Polycyclic Aromatic Hydrocarbons (PAHs) and nitrated analogs associated to particulate matter emission from a Euro V-SCR engine fuelled with diesel/biodiesel blends

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HIGHLIGHTS

- Unregulated carcinogenic emission from heavy-duty engine with SCR aftertreatment
- PM sampling using Biodiesel blends and 13 steady-state engine operation cycle
- The synergic effect of biodiesel/SCR reduces PAHs and Nitro-PAHs particle emission.
- The tested SCR system does not appear to promote PAHs nitration.
- Biodiesel addition may reduce the emission toxicity and the risk to human health.

GRAPHICAL ABSTRACT
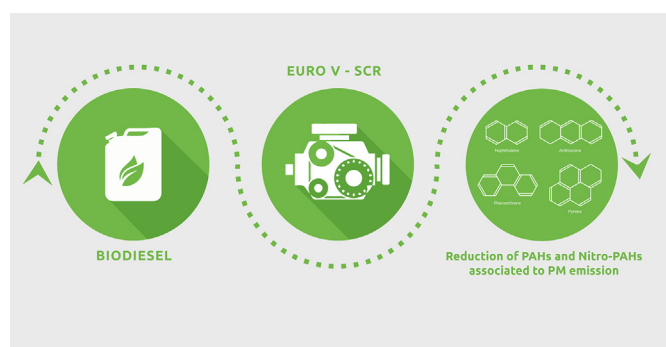
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ABSTRACT

Among the new technologies developed for the heavy-duty fleet, the use of Selective Catalytic Reduction (SCR) aftertreatment system in standard Diesel engines associated with biodiesel/diesel mixtures is an alternative in use to control the legislated pollutants emission. Nevertheless, there is an absence of knowledge about the synergic behaviour of these devices and biodiesel blends regarding the emissions of unregulated substances as the Polycyclic Aromatic Hydrocarbons (PAHs) and Nitro-PAHs, both recognized for their carcinogenic and mutagenic effects on humans. Therefore, the goal of this study is the quantification of PAHs and Nitro-PAHs present to total particulate matter (PM) emitted from the Euro V engine fuelled with ultra-low sulphur diesel and soybean biodiesel in different percentages, B5 and B20. PM sampling was performed using a Euro V – SCR engine operating in European Stationary Cycle (ESC). The PAHs and Nitro-PAHs were extracted from PM using an Accelerated Solvent Extractor and quantified by GC–MS. The results indicated that the use of SCR and the largest fraction of biodiesel studied may suppress the emission of total PAHs. The Toxic Equivalent (TEQ) was lower when using 20% biodiesel, in comparison with 5% biodiesel on the SCR system, reaffirming the low toxicity emission using higher percentage biodiesel. The data also reveal that use of SCR, on its own, suppress the Nitro-PAHs compounds. In

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Nitro-PAHs
Toxic Equivalent (TEQ)

general, the use of larger fractions of biodiesel (B20) coupled with the SCR aftertreatment showed the lowest PAHs and Nitro-PAHs emissions, meaning lower toxicity and, consequently, a potential lower risk to human health. From the emission point of view, the results of this work also demonstrated the viability of the Biodiesel programs, in combination with the SCR systems, which does not require any engine adaptation and is an economical alternative for the countries (Brazil, China, Russia, India) that have not adopted Euro VI emission standards.

1. Introduction

Diesel engine exhaust emissions were classified as a carcinogen by the International Agency for Research on Cancer (IARC) in 2013, thereby increasing the prior challenges that policymakers in several countries face (Diaz-Sanchez et al., 1994; Lighty et al., 2000; Ravindra et al., 2008; Reşitoğlu et al., 2015; Zielinska et al., 2004). Polycyclic Aromatic Hydrocarbons (PAHs) and Nitro-PAHs (nitrated PAHs) are the most toxic compounds among the complex mixture of gases and particles that comprise Diesel engine exhaust aerosols (Hu et al., 2013; HHS USA, 2004; Slezakova et al., 2013; Wang et al., 2013; Yilmaz and Davis, 2016). Composed of two or more fused aromatic rings, these organic compounds have been tested for their carcinogenic activity by the IARC, with benzo[a]pyrene being classified as group 1 (carcinogenic to humans), by this agency. Dibenzo[a,l]pyrene is considered as probably carcinogenic to humans (group 2A) and dibenzo[a,i]pyrene and dibenzo[a,h]pyrene as possibly carcinogenic to humans (group 2B) (IARC, 2018; Zielinska et al., 2004). When these compounds are associated with diesel/biodiesel blends exhaust particle-phase emissions, which are characterized by high concentrations of fine particulate matter ($PM_{2.5}$) (Guan et al., 2017; He, 2016), there is an intensification of many acute and chronic cardiopulmonary diseases, including asthma, respiratory system inflammation and lung cancer (Martin et al., 2017; HHS USA, 2004; Ravindra et al., 2008).

Current emission regulations implemented in the United States of America (U.S.) and European Union (EU), US 2010 and Euro VI, respectively, adopt a limit for NO_x and PM emission that is ten times lower than the levels allowed in 2000. Countries where these emission limits are enforced and implemented (U.S., EU, Canada, Japan and South Korea) project a 26-fold reduction in PM emissions by 2045 (Posada et al., 2016). On the other hand, Brazil, Russia, India, China, Australia and Mexico whose gross domestic product heavily depends on heavy-duty vehicle transport, have yet to fully implement the equivalent emission standards, even though the increased risks are acknowledged. These regulations require extensive deployment of advanced engine tuning, the addition of two or more aftertreatment devices and the use of low sulphur diesel content, therefore potentially fleet renovations. Instead, these countries still enforce the Euro V and equivalent regulations where Selective Catalytic Reduction (SCR) or Exhaust Gas Recirculation (EGR) aftertreatment systems remain the main strategies to reduce NO_x and PM emission (Du and Miller, 2017).

As an additional strategy to reduce pollutants from Diesel vehicles, many countries like Canada, Australia, Brazil, China and Germany are promoting the development, production and use of alternative fuels (biofuels and natural gas) seeking a better balance to fuel economy and thereby improving green freight programs in the long term (Du and Miller, 2017). Biodiesel is already used in several countries and seems to be a promising alternative, as it can be used in diesel engines without major modifications. Despite the high cost of production when compared to diesel, biodiesel can qualitatively and quantitatively reduce regulated pollutant emissions (He et al., 2010; Ratcliff et al., 2010; Sadiktsis et al., 2014). Several researches successfully demonstrated a consistent reduction for hydrocarbons (HC), PM and carbon monoxide (CO) emissions while recognizing an increase in nitrogen dioxide (NO_x) when biodiesel is used (He, 2016; Ravindra et al., 2008; Sadiktsis et al., 2014). On the other hand, there is no agreement whether

the biodiesel promote or not a reduction on PAHs and Nitro-PAHs emissions. Guarieiro et al. (2014) concluded that the biodiesel additions decrease PAHs emissions, which is in agreement with the conclusions made by He et al. (2010), Lim et al. (2014) and Yilmaz and Davis (2016). Westphal et al. (2013) tested PAHs emissions using a turbo-intercooled engine with 6 cylinders operating in the European Stationary Cycle (ESC) fuelled with hydrotreated vegetable oil and jatropha methyl ester. The authors also demonstrated a slight reduction in PAHs emission when low percentages of biodiesel were added and showed that toxicological effects depend on the biodiesel origin. Casal et al. (2014) tested a Euro III engine fuelled with standard diesel (B0), B5 (5% biodiesel) and B20 (20% biodiesel) and concluded that biodiesel mixed with diesel increases the production of PAHs and Alkyl PAHs in the engine exhaust emissions.

Changes in fuel alone are however not sufficient to meet the new or the old standards and use of aftertreatment systems is crucial. The SCR system is still the most widely used in many countries, due to its selectivity to reduce NO_x emissions (Tadano et al., 2014). The injection of urea and a catalyst ensures reductions of up to 90% in NO_x emissions, through a reduction reaction of NO_x and NH_3 resulting in nitrogen and water (Amanatidis et al., 2014; Bacher et al., 2015). Nevertheless, SCR technology is not without its challenges, such as the emission of NH_3, stoichiometric disproportion of urea consumption, cost, and deactivation of the catalyst by deposition (Cheruiyot et al., 2017). The best reported SCR efficiency is achieved at high engine loads and temperatures (approximately 400 °C) (Cheruiyot et al., 2017). However, the added urea increases the probability of unintended formation of Nitro-PAHs through PAHs nitration (Liu et al., 2015).

The combination of low sulphur fuels (ultra-low sulphur diesel-ULSD), new engine technologies, aftertreatment systems (SCR, EGR, DOC – Diesel oxidation catalyst, DPF – Diesel particulate filter) and the use of biofuels are the current strategy to achieve the regulatory reductions worldwide (Wang et al., 2009; Ratcliff et al., 2010; Carrara and Niessner, 2011; Hu et al., 2013; Sadiktsis et al., 2014; Reşitoğlu et al., 2015; He, 2016). However, there is insufficient knowledge and some disagreement in open literature with regards to the potential synergistic effect on unregulated emissions by vehicles equipped with SCR and the use of different biodiesel blends.

This paper describes the PAHs and Nitro-PAHs emission concentrations from a Diesel engine, which is in compliance with the standard emissions determined in PROCONVE P7/Euro V. Furthermore, the potential synergistic effect of the SCR after-treatment and the use of different soybean biodiesel blends (B5 and B20) on emissions have been investigated. Those pollutants are not regulated worldwide, even though they are proven to present several harmful effects on human health.

2. Material and methods

2.1. Sampling and engine parameters

The engine emission tests were performed at the Lactec Institute's Laboratory for Vehicular Emissions in partnership with the Federal University of Paraná, Curitiba, Brazil. The tested engine is currently used in trucks and buses around the world, and has an individual four-valve cylinder head, cross-flow arrangement, common rail injection and SCR

aftertreatment system. The test engine fulfils the European Union Regulation (Directive 2005/55/EC of the European Parliament and of the Council of 28 September 2005) requirements for Euro V emission standards with a urea-SCR system and is in accordance with the P7 phase of the PROCONVE (Vehicular Air Pollution Control Program) in Brazil. The engine details are specified in Table 1.

The engine works in conjunction with a dynamometer and a data acquisition system, both from AVL (Graz, Austria) to perform the emission and engine parameters measurements. The dynamometer can absorb power up to 440 kW at 6000 rpm and a torque of 2334 Nm at 1200–1600 rpm. The European Steady Cycle (ESC) was selected as driving cycle for the dynamometer operation to allow PM sampling. It was designed to achieve high load factors and very high temperature on the exhaust gas (Ericsson, 2001; Mock et al., 2012). The PM emission is collected over a sequence of 13 steady-state modes of load and engine speed. The sampling time was 28 min per cycle. In each mode the exhaust flow and the power are also measured, which are used as weighting parameters for the conversion of the results to g kWh^{-1}. Sixty-five percent of the calculated emission responds to load and engine speed above 50%. That is conservative and captures most of the stop-and-go conditions of the drive cycle experienced by urban buses in rush hours (Tadano et al., 2014).

The PM sampling was performed using an AVL dilution system (Smart Sampler SPC 472 - Graz, Austria). This system prevents filter saturation, reduces the exhaust temperature and adjusts the dilution ratio. The sampling equipment has two filter supports, arranged in sequence, to achieve higher PM retention. The sampling flow rate collected into PM sampler from the engine exhaust was 1.5 g s^{-1} and the dilution air was adjusted to obtain a diluted exhaust gas temperature, measured just before the primary filter, of 325 K (52 °C) in each mode. The dilution ratio should not be <4.

For PAHs and Nitro-PAHs analysis, total PM was collected on two borosilicate glass fiber filters, 70 mm of diameter, coated with fluorocarbon (Pallflex T60A20 fiberfilm). The filters were weighted prior and after the sampling using a Sartorius micro-balance (MSA2.7S-000-DF - Goettingen, Germany) following the NIOSH method 5000 and were stored below −18 °C in cleaned glass containers until analysis. To certify the correct function of SCR system, the NO$_x$ emissions were measured in-line by a SESAM i60 FT, Fourier transform infrared (FTIR) multi-component measurement system from AVL (Graz, Austria). In addition, the catalyst temperature was monitored to archive the best operation condition. Table S.1 shows the experimental conditions set for the FTIR analysis.

2.2. Fuels

Ultra-Low Sulphur Diesel (ULSD – maximum of 10 ppm or mg kg^{-1} of sulphur) and soybean biodiesel were used to prepare two mixtures: B5 (ULSD with 5% of biodiesel) and B20 (ULSD with 20% of biodiesel). The B5 and B20 fuels were collected in amber glass bottles and stored protected from light at 25 °C. The fuel samples were previously characterized according to methods and essays described on American Society

for Testing and Materials (ASTM) in Lacaut – Automotive Fuels Laboratory (certified on ISO 9001, ISO 14001 and ISO 17025) of the Federal University of Paraná, Curitiba, Brazil. Table 2 shows the fuel properties of the biodiesel blend used in this research, tested according with Standard ASTM Test Methods.

2.3. Extraction

All the 27 sampled filters were extracted, using an Accelerated Solvent Extractor (ASE – Dionex, USA), with dichloromethane and methanol (4:1) at a pressure of 1500 psi and temperature of 120 °C in three static extraction cycles of 5 min each. The total extracted volume was concentrated to near dryness with a slight nitrogen flow and recovered with 1.5 ml of dichloromethane. This procedure has been optimized, using different temperatures (100, 120, 150 and 180 °C) and extraction cycles (1, 2 and 3 cycles), based on the 'EPA' Standard Operation Procedure (California Standard Operation Procedure - SOP No. 144/2006) for the determination of PAH in particulate matter using Gas Chromatography with Mass Spectrometry (GC–MS). To assess the extraction efficiency, Naphthalene d_8 and Benz[a]anthracene-d12 were used as recovery standards. The recovery, in percentage, of Naphtalene d_8 was slightly lower (65–80%) than the recovery of Benz[a]anthracene-d12 (84–114%).

2.4. Analysis

Samples and standards were analysed in triplicate, using a gas chromatograph (Perkin Elmer Clarus 680) coupled to a mass spectrometer (Perkin Elmer Clarus SQ 8 T Perkin Elmer - Waltham, USA). A fused silica capillary column (MS-5 30 m × 0.25 mm × 0.25 mm) from Sigma Aldrich (St. Louis, USA) was used to separate the PAHs and Nitro-PAHs. Helium was used as carrier gas at a constant flow rate of 1.0 ml min^{-1}. The volume injected was 1.5 μl in splitless mode with a pressure pulse. The oven temperature was programmed as follows: 1 min at 40 °C, heated at a rate of 10 °C min^{-1} to 200 °C and maintained for 5 min, heated in sequence at a rate of 6 °C min^{-1} to 240 °C and maintained for 10 min and, finally heated to 300 °C at a rate of 10 °C min^{-1} and maintained for 5 min. The injector temperature, GC–MS interface and detector were maintained at 300 °C, 270 °C and 260 °C, respectively. The mass spectrometer emission current was set at 350 μA, the electron energy at 70 eV (nominal) and analysis occurred with SIM (selected-ion monitoring) mode.

Acenaphthene-D10, Phenanthrene-D10 and Perylene-D12 (Sulpeco Analytical - Bellefonte, USA) were used as internal standards. Sixteen PAHs recognized by USEPA (United States Environmental Protection Agency) as priority pollutants were analysed: Naphthalene, Acenaphthene, Acenaphthylene, Anthracene, Phenanthrene, Fluorene, Fluoranthene, Benzo[a]anthracene, Chrysene, Pyrene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Dibenzo[a,h]anthracene, Benzo[g,h,i]perylene, Indeno[1,2,3-c,d]pyrene. In addition, Benzo[e]pyrene, Perylene, 1-Nitronaphtalene, 2-Nitrofluorene, 3-Nitrofluoranthene, 1-Nitropirene and 7-Nitrobenz[a]anthracene were also analysed (standards solutions supplied by Dr. Ehrenstorfer - Augsburg, Germany). The list with all investigated compounds with their respective molecular mass, quantification ion and quantification limits (LoQ) can be found in Table S.2 of the Supplementary material. Four

Table 1
Engine specifications.

Specifications	
Emission	Euro V "heavy duty"/PROCONVE P7
Configuration	4 cylinders, inline
Displacement	4.8 liters
Bore × stroke	105 × 137 mm
Combustion system	Direct injection
Injection system	Common rail electronic
Aspiration	TGV intercooler
Power output	187 hp (139.7 kW) 2200 rpm
Peak torque	720 Nm (73 kgf·m) 1200–1600 rpm
Aftertreatment	SCR

Table 2
Fuel properties of B5 and B20 blends.

Property	B5	B20	Method
Sulphur, mg kg^{-1}	4	6	ASTM D5453
Cetane number	53.8	51.0	ASTM D6890
Flash point (°C)	45.5	70.5	ASTM D93
Viscosity at 40 °C (mm^2 s^{-1})	3.0	3.2	ASTM D445
Specific mass at 20 °C (kg m^{-3})	830.5	848.1	ASTM D4052

blank filters were analysed to determine possible interferents. The method accuracy was verified using the reference material SRM 1650b from NIST (National Institute of Standards and Technology).

The PAHs and Nitro-PAHs concentrations were tested for significant differences using Analysis of Variance (ANOVA). For this purpose, "R" software was used, and significance was determined at a 95% confidence level. The uncertainties were calculated using the Guide to the expression of uncertainty in measurement from the BIPM is an international organization (JCGM, 2008).

3. Results and discussion

Particle emissions from a Euro V engine, operating with and without Selective Catalytic Reduction aftertreatment (SCR-on and SCR-off), and testing ULSD with 5% of biodiesel (B5) and ULSD with 20% of biodiesel (B20), were analysed for their PAHs and Nitro-PAHs content. The compounds average concentrations are presented together with their expanded uncertainties at the 95% of confidence level. To the experiential condition with number of valid samples (n) equal to 1 the uncertainties were estimated using the standard deviation (SD) of other conditions to the same compound. Which respect to number of samples, the differentiation between groups of data is connected to difference in group's mean and the corresponding uncertainties. The best number of samples (n) is determined by a commitment between mean, SD and SD of the mean. Consequently, a minimum of 5 samples were collected for each experimental condition.

3.1. Particle-phase PAHs

Table 3 displays the PAHs emitted from a Euro V engine operating with an ESC cycle, using two different fuels and after treatment conditions, as well as their respective concentrations (in µg kWh^{-1}).

Only 8 of the 23 quantified PAHs were not detected or were found below the quantification limit (Anthracene, Chrysene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Perylene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene - Table S.2).

Considering the sum of all PAHs, the B5 SCR-off condition had the highest value among the sampling conditions (3.37 ± 0.56 µg kWh^{-1}), followed by B5 SCR-on (3.13 ± 0.40 µg kWh^{-1}), B20 SCR-off (2.54 ± 0.28 µg kWh^{-1}) and the B20 SCR-on (2.12 ± 0.15 µg kWh^{-1}). The results indicate therefore a slight reduction (7% and 16% respectively for B5 and B20) in total PAHs emissions when the aftertreatment technology is applied. The reason for this slight reduction may be because of a moderate decrease in total particulate emissions when SCR technology is applied as indicated by Mayer et al. (2007), Czerwinski et al. (2011) and Lee et al. (2015). These reductions

for Euro V engines have been reported, by the cited authors, to be in the same order of magnitude as observed here.

What is more noticeable, however, is that the addition of 20% of biodiesel in the fuel mixture resulted in a decrease of 25% in PAHs emissions in the particle-phase for SCR-off and 32% for SCR-on. Similar results were found by previous studies (Turrio-Baldassarri et al., 2004; He et al., 2010; He, 2016; Yilmaz and Davis, 2016; Martin et al., 2017), however without test the simultaneous effect of biodiesel blends and SCR aftertreatment system. Our results concur with the findings of He et al. (2010), who compared several studies, concluding that, on average, a reduction of 23% in PAHs emissions can be expected with a 20% addition of biodiesel to the fuel. Therefore, our results demonstrated that SCR and Biodiesel, when combined, can be more efficient on PAHs reduction. Additionally, He et al. (2010) showed that PAHs emissions from Euro II engines were two orders of magnitude higher than those reported in the present research, therefore enlightening a decrease in PAHs emissions due to the engine technology evolution. Similarly, the possibly carcinogenic to humans PAHs (PAHsC) were reduced by when B5 was replaced by B20 with and without the SCR system. These results demonstrate the beneficial influence on PAHs emissions if biodiesel additions to fuel are made in conjunction to SCR system.

These results indicate a difference in combustion products between diesel and biodiesel, as highlighted by Ravindra et al. (2008), who stated that the pyrolysis and pyro synthesis processes that diesel undergoes during combustion (in reduced oxygen conditions), will result in the formation of aromatic rings through condensation products. The gaseous hydrocarbons radicals can rapidly reorganize participating on PAHs formation and growth. Through alkyl PAHs formation mechanism, the addition of hydrocarbon radicals to lower molecular weight PAHs, present in diesel, can form higher molecular PAHs. In the case of biodiesel combustion, PAHs formation involves the thermal polymerization of the fatty acid methyl esters forming cyclohexane (Ratcliff et al., 2010), as there are no aromatic organic compounds present. Therefore, the incorporation of biodiesel in the mixture can lead to a reduction in PAHs emissions due to the natural absence of PAH in biodiesel, and to its higher oxygen content. The observed result represents the different chemistry path of biodiesel combustion in relation to diesel and an improvement of the combustion process, reducing the PAHs generated by incomplete combustion of fuel and lubricant oils.

The average and uncertainties for the individual PAHs associated with PM emission are presented in Fig. 1. The major compound quantified in all the experimental conditions was Fluorene followed by Phenanthrene, Pyrene, Fluoranthene, Benzo[b]fluoranthene and Benzo[g,h,i]perylene. The latter compound presented concentrations below the LoQ for B20 during the SCR-on condition. The high molecular weight PAHs with three or more aromatic rings, recognized for their toxicity, contributed more to the total particle PAHs emission, as they have a

Table 3
PAHs concentrations associated to PM exhaust emissions, in µg kWh^{-1}.

PAHs (µg kWh^{-1})	B5 SCR-off		B5 SCR-on		B20 SCR-off		B20 SCR-on	
	Average ± u	n	Average ± u	n	Average ± u	n	Average ± u	n
Naphthalene[a]	0.076 ± 0.014	1	0.036 ± 0.014	2	<LoQ		<LoQ	
Acenaphthylene	0.047 ± 0.006	1	<LoQ		<LoQ		0.043 ± 0.006	2
Acenaphthene	0.138 ± 0.020	1	0.075 ± 0.020	2	<LoQ		<LoQ	
Fluorene	0.841 ± 0.064	2	0.845 ± 0.215	5	0.759 ± 0.129	5	0.867 ± 0.085	2
Phenanthrene	0.786 ± 0.064	5	0.642 ± 0.081	4	0.669 ± 0.088	8	0.658 ± 0.107	2
Fluoranthene	0.317 ± 0.221	5	0.319 ± 0.111	5	0.225 ± 0.085	9	0.128 ± 0.016	4
Pyrene	0.738 ± 0.500	5	0.724 ± 0.253	5	0.587 ± 0.209	9	0.307 ± 0.043	4
Benzo[a]anthracene[a]	0.085 ± 0.016	1	0.081 ± 0.016	2	<LoQ		<LoQ	
Benzo[b]fluoranthene[a]	0.152 ± 0.021	4	0.229 ± 0.173	2	0.128 ± 0.009	9	0.121 ± 0.016	3
Benzo[g.h.i]perylene	0.188 ± 0.014	3	0.183 ± 0.003	2	0.176 ± 0.002	3	<LoQ	
∑PAHs (particles)	3.37 ± 0.56[b]		3.13 ± 0.40[b]		2.54 ± 0.28[b]		2.12 ± 0.15[b]	
PAHsC - possibly carcinogenic for humans[a]	0.313 (9.2%)		0.347 (11.1%)		0.128 (5.0%)		0.121 (5.7%)	

u – expanded uncertainties (95% level of confidence); n – number of valid samples; <LoQ – below quantification limit.
[a] IARC – group 2B (possibly carcinogenic to humans).
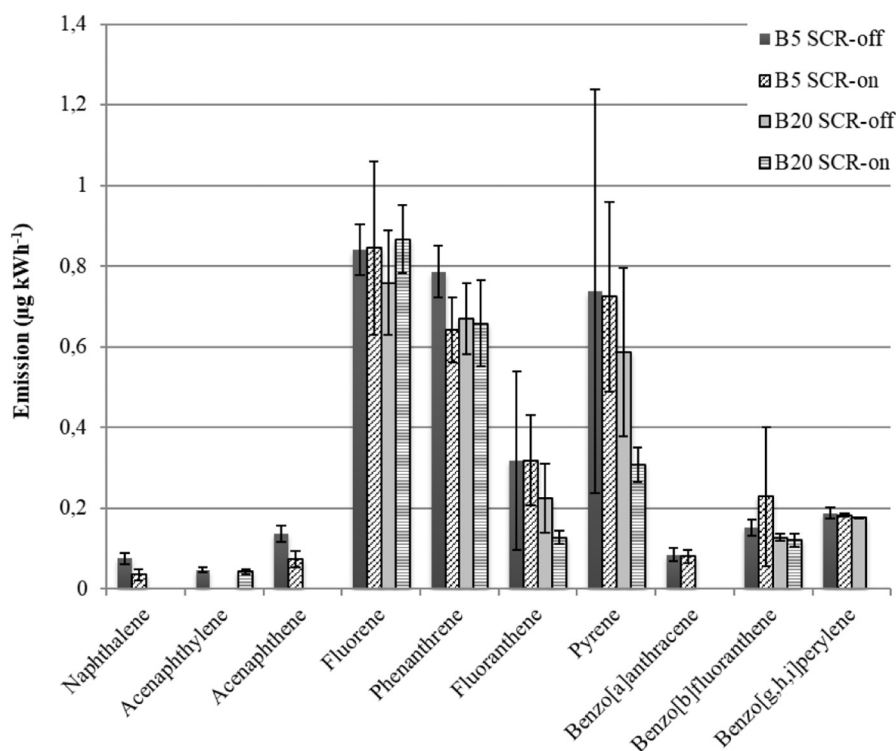[b] Uncertainties propagation for PAHs sum.

Fig. 1. Average concentrations in μg kWh^{-1} (columns) and standard deviation (bars) for individual PAHs associated with total PM emission for all experimental conditions.

higher probability to condense during the combustion process (Ballesteros et al., 2010). Benzo[*a*]pyrene, the most toxic among PAHs species, was not quantified for any of the conditions (LoQ = 3.36 ng ml^{-1}).

The ANOVA test was performed for the substances that presented two or more valid samples: Fluorene, Phenanthrene, Fluoranthene, Pyrene and Benzo[*b*]fluoranthene, to identify if the differences between tested conditions are significant. No statistical difference (95% confidence level) was found for the tested conditions, except for Benzo[*b*] fluoranthene when comparing B5 SCR-off to B20 SCR-off and B5 SCR-on to B20 SCR-off. A similar result was obtained by Shah et al.(Shah et al., 2012) who found no significant difference in PAHs emissions considering the use of the SCR system and a low sulphur diesel. The more noticeable reduction on average emission was observed to Fluoranthene and Pyrene when B20 and the SCR system were tested, 60% and 58% respectively, comparing to B5 SCR-off.

Considering biodiesel, Ballesteros et al. (2010) studied the particle-associated PAHs emission using three diesel (ULSD)/biodiesel mixtures (B30, B70 and B100) with a 4-cylinder, 4-stroke, turbocharged, intercooled, 2.2 l Nissan diesel engine without any aftertreatment system operating in a transient cycle. The authors showed that the biodiesel addition decreased the low molecular weight PAHs concentration (three aromatic rings) in relation to pure diesel and concluded that these emissions depend on the biodiesel origin. In agreement to Ballesteros et al. (2010), in present study, no significant difference was found in the individual PAHs emission and a decrease was observed to low molecular weight PAHs when biodiesel and SCR were tested at once. The same results were reported by Rojas et al. (2011) for 10 out the 16 priority PAHs (as proposed by US EPA) when they monitored the particle emissions from a 20-year-old engine fuelled with pure diesel (1000 ppm of sulphur) and B15. The authors also quantified high concentrations of Pyrene, Benzo[*k*]fluoranthene and Benzo[*g,h,i*] perylene when B15 was used. Despite the results similarities, theses researches did not test the effect of biodiesel and SCR simultaneously.

Total PAHs emission reductions were observed (up to 28%) with the replacement of diesel fuel with biodiesel, which has been

ascribed to the different chemistry pathway during the pyrolysis of the biodiesel. These reductions were more pronounced if the SCR aftertreatment system was used. In addition, the fuel composition also played a significant role in the amount of carcinogens PAH emitted.

The individual PAHs results (Fig. 1) also reveal a reduction on concentration of Naphthalene, Acenaphthylene, Acenaphthene and Benzo [*a*]anthracene when B20 was tested without the SCR system. Considering the B20 with SCR Benzo[*g,h,i*]Perylene similarly have reduced to low concentrations being above the quantification limit. The beneficial effects of the biodiesel/SCR system equally can be confirmed by the Toxic Equivalent (TEQ) values.

The Toxic Equivalency Factors (TEFs) for each PAHs and the TEQ calculation procedure were the same as those proposed by Nisbet and LaGoy (1992) and US EPA (United States Environmental Protection Agency, 2006). The results indicate that the highest TEQ was found for the B5 SCR-on combination (0.036 μg kWh^{-1}), followed by the B5 SCR-off (0.029 μg kWh^{-1}), B20 SCR-off (0.017 μg kWh^{-1}) and the lowest for the B20 SCR-on combination (0.014 μg kWh^{-1}). The highest TEQ value, 0.036 μg kWh^{-1}, match the highest PAHsC, 0.347 μg kWh^{-1} (Table 3), for the B5 SCR-on condition, suggesting that Benzo[*b*]fluoranthene was mostly responsible for the increased toxicity. Shah et al. (2012) tested the influence of the SCR system on the TEQ values and concluded that the aftertreatment increased the quotient value due to the increase in PAHs with high TEFs.

The preponderant factor leading to the reduction of the TEQ was the fuel variation. The reduction from B5 SCR-off to B20 SCR-off was 41% and B5 SCR-on to B20 SCR-on was 60%. Yilmaz and Davis (2016) found low particle-bound PAHs TEQ values in the same order of magnitude for B10 and B20 mixture, using waste oil biodiesel and no aftertreatment. The authors also reported that B10 reduced toxicity by 49% and B20 by 46%, compared to B100. In addition to the discussion about the biodiesel life cycle and the economical/environment sustainability, this biofuel is an alternative to reduce PAHs in particle-phase of Diesel engine emissions and toxicity, when the proportions are limited to 20% on diesel mixture.

3.2. Particle-phase Nitro-PAHs

The concentration of five Nitro-PAHs associated with PM emissions from a Euro V (SCR) engine using diesel/biodiesel blends (B5 and B20) as fuels were assessed in this research and the results are shown in Table 4 and Fig. 2. The 1-Nitropyrene was quantified in one sample of each experimental condition. 2-Nitrofluoranthene and 7-Nitrobenzo[a]anthracene were below the quantification limit for all conditions. The Nitro-PAHs that were present in quantifiable amounts were 1-Nitronaphthalene and 2-Nitrofluorene. It is observed that 2-Nitrofluorene was up to 8.5 times higher than the other Nitro-PAHs quantified and in general higher than any other individual PAHs identified and quantified as indicated in Table 3. According to the World Health Organization (Kielhorn et al., 2003) both 2-Nitrofluorene and 1-Nitropyrene are found in diesel combustion particulate emissions and are the major contributors to the increase in mutagenic emission potential. When considering the Nitro-PAHsC sum (Table 4), it is observed that these compounds represents 87–92% of the total Nitro-PAHs emissions and are therefore of concern, since they are currently classified as group 2B and 2A by the IARC.

Unlike the results obtained in the PAHs analysis, in which the fuel had the greatest reduction influence on the total emissions, the determining factor is a combination of fuel composition and the use of the SCR aftertreatment system. The SCR aftertreatment resulted in a 48% reduction when the B20 fuel was used and 5% in the case of B5. This suggests that the SCR aftertreatment was more effective when larger biodiesel additions are made. The only substantial reduction was observed for B20 with aftertreatment in comparison to the other experimental conditions. It seems therefore that only in the case of a combination of increased biodiesel additions and aftertreatment use, a reduction of Nitro-PAHs emissions was observed. This contrasts with Martin et al. (2017) who found that B20 can reduce overall Nitro-PAHs concentrations in particle phase emissions in comparison to diesel, without aftertreatment.

The analysis of variances for 1-Nitronaphthalene and 2-Nitrofluorene showed no significant difference (95% confidence level) among the different experimental conditions (B5 SCR on, B5 SCR off, B20 SCR on and B20 SCR off). The same outcome was determined for its precursor PAHs, Naphthalene and Fluorene, that presented no significant difference (95% confidence level) in fuel and aftertreatment variation. These two precursors PAHs also have high emission values comparing to the other PAHs.

The formation mechanism of Nitro-PAHs through the nitration reaction during the combustion process in the cylinder has been investigated by several researches. Nevertheless, the knowledge about this process remains inconclusive (Kielhorn et al., 2003; Heeb et al., 2008; Liu et al., 2015). During the combustion, Nitro-PAHs can be formed by electrophilic substitution reactions in the presence of NO_x and the combination of high temperatures. The presence of precursor PAHs and long residence time inside the aftertreatment system also can promote the formation of these compounds (Heeb et al., 2008). During the tests the SCR system reduced NO_x emission in 69% to B5 and 78% to B20;
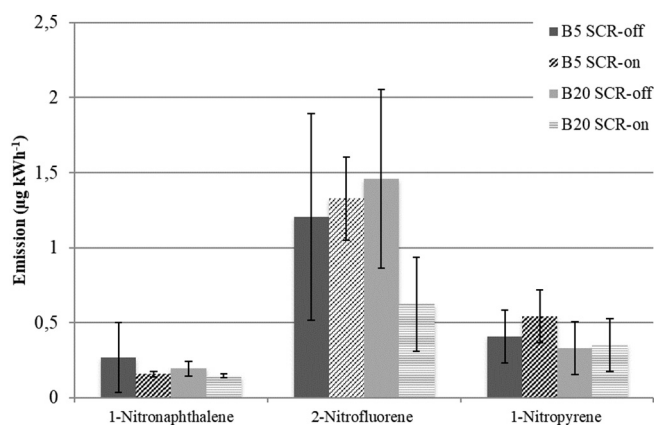

Fig. 2. Average (columns) and standard deviation (bars) for individual Nitro-PAHs associated to total PM emission to all experimental conditions in µg kWh^{-1}.

and showed an increase on NH_3 and N_2O emission when the SCR was used for both fuels. These results are detailed presented in a previous publication (Borillo et al., 2015). In the present study, 1-Nitronaphthalene and 1-Nitropyrene did not show any trends due fuel and aftertreatment changes, considering the average value. On the other hand, 2-Nitrofluorene shows an increase trend when SCR was function with B5 and when B20 was tested without SCR system. As the NO_x emission decrease about 69% and 78% when SCR aftertreatment is used and no correlated decrease was observed in Nitro-PAHs emission, is unlikely that SCR system promote Nitro-PAHs formation in large scale.

In a recent study, Liu et al. (2015) examined the emission of Nitro-PAHs using various types of aftertreatment systems in different configurations. When testing DOC + SCR, the emissions of PAHs increased compared to the results of the engine without any after-treatment system. When studying only the SCR system, a reduction in the emission of Nitro-HPAs was observed by Liu et al. (2015). However, the authors also concluded that the formation of Nitro-PAHs by the SCR system is questionable, since this system significantly reduces NO_2 concentrations, decreasing their availability for the conversion of PAHs into their nitrated forms. In addition, the pores of the SCR system exclude large molecules such as PAHs, reducing their residence time and their interaction with NO_x. Hu et al. (2013) evaluated the use of two SCR systems' composition (vanadium and copper) after a DOC + DPF system and none appeared to promote the nitration of PAH as a whole, but may lead to the selective nitration of some PAHs, such as Phenanthrene. Inomata et al. (2015) studying 4-Nitrophenol, 1-Nitropyerene and 9-Nitroanthracene compounds from 3 different Diesel vehicles emission with DOC, DPF and SCR as aftertreatment systems, concluded that the SCR aftertreatment suppress Nitro-PAHs emission.

Considering the biodiesel effect on the Nitro-PAHs emissions, Ratcliff et al. (2010) and Guan et al. (2017) observed that the use of biodiesel

Table 4
Nitro-PAHs concentrations associated to PM exhaust emissions, in µg kWh^{-1}.

Nitro-PAHs (µg kWh^{-1})	B5 SCR-off		B5 SCR-on		B20 SCR-off		B20 SCR-on	
	Average ± u	n	Average ± u	n	Average ± u	n	Average ± u	n
1-Nitronaphthalene	0.270 ± 0.233	2	0.161 ± 0.020	3	0.193 ± 0.051	2	0.146 ± 0.013	2
2-Nitrofluorene[a]	1.339 ± 0.689	5	1.223 ± 0.276	5	1.624 ± 0.596	5	0.624 ± 0.314	2
1-Nitropyrene[b]	0.408 ± 0.177	1	0.542 ± 0.177	1	0.360 ± 0.177	1	0.350 ± 0.177	1
∑Nitro-PAHs (particles)	2.02 ± 0.75[c]		1.93 ± 0.33[c]		2.17 ± 0.62[c]		1.12 ± 0.36[c]	
Nitro-PAHsC - IARC group 2A and 2B	1.75 (87%)		1.76 (92%)		1,98 (91%)		0.974 (87%)	

u – expanded uncertainties (95% level of confidence); n – number of valid samples.

[a] IARC – group 2B (possibly carcinogenic to humans).
[b] IARC – group 2A (probably carcinogenic to humans).
[c] Uncertainties propagation for PAH sum (estimative).

and oxygenated fuels, respectively, significantly reduces the emission of Nitro-PAHs associated to PM with proportions above 20%. Sharp et al. (2000) studied the effects of biodiesel on unregulated emissions in 3 different heavy-duty vehicles (119, 205 and 176 kW) operating with a transient cycle. Their results showed that Nitro-PAHs emissions associated with PM were lower for biodiesel (B100) compared to the S500 diesel. This result was expected since biodiesel has low concentrations of aromatic compounds, the precursor PAHs in its composition. He (2016) described an increase in Nitro- and Oxy-PAHs when using soybean biodiesel, palm biodiesel and oxidized biodiesel from used fried oil. 1-Nitropyrene has been reported by other studies and can be considered as a diesel emission marker (Bagley et al., 1998; Karavalakis et al., 2010; He, 2016; Guan et al., 2017).

Even with the injection of a urea solution and the consequent reduction on NO_x emission and NH_3 formation, there is no favouring of the nitration process in the SCR aftertreatment system when using biodiesel blends. The results suggest that the opposite occurs: the SCR system combined with biodiesel addition above 20% helps to reduce Nitro-HPAs formation in the aftertreatment by suppressing NO_x and improving the combustion process due to the higher oxygen concentration in biodiesel. However, there is indications that SCR and biodiesel, separately, can increase the emission of some individual Nitro-PAHs, as 2-Nitrofluorene.

In brief, the combination of B20 and SCR after-treatment systems resulted in a consistent reduction of Nitro-PAHs emissions. However, there is evidence that the SCR system selectively promotes the formation of some individual Nitro-PAHs, as 2-Nitrofluorene. Therefore, the higher oxygen content and the absence of aromatic compounds in biodiesel together with PM emission reduction by the SCR system seem to be able to reduce human health risks associated with PAHs and Nitro-PAHs exposure.

4. Conclusion

This study brings an important contribution to a better understanding regarding the synergistic effects of new engine technologies, after-treatment systems and biofuels, on the unregulated PAHs and nitro-PAHs emissions from heavy-duty diesel engines still in use in most developing countries. Total PAHs emission reductions were observed (up to 28%) with the replacement of diesel fuel with biodiesel, which has been ascribed to the different chemistry pathway during the pyrolysis of the biodiesel. These reductions were more pronounced if the SCR aftertreatment system was used. In addition, the fuel composition also played a significant role in the amount of carcinogens PAH emitted. The results were tested against the Toxic Equivalent (TEQ) and the lowest toxicity values were observed with the B20 SCR-on condition, followed by B20 SCR-off, B5 SCR-off and B5 SCR-on. The combination of B20 and SCR after-treatment systems resulted in a consistent reduction of total Nitro-PAHs emissions. Due no correlation between the decrease in NO_x and Nitro-PAHs emission it is unlikely that the SCR system promote PAHs nitration. However, there is evidence that the SCR system selectively promotes the formation of some individual Nitro-PAHs, as 2-Nitrofluorene. Therefore, the higher oxygen content and the absence of aromatic compounds in biodiesel together with the SCR system seem to be able to reduce human health risks associated with PAHs and Nitro-PAHs exposure. These findings can assist in policy making, especially setting new emission standards that include limits for persistent organic pollutants such as PAHs and nitro-PAHs. In addition, the authors recognise that the reduction of tailpipe emissions from diesel-type fuels is a challenging task and therefore hope that the data from this study could help planning the best pathway to assess and reduce vehicular emissions since it depends on fuel type, experimental approaches, engines size and technologies, operating cycles, and aftertreatment systems.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.07.007.

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