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Measurements and Correlations of MTBE and BETX in Traffic Tunnels

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ABSTRACT

In this study, the concentrations of five volatile organic compounds (VOCs), including BTEX and methyl tertiary-butyl ether (MTBE), were investigated in five different traffic tunnels (including Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels) in southern Taiwan. Results showed that Guogang Tunnel was the most polluted with the highest average levels of both MTBE and BTEX while ethylbenzene had the lowest levels. The range of measured concentration of toluene in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were from 5.6 to 6.2 (mean = 1.6), from 0.0 to 62.3 (mean = 17.6), from 2.7 to 26.7 (mean = 13.1), from 15.2 to 125.5 (mean = 57.5), and from 43.7 to 197.1 (mean = 115.8) µg/m^3, respectively. In Guogang Tunnel, the average MTBE–BTEX ratios at two peak rush periods were (5.0:1, 5:3, 4:1, 0:1, 5:1.1) and (5.7:1, 3:3, 2:1, 0:1, 4:1.1). From morning till night, the ratios at different sampling periods in the five different tunnels suggest the existence of both different traffic flow and variations in traffic fleet type in different tunnels. T/B ratio ranged from 0 to 2.3, from 0 to 1.9, from 0.6 to 2.5, from 0.9 to 2.6 and from 0 to 10.5 in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels, respectively. We also observed a wide range of (*m*+*p*+*o*)-xylenes/ethylbenzene (ΣX/E) or *m,p*-X/E ratio in all five tunnels. The *m,p*-xylene/ethylbenzene ratio ranged from 2.2 to 5.7, from 1.4 to 3.3, from 2.0 to 7.7, from 1.4 to 1.5 and from 5.5 to 8.1 in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao Tunnels, respectively. Notably, those high ΣX/E ratios in all tunnels reflect a fresh air parcel in the tunnels due to the enclosed/half-enclosed environment. Nevertheless, it is important that the characteristics of X/E in different traffic tunnels are explored.

Keywords: Characteristic ratio; Tunnel; Traffic; BTEX; MTBE.

INTRODUCTION

Over the last few decades, there has been a dramatic increase in the number of publications on traffic-related volatile organic compounds (VOCs) (Carter, 1990, 1991, 1994; Carter and Atkinson, 1995; Kurtenbach *et al*., 2001; Lee *et al*., 2002; Cheng *et al*., 2006; Chiang *et al*., 2007; Kuykendall *et al*., 2009; Ropkins *et al*., 2009). Edgerton *et al*. (1989) indicate that automobiles in urban regions are the dominant source of benzene, toluene, ethylbenzene and the isomers of xylene, commonly called BTEXs. The BTEX group is an important target in ambient air (Hsieh *et al*., 2011). In particular, such non-methane hydrocarbons (NMHC) have been found to be ubiquitous in the urban air. Many studies reveal that BTEXs are known to be toxic and genotoxic, and they also actively participate in the photochemical reactions. Cytotoxic studies have demonstrated that it is the fine and nanoparticles that play more important, dangerous and deleterious roles on a per mass basis and that even very low mass concentrations of nanoparticles are influential (Chen *et al*., 2006; Lin *et al*., 2008).

Except for BTEXs in ambient air, automobiles in urban regions are the dominant source of Methyl *tertiary*-butyl ether (MTBE). Since the 1970s, MTBE has become a common ingredient in gasoline owing to its excellent octane rating and low impact on air quality in large cities. As far as

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chemical property is concerned, MTBE is more suitable than other volatile organic compounds as a reference compound for indicating traffic emissions, owing to the fact that it is a compound consumed in the formation of gasoline (Hsieh *et al*., 2006). Chang *et al*. (2003) indicated that besides some minor leakage from gas stations during pumping, MTBE in ambient air is assumed to derive almost exclusively from car exhaust and evaporative emissions (Chang *et al*., 2003). Clark *et al*. (1984) also indicated that these compounds are added to fuels to increase the octane number and are emitted to the urban atmosphere as a component of automobile exhaust and by gasoline evaporation and spillage. Moreover, Geiss *et al*. (2010) suggest that exposure to pollutants (VOCs and particles) inside car cabins is often very high, compared to other outdoor or indoor micro-environments.

In general, a tunnel environment is capable providing appropriate conditions for *in situ* measurement of different compositions of vehicular emissions and their characteristic ratios. Touaty and Bonsang (2000) indicated that a tunnel atmosphere provides appropriate conditions for the *in situ* measurement of the average composition of vehicular emissions, because the measured concentrations of exhaust emissions are significantly higher than levels in ambient air. Tunnels also offer the advantage of providing an accurate appraisal of the traffic composition and the volume into which these emissions are released. Nelson and Quigley (1983, 1984) studied the hydrocarbon composition of exhaust emitted from gasoline-fueled vehicles and proposed that the ratio value of "*m,p*-xylenes:ethylbenzene" is a simple technique for estimating hydrocarbon age in ambient atmospheres. They also demonstrated that the ratio between (*m*+*p*)-xylene and ethylbenzene (X/E) can indicate the extent of atmospheric photochemical reactivity. Moreover, the study by Monod *et al*. (2001) also identified the X/E ratio as a useful tool for estimating the photochemical age of air mass. Thus, based on the point of characteristic ratio in air pollutant mass, toluene/benzene (T/B) or xylene/ethylbenzene (X/E) ratios can clarify the characteristics of BTEX emission.

In Taiwan, by applying the characteristic ratios, Hsieh *et al*. (2005, 2006) have been able to characterize the ambient BTEX and MTBE in some representative sites, including: (1) in the ambient air of night markets in southern Taiwan; (2) in the neighborhoods of different industrial parks in southern Taiwan. In Hanoi, Vietnam, Truc and Oanh (2007) investigated roadside BTEX and other gaseous air pollutants in relation to emission sources. They also used the ratio of (*m*+*p*)-xylenes/ethylbenzene (X/E) to understand the characteristics of pollutant VOCs. The X/E ratio was calculated for each sampling site, and the geometric mean and geometric standard deviation of the X/E ratios for TC, DBP and NT are 2.9 and 1.3; 2.8 and 1.3; and 2.3 and 1.2, respectively, were determined. In fact, characteristics of traffic-related VOC emissions are different from those of traffic-related aerosols (Chakraborty, A. and Gupta, T. 2010; Cheng *et al*., 2010; Chuang *et al*., 2010a, 2010b; Pawar *et al*., 2010; Shen *et al*., 2010; Wu *et al*., 2010).

As far as tunnel is concerned, BTEX-ratios have been determined by Yassaa *et al*. (2006) in an air tunnel and in on-road, suburban and rural forest atmosphere. They concluded that the ethylbenzene/m-xylene ratios could provide a deep insight into anthropogenic-related NMHC patterns at different locations and under different meteorological conditions, and may reflect photochemical processes in the best way. Yassaa *et al*. (2006) indicated that aromatic hydrocarbon ratios were found to be useful as a tool to investigate photochemical processes. In particular, BTEX-compounds seem to take part effectively in photochemical processes even in areas more distant from primary emittents. They also concluded that within BTEX-compounds, m-xylene could be selected as a key compound in discriminating different locations. Moreover, in their study, ethylbenzene/m-xylene ratio was found to be a good indicator of the impact of anthropogenic-related hydrocarbon atmospheric chemistry (Yassaa *et al*., 2006).

In Taiwan, based on the number of registrations, there are about 5.7 million passenger cars, 0.83 million light-duty vehicles, 0.16 million heavy-duty vehicles, 27,808 buses, and 14.6 million motorcycles (MTC, 2010). In general, unleaded gasoline #92, unleaded gasoline #95, unleaded gasoline #98, and diesel are commonly used in Taiwan. In light of the high density of vehicle numbers in Taiwan and the economic and social progress this signifies, the high level of VOC pollutants on roads and in traffic tunnels is a necessary consequence. Therefore, given the theoretical positions of characteristic ratios taken for the study and the status of the field as briefly reviewed above, this study aimed to provide an insightful understanding of characteristic ratios of volatile organic compounds measured in traffic tunnels. The present study was carried out in the five tunnels (Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao) in southern Taiwan, where vehicle emissions of MTBE and BTEX have not been evaluated completely. Moreover, this study signifies the important attempt in southern Taiwan to differentiate these emissions from other possible industrial sources, and to obtain characteristics of VOC concentrations in tunnels. These measurements in the selected tunnels are expected to aid in the analysis and understanding of additional data collected in southern Taiwan.

MATERIALS AND METHODS

Sampling Strategy

To examine the characteristic ratios and spatial distribution of VOCs in different traffic tunnels, five representational tunnels were chosen based on their different locations, functional connections, and traffic densities. Fig. 1 displays the sampling locations for MTBE and BTEXs in southern Taiwan. The Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels chosen for VOC monitoring are described as follows:

Liangshan Tunnel: The Liangshan Tunnel is located on the road connecting Liangshan Village to Ailiao Village in Neipu. Residents in this area number less than 35,000. The tunnel is a two-lane, single bore, 119 m in length, with no

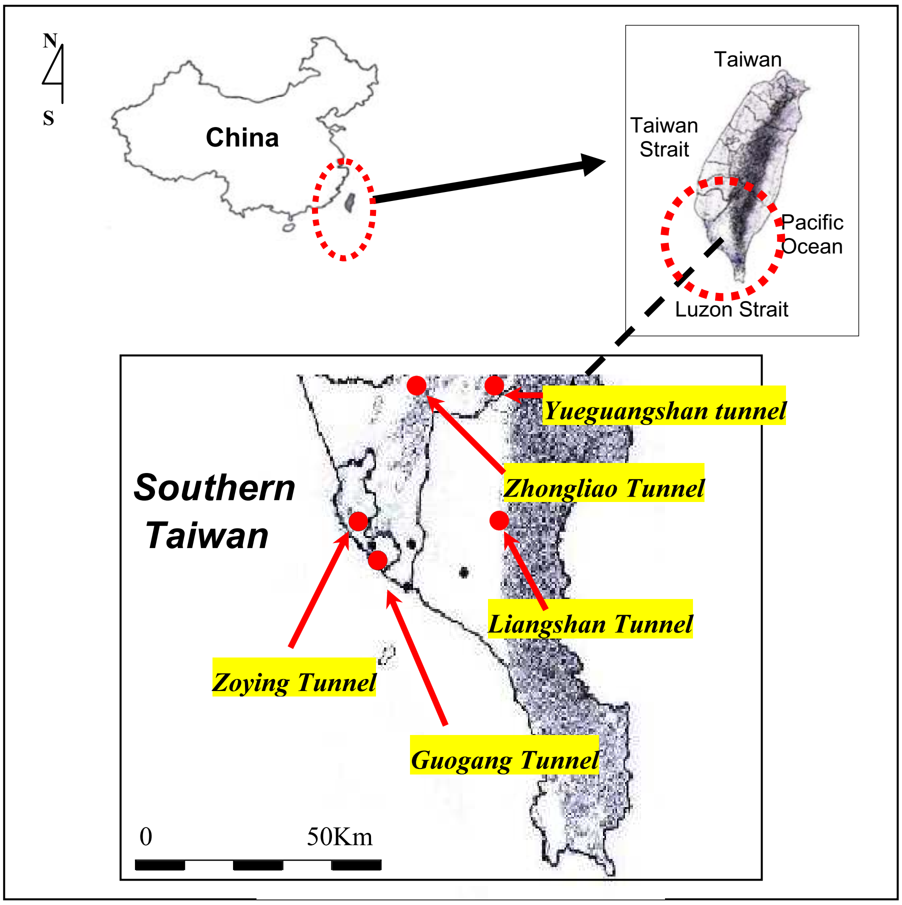

Fig. 1. Sampling locations for MTBE and BTEXs in southern Taiwan.

signal light. Also, it contains a sidewalk ~1 m wide on one side of the road, thus providing space for mounting the instruments in our experiment. The tunnel's orientation is rather straight and the grade is minimal. Since the traffic light is located beyond 1.5 km from the tunnel's entrance, traffic speed within it varies mainly by the congestion factor. Vehicle operation can be safely assumed to be in the hot stabilized mode. There is no axial-type blower mounted under the tunnel's ceiling in this particular tunnel. Note that Liangshan Tunnel is typical for a countryside tunnel with a short length in southern Taiwan.

Yueguangshan Tunnel: The Yueguangshan Tunnel is located on the road connecting Meinong Township to Shanlincun in Meinong. It is a single-bore, 1670 m in length, with two lanes. A sidewalk ~1 m wide is located on one side of the road, thus providing room to mount sampling instruments. The tunnel's orientation is a little curved and the grade is minimal. Since a traffic light is located near the entrance of this tunnel, traffic speed within it varies both from traffic control and the congestion factor. Twelve axial-type blowers are mounted under the tunnel's ceiling. Note that Yueguangshan Tunnel is typical of a countryside tunnel with long length in southern Taiwan.

Zoying Tunnel: The Zoying Car Tunnel is located on the Cuihua Road in Kaohsiung. It is a two-bore for cars, with two lanes in each bore, each of which is 118 m in length. In addition, there is a right-hand outside bore for motorcycles in each bore. A wall separates car and motorcycle lanes. In this study, the measurement was only carried out in the section for cars. No blowers are mounted in this tunnel. Zoying Car Tunnel is a typical urban tunnel with a short length in southern Taiwan.

Guogang Tunnel: The Guogang Tunnel (namely, Cross-Harbor Tunnel) is located on the connection from Qianzhen District to Chi-Chin District in Port of Kaohsiung in Kaohsiung. The Port of Kaohsiung, well-developed for container shipping, is the largest international seaport in Taiwan and one of the largest container trans-shipment centers in the Far East. The Cross-Harbor Tunnel is located from Hsin-Shen Road, Passing Yukong S. 3rd Road in between Chien-Chen Fishery Harbor and Container Terminal No. 3 and across a 440-meter-wide and 14-meter-deep fairway, to the Chung-Hsin Commercial Harbor Area at Chi-Chin District on the opposite bank. The designed max longitudinal gradient is 4% and the min gradient is 0.15%. The designed min radius of sag curve is 1200 m and the min radius of crest curve is 3000 m. The tunnel is a two-bore, with a signal light and divided roads for westbound and eastbound traffic. There are two lanes on each one-way bore, and each bore is 1550 m in length, with approach ramps 729.8 m long. This tunnel is designed as a dual two-lane carriage way, each way with 7 m in net width and 4.6 m in net high, to serve container lorries. The designed traffic volume is 15,100 vehicles per day and 1,270 vehicles per peak hour each way. The designed speed of the highway is 60 km/h. In addition, each bore has eight axial-type blowers mounted under the tunnel's ceiling. Note that Guogang Tunnel is also a typical urban tunnel with long length in southern Taiwan.

Zhongliao Tunnel: The Zhongliao Tunnel is located on the highway between Tianliao and Yanchao areas. It is a two-bore with no signal light control, and is a divided highway for northbound and westbound traffic. There are three lanes (3.8 m per lane) on each one-way bore, and each bore is 88 m^2 in cross-section, 1828 m in length (south to north), 13.40 m in width, and 7.0 m in height.

Sampling and Instruments

Sampling was performed at five selected sites (Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels) five times of the day (5:00–7:00, 7:00–9:00, 12:00–14:00, 17:00–19:00 and 19:00–21:00) from July 2004 to December 2004 to clarify the characterization of VOCs in the air of different vehicle tunnels in southern Taiwan. Three samples were taken simultaneously during each period at each site, including the inlet-, middle- and outlet-streams based on the direction of driving vehicles during the sampling period. The inlet, middle and outlet positions of the tunnels selected for this study are considered representative for evaluating VOC concentrations. Sampling height was 1.5 m for each site. In addition, basic meteorological conditions were obtained by using portable meteorological machines (LM-8000 type) and recorded during sampling times. A portable sampling pump (SKC 224-XR Series Pumps, SKC Inc.) was used to draw in the air. The pump was calibrated with a standard SKC flow meter (SKC UltraFloTM, SKC Inc.) before and after sampling. The sampling airflow rate was 200 mL/min. The sampling duration was fixed at 120 min during each period at each sampling site for all investigated tunnels. In this study, the sampling was active and the sorbent was an activated carbon material (ORBO-32). In this study, the extraction procedure is according to the procedure of USEPA Method 1615. The Method 1615 which was suggested by the US National Institute for Occupational Safety and Health (NIOSH) was adopted for conducting VOC samplings (NIOSH, 1994). The sampling system consisted of a sorbent tube (ORBO-32 charcoal tube, 100 mg/50 mg) and low-flow sampling pumps (Model 222-3, SKC Inc., Eighty-Four, PA) with a sampling flow rate specified at about 150 ml/min. The more detail standard of procedures about the extraction is in the reference (NIOSH, 1994). It is indicated that a general trend of decreasing VOC outgassing with time from background and both filters was observed (Zuo *et al.*, 2010). Therefore, QA/QC is very important. For the individual sampling duration, the sample volume reached 2.4 l. Throughout the study period, we replaced a new ORBO tube at the beginning of each sampling period (5:00–7:00, 7:00–9:00, 12:00–14:00, 17:00–19:00 and 19:00–21:00) to ensure the sampled volume within the confidence volume (under the breakthrough condition). Our experimental results indicate a mean calculated sampling efficiency of higher than 93%. For each collected sample, MTBE and BTEX (including benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) were analyzed by gas chromatography with a flame ionization detector (GC/FID, Agilent Technologies, 6890N Network GC System) using the NIOSH Method 1615 (Hsieh *et al*., 2005; Hsieh *et al*., 2006). Identification and quantification of VOCs were accomplished by using a GC with a Agilent Technologies capillary column (DB-1 30 m × 0.53 mm i.d., 3.0m film thickness), a flame ionization detector (FID). This GC/FID was controlled by a computer workstation and equipped with an Agilent Technologies 7683 Series automatic sampler. The GC oven temperature was set initially at 30°C for 5 min. It was then raised incrementally at 15°C p/min until 90°C and held there for 2 min, then raised at 20 °C p/min to 200°C and held for 5 min. The stock solution was prepared using VOCs Mix 2 (Supelco, from Liu-Ho Co., Taiwan). The established calibration curves for the six investigated VOCs were found to have R-square values > 0.996. Seven replicate analyses were performed on a sample, using the lowest previously specified concentrations for establishing calibration curves for the six VOCs. The resulting standard deviation (STD) for each VOC compound was used to estimate its method detection limit (that is, MDL= 3× STD). The analytical results displayed that the MDLs for the six VOC compounds of MTBE, benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) were 1.25, 0.38, 1.024, 0.833, 0.402 and 0.404 $\mu g/m^3$, respectively. Three replicate analyses were performed on each of the three samples with known specified concentrations, and the relative standard deviations (RSDs) thus obtained were employed to assess the accuracy of the method.

RESULTS AND DISCUSSION

Descriptions of Vehicles in Five Investigated Tunnels

In Liangshan, Yueguangshan, and Guogang tunnels, vehicles were divided into three types: (a) motorcycles (including, two-stroke motorcycles and four-stroke motorcycles); (b) light-duty (including, passenger gasoline vehicles, light-duty gasoline vehicles, and light-duty diesel vehicles); (c) heavy-duty (including, buses, trucks, heavy-duty trailer vehicles). In both Zoying and Zhongliao tunnels, the vehicles were divided into two types: light-duty (including, passenger gasoline vehicles, light-duty gasoline vehicles, and light-duty diesel vehicles), and heavy-duty (including, buses, trucks, heavy-duty trailer vehicles). Descriptions of vehicle profiles in the five investigated tunnels are summarized as follows:

Liangshan Tunnel: The flow of motorcycles, light-duty vehicles and heavy-duty vehicles experienced two peak rush periods, one from 07:00 to 09:00 and the other from 17:00 to 19:00, which reflect standard working hours in southern Taiwan. In general, there was little flow from 19:00 to 21:00. Heavy-duty trucks were abundant only from 07:00 to 09:00 due to the transport of crop products from the countrysides to Kao-Ping area. The flow of heavy-duty vehicles between 07:00 and 09:00 was higher than between 12:00 and 21:00. Comparing light-duty vehicle flow, the peak hours between 07:00 and 09:00 were higher than between 17:00 and 19:00. Based on total count numbers in Liangshan Tunnel, motorcycles, light-duty vehicles and heavy-duty vehicles contributed 36% (126/h), 53% (189/h), and 11% (39/h) of the flow from 07:00 to 09:00, respectively, and 48% (80/h), 47% (79/h), and 5% (9/h) of the flow from 17:00 to 19:00 during the sampling days, respectively.

Yueguangshan Tunnel: The flow of motorcycles and passenger cars experienced two peak rush periods, one from 07:00 to 09:00 and the other from 17:00 to 19:00, which reflect standard working hours. Two such peak rush periods are also associated with the fact that many people work in Kaohsiung or Pingtung and live in the suburbs. There was little flow from 19:00 to 21:00. Heavy-duty trucks were abundant from 07:00 to 09:00 and from 12:00 to 14:00 due to the transport of both agricultural and manufacturing products from Meinong Area to Kao-Ping Area. The flow of heavy-duty vehicles between 07:00 and 09:00 was higher than between 19:00 and 21:00. Comparing the light-duty vehicle flow of the two sampling periods, the peak hours between 07:00 and 09:00 were higher than between 17:00 and 19:00. Based on total count numbers in Yueguangshan Tunnel, motorcycles, light-duty vehicles and heavy-duty vehicles contributed 20% (14/h), 64% (45/h), and 16% (11/h) of the flow from 07:00 to 09:00, respectively, and 15% (23/h), 78% (124/h), and 7% (11/h) of the flow from 17:00 to 19:00 during the sampling days, respectively.

Zoying Tunnel: The flow of light-duty vehicles experienced two peak rush periods, one from 07:00 to 09:00 and the other from 17:00 to 19:00, which reflect standard working hours. Such two peak rush periods are related to the fact that many people, who are non-resident workers, work in Nan-Zi Industrial Park. Heavy-duty vehicles were abundant only from 07:00 to 09:00 and were showed similar traffic flow tendencies as others periods. Based on total count numbers in Zoying Tunnel, light-duty vehicles and heavy-duty vehicles contributed 97% (594/h) and 4% (24/h) of the flow from 07:00 to 09:00, respectively, and 98% (657/h) and 3% (18/h) of the flow from 17:00 to 19:00 during the sampling days, respectively.

Guogang Tunnel: The two peak hours for motorcycles were from 07:00 to 09:00 and 17:00 to 19:00, while traffic was low in the morning from 05:00 to 07:00. There were two off-peak periods, one from 05:00 to 07:00 and the other from 05:00 to 07:00. Based on total count numbers in Guogang Tunnel, motorcycles, light-duty vehicles and heavy-duty vehicles contributed 42% (726/h), 43% (744/h), and 15% (252/h) of the flow from 07:00 to 09:00, respectively, and 45% (519/h), 33% (386/h), and 22% (259/h) of the flow from 17:00 to 19:00 during the sampling days, respectively.

Zhongliao Tunnel: The flow of both light-duty vehicles and heavy-duty vehicles experienced peak rush periods from 07:00 to 19:00 which reflect the characteristics of freeway traffic in southern Taiwan. There were two off-peak periods, one from 05:00 to 07:00 and the other from 05:00 to 07:00. Based on the total count numbers in Zhongliao Tunnel, light-duty vehicles and heavy-duty vehicles contributed 63% (1059/h) and 37% (633/h) of the flow from 07:00 to 09:00, 58% (798/h) and 42% (573/h) of the flow from 12:00 to 14:00, and 60% (822/h) and 40% (540/h) of the flow from 17:00 to 19:00 during the sampling days, respectively.

In total, the temporal patterns of the traffic fleet are similar in the five investigated tunnels in southern Taiwan, normally high at peak hours in the morning and evening, and low at around noon and off-peak hours.

Concentrations of MTBE and BTEX in Different Tunnels

In this study, we measured basic meteorological conditions (including temperature, relative humidity, wind speed, sunlight, and atmospheric pressure) in the five sampling tunnels. We obtained these meteorological data simultaneously in the tunnels during sampling periods. These averages were calculated during all sampling periods in this study. The results show the mean temperatures in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were 29.3, 30.6, 28.1, 30.4 and 17.2°C, respectively. The mean relative humidities in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were 68.8, 69.3, 75.7, 75.6 and 71.0%, respectively. The mean wind speeds in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were 0.8, 1.2, 1.7, 2.5 and 3.0 m/s, respectively. The mean sunlights in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were 183.0, 168.2, 224.4, 153.8 and 91.8 lux, respectively. The mean wind speeds in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were 0.8, 1.2, 1.7, 2.5 and 3.0 m/s, respectively. The mean sunlights in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were 183.0, 168.2, 224.4, 153.8 and 91.8 lux, respectively. The mean atmospheric pressures in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were 754.5, 758.2, 759.6, 758.2 and 762.0 lux, respectively.

Mean and total concentrations of MTBE and BTEX recorded in tunnel air of the five selected tunnels are summarized in Table 2, respectively. In this study, Guogang Tunnel was the most polluted with the highest average levels of both MTBE and BTEX. The range of measured concentration of MTBE in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels was from 5.6 to 21.2 (mean = 11.4), 0.0 to 81.7 (mean = 32.7), 10.0 to 42.8 (mean = 26.2), 42.6 to 174.4 (mean = 98.3), and 0.0 to 31.9 (mean=12.7) μg/m^3, respectively. The range of measured concentration of benzene in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels was from 0.0 to 6.9 (mean = 1.9), 0.0 to 33.2 (mean = 11.7), 2.1 to 14.6 (mean = 7.4), 14.4 to 50.4 (mean = 26.5), and 0.0 to 39.6 (mean = 18.1) μg/m^3, respectively. In total, the mean concentration of MTBE was several times higher than that of benzene in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels.

The range of measured concentration of toluene in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels was from 5.6 to 6.2 (mean = 1.6), 0.0 to 62.3 (mean = 17.6), 2.7 to 26.7 (mean = 13.1), 15.2 to 125.5 (mean = 57.5), and 43.7 to 197.1 (mean = 115.8) μg/m^3, respectively.

Table 1. Description of sampling information in different traffic tunnels.

Sampling site	Sampling time	Mean total vehicle flow (#/hr)	Description
Liangshan Tunnel	05:00–07:00	47	● a two-lane, single bore, 119 m in length, with no signal light. ● a countryside tunnel with a short length
	07:00–09:00	354	
	12:00–14:00	121	
	17:00–19:00	168	
	19:00–21:00	110	
Yueguangshan Tunnel	05:00–07:00	70	● a single-bore, 1670 m in length, with two lanes ● a countryside tunnel with long length
	07:00–09:00	387	
	12:00–14:00	139	
	17:00–19:00	158	
	19:00–21:00	93	
Zoying Tunnel	05:00–07:00	99	● a two-bore for cars, with two lanes in each bore, each of which is 118 m in length ● an urban car tunnel with a short length
	07:00–09:00	618	
	12:00–14:00	404	
	17:00–19:00	675	
	19:00–21:00	405	
Guogang Tunnel	05:00–07:00	352	● two lanes on each one-way bore, and each bore is 1550 m in length, with approach ramps 729.8 m long ● an urban tunnel with long length
	07:00–09:00	1722	
	12:00–14:00	803	
	17:00–19:00	1164	
	19:00–21:00	760	
Zhongliao Tunnel	05:00–07:00	471	● a two-bore and a divided highway for traffic ● three lanes (3.8 m per lane) on each one-way bore, and 1828 m in length (south to north)
	07:00–09:00	1692	
	12:00–14:00	1371	
	17:00–19:00	1362	
	19:00–21:00	807	

* Total vehicle flows = motorcycle flows + light-duty vehicle flows + heavy-duty vehicle flows.

In addition, the range of measured concentration of ethylbenzene in all five tunnels was from 0.0 to 10.6 (mean = 1.7), 0.0 to 19.0 (mean = 7.1), 0.0 to 9.1 (mean = 3.6), 9.5 to 32.9 (mean = 18.6), and 0.0 to 44.5 (mean = 9.5) µg/m^3, respectively. The range of measured concentration of *m,p*-Xylene in all five tunnels was from 2.5 to 9.7 (mean = 6.6), 0.0 to 28.0 (mean = 12.0), 3.6 to 13.0 (mean = 9.5), 14.7 to 50.0 (mean = 27.2), and 0.0 to 118.7 (mean = 60.3) µg/m^3, respectively. Moreover, the range of measured concentration of *o*-Xylene in all five tunnels was from 0.0 to 6.0 (mean = 2.0), 0.0 to 21.1 (mean = 8.1), 1.8 to 9.5 (mean = 6.3), 9.3 to 39.7 (mean = 20.1), and 0.0 to 39.8 (mean = 13.5) µg/m^3, respectively. The maximum total concentration of VOCs in all five tunnels was 54.7, 243.6, 111.3, 472.7 and 410.2 µg/m^3, respectively. The high traffic volume in Guogang Tunnel, coupled with emissions related to industrial activities, may be the cause for the higher pollution. In fact, urban-air chemical removal of BTEXs can occur through reaction with the OH radical during daytime, and the important contribution to the enhancement of ozone production by the oxidation of m-xylene may not be ruled out (Yassaa *et al*., 2006). According to the study by Yassaa *et al*. (2006), such photochemical impact of the other BTEX-aromatics is estimated to be between the potential levels of m-xylene and benzene.

In Table 2, all compounds peaking at the same time (i.e., 05:00–09:00) in Liangshan, Yueguangshan and Guogang tunnels. This similar trend reflects their similar high traffic density at the same period. Contrary to Liangshan, Yueguangshan and Guogang tunnels, all compounds in Zoying and Zhongliao Tunnel are 19:00–21:00 and 05:00–07:00, respectively. In Zhongliao Tunnel, for example, there was an off-peak period about traffic densities, from 05:00 to 07:00. This means that the low traffic-flow reduces the piston effect inside the tunnel and push/move slowly the air mass exit from the tunnel environment. In fact, Ma *et al*. (2011) reported that the number of vehicles at rush hour in the Hsueh-shan Tunnel in Taiwan was about 1400 per hour, three times higher than during non-rush hour. They suggest that the piston effect is very obvious since pollutant concentrations are elevated with increasing distance from the inlet (Ma *et al*., 2011).

In order to show more clearly in the results if the target concentrations were dependent on them, we perform the regression test and obtain the following results.

In Liangshan tunnel, we found that the investigated VOCs concentrations were dependent on their traffic densities, as follows. It is notice that the concentration of VOCs (Y, µg/m^3) vs. traffic densities (X, #/h) give as the equations and each correlation (R) is significant at the 0.01 level in the Eqs. (1)–(18).

MTEB:

motorcycles: $Y = 0.1169X + 3.4107$ $(R = 0.820)$ (1)

light-duty vehicles: $Y = 0.0663X + 6.0954$ $(R = 0.791)$ (2)

heavy-duty vehicles: $Y = 0.2702X + 8.2694$ $(R = 0.781)$ (3)

Table 2. Mean concentrations (μg/m^3) of MTBE and BTEXs recorded in five investigated tunnels in southern Taiwan.

Sampling Site	MTBE	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene	total
Liangshan Tunnel							
05:00–07:00	9.02	1.50	N.D.	N.D.	5.93	0.83	17.28
05:00–09:00	18.27	4.47	3.54	4.05	8.94	5.43	44.70
12:00–14:00	6.04	0.75	N.D.	0.95	5.39	N.D.	13.12
17:00–19:00	16.00	1.97	4.04	3.52	7.78	3.52	36.83
19:00–21:00	7.69	0.80	0.34	N.D.	5.13	N.D.	13.97
Yueguangshan Tunnel							
05:00–07:00	21.37	6.90	7.67	4.76	8.43	5.16	54.29
05:00–09:00	52.52	20.20	33.89	12.39	17.27	13.67	149.93
12:00–14:00	42.07	15.60	27.93	10.07	14.01	10.90	120.58
17:00–19:00	31.05	10.91	14.45	5.78	11.75	8.01	81.95
19:00–21:00	16.49	4.62	4.05	2.53	8.41	2.62	38.70
Zoying Tunnel							
05:00–07:00	18.77	6.52	7.49	1.31	7.27	4.73	46.09
05:00–09:00	25.61	7.50	11.67	4.99	9.98	6.74	66.48
12:00–14:00	17.10	4.94	4.21	1.04	7.97	4.59	39.85
17:00–19:00	32.18	8.84	19.70	3.72	10.61	7.49	82.54
19:00–21:00	37.56	9.20	22.23	6.96	11.85	8.05	95.85
Guogang Tunnel							
05:00–07:00	97.95	27.25	62.19	19.37	27.66	18.73	253.15
05:00–09:00	118.24	36.20	81.26	23.80	36.36	27.36	323.22
12:00–14:00	82.70	19.82	38.96	13.45	20.61	14.23	189.78
17:00–19:00	123.95	28.54	70.19	21.83	31.04	25.03	300.58
19:00–21:00	67.78	20.77	34.95	14.43	20.45	15.19	173.57
Zhongliao Tunnel							
05:00–07:00	21.73	24.13	160.67	14.85	81.65	24.34	327.37
05:00–09:00	12.10	19.72	116.34	10.98	61.32	15.85	236.30
12:00–14:00	9.28	17.39	110.84	7.10	39.58	14.69	198.87
17:00–19:00	11.20	16.23	94.81	7.58	61.35	6.68	197.85
19:00–21:00	9.31	13.22	96.17	7.21	57.62	6.09	189.61

Benzene:

motorcycles: Y = 0.0339X – 0.4194 (R = 0.842) (4)

light-duty vehicles: Y = 0.0217X + 0.1652 (R = 0.915) (5)

heavy-duty vehicles: Y = 0.0927X + 0.8247 (R = 0.949) (6)

Toluene

motorcycles: Y = 0.0431X – 1.3621 (R = 0.806) (7)

light-duty vehicles:Y = 0.0224X – 0.208 (R =0 .712) (8)

heavy-duty vehicles: Y = 0.0857X + 0.5908 (R = 0.660) (9)

Ethybenzene

motorcycles: Y = 0.0454X – 1.4011 (R = 0.883) (10)

light-duty vehicles: Y = 0.0253X – 0.3244 (R = 0.837) (11)

heavy-duty vehicles: Y = 0.099X + 0.5553 (R = 0.793) (12)

m,p-Xylene

motorcycles: Y = 0.0367X + 4.1242 (R = 0.841) (13)

light-duty vehicles: Y = 0.0218X + 4.893 (R = 0.848) (14)

heavy-duty vehicles: Y = 0.0896X + 5.5948 (R = 0.847) (15)

o-Xylene

motorcycles: Y = 0.0552X – 1.82 (R=0.846) (16)

light-duty vehicles: Y = 0.0326X – 0.6536 (R = 0.867) (17)

heavy-duty vehicles: Y = 0.1341X + 0.3983 (R = 0.865) (18)

In Yueguangshan tunnel, we found that the investigated VOCs concentrations were dependent on their traffic densities, as follows. It is notice that the concentration of VOCs (Y, μg/m^3) vs. traffic densities (X, #/h) give as the equations and each correlation (R) is significant at the 0.01 level in the Eqs. (19)–(36).

MTEB

motorcycles: Y = 0.2931X+ 23.085 (R = 0.772) (19)

light-duty vehicles: Y = 0.1503X + 14.205 (R = 0.858) (20)

heavy-duty vehicles: Y = 2.2824X + 1.6576 (R = 0.962) (21)

Benzene

motorcycles: Y = 0.1265X + 7.4973 (R = 0.776) (22)

light-duty vehicles: Y = 0.0646X + 3.699 (R = 0.858) (23)

heavy-duty vehicles: Y = 0.9816X – 1.703 (R = 0.961) (24)

Toluene

motorcycles: Y = 0.2383X + 9.7787 (R = 0.720) (25)

light-duty vehicles: Y = 0.124X + 2.3443 (R = 0.812) (26)

heavy-duty vehicles: Y = 2.0188X – 9.8603 (R = 0.976) (27)

Ethybenzene

motorcycles: Y = 0.0769X + 4.5837 (R = 0.744) (28)

light-duty vehicles: Y = 0.0383X + 2.3914 (R = 0.802) (29) heavy-duty vehicles: Y = 0.6407X – 1.608 (R = 0.991) (30)

m,p-Xylene
motorcycles: Y = 0.07282X + 9.4041 (R = 0.804) (31)
light-duty vehicles: Y = 0.0406X + 6.976 (R = 0.903) (32)
heavy-duty vehicles: Y = 0.561X + 4.341 (R = 0.921) (33)

o-Xylene
motorcycles: Y = 0.0838X + 5.3233 (R = 0.741) (34)
light-duty vehicles: Y = 0.043X + 2.7811 (R = 0.824) (35)
heavy-duty vehicles: Y = 0.6824X – 1.2085 (R = 0.965) (36)

In Zoying tunnel, we found that the investigated VOCs concentrations were dependent on their traffic densities, as follows. It is notice that the concentration of VOCs (Y, μg/m^3) vs. traffic densities (X, #/h) give as the equations and each correlation (R) is significant at the 0.01 level in the Eqs. (37)–(48).

MTEB
light-duty vehicles: Y = 0.0187X + 18.31 (R = 0.482) (37)
heavy-duty vehicles: Y = 0.0555X + 25.345 (R = 0.032) (38)

Benzene
light-duty vehicles: Y = 0.0034X + 5.9736 (R = 0.432) (39)
heavy-duty vehicles: Y = 0.0711X + 6.248 (R = 0.205) (40)

Toluene
light-duty vehicles: Y = 0.016X + 6.2959 (R = 0.463) (41)
heavy-duty vehicles: Y = 0.064X + 12.026 (R = 0.045) (42)

Ethybenzene
light-duty vehicles: Y = 0.0051X + 1.4473 (R = 0.455) (43)
heavy-duty vehicles: Y = 0.1036X + 1.9255 (R = 0.027) (44)

m,p-Xylene
light-duty vehicles: Y = 0.0054X + 7.2618 (R = 0.635) (45)
heavy-duty vehicles: Y = 0.0493X + 8.7352 (R = 0.130) (46)

o-Xylene
light-duty vehicles: Y = 0.0044X + 4.4503 (R = 0.624) (47)
heavy-duty vehicles: Y = 0.0723X + 5.1494 (R = 0.230) (48)

In Guogang tunnel, we found that the investigated VOCs concentrations were dependent on their traffic densities, as follows. It is notice that the concentration of VOCs (Y, μg/m^3) vs. traffic densities (X, #/h) give as the equations and each correlation (R) is significant at the 0.01 level in the Eqs. (49)–(60).

MTEB
motorcycles: Y = 0.1169X+ 3.4107 (R = 0.649) (49)
light-duty vehicles: Y= 0.0663X + 6.0954 (R = 0.597) (50)
heavy-duty vehicles: No significance level

Benzene
motorcycles: Y = 0.019X+ 19.534 (R = 0.729) (51)
light-duty vehicles: Y = 0.0261X + 16.516 (R = 0.828) (52)
heavy-duty vehicles: No significance level

Toluene
motorcycles: Y = 0.0514X+ 38.576 (R = 0.656) (53)
light-duty vehicles: Y = 0.0673X + 31.715 (R = 0.709) (54)
heavy-duty vehicles: No significance level

Ethybenzene
motorcycles: Y = 0.0122X + 14.096 (R = 0.686) (55)
light-duty vehicles: Y = 0.0152X + 12.748 (R = 0.708) (56)
heavy-duty vehicles: No significance level

m,p-Xylene
motorcycles: Y = 0.0198X + 19.919 (R = 0.739) (57)
light-duty vehicles: Y = 0.0258X + 17.337 (R = 0.793) (58)
heavy-duty vehicles: No significance level

o-Xylene
motorcycles: Y = 0.019X + 13.118 (R = 0.826) (59)
light-duty vehicles: Y = 0.0223X + 11.584 (R = 0.799) (60)
heavy-duty vehicles: No significance level

In Zhongliao tunnel, we found that the investigated VOCs concentrations were dependent on their traffic densities, as follows. It is notice that the concentration of VOCs (Y, μg/m^3) vs. traffic densities (X, #/h) give as the equations and each correlation (R) is significant at the 0.01 level in the equations (61)–(70).

MTEB
light-duty vehicles: Y = –0.0111X + 20.451 (R = 0.657) (61)
heavy-duty vehicles: Y = –0.0151X + 19.465 (R = 0.556) (62)

Benzene
light-duty vehicles: Y = –0.0042X + 21.074 (R = 0.316) (63)
heavy-duty vehicles: No significance level

Toluene
light-duty vehicles: Y = –0.0519X + 151.86 (R = 0.594) (64)
heavy-duty vehicles: Y = –0.0654X + 144.94 (R = 0.466) (65)

Ethybenzene
light-duty vehicles: Y = –0.0051X + 13.11 (R = 0.466) (66)
heavy-duty vehicles: Y = –0.0072X + 12.77 (R = 0.409) (67)

m,p-Xylene
light-duty vehicles: Y = –0.0281X + 79.813 (R = 0.575) (68)
heavy-duty vehicles: Y = –0.0471X + 81.316 (R = 0.601) (69)

o-Xylene
light-duty vehicles: Y = –0.0092X + 19.929 (R = 0.375) (70)
heavy-duty vehicles: No significance level

MTBE–BTEX Ratios in Different Tunnels

In this study, we use three types of the characteristic ratios, including MTBE–BTEX, Toluene/benzene (T/B) and Xylene/ethylbenzene Ratios, to present the different atmospheric environment in southern Taiwan. From the point of view of air toxics, we often apply such characteristic ratios to understand some fingerprints about related pollutants.

In this study, the average MTBE–BTEX ratios were evaluated and used to compare the VOC emissions among the five selected tunnels. For the convenience of comparison with different tunnels (as shown in Table 3), the MTBE–BTEX ratio means the ratios between MTBE, benzene, toluene, ethylbenzene, *m,p*-xylene, and *o*-xylene concentrations based on the normalization by minimum level. In Liangshan Tunnel, the average MTBE–BTEX ratios at at peak rush periods 07:00 to 09:00 and 17:00 to 19:00, were 5.2:1, 3:1, 0:1, 1:2, 5:1.5 and 8.1:1, 0:2, 1:1, 8:4, 0:1.8, respectively. Similarly, in Yueguangshan Tunnel, the average MTBE–BTEX ratios at peak rush periods 07:00 to 09:00 and 17:00 to 19:00, were 4.2:1, 6:2, 7:1, 0:1, 4:1.1 and 5.4:1, 9:2, 5:1, 0:2, 0:1.4, respectively.

In Zoying Tunnel, the average MTBE–BTEX ratios from 07:00 to 09:00 and 17:00 to 19:00, were 5.1:1, 5:2, 3:1, 0:2, 0:1.4 and 8.6:2, 4:5, 3:1, 0:2, 8:2.0, respectively. Moreover, in Guogang Tunnel, the average MTBE–BTEX ratios at peak rush periods of 07:00 to 09:00 and 17:00 to 19:00, were 5.0:1.5:3.4:1.0:1.5:1.1 and 5.7:1.3:3.2:1.0:1.4:1.1, respectively. As mentioned before in Section 3.1, in Zhongliao Tunnel the flow of both light-duty vehicles and heavy-duty vehicles experienced peak rush periods from 07:00 to 19:00 which reflect the characteristics of freeway traffic transportation in southern Taiwan. Notably, the average MTBE–BTEX ratios at two peak rush periods (for the convenience of comparison with other tunnels), one from 07:00 to 09:00 and 17:00 to 19:00, were 1.1:1, 8:10, 6:1, 0:5, 6:1.4 and 1.7:2, 4:14 , 2:1, 1:9, 2:1.0, respectively. From morning till night (as shown in Table 3), the ratios at different sampling periods in the five different tunnels suggest the existence of both different traffic flows and variations in traffic fleet type in different tunnels. As far as Zoying and Guogang tunnels are concerned, these two tunnels adjoin different industrial parks in the Kaohsiung area. Therefore, it is possible that such multiple industrial sources of VOCs can coexist and are spread into Zoying and Guogang tunnels by the air flow/wind as long as traffic fleets move in the tunnels. This observation agrees with the point of view of Hsieh *et al*. (2006), who indicate that in neighborhoods where multiple sources of VOCs coexist, the concentration ratio of MTBE to any VOC tends to be smaller than when traffic is the main source, as the contribution of VOC from these multiple sources is superimposed upon the traffic emissions, whereas MTBE comes only from traffic.

Toluene/Benzene (T/B) Ratios in Different Tunnels

Some investigated studies revealed that toluene/benzene (T/B) ratio increases with increasing traffic volume,

Table 3. The characteristic ratios of MTBE and BTEXs in different traffic tunnels.

Characteristic Ratios	MTBE	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Liangshan Tunnel						
05:00–07:00	10.9	1.8	---	---	7.2	1.0
07:00–09:00	5.2	1.3	1.0	1.1	2.5	1.5
12:00–14:00	8.0	1.0	0.0	1.3	7.2	0.0
17:00–19:00	8.1	1.0	2.1	1.8	4.0	1.8
19:00–21:00	22.4	2.3	1.0	---	15.0	---
Yueguangshan Tunnel						
05:00–07:00	4.5	1.4	1.6	1.0	1.8	1.1
07:00–09:00	4.2	1.6	2.7	1.0	1.4	1.1
12:00–14:00	4.2	1.5	2.8	1.0	1.4	1.1
17:00–19:00	5.4	1.9	2.5	1.0	2.0	1.4
19:00–21:00	6.5	1.8	1.6	1.0	3.3	1.0
Zoying Tunnel						
05:00–07:00	14.3	5.0	5.7	1.0	5.5	3.6
07:00–09:00	5.1	1.5	2.3	1.0	2.0	1.4
12:00–14:00	16.5	4.8	4.1	1.0	7.7	4.4
17:00–19:00	8.6	2.4	5.3	1.0	2.8	2.0
19:00–21:00	5.4	1.3	3.2	1.0	1.7	1.2
Guogang Tunnel						
05:00–07:00	5.2	1.5	3.3	1.0	1.5	1.0
07:00–09:00	5.0	1.5	3.4	1.0	1.5	1.1
12:00–14:00	6.1	1.5	2.9	1.0	1.5	1.1
17:00–19:00	5.7	1.3	3.2	1.0	1.4	1.1
19:00–21:00	4.7	1.4	2.4	1.0	1.4	1.1
Zhongliao Tunnel						
05:00–07:00	1.5	1.6	10.8	1.0	5.5	1.6
07:00–09:00	1.1	1.8	10.6	1.0	5.6	1.4
12:00–14:00	1.3	2.4	15.6	1.0	5.6	2.1
17:00–19:00	1.7	2.4	14.2	1.1	9.2	1.0
19:00–21:00	1.5	2.2	15.8	1.2	9.5	1.0

industrial emissions and other urban sources in denser areas (Lee *et al*., 2002; Hsieh *et al*., 2006). Therefore, T/B ratios in different tunnels were also calculated and examined in this study (as shown in Table 4). T/B ratio ranged from 0 to 2.3, 0 to 1.9, 0.6 to 2.5, 0.9 to 2.6 and 0 to 10.5 in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels, respectively. Moreover, average T/B ratios for each sampling period in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels are listed in Table 4, respectively. In this study, average T/B ratios in all five tunnels were 0.7, 1.4, 1.6, 2.1 and 6.4, respectively.

It would be helpful for researchers to compare the ambient T/B ratios in the neighborhoods of different industrial parks and in the five different tunnels in southern Taiwan. Hsieh *et al*. (2006) investigated the ambient BTEX and MTBE in the neighborhoods of different industrial parks in southern Taiwan. They found that the T/B ratio ranged from 0.1 to 5.2, 0 to 5.5, 0.2 to 8.2, 4.1 to 16.3, 0.2 to 4.6 and 0.7 to 9.4 in the Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi industrial parks, respectively. In the study by Hsieh *et al*. (2006), average T/B ratios in Nei-Pu, Ping-Tung, Ping-Nan, Ren-Wu, Lin-Yuan and Nan-Zi were 1.3, 1.7, 2.6, 8.6, 0.9 and 2.9, respectively. In total, in the five investigated tunnels in southern Taiwan, the average T/B ratios ranged from 0.7 to 6.4, revealing a wide variation in values. Moreover, the ratios of T/B in Zhongliao Tunnel were significantly higher at two rush periods, suggesting again that T/B ratio increases with increasing traffic volume in the tunnel environment. Notably, Zhongliao Tunnel is the longest half-enclosed tunnel among the five investigated tunnels in this study.

Xylene/Ethylbenzene (X/E) Ratio in Different Tunnels

We used the Σxylene/ethylbenzene (ΣX/E) ratio to evaluate the relative age of air parcels. The ΣX/E ratio is also used by many researchers to evaluate the relative age of the air parcels in ambient VOC investigation (Monod *et al*., 2001; Hsieh *et al*., 2006; Truc and Oanh, 2007). In general, xylenes are considered a highly reactive species, while ethylbenzene is considered a low reactivity species. Thus, low X/E ratio suggests an aged air parcel. As shown in Table 4, ΣX/E ratio ranged from 3.2 to 5.7, 2.5 to 4.4, 2.9 to 12.1, 2.4 to 2.7 and 7.0 to 8.8 in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels, respectively.

Table 4. The characteristic ratios of MTBE and BTEXs normalized by benzene in five investigated tunnels in southern Taiwan.

Characteristic Ratios	MTBE / B	Toluene / B	Ethylbenzene / B	m,p-Xylene / B	o-Xylene / B	ΣXylene / B	ΣXylene / Ethylbenzene	m,p-Xylene / Ethylbenzene
Liangshan Tunnel								
05:00–07:00	6.0	---	---	3.9	0.5	4.5	---	---
07:00–09:00	4.1	0.8	0.9	2.0	1.2	3.2	3.5	2.2
12:00–14:00	8.0	0.0	1.3	7.2	0.0	7.2	5.7	5.7
17:00–19:00	8.1	2.1	1.8	4.0	1.8	5.7	3.2	2.2
19:00–21:00	9.6	0.4	---	6.4	---	6.4	---	---
Yueguangshan Tunnel								
05:00–07:00	3.1	1.1	0.7	1.2	0.7	2.0	2.9	1.8
07:00–09:00	2.6	1.7	0.6	0.9	0.7	1.5	2.5	1.4
12:00–14:00	2.7	1.8	0.6	0.9	0.7	1.6	2.5	1.4
17:00–19:00	2.8	1.3	0.5	1.1	0.7	1.8	3.4	2.0
19:00–21:00	3.6	0.9	0.5	1.8	0.6	2.4	4.4	3.3
Zoying Tunnel								
05:00–07:00	2.9	1.1	0.2	1.1	0.7	1.8	9.2	5.5
07:00–09:00	3.4	1.6	0.7	1.3	0.9	2.2	3.4	2.0
12:00–14:00	3.5	0.9	0.2	1.6	0.9	2.5	12.1	7.7
17:00–19:00	3.6	2.2	0.4	1.2	0.8	2.0	4.9	2.8
19:00–21:00	4.1	2.4	0.8	1.3	0.9	2.2	2.9	1.7
Guogang Tunnel								
05:00–07:00	3.6	2.3	0.7	1.0	0.7	1.7	2.4	1.4
07:00–09:00	3.3	2.2	0.7	1.0	0.8	1.8	2.7	1.5
12:00–14:00	4.2	2.0	0.7	1.0	0.7	1.8	2.6	1.5
17:00–19:00	4.3	2.5	0.8	1.1	0.9	2.0	2.6	1.4
19:00–21:00	3.3	1.7	0.7	1.0	0.7	1.7	2.5	1.4
Zhongliao Tunnel								
05:00–07:00	0.9	6.7	0.6	3.4	1.0	4.4	7.1	5.5
07:00–09:00	0.6	5.9	0.6	3.1	0.8	3.9	7.0	5.6
12:00–14:00	0.5	6.4	0.4	2.3	0.8	3.1	7.6	5.6
17:00–19:00	0.7	5.8	0.5	3.8	0.4	4.2	9.0	8.1
19:00–21:00	0.7	7.3	0.5	4.4	0.5	4.8	8.8	8.0

* In this table, B denotes Benzene.

Obviously, those high ΣX/E ratios reflect a fresh air parcel in the environment of all investigated tunnels due to the enclosed/half-enclosed environment.

Other than using Σxylene/ethylbenzene (ΣX/E) ratio, the *m,p*-xylene/ethylbenzene (*m,p*-X/E) ratio is also used by some researchers to understand the characteristics of pollutant VOCs (Monod *et al*., 2001; Truc and Oanh, 2007). As shown in Table 4, *m,p*-xylene/ethylbenzene (*m,p*-X/E) ratio ranged from 2.2 to 5.7, 1.4 to 3.3, 2.0 to 7.7, 1.4 to 1.5 and 5.5 to 8.1 in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels, respectively. Truc and Oanh (2007) indicated that there is a wide range of ratios (*m,p*-X/E) reported for different urban samples, ranging from 1.3 for Tokyo to above 4.8 in Athens, but the most common values are between 2.0 and 3.0 (Monod *et al*., 2001).

In addition, Monod *et al*. (2001) reported a higher *m,p*-X/E ratio for evaporative emission, ranging from 3.8 to above 4.5, while the ratios for vehicle exhausts and roadside samples were lower, from 2.8 to 3.6 (Monod *et al*., 2001). The ratios found in the study by Truc and Oanh (2007) for the TC and DBP streets were also in the range reported for the roadsides. In contrast, the ratios in traffic tunnels in southern Taiwan are slightly to significantly higher, suggesting that BTEX in both Liangshan and Zhongliao tunnels may also come from other non-traffic sources (for example, emergency generators in Zhongliao Tunnel). As mention before, unleaded gasoline #92, unleaded gasoline #95, unleaded gasoline #98, and diesel are commonly used in Taiwan. Therefore, another reason for the high ratios in traffic tunnels in southern Taiwan is associated with the fact that such emissions and ratios depend greatly on the used gasoline in different investigated countries. We also observed a wide range of ΣX/E or *m,p*-X/E ratios in the five investigated tunnels in southern Taiwan. Nevertheless, it is important to explore the characteristics of X/E in different traffic tunnels.

Percentage of MTBE and BTEX in Different Tunnels

Table 5 shows the average percentage of MTBE and BTEX for a whole sampling period. In Liangshan tunnel, MTBE, benzene and *m,p*-Xylene are the three most abundant species and contribute approximately 40.9–55%, 20–41.1% and 5.4–10%, respectively. It was observed that MTBE, toluene and *m,p*-Xylene are the three most abundant species three other tunnels and contribute approximately 34.9–42.6%, 10.5–23.2% and 11.5–21.7% in Yueguangshan Tunnel; 38.5–42.9%, 10.6–23.9% and 12.4–20% in Zoying Tunnel, and; 36.6–43.6%, 20.1–25.1% and 10.3–11.8% in Guogang Tunnel, respectively. In Zhongliao Tunnel, toluene, *m,p*-Xylene and benzene are the

Table 5. Distribution (%) of MTBE and BTEXs in five investigated tunnels.

Composition (%)	MTBE	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Liangshan Tunnel						
05:00–07:00	52.2	8.7	0.0	0.0	34.3	4.8
07:00–09:00	40.9	10.0	7.9	9.1	20.0	12.1
12:00–14:00	46.0	5.7	0.0	7.2	41.1	0.0
17:00–19:00	43.5	5.4	11.0	9.6	21.1	9.6
19:00–21:00	55.0	5.8	2.5	0.0	36.8	0.0
Yueguangshan Tunnel						
05:00–07:00	39.4	12.7	14.1	8.8	15.5	9.5
07:00–09:00	35.0	13.5	22.6	8.3	11.5	9.1
12:00–14:00	34.9	12.9	23.2	8.4	11.6	9.0
17:00–19:00	37.9	13.3	17.6	7.1	14.3	9.8
19:00–21:00	42.6	11.9	10.5	6.5	21.7	6.8
Zoying Tunnel						
05:00–07:00	40.7	14.1	16.3	2.8	15.8	10.3
07:00–09:00	38.5	11.3	17.6	7.5	15.0	10.1
12:00–14:00	42.9	12.4	10.6	2.6	20.0	11.5
17:00–19:00	39.0	10.7	23.9	4.5	12.9	9.1
19:00–21:00	39.2	9.6	23.2	7.3	12.4	8.4
Guogang Tunnel						
05:00–07:00	38.7	10.8	24.6	7.7	10.9	7.4
07:00–09:00	36.6	11.2	25.1	7.4	11.3	8.5
12:00–14:00	43.6	10.5	20.5	7.1	10.9	7.5
17:00–19:00	41.2	9.5	23.4	7.3	10.3	8.3
19:00–21:00	39.1	12.0	20.1	8.3	11.8	8.8
Zhongliao Tunnel						
05:00–07:00	6.6	7.4	49.1	4.5	24.9	7.4
07:00–09:00	5.1	8.4	49.2	4.7	26.0	6.7
12:00–14:00	4.7	8.7	55.7	3.6	19.9	7.4
17:00–19:00	5.7	8.2	47.9	3.8	31.0	3.4
19:00–21:00	4.9	7.0	50.7	3.8	30.4	3.2

three most abundant species and contribute approximately 47.9–55.7T% 19.9–31% and 7–8.7%, respectively. In total, MTBE, toluene and *m,p*-Xylene are the three most abundant species in all the five investigated tunnels.

CONCLUSION

In this study, the concentrations of five volatile organic compounds (VOCs), including BTEX (the acronym for benzene, toluene, ethylbenzene, and xylene) and methyl tertiary-butyl ether (MTBE), were investigated in five different traffic tunnels (Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao) in southern Taiwan. In total, the mean concentration of MTBE was several times higher than that of benzene in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnel. The maximum total concentration of VOCs in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunneltunnels were 54.7, 243.6, 111.3, 472.7 and 410.2 $\mu g/m^3$, respectively. The high traffic volume in Guogang Tunnel, coupled with the emission related to the industrial activities, may be the cause for the higher pollution. From morning till night, the ratios during different sampling periods in the five different tunnels suggest the existence of both, different traffic flow and variations in traffic fleet type in different tunnels. In this study, average T/B ratios in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels were 0.7, 1.4, 1.6, 2.1 and 6.4, respectively. ΣX/E ratio ranged from 3.2 to 5.7, 2.5 to 4.4, 2.9 to 12.1, 2.4 to 2.7 and 7.0 to 8.8 in Liangshan, Yueguangshan, Zoying, Guogang and Zhongliao tunnels, respectively. Obviously, those high ΣX/E ratios in all investigated traffic tunnels reflect a fresh air parcel in the tunnel due to the enclosed/half-enclosed environment. Finally, MTBE, toluene and *m,p*-Xylene are the three most abundant species in all the five investigated tunnels.

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