



# Assessment of PM<sub>2.5</sub> and PAH content in PM<sub>2.5</sub> emitted from mobile source gasoline-fueled vehicles in concomitant with the vehicle model and mileages

Yuan-Chung Lin<sup>a, b, c, d, \*</sup>, Ya-Ching Li<sup>a</sup>, Sumarlin Shangdiar<sup>a</sup>, Feng-Chih Chou<sup>a</sup>, Yih-Terng Sheu<sup>a</sup>, Pei-Cheng Cheng<sup>a</sup>

<sup>a</sup> Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, 804, Taiwan

<sup>b</sup> Center for Emerging Contaminants Research, National Sun Yat-Sen University, Kaohsiung, 804, Taiwan

<sup>c</sup> Research Center for Environmental Medicine, Kaohsiung Medical University, Kaohsiung, 807, Taiwan

<sup>d</sup> Ph.D. Program in Toxicology, College of Pharmacy, Kaohsiung Medical University, Kaohsiung, 807, Taiwan

## HIGHLIGHTS

- Emission from vehicles is one of the most important sources of PAHs.
- 21 gasoline-fueled vehicles were characterized and determined.
- Total PAHs content was attained from the sum of 21 PAHs compounds.
- The average concentration of total PAHs discharged was 0.377ng/L-fuel.

## ARTICLE INFO

### Article history:

Received 12 December 2018

Received in revised form

16 March 2019

Accepted 20 March 2019

Available online 30 March 2019

Handling Editor: R Ebinghaus

### Keywords:

PM<sub>2.5</sub>

Gasoline vehicles

PAHs

Toxic

## ABSTRACT

This study investigates the PM<sub>2.5</sub> emission and analyses the PAHs content in PM<sub>2.5</sub> emitted from gasoline-fueled vehicles. Outflow from the vehicles appear to be the ultimate source of PAHs in metro urban communities since the emission from gasoline vehicle increases the wellbeing hazard due to contiguity of exposure to gasoline exhaust. In this study, fifteen vehicles were randomly taken for sampling, where sixteen priority PAHs concentration were investigated. The study was performed on the vehicles with different Euro standard emission by taking into consideration the European legislative levels for vehicles on the toxic gaseous emission. Among all the PAHs outflow components of PM<sub>2.5</sub> radiated in the exhaust of gasoline engines, the average concentration of total PAHs discharged was 0.377ng/L-fuel, while the total BaP<sub>eq</sub> concentration was 0.00993ng/L-fuel.

© 2019 Elsevier Ltd. All rights reserved.

## 1. Introduction

The exhaust gas emitted from the on-road vehicles are recognized as one of the main causes of air pollution in many cities in the world. With expansion in the number of vehicles, movement stream increases the volume of pollutant emissions into the atmosphere. The core pollutants emitted are predominantly hydrocarbon (HC), nitrogen oxides (NOx), carbon monoxide (CO), Volatile

\* Corresponding author. Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, 804, Taiwan.

E-mail address: [yclin@faculty.nsysu.edu.tw](mailto:yclin@faculty.nsysu.edu.tw) (Y.-C. Lin).

organic carbon (VOC), aerosols (PM<sub>2.5</sub>) and Polycyclic aromatic hydrocarbons (PAHs) (Überall et al., 2015; Tsai et al., 2010; Lin et al., 2006a). Fine particles with diameter less than 2.5 μm (PM<sub>2.5</sub>) cause remarkable damage to human wellbeing, progressively entering the respiratory system, deposited in lungs and infiltrate through lung cells into the circulation system (Muñoz et al., 2018; Libalova et al., 2018). PAHs (Polycyclic aromatic hydrocarbons) are pervasive, semi volatile and highly carcinogenic organic pollutants in nature causing metabolic activation and genetic mutation in both humans and animals. VOCs and NOx discharged by means of transportation contributed in the formation of secondary pollutants such as photochemical smog.

PAHs emission occurs predominantly in areas where populace densities are considerably higher than that of the global average (Ma et al., 2018; Yinhui et al., 2016). Despite the fact that emissions have been diminished over the past decades with the advancement of elective engines and modification in vehicle exhaust treatment, the number of vehicle ceaselessly increases and the toxic emission related with the exposure to vehicle engine discharge regularly muddled by different composition of the fuel exhaust. An advanced gasoline engine with three-way catalyst system fitted to the vehicles initially tends to control the emission of PM<sub>2.5</sub>, CO and NO<sub>x</sub> (Ahmed et al., 2018). The catalyst typically comprises of Platinum, Palladium, or Rhodium either separately or in blend. The studies conducted by Zhang and Tao in 2009 shows that contribution of engine vehicles to PAH discharge is much more than that of biomass burning and wildfire (Samburova et al., 2016; Zhang and Tao., 2009). In this manner, PAH from engine vehicles are at substantially higher hazard to human exposure than that contribution to emission itself. The emissions emitted from the vehicles and off-way transportation contains fine suspended particles, therefore the contribution rate of mobile originated source cannot be overlooked. According to the European Union, the air pollutant emission from vehicle transport is a significant contribution to the overall state of air quality in Europe. Therefore, the main aim of Euro emission standard is mainly to reduce the exhaust of harmful gases such as NO<sub>x</sub>, CO, HC, and Particulate matter. The emission from the gasoline vehicles was found to be reduced according to the Euro legislative level. (Tsai et al., 2010; Zheng et al., 2017b; Pei et al., 2014).

The emission regulations for total hydrocarbon comprise of a broad range from basic atomic weight compound, to high sub-atomic weight polycyclic aromatic hydrocarbons (PAHs). Numerous PAHs have a boiling point of 200–300 °C and the area sufficiently volatile to exist predominantly in the gas phase at temperatures above 200 °C. PAHs generated from coal, crude oil and gasoline binds to form small particles in the air, hence, they are mostly identified in automotive fuel emissions and the range of specific analytical structures used at different laboratories varies greatly (Zheng et al., 2017a; Ren et al., 2017). PAHs are widespread environmental pollutants and the actual threat from PAHs depends on the loading rate that remains in the environmental tenacity (Greenfield and Davis, 2005). Indoor PAHs exist for two or three rings contribute mainly by the outdoor PAHs (Environmental Protection Administration, 2017; Baek et al., 1991). The major impact for outdoor PAHs in urban areas is mainly from the commuter traffic which plays as the main source of contribution to PAHs emission. The contribution from gasoline and diesel engine are predominant, however, most of the studies principally focused on the emission from diesel vehicles while emission from gasoline vehicles are rarely addressed. The study conducted by Cao et al. (2017) in China illustrated that, PAHs emitted from vehicles accounted for about 86.0% of gasoline emission, whereby diesel engines are widely used in heavy duty vehicles because of higher fuel efficiency. The emission from diesel vehicles contains carcinogenic compounds such as carbonyl compounds and particulate matter. Nevertheless, studies shows that fuel blends can help to reduce the toxic emission from diesel engine under steady condition. Additionally, Yang et al. (2017) shows that diesel blending with butanol could be an alternative fuel for diesel engines, reducing the emission of PM<sub>10</sub> and PM<sub>2.5</sub> by 59.4%–57.7%.

In this study, 16 PAHs listed in US EPA priority pollutants were taken into consideration as a distinctive example (U.S Environmental protection Agency, 1998). PAHs from vehicular exhaust present in respirable ranges are of specific concern due to their higher intake fraction than that of other fuel emanation zones. PAHs are of great alarm to the environment because of its horrendous widespread combined with high toxicity, mutagenicity

and carcinogenic health effects (Zheng et al., 2017a; Shen et al., 2013; Zhang and Tao, 2009). Considerable amount of airborne PAHs are expected to present in the accumulation mode of the particles with large specific surface area. The main objective of this study is to investigate the concentration of PAH in PM<sub>2.5</sub> emission from mobile source gasoline-fueled vehicles by taking into consideration the model year and various mileages of the vehicle. This study intends to explore the status of pollutant emissions from gasoline vehicles traveling in Kaohsiung city, located in the South-Western part of Taiwan, by estimating the emission factors and emission of pollutant sources through testing data and establishing a pollution discharge inventory to clarify the sources of mobile pollution contributed in Kaohsiung city.

## 2. Experimental section

### 2.1. Details of gasoline vehicles and test procedures

In this study, a number of test conditions recorded include the vehicle type, manufacturing year, Displacement (c.c), and total kilometers as shown in Table 1. Three vehicles were tested for Euro 3 and Euro 4, five vehicles for Euro 5, and four vehicles for Euro 6. Each vehicle was sampled for PM<sub>2.5</sub> emissions and PAHs content in PM<sub>2.5</sub> from the exhausts of gasoline vehicles.

The schematic diagram of the gasoline vehicle and the experimental set up is shown in Fig. 1. The gaseous contamination discharge from the tail pipe exhaust was observed online by using a transferable gaseous pollutant analyzer (Telegan Sprint V4). Analysing of pollutants such as NO<sub>x</sub> and CO was evaluated by using different detection equipment; NO<sub>x</sub> was analyzed by using a chemiluminescent detection (CLD) (model 404, Rosemount, UK) and CO was sensed by using a nondispersive infrared detector (NDIR) (model 880A, Rosemount, UK). Each filtered particulate matter was weighed and calibrated by utilizing an electronic systematic adjustment with complete programmed alignment innovation (AT200, Mettler, Switzerland), keeping in mind the target to determine the net mass of gathered particulate matter (Yang et al., 2015., Tsai et al., 2014; Lin et al., 2006a).

### 2.2. Test analysis

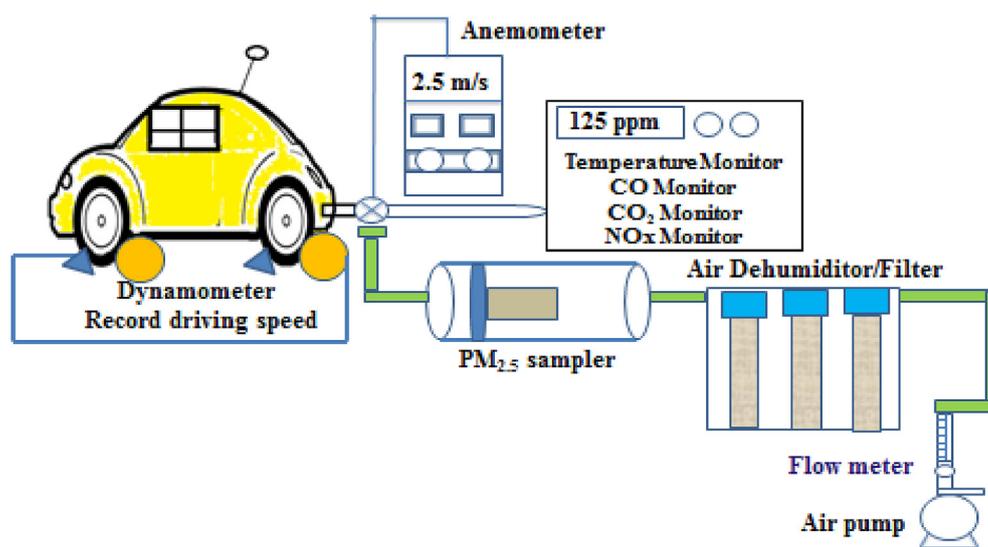
#### 2.2.1. PAH analysis

For analyzing PAH, the sample was separated in a Soxhlet extractor with a blended dissolvable (n-hexane and dichloromethane; vol/vol, 1:1; 500 ml each) for 24 h. The PAH substance was regulate by HP gas chromatograph (GC) (HP 5890A; Hewlett-Packard, Wilmington, DE, USA), a mass selective detector (MSD) (HP 5972), and a PC workstation (Aspire C500; Acer, Taipei, Taiwan). The extract was concentrated and cleaned up by utilizing a silica segment loaded with silica gel particles positioned under a layer of Na<sub>2</sub>SO<sub>4</sub> and specifically reconcentrated with ultra-pure nitrogen to precisely 0.2 mL for GC/MS analysis. The scientific technique for GC/MS was practically identical with those found in our previous studies (Yang et al., 2017; Tsai et al., 2010; Lin et al., 2006a, 2006b).

In this study, 21 PAHs were analyzed as per the sub-atomic weight of the compound. The PAHs were subdivided into three sets; LMW-PAH (Lower molecular weight-Polycyclic aromatic hydrocarbon), MMW-PAH (Medium molecular weight-Polycyclic aromatic hydrocarbon), and HMW-PAH (High molecular weight-Polycyclic aromatic hydrocarbon). The LMW-PAHs include (Nap), (AcPy), (Acp), (Flu), (PA), and (Ant) while the MMW-PAHs were (FL), (Pyr), (BaA), and (CHR). The HMW-PAHs were the groups of (CYC), (BbF), (BkF), (BeP), (BaP), (PER), (DBA), (BbC), (IND), (Bghip), and (COR). The total PAH data for fuel exhaust is given by the sum of 21

**Table 1**  
Details of gasoline fueled vehicles tested for PM<sub>2.5</sub> emissions and PAHs content in PM<sub>2.5</sub>.

No. of vehicles	Brand	Year	Displacement (c.c)	Total Kilometers (Km)
1	TOYOTA	2004	1998	11,266
2	TOYOTA	2004	1798	143,331
3	SUZUKI	2004	1328	155,779
4	TOYOTA	2012	1798	9488
5	TOYOTA	2004	1497	130,713
6	NISSAN	2015	1598	26,984
7	TOYOTA	2014	1987	157,148
8	MITBISHI	2000	2378	46,932
9	TOYOTA	2004	1998	130,304
1	TOYOTA	2016	1978	23,683
11	TOYOTA	2006	1496	102,286
12	CMC Motor	2009	1998	998,857
13	TOYOTA	2010	1978	144,008
14	TOYOTA	2014	1987	194,229
15	TOYOTA	2014	1987	38,447



**Fig. 1.** Schematic diagram of the experimental set up.

individual PAHs.

Impeccable quality assurance and control measures were firmly maintained during the experiment. Field control blanks including both the field and laboratory blanks were analyzed to determine the concentration of PAHs. The GC/MSD was adjusted with diluted standard solutions of 16 PAHs with five additional individual PAHs obtained from Merck (Darmstadt, Germany). The limit of detection (LOD) of 16 PAHs is shown in Table S1. An in-depth information on the GC/MSD activity, PAH measurement, QA/QC, and technique recognition breaking points can be discovered elsewhere in the reference (Lin et al., 2006a, 2006b, 2008., Lin et al., 2008; Zhang and Tao, 2009). Keeping in view retaining the quality of sampling system, the isokinetic sampling procedure was adopted, where the particle phase PAHs was collected by utilizing an examining framework from the tailpipe exhaust of gasoline powered engines on a quartz fiber filter. Furthermore, two internal standards were utilized to check the reaction factor, to determine the final concentration and the recovery efficiencies for PAH analysis. According to the test results, recovery efficiencies for 21 PAHs compound vary from 83.5 to 96.1% with an average value of 94.73%. Analysis of field blank and glass fiber filter revealed no substantial contamination.

### 2.3. Data analysis

The total PAHs content for each sample was attained from the

sum of 21 PAHs compounds. Additionally, the PAH homolog dissemination was analyzed for 21-PAHs and various atomic weight PAHs. Considering the fact that PAHs compound are human carcinogens, the carcinogenic impact of discharged PAHs compound were determined based on benzo[a]pyrene concentration (BaP<sub>eq</sub>) by using TEF (Toxic Equivalent Factor) of a PAHs compound to ascertain its BaP<sub>eq</sub> concentration (Ren et al., 2017; Samburova et al., 2017; Liu et al., 2015; Baek et al., 1991). TEF represents the comparative carcinogenic strength of a given PAHs compound utilizing benzo[a]pyrene as a perspective compound to regulate with its unique concentration. In this study, TEFs detailed by Nisbet and LaGoy was adopted (Huang et al., 2019; An et al., 2016; Yang et al., 2015; Nisbet and LaGoy, 1992). Likewise, the carcinogenic intensity of total PAHs (i.e. total BaP<sub>eq</sub>) was evaluated by summing up the BaP<sub>eq</sub> concentration assessed for each PAHs compound compared with the TEF in the total PAHs.

## 3. Result and discussion

### 3.1. Emission concentration and emission factors for CO and NO<sub>x</sub> compound

The emission concentration emitted from gasoline engines were recorded at the range of 17.5–233 (ppm) for CO and 1.26–20.0 (ppm) for NO<sub>x</sub> as shown in Table 2. The product of complete

**Table 2**  
Concentration of CO and NOx emitted from Vehicle (ppm).

Compounds	Range	Mean	SD	RSD (%)
CO	17.5–233	116	65.1	56.3
NOx	1.26–20.0	9.34	5.02	53.7

combustion of gasoline are carbon dioxide and water; however, gasoline engines are affected by many factors, therefore, combustion from gasoline engine are not completely turned into carbon dioxide and water during the combustion process. These factors include the external temperature, fuel atomization, air-fuel ratio and engine load. The harmful components in the exhaust of gasoline engine are mainly CO, HC, NOx and PAHs (Yinhui et al., 2016; An et al., 2016; Zhu et al., 2016). With respect to different combustion methods and conditions, PAHs have their own unique emission characteristics, that is, different emission sources have their own unique PAHs profile, where some PAHs have been identified as mutagenic and carcinogenic PAHs (Zheng et al., 2017a; Shen et al., 2013; Zhang and Tao, 2009).

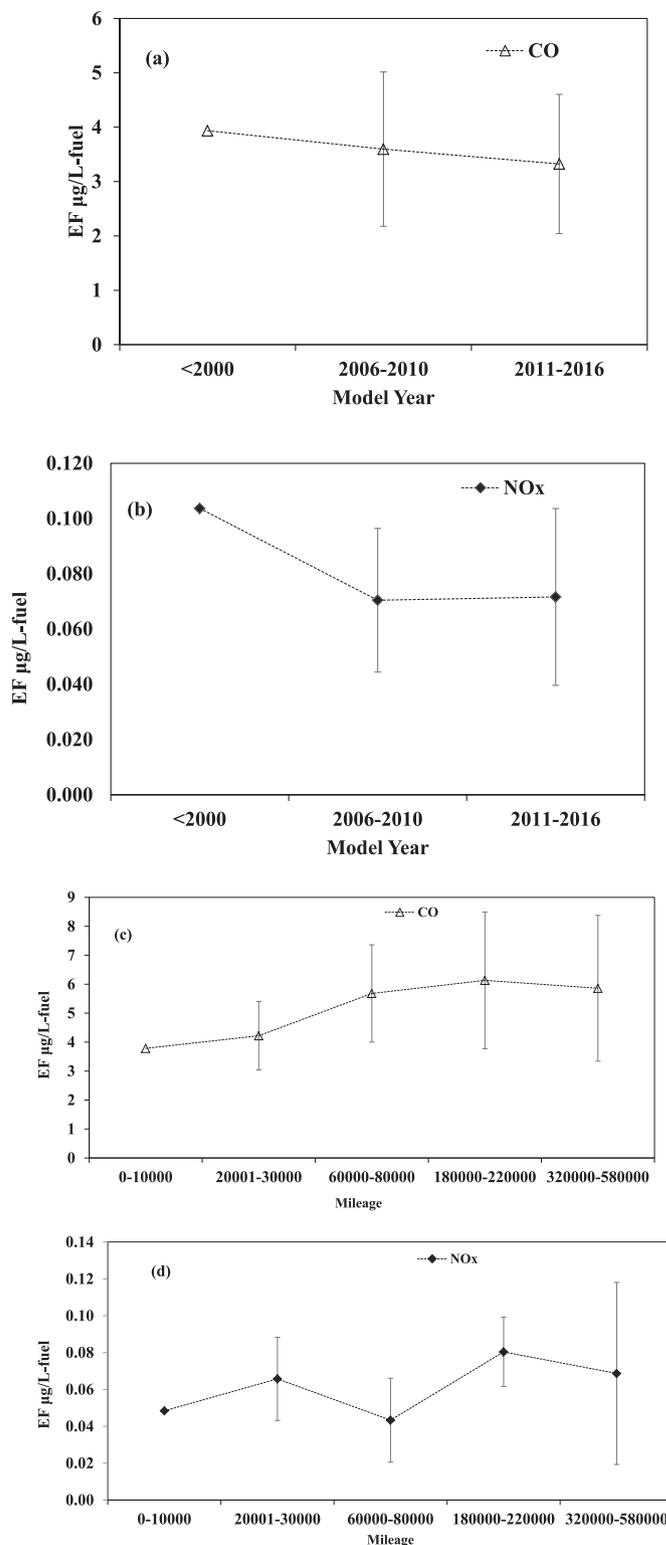
The emission factors (EFs) of CO and NOx emitted from gasoline vehicles with respect to the model year and various mileages is shown in Fig. 2. According to the figure, low cumulative mileages (mileage < 10,000 km) emits less CO and NOx emission factors, however, the mileage with the range higher than 20,000 km shows an increasing trend. It was also observed that CO tends to increase with an increasing vehicle mileage, but on the contrary NOx emission tends to decrease with certain mileage range in the newly modified vehicle as a result of advanced development of the catalyst that are fitted in the vehicle. The emission factor in the exhaust of gasoline vehicle for CO and NOx was derived from PM<sub>2.5</sub> measurements of NOx and CO concentrations. The CO and NOx emission factor from the exhaust of gasoline engines were recorded at the range of 0.412–4.75 for CO, and 0.256–0.779 for NOx emissions respectively. As per the study conducted, the emission factors resulting from 15 gasoline-fueled vehicles is in accordance with the study conducted by Pierson and Brachaczek (1982) and Pierson et al., (1996) (Fang et al., 2018; Pierson et al., 1996; Pierson and Brachaczek, 1982).

### 3.1.1. PM<sub>2.5</sub> concentration and emission factor

In this study, the concentration of PM<sub>2.5</sub> emitted from gasoline engines ( $\mu\text{g}/\text{m}^3$ ) were at the range of 361–1020  $\mu\text{g}/\text{m}^3$ . The emission factor corresponding with the model year and vehicle mileages are shown in Fig. 3. The emission factor of PM<sub>2.5</sub> in the exhaust of 15 gasoline engines were found at the range of 0.814–2.26  $\mu\text{g}/\text{L-fuel}$ . It is known that the concentration of PM<sub>2.5</sub> and the emission factor emitted from vehicle exhaust could be affected by numerous factors such as, vehicle type (Muñoz et al., 2018, Shen et al., 2013b), fuel quality [41, 42], displayed year of the vehicles (Menichini et al., 2006), vehicle speed (Zheng et al., 2017b) and the features of the road (Libalova et al., 2018). According to the results obtained, it is noted that PM<sub>2.5</sub> emitted from the gasoline vehicle tends to increase with the increasing mileage of the vehicle but shows recover with the progression of the model year. Hence, PM<sub>2.5</sub> emission factor can be reduced with the emission control strategies of air pollutant for transport vehicles constraining the discharge estimation of a wide range of vehicle. Therefore, the control of new model vehicles with more stringent emission standard creates the new car with low pollution emission to gradually replace the old car with high pollution emission.

### 3.1.2. Soluble Organic Fraction (SOF) emission

The contents of SOF in the exhausts of gasoline engines is



**Fig. 2.** CO, NOx emission factor with model year (a), (b) and various mileages (c), (d).

recorded at the range of 6.34–53.9% with 37.2%. The relative substance of Soluble Organic Fraction (SOF) in PM<sub>2.5</sub> has a diminishing propensity with expanding load, whereas the relative substance of diversified Insoluble Fraction (ISF) has an expanding inclination with diminishing load. When the engine activates at lower loads, the excess PM, SOF, and ISF at idle speed air coefficient has higher

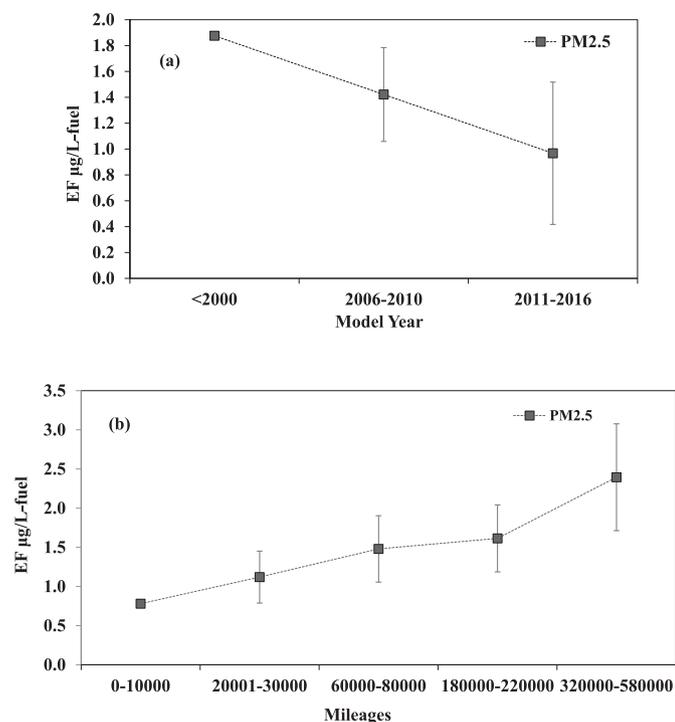


Fig. 3. PM<sub>2.5</sub> emission factor with model year (a) and various mileages (b).

esteem and the temperature in the burning chamber is lower, consequently, the concoction response rate is lower (Ahmed et al., 2018; Fang et al., 2018; Muñoz et al., 2018). Hence, the emission of soluble organic particles and PAHs increases with the decreasing loads.

### 3.2. PAH content in PM<sub>2.5</sub>

The total evaluated particle bound PAHs content ( $\Sigma$ PAHs) produced from the test vehicles were in the order of LMW-PAHs > MMW-PAHs > HMW-PAHs as shown in Table 3. The overall PAHs content of PM<sub>2.5</sub> emitted from gasoline engines ( $\text{ng/m}^3$ ) and the average concentrations of total-PAHs emitted was  $206 \text{ ng/m}^3$  whereas the total-BaPeq concentrations emitted was  $5.37 \text{ ng/m}^3$ .

The masses and quantification of PAHs ion was detected by scanning and selective ion monitoring (SIM) system according to their elution orders. The 21 PAHs quantified in SIM mode are as follows: naphthalene (Nap = 42.9%), acenaphthylene (Ace = 44.2%), acenaphthene (Acen = 57.7%), fluorene (Flu = 52.3%), phenanthrene (Phen = 33.8%), anthracene (An = 57.0%), fluoranthene (Fluo = 48.6%), pyrene (Pyr = 58.8%), benzo(a)anthracene (BaA = 49.9%), chrysene (Chry = 48.9%), benzo(b)fluoranthene (BbF = 50.5%), benzo(k)fluoranthene (BkF = 57.9%), benzo (a) pyrene (BaP = 58.3%), benzo[e]pyrene (BeP = 42.4%), cyclopenta[cd]pyrene (CYC = 55.4%), indeno(1,2,3,-cd)pyrene (Indeo = 276), dibenzo(a,h)anthracene (DiBa = 59.9%), perylene (PER = 52.7%), indeno[1,2,3,-cd]pyrene (IND = 59.2%), benzo[b]chrycene (BbC = 51.1%), benzo[ghi]perylene (Bghip = 57.1%), and coronene (COR = 47.3%).

### 3.3. Emission factor of PAH in PM<sub>2.5</sub> concentration

The emission factors of 21 PAHs in the exhausts of gasoline engines ( $\text{ng/L-fuel}$ ) were categorized and the emission factors of PM<sub>2.5</sub> and total particle-bound PAH concentrations ( $\Sigma$ PAHs) were

Table 3  
PAHs content of PM<sub>2.5</sub> emitted from gasoline engines ( $\text{ng/m}^3$ ).

Compounds	Mean	SD	RSD (%)
Nap	60.2	25.0	42.9
AcPy	3.17	1.35	44.2
Acp	3.39	2.69	57.7
Flu	9.77	7.33	52.3
PA	54.8	28.7	33.8
Ant	10.2	7.18	57.0
FL	18.8	10.4	48.6
Pyr	13.9	11.2	58.8
BaA	2.20	1.61	49.9
CHR	2.64	1.68	48.9
BbF	2.66	1.96	50.5
BkF	3.16	1.77	57.9
BaP	2.64	2.86	58.3
BeP	1.76	1.92	42.4
CYC	1.70	1.49	55.4
DBA	1.56	1.70	59.9
PER	2.05	1.42	52.7
IND	2.29	0.939	59.2
BbC	2.60	2.44	51.1
BghiP	3.33	1.68	57.1
COR	2.78	1.27	47.3
$\Sigma$ LMW	141	34.2	41.3
$\Sigma$ MMW	38.0	13.8	52.7
$\Sigma$ HMW	26.1	12.7	54.2
Total PAHs	206	42.4	
Total-BaPeq	5.37	2.70	

quantified as shown in Table 4. The PAHs emitted were mostly LMW-PAHs with the total of 0.254, followed by some MMW-PAHs with 0.0661 and HMW-PAHs with 0.0574. Gasoline vehicle shows higher fraction of medium and high molecular weight p-PAHs in compare to diesel vehicles (Zheng et al., 2018). Recently, the study conducted by Hao et al. (2018), on the on-road emissions of gasoline vehicles in Beijing with different emission standard, shows that an improved emission standard reduces the impact of PAHs and NPAHs (nitro- Polycyclic Aromatic Hydrocarbon) (Hao et al., 2018), whereby the emission factor were mostly detected in non-highway

Table 4  
PAHs emission factor of PM<sub>2.5</sub> in the exhaust of gasoline engines ( $\text{ng/L-fuel}$ ).

Compounds	Mean	SD	RSD (%)
Nap	0.111	0.0752	53.3
AcPy	0.00592	0.00422	47.6
Acp	0.00532	0.00389	37.2
Flu	0.0135	0.0126	51.8
PA	0.103	0.0765	51.5
Ant	0.0145	0.0131	48.3
FL	0.0350	0.0198	48.4
Pyr	0.0198	0.0209	37.6
BaA	0.00502	0.00258	53.2
CHR	0.00582	0.00258	46.0
BbF	0.00546	0.00570	53.6
BkF	0.00498	0.00514	51.8
BaP	0.00527	0.00558	55.2
BeP	0.0131	0.03987	43.7
CYC	0.00256	0.00320	47.7
DBA	0.00207	0.00243	40.1
PER	0.00326	0.00233	50.4
IND	0.00487	0.00206	36.5
BbC	0.00349	0.00397	52.9
BghiP	0.00697	0.00356	48.0
COR	0.00584	0.00322	57.0
$\Sigma$ LMW	0.254	0.142	54.8
$\Sigma$ MMW	0.0661	0.0318	43.9
$\Sigma$ HMW	0.0574	0.0559	50.1
Total PAHs	0.377	0.157	
Total-BaPeq	0.00993	0.00579	

roads than in highway roads because of the incomplete combustion. In addition, [Hao et al., 2018](#), stated that the emission factor of CO, HC, and PM<sub>2.5</sub> for diesel engines shows a decreasing trend with the improved stringency of the emission standard for the on-road vehicles though; the emission standard did not include the regulation standard for PAHs and NPAHs ([Cao et al., 2017](#)).

Taking into consideration the model year and mileages of the vehicle as shown in [Fig. 4](#), it can be illustrated that the PAHs emission factor tends to decrease with the increase in model year of the vehicle which results from the high combustion efficiency of the newly fitted catalyst. PAHs from mobile sources are mainly contributed from medium and high sub-atomic weight PAHs with higher average toxicity. In addition, it is predictable that the LMW-PAHs are connected with diesel engines, while the HMW-PAHs are related with gasoline engine emissions ([Hergueta et al., 2017](#); [Zheng et al., 2017a](#); [An et al., 2016](#); [Yinhui et al., 2016](#); [Überall et al., 2015](#)). The study conducted by [Huang et al., 2019](#), [Ren et al. \(2017\)](#), [Lin et al. \(2008\)](#), [Lin et al. \(2006a\)](#), [Baek et al. \(1991\)](#), stated that emissions of PAHs usually start from three distinct mechanisms, specifically, blending from less complex atoms in the fuel predominantly from aromatic compounds, storage in engine deposits, resultant outflow of PAHs effectively exhibit in the fuel and pyrolysis of lubricant.

### 3.4. PAH contribution from gasoline vehicles

PAHs homolog grouped by the quantity of ring contributed from the test vehicle sampled is shown in [Fig. 5](#). The average sums of 21 PAHs highlighted in the histogram shows that the driving cycle and regulations made by the European legislative level for vehicles has brought about a drastic changes in the vehicle emissions where the toxic exhaust from the vehicle lessens in Euro 5 and Euro 6 according to the emission standard for the passenger cars in compare with that of Euro 3 and Euro 4 vehicles. Conversely, Euro 5 shows an increasing trend in PAHs with ring 3 and 5 in the test gasoline vehicle which is considered to be affected by the factors such as an

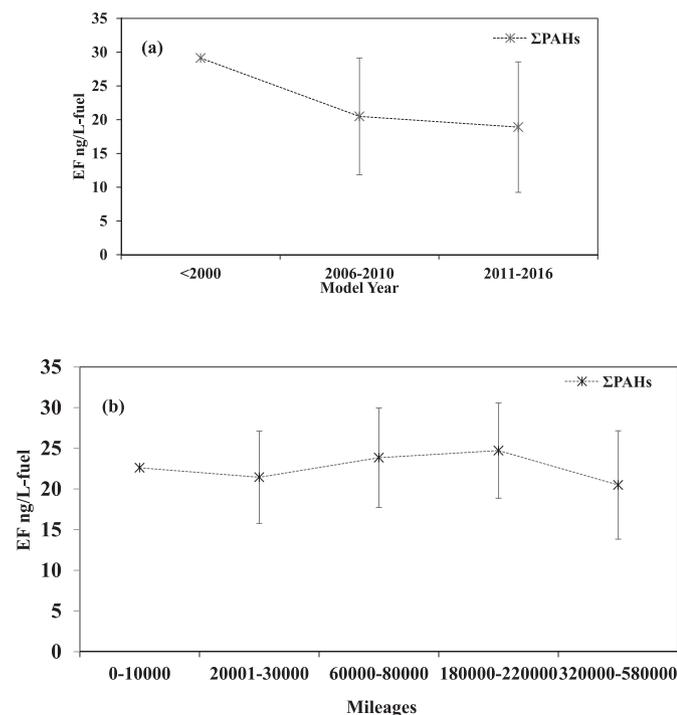


Fig. 4. PAHs emission factor with model year (a) and various mileages (b).

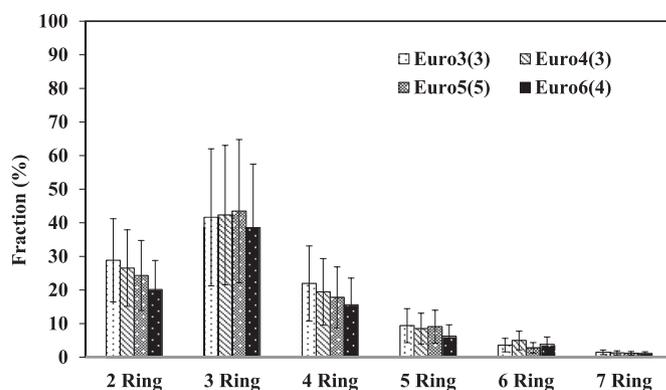


Fig. 5. PAHs (ring-wise) contribution (%) of PM<sub>2.5</sub> emitted from gasoline Vehicle.

environmental conditions, temperature, road surface and the vehicle maintenance of the users.

The detailed contribution of 21 PAHs compound studied is outlined in [Fig. S1](#). Lower molecular weight PAHs with 2–3 ring include Nap, AcPy, Acp, Flu, PA and Ant accounted for about 66.6% of total PAHs contribution, Medium molecular weight PAHs with 4 ring include FL, Pyr, BaA and CHR accounting for 18.7% of total PAHs contribution, and Higher molecular weight PAHs with 5–7 ring include CYC, BbF, BkF, BeP, BaP, PER, DBA, BbC, IND, Bghip and COR accounting for 14.42% of total PAHs contribution ([Fang et al., 2018](#); [Samburova et al., 2016](#)). In reference ([Fang et al., 2018](#); [Chen et al., 2017](#); [Black et al., 2016](#); [Zhu et al., 2016](#); [Shen et al., 2013](#); [Tsai et al., 2010](#); [Lin et al., 2006a](#)), PAHs compound comprising of C and H component with chemical structures of at least two melded benzene ring in straight, angular, or cluster arrangement can be shaped in deficient ignition or high temperature pyrolytic procedures.

## 4. Conclusion

A comprehensive assessment of PM<sub>2.5</sub> emissions and PAHs concentration in PM<sub>2.5</sub> from the exhausts of 15 gasoline vehicles and chemical characterization of PM<sub>2.5</sub> conducted in Kaohsiung City of Taiwan, shows that the emission concentration (ppm) for CO and NO<sub>x</sub> emitted from the test vehicles accounted for about 56.3% and 53.7%, respectively. The study likewise uncovered that PM<sub>2.5</sub> emission factor of vehicles could be influenced by several features such as vehicle type, the nature of the fuel utilized, vehicle mileages, model year of the vehicles, vehicle driving speed and the features of the road. Therefore, results acquired can be seen as profitable information concerning the assessment of PM<sub>2.5</sub> discharges and PAHs content in PM<sub>2.5</sub> from the exhausts of gasoline engine vehicles. Subsequently, this study will help in establishing limits in the emission standard for vehicles in urban areas ambient air quality as well as limiting the exhaust emissions of many pollutants from road transport.

## Conflicts of interest

All contributing authors declare no conflicts of interest and the manuscript is approved by all the authors for publication.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.03.137>.

## References

- Ahmed, T.F., Bergvall, C., Westerholm, R., 2018. Emissions of particulate associated oxygenated and native polycyclic aromatic hydrocarbons from vehicles powered by ethanol/gasoline fuel blends. *Fuel* 214, 381–385.
- An, Y.Z., Teng, S.P., Pei, Y.Q., Qin, J., Li, X., Zhao, H., 2016. An experimental study of polycyclic aromatic hydrocarbons and soot emissions from a GDI engine fueled with commercial gasoline. *Fuel* 164, 160–171.
- Baek, S.O., Goldstone, M.E., Kirk, P.W.W., Lester, J.N., Perry, R., 1991. Phase distribution and particle size dependency of polycyclic aromatic hydrocarbons in the urban atmosphere. *Chemosphere* 22, 503–520.
- Black, R.R., Aurell, J., Holder, A., George, I.J., Gullett, B.K., Hays, M.D., Geron, C.D., Tabor, D., 2016. Characterization of gas and particle emissions from laboratory burns of peat. *Atmos. Environ.* 132, 49–57.
- Cao, X., Hao, X., Shen, X., Jiang, X., Wu, B., Yao, Z., 2017. Emission characteristics of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons from diesel trucks based on on-road measurements. *Atmos. Environ.* 148, 190–196.
- Chen, L., Liang, Z., Zhang, X., Shuai, S., 2017. Characterizing particulate matter emissions from GDI and PFI vehicles under transient and cold start conditions. *Fuel* 189, 131–140.
- Environmental Protection Administration, 2017. Environment Resource Database. Taiwan (ROC).
- Fang, X., Wu, L., Zhang, Q., Zhang, J., Wang, A., Zhang, Y., Zhao, J., Mao, H., 2018. Characteristics, emissions and source identifications of particle polycyclic aromatic hydrocarbons from traffic emissions using tunnel measurement. *Transport. Res. D Transport Environ.* (in press) <https://doi.org/10.1016/j.trd.2018.02.021>.
- Greenfield, B.K., Davis, J.A., 2005. A PAH fate model for san Francisco bay. *Chemosphere* 60 (4), 515–530.
- Hao, X., Zhang, X., Cao, X., Shen, X., Shi, J., Yao, Z., 2018. Characterization and carcinogenic risk assessment of polycyclic aromatic and nitro-polycyclic aromatic hydrocarbons in exhaust emission from gasoline passenger cars using on-road measurements in Beijing, China. *Sci. Total Environ.* 645, 347–355.
- Hergueta, C., Bogarra, M., Tsolakis, A., Essa, K., Herreros, J.M., 2017. Butanol-gasoline blend and exhaust gas recirculation, impact on GDI engine emissions. *Fuel* 208, 662–672.
- Huang, Y., Sun, X., Liu, M., Zhu, J., Yang, J., Du, W., Zhang, X., Gao, D., Qadeer, A., Xie, Y., Nie, N., 2019. A multimedia fugacity model to estimate the fate and transport of polycyclic aromatic hydrocarbons (PAHs) in a largely urbanized area, Shanghai, China. *Chemosphere* 217, 298–307.
- Libalova, H., Rossner, P., Vrbova, K., Brzicova, T., Sikorova, J., Vojtisek-lom, M., Beranek, V., Klema, J., Ciganek, M., Neca, J., Machala, M., Topinka, J., 2018. Transcriptional response to organic compounds from diverse gasoline and biogasoline fuel emissions in human lung cells. *Toxicol. Vitro* 48, 329–341.
- Lin, Y.C., Lee, W.J., Chen, C.B., 2006a. Characterization of Polycyclic Aromatic Hydrocarbons from the diesel engine by adding light cycle oil to premium diesel fuel. *J. Air Waste Manag. Assoc.* 56, 752–758.
- Lin, Y.C., Lee, W.J., Hou, H.C., 2006b. PAH emissions and energy efficiency of palm-biodiesel blends fueled on diesel generator. *Atmos. Environ.* 40, 3930–3940.
- Lin, Y.C., Tsai, C.-H., Yang, C.-R., Wu, C.H.J., Wu, T.-Y., Chang-Chien, G.-P., 2008. Effects on aerosol size distribution of polycyclic aromatic hydrocarbons from the heavy-duty diesel generator fueled with feedstock palm-biodiesel blends. *Atmos. Environ.* 42, 6679–6688.
- Liu, Y., Gao, N., Yu, N., Zhang, C., Wang, S., Ma, L., Zhao, J., Lohmann, R., 2015. Particulate matter, gaseous and particulate polycyclic aromatic hydrocarbons (PAHs) in an urban traffic tunnel of China: emission from on-road vehicles and gas-particle partitioning. *Chemosphere* 134, 52–59.
- Ma, W.L., Liu, L.Y., Jia, H.L., Yang, M., Li, Y.F., 2018. PAHs in Chinese atmosphere Part I: concentration, source and temperature dependence. *Atmos. Environ.* 173, 330–337.
- Menichini, E., Belladonna, V., Bergoglio, F., Gabrieli, C., Ceccanti, M., Rossi, I., Cellini, L., Corradetti, E., Grechi, D., Tricarico, V., Rosa, M., Zamello, C., Spiazzi, A., Stella, a., Valerio, F., Trevisani, G.R., Villalta, R., 2006. Trend of atmospheric benzo (a) pyrene in Italy before the adoption of the European directive on PAHs. *Polycycl. Aromat. Comp.* 26, 79–92.
- Muñoz, M., Haag, R., Honegger, P., Zeyer, K., Mohn, J., Cornte, P., Czerwinski, J., Heeb, N.V., 2018. Co-formation and co-release of genotoxic PAHs, alkyl-PAHs and soot nanoparticles from gasoline direct injection vehicles. *Atmos. Environ.* 178, 242–254.
- Nisbet, I.C.T., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharmacol.* 16, 290–300.
- Pei, Y., Qin, J., Pan, S., 2014. Experimental study on the particulate matter emission characteristics for a direct-injection gasoline engine. *Proc. Inst. Mech. Eng. - Part D J. Automob. Eng.* 228, 604–616.
- Pierson, W.R., Brachaczek, W.W., 1982. Particulate matter associated with vehicles on the Road. II. *Aerosol Sci. Technol.* 2, 1–40.
- Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinska, B., Bishop, G.A., Stedman, D.H., Zweidinger, R.B., William, D.R., 1996. Real-world automotive emissions-summary of studies in the fort McHenry and Tuscarora mountain tunnels. *Atmos. Environ.* 30 (21), 2233–2256.
- Ren, Y., Zhou, B., Tao, J., Cao, J., Zhang, Z., Wu, C., Wang, J., Li, J., Zhang, L., Han, Y., Liu, L., Cao, C., Wang, G., 2017. Composition and size distribution of airborne particulate PAHs and oxygenated PAHs in two Chinese megacities. *Atmos. Res.* 183, 322–330.
- Samburova, V., Connolly, J., Gyawali, M., Yatavelli, R.L.N., Watts, A.C., Chakrabarty, R.K., Zielinska, B., Moosmüller, H., Khlystov, A., 2016. Polycyclic aromatic hydrocarbons in biomass-burning emissions and their contribution to light absorption and aerosol toxicity. *Sci. Total Environ.* 568, 391–401.
- Samburova, V., Zielinska, B., Khlystov, A., 2017. Do 16 polycyclic aromatic hydrocarbons represent PAH air toxicity? *Toxics* 5, 17.
- Shen, H., Tao, S., Wang, R., Wang, B., Shen, G., Li, w., Su, S., Huang, Y., Wang, X., Liu, W., Li, B., Sun, K., 2013. Global time trends in PAH emissions from motor vehicles. *Atmos. Environ.* 45, 2067–2073.
- Tsai, J.H., Chen, S.J., Huang, K.L., Lin, Y.C., Lee, W.J., Lin, C.C., Lin, W.Y., 2010. PM, carbon, and PAH emissions from a diesel generator fuelled with soy-biodiesel blends. *J. Hazard Mater.* 179, 237–243.
- Tsai, J.-H., Chen, S.J., Huang, K.-L., Lin, W.-Y., Lee, Wen-J., Lin, C.-C., H L-T, Chiu, J.-Y., Kuo, W.-C., 2014. Emissions from a generator fueled by blends of diesel, biodiesel, acetone, and isopropyl alcohol: analyses of emitted PM, particulate carbon, and PAHs. *Sci. Total Environ.* 466–467, 195–202.
- U.S. Environmental Protection Agency, 1998. Locating and Estimating Air Emissions from Sources of Polycyclic Organic Matter. EPA, Washington, Dc.
- Überall, A., Otte, R., Eilts, P., Krahl, J., 2015. A literature research about particle emissions from engines with direct gasoline injection and the potential to reduce these emissions. *Fuel* 147, 203–207.
- Yang, P.M., Wang, C.C., Lin, Y.C., Jhang, S.R., Lin, L.J., Lin, Y.C., 2017. Development of novel alternative biodiesel fuels for reducing PM emissions and PM-related genotoxicity. *Environ. Res.* 156, 512–518.
- Yang, P.M., Lin, Y.C., Lin, K.C., Jhang, S.R., Chen, S.C., Wang, C.C., Lin, Y.C., 2015. Comparison of carbonyl compounds emissions from a diesel engine generator fueled with blends of n-butanol, biodiesel and diesel. *Energy* 90, 266–273.
- Yinhui, W., Rong, Z., Yanhong, Q., Jianfei, P., Mengren, L., Jianrong, L., Yusheng, W., Min, H., Shijin, S., 2016. The impact of fuel compositions on the particulate emissions of direct injection gasoline engine. *Fuel* 166, 543–552.
- Zhang, Y.X., Tao, S., 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmos. Environ.* 43, 812–819.
- Zheng, X., Wu, Y., Zhang, S., Hu, J., Zhang, K.M., Li, z., He, L., Hao, J., 2017a. Characterizing particulate polycyclic aromatic hydrocarbon emissions from diesel vehicles using a portable emissions measurement system. *Nat. Sci. Rep.* <https://doi.org/10.1038/s41598-017-09822-w>.
- Zheng, X., Zhang, S., Wu, Y., Zhang, K.M., Wu, X., Li, Z., 2017b. Characteristics of black carbon emissions from in-use light-duty passenger vehicles. *Environ. Pollut.* 231, 348–356.
- Zheng, X., Zhang, S., Wu, Y., Xu, G., Hu, J., He, L., Wu, X., Hao, J., 2018. Measurement of particulate polycyclic aromatic hydrocarbon emissions from gasoline light-duty passenger vehicles. *J. Clean. Prod.* 185, 797–804.
- Zhu, R., Hu, J., Bao, X., He, L., Lai, Y., Zu, L., Li, Y., Su, S., 2016. Tailpipe emissions from gasoline direct injection (GDI) and port fuel injection (PFI) vehicles at both low and high ambient temperatures. *Environ. Pollut.* 216, 223–234.