} using a Model 910 Pressurized Canister Sampler (Xonteck, Inc., CA, USA) on two weekdays and two weekends. The VOC samples were collected at time intervals of 02:00-03:00, 07:00-08:00, 08:00-09:00, 09:00-10:00, 10:30-11:30, 14:00-15:00, 17:00-18:00, 18:00-19:00, and 19:00-20:00 on each sampling day. Detailed descriptions of the tunnel, *in situ* field measurements, and sample collection, can be found in our previous studies (Zhang et al., 2015a, 2016) and are also available in the supporting information.

Carbon dioxide (CO_2) was monitored *in situ* by an eddy covariance system (IRGASON, Campbell Scientific, Inc., UT, U.S.), with an integrated open-path CO_2/H_2O gas analyzer and a 3-D Sonic Anemometer. Carbon monoxide (CO) was measured from canister air samples by gas chromatography (Zhang et al., 2012).

2.2. Laboratory analysis

We analyzed VOCs by using a Model 7100 Preconcentrator (Entech Instruments Inc., California, USA) combined with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). The detailed cryogenic concentration steps are described elsewhere (Zhang et al., 2013a). Briefly, VOCs were concentrated inside canisters by three-stage liquid nitrogen cryogenic trapping, then injected to the GC-MSD/FID system for quantification. Details regarding the instrumentation and parameters, analytical conditions, calibration methods, and quality control and quality assurance procedures, can be found elsewhere (Zhang et al., 2012, 2015a,b) and are also available in the supporting information.

2.3. EF calculations for individual VOCs

The average EF of individual VOCs from vehicles passing through the tunnel during a time interval, *T*, was calculated as follows

(Zhang et al., 2016):

$$EF_i = \frac{(C_{outlet,i} - C_{inlet,i}) \times V_{air} \times T \times A}{N \times L} \quad (1)$$

where $\boldsymbol{EF_i}$ (mg km^{-1} veh^{-1}) is the mean EF of VOC species $\boldsymbol{i}$ during the time interval $\boldsymbol{T}$ (s; 1 h in this study); $\boldsymbol{C_{outlet,i}}$ and $\boldsymbol{C_{inlet,i}}$ (mg m^{-3}) are the paired average concentrations of VOC species $\boldsymbol{i}$ measured at the outlet station and inlet station during the same time interval, respectively; $\boldsymbol{V_{air}}$ (m s^{-1}) is the air velocity parallel to the tunnel measured by the 3-D sonic anemometer, $\boldsymbol{A}$ (m^2) is the tunnel cross-section area, N is the total vehicle number passing through the tunnel during the time interval, and $\boldsymbol{L}$ (km) is the length of the tunnel between the outlet and inlet stations. For the piston effect of the traffic in a one-way tunnel assures, the equation requires that the exit end is the same for both the air and the traffic.

It is vital to evaluate if emission factors would be influenced by oxidation processes, in which NO_3 radical usually plays an important role under the dark environment. With the available rate constants (Atkinson and Arey, 2003; Finlayson-Pitts and Pitts, 1999), the consumption of VOC via reactions with NO_3 was estimated to be less than 0.1% during their residency in the tunnel even under a NO_3 radical concentration as high as 20 ppt, which is near the upper limit of ambient NO_3 levels observed during nighttime in polluted urban atmosphere (McLaren et al., 2010; Wang et al., 2013b). Thus VOC loss by reactions with NO_3 radical in the tunnel is negligible.

3. Results and discussion

3.1. Diurnal variations in traffic flow, fleet composition, and incremental VOCs/CO/CO_2 concentrations

The total number of vehicles passing through the tunnel ranged from 660 to 2644 per hour, with an average of 2108 per hour. This is comparable to findings from Fu et al. (2005), who reported an average of 2528 per hour in the same tunnel in 2004. Fig. 1 shows variations in vehicle numbers by fuel types, including gasoline vehicles (GVs), diesel vehicles (DVs), and LPG vehicles (LPGVs, mostly taxi and buses). The number of GVs, DVs, and LPGVs passing through the tunnel ranged 263-1877, 96-587, and 279-540 vehicles per hour, respectively. As expected, GVs and DVs displayed significant diurnal variations, with minimums during the night and maximums between the rush hours of 17:00–18:00. The flow of LPGVs was relatively stable, with less distinctive diurnal variation. The vehicle fleet compositions were quite near that recorded in 17 roads in Guangzhou in 2010 (Yao et al., 2013). For example, in average taxi and bus occupied 26.7% and 22.7%, respectively, in vehicle fleet passing through tunnel; and as reported by Yao et al. (2013), they occupied 20.9% and 21.4% before the first traffic control drill (normal days), and 26.1% and 23.3% before the second traffic control drill (normal days), respectively.

Incremental concentrations (Δ) from the tunnel inlet station to the outlet station for selected VOCs, CO_2, and CO are also shown in Fig. 1. Traffic-related aromatic hydrocarbons, including benzene, toluene, and ethylbenzene (Wang et al., 2002), as well as the LPG-related emission markers propane, *n*-butane, and *i*-butane (Blake and Rowland, 1995), peaked during the morning and afternoon rush hours on the weekdays of June 25th and 26th; in contrast, only one afternoon peak appeared on the weekend days of June 27th and 28th. Similar diurnal variations were observed for incremental concentrations of CO_2 and CO, with peak values during the late afternoon rush hours from 17:00 to 19:00 and lowest concentrations registered during the night.

3.2. NMHC composition profiles

3.2.1. NMHC composition from on-road vehicles passing through the tunnel

The inlet to outlet incremental concentrations of VOCs represents the composition of VOCs from vehicles passing through the tunnel. Table 1 lists the average weight percentages (wt%) with 95% confidence intervals (95% C.I.) and ranges for 64 VOC species from vehicle exhaust. Alkanes accounted for 74.8 ± 2.2% of the total, which was comprised of *n*-alkanes (58.1 ± 2.6%), branched alkanes (15.6 ± 1.0%), and saturated cycloalkanes (1.1 ± 0.1%). Aromatic hydrocarbons constituted the second largest fraction (14.1 ± 1.6%), followed by alkenes (9.4 ± 0.6%), and alkynes (acetylene) (1.7 ± 0.3%).

The individual NMHCs with the highest weight percentages were propane, *n*-butane, and *i*-butane, with weight percentages ranging from 16.5–51.3%, 7.0–16.8%, and 4.3–10.4% and averages of 40.5 ± 2.6%, 11.7 ± 0.8%, and 6.8 ± 0.5%, respectively. Ethylene and propene were the most prevalent alkene species, with fractions of 3.8 ± 0.3% and 2.2 ± 0.1%, respectively. Toluene, m,p-xylene, and benzene were the most abundant aromatic hydrocarbons, contributing 2.5 ± 0.3%, 1.9 ± 0.2%, and 1.0 ± 0.1% to the total, respectively.

A comparison of results between the current and a previous study from the same tunnel (Fu et al., 2005) revealed significant changes in vehicle exhaust VOC compositions following upgraded fuel standards, more stringent emission standards, and increasing use of environmentally friendly fuels such as LPG (Fig. 2). Alkanes (35.1%) and alkenes (31.2%) had similar fraction contributions and were the most abundant VOCs in 2004; in 2014, however, alkanes dominated, with a fraction of 74.8%, and alkenes and aromatic hydrocarbons were significantly lower than in 2004 (Fu et al., 2005).

Whereas most VOC species have decreased since 2004, propane and butanes increased. Propane increased by an order of magnitude from 3.1% in 2004 (Fu et al., 2005) to 40.5 ± 2.6% in 2014. N-butane and *i*-butane also increased from 2.1% and 1.0% in 2004 to 11.7 ± 0.8% and 6.8 ± 0.5% in 2014, respectively. In contrast, alkene species were lower in 2014 than in 2004, with percentages of ethylene, propene, and 1-butene decreasing from 10.8%, 4.6%, and 13.6% in 2004 to 3.8 ± 0.3%, 2.2 ± 0.1%, and 3.6 ± 0.6% in 2014, respectively. All aromatic hydrocarbons, including benzene, which decreased from 3.8% to 1.0 ± 0.1%, toluene, which decreased from 6.5% to 2.5 ± 0.4%, and C_8-AHs (ethylbenzene and xylenes), which decreased from 8.8% in 2004 to 2.8 ± 0.5% in 2014. Acetylene also decreased from 2.1% in 2004 to 1.7 ± 0.3% in 2014.

Compositional changes in VOCs from vehicle exhaust can largely be explained by differences in vehicle fleet composition, vehicle emission standards, and fuel type and quality. The sharp increases in propane and butanes fractions can be attributed to the widespread use of LPG as bus and taxi fuel beginning in 2004 (Tang et al., 2007). There were no LPG-powered vehicles in Guangzhou in 2004; however, by 2014, there were 11,000 LPG-powered taxis and 22,000 powered buses (Guangzhou Statistical Yearbook, 2015). LPG vehicles constituted over 20% of the vehicles passing through the tunnel in 2014 (Fig. 1). Propane, *n*-butane, and *i*-butane were determined to be major components of LPG (Blake and Rowland, 1995) and LPG taxi exhaust in Guangzhou (Tang et al., 2007, 2008) and Hong Kong (Guo et al., 2011) (Fig. S1); thus, the increased percentages of propane and butanes detected here likely reflect the transition in the fuels used by taxis and buses from gasoline or diesel to LPG. The decrease in alkenes can be attributed to upgraded fuel quality and vehicle emission standards. The fuel quality standards for diesel vehicles were upgraded from China II in 2004 and to China III in 2014. Gasoline oil standards for motor vehicles were upgraded from China II in 2004 to China IV in 2014.

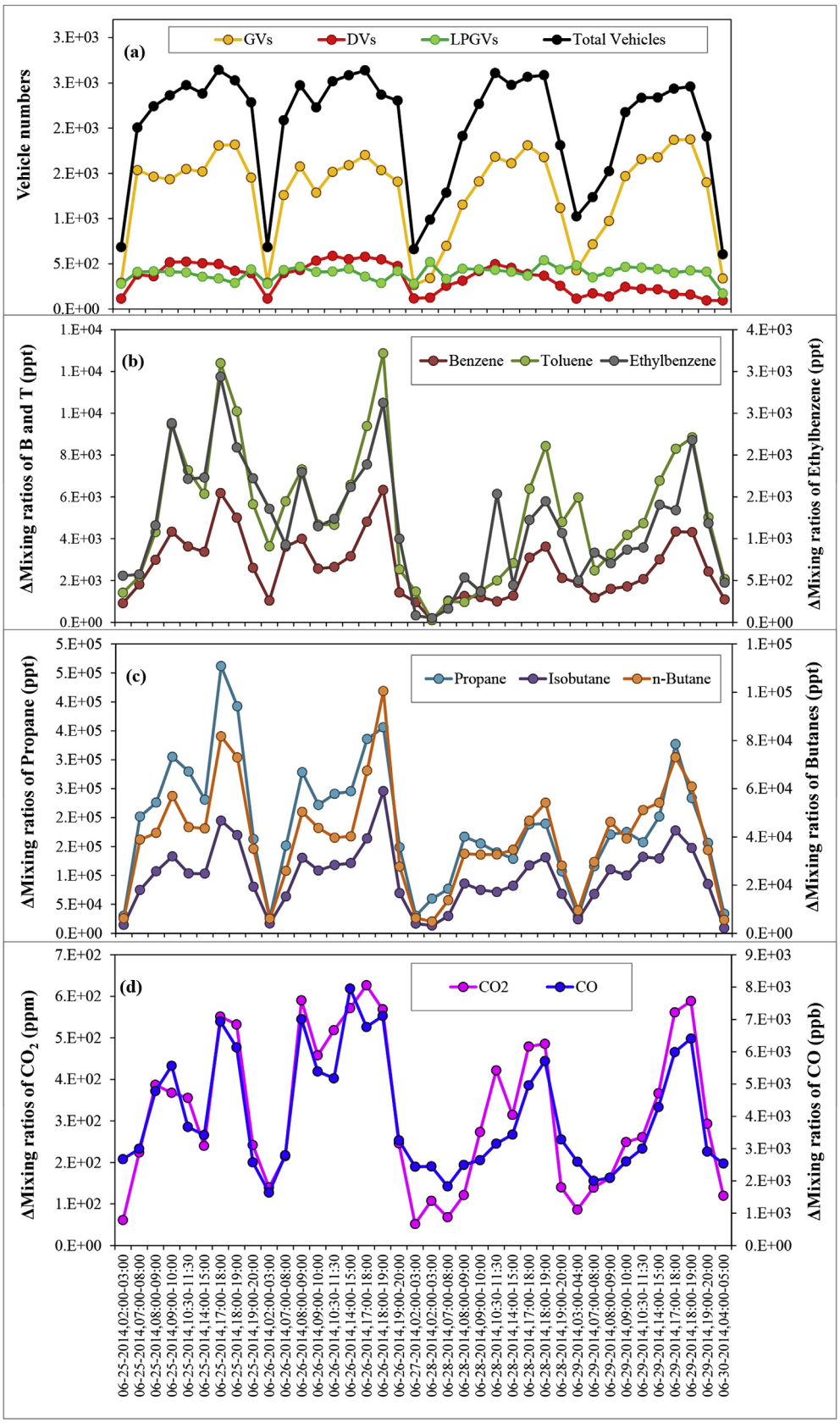

Fig. 1. Traffic flow and incremental mixing ratios (Δ) of selected VOCs, CO_2, and CO during the sampling period (B: benzene; T: toluene).

Table 1
Weight percentages (wt%) of VOCs in vehicle exhaust based on tests in the Zhujiang Tunnel.

Species	Mean ± 95% C.I.	Ranges	Species	Mean ± 95% C.I.	Ranges
Ethane	2.02 ± 0.26	0.30–4.63	*1,3-Butadiene*	0.25 ± 0.13	0.02–0.88
Propane	40.53 ± 2.56	16.49–51.32	*Trans-2-butene*	0.42 ± 0.06	0.18–0.96
n-Butane	11.67 ± 0.79	7.02–16.80	*Cis-2-butene*	0.30 ± 0.04	0.13–0.64
n-Pentane	1.71 ± 0.25	0.79–4.02	*3-Methyl-1-butene*	0.09 ± 0.01	0.04–0.19
n-Hexane	0.54 ± 0.12	0.10–1.80	*1-Pentene*	0.17 ± 0.02	0.08–0.32
n-Heptane	0.43 ± 0.04	0.22–0.80	*2-Methyl-1-butene*	0.36 ± 0.04	0.17–0.70
n-Octane	0.18 ± 0.02	0.09–0.36	*Trans-2-pentene*	0.34 ± 0.05	0.12–0.71
n-Nonane	0.14 ± 0.02	0.01–0.33	*Cis-2-pentene*	0.18 ± 0.03	0.08–0.38
n-Decane	0.20 ± 0.03	0.06–0.47	*2-Methyl-2-butene*	0.51 ± 0.06	0.14–0.95
n-undecane	0.43 ± 0.08	0.03–1.27	*Cyclopentene*	0.08 ± 0.01	0.04–0.20
n-dodecane	0.45 ± 0.12	0.19–2.07	*1-Hexene*	0.12 ± 0.02	0.07–0.27
Isobutane	6.80 ± 0.46	4.26–10.42	*Trans-2-hexene*	0.07 ± 0.02	0.02–0.16
Isopentane	3.77 ± 0.53	1.62–8.44	*Cis-2-hexene*	0.05 ± 0.01	0.01–0.11
2,2-Dimethylbutane	0.17 ± 0.02	0.08–0.37	*3-Hexene*	0.05 ± 0.01	0.02–0.12
2,3-Dimethylbutane	0.33 ± 0.04	0.15–0.57	*Acetylene*	1.66 ± 0.27	0.42–3.96
2-Methylpentane	1.27 ± 0.15	0.57–2.48	*Benzene*	1.03 ± 0.10	0.15–1.88
3-Methylpentane	0.81 ± 0.09	0.25–1.77	*Toluene*	2.52 ± 0.34	0.61–7.03
2-Methylhexane	0.14 ± 0.01	0.08–0.27	*Ethylbenzene*	0.65 ± 0.09	0.17–1.45
3-Methylhexane	0.58 ± 0.06	0.29–1.12	*m/p-Xylene*	1.90 ± 0.24	0.24–4.24
2,3-Dimethylpentane	0.21 ± 0.02	0.11–0.45	*Styrene*	0.27 ± 0.11	0.02–1.06
2,4-Dimethylpentane	0.68 ± 0.08	0.32–1.43	*o-Xylene*	0.86 ± 0.10	0.26–1.74
2,2,4-Trimethylpentane	0.37 ± 0.03	0.21–0.73	*Isopropylbenzene*	0.10 ± 0.01	0.03–0.21
2,3,4-Trimethylentane	0.14 ± 0.02	0.08–0.30	*n-Propylbenzene*	0.37 ± 0.05	0.11–0.83
2-Methylheptane	0.21 ± 0.03	0.11–0.39	*m-Ethyltoluene*	0.87 ± 0.16	0.12–1.84
3-Methylheptane	0.21 ± 0.02	0.10–0.42	*p-Ethyltoluene*	0.74 ± 0.11	0.32–1.83
Cyclopentane	0.17 ± 0.02	0.05–0.39	*1,3,5-Trimethylbenzene*	0.83 ± 0.11	0.34–1.87
Cyclohexane	0.56 ± 0.06	0.28–1.07	*o-Ethyltoluene*	0.57 ± 0.08	0.24–1.27
Methylcyclopentane	0.13 ± 0.02	0.05–0.38	*1,2,4-Trimethylbenzene*	1.76 ± 0.22	0.78–3.46
Methylcyclohexane	0.25 ± 0.03	0.10–0.50	*1,2,3-Trimethylbenzene*	0.99 ± 0.13	0.52–2.29
Ethylene	3.76 ± 0.32	2.02–6.18	*m-Diethylbenzene*	0.22 ± 0.04	0.06–0.63
Propene	2.19 ± 0.13	1.58–3.31	*p-Diethylbenzene*	0.61 ± 0.10	0.25–1.75
1-Butene	0.65 ± 0.05	0.44–1.06	*o-Diethylbenzene*	0.06 ± 0.02	0.02–0.26

The alkene limit in gasoline decreased from 35% (v/v %) in 2004 to 28% in 2014.

3.2.2. Comparison of compositions with other tunnel studies

Alkanes make up the largest group in most tunnel studies, with weight percentages ranging from 27.0% to 74.8% (Duffy and Nelson, 1996; Wang et al., 2001b; Ho et al., 2009; Liu et al., 2014b). In contrast, alkenes were the most abundant fraction in the Zhujiang Tunnel in 1999 (36.8%; Wang et al., 2006) and the Chung-Cheng Tunnel in 2001 (54.0%, Chen et al., 2003), and total aromatic hydrocarbons were the largest part in the Hsuehshan Tunnel (42.7%; Liu et al., 2014b), the Chungliao Tunnel (48.3%; Chiang et al., 2007) and the Taipei Tunnel (51.5%; Hwa et al., 2002). Acetylene made up 0–6.7% of NMHCs in the tunnel measurements.

N-alkanes were the most abundant group (58.1 ± 2.6%) in the Zhujiang Tunnel in 2014, due largely to a greater fraction of LPG-related species. Branched alkanes made up the largest fraction in the Chung-Bor Tunnel (34.8%; Chen et al., 2003), the Hsuehshan Tunnel (Liu et al., 2014b) for driving speeds of 45 km/h (39.9%) and 65 km/h (36.4%), and in gasoline tailpipe exhaust in Hong Kong (32.7%; Guo et al., 2011).

The weight percentages (w/w%) of selected alkanes, alkenes, aromatic hydrocarbons, and acetylene in the Zhujiang Tunnel were compared to those from tunnel studies in other Asian cities (Table S1), such as Beijing (Wang et al., 2001b), Shanghai (Lu et al., 2010), Taiwan (Hwa et al., 2002; Chen et al., 2003; Chiang et al., 2007; Liu et al., 2014b), and Hong Kong (Ho et al., 2009). Although there were also LPG powered vehicles in vehicle fleets passing the Shing Mun Tunnel in Hong Kong in 2003 (Ho et al., 2009) or the Hsuehshan Tunnel in Taiwan in 2010 and 2013 (Liu et al., 2014b), fractions of typical LPG-related propane (40.5%), n-butane (11.7%), and i-butane (6.8%) in this study showed were significantly higher than that of 5.4%, 8.2%, and 5.0% in the Shing Mun Tunnel (Ho et al., 2009) or 0.3–1.4%, 2.6–8.8% and 1.6–5.0% in the Hsuehshan Tunnel (Liu et al., 2014b), respectively. In this study the average percentage of *i*-pentane (3.8 ± 0.5%), a typical gasoline evaporation (Zhang et al., 2013b), was lower in this study than in all other studies (5.4–14.8%). The only exception was a study conducted in 2001 in the Chung-Cheng and Chung-Bor Tunnels, where no i-pentane was detected (Chen et al., 2003). The ranges of the most abundant alkenes in this study, ethylene (3.8 ± 0.3%) and propene (2.2 ± 0.1%), overlapped with ranges reported in other studies (1.6–10.9% for ethylene and 0.1–25.5% for propene). The average percentage of acetylene in this study (1.7 ± 0.3%) fell within the lower range (0.9–6.2%) of reports from other tunnel studies (Table S1). Fractions of the aromatic hydrocarbons, benzene (1.0 ± 0.1%), toluene (2.5 ± 0.3%), ethylbenzene (0.7 ± 0.1%), and m,p-xylene (1.9 ± 0.2%) in this study were the lowest when compared to the ranges of 1.3–11.3%, 2.7–16.1%, 1.0–3.8% and 2.0–7.6% reported in other tunnel studies, respectively. VOC compositions varied with the on-road vehicle fleet, composition and emission standards imposed on vehicles during the test year; therefore, it is important to measure local VOC composition profiles from vehicles and to update this information as fleet compositions and emission standards change.

A comparison of composition profiles from vehicle-related emission sources (vehicle exhaust and oil evaporation) is presented in Fig. 3. Of the VOC species, *i*-pentane (24.9%) was the most abundant compound from gasoline evaporation (Zhang et al., 2013b). Toluene, ethylene, and *i*-pentane were previously identified as the most abundant compounds from tailpipe exhaust, but results varied with test speed, starting status, fuel type, and the presence or absence of a catalytic converter (Schmitz et al., 2000; Schauer et al., 1999, 2002; Liu et al., 2008a; Guo et al., 2011).

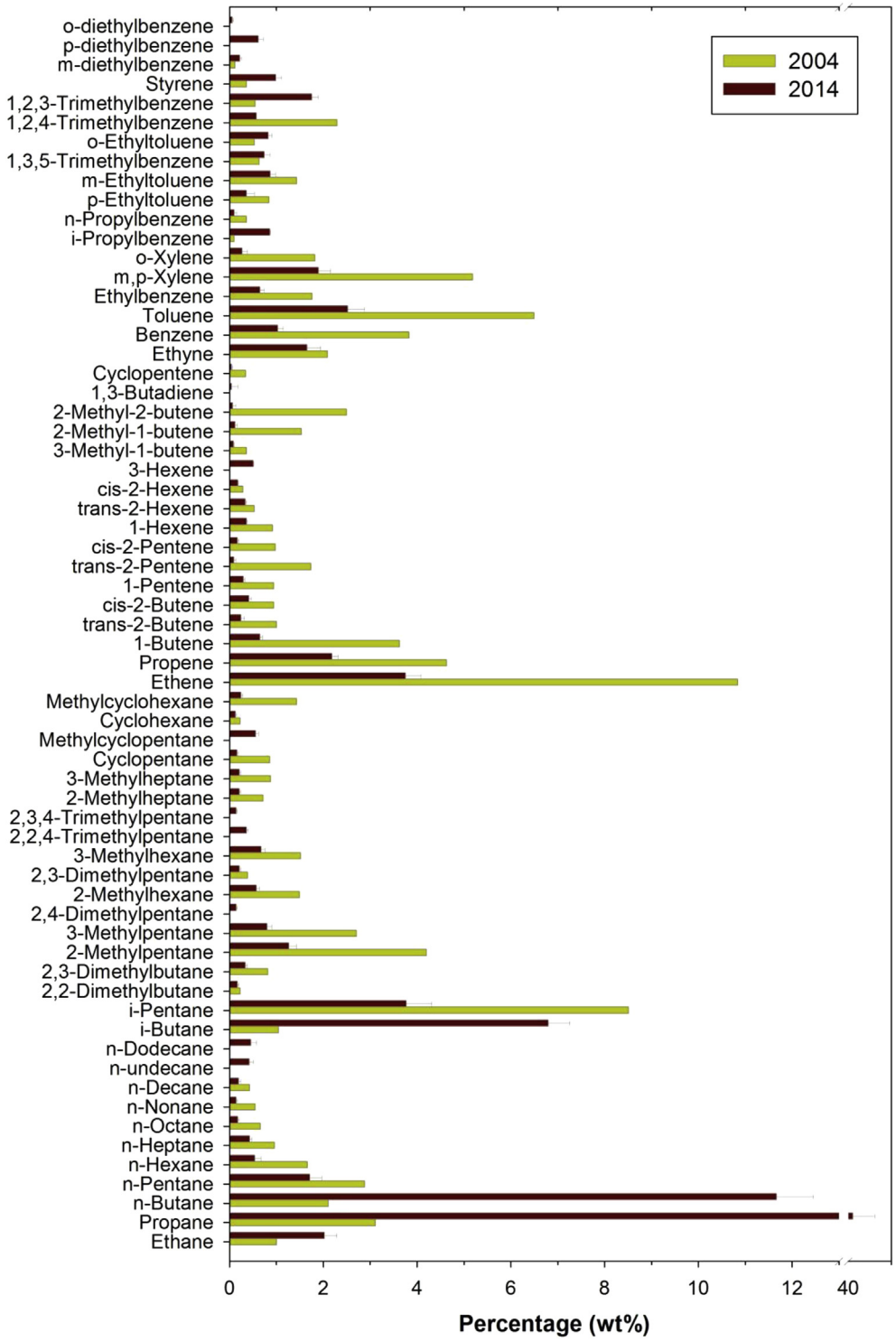

Fig. 2. Comparison of VOC profiles from vehicle exhaust based on tests in the Zhujiang Tunnel in 2004 (Fu et al., 2005) and in 2014.

3.3. NMHC emission factors

3.3.1. Emission factors in the Zhujiang Tunnel

The mean ± 95% C.I., maximum, and minimum EFs (mg km^{-1} veh^{-1}) for each of the 64 VOC species are presented in Table 2. The detection limits (MDL) in parts per trillion (ppt), precision (%), and accuracy (%) of each VOC species are also displayed in Table 2. 95% uncertainty ranges for the EFs were quantified by the uncertainty analysis tool AuvToolPro (Zheng and Frey, 2002; Table S2). The 64 non-methane hydrocarbons had a total EF of 449 ± 40 mg km^{-1} veh^{-1}. By group, alkanes, aromatics, and alkenes had EFs of 338 ± 33, 63 ± 7, and 42 ± 3 mg km^{-1} veh^{-1}, respectively.

Of the alkanes, propane had an average EF of 184 ± 21 mg km^{-1} veh^{-1} and a maximum of 303 mg km^{-1} veh^{-1}. The compounds with the next highest EFs were *n*-butane, *i*-butane, and *i*-pentane, with averages of 53 ± 6, 31 ± 3, and 17 ± 3 mg km^{-1} veh^{-1}, respectively.

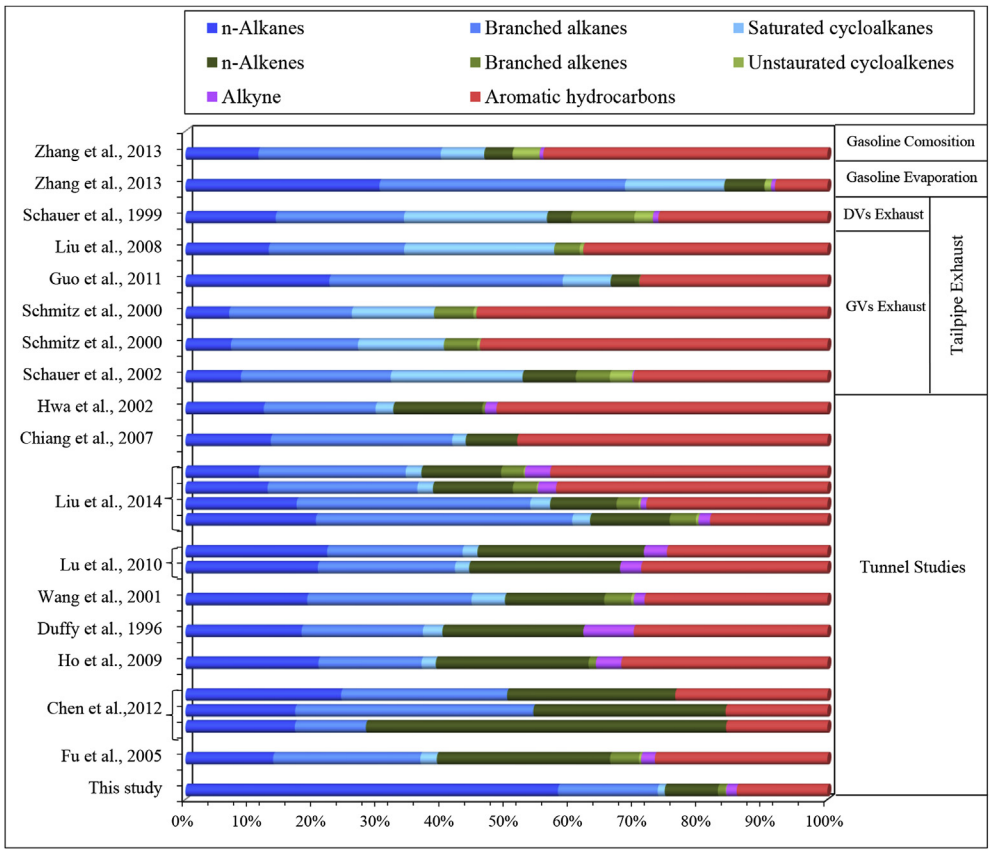

Fig. 3. VOC group percentages among studies of vehicle-related emissions.

Tang et al. (2007, 2008) found that propane was the dominant species detected in the exhaust of LPG-fueled taxis in Guangzhou, with propane and *n*-butane consitituting 47% and 11% of the emitted NMHCs, respectively. The average ratio of propane to *n*-butane was 3.5, which is similar to a previous report of 3.2 for LPG taxi exhaust (Tang et al., 2007, 2008). These results also suggest that the high observed EFs for propane, *n*-butane, and *i*-butane are most likely related to the increasing use of LPG-powered buses and taxis in urban Guangzhou.

Of the alkenes, ethylene and propene were the most abundant species, with EFs of 16 ± 1 and 9.7 ± 0.9 mg km^{-1} veh^{-1}, respectively. Isoprene is a well-known biogenic VOC emitted from plants (Guenther et al., 1995). Based on seasonal and diurnal variations of isoprene (Barletta et al., 2005), ratios of isoprene to the vehicle exhaust markers 1,3-butadiene and ethyne (Reimann et al., 2000; Borbon et al., 2001; Wang et al., 2013a; Chang et al., 2014), and source attribution techniques, such as principal component analysis (PCA) (Derwent et al., 1995; So and Wang, 2004) and receptor models (McLaren et al., 1996; Hellen et al., 2012), vehicle exhaust has previously been proposed as a source of isoprene. In this study, isoprene EFs ranged from −7.7 to 2.7 mg km^{-1} veh^{-1}, with an average of −3 ± 1 mg km^{-1} veh^{-1}. These results suggest that vehicle exhaust does not directly contribute to isoprene concentrations, which is consistent with results from another tunnel study in Taiwan (Liu et al., 2014b). Of the aromatics, toluene and m,y-xylene displayed higher EFs than the other species, with EFs of 11.3 ± 2 and 8.5 ± 1 mg km^{-1} veh^{-1}, respectively.

3.3.2. Comparison of EFs in the Zhujiang Tunnel: 2014 VS 2004

The total NMHC EF decreased from 493 ± 120 mg km^{-1} veh^{-1} in 2004 (Fu et al., 2005, Fig. 4) to 449-449 ± 40 mg km^{-1} veh^{-1} in 2014. The EFs of aromatics and alkenes in 2014 were lower than those in 2004, with reductions ranging from −91% to −5%. In contrast, the EFs of ethane, propane, *n*-butane, and *i*-butane in 2014 were 1.8, 12.1, 5.1, and 6.0 times the EFs in 2004, respectively. The stricter emission limits and increasing use of LPG as fuel likely resulted in the changes in the EFs of total and specific NMHCs. Over the past decade, vehicle emission standards have been updated frequently in Guangzhou. In 2004, most vehicles met the China I and China II emission standards; in 2014, the percentages of vehicles in Guangzhou meeting China I, China II, China III, China IV, and China V emission standards were 12.3%, 9.4%, 39.4, 36.2%, and 2.7%, respectively (Zhang et al., 2015a,b). In 2004, the vehicle fleet consisted of approximately 80% gasoline and 20% diesel vehicles (He et al., 2008); however, LPG, considered to be a cleaner fuel, has been increasing in popularity as a substitute fuel, especially for buses and taxis. In 2014, the percentage of gasoline and diesel vehicles decreased to 61% and 12% (Zhang et al., 2015a) respectively, and LPG vehicles constituted 27% of the vehicle fleet. Furthermore, variations in driving speeds may also contribute to variations in vehicle emission profiles.

It is worth noting that total NMHC EFs decreased less than 10% from 2014 to 2004. Meanwhile, the total number of motor vehicles jumped from 1.7 million in 2004 to 2.7 million in 2014, with an annual rate of increase in Guangzhou of 6% (Guangzhou Statistical Yearbook, 2015) and an even greater increase in total vehicle mileage. Therefore, the reduction of total VOC emissions from vehicle exhaust will remain a challenge in the future.

3.3.3. Changes in ozone and SOA formation potentials: 2014 VS 2004

To evaluate the effect that decadal changes in VOC EFs from on-

Table 2
Emission factors (mg km^{-1}) of NMHCs for on-road vehicles based on tunnel measurements.

Species	MDL (ppt)	Precision (%)	Accuracy (%)	Mean ± 95%C.I.	Max	Min
Ethane	39	2	5	9 ± 1	17	1
Propane	31	2	5	184 ± 21	303	58
n-Butane	21	3	5	53 ± 6	97	25
n-Pentane	8	3	5	7 ± 1	17	3
n-Hexane	6	3	5	2.3 ± 0.5	6.3	0.4
n-Heptane	10	3	5	1.9 ± 0.2	2.8	0.8
n-Octane	6	4	5	0.8 ± 0.1	1.3	0.3
n-Nonane	6	4	5	0.6 ± 0.1	1.1	0.0
n-Decane	6	4	5	0.8 ± 0.1	1.5	0.2
n-undecane	6	4	5	1.8 ± 0.3	4.6	0.1
n-dodecane	6	4	5	1.9 ± 0.4	7.5	0.7
Isobutane	17	3	5	31 ± 3	57	14
Isopentane	14	3	5	17 ± 3	46	7
2,2-Dimethylbutane	14	3	5	0.8 ± 0.1	1.9	0.2
2,3-Dimethylbutane	12	3	5	1.5 ± 0.2	3.0	0.4
2-Methylpentane	8	3	5	5.7 ± 0.8	14.7	1.7
3-Methylpentane	7	3	5	3.6 ± 0.5	8.9	0.7
2-Methylhexane	6	3	5	0.6 ± 0.1	1.0	0.3
3-Methylhexane	6	3	5	2.5 ± 0.3	4.0	1.0
2,3-Dimethylpentane	9	3	5	0.9 ± 0.1	1.6	0.5
2,4-Dimethylpentane	4	3	5	3.0 ± 0.3	5.2	1.1
2,2,4-Trimethylpentane	9	3	5	1.6 ± 0.2	2.6	0.6
2,3,4-Trimethylentane	6	3	5	0.6 ± 0.1	1.1	0.2
2-Methylheptane	4	3	5	0.9 ± 0.1	1.4	0.3
3-Methylheptane	5	3	5	0.9 ± 0.1	1.4	0.3
Cyclopentane	7	5	7	0.8 ± 0.1	1.8	0.1
Cyclohexane	6	5	7	2.4 ± 0.3	4.7	1.2
Methylcyclopentane	9	5	7	0.6 ± 0.1	1.3	0.2
Methylcyclohexane	5	5	7	1.1 ± 0.1	1.8	0.4
Sum of alkanes				**338 ± 33**	**561**	**181**
Ethene	41	2	5	16 ± 1	24	8
Propene	31	3	5	9.7 ± 0.9	16.3	6.0
1-Butene	17	4	8	2.8 ± 0.3	5.4	1.3
1,3-butadiene	8	4	8	0.7 ± 0.4	3.2	0.0
trans-2-butene	13	4	8	1.9 ± 0.3	5.5	0.5
Cis-2-butene	11	4	8	1.3 ± 0.2	3.8	0.4
3-Methyl-1-butene	2	4	8	0.4 ± 0.1	1.0	0.2
1-Pentene	2	4	8	0.8 ± 0.1	1.6	0.3
2-Methyl-1-butene	2	4	8	1.6 ± 0.2	4.0	0.7
Trans-2-pentene	2	4	8	1.5 ± 0.3	4.4	0.3
Cis-2-pentene	1	4	8	0.8 ± 0.1	2.0	0.3
2-Methyl-2-butene	2	4	8	2.3 ± 0.4	6.0	0.5
Cyclopentene	1	4	8	0.4 ± 0.1	1.1	0.1
1-Hexene	5	4	8	0.5 ± 0.1	1.0	0.2
Trans-2-hexene	3	4	8	0.3 ± 0.1	0.6	0.1
Cis-2-hexene	2	4	8	0.2 ± 0.0	0.2	0.1
3-Hexene	1	4	8	0.2 ± 0.0	0.4	0.1
Isoprene	5	4	8	−3 ± 1	3	−8
Sum of alkenes excluding isoprene				**42 ± 3**	**66**	**26**
Acetylene	57	2	5	7 ± 1	14	2
Benzene	14	3	5	4.6 ± 0.5	8.2	0.4
Toluene	9	3	5	11 ± 2	25	3
Ethylbenzene	6	3	5	2.9 ± 0.4	5.3	0.6
m/p-Xylene	9	3	5	9 ± 1	15	0.7
Styrene	8	3	5	1.1 ± 0.4	3.5	0.0
o-Xylene	4	3	5	3.8 ± 0.5	6.6	0.8
Isopropylbenzene	4	3	5	0.4 ± 0.1	0.7	0.0
n-Propylbenzene	4	3	5	1.6 ± 0.2	2.7	0.3
m-Ethyltoluene	3	3	5	3.9 ± 0.9	10.4	0.6
p-Ethyltoluene	1	3	5	3.1 ± 0.4	6.6	1.6
1,3,5-Trimethylbenzene	3	3	5	3.6 ± 0.4	6.1	0.9
o-Ethyltoluene	2	3	5	2.5 ± 0.3	4.1	0.7
1,2,4-Trimethylbenzene	6	3	5	7.7 ± 0.9	12.2	2.3
1,2,3-Trimethylbenzene	2	3	5	4.3 ± 0.5	7.5	1.4
m-Diethylbenzene	1	4	8	0.9 ± 0.1	2.0	0.2
p-Diethylbenzene	1	4	8	2.6 ± 0.3	5.7	0.7
o-Diethylbenzene	1	4	8	0.2 ± 0.3	1.3	0.1
Sum of aromatics				**63 ± 7**	**105**	**23**

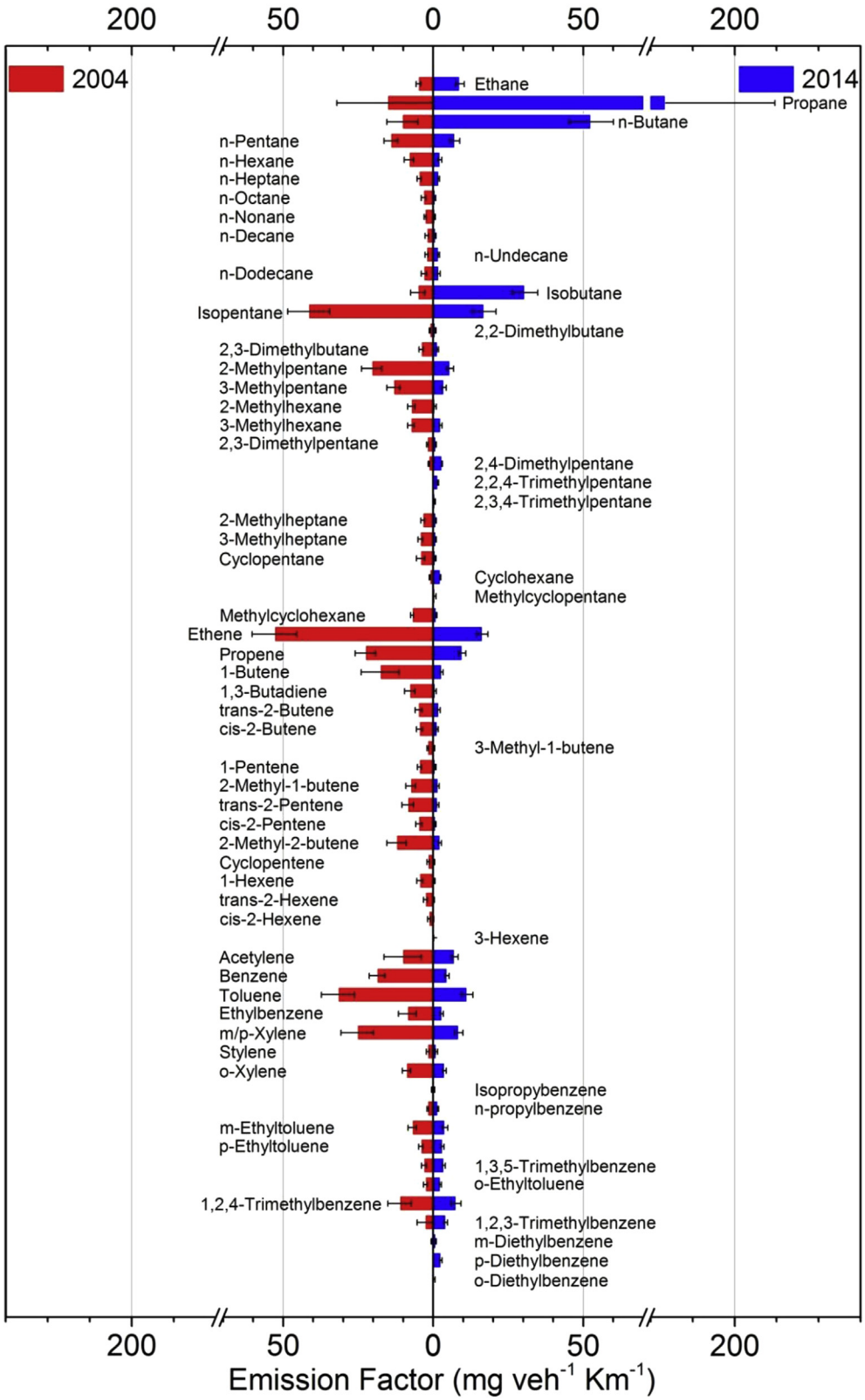

Fig. 4. Comparison of VOC EFs in the Zhujiang tunnel in 2014 with EFs from 2004 (Fu et al., 2005).

road vehicles will have on VOC-generated secondary pollutants, such as ozone and SOA, a maximum incremental relativity (MIR) method (Carter, 1994, 2009) and SOA yields (Odum et al., 1996; Ng et al., 2007; Lim and Ziemann, 2009) were applied to determine ozone formation potentials (OFPs) and SOA formation potentials (SOAFPs). OFPs and SOAFPs were calculated as described in equations (2) and (3):

$$OFPs = \sum_i EF_i \times MIR_i \quad (2)$$

where OFPs is the sum of OFP for all VOC species, EF_i is the emission factor of species i, and MIR_i is the MIR coefficient for VOC species i (Carter, 2009); and

$$SOAFPs = \sum_i EF_i \times Y_i \quad (3)$$

where SOAFPs is the sum of SOAFP for all VOC species, and Y_i is the SOA yield of VOC species i, as determined by chamber studies (Ng et al., 2007; Lim and Ziemann, 2009; Loza et al., 2014). SOA yields of VOCs depend on nitrogen oxide (NO_x) (Ng et al., 2007). Thus, we calculated the SOAFPs under high-NO_x and low-NO_x conditions, approximating the higher and lower limits.

Changes in the EF, OFPs, and SOAFPs of 64 VOC species from on-road vehicle exhaust in 2014 against those in 2004 tested in the Zhujiang Tunnel are showen in Fig. 5, Table S3, and Table S4 in supporting materials. The average total EF was only 9% lower in 2014 than it was in 2004. However, total OFPs decreased by 57%, from 2.5 × 10^3 mg km^{-1} in 2004 to 1.1 × 10^3 mg km^{-1} in 2014. Similarly, total SOAFPs under high-NO_x conditions decreased by 57% from 21 mg km^{-1} in 2004 to 9 mg km^{-1} in 2014, and total SOAFPs under low-NO_x conditions decreased by 50%, from 50 mg km^{-1} in 2004 to 25 mg km^{-1} in 2014.

As discussed above, the large decreases in OFPs and SOAFPs are related to changes in VOC compositions, and these can specifically be attributed to a decrease in reactive alkenes and aromatics. As for group contributions to OFPs, the alkene composition fraction decreased the most, from 63% in 2004 to 39% in 2014. The decrease in total SOAFP was largely due to changes in the contribution of aromatic fractions, which decreased from 41 mg km^{-1} in 2004 to 6 mg km^{-1} in 2014 under high-NO_x conditions and from 44 mg km^{-1} in 2004 to 22 mg km^{-1} in 2014 under low-NO_x conditions.

Previous studies of VOCs in ambient air have demonstrated that alkenes and aromatics contribute the most to ozone formation (Zhang et al., 2012, 2013; 2015b). Aromatics are also known to contribute most to SOA formation, especially in urban areas (Ding et al., 2012). A reduction in alkene and aromatic emissions from vehicles would greatly benefit regional ozone and SOA control.

3.3.4. EF comparison of with other tunnel studies

The EFs of selected VOCs from this study were compared to those from other tunnel studies dating back to the year 2000 (Fig. 6). The tunnel locations, test years, and vehicle fuel types from each study can be found in Table S5. Large differences in EFs were noted among these studies. I-pentane had the highest EF of all VOC species in Mexico's Loma Larga Tunnel in (Araizaga et al., 2013) and in Taiwan's Chung-Liao Tunnel (Chiang et al., 2007). Toluene had the highest EF in Taiwan's Tai Pei Tunnel (Hwa et al., 2002), and ethylene was most abundant in Zurich's Gubrist Highway Tunnel in (Legreid et al., 2007) and Hong Kong's Shing Mun Tunnel (Ho et al., 2009). In contrast, the average propane EF in the current study was 10–918 times of other studies, and the EFs for the other major LPG-related VOCs n-butane and *i*-butane were also 2–10 and 3–18 times higher than those in other studies, respectively. This difference corresponds to the larger fraction of LPG vehicles (27%) in the Zhujiang Tunnel compared to vehicle fleets, most of which consisted of only gasoline and diesel vehicles, in other tunnel studies. In the Shing Mun Tunnel study in Hong Kong (Ho et al., 2009), LPG vehicles accounted for approximately 10% of the total fleet, and the LPG-related EFs were lower than the EFs of gasoline and diesel vehicle exhaust-related species.

Of the individual VOC species, the mean EF of benzene in this study (4.6 ± 0.5 mg veh^{-1} km^{-1}; Table 2) is similar to values found in the Shing Mun Tunnel in Hong Kong (4.5 mg veh^{-1} km^{-1}; Ho

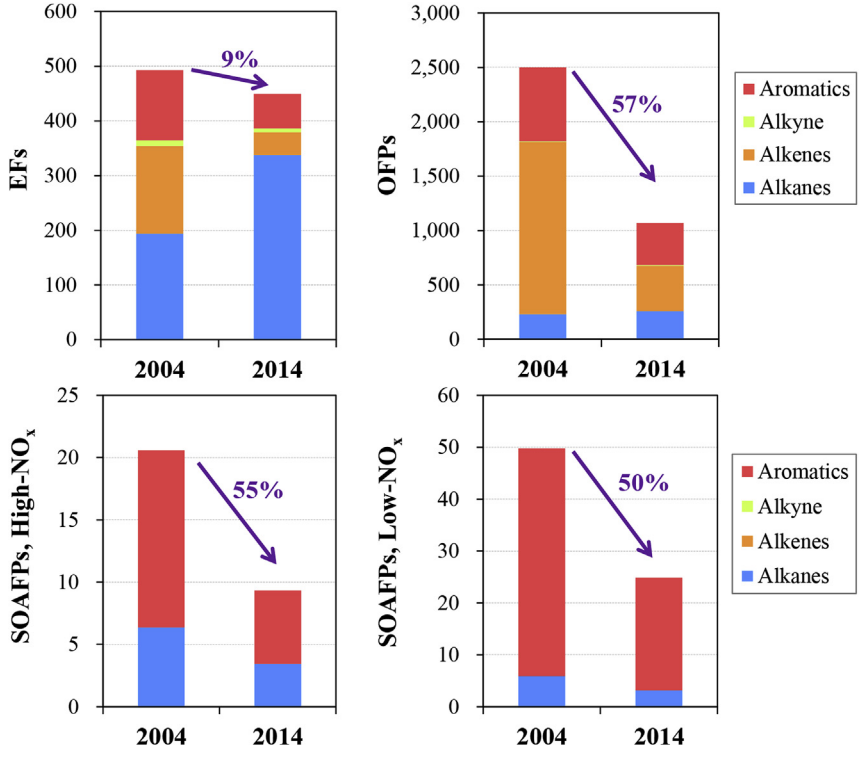

Fig. 5. Decadal changes in EFs (mg km^{-1} veh^{-1}), OFPs, and SOAFPs for VOCs from on-road vehicles in the Zhujiang Tunnel in 2004 (Fu et al., 2005) and in 2014.

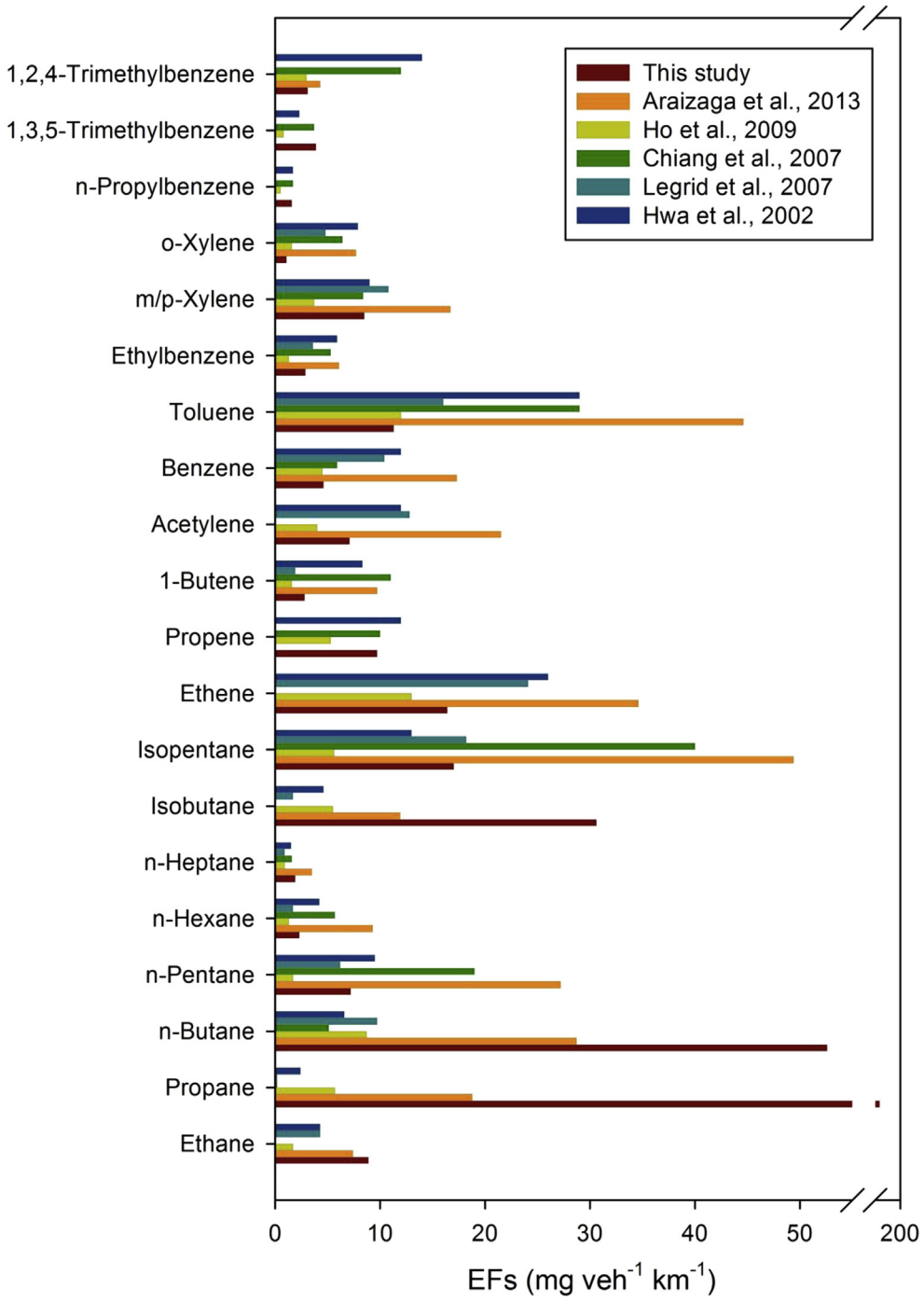

Fig. 6. Comparison of EFs (mg veh^{-1} km^{-1}) for selected VOCs in the Zhujiang Tunnel with other tunnel measurements.

et al., 2009) and the Chung-Liao Tunnel in Taiwan (5.9 mg veh^{-1} km^{-1}; Chiang et al., 2007) but much lower than levels from other studies (10.4–17.3 mg veh^{-1} km^{-1}; Hwa et al., 2002; Legreid et al., 2007; Araizaga et al., 2013). The average toluene EF in this study (11.3 ± 1.5 mg km^{-1} veh^{-1}) is similar to levels in Hong Kong (12.0 mg veh^{-1} km^{-1}; Ho et al., 2009), but lower than EFs in other studies (16.0–44.6 mg veh^{-1} km^{-1}, Hwa et al., 2002; Chiang et al., 2007; Legreid et al., 2007; Araizaga et al., 2013). The mean ethane EF in this study (8.9 ± 1.2 mg veh^{-1} km^{-1}) was the highest of all tunnel studies (1.7–7.4 mg veh^{-1} km^{-1}, Fig. 4), whereas the EFs of *n*-pentane, *n*-hexane, and *n*-heptane reported here (7.8, 2.5, and 2.0 mg veh^{-1} km^{-1}, respectively) were within the ranges of reported in other studies (1.7–27.2, 1.3–9.3, and 0.9–3.5 mg veh^{-1} km^{-1}, respectively).

4. Conclusions

Vehicle emission control is crucial for treating the most intractable air quality problems due to $PM_{2.5}$ and O_3 pollution particularly in urban areas. With the fast changing vehicle numbers and fleet compositions, vehicle emission standards and fuel quality in the last decade, it is important to see what really happened to the

vehicle emission, and to get up-to-date emission factors. As tunnel measurement has its advantages to obtain absolute emission levels by capturing a snap-shot of the on-road vehicle fleet and representing real-world operation conditions, in 2014 we carried out measurements in the Zhujiang Tunnel, a busy tunnel with over 40,000 motor vehicles passing through in each direction per day in urban Guangzhou, and compared the results for speciated VOC emissions with that obtained in the same tunnel in 2004.

The bad news from our study is that EFs of total NMHCs in 2014 was only 9% lower than that in 2004, and the good news is that their ozone and SOA formation potentials reduced over 50%: EFs of total NMHCs decreased from 493 mg km^{-1} in 2004 to 449 mg km^{-1} in 2014, but their OFPs decreased -57% from 2499 mg km^{-1} in 2004 to 1099 mg in 2014, and their SOAFPs under high-NO_x condition decreased -55% from 21 mg km^{-1} in 2004 to 9 mg km^{-1} in 2014, or -50% under low-NO_x condition from 50 mg km^{-1} in 2004 to 25 mg km^{-1} in 2014. The drop of ozone and SOA formation potentials was resulted from declined EFs for more reactive alkenes and aromatics: alkanes, aromatics, and alkenes had average EFs of 338, 63 and 42 mg km^{-1} in 2014 against that of 194, 129, 160 mg km^{-1} in 2004, respectively. These changes in on-road vehicle VOC emission were a combined effect of fuel transition from diesel/gasoline to LPG for taxis and buses, tightened emission limits and improved fuel quality as well.

Specifically, the LPG-related propane and butanes showed large increase of EFs as LPG vehicles shared percentages from 0 in 2004 to 27% in 2014 in the vehicle fleets. In 2014 the LPG-related propane, n-butane and i-butane were the top three abundant NMHCs with average EFs of 183.6 ± 21.0, 52.6 ± 6.1 and 30.6 ± 3.4 mg km^{-1} veh^{-1}. The gasoline evaporation marker i-pentane had an average EF of 17.0 ± 2.9 mg km^{-1} veh^{-1}. Among the alkenes group, ethylene and propene were the top two species with average EFs of 16.4 ± 1.0 and 9.7 ± 0.9 mg veh^{-1} km^{-1}, respectively. Isoprene was confirmed to have no direct emission from vehicles. For the aromatics group, toluene showed the highest average EF of 11.3 ± 1.5 mg km^{-1} veh^{-1}. The typical combustion sources marker acetylene had an average EF of 7 ± 1 mg km^{-1} veh^{-1}. When compared to results in 2004, aromatics and alkenes had reduction rates ranging from −90% to −5% in their EFs.

It is worth noting that although there were also a considerable fraction of LPG vehicles in Hong Kong, when compared to the results from tunnel tests by Ho et al. (2009) in Hong Kong, EFs of LPG-related propane and butanes in Guangzhou based on our tests were disproportionally much higher. While the LPG related species may not significantly contribute to the formation of $PM_{2.5}$ or SOA, they still have potentials to form tropospheric O_3. Therefore enhancing the LPG vehicle emission control as did in Hong Kong (Lyu et al., 2017) or introducing even more environmentally friendly fuels, such as Liquefied Natural Gas (LNG) for taxis and buses might benefit further improving regional air quality.

Acknowledgements

This study was funded by Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB05010200), Natural Science Foundation of China (Project No. 41530641/41571130031/41303078), National Key Research and Development Program (2016YFC0202204), Youth Innovation Promotion Association, CAS (2017406) and Guangzhou Science Technology and Innovation Commission (201505231532347).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2017.10.133.

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