



Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in particulates emitted by motorcycles



Chau Thuy Pham^{a,*}, Takayuki Kameda^{a,b}, Akira Toriba^{a,b}, Kazuichi Hayakawa^{a,b}

^a Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

^b Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

ARTICLE INFO

Article history:

Received 19 September 2012

Received in revised form

3 December 2012

Accepted 5 January 2013

Keywords:

Polycyclic aromatic hydrocarbons

Nitropolycyclic aromatic hydrocarbons

Regulated pollutants

Motorcycles

Direct-acting mutagenicity

ABSTRACT

We determined eleven PAHs and four NPAHs in particulates and regulated pollutants (CO, CO₂, HC, NO_x, PM) exhausted from motorcycles to figure out the characteristics of motorcycle exhausts. Fluoranthene and pyrene accounted for more than 50% of the total detected PAHs. Among four detected NPAHs, 6-nitrochrysene and 7-nitrobenz[*a*]anthracene were the predominant NPAHs and were highly correlated relationship with their parent PAHs ($R = 0.93$ and 0.97 , respectively). The PM and HC emissions tended to be close to the PAH emissions. NO_x and NPAHs were negatively correlated. Despite their small engine size, motorcycles emitted much more PM and PAHs, showed stronger PAH-related carcinogenicity and indirect-acting mutagenicity, but weaker NPAH-related direct-acting mutagenic potency than automobiles. This is the first study to analyze both PAHs and NPAHs emitted by motorcycles, which could provide useful information to design the emission regulations and standards for motorcycles such as PM.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) are widespread pollutants in the environment which have been found in diesel particulates, fly ash, cigarette smoke, and various incomplete combustion processes of organic matters and fossil fuels. NPAHs also come from the reaction of their parent PAHs with OH or NO_x radicals in the atmosphere (Arey et al., 1986) and/or the heterogeneous gas-particle interaction of the parent PAHs adsorbed onto particulates with nitrating agents (Feilberg et al., 2001). Once released into the atmosphere, both PAHs and NPAHs can be carried over thousands of kilometers through the atmosphere from their original sources (Nielsen, 1984). The presence of PAHs and NPAHs in the atmosphere has been receiving attention because of their possible effects on human health. Many PAHs and NPAHs are carcinogenic and/or mutagenic (Pitts et al., 1978). Several NPAHs exhibit higher mutagenicity and carcinogenicity than their parent PAHs (Durant et al., 1996). The mutagenic properties and potential carcinogenicity for some PAHs and NPAHs have been documented in the report of the International Agency for Research on Cancer (IARC, 2010).

Internal combustion engines in motor vehicles generate a wide variety of PM, which are mainly fine particulates with a diameter

smaller than 0.25 μm (Ondov and Wexler, 1998; Kleeman et al., 2000; Yang et al., 2005a). When PM are inhaled, coarse particulates are deposited almost exclusively in the nose and throat, whereas fine and ultrafine particles generally are able to reach the lungs (Cheng and Liu, 2009; Chien and Huang, 2010). Most carcinogenic PAHs and NPAHs have been found to associate with particulates, predominantly with fine particulates (Westerholm et al., 1991; Yang et al., 2005a).

Motorcycles, which are two-wheeler vehicles, are popular means of transportation in South-East Asian countries such as Vietnam, where they account for more than 90% of total vehicles in urban areas (Pham et al., 2012). Exhausts emitted from motorcycles contribute significantly to levels of several air pollutants such as hydrocarbon (HC), carbon monoxide (CO), nitrogen oxides (NO_x) and PAHs (Leong et al., 2001; Ntziachristos et al., 2006; Pham et al., 2012).

Although many studies have examined PAH emissions from automobiles (Kleeman et al., 2000; Abrantes et al., 2004; Robert et al., 2007; Riddle et al., 2007) and motorcycles (Yang et al., 2005a, 2005b, 2008; Spezzano et al., 2007, 2008, 2009), no studies have examined NPAHs emission from motorcycles or their direct-acting mutagenicities. The characterization of PAHs and NPAHs from motorcycle exhausts, their relationship with regulated pollutants, and also their carcinogenic and mutagenic potencies are necessary to fully investigate to be helpful in emission control for motorcycles.

The aims of this study were: i) to determine both PAHs and NPAHs emission from in-use motorcycles and ii) to find out the

* Corresponding author.

E-mail addresses: chauthuy@stu.kanazawa-u.ac.jp, pcthuy@gmail.com (C.T. Pham).

relationship between PAHs and NPAHs in particulates and regulated pollutants as the characteristic of motorcycle exhausts and to further understand the formation mechanism of NPAHs in motorcycle exhausts. Additionally, the carcinogenicity and mutagenicity of emitted particulates were compared between motorcycles and automobiles to better understand the contribution of PAHs and NPAHs from motorcycle exhausts to the atmosphere.

2. Materials and methods

2.1. Motorcycles tested and fuels used

Exhaust emission measurements were carried out using ten in-use motorcycles with different displacements, different years (2002–2010) of registration and different manufacturers. These vehicles equipped with all four-stroke engines and without catalyst converters, which were chosen among the most widely used ones in Hanoi, Vietnam. Table 1 presents the descriptions of 10 tested motorcycles (M1–10). The testing was conducted using two kinds of engines: carburetor engines with engine capacity from 100 to 125 cc (M1–8) and fuel injection engines with engine capacity of 110 cc (M9–10). The accumulated mileage of the tested motorcycles varies from 7394 to 60,299 km (average 39,202 km). The testing was conducted using two kinds of fuels: a commercial fuel A92 (M1–6, 9 and 10) produced by Vietnamese Petroleum Company with an octane number of 92, which was the most widely used gasoline in Vietnam, and E5, the mixture of 95% A92 and 5% ethanol (M7 and 8), which is being put into widespread use as a new choice toward environmentally friendly. All tested motorcycles belong to emission legislation EURO-0.

2.2. Emission testing

The test motorcycles were driven on a AVL-Zöllner chassis dynamometer (Kiel Prüfstand) (Fig. 1), which was located in the motorcycle test bed of Internal combustion engine laboratory, Hanoi University of Science and Technology. The dynamometer system consisted of a fan, a dynamometer, a constant volume sampling system with a mixing tunnel which is typically used to dilute engine exhausts and control the total amount of dilute flow through the system, a combustion emission bench – CEB II for analyzing the gas constituents after dilution, a smart sampler SPC 472 which was a partial-flow dilution system for the gravimetric measurement of particulate matter (PM) exhausted from internal combustion engines, and a personal computer to operate the system according to the program. The mass of PM was calculated from exhaust raw flow through the filter, the weight of PM loaded on the filter, the dilution ratio, distance driven and expressed as mass emitted per kilometer driving.

The European driving cycle for motorcycle ECE R40 (Economic Emission for European Regulation 40) was used for the exhaust emission testing (Fig. 2). This cycle is made by six elementary cycles. Each elementary cycle lasted for 195 s including idling, acceleration, cruising and deceleration. The pattern was designed to be representative of urban driving conditions. The speed for this test cycle varied from 0 to 50 km h⁻¹. The motor was run at idling speed to warm up the engine before testing. The emission measurement started at 41 s at the first cycle, and the idling speed was used in the first 40 s. Dilution ratio of SPC 472 was 1.3 for all samples, except for M3 and M6 whose dilution ratios were 1.4 and 1.5, respectively. The sampling temperature at the exhaust pipe was 165 °C or more and it was reduced to 45–50 °C when diluted. PM was collected on Pall Pallflex Emfab Filters (70 mm diameter) during the whole phase ECE 40 cycle. Before and after sampling, filters were equilibrated in a desiccator at room temperature for 48 h and weighted to determine the mass of collected PM. Each filter with collected PM was stored in a Petri dish, then was wrapped in aluminum foil and kept in a refrigerator at –20 °C

until use. In the gas analyzer, carbon monoxide (CO) was measured by non-dispersive infrared absorption detector, hydrocarbon (HC) was measured by a flame ionization detector (FID) and nitrogen oxides (NO_x) was measured by a chemiluminescence detector (CLD).

2.3. Particle-phase PAHs and NPAHs analysis

2.3.1. Chemicals

The EPA 610 Polynuclear Aromatic Hydrocarbons standard mixture including phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBA), benzo[*ghi*]perylene (BghiPe) and indeno[1,2,3-*cd*]pyrene (IDP) were purchased from Supelco, Inc. (Bellefonte, PA, U.S.A.). NPAHs including 1-nitropyrene (1-NP), 6-nitrochrysene (6-NC), 7-nitrobenz[*a*]anthracene (7-NBaA) and 6-nitrobenzo[*a*]pyrene (6-NBaP) were purchased from AccuStandard, Inc., (New Haven, U.S.A.). Three deuterated PAHs, Phe-*d*₁₀, Pyr-*d*₁₀ and BaP-*d*₁₂, were purchased from Wako Pure Chemical Industries, Ltd., (Osaka, Japan) as internal standards for PAHs analysis. 2-Fluoro-7-nitrofluorene (FNF) was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, U.S.A.) as an internal standard for NPAHs analysis. All of these compounds were dissolved in acetonitrile or ethanol to obtain standard and internal standard solutions. All solvents and other chemicals were HPLC or analytical grade purchased from Wako Pure Chemical Industries, Ltd and Kanto Chemical Company (Tokyo, Japan).

2.3.2. Extraction and clean up

An area of 1 cm² of each Pall Pallflex Emfab filter was cut into smaller pieces and put in a glass flask. Internal standards, Phe-*d*₁₀, Pyr-*d*₁₀ and BaP-*d*₁₂, for PAHs and FNF for NPAHs were added to the flask before extraction. Both PAHs and NPAHs on filter papers were extracted ultrasonically twice with 40 mL benzene/ethanol (3:1, v/v) and the mixture was filtered through a filter paper (Advantec, Toyo No. 6, 125 mm diameter, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) and a membrane filter (HLC-Disk 13, pore size 0.45 μm). The extracts were cleaned-up by using 80 mL of 5% sodium hydroxide solution, 80 mL of 20% sulfuric acid solution and 80 mL distilled water, successively. Then, the filtrate was evaporated to dryness in a round bottom flask after adding 100 μL dimethyl sulfoxide. The residue was dissolved in 900 μL ethanol. Finally, the solution was passed through a membrane filter (HLC-Disk 13, pore size 0.45 μm) and then an aliquot (100 μL) of the solution was injected into each HPLC system.

2.3.3. PAHs and NPAHs analysis by high-performance liquid chromatography (HPLC)

Eleven PAHs (Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, BghiPe and IDP) were determined by using an HPLC with a fluorescence detector. The system (Shimadzu LC-10, Kyoto, Japan) consisted of two HPLC pumps, a fluorescence detector, a system controller, an integrator, an auto sample injector and a column oven. The analytical column and the guard column were Inertsil ODS-P (4.6 i.d. × 250 mm, GL Science Inc., Tokyo, Japan) and ODS-P (4.0 i.d. × 10 mm, GL Sciences Inc.), respectively. The mobile phase was acetonitrile/water with an increasing acetonitrile concentration. The time program of the fluorescence detector was set to detect at the optimum excitation and emission wavelengths for each PAH according to our previous report (Tang et al., 2005).

Four NPAHs (1-NP, 6NC, 7-NBaA and 6-NBaP) were determined by using a Shimadzu LC-10 HPLC system with a chemiluminescence detector (CLD, Shimadzu) and a switching valve according to our previous report (Hayakawa et al., 2001) with some modifications. The system consisted of 6 HPLC columns: a guard column 1 (4.6 i.d. × 30 mm, 20 °C), a guard column 2 (4.6 i.d. × 50 mm, 20 °C), a clean-up column (Cosmosil, 5C₁₈-MS-II, 4.6 i.d. × 150 mm, 20 °C), a reducer column (Pt/Rh, 4.0 i.d. × 10 mm, 80 °C), a concentrator column (ODS, 4.6 i.d. × 30 mm, 20 °C) and two separator columns (Cosmosil, 5C₁₈-AR-II, 4.6 i.d. × 250 mm, 20 °C and Cosmosil,

Table 1
Tested motorcycles and collected particulates.

Motorcycle ^a	Engine capacity (displacement, cc)	Model year	Fuel system ^b	Manufacture	Mileage (km)	Particulate matter (PM)		Fuel consumption rate (L/100 km)
						mg	mg km ⁻¹	
M1	100	2007	Carburetor/A92	Honda	26,000	8.7	4.0	2.35
M2	100	2007	Carburetor/A92	Suzuki	50,000	6.6	3.4	2.50
M3	100	2002	Carburetor/A92	Honda	57,365	181.7	91.5	2.40
M4	110	2006	Carburetor/A92	Yamaha	38,831	64.5	29.8	2.33
M5	125	2006	Carburetor/A92	SYM	45,900	22.9	11.6	2.98
M6	100	2002	Carburetor/A92	Loncin-China	60,299	138.6	91.0	2.09
M7	110	2006	Carburetor/E5	Yamaha	38,831	33.6	15.1	2.39
M8	125	2006	Carburetor/E5	SYM	45,900	8.0	4.4	2.71
M9	110	2007	FI/A92	Honda	21,500	13.6	8.4	2.37
M10	110	2010	FI/A92	Honda	7394	29.0	16.7	2.84

^a All tested motorcycles were equipped with 4-stroke engines.

^b FI: Fuel injection; A92: Commercial fuel (Vietnam Petroleum Company); E5: 95% A92-5% ethanol.

Download English Version:

<https://daneshyari.com/en/article/6318473>

Download Persian Version:

<https://daneshyari.com/article/6318473>

[Daneshyari.com](https://daneshyari.com)