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Fuel Economy and Volatile Organic Compound Exhaust Emission for Motorcycles with Various Running Mileages

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ABSTRACT

The implementation of control measures for motorcycles in urban areas depends on the establishment of baseline measures for fuel economy and emission characteristics. In this study, the fuel economy of motorcycles was determined to be 34.7 ± 1.4, 32.6 ± 1.8 and 29.5 ± 2.5 km L^{-1} for regulation phase V, IV, and III motorcycles, respectively. For regulation phase V motorcycles, the average emission factor was 84.3 ± 40.9 g L^{-1} for CO, 29.4 ± 13.1 g L^{-1} for HC, 8.0 ± 2.3 g L^{-1} for NO_x, and 2098 ± 109 g L^{-1} for CO_2. A comparison of the fuel economy of regulation phase III and IV motorcycles with that of regulation phase V motorcycle showed reductions of 15% and 6.2%, corresponding to increases of 156% and 48% in CO emission, increases of 84% and 9% in HC emission, and decreases of 30% and 17% in NO_x emission, respectively. Based on fuel economy, the emission factors of a total of 67 volatile organic compounds(VOCs) were 25.2 ± 8.0 g L^{-1} for a running mileage of 5,231 ± 4,353 km, with emissions increasing to 47.1 ± 19.8 g L^{-1} for a running mileage of 47,617 ± 8,568 km. The exhaust of VOC groups profiled included paraffins (38–45%), olefins (9.7–15%), aromatics (38–48%), and carbonyls (1.8–3.0%) for various running mileages. Toluene, isopentane, m,p-xylene, o-xylene, 1-butene, 1,2,4-trimethylbenzene, ethylbenzene, n-pentane, and benzene were the main VOCs in motorcycle exhaust. Regarding the ozone formation potential of VOCs, 1-butene, xylene, isoprene, toluene, 1,2,4-trimethylbenzene, propene, and 1-hexene were the most abundant species in motorcycle exhaust.

Keywords: Fuel economy; Dynamometer testing; Ozone formation potential (OFP).

INTRODUCTION

Motor vehicle exhaust is a significant source of air pollution, regulated air pollutants, and organic compounds derived from the incomplete combustion of fuel, especially that from motorcycles with small engine capacities (less than 150 cc) (Graedel *et al.*, 1986; Yao *et al.*, 2013; Zhang and Batterman, 2013; Kamal *et al.*, 2015; Lakshmanan *et al.*, 2015; Yao *et al.*, 2017). These pollutants are easily transported and transformed in ambient air, affecting air quality and impacting human health, especially in urban areas. Motorcycles offer high maneuverability and ease of parking in crowded metropolitan areas (Adak *et al.*, 2016). They are also inexpensive, making them an attractive transportation mode, especially in developing countries.

In 2012, there were about 313 million motorcycles on the road, with a worldwide distribution of 78% in Asia, 14% in Europe, 5% in Latin America, 2% in North America, 1% in Africa, and just a few in the Middle East (Haworth, 2012). In Asia, 100 million motorcycle units were registered in China (the highest number in the world), 40 million in India, and 30 million in Indonesia. In 2016, 16.8 million two- and three-wheelers were sold in China (ICCT, 2017). Most motorcycles in service are inexpensive and have a small engine volume. Motorcycles with engines of less than 150 cc account for 65–75% of on-road vehicles in China, India, Indonesia, Thailand, and Taiwan (The Freedonia Group, 2013). An increase in fuel prices has contributed to an associated increase in the use of small-engine-capacity motorcycles for transportation in India, China, and Vietnam (Haworth, 2012; The Freedonia Group, 2013). Approximately 85% of new motorcycle sales occurred in Asia, where per capita automobile and truck ownership is lower than that in developed countries. Therefore, motorcycle emissions have a substantially higher air quality impact in Asian cities compared to that in non-Asian cities (MECA, 2014).

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According to data from the Energy Information Administration (EIA), global energy consumption could be as high as 409×10^{15} BTU (British thermal unit), with the industrial sector accounting for 54% (222×10^{15} BTU), the transportation sector for 27% (104×10^{15} BTU), the residential sector for 13% (53×10^{15} BTU), and the commercial sector for 7% (29×10^{15} BTU) (USEIA, 2016). Only the industrial sector consumes more fuel than the transportation sector.

According to the Total Motorcycle Website (TWM), the energy consumption of small-engine-volume motorcycles produced by Yamaha and Suzuki was in the range of 36.8–37.2 km L^{-1} in the period 2000–2005. The average fuel economy for motorcycles produced by Honda, Piaggio, Vespa, Kymco, and Yamaha was 31.8 ± 2.3–42.2 ± 8.7 km L^{-1} in the period 2010–2016 (TWM, 2017). In 2016, the Chinese Ministry of Industry and Information Technology released fuel economy standards of 37 (for automatic transmissions) to 40 (for manual transmissions) km L^{-1} for 125- to 150-cc two-wheeled motorcycles (ICCT, 2017). In Taiwan, the motorcycle fuel economy standard was set at 36 (for manual transmissions and some variable transmission (CVT) motorcycles) and 39 (for CVT and hot-start motorcycles) km L^{-1} for 100- to 150-cc engine capacities in the period 2002–2010. After 2011, the fuel economy standard was set at 38 km L^{-1} for 100- to 150-cc engine capacities (Auto Engine, 2017).

Due to photochemical reactions, volatile organic compounds (VOCs) can react with nitrogen oxides (NO_x), OH radicals, and O_3 to form ozone and secondary organic aerosols, reducing visibility and thus directly and seriously affecting atmospheric air quality (Atkinson, 2000; Kroll and Seinfeld, 2008). Therefore, VOCs are regarded as important air pollutants because they are the precursors to ambient ozone and secondary aerosols. Furthermore, many VOCs have been identified as hazardous or toxic air pollutants, with harmful effects on human health following exposure (Pérez-Rial *et al.*, 2010). Reactive aromatics are the dominant ozone-sensitive VOCs, in particular toluene and xylenes, which are emitted from anthropogenic sources such as motor vehicles (Zhang *et al.*, 2007b). Traffic is known to be a major source of non-methane hydrocarbons (NMHCs) in urban areas (Watson *et al.*, 2001), and motor vehicle emissions associated with incomplete combustion exhaust and gasoline evaporation are important sources of VOCs in urban areas (Song *et al.*, 2007, 2008; Shao *et al.,* 2009; Wang *et al.*, 2010; Wu *et al.*, 2012, 2016; Tsai *et al.*, 2017b).

According to a Taiwan Environmental Protection Administration (TEPA) report (TEPA, 2013), 74% of motorcycles in Taiwan have four-stroke engines. Due to high pollutant emissions, the production of two-stroke-engine motorcycles was phased out in Taiwan in 2004. More than 60% of motorcycle emissions are now contributed by four-stroke engines, so this type of motorcycle was selected in this study for evaluation of exhaust emission. Motorcycles contribute approximately 19.6% (178,700 ton yr^{-1}) of CO emission, 10.6% (89,300 ton yr^{-1}) of HC emission, and 2.6% (13,500 ton yr^{-1}) of NO_x emission in Taiwan (TEPA, 2013). To improve air quality, TEPA began creating motorcycle emission standards in 1987. As of 2017, the regulation in Taiwan is regulation phase VI, following Euro 4.

Taiwan has the toughest motorcycle emission standards in the world. The tested driving cycle was changed from hot-start to cold-start in January, 2004. For the motorcycle air pollution control program, testing includes idle testing and dynamometer driving cycle testing for new motorcycles and idle testing for in-use motorcycles. These tests are performed to curb CO, HC, and NO_x emissions by their emission factor. In addition, there are two types of inspection for in-use motorcycles: (1) periodic inspections, where motorcycles older than five years are inspected annually at a certified testing station, and (2) hot-spot inspections performed on vehicles pulled randomly for roadside inspections. Periodic inspection and maintenance tests measure motorcycle emissions and require consumers to perform repairs to reduce emissions, a strategy that could affect pollutant emissions. However, an observed increase in motorcycle population indicates that motorcycles are still a major source of air pollutants in urban areas in Taiwan (CTCI, 2007).

In this study, motorcycle dynamometer testing was employed to determine the fuel economy and emission factors of motorcycle exhaust. The testing followed the Economic Commission for Europe (ECE) driving cycle. CO, HC, and NO_x, as regulated air pollutants, and CO_2 were analyzed during the ECE driving cycle. VOCs, including paraffins, olefins, aromatics, and carbonyls, in motorcycle exhaust were analyzed for the entire driving cycle. In addition, the ozone formation potential of VOCs was determined for the exhaust from motorcycles with various running mileages.

EXPERIMENTS

Selected Motorcycles

Three regulation phases of motorcycle were selected. Seven motorcycles were classified as regulation phase III (phased in progressively between 1998 and 2003), with an average age of 15.0 ± 3.6 years and a running mileage of 45,613 ± 11,947 km. Sixteen motorcycles were under phase IV regulation (implementation phased in from 2004 to 2007), with an average age of 8.2 ± 1.8 years and a running mileage of 30,120 ± 9,067 km. Twenty motorcycles were under phase V regulation (phased in between 2007 and 2017), with an average age of 4.0 ± 1.5 years and a running mileage of 12,179 ± 6,337 km.

The durability testing of motorcycles (≤ 150 cc) is typically conducted between 6,000 and 15,000 km for emission certification, with some of the larger motorcycles (> 280 cc) tested at up to 30,000 km (MECA, 2014). In Taiwan, motorcycle guaranteed mileage was performed at 6,000 km in 1991, increased to 15,000 km in 1998, and increased again to 20,000 km in 2017 (TEPA, 2017). Based on the motorcycle guaranteed mileage of 15,000 km between 1998 and 2016, the running mileages of selected motorcycles were divided into seven groups, namely 0–

10000 (n = 6), 10001–15000 (n = 8), 15001–20000 (n = 8), 20001–30000 (n = 8), 30001–40000 (n = 6), and > 40001 km (n = 7), to determine mileage effects on the pollution emission of motorcycle exhaust.

Test Procedures

Chassis dynamometer measurements are designed to follow regulatory standards. They are arguably the most proven technology and are thus routinely used for road vehicles and engines (Traver *et al.*, 2002; Franco *et al.*, 2013). In this study, a certified laboratory set up by a motorcycle manufacturer was employed to examine the safety of the tested motorcycles and conduct chassis dynamometer testing. The main dynamometer system was integrated with a dilution tunnel, a constant volume system (CVS) unit (HORIBA, CVS-51S), and an exhaust gas analyzer (HORIBA, MEXA-8320). The test room temperature ranged from 25 to 30°C. Exhaust samples were collected for the entire testing cycle. The exhaust gas was initially mixed with air controlled by the CVS unit, and then the diluted mixture air flowed into the sampling bags and analyzer.

The motorcycle drive pattern was the ECE test cycle, which was adopted as the standard test procedure in Taiwan (TEPA, 1996). A complete test cycle is 780 seconds, including 240 seconds for the idle stage, 168 seconds for the acceleration stage, 228 seconds for cruising stages (30 and 50 km hr^{-1}), and 144 seconds for the deceleration stage.

The test gasoline was commercial unleaded gasoline with an octane rating of 95 and 10.2% methyl tert-butyl ether (MTBE) as the oxygenated additive. Oxygen content was 1.8 wt%, aromatics content was 30.0 vol%, olefins content was 10.8%, paraffins content was 10.7%, naphthenes content was 6.1%, benzene content was 0.52%,the heating value was 10275 kcal kg^{-1}, hydrogen content was 10.5 wt%, and carbon content was 88.2%. The fuel was provided by the manufacturer's laboratory; it was purchased from the largest petroleum refinery, China Petroleum Corporation (CPC), in Taiwan. The constituents and physicochemical characteristics of the tested gasoline were similar to those of regulated gasoline in the United States and Europe (European Commission, 2007; USDOE, 2014). Prior to each emissions test, the fuel was replaced and the engine cooled down for drive cycle testing the following day.

Gas Sampling and Analysis

Gas samples were collected for the entire cycle with an automated instrument, which took a constant sample volume (HORIBA, CVS-51S). The tailpipe of each motorcycle was connected directly to a sampling bag for the exhaust analysis during the entire testing cycle. The exhaust gas was analyzed using a non-dispersive infrared analyzer for CO and CO_2, a flame ionization detection analyzer for THC, and a chemiluminescence detection analyzer for NO_x. The background pollutant concentrations were also analyzed routinely and deducted from the test results. The results indicated that the background concentrations were approximately 1 ppm for CO, 4 ppm for THC, 0.2 ppm for NO_x, and 0.01% for CO_2, which were much lower than those of the sampling gas. The schematic diagram of the sampling equipment for criteria and organic air pollutants was the same as that in a previous work (Tsai *et al.*, 2003).

VOC Analysis

VOC samples were collected from the exhaust for the entire cycle. VOC species were pre-concentrated in a purge-and-trap system (Entech 7100 instrument) and subsequently analyzed in a GC/MS (HP-6890 gas chromatograph and HP 5973Nmass spectrometer). The GC was equipped with a fused silica capillary column (non-polar RTx-1, 105 m × 0.25 mm (ID) × 1.0 μm (film thickness)). Certified VOC standard gas (56 Enviro-Mat Ozone Precursor, Matheson, USA) was diluted with ultra-high-purity nitrogen (99.995%) in dilution bottles and served as the VOC species calibration standard. Perfluorotributylamine was used as the standard to evaluate the performance and quality of the GC/MS. The relative standard deviation for all VOCs was < 15%, the accuracy ranged from 92 ± 6% (propene) to 116 ± 8% (*p*-ethyltoluene), and the method detection limit varied from 0.04 (n-undecane) to 0.10 (propene) ppb. A total of 52 VOCs were analyzed: alkanes (27species), alkenes (9 species), and aromatics (16 species).

Carbonyl Analysis

The derivation technique was employed to determine the aldehyde species. After VOC sample collection of the entire cycle, the exhaust was immediately drawn from the Tedlar bag into a pre-coated 2,4-DNPH (dinitrophenylhydrazine) cartridge (LpDNPH S10 Cartridge, Supelco Inc., Bellefonte, PA, USA) at a sampling rate of 0.15 L min^{-1} for 2 min. The cartridges were then capped and stored until analysis. This cartridge had a capacity of 75 μg of formaldehyde, low background (< 0.35 μg of aldehydes), and a sampling temperature in the range of 10–100°C (USEPA, 1999). High-performance liquid chromatography (HPLC) was applied to separate and measure the DNPH derivatives of aldehydes. A Dionex system (Dionex TCC-100 HPLC column compartment and P680 HPLC pump) with an ultraviolet detector (Thermo Finnigan UV 6000LP), a computerized pump, and an eluent delivery system were combined as the HPLC system. The separation column was a SupelcosilLC18 column (25 cm × 4.6 mm (ID), 5-μm particles). The gradient program was conducted in this study. The eluent was 60:40 acetonitrile:water, the flow rate was 1.2 mL min^{-1}, the injection volume was 20 μL, and the detection wavelength was 360 nm. A total of 15carbonyl compounds were analyzed in this work. The recovery, reproducibility (in terms of coefficient of variation), and linearity (in terms of the R-squared value of the regression line) were in the ranges of 85–106%, 2.7–10.2%, and 0.994–0.999, respectively.

The breakthrough of carbonyls was measured using five sets of a series of two cartridges; the results indicated that the carbonyl species concentrations were undetectable in the second cartridge for all five sets prior to the experiments. Therefore, one cartridge was sufficient for the sorption of carbonyls in this study. The method detection limit varied from 0.15 (m-tolualdehyde) to 0.48 (formaldehyde) ppb.

Three duplicated analyses were done for each extracted carbonyl sample from the cartridge.

Statistical Analysis

Differences between groups were analyzed using two-way analysis of variance (ANOVA) followed by Scheffe's test. A p-value of < 0.05 was considered statistically significant.

RESULTS AND DISCUSSION

Regulated Pollutants for Various Phase Motorcycles

Fig. 1 shows the fuel economy of the selected motorcycles. The fuel economy was 34.7 ± 1.4 km L^{-1} for regulation phase V motorcycles, 32.6 ± 1.8 km L^{-1} for regulation phase IV motorcycles, and 29.5 ± 2.5 km L^{-1} for regulation phase III motorcycles. In Taiwan, the energy efficiency for new motorcycles was in the range of 36–39 km L^{-1} for various types of motorcycle and testing conditions (cold/hot start) in the period 2002 to 2010. Since 2011, the fuel efficiency standard has been set at 38 km L^{-1}. The fuel consumption of in-use motorcycles can be as much as 10–30% higher than the regulation standard. According to data from the Motorcycle Fuel Economy Guide, the fuel economy of 124- to 155-cc motorcycles produced by Honda, Piaggio, Vespa, and Yamaha in 2016 was in the range of 30.8–49.8 km L^{-1} (TWM, 2017). The results indicate that fuel economy decreased with increasing age and running mileage. The fuel economy of regulation phase III motorcycles was 20% lower than that of brand-new motorcycles. For the regulation phase V motorcycles (shown in Table 1), the average emission factor was 84.3 ± 40.9 g L^{-1} for CO, 29.4 ± 13.1 g L^{-1} for HC, 8.0 ± 2.3 g L^{-1} for NO_x, and 2,098 ± 109 g L^{-1} for CO_2 (CO_2 is not a regulated air pollutant in motorcycle exhaust). For motorcycles in compliance with regulation phase IV standards, the average emissions for CO, HC, NO_x, and CO_2 were 125 ± 42.6, 32.1 ± 13.8, 6.6 ± 0.94, 1,979 ± 112 g L^{-1}, respectively. The emission factor of regulation phase III motorcycles was 216 ± 74 g L^{-1} for CO, 54.0 ± 15.8 g L^{-1} for HC, 5.6 ± 1.8 g L^{-1} for NO_x, and 1,838 ± 128 g L^{-1} for CO_2.

The CO, HC, and CO_2 emissions and fuel consumption (L km^{-1}) of motorcycles follows the sequence regulation phase III motorcycles > regulation phase IV motorcycles > regulation phase V motorcycles. According to the statistical analysis (shown in Table 1), the CO and HC emissions and

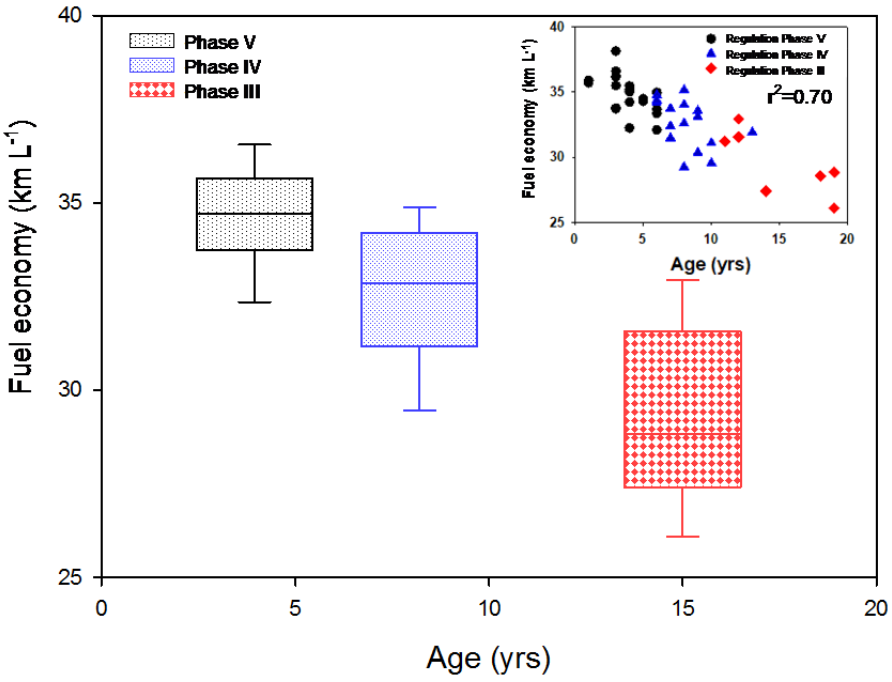

Fig. 1. Relationship between fuel economy and age for selected motorcycles.

Table 1. Exhaust emission (g L^{-1}) and fuel economy (km L^{-1}) for various motorcycles.

Regulation	CO (g L^{-1})	HC (g L^{-1})	NO_x (g L^{-1})	CO_2 (g L^{-1})	Fuel economy (km L^{-1})
Regulation phase III (n = 7)[1]	216 ± 71[2]	54 ± 16	5.57 ± 1.83	1838 ± 127	29.5 ± 2.46
Regulation phase IV (n = 16)	125 ± 43*	32 ± 14*	6.64 ± 0.94	1979 ± 112	32.6 ± 1.85*
Regulation phase V (n = 20)	84 ± 41*[#]	29 ± 13*	7.96 ± 2.28*[#]	2098 ± 109*[#]	34.7 ± 1.45*[#]

[1] n is motorcycle testing number.
[2] Mean value ± standard deviation.
[3] Significance versus regulation phase III: *$p < 0.05$.
[4] Significant difference between regulation phases IV and V: [#]$p < 0.05$.

fuel economy were significantly different (p-value < 0.05) between regulation phase III and IV motorcycles. For regulation phase III and V motorcycles, the CO, HC, NO_x, and CO_2emissions and fuel consumption were significantly different. For regulation phase IV and V motorcycles, only HC was insignificantly different (p-value > 0.05); the other items were different.

For the regulation phase IV motorcycles, there was a 6.2% fuel economy reduction over that of the phase V motorcycles, with a 48% increase in CO emission, a 9% increase in HC emission, and a 17% decrease in NO_x emission. Regulation phase III motorcycles presented a 15% fuel economy reduction over that of regulation phase V motorcycles. There was a 156% CO emission increase, an 84% HC emission increase, and a 30% NO_x emission decrease. This reduction in fuel economy and increase in emissions are attributable to the high running mileage (over 30,000 km) and age (over eight years) of the phase III motorcycles.

Fulper *et al.* (2010) found that newer-model-year vehicles have lower particulate matter emissions. May *et al.* (2014) found that the emissions of regulated gaseous pollutants (CO, THC, and NO_x) of newer light-duty gasoline vehicles (LDGVs) are lower than the emissions of older vehicles. The results in the literature, which are similar to the results in this study, indicate that older vehicles and those with higher running mileage emit relatively high amounts of exhaust pollutants.

Mileage Effect on Motorcycles with Various Running Mileages

Fig. 2 shows that the fuel economy was 35.5 ± 1.6 km L^{-1} at a running mileage of 5,231 ± 4,353 km, and decreased to 29.9 ± 2.6 km L^{-1} at a running mileage of 47,617 ± 8,568 km. CO (Fig. 3(a)) and HC (Fig. 3(b)) emissions increased with increasing running mileage. The results indicate that the average CO emission was 61 ± 30 g L^{-1} at 5,231 ± 4,353 km, increasing to 203 ± 75 g L^{-1} at 47,617 ± 8,568 km. HC emission was 27 ± 11 g L^{-1} at 5,231 ± 4,353 km, increasing to 47 ± 19 g L^{-1} at 47,617 ± 8,568 km. Hydrocarbon emission increased significantly (p-value < 0.05) at running mileages of over 30,000 km, which may be attributed to incomplete combustion and failure of the catalyst system. However, the NO_x emission (Fig. 3(c)) decreased with increasing mileage, decreasing from 9.1 ± 2.5 g L^{-1} at 5,231 ± 4,353 km to 5.4 ± 1.2 g L^{-1} at 47,617 ± 8,568 km.

The average running mileage increase from 5,231 to 47,617 km corresponded to a 16% decrease in fuel economy, a 3.3-fold increase in CO emission, a 1.7-fold increase in HC emission, and a 41% reduction in NO_x emission.

Some studies have investigated the mileage and age effects on motorcycle exhaust constituents in the real world (Tsai *et al.*, 2000; Chen *et al.*, 2009). A slight correlation was observed between CO and HC emissions and mileage and age (Tsai *et al.*, 2000). In addition, CO and HC emissions and fuel consumption increased with increasing odometer mileage (Tsai *et al.*, 2017a), but these findings vary widely. Therefore, more motorcycle exhaust emission testing is required to obtain baseline information for the development of motorcycle air pollution control strategies.

VOC Emission for Motorcycles with Various Running Mileages

Based on fuel economy, the emission factors of a total of 67 VOCs were 19.1 ± 9.7 g L^{-1} for a running mileage of 5,231 ± 4,353 km and 47.1 ± 19.8 g L^{-1} for a running

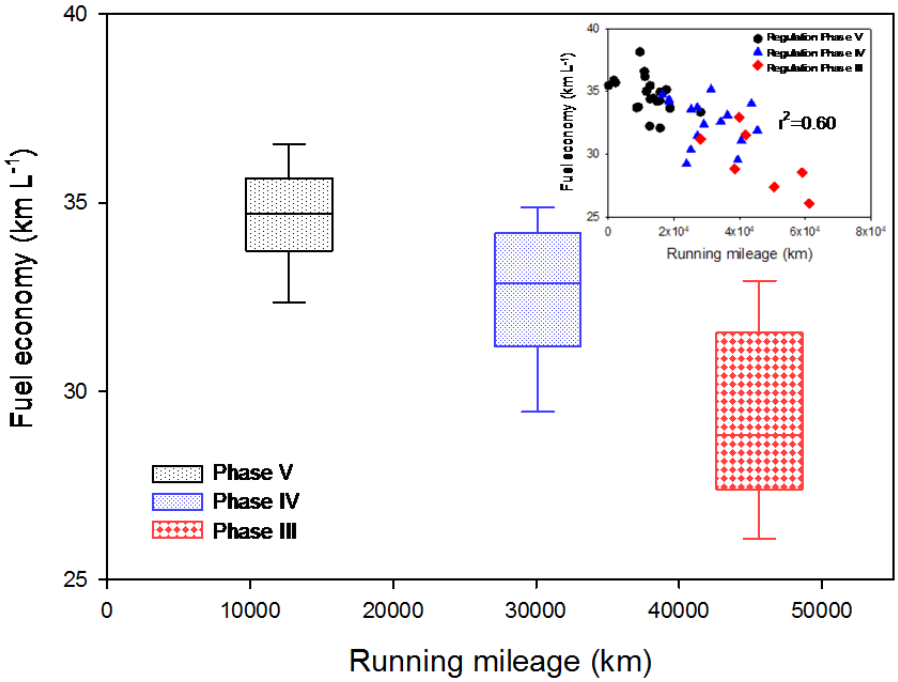

Fig. 2. Relationship between fuel economy and running mileage for selected motorcycles.

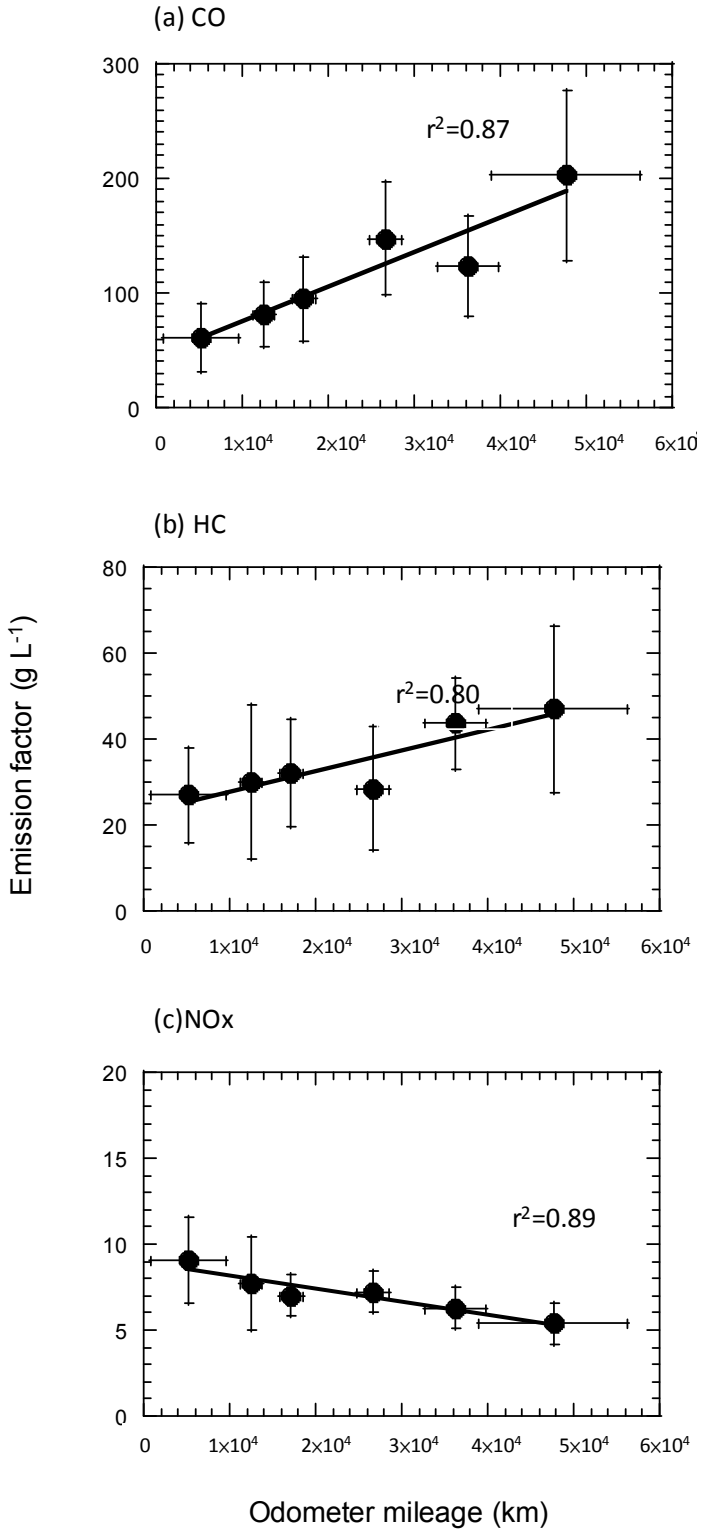

Fig. 3. Emission factors of (a) CO, (b) HC, and (c) NO_x of selected motorcycles with various running mileages.

mileage of 47,617 ± 8,568 km (shown in Fig. 4). For various running mileages, the major VOCs were paraffins (38–45%), olefins (9.7–15%), aromatics (38–48%), and carbonyls (1.8–3.0%). Paraffins and aromatics were the major VOC species, contributing over 80% of the VOC emission in motorcycle exhaust.

The emission of paraffins was 9.0–19 g L^{-1} for various running mileages; isopentane, n-pentane, 2,3-dimethylbutane, 3-methylpentane, n-decane, and n-undecane were the most abundant species (shown in Fig. 5(a)). 1-butene, propene, isoprene, and 1-hexene contributed about 70–82% of the analyzed olefin species (the average emission factors

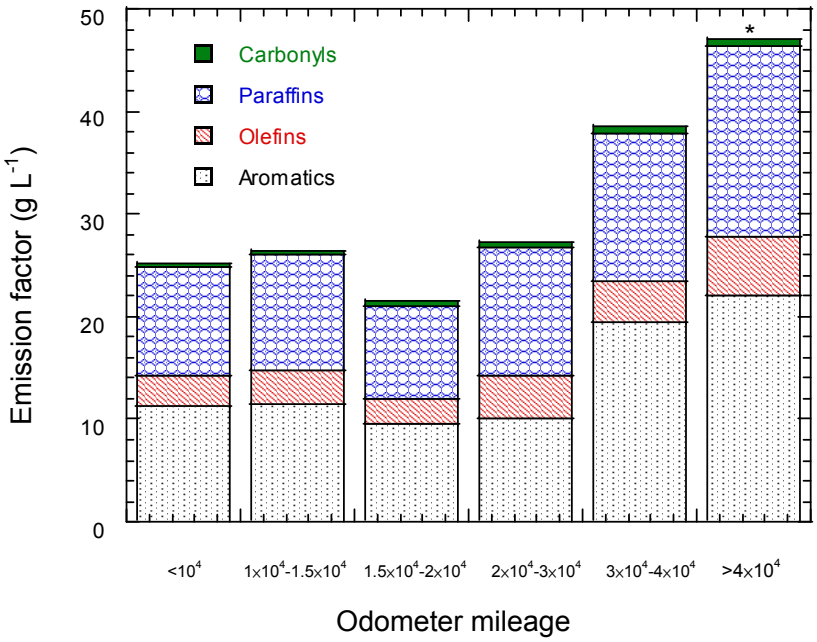

Fig. 4. Emission factors of paraffins, olefins, aromatics, and carbonyls for selected motorcycles with various running mileages (significance versus group with mileage < 10,000 km: *$p < 0.05$).

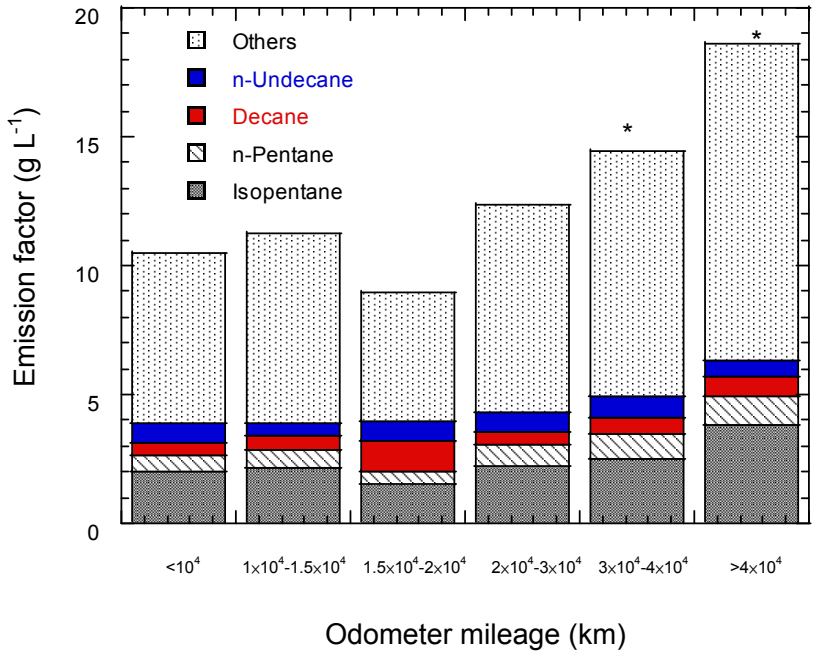

Fig. 5(a). Emission factors of dominant paraffins of selected motorcycles for different running mileage (significance versus group with mileage < 10,000 km: *$p < 0.05$).

ranged from 2.2 g L^{-1} for a running mileage of 5,231 km to 5.7 g L^{-1} for 47,617 km, as shown in Fig. 5(b)). Toluene, m,p-xylene, o-xylene, trimethylbenzene, m-ethyltoluene, ethylbenzene, and benzene were the dominant aromatic species, with total aromatics ranging from 8.9 to 22 g L^{-1} for average running mileages of 5,231 to 47,617 km (shown in Fig. 5(c)). The dominant aromatic species contributed 68–79% of the analyzed aromatic species.

Formaldehyde, acetaldehyde, acetone, butyraldehyde, benzaldehyde, isovaleraldehyde, and valeraldehyde were the most abundant carbonyl species, contributing about 78–84% of carbonyl compounds. Fifteen carbonyl species increased from 0.41 to 0.80 g L^{-1} for average running mileages of 5,231 to 47,617 km (shown in Fig. 5(d)).

Although the VOC species emission increased with increasing running mileage of motorcycles, based on the statistical analysis, the increase of the average VOC group emission factor with increasing mileage was insignificant

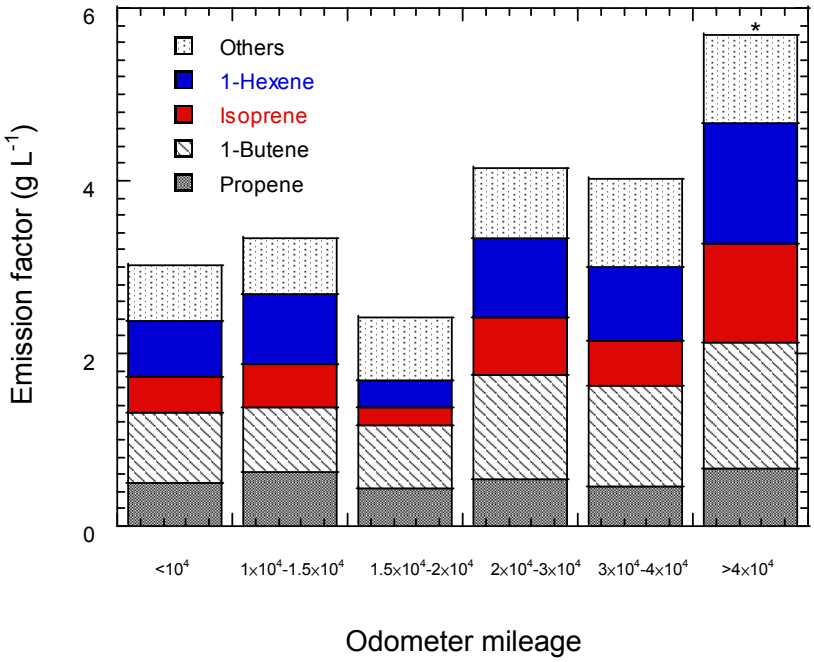

Fig. 5(b). Emission factors of dominant olefins of selected motorcycles for different running mileage (significance versus group with mileage < 10,000 km:*$p < 0.05$).

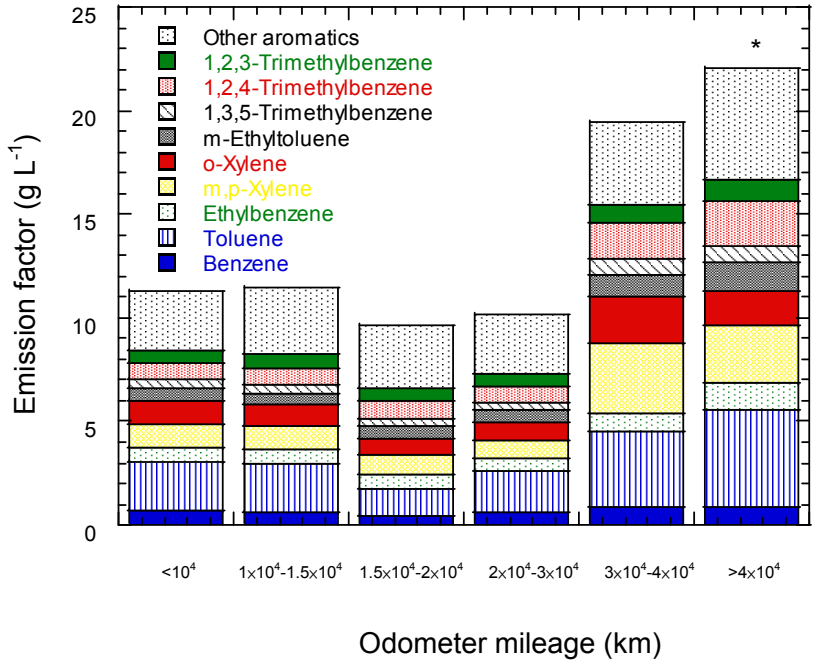

Fig. 5(c). Emission factors of dominant aromatics of selected motorcycles for different running mileage (significance versus group with mileage < 10,000 km: *$p < 0.05$).

(p-value > 0.05) within 40,000 km. For running mileages of over 40,000 km, paraffins, olefins, aromatics, carbonyls, and total of 67 VOCs emissions significantly increased (p-value < 0.05) compared to those of the motorcycle with a running mileage of less than 10,000 km. In addition, some VOC groups and 67 VOCs emissions decreased for odometer mileages of 15,000–20,000 km. Motorcycle exhaust emission is affected by many factors, including equipment (e.g., emission control system and motorcycle and fuel types), utilization parameters (e.g., motorcycle age and odometer mileage, inspection and maintenance), operating and driving conditions (e.g., cold/hot starts, travel volume, and idle, acceleration, deceleration, and average speed fraction during travel), and ambient parameters (e.g., temperature and humidity) (Tsai *et al.*, 2017a). The selected motorcycles and sample size limitation could be the reasons, the

difference in emission factors was found to be insignificant in the statistical analysis.

Over the average running mileage range of motorcycles, from 5,231 to 47,617 km, paraffin emissions increased 2.45 fold, olefins 2.52 fold, aromatics 2.49 fold, and carbonyls 1.92 fold. Pang *et al.* (2014) indicated that the average VOCs in tailpipe emissions of a 2003 fleet decreased by about 80% over those of a 1995 fleet, suggesting that older vehicles emit more VOCs in exhaust.

Gasoline, a mixture of C_4–C_{12} complex hydrocarbons, includes paraffins, olefins, naphthene, and aromatics (Pradelle *et al.*, 2015); therefore, incomplete combustion could cause the emission of various speciated VOCs. The large paraffins decompose during combustion via hydrogen abstraction (abstractors: H, OH, O, CH_3, HO_2, and O_2) and thermal decomposition to form radicals that could subsequently decompose from the β scission to an olefin and a radical forwarded to react with other compounds (Allara and Shaw, 1980; Zhang, 2005).

May *et al.* (2014) indicated that gasoline vehicles can emit over 5–10 times higher NMHC during a cold start compared to a warm start, and that pre-LEV (model years before 1994) vehicles can emit from several grams to more than 50 grams NMHC per kg-gasoline, which is about 10 times the NMHC emission of vehicles with model years after 2004 during a cold start. The non-methane organic gas constituents were 40% normal/branched alkanes, 15% single-ring aromatics, 10% olefins/naphthenes, and 25% unidentified species in LDGVs. A high alkane fraction was found in LDGV exhaust, whereas a high aromatic fraction was found in motorcycle exhaust in this work. The high combustion efficiency, which leads to the decomposition of aromatic constituents, and gasoline composition could be important reasons for LDGV exhaust. Olefins are important sources of allylic radicals, which form the precursors of aromatic species such as propyne, butyne, butene isomers, and most unsaturated species (Zhang, 2005; Zhang *et al.*, 2007a). The above results could be important reasons for the formation of aromatic species in motorcycle exhaust.

The formation of aromatic species and branched aromatic species (benzene, toluene, and xylene) in n-butane combustion systems can be enhanced by propargyl (H_2CCCH) recombination, a propargyl and allyl(C_3H_5) combination reaction and H-atom catalysis, and an allyl and propargyl radical reaction that leads to the formation of benzene and triggers a series of radical reactions (such as propargyl, allyl, 1-methylallenyl, and cyclopentadienyl radicals) (Marinov *et al.*, 1998).

Peroxide radicals can react with olefins via an addition reaction witha double bond to form organic compounds during combustion (Pereira and Pasa, 2006). Peroxyallyl radicals are forwarded to an addition reaction with a carbon double bond and lead to the formation of $\cdot CH_2CHO$ radicals and formaldehyde (Lodhi and Walker, 1991; Battin-Leclerc, 2008). These abstraction reactions yield hydroxymethyl radicals (CH_2OH or CH_3O) that generate formaldehyde through further reactions (Held and Dry, 1998). Aromatic aldehydes and ketones can be formed by the reaction of alkyl radicals with oxygen in gasoline combustion systems (Battin-Leclerc, 2008). The free radical chain processes involve a series formation of VOCs (Heneghan and Zabarnick, 1994).

Volckens *et al.* (2008) showed that the main aromatic species included toluene, 1,2,4 trimethylbenzene, 1-methyl-3-ethylbenzene, and benzene, and that the major paraffin species included isopentane, isooctane, n-pentane, n-butane, n-hexane, 2-methylpentane, and 2,3,4-trimethylpentane for gasoline combustion. The main olefins included propene, 1-hexene, isobutylene, and 1-butene, and the abundant carbonyls included formaldehyde, acetylaldehyde, benzaldehyde, and acetone in the exhaust of gasoline combustion (Schuetzle *et al.*, 1994; Volckens *et al.*, 2008; May *et al.*, 2014).

Ozone Formation Potential of Motorcycles

The maximum incremental reactivity factors (Carter, 2009) were calculated to determine the OFP of VOCs from motorcycle exhaust. The OFP values in the exhaust of a total of 67 VOCs were 90.7–112 g-O_3 L^{-1} for the average motorcycle running mileage, ranging from 5,231 to 26,715 km (shown in Table 2). The OFP significantly increased to 174 g-O_3 L^{-1} for the an average motorcycle running mileage of 36,615 km and to 204 g-O_3 L^{-1} for an average motorcycle running mileage of 48,917 km. The OFP fraction profile was similar for motorcycles with running mileages, with 10–13% for paraffins, 22–34% for olefins, 50–67% for aromatics, and 2–3% for carbonyls.

The highest contribution to OFP was attributed to aromatic chemicals for the test motorcycles. For aromatic species, the high-OFP species were xylene (13.0 g-O_3 L^{-1} for m,p-xylene and 9.6 g-O_3 L^{-1} for o-xylene), toluene (10.5 g-O_3 L^{-1}), 1,2,4-trimethylbenzene (10.3 g-O_3 L^{-1}), 1,2,3-trimethylbenzene (8.1 g-O_3 L^{-1}), 1,3,5-trimethylbenzene (6.3 g-O_3 L^{-1}), and ethyltoluene (6.8 g-O_3 L^{-1}, with about 80% attributed to m-ethyltoluene). The OFP of most paraffins was less than 4.0 g-O_3 L^{-1}. Isopentane and n-pentane were the major OFP paraffin species, with an average OFP of less than 4.0 g-O_3 L^{-1} for both species.1-butene, isoprene, propene, and 1-hexene were high-OFP olefin species, with average OFP values of 13.7, 11.7, 7.7, and 7.4 g-O_3 L^{-1}, respectively.

Low carbonyl species were determined due to their low emission in motorcycle exhaust. Formaldehyde and acetaldehyde contributed 0.47–1.18 and 0.58–0.97 g-O_3 L^{-1}, respectively, for the test motorcycles with different running mileages. The average OFP of acrolein, propionaldehyde, crotonaldehyde, and butyraldehyde was 0.27, 0.19, 0.12, and 0.20 g-O_3 L^{-1}, respectively.

The average running mileage of the motorcycles ranged from 5,231 to 47,617 km; in this range, the OFP increased 1.81 fold for paraffin emission, 1.83 fold for olefins, 2.03 fold for aromatics, and 1.77 fold for carbonyls. There was a 1.95-fold increase for the OFP of the 67 VOCs.

CONCLUSION

The fuel consumption of regulation phase III motorcycles was found to be 20% higher than that the brand-new

Table 2. Ozone formation potential of volatile organic compounds in exhaust of motorcycles with various running mileages.

Mileage range (km)	Formula	0–10,000 (n = 6)	10,001–15,000 (n = 8)	15,001–20,000 (n = 8)	20,001–30,000 (n = 8)	30,001–40,000 (n = 6)	> 40,001 (n = 7)
Toluene	C_7H_8	9.12	8.86	5.01	7.68	14.07	18.18
m,p-Xylene	C_8H_{10}	9.06	8.28	6.96	6.88	25.70	20.82
o-Xylene	C_8H_{10}	7.95	7.55	6.32	6.50	16.81	12.59
1-Butene	C_4H_8	7.62	7.08	6.92	11.40	11.06	13.67
1,2,4-Trimethylbenzene	C_9H_{12}	7.32	7.21	7.21	6.76	14.57	18.77
1,2,3-Trimethylbenzene	C_9H_{12}	6.41	7.20	6.66	6.23	10.03	12.27
Propene	C_3H_6	5.81	7.04	4.93	6.18	5.19	7.72
1,3,5-Trimethylbenzene	C_9H_{12}	4.79	5.18	4.59	4.79	9.09	9.09
m-Ethyltoluene	C_9H_{13}	4.34	3.81	4.02	3.88	7.83	9.73
Isoprene	C_5H_8	4.23	5.25	2.11	6.81	5.39	11.66
m-Diethylbenzene	$C_{10}H_{14}$	3.61	4.24	4.04	3.60	5.07	6.46
1-Hexene	C_6H_{12}	3.43	4.30	1.67	4.80	4.48	7.41
Isopentane	C_5H_{12}	2.77	2.96	2.07	3.03	3.45	5.23
cis-2-Pentene	C_5H_{10}	2.60	2.42	3.29	2.37	3.53	2.52
o-Ethyltoluene	C_9H_{13}	2.37	2.60	3.17	2.36	3.73	4.71
Ethylbenzene	C_8H_{10}	2.07	2.21	2.01	1.86	2.52	3.86
p-Ethyltoluene	C_9H_{13}	1.79	2.06	1.87	1.81	3.00	4.34
trans-2-Pentene	C_5H_{10}	1.63	1.60	1.91	2.86	3.38	3.49
Formaldehyde	HCHO	0.47	0.61	0.71	0.90	1.08	1.18
Acetaldehyde	CH_3CHO	0.65	0.58	0.81	0.91	0.87	0.97
20 species		88	91	76	92	151	175
Paraffins		13	14	10	15	17	23
Olefins		28	31	24	38	37	52
Aromatics		62	62	55	55	116	126
Carbonyls		2.0	1.9	2.4	2.7	2.7	3.5
67 VOCs		105	109	91	111	174	204

motorcycles. Due to their high running mileage (over 30,000 km) and age (over eight years), regulation phase III motorcycles had a 15% fuel economy reduction, a 156% CO emission increase, an 84% HC emission increase, and a 30% NO_x emission decrease compared with those of regulation phase V motorcycles. The results indicate that motorcycle fuel economy decreased with increasing age and running mileage.

High-running-mileage motorcycles had lower fuel economy (a reduction rate of about 1.3 km L^{-1} per 10,000 km) compared to that of low-running-mileage motorcycles. They also had a high air pollutant emission rate (34 g L^{-1} per 10,000 km and 4.7 g L^{-1} per 10,000 km for CO and HC, respectively) and reduced NO_x emission (0.87 g L^{-1} per 10,000 km) due to the combustion efficiency from exhaust. The average running mileage was between 5,231 and 47,617 km; in this range, the increase of paraffin species was 2.60 g L^{-1} per 10,000 km, that of olefin species was 0.81 g L^{-1} per 10,000 km, that of aromatic species was 3.11 g L^{-1} per 10,000 km, and that of carbonyl species was 0.08 g L^{-1} per 10,000 km. The 67 VOC species increased by 6.61 g L^{-1} per 10,000 km. The increase of OFP was 2.41 g L^{-1} per 10,000 km for paraffin species, 5.55 g L^{-1} per 10,000 km for olefin species, 15.1 g L^{-1} per 10,000 km for aromatic species, and 0.36 g L^{-1} per 10,000 km for carbonyl species. The OFP was 23.4 g-O_3 L^{-1} per 10,000 km for the 67 VOC species.

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