

# A Comparison on the Emission of Polycyclic Aromatic Hydrocarbons and Their Corresponding Carcinogenic Potencies from a Vehicle Engine Using Leaded and Lead-Free Gasoline

Hsiao-Hsuan Mi,<sup>1</sup> Wen-Jhy Lee,<sup>1</sup> Perng-Jy Tsai,<sup>2</sup> and Chung-Ban Chen<sup>3</sup>

<sup>1</sup>Department of Environmental Engineering, National Cheng Kung University, Tainan, Taiwan; <sup>2</sup>Department of Environmental and Occupational Health, Medical College, National Cheng Kung University, Tainan, Taiwan; <sup>3</sup>Heavy Duty Diesel Engine Emission Group, Refining and Manufacturing Center, Chinese Petroleum Corporation, Chia-Yi, Taiwan

Our objective in this study was to assess the effect of using two kinds of lead-free gasoline [including 92-lead-free gasoline (92-LFG) and 95-lead-free gasoline (95-LFG), rated according to their octane levels] to replace the use of premium leaded gasoline (PLG) on the emissions of polycyclic aromatic hydrocarbons (PAHs) and their corresponding benzo[*a*]pyrene equivalent (BaP<sub>eq</sub>) amounts from the gasoline-powered engine. The results show that the three gasoline fuels originally contained similar total PAHs and total BaP<sub>eq</sub> contents; however, we found significant differences in the engine exhausts in both contents. The above results suggest that PAHs originally contained in the gasoline fuel did not affect the PAH emissions in the engine exhausts. The emission factors of both total PAHs and total BaP<sub>eq</sub> obtained from the three gasoline fuels shared the same trend: 95-LFG > PLG > 92-LFG. The above result suggests that when PLG was replaced by 95-LFG, the emissions would increase in both total PAHs and total BaP<sub>eq</sub>, but when replaced by 92-LFG would lead to the decreased emissions of both contents. By taking emission factors and their corresponding annual gasoline consumption rates into account, we found that both total PAH and total BaP<sub>eq</sub> emissions increased from 1994 to 1999. However, the annual increasing rates in total BaP<sub>eq</sub> emissions were slightly higher than the corresponding increasing rates in total PAHs. **Key words:** benzo[*a*]pyrene equivalent concentration, engine exhaust, lead-free gasoline, polycyclic aromatic hydrocarbons, premium leaded gasoline. *Environ Health Perspect* 109:1285–1290 (2001). [Online 30 November 2001]

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The premium leaded gasoline (PLG) and two kinds of lead-free gasoline [including 92 lead-free gasoline (92-LFG) and 95 lead-free gasoline (95-LFG) so called for their octane levels] are the three major fuels currently used in Taiwan area for spark-ignition engine vehicles. Recently worldwide efforts to reduce the use of PLG are intended to lower lead emission into the atmosphere and eventually to reduce the lead level in human blood. In Taiwan, the annual PLG consumption rates decreased significantly from  $2,599 \times 10^6$  L/year in 1994 to  $944 \times 10^6$  L/year in 1999. On the other hand, the annual consumption rates of 92-LFG and 95-LFG increased significantly from  $1,321 \times 10^6$  L/year and  $3,485 \times 10^6$  L/year in 1994, to  $2,136 \times 10^6$  L/year and  $6,118 \times 10^6$  L/year in 1999, respectively (Table 1). As a result, one-ring aromatic hydrocarbon in LFG fuels were added to maintain the knock resistance of vehicle engine (1). An important question, therefore, is whether the use of LFG in replacing PLG will increase emissions of some toxic substances, such as polycyclic aromatic hydrocarbons (PAHs), from gasoline-fueled engines.

PAHs and their derivatives are associated with the incomplete combustion of organic material, arising partly from natural combustion, such as forest fires and volcanic eruptions; but most emissions arise from anthropogenic activities, such as the burning

of gasoline in motor vehicles (2–4). For gasoline-powered engines, the emission of PAHs occurs through many factors, including the chemical compositions of the fuels, the types of lubricant and fuel additives, and the engine's operating conditions (1,5–7). However, the emission of PAHs in the above studies was assessed on the basis of total PAH concentration, without taking the carcinogenic potency of each individual PAH compound into account. To date, the International Agency for Research on Cancer (IARC) has classified several PAH compounds into probable (2A) or possible (2B) human carcinogens (8). In principle, the carcinogenic potency of a given PAH compound can be assessed based on its benzo[*a*]pyrene equivalent concentration (BaP<sub>eq</sub>). Calculation of BaP<sub>eq</sub> concentration for a given PAH compound requires the use of its toxic equivalent factor (TEF)—which represents the relative carcinogenic potency of the given PAH compound by reference to the specific compound BaP—to adjust its original concentration. To date, only a few proposals for TEFs are available (9–11). Among them, the list of TEFs completed by Nisbet and LaGoy in 1992 (11) (Table 2) reflects well the actual state of knowledge on the toxic potency of each individual PAH compound (12). On the basis of this TEFs list, the carcinogenic potency of total PAHs

can be assessed by the sum of the BaP<sub>eq</sub> concentrations estimated for each PAH compound in total PAHs.

In this study we aimed first to assess the effect on PAH emissions when different types of LFG replaced PLG in a test gasoline-powered engine. Assuming that PAH compositions in the engine exhaust might be affected by the types of gasoline fuel used in the test engine, we further assessed total BaP<sub>eq</sub> concentrations in engine exhaust as a possible health risk. The results obtained from this study will enhance further examination of the appropriate type of LFG to replace PLG.

## Materials and Methods

**Engine and dynamometer system.** The gasoline-powered engine (nontalyst) used in this study was a Mazda E5 engine with an odometer reading of approximately 100,000 km. The test engine was a four-cylinder carburetor with the ignition order of 1-3-4-2, bore and stroke of  $77 \times 80$  mm<sup>2</sup>, swept volume of 1,490 cm<sup>3</sup>, power generation rate of 6.88 kW/1,500 rpm, and compression ratio of 9:1. The engine was installed and operated on a dynamometer (Model FE 60-100-150S; Borghi & Saveri Corp, Bologna, Italy). The engine was adjusted at the laboratory of the manufacturer before the first experiment was conducted. Before each set of experiments, both the lubricating oil and the oil filter were changed and the fuel tank was emptied. The tank was filled with 20 L fuel, and then the engine was conditioned by simulating a cruising distance of approximately 55 km at a speed of 110 km/hr (rotary speed 3,000 rpm). To eliminate the effect of the type of lubricant on the performance of the test engine, only one commercially available synthetic engine lubricating oil was used (Super-2170; Chinese Petroleum Co., Taipei, Taiwan) in this study. The rotary speeds of 1,000, 1,500, 2,100, and 3,000 rpm simulated the four specified operating conditions of idling and the three cruising speeds of 40

Address correspondence to P.-J. Tsai, Department of Environmental and Occupational Health, Medical College, National Cheng Kung University, 138 Sheng-Li Road, Tainan 70428, Taiwan. Telephone: +886-6-2353535/5806. Fax: +886-6-2752484. E-mail: pjtsai@mail.ncku.edu.tw

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km/hr, 80 km/hr, and 110 km/hr, respectively. Under these four operating conditions, the throttle opening fractions of the air valve were 0%, 20%, 30%, and 40%, the eddy currents on the dynamometer were 1.1, 2.6, 2.6, and 2.3 Amp, and the torques were 0.79, 4.44, 4.39, and 4.32 kg/m, respectively. We performed three runs of the experiment under each of the prescribed operating conditions.

**Gasoline fuels.** We tested three gasoline fuels currently used most often in Taiwan, including PLG, 92-LFG, and 95-LFG (Table 3). For each set of experiments, we determined the volume of gasoline fuel before and after the experiment to obtain the net amount of fuel consumed. Also, before each set of experiments was conducted, we collected three 10-mL gasoline samples for PAH analysis. The fuel consumption rates, inlet airflow rates, and exhaust gas flow rates obtained for each of the three gasoline fuels operated under each of the four specified operating conditions are shown in Table 4.

**PAH sampling system for engine exhaust.** Because PAHs contained in engine exhaust gases are semivolatile, measurements for both particle-phase and gas-phase PAHs were necessary. We used a PAH sampling system (PSS;

Bectech Group Ltd. Co., Taipei, Taiwan) to meet the above requirement. The PSS was equipped with a dilution pipe (internal diameter 30 cm) which was connected to the engine tail pipe, and from which the exhaust gas was drawn, diluted, cooled, and then collected. The dilution factor of pollutants in the dilution pipe was approximately 25. A pump was installed behind the flow meter to draw the gas sample from the dilution pipe. We used a sampling probe with a filter holder to collect particle-phase PAHs in the diluted exhaust. A cooling device was installed after the filter holder to ensure the temperature of gas was below 31°C to prevent the revolatilization of lower molecular-weight PAHs from the glass cartridge. The glass cartridge contained three sections, including a 5-cm polyurethane foam (PUF) plug, followed by 2.5 cm of XAD-2 resin, and finally supported by a 2.5-cm PUF plug. Silicon glue was used to seal and hold the two PUF plugs to prevent XAD-2 resin from leaking out during sampling. The PAH compounds collected by the glass cartridge comprised the gas-phase PAHs. In this study, the operational flow rates of the PSS were specified at 4.5–5.5 L/min.

Before sampling, we cleaned the glass fiber filter with distilled deionized water and *n*-hexane, and placed it in an oven at 450°C for 8 hr to burn off organic compounds that might have been contained in the filters. Finally, the glass fiber filter was stored in a prebaked glass box and wrapped with hexane-washed aluminum foil. The cartridge was first soaked in distilled water and methanol dichloromethane for 1 day and then soaked in *n*-hexane for 4 days. Then the glass cartridge was placed in a vacuum oven at 60°C for 2 hr to evaporate residual solvent.

Finally, the cartridge was wrapped by hexane-washed aluminum foil and stored in clean screw-capped jars with Teflon cap liners.

We performed breakthrough tests on a two-layer XAD-2 cartridge with the sequence PUF-1, XAD-2-1, PUF-2, XAD-2-2, and PUF-3. After sampling, we analyzed the PAH concentrations of the two XAD-2 resin layers and the three PUF plugs. In three breakthrough tests, we found no significant amounts of PAHs in the XAD-2-2 resin, PUF-2, and PUF-3 sections.

**PAH analysis.** After sampling, both glass fiber filter and cartridge were Soxhlet extracted with a mixed solvent (*n*-hexane and dichloromethane, v:v = 1:1, 500 mL each) for 24 hr. The extract was concentrated by purging with ultrapure nitrogen (flow rate 1.0 L/min) to 2 mL, which was followed by the cleanup procedure to remove pollutants that would coelute with PAHs from the gas chromatography (GC) column. The cleanup procedure was done in a cleanup column. The column (internal diameter 1 cm) contained approximately 5 g glasswool at the bottom, filled by 17 g 6% deactivated silica gel (mixed with 60 mL *n*-hexane) in the middle section, and topped with 1 cm of anhydrous sodium sulfate. Before cleanup, we added 60 mL *n*-hexane to wash the sodium sulfate and the silica gel. Just before the sodium sulfate layer was exposed to the air, the elution of *n*-hexane was stopped and the eluant was discarded. During cleanup, the concentrated sample was transferred onto column, and the wall of vessel was rinsed twice with 2 mL *n*-hexane which was also added to the column. Then, 200 mL 6% ethylether in *n*-hexane was added to the column and allowed to flow through the column at a rate of 3–5 mL/min, and the eluant was collected. The collected

**Table 1.** Gasoline consumption rates for PLG, 92-LFG, and 95-LFG in Taiwan, 1994–1999 (10<sup>6</sup> L/year).

Year	PLG	92-LFG	95-LFG	Total
1994	2,599	1,321	3,485	7,405
1995	2,160	1,571	4,166	7,897
1996	1,826	1,792	4,699	8,317
1997	1,488	1,922	5,101	8,511
1998	1,219	2,036	5,681	8,936
1999	944	2,136	6,118	9,198

Data from internal statistics, Chinese Petroleum Co.

**Table 2.** PAH compounds and their TEFs.

PAH	TEF
Naphthalene (Nap)	0.001
Acenaphthylene (AcPy)	0.001
Acenaphthene (Acp)	0.001
Fluorene (Flu)	0.001
Phenanthrene (PA)	0.001
Anthracene (Ant)	0.01
Fluoranthene (FL)	0.001
Pyrene (Pyr)	0.001
Cyclopenta[ <i>c,d</i> ]pyrene (CYC)	— <sup>a</sup>
Benzo[ <i>a</i> ]anthracene (BaA)	0.1
Chrysene (CHR)	0.01
Benzo[ <i>b</i> ]fluoranthene (BbF)	0.1
Benzo[ <i>k</i> ]fluoranthene (BkF)	0.1
Benzo[ <i>e</i> ]pyrene (BeP)	— <sup>a</sup>
Benzo[ <i>a</i> ]pyrene (BaP)	1
Perylene (PER)	— <sup>a</sup>
Indeno[1,2,3- <i>cd</i> ]pyrene (IND)	0.1
Dibenzo[ <i>a,h</i> ]anthracene (DBA)	1
Benzo[ <i>b</i> ]chrysene (BbC)	— <sup>a</sup>
Benzo[ <i>ghi</i> ]perylene (BghiP)	0.01
Coronene (COR)	— <sup>a</sup>

Data from Nisbet and Lagoy (11).

<sup>a</sup>No TEF has been suggested.

**Table 3.** Specifications for PLG, 92-LFG, and 95-LFG.

Specification	PLG	92-LFG	95-LFG
Product no.	13-F11095	113-F12092	113-F12095
Octane no.	95	92	95
Reid vapor pressure (kPa at 37.8°F)	69	69	69
Sulfur content (%wt)	0.10	0.10	0.10
Lead content (g Pb/L)	0.08	0.013	0.013
Distillation (°C)			
10%	74	74	74
50%	127	127	127
90%	190	190	190
End point (°C)	225	225	225
Residue (%vol)	2	2	2

**Table 4.** Gasoline consumption, inlet-air flow rate, and exhaust-gas flow rate for the gasoline-powered engine operated at idling, 40 km/hr, 80 km/hr, and 110 km/hr.

Driving speed	Fuel consumption rate (L/hr)			Inlet air flow rate (L/min)	Exhaust gas flow rate (L/min)
	PLG	92-LFG	95-LFG		
Idling	3.80	2.80	3.70	319	750
40 km/hr	4.16	3.00	4.04	474	1,130
80 km/hr	5.10	4.68	4.60	844	1,650
110 km/hr	6.54	4.96	5.86	1,100	2,250

eluant from the cleanup procedure was re-concentrated to 0.5 mL with nitrogen.

We used a GC (model 5890A; Hewlett-Packard, Wilmington, DE, USA) with a Hewlett-Packard capillary column (HP Ultra 2, 50 m × 0.32 mm × 0.17 μm), a mass selected detector (MSD) (Hewlett-Packard model 5972), and a computer workstation for the PAH analysis. We determined the masses of molecular and fragment ions of PAHs using the scan mode for pure PAH standards. We identified PAHs using the selected ion monitoring (SIM) mode. The

GC/mass spectrometer (MS) was calibrated with a diluted standard solution of 16 PAH compounds (PAH Mixture-610M; Supelco, Bellefonte, PA, USA) plus five additional individual PAHs obtained from Merck (Darmstadt, Germany). These 21 PAH compounds include naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), cyclopenta[*c,d*]pyrene (CYC), benz[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF),

benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene (PER), indeno[1,2,3-*cd*]pyrene (IND), dibenz[*a,h*]anthracene (DBA), benzo[*b*]chrysene (BbC), benzo[*ghi*]perylene (BghiP), and coronene (COR). Analysis of serial dilutions of PAH standards showed the limit of detection (LOD) of GC/MS was 0.023–0.524 ng. The limit of quantification (LOQ) was defined as the limit of detection divided by the sampling volume for the PSS. The LOQ for PAH compounds was 0.077–1.75 ng/m<sup>3</sup>. Ten consecutive injections of a PAH 610-M standard yielded an average relative standard deviation (RSD) of GC/MS integration area of 3.0% (range 0.8–5.1%).

We determined PAH recovery efficiencies by spiking the filter/cartridge with solutions containing known PAH concentrations through the same experimental procedure applied to the field samples. The recovery efficiency of PAHs varied between 0.736 and 1.15 and averaged 0.859. The recovery efficiency yielded for the two internal standards PA-d10 and PER-d12 was between 0.78 and 0.88. The blank tests for PAHs were accomplished by the same procedure as the recovery-efficiency tests without adding the known standard solution before extraction. Analyses of field blanks, including filters and cartridges, found no significant contamination (GC/MS integrated area < detection limit).

## Results and Discussion

*PAH and its corresponding BaP<sub>eq</sub> concentration originally contained in gasoline fuels.* We collected six samples from each of the three gasoline fuels (i.e., PLG, 92-LFG, and

**Table 5.** Mean PAH concentration and its corresponding BaP<sub>eq</sub> concentration originally contained in PLG, 92-LFG, and 95-LFG (*n* = 6).

Compound	PLG (mg/L)		92-LFG (mg/L)		95-LFG (mg/L)	
	PAH	BaP <sub>eq</sub>	PAH	BaP <sub>eq</sub>	PAH	BaP <sub>eq</sub>
Nap	11.4	0.0114	12.83	0.0128	11.5	0.0115
AcPy	0.59	0.00059	0.94	0.00094	0.71	0.00071
Acp	0.17	0.00017	0.30	0.0003	0.24	0.00024
Flu	0.88	0.00088	1.24	0.00124	0.85	0.00085
Ant	0.18	0.0018	0.32	0.0032	0.21	0.0021
PA	0.38	0.00038	0.36	0.00036	0.67	0.00067
FL	0.06	0.00006	0.12	0.00012	0.08	0.00008
Pyr	0.01	0.00001	0.06	0.00006	0.04	0.00004
CYC	0.02	–	0.04	–	0.01	–
BaA	0.04	0.004	0.02	0.002	0.05	0.005
CHR	0.01	0.0001	0.02	0.0002	0.03	0.0003
BbF	0.004	0.0004	0.002	0.0002	0.002	0.0002
BkF	0.003	0.0003	0.01	0.001	0.003	0.0003
BeP	0.002	–	0.002	–	0.01	–
BaP	0.01	0.01	0.01	0.01	0.007	0.007
PER	0.01	–	0.02	–	0.03	–
IND	0.37	0.037	0.31	0.031	0.25	0.025
DBA	0.02	0.02	0.04	0.04	0.04	0.04
BbC	0.10	–	0.10	–	0.05	–
Bghip	0.15	0.0015	0.14	0.0014	0.14	0.0014
COR	0.03	0	0.03	–	0.03	–
Total	13.8	0.09	16.9	0.11	15.0	0.10

**Table 6.** Mean PAH concentrations contained in fuel (*n* = 6) and engine exhausts (*n* = 3) operated at four driving speeds for the tested engine with PLG, 92-LFG, and 95-LFG.

PAHs	PLG Engine exhaust (μg/m <sup>3</sup> )				92-LFG Engine exhaust (μg/m <sup>3</sup> )				95-LFG Engine exhaust (μg/m <sup>3</sup> )			
	Idling	40 km/hr	80 km/hr	110 km/hr	Idling	40 km/hr	80 km/hr	110 km/hr	Idling	40 km/hr	80 km/hr	110 km/hr
Nap	120	75.1	61.5	102	146	96.8	121	88.2	147	95.9	87.5	97.0
AcPy	2.58	7.8	5.24	1.92	0.65	0.59	0.51	0.68	1.22	5.19	8.09	5.52
Acp	0.25	0.32	2.57	6.52	0.42	0.39	0.55	0.86	0.68	0.28	0.32	35.0
Flu	36.6	81.3	82.6	34.6	5.42	3.59	3.48	2.62	72.7	43.8	77.6	212
Ant	14.1	33.6	21.2	33.8	1.26	0.79	0.96	0.95	54.3	67.2	58.5	35.6
PA	2.82	1.35	1.42	1.27	1.12	0.82	0.97	0.89	6.72	9.52	6.85	7.97
FL	9.97	18.2	6.26	4.14	1.11	0.38	0.43	1.02	16.2	14.7	11.0	5.30
Pyr	5.22	11.3	6.32	3.58	0.25	0.23	0.12	0.22	10.6	10.8	9.32	9.99
CYC	0.67	2.83	0.99	0.93	1.05	1.61	1.40	1.50	5.86	4.6	3.44	13.8
BaA	0.55	5.13	2.50	3.53	0.32	0.49	0.99	0.72	4.45	3.71	3.21	3.53
CHR	2.61	6.43	3.21	4.41	0.21	0.47	0.18	0.29	4.57	3.62	5.04	5.49
BbF	1.01	2.94	1.63	3.04	0.27	0.12	0.29	0.28	2.04	1.49	3.13	3.14
BkF	1.08	3.34	2.07	2.91	0.11	0.03	0.05	0.19	1.96	2.19	3.75	4.06
BeP	1.09	0.72	0.55	0.54	0.44	0.15	0.22	0.23	1.19	0.62	0.76	2.12
BaP	0.81	2.20	1.29	1.72	0.06	0.04	0.03	0.08	1.62	1.48	2.73	3.23
PER	0.13	0.22	0.10	0.21	1.78	0.87	1.17	2.26	0.21	0.14	0.31	0.18
IND	1.27	5.06	1.66	6.84	3.15	1.87	3.45	4.27	1.98	1.73	5.60	5.77
DBA	0.39	0.58	0.31	0.64	0.03	0.02	0.03	0.10	0.44	0.38	0.86	1.37
BbC	0.89	1.07	0.95	1.48	0.05	0.04	0.06	0.04	0.40	0.9	1.38	1.19
Bghip	3.21	3.35	5.07	2.28	0.15	0.16	0.23	0.14	2.39	5.11	2.75	5.36
COR	0.03	0.06	0.01	0.01	0.002	ND	ND	0.01	0.02	0.04	0.01	0.03
Total	205	263	207	216	164	109	136	106	337	274	292	458
EF <sub>PAH</sub>	2,430	4,280	4,030	4,470	2,630	2,470	2,880	2,870	4,090	4,590	6,290	10,500
Avg EF <sub>PAH</sub>		3,800 μg/L fuel				2,710 μg/L fuel				6,380 μg/L fuel		

95-LFG) for PAH analyses (Table 5). The results show that the concentrations for each individual PAH compound, total PAHs, individual BaP<sub>eq</sub>, and total BaP<sub>eq</sub> among the three gasoline fuels were comparable (*t*-test, *p*-value < 0.05). The concentrations of total PAHs and total BaP<sub>eq</sub> for PLG, 92-LFG, and 95-LFG were 13.8, 16.9, and 15.0 mg/L, and 0.09, 0.11, and 0.10 mg/L, respectively. Total PAHs obtained for PLG, 92-LFG, and 95-LFG were contributed mostly by Nap, which accounted for 83%, 76%, and 77% of total PAHs for the three types of gasoline fuel, respectively. However, total BaP<sub>eq</sub> was contributed mainly by the three carcinogenic compounds—BaP, IND, and DBA—and their sum accounted for 74%, 74%, and 72% of total BaP<sub>eq</sub> for the three types of gasoline fuel, respectively. These results clearly indicate that the three gasoline fuels contained not only similar PAH compositions, but also similar carcinogenic potencies.

**PAHs contained in engine exhaust.** In this study, the test engine was operated under four specified operating conditions, including idling, and three cruising speeds of 40 km/hr, 80 km/hr, and 110 km/hr for each of the three gasoline fuels. For each set of experiments (i.e., the test engine was filled with one specific type of gasoline fuel and operated under one specific operating condition), we collected three samples from the engine exhaust by using the PSS. The mean concentrations (micrograms per cubic meter) obtained for each of the 21 PAH compounds and the total PAHs (micrograms per cubic meter) are shown in Table 6. Total PAH concentrations for each of the three

gasoline fuels operated under the four specified operating conditions were not consistent. The magnitude of total PAHs presented in sequences for PLG, 92-LFG, and 95-LFG operated under the four specified operating conditions were, respectively, 110 km/hr > 40 km/hr > 80 km/hr > idling; 80 km/hr > 110 km/hr > idling > 40 km/hr; and 110 km/hr > 40 km/hr > 80 km/hr > idling. These results are not surprising because the fuel consumption rates and inlet air flow rates were different for the three types of gasoline fuel when operated under the four specified operating conditions (Table 4). Moreover, given that the exhaust gas flow rates were also different (Table 4), the above total PAH concentrations were not adequate to describe the amount of PAH emission for each of the three types of gasoline fuel when operated under each of the four specified operating conditions.

Table 6 also shows the emission factors for total PAHs (i.e., EF<sub>PAHs</sub>, micrograms per liter of fuel) for each of the three types of gasoline fuel when operated under each of the four operating conditions. Here, EF<sub>PAHs</sub> was defined as the amount of total PAHs (micrograms) expelled from the test engine when 1 L of gasoline fuel was consumed, and was calculated based on the following equation:

$$EF_{PAH} = \frac{[(\text{Total PAHs}) \times (\text{Exhaust gas flow rate}) \times 10^{-3}]}{[(\text{Fuel consumption rate}) \times \frac{1}{60}]}$$

From this equation, total PAHs (micrograms per cubic meter) can be found in Table 6, and the exhaust gas flow rate (liters

per minute) and the fuel consumption rate (liters per hour) can be seen in Table 4. The results show the magnitude of EF<sub>PAH</sub> presented in sequence for the four specified operating conditions shared the same trend as 95-LFG > PLG > 92-LFG. Because the three types of gasoline fuel contain similar PAH concentrations (Table 5), the above results suggest that PAHs originally contained in gasoline fuels did not affect PAH emissions in the engine exhaust. PAHs in the engine exhaust were contributed both by the survival of PAHs originally contained in the fuel and by PAHs generated during pyrosynthesis (13). At this stage, because the mechanisms of survivability and pyrosynthesis of PAHs in the engine are not well understood, the results obtained from this study warrant further research.

**BaP<sub>eq</sub> contained in the engine exhaust.** Table 6 shows that Nap contributed to the majority of total PAHs for the three types of gasoline fuel operated under the four specified operating conditions. Therefore, the measurement of total PAHs might be deceptive on assessing the health-risks that associated with total PAH exposures because some PAH compounds, such as BaP, DBA, BaA, BbF, BkF, and IND, are more carcinogenic than Nap. Therefore, we must examine further the emission of BaP<sub>eq</sub> as a health risk. Table 7 shows the mean concentrations of BaP<sub>eq</sub> for each of the 21 PAH compounds and the total BaP<sub>eq</sub> for each type of gasoline when operated under the four specified operating conditions. The magnitudes of total BaP<sub>eq</sub>, in sequence for PLG, 92-LFG, and 95-LFG, were 110 km/hr > 40 km/hr > 80

**Table 7.** Mean BaP<sub>eq</sub> concentrations (µg/Nm<sup>3</sup>) contained in engine exhausts (*n* = 3) operated at four driving speeds for the tested engine using the fuel of PLG, 92-LFG, and 95-LFG.

PAHs	PLG Engine exhaust (µg/Nm <sup>3</sup> )				92-LFG Engine exhaust (µg/Nm <sup>3</sup> )				95-LFG Engine exhaust (µg/Nm <sup>3</sup> )			
	Idling	40 km/hr	80 km/hr	110 km/hr	Idling	40 km/hr	80 km/hr	110 km/hr	Idling	40 km/hr	80 km/hr	110 km/hr
Nap	0.120	0.0751	0.0615	0.102	0.146	0.0968	0.121	0.0882	0.147	0.0959	0.0875	0.097
AcPy	0.00258	0.0078	0.00524	0.00192	0.00065	0.00059	0.00051	0.00068	0.00122	0.00519	0.00809	0.00552
Acp	0.00025	0.00032	0.00257	0.00652	0.00042	0.00039	0.00055	0.00086	0.00068	0.00028	0.00032	0.035
Flu	0.0366	0.0813	0.0826	0.0346	0.00542	0.00359	0.00348	0.00262	0.0727	0.0438	0.0776	0.212
Ant	0.141	0.336	0.212	0.338	0.0126	0.0079	0.0096	0.0095	0.543	0.672	0.585	0.356
PA	0.00282	0.00135	0.00142	0.00127	0.00112	0.00082	0.00097	0.00089	0.00672	0.00952	0.00685	0.00797
FL	0.00997	0.0182	0.00626	0.00414	0.00111	0.00038	0.00043	0.00102	0.0162	0.0147	0.011	0.0053
Pyr	0.00522	0.0113	0.00632	0.00358	0.00025	0.00023	0.00012	0.00022	0.0106	0.0108	0.00932	0.00999
CYC	—	—	—	—	—	—	—	—	—	—	—	—
BaA	0.055	0.513	0.250	0.353	0.032	0.049	0.099	0.072	0.445	0.371	0.321	0.353
CHR	0.0261	0.0643	0.0321	0.0441	0.0021	0.0047	0.0018	0.0029	0.0457	0.0392	0.0504	0.549
BbF	0.101	0.294	0.163	0.304	0.027	0.012	0.029	0.028	0.204	0.149	0.313	0.314
BkF	0.108	0.334	0.207	0.291	0.011	0.003	0.005	0.019	0.196	0.214	0.375	0.406
BeP	—	—	—	—	—	—	—	—	—	—	—	—
BaP	0.810	2.20	1.29	1.72	0.06	0.04	0.03	0.08	1.62	1.48	2.73	3.23
PER	—	—	—	—	—	—	—	—	—	—	—	—
IND	0.127	0.506	0.166	0.684	0.315	0.187	0.345	0.427	0.198	0.173	0.56	0.577
DBA	0.390	0.58	0.31	0.64	0.03	0.02	0.03	0.1	0.44	0.38	0.86	1.37
BbC	—	—	—	—	—	—	—	—	—	—	—	—
Bghip	0.0321	0.0335	0.0507	0.0228	0.0015	0.0016	0.0023	0.0014	0.0239	0.0511	0.0275	0.0536
COR	—	—	0	—	—	—	—	—	—	—	—	—
Total	1.97	5.06	2.85	4.55	0.65	0.43	0.68	0.83	3.97	3.71	6.02	7.09
EF <sub>BaP<sub>eq</sub></sub>	23.3	82.4	55.3	93.9	10.4	9.67	14.4	22.7	48.3	62.3	130	163
Avg EF <sub>BaP<sub>eq</sub></sub>	63.7 µg/L fuel				14.3 µg/L fuel				101 µg/L fuel			



km/hr > idling; 110 km/hr > 80 km/hr > idling > 40 km/hr; and 110 km/hr > 80 km/hr > idling > 40 km/hr. At this stage, we do not have enough knowledge to address the above findings because the fuel consumption rates and inlet air flow rates were different for the three types of gasoline fuel operated under the four specified operating conditions (Table 4), and particularly because the mechanism regarding the PAH emissions in the engine are not well understood.

Table 7 also shows the emission factors for total BaP<sub>eq</sub> (i.e., EF<sub>BaP<sub>eq</sub></sub>, micrograms per liter of fuel) for each type of gasoline fuel when operated under the four operating conditions. Here, the emission factor EF<sub>BaP<sub>eq</sub></sub> (micrograms per liter of fuel) was defined as the amount of BaP<sub>eq</sub> (micrograms) exhausted from the test engine when 1 L of gasoline fuel was consumed, and was calculated based on the following equation:

$$EF_{BaP_{eq}} = \frac{[(Total\ BaP_{eq}) \times (Exhaust\ gas\ flow\ rate) \times 60]}{[(Fuel\ consumption\ rate) \times 10^3]}$$

The results show that the magnitude of EF<sub>BaP<sub>eq</sub></sub> presented in sequence for the four specified operating conditions were not consistent. The sequences were 95-LFG > PLG > 92-LFG, for the test gasoline engine when operated under 110 km/hr, 80 km/hr, and idling conditions, and PLG > 95-LFG > 92-LFG when operated at 40 km/hr. Although the three types of fuel originally contained quite similar BaP<sub>eq</sub> contents (Table 5), the above results indicate that PAHs originally contained in the fuel did not affect the emission of BaP<sub>eq</sub>. One recent study indicated that the combustion process not only might decrease the lower molecular weight PAHs originally contained in raw materials, but also might increase some more toxic compounds, such as BaP, in the exhaust gas (14). At this stage, because the mechanisms regarding the decomposition and pyrosynthesis of PAHs for the gasoline-powered engine are not well understood, the results obtained from this study warrants further research.

**The effect of using lead-free gasoline on total PAH and BaP<sub>eq</sub> emissions.** Table 8 shows the annual emission rates (kilograms per year) of total PAHs (i.e., ER<sub>PAH</sub>) and total BaP<sub>eq</sub> (i.e., ER<sub>BaP<sub>eq</sub></sub>) for each type of

gasoline from 1994 to 1999. Here, ER<sub>PAH</sub> and ER<sub>BaP<sub>eq</sub></sub> were calculated according to following equations

$$ER_{PAH} = (Avg\ EF_{PAH}) \times (Fuel\ consumption\ rate) \times 10^{-3}$$

$$ER_{BaP_{eq}} = (Avg\ EF_{BaP_{eq}}) \times (Fuel\ consumption\ rate) \times 10^{-3},$$

where Avg EF<sub>PAH</sub> = the averaged EF<sub>PAH</sub> values for the given type of gasoline operated under the four specified cruising speeds (micrograms per liter of fuel) (Table 6). Ave EF<sub>BaP<sub>eq</sub></sub> = the averaged EF<sub>BaP<sub>eq</sub></sub> values for the given type of gasoline operated under the four specified cruising speeds (micrograms per liter of fuel) (Table 7).

The results show the ER<sub>PAH</sub> for PLG reduced significantly from 9,876 kg/year in 1994 to 3,587 kg/year in 1999. But for 92-LFG and 95-LFG, the ER<sub>PAH</sub> increased significantly from 3,580 L/year and 22,234 kg/year in 1994 to 5,798 kg/year and 39,033 kg/year in 1999, respectively. Total ER<sub>PAH</sub> (i.e., the sum of ER<sub>PAH</sub> values for the three type of gasoline) increased from 35,690 kg/year in 1994 to 48,409 kg/year in 1999. Obviously, the above results could not be explained simply by the annual consumption rates of the three types of gasoline fuel. The Avg EF<sub>PAH</sub> (Table 6) for the three types of gasoline fuel also played important roles for ER<sub>PAH</sub> and total ER<sub>PAH</sub>. As shown in Table 6, the magnitude of Avg EF<sub>PAH</sub> presented in sequence for the three types of gasoline was 95-LFG > PLG > 92-LFG (i.e., 6,380 µg/L fuel > 3,800 µg/L fuel > 2,710 µg/L fuel). Therefore, use of 95-LFG to replace PLG would increase total ER<sub>PAH</sub>, but use of 92-LFG would decrease total ER<sub>PAH</sub>. Annual consumption rates of the three types of gasoline show that PLG decreased from 2,599 × 10<sup>6</sup> L/year in 1994 to 944 × 10<sup>6</sup> L/year in 1999. On the other hand, 92-LFG and 95-LFG increased from 1,321 × 10<sup>6</sup> L/year and 3,485 × 10<sup>6</sup> L/year in 1994 to 2,136 × 10<sup>6</sup> L/year and 6,118 × 10<sup>6</sup> L/year in 1999, respectively. The increase of fuel consumption for 95-LFG was more significant than for 92-LFG during the period. That the magnitude of Avg EF<sub>PAH</sub> for 95-LFG (i.e., 6,380 µg/L fuel) was also

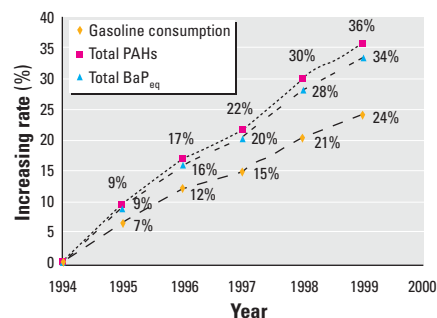
higher than for 92-LFG (i.e., 3,800 µg/L fuel) suggests that the increases of total ER<sub>PAH</sub> were caused mainly by increases in 95-LFG consumption during the period.

Figure 1 shows the annual increasing rates for both total gasoline consumption and total ER<sub>PAH</sub> from 1995 to 1999 (by reference to the values obtained in 1994). The increasing rate for total ER<sub>PAH</sub> (36%) was higher than the corresponding increasing rate for annual gasoline consumption (24%) over the same period. Therefore, when PLG was replaced by LFG for the test gasoline engine, it might reduce lead emissions, but would increase PAH emissions, specifically when 95-LFG was used. The above result suggests that lower-octane LFG may be a more desirable substitute for PLG. However, PAH emissions from the gasoline-powered engine might not completely reflect humans' environmental exposure level. For instance, the particle size of particle-phase PAHs expelled from the gasoline engine might be increased in the atmosphere via aggregation with other aerosols. The resultant aggregates could be removed from the atmosphere through gravitational precipitation, and thus might not affect human exposure levels. Gas-phase PAHs could be adsorbed and bounded by large particles, which might in turn decrease their bioavailabilities and eventually decrease the internal dose in the human body. Because these factors were not considered, the results obtained from this study might be suggestive but should be used with caution for policy decisions.

As shown in Table 8, the ER<sub>BaP<sub>eq</sub></sub> for PLG decreased significantly from 166 kg/year in 1994 to 60 kg/year in 1999. But for 92-LFG and 95-LFG, the ER<sub>BaP<sub>eq</sub></sub> increased from 19 L/year and 352 kg/year in 1994 to 31 kg/year and 618 kg/year in 1999, respectively. The amounts of total ER<sub>BaP<sub>eq</sub></sub> (i.e., the sum of ER<sub>BaP<sub>eq</sub></sub> values for the three types of gasoline) increased from 536 kg/year in 1994 to 709 kg/year in 1999. In addition, the increasing rates for total ER<sub>BaP<sub>eq</sub></sub> were higher than the corresponding increasing rates for total gasoline consumption from 1995 to

**Table 8.** Emission rates of total PAHs and total BaP<sub>eq</sub> for PLG, 92-LFG, and 95-LFG in a gasoline-powered engine in Taiwan, 1994–1999 (kg/year).

Year	PLG		92-LFG		95-LFG		Total	
	ER <sub>PAH</sub>	ER <sub>BaP<sub>eq</sub></sub>	ER <sub>PAH</sub>	ER <sub>BaP<sub>eq</sub></sub>	ER <sub>PAH</sub>	ER <sub>BaP<sub>eq</sub></sub>	ER <sub>PAH</sub>	ER <sub>BaP<sub>eq</sub></sub>
1994	9,876	166	3,580	19	22,234	352	35,690	536
1995	8,208	138	4,257	22	26,579	421	39,044	581
1996	6,939	116	4,856	26	29,980	475	41,775	617
1997	5,654	95	5,209	27	32,544	515	43,407	637
1998	4,632	78	5,518	29	36,245	574	46,395	681
1999	3,587	60	5,789	31	39,033	618	48,409	709



**Figure 1.** Annual increasing rates for total gasoline consumption, total PAHs, and total BaP<sub>eq</sub> from 1995 to 1999 (based on values found in 1994).

1999 (Figure 1). The above results again suggest that the increase of total  $ER_{BaP_{eq}}$  could not be explained simply by the increase in total gasoline consumption. This was also affected by the magnitude of Avg EF  $ER_{BaP_{eq}}$  for the three types of gasoline. As shown in Table 7, the magnitudes of Avg EF  $ER_{BaP_{eq}}$  presented in sequence for the three types of gasoline were 95-LFG > PLG > 92-LFG (i.e., 101  $\mu\text{g/L fuel}$  > 63.7  $\mu\text{g/L fuel}$  > 14.3  $\mu\text{g/L fuel}$ ). Therefore, the increases of total  $ER_{BaP_{eq}}$  were caused mainly by the increases of 95-LFG consumption during the period.

The above results suggest the use of LFG to replace LPG in gasoline engines would significantly increase the emission of carcinogenic PAHs, particularly when 95-LFG was used instead of 92-LFG. However, the increasing rates obtained for both total  $ER_{PAH}$  and total  $ER_{BaP_{eq}}$  show that the values for the former were slightly higher than the corresponding values for the latter (Figure 1). This result suggests that the use of LFG to replace LPG for the test gasoline-powered engine would produce approximately equal significance for the increase of both total  $ER_{PAH}$  and total  $ER_{BaP_{eq}}$ .

The results obtained from this study are applicable only for gasoline fuels with similar chemical compositions when tested against the same type of gasoline-powered engine. Both LPG and LFG found outside Taiwan might contain different chemical compositions (even the fuel with the same RON/MON range), so the PAH emissions in the engine exhaust could be different. Therefore, the results obtained in this study should not be adopted directly for policy decisions in other countries. Moreover, recent studies have indicated the PAH emissions from the gasoline-powered engine might also be affected by the types of lubricant (15) and catalytic converter (16). Because other types of engine, gasoline fuel, lubricant, and catalytic converter will affect PAHs emission in the engine exhaust, further

studies should be conducted to extend the generality of the above findings.

## Conclusions

In this study, we found the three types of fuel originally contained comparable total PAH content. However, the emissions of total PAHs in exhaust gas from the test gasoline-fueled engines were different when produced under different operating conditions. The averaged emission factors (Avg EF  $ER_{PAH}$ ) for the gasoline-powered engine operated under the four test cruising speeds were 95-LFG > PLG > 92-LFG, indicating that the PAHs originally contained in the fuel did not affect the PAH emissions in the engine exhaust. We also examined the emissions of  $BaP_{eq}$  from the health-risk point of view. Again, we found that the average  $BaP_{eq}$  emission factors (Avg EF  $ER_{BaP_{eq}}$ ) for the gasoline-powered engine operated under the four test cruising speeds also shared the same trend of 95-LFG > PLG > 92-LFG. Therefore, using 95-LFG to replace PLG would increase both Avg EF  $ER_{PAH}$  and Avg EF  $ER_{BaP_{eq}}$ , whereas using 92-LFG as the substitute would decrease of both amounts. By taking both emission factors and gasoline consumption rates into account, we found that both the total PAH emission rate (total  $ER_{PAH}$ ) and total  $BaP_{eq}$  emission rate (total  $ER_{BaP_{eq}}$ ) consistently increased from 1995 to 1999. However, the increasing rates for total  $ER_{PAH}$  were slightly higher than the corresponding rates for total  $ER_{BaP_{eq}}$ . Given that gasoline fuels outside Taiwan might contain different chemical compositions, PAH emissions in engine exhausts could be different. Therefore, the results obtained from this study should be used with caution for policy decisions in other countries.

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