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Characterization of $PM_{2.5}$ and Particulate PAHs Emitted from Vehicles via Tunnel Sampling in Different Time Frames

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ABSTRACT

The present study investigated the emission characteristics of $PM_{2.5}$ and particulate PAHs (25 congeners) emitted from vehicles in real running conditions via air sampling in the longest tunnel in Taiwan. The average $PM_{2.5}$ concentrations measured in the tunnel inlet and outlet were 21.9 ± 6.9 μg m^{-3} and 46.1 ± 12 μg m^{-3}, respectively, which are significantly higher than that measured at an ambient station nearby (12.5 ± 6.2 μg m^{-3}). Total particulate PAHs (P-PAHs) concentration measured at the inlet of the tunnel was 1.68 ± 1.4 ng m^{-3}, which was significantly lower than that measured at the outlet of the tunnel (6.31 ± 4.8 ng m^{-3}). Meanwhile, the average concentration of P-PAHs found in ambient air station was only 0.275 ± 0.062 ng m^{-3}. A higher concentration difference ($\Delta C = C_{out} - C_{in}$) of particulate PAHs was found on weekday compared with that observed during the weekend due to the higher number of diesel vehicles passing through the tunnel. The concentration differences of these pollutants were higher in the daytime compared with that in the nighttime because of higher vehicle number. Pyr and PL were the dominant contributors in terms of mass concentration while BcFE was the main contributor to TEQ concentration. The results also indicate that the list of 15 EU-PAHs should be considered for evaluation of the health risk associated with the emission of PAHs from vehicles.

Keywords: Mobile sources, Tunnel sampling, timeframe emission, EU-PAHs, Benzo[c]fluorene

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1 INTRODUCTION

Exposure to the high concentration of particulate matter (PM) causes numerous adverse health effects such as exacerbation of chronic respiratory and cardiovascular diseases, decreased lung function, and premature mortality (Guaita *et al.*, 2011; Halonen *et al.*, 2009; Perez *et al.*, 2012; Samoli *et al.*, 2008, Xing *et al.*, 2016). Especially, fine particles ($PM_{2.5}$) are the main causes of visibility reduction and climate change due to direct effects of scattering and absorption of solar radiation, and their association with cloud formation (Adesina *et al.*, 2016; Samset *et al.*, 2016; Srivastava *et al.*, 2018). Additionally, polycyclic aromatic hydrocarbons (PAHs) are a group of chemically related compounds that are environmentally persistent with various structures and varied toxicity (Nisbet and LaGoy, 1992). Association of PM with toxic PAHs has been investigated and reported worldwide due to their synergistic effect on human health (Dat and Chang, 2016). Both $PM_{2.5}$ and particulate PAHs emitted from mobile sources are regarded as a major contributor to air quality degradation in urban areas (Guo *et al.*, 2003; Zhang *et al.*, 2013; Liang *et al.*, 2020; Wang *et al.*, 2020; Xing *et al.*, 2020; Nadali *et al.*, 2021), indicating that they need to be controlled for reducing their levels in the environment. Vehicles are reported as one of the main contributors to

ambient PAHs in urban areas of Taiwan, such as in Kaohsiung (Lai *et al.*, 2016), Hsinchu (Yang *et al.*, 2016) and Taoyuan (Dat *et al.*, 2018). Therefore, investigation of emission factor and characteristics of PM and particle-bound PAHs (P-PAHs) emitted from mobile sources is deemed necessary for enacting effective regulations on reducing the occurrence of PAHs in the environment.

PAHs are discharged from vehicles via three main mechanisms, including the synthesis of low-molecular-weight PAHs through combustion processes, emission of the PAHs originally present in the fuel, and the cracking of the lubricating oil (Sonntag *et al.*, 2012). Emission factors and characteristics of particulate PAHs emitted from vehicles are mainly affected by engine type, operating condition, compositions of fuel and lubricant used, vehicle mileage, and the catalytic converter adopted (Cheruiyot *et al.*, 2015). Lyu *et al.* (2019) investigated the emission of 27 PAHs including 16 US-EPA and 15+1 EU-PAHs from coal-fired processes and indicated that 15+1 EU-PAHs contributed to 99% total Ba-P TEQ concentration of PAHs emitted from a coal-fired plant. Similar results were obtained by the investigation of PAHs in different environmental matrices (Richter-Brockmann and Achten, 2018), suggesting the importance of including EU-PAHs as target compounds for evaluating the health risk of PAHs. However, limited information regarding these PAHs emitted from vehicles has been reported worldwide. Therefore, the 15 EU-PAHs are included as the target compounds (25 congeners) in this study for evaluating their contributions on the total emission and TEQ. Additionally, the contribution of 15 EU-PAHs to total PAHs in terms of mass and TEQ concentrations will be compared, which would provide useful information for future research regarding the emission and risk assessment of PAHs.

The tunnel with a semi-enclosed space can be selected to investigate the characteristic of pollutants discharged from a wide ranges of vehicle type (or fleet composition) operated at different conditions because of the least influences of meteorological parameters and atmospheric reactions occurring inside the tunnel (Kim *et al.*, 2012). This study conducted the tunnel sampling with the primary aims to (1) characterize the distribution of 25 PAHs in particulate phase ($PM_{2.5}$); (2) assess the influence of fleet composition on emission characteristics of $PM_{2.5}$ and particulate PAHs at different sampling time frames including weekday, weekend, daytime and nighttime; (3) evaluate the diagnostic ratios and emission factors of $PM_{2.5}$ and particulate PAHs emitted from vehicles. This study is expected to provide the comparison between characteristics of 16 popular PAHs and EU-PAHs in particulate phase of a tunnel in different timeframes, which would provide good insights into the PAHs emission from mobile sources.

2 MATERIALS AND METHOD

2.1 Tunnel Sampling

The tunnel with a length of 1,875 m connecting New Taipei City and Keelung City in northern Taiwan (as shown in Fig. 1) was selected to investigate the characteristics of PAHs emitted from vehicles. The tunnel has two separate bores with three lanes per bore, which was equipped with a vertical flow ventilation jet fan with a total width of 10.3 meters. There are 1.0-meter wide pedestrian walkways on both sides of the road. The height of the tunnel is 8.5 m and the sectional area is about 106 m^2. In the tunnel, samples were collected at two sampling points 50 m away from the tunnel inlet (located in Keelung City, Station A) and the outlet (located in New Taipei City, Station B), respectively. Furthermore, ambient air samples were also collected at the same time at an air quality monitoring station nearby the tunnel (Station C). To evaluate the characteristics of PAHs emitted in different periods, samples were collected simultaneously at three stations in a period of seven days, being divided into weekdays (Monday–Friday) and weekend (Saturday and Sunday) samples. Furthermore, single-day samples were divided into daytime (7:00 AM–19:00 PM) and nighttime (19:00 PM–7:00 AM) samples. The sampling campaign was conducted from 5th March 2019 to 11th March 2019, and the number and type of vehicles crossing the tunnel were identified via a radar vehicle counter and a video recorder.

All samples were collected by high flow rate samplers operating with the sampling flow rate of 500 L min^{-1}. The $PM_{2.5}$ and particulate PAHs were collected on a 150 mm round quartz fiber filter (QFF) which was pre-cleaned in a furnace at the temperature of 900°C. After the sampling campaign, the QFF was stored in a tight box with ice, sent back to the laboratory immediately and then stored in a refrigerator until extraction. PAHs were extracted and analyzed within three weeks after sampling.

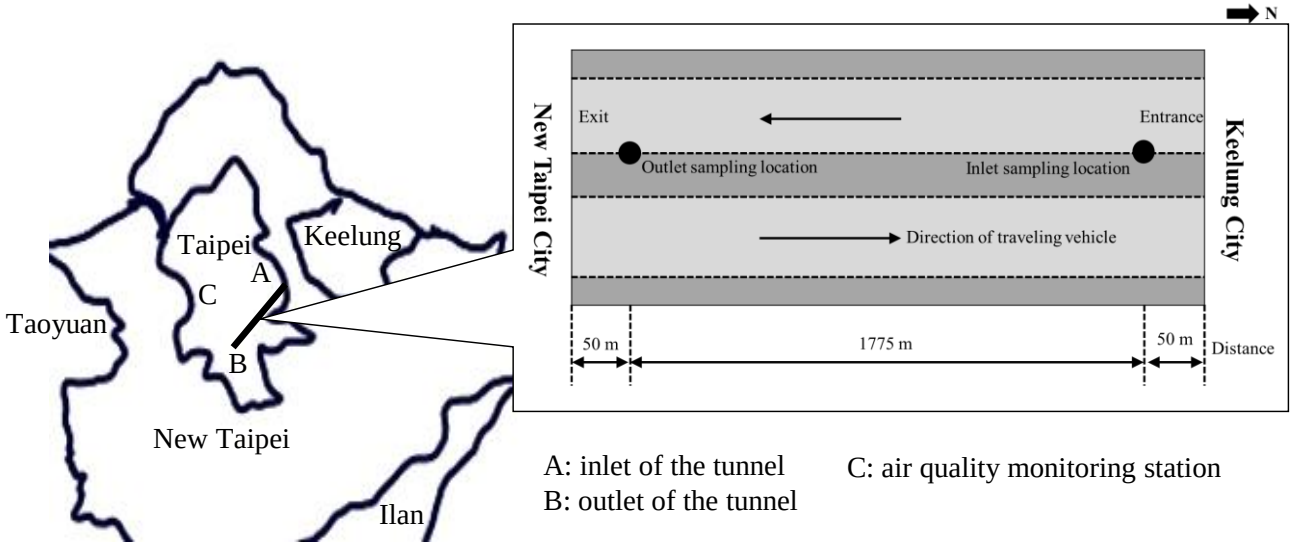

Fig. 1. Relevant locations for tunnel and ambient samplings.

2.2 Analysis of $PM_{2.5}$ and Particulate PAHs

Before analysis, the filters were conditioned under specific conditions (20°C, and relative humidity of 40%) for 24 hrs and weighed to obtain the mass of particle collected for calculating $PM_{2.5}$. For the analysis of particulate PAHs, all QFFs were then spiked with internal standards (PAH-LCS-B, Wellington Laboratories Inc.) and extracted for 24 hours by Soxhlet extraction with dichloromethane (DCM). The DCM extract was then concentrated to approximately 10 mL by rotary evaporation. Thereafter, DCM was replaced with n-hexane for three times by adding 70–80 mL of n-hexane and concentrating to completely remove DCM. The sample was then passed through a clean-up column packed with 10 g of activated silica gel and 1 g Na_2SO_4. The column was eluted by hexane and DCM to obtain PAHs in the purifying solution and then, the extract was condensed to 2 mL by rotary evaporation. The collected eluent was reconcentrated to approximately 500 μL with a gentle nitrogen stream, and the recovery standards were for analysis. In this study, 25 PAHs were analyzed by gas chromatography-mass spectrometry (Agilent 6890-5973N) using a fused silica capillary column DB-5 MS (60 m × 0.25 mm × 0.25 m) under positive EI conditions, and data were obtained in the selected ion monitoring (SIM) mode. The relevant information regarding target compounds and their abbreviations was presented in Table S1.

2.3 Emission Factor and BaP Equivalency Factors

In this study, emission factor (EF) of particulate PAHs was calculated for vehicles passing through the tunnel during the sampling period. The EF was calculated following Riccio *et al.* (2016) using the vehicle kilometers traveled-based emission factors (EF_{VKT}) calculation method as shown in Eq. (1):

$$EF_{VKT} = \frac{V \times A}{N \times L} \Delta C \quad (1)$$

where EF_{VKT} is the emission factor of vehicle mileage (ng PAHs emitted km-vehicle traveled^{-1}); V is the air flow velocity (m s^{-1}); A is the tunnel cross-sectional area (m^2); N is the number of vehicles per unit time (number-of-vehicles total-time^{-1}); L is the distance between two sampling points (km) and Δc is the difference in PAHs concentrations (ng m^{-3}) measured at the two sampling points of the tunnel.

The BaP equivalent concentration (BaP_{eq}) was used to assess the carcinogenic risk of PAHs, and the toxic equivalency factors (TEFs) were obtained from previous studies (Nisbet and LaGoy, 1992; Richter-Brockmann and Achten, 2018; U.S. EPA, 2010; Andersson *et al.*, 2015; OEHHA, 1994). The BaP_{eq} of the PAHs was calculated according to Eq. (2):

$$Bap_{eq} = \sum_{n}^{i} PAH_i \times TEF_i \quad (2)$$

where PAH_i is the concentration of the individual PAH in each sample and TEF_i is the TEF of the individual PAH. The carcinogenic risk of 25 PAHs is calculated based on the sum of individual BaP_{eq}. The TEF values of individual PAH are summarized in Table S1.

2.4 Quality Assurance and Quality Control (QA/QC)

The QC and QA for analysis of $PM_{2.5}$ and PAHs were carried out according to the methods prescribed by the European Commission and Taiwan EPA, including EN-14907 and NIEA A212.10B for sampling and analysis of $PM_{2.5}$ and particulate PAHs in tunnel and ambient air, respectively. Field blanks and method blanks were extracted and analyzed simultaneously with field samples. Only low contents of PHE, Ant, FL, and Pyr were detected in the PUF and filter of field blank samples (< 2 μg, < 0.3 μg, < 0.1 μg, < 0.1 μg and < 0.2 μg per cartridge, respectively). The recoveries of internal standards ranged from 75 to 110% for most PAHs.

3 RESULTS AND DISCUSSION

3.1 Traffic Flow and $PM_{2.5}$ Emission

The vehicles passing through the tunnel were divided into two categories including diesel and gasoline engines. The average speed of vehicles in daytime and nighttime were 80.9 ± 1.2 and 91.3 ± 0.87 (km hr^{-1}), respectively, and no significant difference between weekend and weekday was found. The average volume and composition of the fleet recorded at different time frames are presented in Fig. 2. The vehicle number ranged from 52,000 to 57,000 per day with a slightly lower traffic flow during weekdays (4,400 ± 200 vehicles hr^{-1}) compared with the weekend (4,600 ± 100 vehicles hr^{-1}). The number of vehicles recorded in nighttime accounted for 26 ± 2% of total vehicles passing through the tunnel on weekdays, while this figure increased to 32 ± 1% for the weekend. Gasoline vehicles predominated at all time and the diesel vehicle accounted for 16.2% and 8.6% of the fleet on weekday and weekend, respectively. Furthermore, the proportion of diesel vehicles in the fleet was higher in the daytime compared with nighttime, especially a significant difference was observed on weekdays.

The average $PM_{2.5}$ concentrations measured at the inlet and outlet of the tunnel were 21.9 ± 6.9 μg m^{-3} and 46.1 ± 12 μg m^{-3}, respectively, which are significantly higher than that measured at ambient station (12.5 ± 6.2 μg m^{-3}), indicating that vehicle emissions contributed significantly to the level of $PM_{2.5}$ in the tunnel. The concentration of $PM_{2.5}$ measured in this study was relatively lower than those reported worldwide for $PM_{2.5}$ concentration measured in tunnel (Zhang *et al.*, 2015; Pant *et al.*, 2017; de P. Pereira *et al.*, 2002). Interestingly, the ambient $PM_{2.5}$ concentration (Fig. 2(b)) measured during the weekend (13.5 ± 7.9 μg m^{-3}) was slightly higher than that measured during the weekdays (11.7 ± 5.8 μg m^{-3}), while the $PM_{2.5}$ concentrations measured at the inlet and outlet of tunnel during the weekday (inlet: 26.3 ± 11 μg m^{-3}, outlet: 55.3 ± 16 μg m^{-3}) were higher than those measured during the weekend (inlet: 17.2 ± 3.3 μg m^{-3}, outlet: 33.3 ± 7.2 μg m^{-3}). It is noted that the difference of inlet and outlet $PM_{2.5}$ concentrations measured during weekday and weekend are 29.0 μg m^{-3} and 16.1 μg m^{-3}, respectively, which is consistent with the significantly higher number of diesel vehicle passing through the tunnel during the weekday (1.76 times higher) in comparison with that on the weekend. Additionally, the difference of inlet and outlet $PM_{2.5}$ concentration measured during the daytime (27.4 μg m^{-3}) was significantly higher than that measured during the nighttime (16.4 μg m^{-3}), resulting from the higher traffic volume in the daytime compared with that in the nighttime (Fig. 2(c)). A similar trend was also reported by Perez-Martinez *et al.* (2014) for the levels of NO_x and PM_{10} measured in a tunnel located in Brazil.

3.2 Mass Concentration and Distribution of PAHs on $PM_{2.5}$

The concentrations of particulate PAHs (P-PAHs) measured at the inlet and outlet of the tunnel, respectively, are shown in Fig. 3. The total P-PAHs measured at the inlet of the tunnel was 1.68 ± 1.4 ng m^{-3}, which is significantly lower than that measured at the outlet of the tunnel (6.31 ±

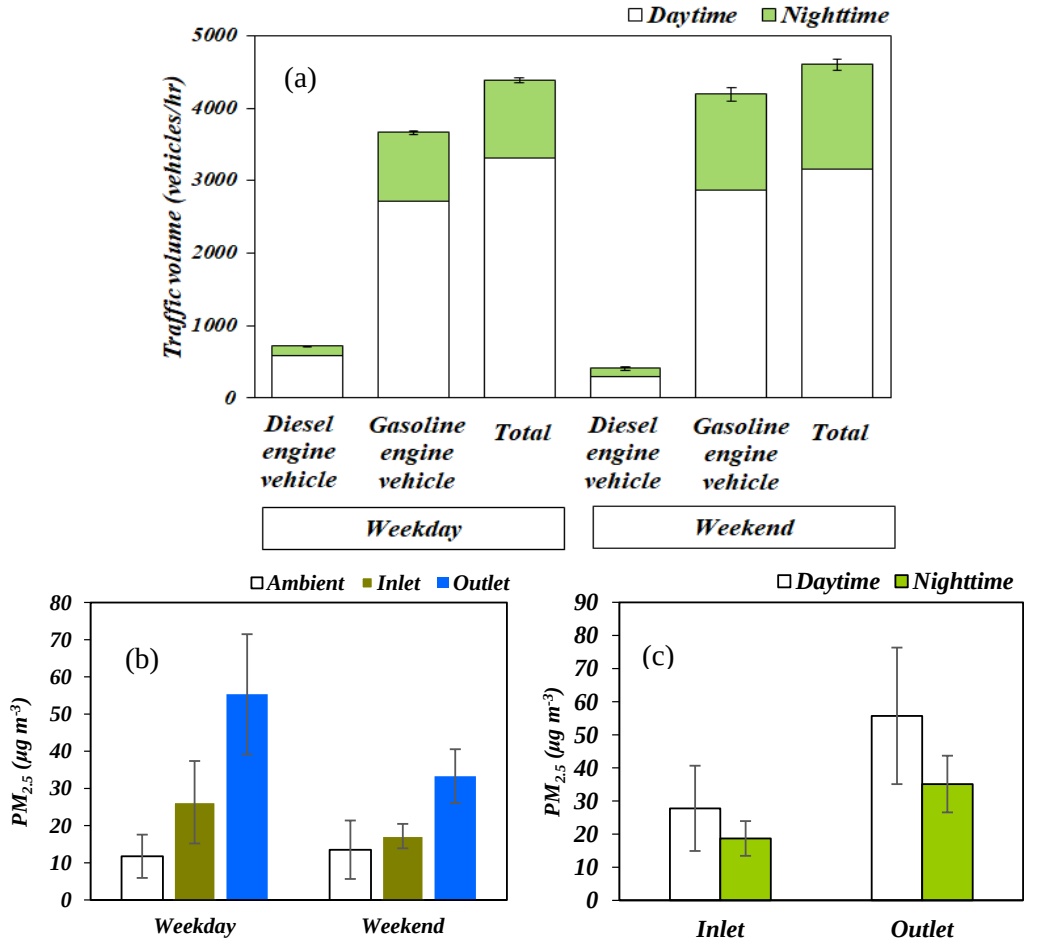

Fig. 2. (a) Composition and fleet number in different time frames; (b) Average $PM_{2.5}$ concentrations measured at the ambient air, tunnel inlet and outlet on weekday and weekend, respectively; (c) Average $PM_{2.5}$ concentrations measured at the inlet and outlet of the tunnel in daytime and nighttime, respectively. The error bar refers to the standard deviation (± SD).

4.8 ng m^{-3}), while the average concentration of P-PAHs found in ambient air station was only 0.275 ± 0.062 ng m^{-3}. Interestingly, the levels of P-PAHs measured in this study were notably lower than those reported by previous studies. For instance, Fang *et al.* (2018) indicate that the levels of 15 PAHs in $PM_{2.5}$ measured at the inlet and outlet of the tunnel in Nanjing (China) were 6.34 ± 3.1 and 32.1 ± 7.5 ng m^{-3}, respectively. Kim *et al.* (2014) revealed that the levels of particle-PAHs measured in three tunnels located in South Korea were in the range of 28.2 to 37.4 ng m^{-3}. The differences ($\Delta C = C_{outlet} - C_{inlet}$) of $PM_{2.5}$-PAH congeners (outlet – inlet) measured at the tunnel at different time frames of this study are presented in Fig. 4. The differences found in daytime, nighttime, weekday and weekend were 4.28 ± 3.9 and 4.46 ± 2.4, 5.27 ± 3.6 and 4.28 ± 1.2 ng m^{-3}, respectively. Although the fleet number in the daytime was significantly higher than that in the nighttime, the differences of P-PAH concentration measured in daytime and nighttime were comparable, even the $PM_{2.5}$ concentration measured in the daytime was significantly higher than that measured in nighttime (Fig. 2). The level of PAHs on $PM_{2.5}$ collected in nighttime at the outlet of tunnel (0.166 ± 0.069 ng μg^{-1}) was significantly higher than that in daytime (0.108 ± 0.087 ng μg^{-1}). Similar results were also reported by Ho *et al.* (2009) for particulate-PAHs in different time frames. It might be attributed to the adsorption/desorption of PAHs onto particles and the decline of temperature at nighttime. After being emitted into the atmosphere of the tunnel at a low temperature, gas-phase PAHs of high affinity with particles (normally high-ring PAHs) would immediately associate with fine particles, resulting in the higher level of PAHs on $PM_{2.5}$ collected in nighttime (Dat *et al.*, 2017). On the other hand, a higher difference of P-PAHs concentration was found during weekdays compared with that on weekends, while the total number of vehicles

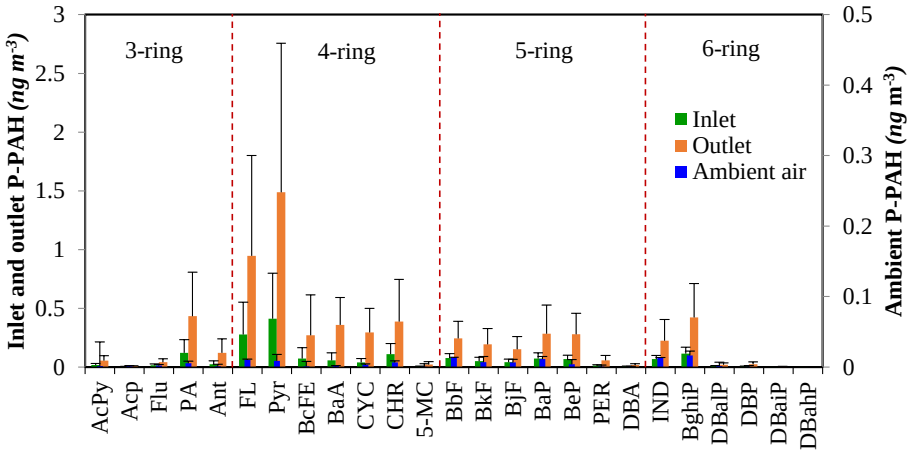

Fig. 3. The concentrations of P-PAHs measured at the ambient air station, and inlet, outlet of the tunnel, respectively (the error bar represents one SD of the data).

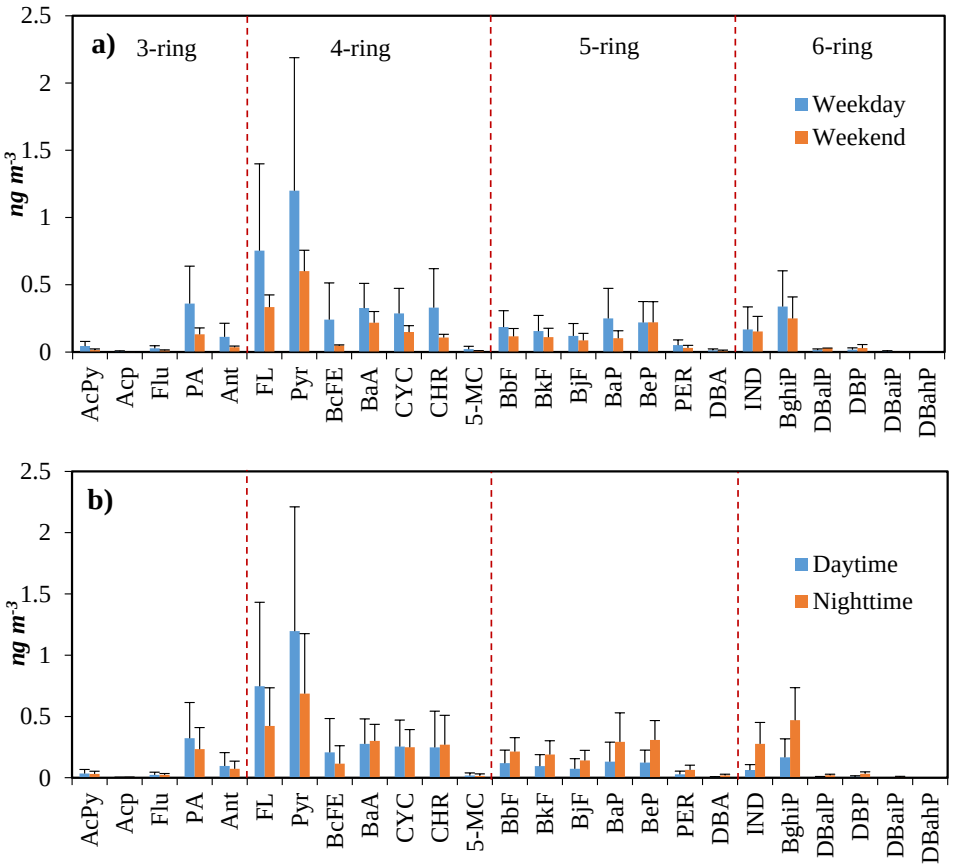

Fig. 4. The differences of P-PAH concentrations measured at different time frames: (a) weekend and weekday, (b) daytime and nighttime (the bar represents one SD of the data).

recorded on weekends was slightly higher than that on weekdays. This trend was similar to that of $PM_{2.5}$, which was resulted from the higher number of diesel vehicles compared with gasoline vehicles in the daytime. Previous studies indicated that the PM and PAH emission factors of diesel engines were significantly higher than that of gasoline engines. For example, Yang *et al.* (2019) investigated the emission factors of $PM_{2.5}$ from gasoline and diesel vehicles in Taiwan, and they revealed that average emission factor of $PM_{2.5}$ from diesel engines (57.8 mg km^{-1}) was significantly higher than that from gasoline engines (1.57 mg km^{-1}). Chen *et al.* (2013) reported that the emission

factor of PAHs from diesel vehicles was 3.37 times higher compared with that from gasoline vehicles. Ho *et al.* (2009) indicated that diesel vehicles emitted 5.45 times PAHs compared to gasoline vehicles. Several factors are reported to affect the PAH emission factor of vehicles, such as engine type, engine temperature, service age, mileage, and maintenance (Cheruiyot *et al.*, 2015). Survival of PAHs in the fuel and pyrosynthesis of PAHs in combustion chamber are two major mechanisms of PAHs formation in vehicular engines (Elghawi *et al.*, 2010). Souza and Corrêa (2016) indicated that 1–5% of diesel was not destroyed in diesel engines, which could be the reason for higher PAHs emission from diesel vehicles compared to that from gasoline vehicles because of the significantly higher level of PAHs in diesel fuel compared with that in gasoline (Pohjola *et al.*, 2010). The result indicates that the emission of PAHs from diesel vehicles constituted a major contribution to total P-PAHs measured in the tunnel despite of lower diesel vehicles in the total fleet number.

Fig. 3 also presents the congener profile of PAHs on $PM_{2.5}$ collected at the inlet and outlet of the tunnel. It can be seen that the profile of P-PAHs collected in the ambient air station was significantly different from those collected at the inlet and outlet of the tunnel. In the samples collected from ambient station, the 5-ring PAHs dominated, accounting for 36.6 ± 8.7% of total PAHs, followed by 6-ring and 4-ring PAHs, which made up 28.9 ± 5.7% and 24.1 ± 5.7% of total P-PAHs, respectively; and the 3-ring PAHs only contributed to 10.5 ± 8.7% of total P-PAHs. Specifically, BbF and BaP were the dominant congeners among the 5-ring group, contributing to 11.7 ± 2.2% and 9.5 ± 1.6%, respectively, of total P-PAHs. As for the 6-ring PAHs group, the main contributors to total P-PAHs include BghiP (16.0 ± 6.2%) and IND (11.4 ± 1.5%). FL (7.5 ± 2.8%) and Pyr (6.6 ± 1.6%) were the major contributors to total P-PAHs in the 4-ring group, while PA of 3-ring group contributed to 4.7 ± 1.5% of total P-PAHs. On the other hand, Fig. 3 also reveals a similar profile of P-PAHs collected at the inlet and outlet of the tunnel, with the dominance of 4-ring PAHs (54.0–57.8%), followed by 5-ring PAHs (19.7–21.4%), 6-ring PAHs (12.5–14.3%), 3-ring PAHs (9.9–10.3%). The results are consistent with those reported by Ho *et al.* (2009) and Liu *et al.* (2015) for the P-PAHs collected in the tunnel located in Hongkong and Shanghai, respectively. It is noted that the dominant congener found at the inlet and outlet of the tunnel was Pyr (4-ring congener), accounting for 23.7 ± 7.3% and 23.5 ± 7.6%, respectively, which is remarkably higher than that found in the ambient air samples. BeP was the highest contributor to total P-PAHs in the 5-ring group, constituting 5.0 ± 2.7%, while BghiP was the major contributor of 6-ring PAHs with 7.1 ± 3.3% of total P-PAHs. PA was the biggest congener contributing to total P-PAHs among the 3-ring group, accounting for 6.6 ± 1.9%. The congener profile of PAHs was routinely employed as basic information for suggesting major sources of PAHs. Different congener profiles of PAHs in the samples collected from ambient air station and the tunnel indicated different sources contributed to PAHs collected at two sampling locations. The PAHs collected from ambient air might be originated from several sources, while those found in the tunnel should be resulted from the evaporation or/and incomplete combustion of diesel and gasoline fuels (Wallington *et al.*, 2006). Some studies reported that the enrichment of low-ring PAHs (≤ 4-ring PAHs) denotes the contribution of diesel engine emission, while the dominance of high-ring PAHs (5- and 6-ring PAHs) indicates the emission of gasoline engines (Ancelet *et al.*, 2011; Kam *et al.*, 2012). Although the fleet composition showed that gasoline engines were the major vehicle, the high contribution of 4-ring PAHs indicates the emission of PAHs from diesel vehicles contributed mainly to the PAHs collected. This result confirms that diesel engines emitted significantly higher PAHs than gasoline engines.

Fig. 4 depicts the concentration differences of PAHs in $PM_{2.5}$ collected at different time frames. The differences observed in the weekday and weekend were 5.25 ± 3.6 and 2.81 ± 2.8 ng m^{-3}, respectively, while the differences found in daytime and nighttime were 4.25 ± 3.9 and 4.46 ± 2.4 ng m^{-3}, respectively. As presented in Fig. 4(a), the profiles of P-PAHs emitted in the tunnel are similar at all different time frames with the dominance of 4-ring PAHs (Pry and PL). A higher P-PAHs concentration was found in the tunnel during weekday compared with that on the weekend, which is in line with the higher number of vehicles recorded on the weekday. Fig. 4(b) shows the concentrations of PAHs measured in daytime and nighttime, respectively, which reveals that the concentrations of low-ring PAHs (3- and 4-ring groups) were higher in daytime compared with those in nighttime, however, the opposite trend was found for high-ring PAHs (5- and 6-ring groups). It is noted that the proportion of diesel vehicles in nighttime was lower than in day time.

Many studies indicated that diesel engines mainly emit low-ring PAHs, while high-ring PAHs dominate in gas exhaust emitted from gasoline engines (Zielinska *et al.*, 2004; Oliveira *et al.*, 2011; Kou *et al.*, 2012). This might be the reason for different distributions of PAHs in particles in night and day times.

3.3 TEQ Concentration and Distribution

The TEQ concentration of P-PAHs measured at ambient air station and inlet, outlet of the tunnel, and the TEQ concentration difference at different time frames are shown in Fig. 5. The TEQ concentration of P-PAHs measured in ambient air station was low (0.051–0.217 ng BaP-TEQ m^{-3}), which is lower than 1 ng BaP-TEQ m^{-3} for the ambient PAHs standard as recommended by the European Commission (European Commission, 2005) and within the range reported by Dat *et al.* (2018) for P-PAHs concentration in northern Taiwan, while those measured at the inlet and outlet of the tunnel were in the ranges of 0.405–7.14 and 1.55–23.2 ng BaP-TEQ m^{-3}, respectively. In terms of concentration differences ($\Delta C = C_{out} - C_{in}$), as shown in Fig. 5, the average concentration differences measured during weekday, weekend, daytime, and nighttime were 5.41, 1.56, 4.44, 3.07 ng BaP-TEQ m^{-3}, respectively.

Furthermore, Fig. 5 also reveals that the BcFE is the predominant congener contributing to the total BaP-TEQ concentration of P-PAHs collected in the tunnel, accounting for 63.8–92.8% of total TEQ. The following major contributors to total TEQ concentration are BaP (2.94–9.52%) and DBalP (1.44–19.45%), and all other congeners contribute less than 1% of total TEQ (as shown in Fig. S1). These results are conceivable considering the relatively high toxic equivalent factors of these species (BcFe: 20; BaP: 1; DBalP: 10), which is in agreement with those reported by previous studies if these congeners are included in the target compounds. Richter-Brockmann and Achten (2018) investigated the occurrence of 24 PAHs in various kinds of environmental samples and found that BcFe contributed to about 93% of the total TEQ concentration. Lyu *et al.* (2019) reported that BcFe, DalP were the main contributors to total TEQ of P-PAHs emitted from coal-fired power plants.

It is important to evaluate the contribution of 15 EU-PAHs to the total TEQ concentration. The lists of US-EPA PAHs and EU-PAHs and their toxic equivalent factors are presented in Table S1. In this study, 15 EU-PAHs consistently contributed to 99.9% of the total TEQ concentration in all samples collected in the tunnel, which is consistent with those reported by Richter-Brockmann and Achten (2018) and Lyu *et al.* (2019) for environmental samples and stack gas samples emitted from a coal-fired power plant, respectively. The figure for ambient air samples ranges from 59.3 to 82.7%. On the other hand, 15 US-EPA PAHs only contribute to 4.96 to 15.0% of total TEQ for tunnel samples and 87.6 to 93.1% of total TEQ for ambient air samples. This finding implies that 15 EU-PAHs should be included for the evaluation of health risk associated with PAHs.

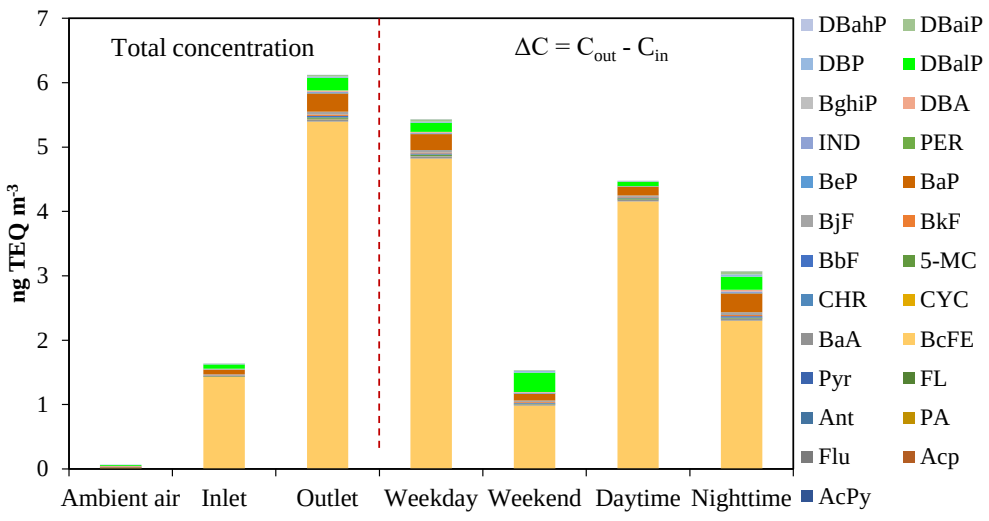

Fig. 5. TEQ concentrations of P-PAHs measured at three sampling sites and the TEQ concentration differences found in the tunnel at different time frames.

Table 1. Comparison of diagnostic ratios obtained in this study and literature.

Ratio	Range	Average	Sources	Reference
Flu/(Flu + Pyr)	0.019–0.034	0.02	Diesel: 0.40–0.60 Gasoline: 0.4	Sicre *et al.* (1987) and Rogge *et al.* (1993)
IND/(IND + BghiP)	0.23–0.45	0.32	Cars: 0.18 Diesel: 0.35–0.70	Grimmer *et al.* (1983), Kavouras *et al.* (2001), and Ravindra *et al.* (2006)
BaA/(BaA + Chr)	0.5–0.61	0.55	Diesel: 0.38–0.65 Gasoline: 0.22–0.55 Vehicular emission: > 0.35	Sicre *et al.* (1987), Simcik *et al.* (1999), and Kavouras *et al.* (2001)
BbF/BkF	1.08–1.55	1.27	Diesel: > 0.5	Pandey *et al.* (1999) and Park *et al.* (2002)
Pyr/BaP	1.24–9.90	5.17	Diesel: ~10 Gasoline: ~1	Ravindra *et al.* (2008)
Flu/BeP	0.02–0.20	0.10	Automobiles: 3.5 ± 0.5	Oda *et al.* (2001)
BaP/BghiP	0.34–0.96	0.65	Traffic emission: > 0.5	Katsoyiannis *et al.*, 2007

3.4 Diagnostic Ratio and Emission Factor (EF)

In PAH study, diagnostic ratios were usually used as a common tool to identify preliminary sources of PAHs (Tobiszewski *et al.*, 2012). Several diagnostic ratios used for distinguishing diesel and gasoline-related emissions calculated from the data of concentration differences obtained in this study are listed and compared in Table 1. It can be seen that the BaA/(BaA + Chr) > 0.35 and BaP/BghiP = 0.65 (on average) > 0.5 are in agreement with the literature for identifying vehicular emission. The ratios of IND/(IND + BghiP), BaA/(BaA + Chr), BbF/BkF, Pyr/BaP reveal that the PAHs collected were closer to diesel vehicles rather than gasoline vehicles. The ratios of Flu/(Flu + Pyr) and Flu/BeP are out of the ranges reported in the literature (Sicre *et al.*, 1987; Rogge *et al.*,1993; Oda *et al.*, 2001), which should be carefully considered if they are employed for identifying the sources of PAHs in ambient air.

The average EF_{VKT} ($PM_{2.5}$) of the tunnel sampling calculated in this study is 10.9 ± 1.1 mg km-vehicle^{-1}, which is lower than those reported previously. For instance, Ferm and Sjöberg (2015) reported that the EF of $PM_{2.5}$ in Sweden was 20 mg km-vehicle^{-1}, and 22.8 ± 7.4 mg km-vehicle^{-1} was reported by Mancilla and Mendoza (2012) for the tunnel study conducted in Mexico. Marinello *et al.* (2020) reviewed various studies conducted at different countries and indicated that the EF of $PM_{2.5}$ was in a wide range of 3–715 (mg km-vehicle^{-1}). Many reasons might be attributed to the lower EF of PM found in this study compared with previous studies such as the ventilation rate in the tunnel, the detailed composition fleet and the maintenance quality of vehicles passing through the tunnel during sampling time, which should be clarified in the future studies.

The EFs of particulate PAHs emitted from vehicles passing through the tunnel at different time frames are shown in Table 2. The emission factors of total P-PAHs are higher in weekday and nighttime compared with weekend and daytime, respectively. The contribution of individual PAHs to total EF follows the trend of concentration difference with the highest EF of Pyr (6.61 μg km-vehicle^{-1}), followed by FL (4.11 μg km-vehicle^{-1}) and PA (1.91 μg km-vehicle^{-1}). The total EFs ranged from 9.29 to 81.7 (μg km-vehicle^{-1}) or 28.0 ± 22 (μg km-vehicle^{-1}) on average, which are in the ranges of 22.0 to 354.2 and 71.1 ± 15 and 43.11 ± 15 (μg km-vehicle^{-1}) found in tunnels in Hongkong, Portugal, and China, respectively (Ho *et al.*, 2009; Alves *et al.*, 2016; and Fang *et al.*, 2018).

4 CONCLUSIONS

This study investigated the characteristics of $PM_{2.5}$ and 25 PAHs on $PM_{2.5}$ emitted from vehicles in different time frames via air sampling conducted in a tunnel located in northern Taiwan. The emissions of $PM_{2.5}$ and P-PAHs depended on the size and composition of the fleet. Generally, higher concentration differences of $PM_{2.5}$ and P-PAHs were found on weekday compared with that on weekend due to the higher number of diesel vehicles. Furthermore, the concentration differences of these pollutants were higher in the daytime compared with that in the nighttime because of the larger fleet size in daytime. In terms of mass concentration, 4-ring PAHs (Pyr and

Table 2. The emission factors of particulate PAHs measured in the tunnel investigated.

μg km-vehicle^{-1}	Weekday	Weekend	Daytime	Nighttime
AcPy	0.269	0.069	0.160	0.230
Acp	0.0296	0.00760	0.0194	0.0195
Flu	0.165	0.065	0.118	0.154
PA	2.19	0.660	1.16	2.16
Ant	0.679	0.183	0.376	0.644
FL	4.66	1.70	1.97	5.00
Pyr	7.40	3.06	3.12	7.99
BcFE	1.49	0.26	0.62	1.40
BaA	1.93	1.09	1.42	1.85
CYC	1.70	0.752	1.24	1.70
CHR	1.94	0.550	1.44	1.66
5-MC	0.129	0.053	0.0772	0.122
BbF	1.06	0.576	1.08	0.796
BkF	0.882	0.541	0.930	0.630
BjF	0.685	0.424	0.685	0.491
BaP	1.40	0.508	1.58	0.879
BeP	1.23	1.07	1.42	0.823
PER	0.286	0.147	0.328	0.186
DBA	0.0678	0.0440	0.0970	0.0370
IND	0.894	0.734	1.37	0.414
BghiP	1.86	1.21	2.34	1.11
DBalP	0.0683	0.0696	0.0884	0.0257
DBP	0.0818	0.140	0.129	0.0416
DBaiP	0.0136	0.00241	0.0289	0.00131
DBahP	n.a.	n.a.	n.a.	n.a.
Total	**31.1**	**13.9**	**21.8**	**28.4**

n.a.: not available.

PL) were the dominant contributors in all samples; however, another 4-ring PAHs (BcFE) was the major contributor to total TEQ concentration due to its high toxic equivalence. On the other hand, the predominant contribution of 15 EU-PAHs indicates that they should be included for the evaluation of the health risk associated with PAHs emission. The diagnostic ratios reveal that the source of P-PAHs collected was closer to emission of diesel vehicles, which is consistent with the higher emission factor of diesel vehicles compared with gasoline vehicles. The EF of $PM_{2.5}$ was lower than those reported in previous studies, while the EF of P-PAHs was within the range of those reported worldwide.

As indicated in this study, different characteristics of PM and particulate PAHs emitted from vehicles passing through this tunnel in different time frames were attributed from different fleet compositions and number of vehicles in different time frames. To the best of our knowledge, this study is the first investigation including 15 EU-PAHs emitted from vehicles via tunnel sampling and the results obtained suggest that these PAHs are important to be taken into account as the risk of PAHs is assessed. Benzo[c]fluorine was found as the main contributor to total TEQ concentration of particulate PAHs emitted from vehicles. Therefore, this study could provide useful insights for future research regarding the emission characteristics of PAHs from mobile sources.

This study only investigated the particulate PAHs emitted from two types of vehicle based on fuels used (diesel and gasoline) in a tunnel in different time frames. Therefore, it is suggested that future studies should investigate emission characteristics of PAHs from different kinds of vehicles based on powers. The gas-phase PAHs normally are the main contributors to total PAHs emitted from vehicles, which should be included in the next investigation. Furthermore, the emission of 15-EU PAHs should be characterized for not only mobile sources but also stationary sources because of their highly adverse effects to human health and environment.

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SUPPLEMENTARY MATERIAL

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