# Characteristics of polycyclic aromatic hydrocarbons emissions of palm-biodiesel blends

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Pure diesel fuel and biodiesel/diesel blends are widely used as important materials in manufacturing and transportation industries because of increasing industrialisation rate and consumption of energy worldwide. However, it causes environmental damages because of spills during their extraction, transportation, processing and distribution. The spill simulations with pure diesel and pure palm-biodiesel as well as their blends have been carried out in laboratory, aiming at analysing their polycyclic aromatic hydrocarbons. The spill simulations with pure diesel and pure palm-biodiesel as well as their blends have been carried out in laboratory, aiming at analysing their polycyclic aromatic hydrocarbons by using chromatography–mass spectrometry analysis. Total 14 compounds of polycyclic aromatic hydrocarbons were found in this study that known as toxicity potential stated by United States of Environmental Protection Agency. The results showed that higher proportion of biodiesel fuel in the mixture resulted lower amount of polycyclic aromatic hydrocarbons. Most of quantification limits obtained for all of these compounds exceeded the permitted limits recommended by Netherland, UK and Canada soil quality guidelines.

**Keywords:** PAHs, Biodiesel/diesel-contaminated soil, Extraction, GC–MS, Biodiesel/diesel blends, Palm-based biodiesel

## Introduction

The fossil fuel resources are decreasing day by day as number of motor vehicles increases. The scarcity of known petroleum reserves will make renewable energy sources more attractive. An alternative fuel to petroleum diesel must be technically feasible, competitive, environmentally acceptable and easily available. Currently, the best option for a petroleum diesel fuel substitution is biodiesel. The fuel strategy of the EU (Biofuels Directive 2003/30/EU) has resulted in the emergence of mixtures of both types of fuels (biodiesel and their diesel blends) on the markets of many countries. Since then, biodiesel fuels have attracted increasing attention worldwide as blending components or direct replacements for diesel fuel in conventional diesel engines. It can be legally blended and used in many different proportions such as B2 (mixture of 2% biodiesel and 98% diesel), B5 (mixture of 5% biodiesel and 95% diesel), B20 (mixture of 20% biodiesel and 80% diesel) and B100 (100% biodiesel). However, the most common biodiesel blend is B20, which qualifies for fleet compliance under the Energy Policy Act of 1992.[1] These benefits are good evident that pure biodiesel and their diesel blends will be used in the energy sector attending to transport vehicles driven by conventional diesel engines in the near future; however, this means new threats to the environment in case of their spillage.

As occurs to the diesel fuel, the commercialisation of biodiesel or their diesel blends on the market of many countries can create environmental damages because of accidental spills such as leakage from underground storage tank, pipelines and container tank truck or rail accidents. Continuous low-level inputs are not often noticed, and possibly pose a serious threat to the environment as contamination accumulates. These contaminants contain polycyclic aromatic hydrocarbons (PAHs) in soil which is toxic to humans, plants and soil microorganisms.[2]

Polycyclic aromatic hydrocarbon, also known as polynuclear aromatic hydrocarbons, are group of chemical compounds containing carbon (C) and hydrogen (H) atoms, composed of two or more fused aromatic rings in linear, angular and cluster arrangements.[3] They originated mainly from human activities, including incomplete combustion of carbon-based fuels and pyrolysis of

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organic matter.[4] Polycyclic aromatic hydrocarbon are also formed from natural sources such as forest fires and volcanic eruptions. However, most PAHs are released to the environment from anthropogenic sources such as oil spills and the burning of fossil fuels.[5] Petroleum diesel containing PAHs raise substantial concern because of their widely known toxic potential such as mutagenic, teratogenic, carcinogenic, photo-induced toxicity and endocrine-disrupting activities.[6] Therefore, up to 16 compounds of PAHs are listed by the US Environmental Protection Agency (US EPA) and the European Community as priority pollutants. They are naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorine, fluoranthene, benz[*a*]anthracene, chrysene, pyrene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, dibenz[*a,h*]anthracene, benzo[-*g,h,i*]perylene and indeno[*1,2,3-cd*]pyrene. The most potent carcinogens among the PAHs are the crysene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, dibenz[*a,h*]anthracene, benzo[*g,h,i*]perylene and indeno[*1,2,3-cd*]pyrene.[7]

Previously, Leme[8] studied the cytotoxic and genotoxic potential of soy-based biodiesel (B100), diesel (D100) and their blends (B5, B20 and B50) contaminated in soil. Result of PAHs chemical analysis from the spill simulations shows that sample D100 contains higher amount of total PAHs followed by B5, B20, B50, B100 and control. Their results verified that soy-based biodiesel does contain lower PAHs compared to other samples.

Therefore, this study aims on PAHs contamination in soil for different origins, which is palm-based biodiesel. The concentration of PAHs in the contaminated soil was examined and evaluated in spillage simulation. The level of PAHs in biodiesel and diesel was compared. Our study is significant for understanding the background of PAHs level in biodiesel/diesel contaminated soil.

## Materials and methods

The mixed standard solution of 16 EPA-PAHs was purchased from USA and further diluted to the concentration of 0·5, 1·0, 3·0 and 5·0 ppm. The surrogate, 2-fluorobiphenyl (2-FBP) and d10 anthracene, silica gel 60 (0·040–0·063 mm) as well as anhydrous sodium sulphate were also purchased from USA. All solvents (hexane and acetone) were prepared for analytical purity and redistilled in all-glass system. The silica gel was activated in dry oven at 130°C for 16 hours while anhydrous sodium sulphate was heated at 400°C for 4 hours.

## Experiments and sample preparation procedures

The diesel (EN 590) was obtained from diesel pump station at Parit Raja, Johor and biodiesel (palm-based biodiesel produced by transesterification with methanol) from Biodiesel Pilot Plant, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia (UTHM).

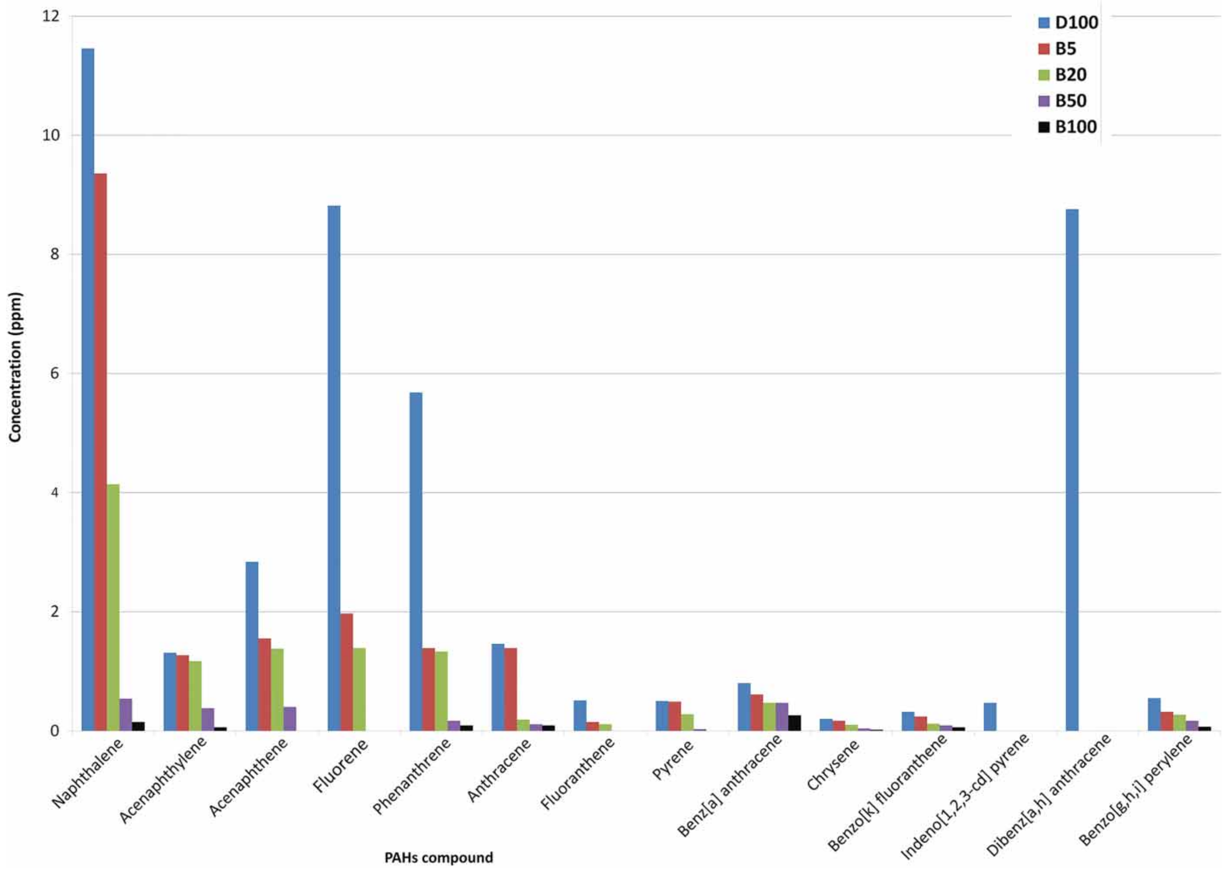
The spill simulations with biodiesel, diesel and their blends in soils were performed according to Taylor[9] with modifications. A 5% of biodiesel (20 mL) and 95% of diesel (480 mL) were added to other container containing 1000 g of soil for sample B5. This step was repeated by replacing the mixture of 5% of the biodiesel and 95% of the diesel with 20% of the biodiesel (100 mL) and 80% diesel (400 mL), 50% biodiesel (250 mL) and 50% diesel (250 mL), 100% biodiesel (500 mL) and then 100% diesel (500 mL), for samples B20, B50, B100 and D100, respectively. After that, samples were incubated in dark condition at room temperature before further testing parameters.

The soil samples were extracted according to a US EPA Method 3540C.[10] According to the method, a 10 g of dried soil samples were ground with 10 g of anhydrous sulphate. The samples were spiked with 1 mL of 2-fluorobiphenyl and extracted using mixtures of hexane/acetone via reflux circle for about 24 hours at 4–6 cycles per hour. The obtained extracts were then cleanup based on standard column chromatograph cleanup technique in a US EPA Method 3630.[11] After that, the collect elutes were concentrated using dry nitrogen gas blow down technique and submitted to gas chromatography–mass spectrometry (GC–MS) qualitative analysis aiming to identify PAHs compounds. For GC–MS qualitative analysis, the extracts were analysed using a gas chromatograph (Agilent model TD-6890) coupled to TD-7683 autosampler, capillary column fused silica: FactorFour HP-5 ms, 30 m × 0·25 mm × 0·25 μm (5% phenyl, 95% methylpolisiloxane) from Agilent Inc. The instrument conditions used for analysis of extracts by GC–MS were as follows: acquisition mass range 30–450 Da, ionisation mode by electronic impact (70 eV). The injection volume was 1·0 μL in splitless mode, injector temperature 325°C helium as carrier gas at 1·5 mL per minute, linear velocity: 45 cm per second. Oven temp.: 50°C (hold 1 minutes) to 200°C at 25°C per minute to 326°C at 8°C per minute.

## Results and discussion

The chemical analysis of the pure diesel extracts proved the presence of different PAHs whose main pollutant was naphthalene. Most of the PAHs compounds have higher concentration in pure diesel (D100) than biodiesel (B100) and their diesel blends (B5, B20 and B50) extracts. Therefore, sample D100 is considered to have more toxic substances than other samples especially B100. In this study, sample D100 was over the limit of Netherland 'Maximum Permissible Concentration for PAHs', The New Dutchlist United Kingdom and Canadian Soil Quality Guidelines 'Carcinogenic and other PAHs'. In this sensed, spillage of diesel in soils can restrain microbial activities and also result in larger health impact because of their toxic potential such as cytotoxic, genotoxic, mutagenic, ferotegenic, carcinogenic, photo-induced toxicity and endocrine-disrupting activities.[12] According to Schirmer[13] PAHs can cause cytotoxicity directly or after their metabolic activation via cytochrome P450. They also stated that two- and three-ring PAHs such as naphthalene, acenaphthylene, acenaphthene and phenanthrene are recognised as direct cytoxic inducers.

No PAH was detected in control sample throughout this experiment possibly due to no addition of biodiesel and diesel in sample. Summarised in Fig. 1 is amount of PAHs examined from GC–MS qualitative analysis for all samples. The compounds such as acenaphthene, fluorene, fluoranthene, pyrene, indeno (1, 2, 3-c, d)




**1 Summarised of PAHs detected in soil samples from the spill simulations**

pyrene and dibenz (a, h) anthracene were not detected in sample B100 as shown in Table 1. No contains of fluorene, fluoranthene and indeno (1, 2, 3-c, d) pyrene as well as dibenz (a, h) anthracene were detected in sample B50. Meanwhile for samples B5 and B20 compound of indeno (1, 2, 3-c, d) pyrene and dibenz (a, h) anthracene were not detected. The results show that the highest amount of naphthalene, acenaphthylene, phenanthrene, anthracene, benz (a) anthracene, chrysene, benzo (k) fluoranthene, benzo (g, h, i) perylene were found in sample D100 followed by B5, B20, B50 and B100. The highest amount of acenaphthene and pyrene was found in sample D100 followed by B5, B20 and B50. Meanwhile, the amount of fluorene and fluoranthene was found to be highest in sample D100 followed by B5 and B20. The indeno (1, 2, 3-c, d) pyrene dibenz (a, h)

**Table 1 PAHs detected in soil samples from the spill simulations**

| PAHs | SC (ppm) | D100 (ppm) | B5 (ppm) | B20 (ppm) | B50 (ppm) | B100 (ppm) | Standard (ppm) |
|---|---|---|---|---|---|---|---|
| Naphthalene | nd | 11·46 | 1·36 | 1·14 | 0·44 | 0·05 | 0·14* |
| Acenaphthylene | nd | 1·31 | 1·27 | 1·17 | 0·38 | 0·06 | 0·01† |
| Acenaphthene | nd | 2·84 | 1·55 | 1·38 | 0·40 | nd | 0·01† |
| Fluorene | nd | 8·82 | 1·97 | 1·39 | nd | nd | 0·01† |
| Phenanthrene | nd | 5·68 | 1·39 | 1·33 | 0·17 | 0·09 | 0·51* |
| Anthracene | nd | 1·46 | 1·39 | 0·19 | 0·11 | 0·09 | 0·12* |
| Fluoranthene | nd | 0·51 | 0·15 | 0·11 | nd | nd | 0·04† |
| Pyrene | nd | 0·50 | 0·49 | 0·28 | 0·03 | nd | 10‡ |
| Benz[a] anthracene | nd | 0·80 | 0·61 | 0·47 | 0·47 | 0·26 | 0·25* |
| Chrysene | nd | 0·20 | 0·17 | 0·1 | 0·04 | 0·02 | 0·05‡ |
| Benzo[k] fluoranthene | nd | 0·32 | 0·24 | 0·12 | 0·09 | 0·06 | 0·5‡ |
| Indeno[1,2,3-c,d] pyrene | nd | 0·47 | nd | nd | nd | nd | 0·05‡ |
| Dibenz[a,h] anthracene | nd | 8·76 | nd | nd | nd | nd | 0·7† |
| Benzo[g,h,i] perylene | nd | 0·55 | 0·32 | 0·27 | 0·17 | 0·07 | 0·05‡ |
| Total | nd | 43·21 | 10·91 | 7·95 | 2·3 | 0·7 | |

SC, soil control; D100 = pure diesel; B5 = blend 5% biodiesel + 95% diesel; B20 = blend 20% biodiesel + 95% diesel; B50 = blend 50% biodiesel + 50% diesel, B100 = pure biodiesel.
*Based on Netherlands 'Maximum Permissible Concentration' (MPCs) for PAHs.
†Based on Canadian Council of Ministers of the Environment environmental quality guidelines for PAHs.
‡Based on The New Dutchlist United Kingdom.
nd, not detected (below detection limit).

anthracene were only found in sample D100 at 0·47 and 8·76 ppm, respectively. Overall, this study found that the trend of amount of PAHs was highest in sample D100 followed by B5, B20, B50 and B100.

Biodiesel degrades about four times faster than petroleum diesel. In fact, it contains 11% oxygen by weight which improves the biodegradation process and further leading to an increased level of quick biodegradation.[14] The amount of PAHs found in sample B100 was lower than other samples especially D100 possibly because of the differences on proportions and level of biodegradability in biodiesel blends. It does contain sulphur and phosphate[15–17] as well as PAHs with high biodegradability.[18]

Typically, biodiesel is more easily biodegraded and less toxic than diesel. Zhang[18] has verified that biodiesel can promote and speed up the biodegradation of diesel by means of co-metabolism, that is a term used to describe the process in which microorganisms use a second substrate (readily degradable) as the carbon (energy) source to degrade the first substrate which otherwise is scarcely attacked by the microorganisms when it is the sole carbon source. Besides, fuel spillages in soil were influenced by several environmental factors which can promote changes in the chemical structures of pollutants[8] in this case for PAHs. Therefore, further studies combining the environmental factors and accurate chemical analyses are recommended for additional elucidate.

## Conclusion

In conclusion, soil polluted with petroleum-based diesel has higher PAHs compared to biodiesel blends and pure palm-based biodiesel. The amount of PAHs in soils contaminated was decreased with the increase of bio-diesel proportion in blends. Even though biodiesel is considered an eco-friendly choice to petroleum-based diesel, this study found the level of some PAHs was exceeding the permissible limit stated in regulated guidelines. This condition could create a world-wide problem of diesel and biodiesel in soil contamination which requires further decontamination. Nevertheless, other several environmental factors that influence change of PAHs during fuel spillages in soil should be considered and examined as future necessary tools.

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