



Full Length Article

Polycyclic aromatic hydrocarbons in diesel emission, diesel fuel and lubricant oil



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HIGHLIGHTS

- PAHs were evaluated in diesel vehicle exhaust, in diesel fuel and in lubricant oil.
- 95–99% of the PAHs in diesel were destroyed, converted, or retained in the lubricant oil.
- PAHs with higher concentrations in diesel also had higher exhaust emission factors.
- The PAH profile in lubricant oil was similar to diesel and in exhaust.
- 4.5% of the total PAHs were present in nanoparticles smaller than 56 nm.

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ABSTRACT

This study determined the priority PAHs concentrations in diesel fuel sold in Brazil and in lubricant oil sampled in different usage times. The solid phase extraction (SPE) technique using florisil (magnesium silicate) as solid phase was used to separate the fraction containing aromatic components present in the diesel fuel and lubricating oil samples. The measurements were performed by gas chromatography coupled to mass spectrometry. The PAH priority profile in lubricant oil was similar to the PAH profile in diesel where Naphthalene, Phenanthrene and Pyrene were dominant. The PAHs concentration in Brazilian diesel fuel sample were compared with the emission factors of their PAHs respective in exhaust of a vehicle fueled with the same Brazilian diesel fuel in order to estimate how much of the PAHs present in diesel remains unchanged during combustion. The ratio between the PAHs emission factors in exhaust ($\mu\text{g L}^{-1}$ diesel) and their respective concentrations in diesel fuel ($\mu\text{g L}^{-1}$) ranged from 0.01 ± 0.02 to 0.05 ± 0.029 , depending on the PAH. These values indicate that at least 95–99% of the PAHs identified in diesel fuel were destroyed, converted into other compounds during the combustion, and/or retained in the lubricant oil reservoir. On the other hand, PAHs with higher concentrations in diesel also had higher exhaust emission factors, which suggests that the PAHs from diesel have a contribution to total PAH emissions. Therefore, reducing the PAHs content in diesel will probably contribute to curbing emissions of these compounds and help improve air quality.

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1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are known worldwide for their potential carcinogenic and mutagenic effects [1–4]. Because of these effects, the United States Environmental Protection Agency (U.S.EPA) listed sixteen PAHs as priority pollutants. Table 1 shows the number of aromatic rings and molecular mass of 16 priorities PAHs.

PAHs are introduced into the environment mainly from processes involving combustion, and diesel engines are significant sources of PAH emissions into urban air [5,6]. Despite the dangers

that PAHs present to humans, there are no motor vehicle emission limits for these compounds in most countries. The PAHs emitted by diesel vehicles can be associated with their presence in the unburned fuel (petrogenic source) and may be formed during combustion (pirogenic source) [5,3,7–9]. During engine use, lubricating oil can accumulate significant amounts of PAHs and therefore influence PAH emissions [9,10]. Combustion in diesel engines is very complex and involves a series of reactions and physical processes. Factors that favor PAH formation and/or destruction during combustion and the relative contributions of PAHs present in diesel emissions are not yet fully clear.

Several studies have been performed in recent years in order to identify and quantify PAHs in gases-phase and particle matter in exhaust vehicle diesel [5,7,11–18]. However, few studies were

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Table 1
Number of aromatic rings and molecular mass of 16 priorities PAHs.

Compound - code	Number of rings	Molecular mass
Naphthalene - NAP	2	128
Acenaphthylene - ACY	2	152
Acenaphthene - ACE	2	154
Fluorene - FLU	2	166
Phenanthrene - PHE	3	178
Anthracene - ANT	3	178
Fluoranthene - FLT	3	202
Pyrene - PYR	4	202
Benzo[a]anthracene - BAA	4	228
Chrysene - CRY	4	228
Benzo[b]fluoranthene - BBF	4	252
Benzo[k]fluoranthene - BKF	4	252
Benzo[a]pyrene - BAP	5	252
Dibenzo[a,h]anthracene - DBA	5	278
Benzo[g,h,i]perylene - BGP	5	276
Indeno[1,2,3-cd]pyrene - IND	5	276

found that examined the concentration of PAHs in diesel oil samples and lubricating oil samples from the engine [5,8,16,19,20]. These studies are not recent and since then diesel sold in most countries has undergone several changes, among them, a reduction in the concentration of aromatic compounds, with the purpose of reducing the pollutants emissions. The individual PAHs determination in diesel fuel and lubricant oil engine require analytical methods which have high selectivity, since these samples have complex matrices. Marr et al. [5] and Dobbins et al. [8] employed the solid phase extraction (SPE) technique followed by gas chromatography coupled mass spectrometry to analyse PAHs in diesel fuel samples. The solid phase of the SPE should be chosen according the desired retention mechanisms. Marr et al. [5] used silica and Dobbins et al. [8] used aminosilane as solid phase to separate the aromatic fraction in diesel fuel samples. The liquid-liquid extraction (LLE) technique followed by SPE technique were used by Wong and Wang [16] to separate the aromatic fraction in engine lubricating oil. It is difficult to separate PAHs from the diesel fuel and lubricating oil sample matrix without some loss. Therefore, this study determined the priority PAHs concentrations in diesel fuel sold in Brazil and in lubricant oil sampled in different usage times. Two different methods have been developed, one to analyse priority PAHs in diesel fuel and other to analyse priority PAHs in lubricant oil. The SPE technique using florasil (magnesium silicate) as solid phase was used to separate the fraction containing aromatic components present in the diesel fuel and lubricating oil samples. Although this solid phase is indicated for PAHs [21], it was not found studies that have used florasil to determine PAHs in diesel fuel and lubricating oil samples. Also no studies were found in the literature searches that have analyzed the PAHs concentration in diesel fuel and oil lubricant samples sold in Brazil.

The PAHs concentration in Brazilian diesel fuel sample was compared with their respective emission factors in a vehicle exhaust fueled with the same Brazilian diesel in order to estimate how much of the PAHs present in diesel remained unchanged during combustion. In this case, the PAH emission factor was calculated in PAH mass in the exhaust per fuel volume consumed during the vehicle testing. Only one study were found in the literature searches which compared the PAHs emission factors from a diesel vehicle with their respective concentrations in diesel fuel used during the vehicle test. But it is important to note that this study was performed using other vehicle test conditions, other vehicle model and other diesel fuel.

2. Methodology

2.1. Vehicle emission tests, sampling and extraction of samples

Vehicle emission tests were performed to collect the PAHs in the gas phase and particulate matter (PM) phase present in the exhaust. The tests were performed in triplicate using a 2012 Renault Master 2.5 L 16-valve engine with 84 kW at 3500 rpm; this engine is typical of the fleets in Brazilian cities. The tests were performed with a stationary pre-heated engine, with constant rotation at 1500 rpm without load. A carbon 2-m long steel pipe was attached to the end of the vehicle's exhaust pipe to lower the temperature gradient of the combustion products before they were collected at the end of the tube. A constant-volume sampler system without dilution of exhaust gases collected gross emissions at a temperature of 55 ± 2 °C. The vehicle was fueled with S10 (10 mg kg⁻¹ of sulfur) and B5 (5% v/v biodiesel) commercial diesel provided by Petrobras distributor. This vehicle had no after-treatment device. To evaluate emissions of PAHs in PM, a MSP nano MOUDI (Micro-Orifice Uniform Deposit Impactor) II model 120R was used at a flow rate of 30 L min⁻¹ for 20 min. Glass fiber filters (Whatman grade GF/C 0.7 µm) were used as substrates at the impactor plates. The gas phase PAHs were collected using three double-bed XAD-2 cartridges (400/200 mg Supelco ORBO 32) positioned in series at a flow rate of 1.5 L min⁻¹ for 20 min. After the tests, the samples were stored in a freezer before extraction and analysis. The second cartridge bed was analyzed separately to assess possible loss of PAHs in the gas phase. No losses of PAHs in the gas phase were found when using a flow rate of 1.5 L min⁻¹ for 20 min. Fig. 1 shows a schematic of the PAH exhaust sampling system.

The PAHs in filters and cartridges were extracted in cold ultrasonic baths for two hours at 20 °C with 70 mL dichloromethane and then filtered using a 0.2 µm PTFE membrane. The filtered extracts were concentrated in a rotary evaporator under a gentle flow of nitrogen to a final volume of 1.0 mL. The efficiency of

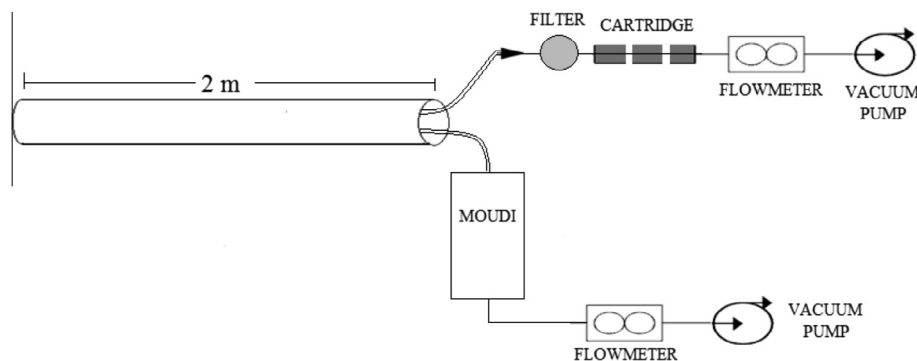


Fig. 1. PAH sampling system in the exhaust.

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