White Paper

A Review of Polycyclic Aromatic Hydrocarbon and Polycyclic Aromatic Hydrocarbon Derivative Emissions from Off-Road, Light-Duty, Heavy-Duty, and Stationary Sources

Contract #18RD011

Prepared for:

California Air Resources Board

June 2020

Submitted by:
Dr. Georgios Karavalakis
Mr. Tianyi (Jerry) Ma
Mr. Miguel Robledo

University of California
CE-CERT
Riverside, CA 92521
951-781-5799
951-781-5790 (fax)

Disclaimer

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board or other participating organizations and their employees. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

Acknowledgments

This report was prepared at the University of California, Riverside, and Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT). The authors thank the following organizations and individuals for their valuable contributions to this project.

We acknowledge funding from California Air Resources Board under contract 18RD011. We thank CARB staff, including Jenny Melgo, Wenli Yang, Mary Beth Schwehr, Gabe Ruiz, and David Edwards from the Air Quality Planning and Science Division, for their helpful reviews of this document. Finally, we thank Chris Ruehl in CARB’s Research Division for his valuable help in initiating this important study.

Table of Contents

Executive Summary

Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic pollutants and their primary source in the environment is from the incomplete combustion of carbonaceous materials. PAHs are of great concern because of their widespread occurrence and toxic effects on ecosystem and human health. Although there is no definitive legislation concerning PAH abatement, the Environmental Protection Agency (EPA) has designated 16 PAH as priority pollutants, the latest being effective from 1997.

In this white paper, an extensive literature review on past and current studies on PAH emissions from different combustion sources was performed. We summarized the results of 14 peer-reviewed studies conducted on off-road combustion sources, including diesel generators and off-road engines used for construction or agricultural activities. We also summarized the findings of 37 peer-reviewed studies conducted on on-road heavy-duty diesel engines or heavy-duty diesel vehicles. Finally, we included the results from 50 peer-reviewed studies on light-duty diesel and gasoline engines and vehicles.

PAH emission concentrations are generally high with older technology diesel generators without emissions control aftertreatment. Diesel generators and off-road diesel engines equipped with diesel particulate filters (DPFs) show significant reductions in PAH emissions, especially in the particle-phase. The same observation holds for heavy-duty diesel vehicles and engines. For gasoline vehicles and engines, PAH emissions are generally higher than diesel vehicles. Our literature review showed elevated PAH emissions for gasoline vehicles equipped with gasoline direct injection (GDI) engines compared to diesel vehicles equipped with DPFs, indicating that the larger source of airborne PAHs is from the light-duty GDI fleet.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic chemicals with two to seven fused aromatic rings. Chemically the PAHs are comprised of two or more benzene rings bonded in linear, cluster, or angular arrangements. PAHs may also contain additional fused rings that are not six-sided. Some PAHs are well known as carcinogens, mutagens, and teratogens and therefore pose a serious threat to the health of humans. The International Agency for Research on Cancer (IARC) has classified certain individual PAHs as carcinogenic to animals and probably carcinogenic to humans (IARC, 2010). PAHs known for their carcinogenic and teratogenic properties are benzo[a]anthracene and chrysene ($C_{18}H_{12}$); benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene ($C_{20}H_{12}$); indeno[1,2,3-cd]pyrene ($C_{22}H_{12}$); and dibenzo[a,h]anthracene ($C_{20}H_{14}$). Benzo[a]pyrene is being classified as Group 1 by IARC, while dibenzo[a,l]pyrene and dibenzo[a,h]pyrene are considered as probably carcinogenic to humans (Group 2A) and possible carcinogenic to humans (Group 2B), respectively. Benzo[a]pyrene, a well-studied carcinogen with high potency, has been considered as an index compound and a ‘gold standard’ for its carcinogenic activity defines as 1.0 according to the US EPA (US EPA, 1993).

PAHs are formed primarily during the incomplete combustion of fossil and biomass fuels, and other organic material such as coal, and wood (Stogiannidis and Laane, 2015; Samburova et al., 2017; Zhang and Tao, 2009; Ravindra et al., 2008). The most abundant and potent PAH compounds found as products of incomplete combustion are shown in Figure 1. PAHs formation has three different pathways: 1. PAH fragments in the fuel can survive the combustion process retaining the original carbon skeleton. 2. Pyrosynthesis during combustion of lower molecular weight aromatic compounds. PAHs isolated from exhaust gases could be produced by the recombination of fragments of previous partially destroyed compounds to form new PAHs. 3. Pyrolysis of lubricant oils and unburnt fuel.

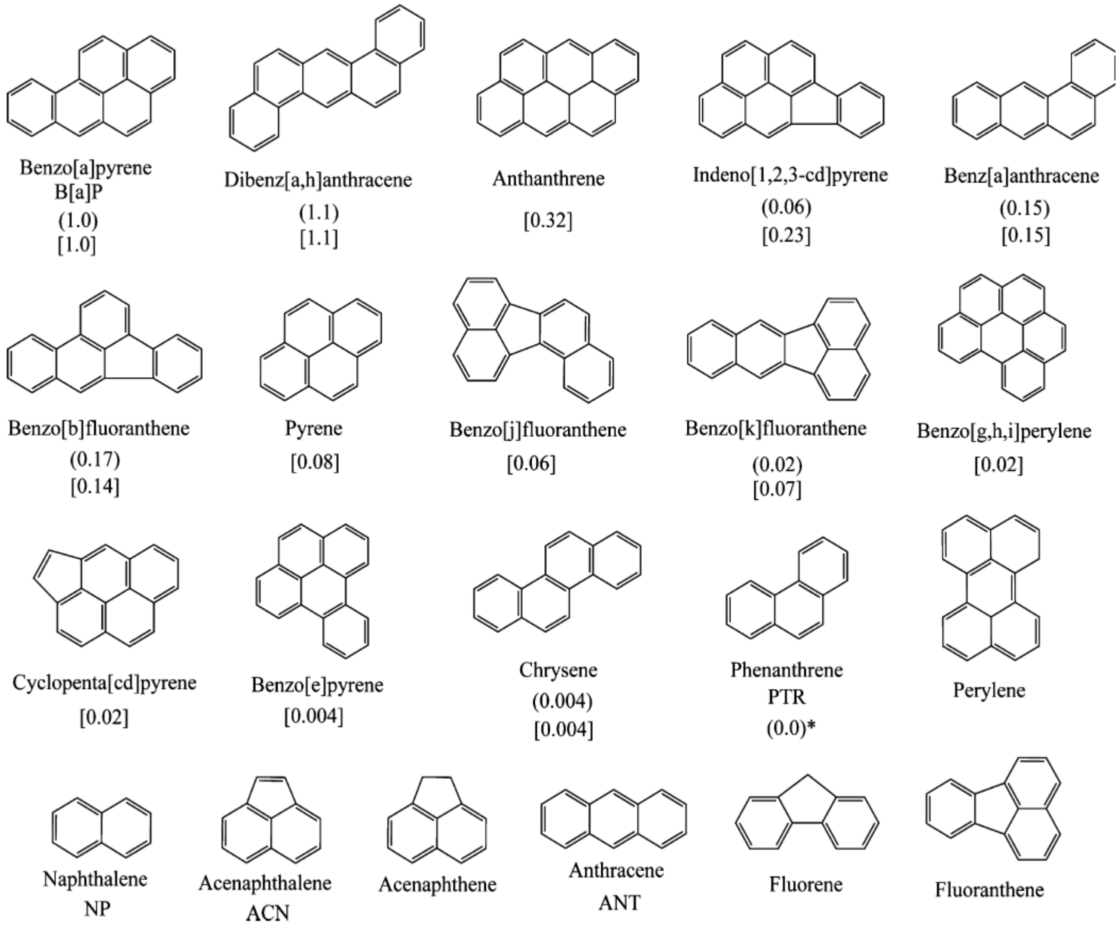


Figure 1: Most abundant PAHs found in the exhaust. Numbers represent carcinogenic potency factors relative to benzo[a]pyrene.

When the temperature exceeds 500 °C, carbon-hydrogen and carbon-carbon bonds are broken to form free radicals. These radicals combine to form ethylene, acetylene, and 1,3-butadiene which further condense with aromatic ring structures, which are resistant to thermal degradation. Although radical PAH formation mechanisms are favored due to the faster combustion processes in the internal combustion engine, other possible PAH formation pathways exist, including the

Diels-Alder reactions, rapid radical reactions, and ionic reaction mechanisms (Kislov et al., 2005). It should be noted, however, that the hydrogen abstraction-acetylene addition (HACA) mechanism is the most commonly accepted as the major reaction route leading to the formation of PAHs in combustion engines (Kislov et al., 2013; Richter and Howard, 2000; Frenklach and Wang, 1991).

Fuel structure could play an important role in PAH formation (Pena et al., 2018; Yinhui et al., 2016). Aromatic hydrocarbons present in diesel and gasoline fuels, especially mono-aromatic species (benzene, toluene, and xylene isomers), may provide a base for PAH and soot growth (Anderson et al., 2000). For instance, benzene combustion generates phenyl radicals, which are highly reactive and can undergo oxidation and ring fragmentation reactions (Li et al., 2010). They can also form phenoxy radicals that oxidizes to cyclopentadiene, a species known to produce naphthalene through cyclopentadienyl recombination (Saggese et al., 2013). In contrast, toluene combustion generates benzyl radicals that are resonantly stabilized and can survive for a long time in the combustion environment (Talibi et al., 2018). They provide a base for the formation of naphthalene and larger PAHs and soot (Anderson et al., 2000).

Beside parent PAHs, some derivatives, like nitrated PAHs (nitro-PAHs), oxygenated PAHs (oxy-PAHs), and hydroxyl PAHs (HO-PAHs) are also of growing concern since it is generally considered that these derivatives are more toxic than the parent PAHs (Albient et al., 2008; Andreou and Rapsomanikis, 2009; Durant et al., 1996; Walgraeve et al., 2010; Ravindra et al., 2008). Nitrated and oxygenated PAHs (mostly quinones) can be directly emitted from combustion sources, formed secondary inside the catalyst system from nitration reactions of the parent PAHs, or formed secondary from the radical reactions with the parent PAHs and/or other precursors (Albient et al., 2007; Walgraeve et al., 2010; Perrini et al., 2005; Yaffe et al., 2001; Jakober et al., 2007). Like their parent PAHs, nitro-PAHs and oxy-PAHs are semi-volatile organic compounds, partitioning between the particle and vapor phase. Although concentrations are far lower than levels of parent PAHs, nitro-PAHs can have stronger carcinogenic and mutagenic activity (Schantz et al., 2001; Khalek et al., 2011). Several nitro-PAHs are direct-acting mutagens, e.g., dinitropyrene and 1-nitropyrene in diesel particulate matter (Perrini et al., 2005). Oxygenated PAHs, containing one or more oxygen(s) attached to the aromatic structure, are also known for their toxicity and mutagenicity, especially several ketones and quinones like benzanthrone and anthraquinone (Durant et al., 1996; Lundstedt et al. 2007). Oxygenated PAHs may affect human health via the formation of proteins and DNA adducts, the depletion of glutathione, and generation of reactive oxygen species (ROS) that can enhance the oxidative stress (Li et al., 2003; Verma et al., 2015). Gas-phase reactions of PAHs to form nitro-PAHs or oxy-PAHs are initiated by either OH or NO_3 radical attack at the position of highest electron density on the aromatic ring, followed by NO_2 addition with a subsequent loss of H_2O or HNO_3, respectively (Jariyasopit et al., 2014; Atkinson et al., 1990; Keyte et al., 2013). In addition, heterogeneous reactions may also occur, including nitration reactions of pyrene and fluoranthene with NO_3/N_2O_5 to yield different nitropyrene and nitrofluoranthene isomers (Zimmermann et al., 2013; Atkinson et al. 1990).

The literature review was selective and critical. Journals obtained from scientific indices were the preferred choice, although other non-indexed publications, such as Society of Automotive Engineers (SAE) technical papers and some internal and published reports from organizations such as the California Air Resources Board have also been cited. This literature review emphasizes on the emissions of PAHs and their nitrated and oxygenated derivatives from on-road and off-road engines. Figure 2 summarizes the compound-specific emission factors included in this review. The following sections show PAH emission factors categorized by source, including off-road diesel engines and generators, light-duty gasoline vehicles, light-duty diesel vehicles, and heavy-duty diesel vehicles. For the light-duty gasoline vehicles category, our intent is to provide two subcategories that represent PAH emission factors from port fuel injection (PFI) engines and gasoline direct injection (GDI) engines.

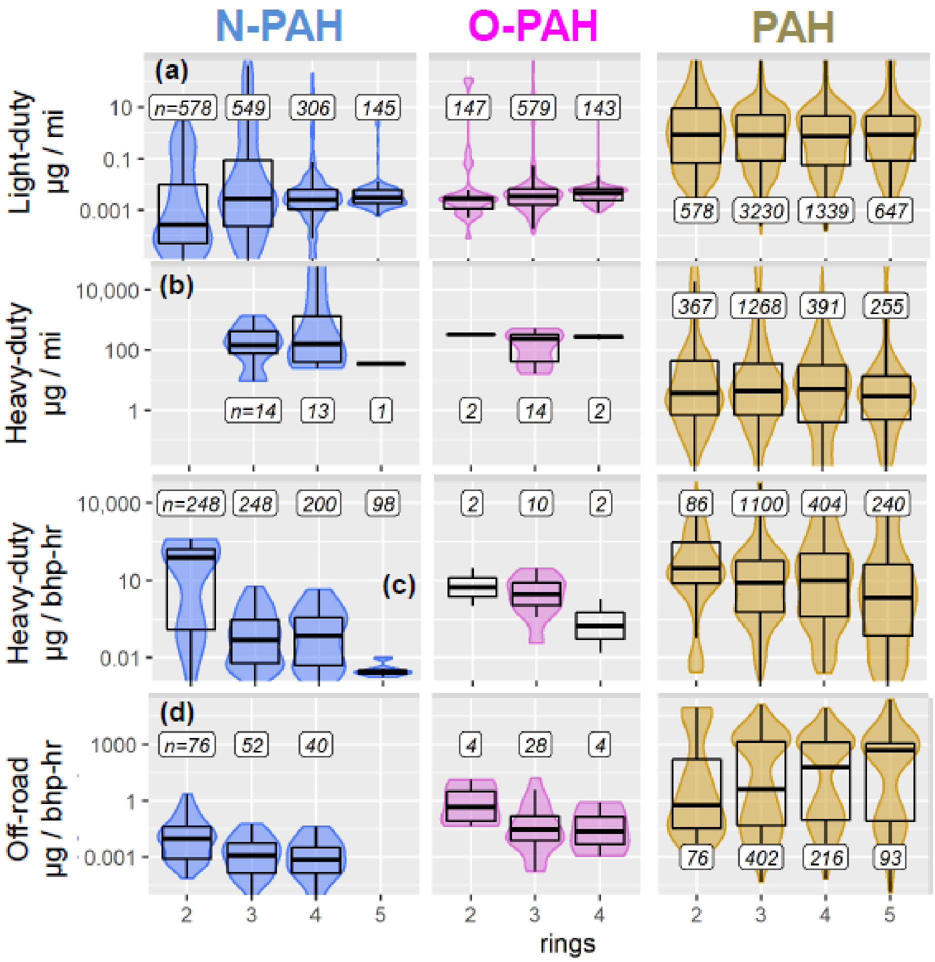


Figure 2. Distribution of compound specific emissions factors (EFs) from (a) light-duty vehicles, (b) heavy-duty vehicles, (c) heavy-duty engines, and (d) off-road engines. EFs are grouped by compound class: nitrogenated (blue), oxygenated (purple), and hydrocarbon PAHs (yellow). Total number of EFs are given in italics. Superimposed are box plots in black indicating median and interquartile range.

References

Albient et al. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): concentrations and sources. Sci Total Environ. 2007, 384, 280-92.

Albient et al. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys Part 1: concentrations, sources and gas/particle partitioning. Atmospheric Environment. 2008, 42, 43–54.

Anderson et al. Experimental study of naphthalene formation pathways in non-premixed methane flames doped with alkylbenzenes. Proc. Combust. Inst., 2000, 28, 2577-2583.

Andreou G., Rapsomanikis S. Polycyclic aromatic hydrocarbons and their oxygenated derivatives in the urban atmosphere of Athens. J Hazard Mater. 2009, 172, 363-73.

Atkinson et al. Kinetics and Nitro-Products of the Gas-Phase OH and NO3 Radical-Initiated Reactions of Naphthalene-d8, Fluoranthene-d10, and Pyrene. Int. J.Chem. Kinet. 1990, 22, 999−1014.

Durant et al. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. Mutat Res. 1996, 371, 123-57.

Frenklach, M.; Wang, H. Detailed Modeling of Soot Particle Nucleation and Growth. Proc. Combust. Inst. 1991, 23, 1559−1566.

International Agency for Research on Cancer. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Volume 94 World Health Organisation; Geneva, Switzerland: 2010. Working Group on the Evaluation of Carcinogenic Risks to Humans, IARC monographs on the evaluation of carcinogenic risks to humans. Ingested nitrate and nitrite, and cyanobacterial peptide toxins.

Jakober et al. Quinone emissions from gasoline and diesel motor vehicles. Environ. Sci. Technol. 2007, 41, 4548-4554.

Jariyasopit et al. Novel nitro-PAH formation from heterogeneous reactions of PAHs with NO2, NO3/N2O5, and OH radicals: Prediction, laboratory studies, and mutagenicity. Environ. Sci. Technol. 201448, 412-419.

Keyte et al. Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons - a review. Chem. Soc. Rev. 2013, 42, 9333-9391.

Khalek et al. Regulated and unregulated emissions from highway heavy-duty diesel engines complying with U.S. Environmental Protection Agency 2007 emissions standards. J Air Waste Manag Assoc. 2011, 61, 427-42.

Kislov et al. Hydrogen Abstraction Acetylene Addition and Diels-Alder Mechanisms of PAH Formation: A Detailed Study Using First Principles Calculations. J. Chem. Theory Comput. 2005, 1, 908−924.

Kislov et al. Formation mechanism of polycyclic aromatic hydrocarbons beyond the second aromatic ring. J. Phys. Chem A 2013, 117, 4794-4816.

Li et al., Particulate air pollutants and asthma. A paradigm for the role of oxidative stress in PM-induced adverse health effects. Clin Immunol. 2003, 109, 250-65.

Li et al. Investigation on fuel-rich premixed flames of monocyclic aromatic hydrocarbons: Part I. Intermediate identification and mass spectrometric analysis. Combustion and Flame 2010, 157, 143-154.

Lundstedt et al. Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. Ambio 2007, 36, 475-85.

Pena et al. Effects of fuel-bound methyl groups and fuel flow rate in the diffusion flames of aromatic fuels on the formation of volatile PAHs. Combustion and Flame 2018, 198, 412-427.

Perrini et al. Nitrated polycyclic aromatic hydrocarbons in the environment: formation, occurrences and analysis. Ann Chim. 2005, 95, 567-77.

Ravindra et al. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment 2008, 42, 2895-2921.

Richter H. Howard J.B. Formation of Polycyclic Aromatic Hydrocarbons and Their Growth to Soot - a Review of Chemical Reaction Pathways. Prog. Energy Combust. Sci. 2000, 26, 565−608.

Saggese et al. A wide range kinetic modeling study of pyrolysis and oxidation of benzene. Combustion and Flame 2013, 160, 1168-1190.

Samburova et al. Do 16 polycyclic aromatic hydrocarbons represent PAH air toxicity? Toxic 2017, 5, 17.

Schantz et al. Stability of Polycyclic Aromatic Hydrocarbons in Frozen Mussel Tissue. Polycyclic Aromatic Compounds. 2001, 19, 253–262.

Stogiannidis E, Laane R. Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: an overview of possibilities. Rev Environ Contam Toxicol. 2015, 234, 49-133.

Talibi et al. Impact of increasing methyl branches in aromatic hydrocarbons on diesel engine combustion and emissions. Fuel 2018, 216, 579-588.

U.S. Environmental Protection Agency. Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. Office of Research and Development; Washington, DC, USA: 1993.

Verma et al. Fractionating ambient humic-like substances (HULIS) for their reactive oxygen species activity-assessing the importance of quinones and atmospheric aging. Atmos. Environ. 2015, 120, 351-359.

Walgraeve et al. Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: Molecular characterization and occurrence. Atmospheric Environment 2010, 44, 1831–1846.

Yaffe et al. Multimedia analysis of PAHs and nitro-PAH daughter products in the Los Angeles Basin. Risk Anal. 2001, 21, 275-94.

Yinhui et al. The impact of fuel compositions on the particulate emissions of direct injection gasoline engine. Fuel 2016, 166 543-552.

Zhang Y.X., Tao S. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. Atmos. Environ. 2009, 43, 812–819.

Zimmermann et al. Formation of nitro-PAHs from the heterogeneous reaction of ambient particle-bound PAHs with N2O5/NO3/NO2. Environ. Sci. Technol. 2013, 47, 8434-8442.

2. Off-Road Sources

The following section provides information about the emissions factors of PAH and nitro-PAH species from off-road (diesel) engines and diesel generators (stationary sources). For each study, tables including PAH and nitro-PAH emissions will be presented, as well as the sampling procedure and method of analysis.

2.1 Diesel Off-Road Engines

The first study by **Liu et al. (2015)** [Mitigation of PAH and Nitro-PAH Emissions from Nonroad Diesel Engines, Environmental Science and Technology] used a source dilution sampling system to characterize PAH and nitro-PAH emissions in the exhaust of a nonroad, Tier 4 Final diesel engine equipped with various aftertreatment systems. These were including DOC+copper zeolite selective catalytic reduction (CuZ-SCR) catalyst+ammonia oxidation (AMOX) catalyst, vanadium-based SCR (V-SCR) catalyst+AMOX, and DOC+DPF+CuZ-SCR+AMOX. Experiments were performed over the Nonroad Transient Cycle (NRTC). An 8.9 L engine rated for 380 HP (283 kW) at 2100 rpm was used for this study. The engine was turbocharged and charge air cooled and was equipped with electronically controlled high pressure common rail fuel injection and cooled exhaust gas recirculation. This is an industrial nonroad U.S. Tier 4 Final/Euro Stage IV engine rated for use with ultralow-sulfur diesel (ULSD).

Engine exhaust samples were collected with a source dilution sampling (SDS) system composed of a critical flow venturi-constant volume system (CFV-CVS) for primary dilution, a residence time chamber (RTC) used to simulate atmospheric aging of exhaust samples, isokinetic sampling probes, and multiple mass flow-controlled sample trains for filter- and cartridge-based sample collection. Dilution air was humidity and temperature controlled, and high-efficiency particulate air (HEPA) and activated carbo filters removed background particles and organic compounds. Emissions of PAHs and nitro-PAHs were collected with a high-volume sampler. A 90 mm PTFE impregnated glass fiber (TIGF) filter was used to trap PM-phase emissions and was located upstream of an Amberlite XAD-4 polymeric adsorbent cartridge (Sigma-Aldrich Corp.) which trapped volatile and semivolatile species that were not PM-bound in the sampling apparatus.

The XAD prefilter was sonicated for 10 min twice in both dichloromethane (DCM) and methanol and was then dried in a vacuum oven at 50 °C for a minimum of 24 h. The XAD-4 resin was washed with liquinox soap and rinsed with hot water, deionized water, and methanol before being extracted with DCM and then acetone at 1500 pounds per square inch (psi) and 80 °C. The XAD-4 resin was then dried in a vacuum oven at 50 °C and finally loaded in a glass sampling cartridge. After sampling, the TIGF prefilter and XAD-4 resin were spiked with deuterated PAH and nitro-PAH standards and then extracted separately with DCM followed by acetone at 1500 psi and 80 °C. The PAH and nitro-PAH compounds of interest were isolated with the use of a solid-phase extraction aminopropyl Sep-Pak cartridge (Waters). PAH compounds were either measured with a Varian 4000 gas chromatograph/mass spectrometer (GC/MS) or a Scion 456 GC coupled to a Scion triple quadrupole (TQ) MS for XAD-4 and prefilter extracts, respectively. Nitro-PAHs were analyzed by negative ion chemical ionization mass spectrometry (NICI-MS) with methane as the reagent gas. A 6-level calibration was performed for all analytes, and a midlevel standard was run at least once every 10 samples.

Table 1: Emissions of PAH as a function of aftertreatment system (g/bhp-hr)

	engine out	**DOC+SCR**	**V-SCR**	**DOC+DPF+SCR**
Naphthalene	1.48E-04	2.34E-06	4.51E-07	1.80E-06
quinoline	5.78E-06	1.98E-08	ND	ND
2-methylnaphthalene	1.68E-04	4.38E-07	1.86E-07	1.27E-07

2,6+2,7-dimethylnaphthalene	1.25E-04	1.44E-07	6.41E-08	4.22E-08
1,3+1,6+1,7dimethylnaphth	1.29E-06	6.22E-08	9.24E-08	4.96E-08
1,4+1,5+2,3-dimethylnaphth	1.02E-04	4.77E-08	2.41E-08	2.04E-08
Acenaphthylene	2.18E-05	1.03E-08	2.63E-09	ND
1,2-dimethylnaphthalene	2.96E-05	1.44E-08	ND	1.04E-08
Acenaphthene	4.71E-06	4.84E-08	3.19E-09	1.02E-07
Dibenzofuran	6.62E-06	1.68E-07	ND	1.68E-08
1,8-dimethylnaphthalene	ND	ND	ND	ND
1-ethyl-2-methylnaphthalene	9.89E-06	1.68E-08	7.20E-09	7.12E-09
2,3,5+I-trimethylnaphthalene	2.40E-05	5.55E-08	3.16E-08	3.00E-08
B-trimethylnaphthalene	3.46E-05	2.85E-09	5.19E-08	3.34E-08
A-trimethylnaphthalene	4.43E-05	1.11E-07	9.12E-08	3.12E-08
C-trimethylnaphthalene	2.96E-05	8.74E-08	1.17E-07	3.21E-08
1+2ethylnaphthalene	2.56E-05	5.08E-07	7.40E-08	3.35E-07
2-ethyl-1-methylnaphthalene	1.54E-06	2.08E-08	1.25E-08	2.91E-09
E-trimethylnaphthalene	2.14E-05	1.25E-07	6.90E-08	1.24E-08
2,4,5-trimethylnaphthalene	4.22E-06	3.52E-08	1.45E-08	1.65E-08
F-trimethylnaphthalene	1.80E-05	ND	2.85E-08	1.89E-08
Fluorene	6.56E-06	2.90E-07	1.21E-07	1.45E-07
1,4,5-trimethylnaphthalene	7.37E-06	ND	3.31E-08	ND
J-trimethylnaphthalene	1.45E-05	3.63E-08	2.67E-08	1.22E-08
A-Methylfluorene	1.34E-05	2.25E-08	1.04E-08	5.64E-09
B-Methylfluorene	5.10E-06	8.08E-09	ND	ND
1-Methylfluorene	7.71E-06	5.91E-08	2.75E-08	1.73E-09
Dibenzothiophene	8.57E-08	2.19E-08	1.44E-08	ND
Phenanthrene	1.64E-05	2.55E-07	1.81E-07	8.18E-08
Anthracene	3.18E-06	5.86E-09	2.68E-08	2.49E-09
3-methylphenanthrene	9.21E-06	5.80E-08	1.33E-07	2.88E-08
2-methylphenanthrene	9.09E-06	6.90E-08	1.91E-07	3.77E-08
2-methylanthracene	1.58E-06	2.43E-09	2.00E-08	1.64E-09
4,5-methylenephenanthrene	4.78E-07	1.32E-08	2.40E-08	4.91E-09
9-methylphenanthrene	5.97E-06	4.34E-08	7.68E-08	1.47E-08
1-methylphenanthrene	3.98E-06	2.70E-08	7.94E-08	1.85E-08
9-methylanthracene	2.90E-07	1.16E-09	3.95E-09	1.15E-09
2-phenylnaphthalene	6.16E-07	9.19E-09	2.09E-08	3.13E-09
A-dimethylphenanthrene	3.93E-06	2.74E-08	1.46E-07	1.41E-08
B-dimethylphenanthrene	1.73E-06	1.70E-08	7.70E-08	9.94E-09
7-methylbenz(a)anthracen	3.78E-09	8.55E-10	5.19E-09	ND
7,12-dimethylbenz(a)anthrace	1.62E-08	8.37E-09	ND	1.56E-08
Benzo(b)fluoranthene	9.62E-08	2.66E-09	7.32E-09	ND
Benzo(k)fluoranthene	3.93E-08	1.15E-09	3.42E-09	ND
Benzo(j)fluoranthene	6.67E-08	2.43E-09	5.85E-09	ND
Benzo(a)fluoranthene	1.76E-08	1.03E-09	6.53E-09	ND

Benzo[e]pyrene	7.40E-08	2.27E-09	7.80E-09	ND
Benzo[a]pyrene	5.96E-08	5.37E-10	6.40E-09	ND
Perylene	1.70E-08	ND	2.34E-09	ND
3-methylcholanthrene	ND	3.98E-09	1.68E-09	ND
7-methylbenzo(a)pyrene	ND	9.38E-10	ND	ND
Indeno[123-cd]fluoranthene	ND	9.11E-10	ND	ND
dibenzo(a,h)acridine	ND	6.15E-10	ND	ND
1,7-dimethylphenanthrene	1.80E-06	2.02E-08	9.32E-08	1.94E-08
3,6-dimethylphenanthrene	2.13E-06	9.87E-09	5.64E-08	4.21E-09
D-dimethylphenanthrene	1.03E-06	2.24E-08	1.14E-07	1.34E-08
E-dimethylphenanthrene	2.01E-06	4.06E-09	1.26E-08	6.06E-09
C-dimethylphenanthrene	5.46E-06	4.21E-08	2.18E-07	2.34E-08
Fluoranthene	1.45E-06	1.27E-07	5.92E-08	5.83E-09
Pyrene	6.09E-06	3.63E-08	2.50E-07	2.38E-08
9-Anthraaldehyde	5.39E-08	1.70E-10	2.35E-09	1.73E-09
Retene	1.59E-09	6.44E-10	2.69E-09	ND
benzo(a)fluorene	1.52E-07	5.21E-10	8.06E-09	4.76E-11
benzo(b)fluorene	4.04E-09	ND	1.73E-09	ND
B-MePy/MeFl	2.78E-08	3.45E-09	2.05E-08	ND
1-MeFl+C-MeFl/Py	1.75E-08	ND	ND	ND
1+3-methylfluoranthene	4.22E-07	7.47E-10	3.53E-08	1.18E-09
4-methylpyrene	2.24E-06	9.87E-09	1.36E-07	7.26E-09
C-MePy/MeFl	1.04E-08	7.48E-11	4.44E-09	8.27E-10
D-MePy/MeFl	1.48E-06	1.47E-08	1.53E-07	7.52E-09
1-methylpyrene	1.12E-06	6.96E-09	6.52E-08	3.08E-09
Benzonaphthothiophene	7.44E-09	9.56E-10	3.52E-09	3.21E-09
benzo(c)phenanthrene	1.97E-07	1.85E-09	1.48E-08	3.29E-10
Benzo(ghi)fluoranthene	7.25E-07	5.59E-09	3.65E-08	4.94E-09
9-phenylanthracene	1.07E-08	ND	4.55E-10	ND
Cyclopenta(c,d)pyrene	7.20E-08	9.48E-10	2.28E-09	1.21E-09
Benz(a)anthracene	2.03E-07	2.11E-09	1.02E-08	ND
Chrysene	2.54E-07	4.84E-09	1.86E-08	ND
Triphenylene	6.22E-08	5.88E-10	3.71E-09	4.65E-09
3-methylchrysene	3.35E-08	1.01E-09	3.86E-09	1.43E-10
5-methylchrysene	ND	ND	ND	ND
6-methylchrysene	ND	ND	1.28E-09	ND
Dibenzo(ah)anthracene	2.75E-09	8.20E-10	1.82E-09	ND
7H-dibenzo[c,g]carbazole	ND	4.50E-09	1.79E-08	ND
Benzo(ghi)perylene	7.32E-08	7.80E-09	2.98E-08	1.11E-10
Dibenzo(a,l)pyrene	ND	1.70E-09	ND	ND
Coronene	4.81E-09	2.08E-09	1.92E-08	3.40E-10
Dibenzo(a,e)pyrene	ND	ND	5.40E-08	ND
Dibenzo(a,i)pyrene	ND	ND	ND	ND

Dibenzo(a,h)pyrene	ND	ND	ND	ND
Dibenzo(b,k)fluoranthene	ND	ND	ND	ND
Anthraquinone	7.67E-07	9.76E-08	3.21E-07	3.55E-08
Picene	4.56E-08	9.38E-09	3.03E-08	1.28E-11
Benzo(b)chrysene	ND	1.06E-10	ND	ND
Perinaphthenone	1.27E-05	9.80E-08	2.04E-06	4.46E-08
9-fluorenone	4.01E-06	7.60E-07	1.50E-07	8.49E-08
Acenaphthenequinone	ND	3.58E-10	1.07E-08	ND
Xanthone	1.59E-05	9.72E-09	6.95E-09	8.28E-09
Benzanthrone	8.08E-07	7.49E-09	7.55E-08	1.20E-09
Benz(a)anthracene-7,12-dione	3.93E-08	2.85E-10	7.54E-09	ND
Anthrone	1.25E-06	8.06E-09	2.87E-08	7.74E-09
Anthanthrene	ND	5.50E-10	2.40E-09	1.39E-11
dibenzo(a,j)acridine	ND	2.35E-09	6.64E-09	2.39E-10
Indeno[123-cd]pyrene	2.53E-08	1.91E-09	6.72E-09	6.94E-11
Dibenzo(ah+ac)anthracene	ND	ND	ND	ND
Dibenzo(ac)anthracene	1.09E-09	5.72E-10	4.79E-10	ND

ND: Not Detected

Table 2: Emissions of nitro-PAHs as a function of exhaust aftertreatment system (g/bhp-hr)

	engine out	**DOC+SCR**	**V-SCR**	**DOC+DPF+SCR**
1-nitronaphthalene	4.83E-08	1.42E-06	5.62E-08	2.30E-06
1-methyl-5-nitronaphthalene	3.77E-08	1.13E-07	9.18E-10	4.07E-07
2-nitronaphthalene	2.03E-07	4.58E-07	1.34E-08	1.43E-07
2-nitrobiphenyl	1.71E-08	1.87E-08	6.10E-10	1.93E-08
2-methyl-4-nitronaphthalene	1.64E-08	5.82E-09	9.75E-10	2.19E-08
1-methyl-4-nitronaphthalene	ND	6.61E-09	4.83E-10	2.16E-08
1-methyl-6-nitronaphthalene	4.09E-08	2.13E-10	7.03E-10	6.10E-10
3-nitrobiphenyl	1.07E-08	9.55E-09	6.35E-10	6.57E-10
4-nitrobiphenyl	2.47E-08	2.12E-07	4.02E-09	8.91E-08
1,3-dinitronaphthalene	5.91E-09	5.28E-09	2.39E-09	7.44E-11
1,5-dinitronaphthalene	4.18E-10	1.68E-08	4.81E-09	3.29E-09
5-nitroacenaphthene	1.42E-09	1.55E-10	1.69E-09	7.10E-11
2-nitrofluorene	2.74E-09	1.90E-10	1.18E-09	9.79E-11
4-nitrophenanthrene	4.34E-09	1.10E-08	5.04E-09	6.13E-11
9-nitroanthracene	2.12E-08	4.79E-10	2.63E-09	8.99E-11
9-nitrophenanthrene	3.57E-08	1.30E-09	2.36E-08	6.25E-09
1,8-dinitronaphthalene	6.59E-10	4.35E-09	2.98E-10	3.22E-10
3-nitrophenanthrene	5.54E-08	6.27E-10	6.63E-09	9.30E-10
2-nitrophenanthrene	2.69E-08	6.75E-11	8.82E-10	
2-nitroanthracene	ND	ND	ND	1.53E-10

2-nitrofluoranthene	5.34E-09	7.18E-12	ND	ND
3-nitrofluoranthene	6.72E-10	5.06E-13	ND	ND
4-nitropyrene	1.48E-08	2.53E-12	1.35E-10	ND
1-nitropyrene	3.90E-08	1.71E-09	2.80E-09	ND
2-nitropyrene	8.93E-09	ND	2.57E-11	1.98E-10
2,7-dinitrofluorene	ND	ND	ND	ND
2,7-dinitrofluoren-9-one	ND	ND	ND	ND
7-nitrobenz(a)anthracen	5.35E-09	2.20E-11	1.27E-10	ND
6-nitrochrysene	7.15E-10	ND	ND	ND
3-nitrobenzanthrone	ND	ND	ND	ND
1,3-dinitropyrene	4.23E-10	ND	ND	ND
1,6-dinitropyrene	1.35E-10	ND	ND	ND
1,8-dinitropyrene	3.05E-09	ND	ND	ND
6a+1e-nitrobenzopyrene	ND	ND	ND	ND
3-nitrobenzo[e]pyrene	ND	ND	ND	ND

ND: Not Detected

Rajput and Lakhani (2009) [PAHs and their Carcinogenic Potencies in Diesel Fuel and Diesel Generator Exhaust, Human and Ecolo Risk Assessment] characterized PAH emissions from two engines; a 10 hp four-stroke Skoda, Type 15110 engine (E1) and a 5 hp diesel generator. Exhaust samples were collected on 19 mm x 90 mm Glass micro fiber thimbles using a Vayibodhan Stack Sampler (VSS1). Diesel fuel samples were diluted thrice in HPLC grade dichloromethane while the exhaust samples were extracted ultrasonically in 100ml dichloromethane. These samples were cleaned using silica gel (Fluka, 230 mesh) packed glass columns (10 cm × 1 cm i.d.) and were concentrated to 1 ml. Both fuel and exhaust samples were stored in Teflon vials and were then analyzed in splitless mode using a temperature gradient program by a gas chromatograph (Shimadzu 17AATF, ver 3) equipped with an FID detector and capillary column (25 m length 0.3 mm internal diameter; BP1; with dimethyl polysiloxane as stationary phase). The GC was calibrated and quantified with a standard solution of 16 PAH compounds (Supelco USEPA 610 PAH mixture). Quantification of PAHs was done with a reference to standard PAH mixture by comparing the retention times and peak areas to the external calibration.

Exhaust concentration PAH emission factors (mg/lfuel) were calculated for both engines as:

$$\text{Emission Factor (mg/l)} = \frac{[\text{PAH concentration (mg m}^{-3}) \times \text{Flow rate of exhaust gas (m}^{3}\ \text{min}^{-1})]}{\text{Fuel consumption (1 min}^{-1})}$$

Authors also calculated the out/input ratio (O/I) of individual PAHs. This ratio is defined as the ratio of its emission factor to its fuel consumption. The O/I ratio can help explain the PAH fate during combustion process. It is calculated as:

$$\text{O/I ratio} = [\text{Emission Factor (mg/l)}]/[\text{Fuel concentration (mg/l)}]$$

Table 3: PAHs concentration in the exhaust samples and their/I ratio

	Exhaust concentration		Emission factors		O/I ratio	
	(μg m^{-3})		(mg/l)			
PAH	E1, n = 10	E2, n = 10	E1	E2	E1	E2
Naphthalene	26 ± 3.1	—	6.5 ± 8.1	—	1.5 × 10−2	—
Acenaphthylene	5 ± 1.2	16.8 ± 6.3	1.1 ± 0.2	2.1 ± 1.2	0.08 × 10−2	0.15 × 10−2
Acenaphthene	4 ± 2.3	—	0.9 ± 0.6	—	0.05 × 10−2	—
Fluorene	9 ± 1.1	10.1 ± 5.8	2.2 ± 2.8	1.3 ± 0.9	0.15 × 10−2	0.09 × 10−2
Phenanthrene	33 ± 29	3.15 ± 1.2	8.2 ± 7.6	0.4 ± 0.2	0.62 × 10−2	0.03 × 10−2
Anthracene	18 ± 6.7	—	4.1 ± 1.4	—	0.33 × 10−2	—
Fluoranthene	111 ± 36	1.96 ± 0.8	26.7 ± 8.9	0.2 ± 0.1	2.13 × 10−2	0.02 × 10−2
Pyrene	69 ± 49	49.4 ± 12.4	16.7 ± 12.6	6.0 ± 1.6	3.4 × 10−2	1.2 × 10−2
Benz[a]anthracene+Chrysene	195 ± 50	30.3 ± 14.5	48.5 ± 44.6	3.3 ± 2.6	40.6 × 10−2	2.6 × 10−2
Benzo[b]fluoranthene +Benzo[k]fluoranthene	276 ± 159	99.1 ± 28.5	67.6 ± 32.8	11.3 ± 8.9	11.26	179.8 × 10−2

Benzo[a]pyrene	102 ± 60	70.7 ± 36.6	25.3 ± 30.2	7.8 ± 8.2	2.55	79.2 × 10−2
Dibenzo[a,h]anthracene+ Indeno[1,2,3cd]pyrene	219 ± 123	115 ± 75	53.57 ± 43.1	13.7 ± 8.8	—	—
Benzo[ghi]perylene	194 ± 76	77.5 ± 20.8	48.1 ± 10.7	9.4 ± 3.1	—	—

Cui et al. (2017) [Measurement of PM and its chemical composition in real-world emissions from non-road and on-road diesel vehicles, Atmo Chem Phys] investigated the PAH emissions from six excavators and five trucks. Detailed information for the selected engines is shown below:

ID	Manufacturer	Model Year	Emission standards	Power (kW)	Total weigh (kg)	Displacement (L)
E1	Volvo	2013	Stage 2	169	30500	7.1
E2	Hitachi	2007	Pre-stage 1	162	30200	9.8
E3	Sany	2012	Stage 2	128	22900	-
E4	Doosan	2004	Pre-stage 1	110	22000	8.1
E5	Doosan	2007	Pre-stage 1	40	5250	2.8
E6	Kumatsu	2013	Stage 2	35	5300	2.4
T1	Futian	2010	China III	68	4495	2.6
T2	JAC	2014	China IV	88	4495	2.8
T3	Futian	2011	China III	70	11190	3.9
T4	Chunlan	2002	China II	125	15480	-
T5	JAC	2011	China III	105	15590	4.3

The excavators in this study were categorized into three types, low (0–75 kw), medium (75–130 kw), or high (130–560 kw) power, under different emission standards. Three operational modes were selected for the excavators to reflect actual use conditions, such as idling, moving, and working. Three types of diesel trucks were selected in this study, including one China II standards truck, three China III standards trucks, and one China IV standards truck. The China III trucks included one of each light-duty, medium-duty, and heavy-duty diesel truck.

The onboard PM sampling system consisted of a dilution system followed by five exhaust channels. Two channels were connected to PM samplers, and the other three were blocked. Before sampling, the emission measurement system was in-stalled on a truck and was connected to the excavator exhaust tube by a stainless steel pipe. Quartz-fiber filters were used to collect PM samples for PAH analysis. Quartz filter samples were spiked with internal standards (including acenaphthene-d10, benzo[a]anthracene-d12, pyrene-d10, coronene-d12, cholestane-d4, n-C15-d32, n-C20-d42, n-C24-d50, n-C30-d58, n-C32-d66, n-C36-d74) and were ultrasonically extracted twice in 30 mL of a 1:1 mixture of hexane and dichloromethane for 10 min. All extracts from each sample were combined, filtered, and concentrated to approximately 0.5 mL. PAHs were analyzed using GC-MS (Agilent 7890AGC-5975C MS) with a DB-5MS column of 30 m in length, an inner diameter of 0.25 mm, and thickness of 0.25 μm. The following GC operating program was used: 60◦C for 4 min, then increase 5◦C min^{-1}to 150◦C with 2 min static time, and finally increase 3◦C min^{-1} to 306◦C with a 20 min static time.

Table 4: PAH constituents of PM for different vehicles (%)

PAH	E1	E3	E4	E5	T1	T2	T3	T4	T5
Naphthalene	0.012	0.01	0.006	0.004	nd	0.001	nd	0.004	nd
Acenaphthylene	0.006	0.007	0.006	0.002	nd	nd	nd	0.001	nd
Acenaphthalene	0.002	0.002	0.001	0.0004	nd	nd	nd	0.0002	nd
Fluorene	nd	0.0001	0.006	0.00001	nd	nd	0.0004	nd	nd
Phenanthrene	0.001	0.003	0.017	0.0004	0.0002	0.001	0.103	0.001	0.001
Anthracene	0.0001	0.001	0.002	0.00003	nd	nd	0.005	nd	0.001
Fluoranthene	0.004	0.069	0.027	0.004	0.001	0.009	0.032	0.004	0.003
Pyrene	0.013	0.087	0.004	0.006	0.002	0.026	0.382	0.022	0.008
Benzo(a)Anthracene	0.002	0.019	0.005	0.001	0.0001	0.002	0.001	0.001	0.0002
Chrysene	0.005	0.025	0.001	0.001	0.0001	0.005	0.002	0.001	0.001
Benzo(b)Fluoranthene	0.001	0.007	0.001	0.001	nd	0.001	0.001	0.0004	nd
Benzo(k)Fluoranthene	0.0001	0.002	0.001	0.0001	nd	0.0002	0.0002	0.0001	nd
Benzo(a)Pyrene	nd	0.001	0.0004	0.00002	nd	nd	0.0001	nd	nd
Indeno[1,2,3-cd]pyrene	0.001	0.001	0.001	0.002	nd	nd	0.0001	nd	nd
Dibenzo(a,h)anthracene	nd	0.0003	0.001	nd	0.0001	0.002	0.002	0.0004	0.0001
Benzo(ghi)perylene	0.004	0.003	nd	0.005	0.001	0.009	0.009	0.002	0.001

Gao et al. (2016) [Polycyclic aromatic hydrocarbon emissions of non-road diesel engine treated with non-thermal plasma technology, Korean J. Chem. Eng.] studied the gas- and particle-phase PAH emissions from a low power non-road diesel engine at different loads. The engine was tested in its original configuration and with the use of non-thermal plasma (NTP), which was designed as an effective aftertreatment to reduce PAH emissions. the engine was a single cylinder, 0.418L engine without any aftertreatment control that was manufactured by KEPU (model KD186FA). PAH emissions were measured at three different loads, namely at 40%, 60%, and 80%. The speed of the diesel engine was constant.

Particle- and gas-phase PAHs were collected using glass fiber filter paper (Whatman GF/A55) and self-made "PUF/XAD-2/PUF" at 35C, respectively. Glass fiber filter papers were baked for 6hours at 400C in a muffle furnace before sampling. Particle- and gas-phase PAHs were sampled at 10L/min exhaust flow rate for 10min, and PM aggregation was undertaken at 200L/min over dozens of minutes. Particle- and gas-phase PAHs were extracted from glass fiber filter paper and PUF/XAD-2/PUF, respectively, by using an accelerated solvent extraction system (Dionex ASE 200), and the extraction conditions were as follows: mixed solvent (acetone: n-hexane, 1:1), pressure (1,500 psi (10.34MPa)), temperature (100C), pre-heating time (2 min), cycle index (3). The extracts were concentrated in a rotary evaporator to 1mL then stored below 4C. Qualitative and quantitative analysis of PAHs were performed using a gas chromatograph-mass spectrometer (GC-MS, Agilent 7890A/5975C) under selected ion monitoring (SIM) scanning. The GC-MS was equipped with a capillary column (HP-5, 30m×250 µm×0.25µm) with an injection volume (1µL) and delay time (5 min). The splitless injection and ion source temperatures were 280 and 230C, respectively. The oven temperature was held at 70C for 2min and programmed to increase to 280C at 10C/min (held for 5min), and then to 300C at 5C/min (held for 5min). Relative standard deviation (RSD), limits of detection and recoveries of 16 PAHs were 0.5%-10.1%, 0.03mg/L-0.67mg/L and 55.78%-103.46%, respectively.

Table 5: Particle-phase PAHs, expressed in µg/m^3

Engine Load	40%		60%		80%	
	Without NTP	With NTP	Without NTP	With NTP	Without NTP	With NTP
Naphthalene	NA	NA	20.02	NA	2.21	NA
Acenaphthene	4.83	2.36	120.44	NA	48.16	NA
Acenaphthylene	NA	4.46	42.50	NA	3.15	NA
Fluorene	17.85	6.32	339.58	NA	37.47	NA
Phenanthrene	109.53	35.95	NA	34.74	297.33	1.40
Anthracene	10.54	NA	153.53	8.03	33.89	NA
Fluorene	68.93	1.24	544.80	17.91	233.30	21.38
Pyrene	76.61	2.23	600.41	17.71	263.89	30.98
Benzo[a]Fluoranthene	7.44	3.22	94.42	NA	38.57	5.68
Chrysene	8.18	1.86	100.65	NA	43.37	5.10

Benzo[b]Fluoranthene	8.16	0.91	82.98	1.870	45.22	6.29
Benzo[k]Fluoranthene	NA	NA	7.38		21.18	1.36
Benzo[a]Pyrene	3.85	0.30	91.06	1.696	23.65	4.87
Indeno[1,2,3-cd]Pyrene	4.50	NA	80.85	1.559	26.70	3.87
Dibenzo[a,h]Anthracene	NA	NA	5.81	NA	2.67	NA
Benzo[g,h,i]Perylene	6.25	NA	2.10	2.179	35.23	5.11

Table 6: Gas-phase PAHs, expressed in μg/m^3

Engine Load	40%		60%		80%	
	Without NTP	With NTP	Without NTP	With NTP	Without NTP	With NTP
Naphthalene	178.96	195.26	1.94	84.49	1.55	61.46
Acenaphthene	127.70	84.83	364.99	273.74	511.55	417.41
Acenaphthylene	66.96	32.83	96.32	117.92	129.69	116.12
Fluorene	140.54	72.22	222.10	87.01	375.50	102.46
Phenanthrene	21.63	5.92	1.28	NA	5.43	1.78
Anthracene	49.38	16.71	60.06	25.23	1.69	NA
Fluorene	43.67	29.24	NA	NA	1.82	NA
Pyrene	36.47	3.29	1.26	NA	2.36	1.63
Benzo[a]Fluoranthene	NA	NA	8.86	3.47	NA	NA
Chrysene	NA	NA	NA	NA	NA	NA
Benzo[b]Fluoranthene	6.27	NA	6.98	NA	5.67	3.34
Benzo[k]Fluoranthene	NA	NA	NA	NA	4.26	NA
Benzo[a]Pyrene	6.27	1.16	9.86	3.50	NA	NA
Indeno[1,2,3-cd]Pyrene	NA	NA	5.13	NA	NA	NA
Dibenzo[a,h]Anthracene	NA	NA	NA	NA	2.83	NA
Benzo[g,h,i]Perylene	NA	NA	NA	NA	NA	NA

Zhang et al. (2020) [Emission characteristics and chemical composition of particulate matter emitted by typical non-road construction machinery, Atmospheric Pollution Research] investigated PAH emissions from three types of construction machinery (1 excavator, 1 loader, and 1 forklift) when operated under different working conditions using PEMS. During the experiment, the on-line analysis was performed on vehicle exhausts and sample collections of particulate matter obtained under three working conditions: idling, moving and working. Each working condition lasted at least 10–20 min, and the test were repeated 3–6 times for each non-road construction machinery. The fuel used in this study was China V diesel.

A portable particle matter collection sampler (HY–100WS particle sampler, Qingdao Hengyuan) was simultaneously used to collect the exhaust particulate matter. The PM was collected using a Teflon filter (90 mm, Whatman, America) to study the chemical composition of the particulate matter.

The polycyclic aromatic hydrocarbons (PAHs) were detected based on the EPA TO-13A standard, and gas chromatography-mass spectrometry (GC-MS, Agilent 7890b-5977A, Agilent, USA) was used t analyse 18 kinds of PAHs present in the samples, which included Naphthalene (NA), Acenaphthylene (ACL), Acenaphthene (AC), Fluorene (FL), Phenanthrene (PHE), Anthracene (AN), Fluoranthene (FA), Pyrene (PY), Benzo (a) anthracene (BaA), Chrysene (CHR), Benzo (b) fluoranthene (BbFA), Benzo (k) fluoranthene (BkFA), Benzo (e) pyrene (BeP), Benzo (a) pyrene (BaP), Dibenzo (a,h) anthracene (DBahA), Benzo (g,h,i) perylene (BghiP), Indeno (1,2,3-cd) pyrene (IP), Coronene (COR).

Table 7: PAH emissions in PM2.5 in μg/m^3 for the three different construction equipment

PAHs	**Loader**	**Excavator**	**Forklift**
Naphthalene	0.031	0.039	0.035
Acenaphthylene	0.016	0.031	0.000
Acenaphthene	0.212	0.035	0.020
Fluorene	0.302	0.302	0.204
Phenanthrene	0.282	0.223	0.000
Anthracene	0.321	0.200	0.172
Fluoranthene	0.063	0.000	0.031
Pyrene	0.345	0.478	0.188
Benzo(a)anthracene	0.110	0.000	0.031
Chrysene	1.406	1.786	1.003
Benzo(b)fluoranthene	0.274	0.474	0.188

Benzo(k)fluoranthene	0.690	1.610	0.180
Benzo(e)pyrene	0.153	0.317	0.106
Benzo(a)pyrene	0.176	0.325	0.110
Dibenzo(a,h)anthracene	1.481	4.944	1.826
Benzo(g,h,i)perylene	0.043	0.110	0.055
Indeno(1,2,3-cd)pyrene	0.125	0.157	0.063
Coronene	0.051	0.063	0.000

Peng et al. (2016) [Real-World emission from in-use construction equipment in China, Aerosol and Air Quality Research] studied the in-use PAH emissions of construction equipment using PEMS. The construction equipment were all in-use vehicles selected at construction sites in the city of Dalian, China. No emission aftertreatment was employed in these vehicles. The selected vehicles were of either China Stage 0 (not certified to any emission standard) or China Stage 2 (equivalent to Euro 2). Emissions testing was done on three operating modes: idling, moving, and working.

The particle sampler used to collect PM in the exhaust contained two sampling channels without size-selective inlet. Each channel contained a quartz-fiber filter whose diameter was 47 mm. The sampling volumetric flow rate was set to 10 L min^{-1}. Before entering the sampler, the exhaust was diluted by a two-stage diluter with a constant dilution ratio of 64. The diluted exhaust in the first stage was heated up to 190 °C while the second stage was not heated.

PAH emissions were analyzed by GCMS (Agilent 5975-6890) to determine particle-phase PAHs. Before tested by GC-MS, the sample was soaked in dichloromethane for 24 hr to extract particle-phase PAHs. The analysis followed the procedure provided in Chinese environmental standard HJ 646-2013.

Table 8: Fuel-based PAH emission factors in mg/kg fuel for the Stage 0 and Stage 2 construction equipment during idling, moving, and working modes

Particle-Phase PAHs	**Idling Mode**		**Moving Mode**		**Working Mode**	
	Stage 0	**Stage 2**	**Stage 0**	**Stage 2**	**Stage 0**	**Stage 2**
Naphthalene	1.115	0.154	0.920	0.279	1.074	0.515
Acenaphthylene	0.962	0.179	0.693	0.310	1.270	0.501
Acenaphthene	0.321	ND	0.052	ND	0.089	ND
Fluorene	0.340	0.048	0.274	0.088	0.310	0.139
Phenanthrene	1.260	0.192	1.093	0.393	0.641	0.406
Anthracene	1.519	0.224	1.295	0.463	0.633	0.486
Fluoranthene	0.340	0.083	0.336	0.145	0.170	0.132
Pyrene	0.859	0.215	0.801	0.401	0.374	0.286
Benzo[a]anthracene	0.077	0.013	0.096	0.039	0.019	0.012
Chrysene	0.083	0.013	0.085	0.041	0.025	0.017
Benzo[b]fluoranthene	0.013	ND	ND	ND	ND	ND
Benzo[k]fluoranthene	ND	ND	ND	ND	ND	ND
Benzo[a]pyrene	0.042	ND	0.044	0.044	0.074	ND
Indeno[1,2,3-c,d]pyrene	0.042	ND	0.052	0.049	0.110	ND
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	0.035	0.013	0.070	0.070	0.217	0.134

ND: Not Detected

2.2 Diesel Generators (Stationary Sources)

Tsai et al. (2011) [Particle-bound PAHs and Particle-extract-induced Cytotoxicity of Emission from a Diesel-generator Fueled with Soy-biodiesel, Aerosol and Air Quality Research] characterized the particle-bound PAH emissions and their cytotoxicity properties from a diesel engine power generator when operated on diesel fuel and 20 vol% soybean biodiesel (S20). Testing was performed in the unload (0 kW) and load (3 kW or 75% of max output power) phases of the generator. The diesel engine was a water-cooled, direct injection single cylinder four-stroke diesel engine (Model: TF110E, Yanmar Corporation, Japan).

The size distributions of particle-bound PAHs that were emitted from the generator using different fuels were measured using a micro-orifice uniform deposit impactor (MOUDI) and a Nano-MOUDI (with 0.01–18 μm aerodynamic diameters). The flow rates of the MOUDI and Nano-MOUDI were set to 30 and 10 L/min, respectively; these two samplers used 37- and 47-mm quartz filters (Pall Ltd., USA), respectively. The impactors in the MOUDIs and Nano-MOUDI separated the particulate matter into 13 size ranges (at 50% efficiency) with the following equivalent cutoff diameters: 0.010–0.018, 0.018–0.032, 0.032–0.056, 0.056–0.1, 0.1–0.18, 0.18–0.32, 0.32–0.56, 0.56–1.0, 1.0–1.8, 1.8–3.2, 3.2–5.6, 5.6–10, and 10–18 μm. The particles were divided into six size groups: PM0.01–0.056 (nanoparticles: 0.01 μm < Dp < 0.056 μm), PM0.01–0.1 (ultrafine particles: 0.01 μm < Dp < 0.1 μm), PM0.01–1 (submicron particles: 0.01 μm < Dp < 1 μm), PM0.01–2.5 (fine particles: 0.01 μm < Dp < 2.5 μm), PM0.01–10 (0.01 μm < Dp < 10 μm), and PM0.01–18 (0.01 μm < Dp < 18 μm).

The extraction of PAHs from the paper filters and the glass sleeves that were used in the sampling was performed using the Soxhlet-extraction method. The extraction solvent was a mixture of n-hexane and dichloromethane (1:1 volume ratio). The extraction reflux time was 24 h.

After extraction, the extract was concentrated to 2 mL using highly pure nitrogen gas. The extract was then poured into a purification tube that contained pretreated silica gel (dried at 105°C for 8 h and then activated with distilled water for 24 h) and n-hexane to remove moisture and highly polar substances. The purified solution was further concentrated to 1 mL using a nitrogen gas stream and then stored in brown sample vials for the subsequent identification of 15 PAHs using a gas chromatograph/mass selective detector (GC/MSD; model: GC 6890N/HP 5973; Hewlett-Packard, Wilmington, DE, USA). The GC/MSD, equipped with a capillary column (HP Ultra 2, 50 m × 0.32 mm × 0.17 μm) and an automatic sampler (HP-7683), was operated under the following conditions; GC/MSD injection volume of 1 μL, splitless injection temperature of 310°C, and ion source temperature of 310°C. The oven temperature increased from 50°C to 100°C at a rate of 20 °C/min, and then from 100°C to 290°C at a rate of 3 °C/min; this temperature, 290°C, was maintained for 40 min. The GC/MSD was calibrated with a diluted standard solution of 16 PAH compounds (EPA610 PAH mixtures; Supelco, Bellefonte, PA, USA) and five additional individual PAHs (Pyr, CYC, BeP, BbC, and COR) obtained from Merck (Darmstadt, Germany). The method detection limits (MDLs) for the 21 PAH compounds were 0.023–0.106 ng, and the R2 values of calibration curves applied for GC/MSD analysis were 0.991–0.999. The recovery efficiencies were 83.9–92.6% (average = 86.4%). The 15 identified PAH species were four 4-ring (fluoranthene (FL), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (CHR)), six 5-ring (cyclopenta(c,d)pyrene (CYC), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), perylene (PER)), four 6-ring (indeno(1,2,3,cd)pyrene (IND), dibenzo(a,h)anthrance (DBA), benzo(b)chrycene (BbC), benzo(ghi)perylene (BghiP)), and one 7-ring (Coronene (COR)) PAH compound. The 4-ring and

5-/6-/7-ring PAHs are referred to as having a middle molecular weight (MMW) and a high molecular weight (HMW) PAHs, respectively.

Table 9: Concentrations (µg/m^3) of tested 4–7 ring PAHs in DEPs emitted from diesel-engine generator fueled with diesel (D100) and S20 under 0 (unload) kW

	PM 0.01-18		PM 0.01-10		PM0.01-2.5		PM 0.01-1		PM 0.01-.1		PM 0.01 -0.056	
µg/m^3	D100	S20	D100	S20	D100	S20	D100	S20	D100	S20	D100	S20
Fluorene	31.7	5.88	30.7	5.54	27.2	4.78	22.8	4.19	5.63	2.4	4.77	2.15
Pyrene	35.6	5.76	34.4	5.5	29.5	4.75	24	4.2	5.71	2.44	4.84	2.22
six 5-ring (cyclopenta(c,d)pyrene	7.46	2.36	7.25	2.34	6.86	2.18	6.12	2.02	0.7	0.19	0.53	0.14
Benzo(a)anthracene	3.19	0.44	3.12	0.43	3.02	0.38	2.69	0.33	0.19	0.18	0.17	0.17
Chrysene	9.92	3.14	9.71	2.97	9.04	2.67	7.98	2.33	0.78	0.34	0.6	0.21
Benzo(b)fluoranthene	5.22	1.68	5.13	1.65	4.94	1.35	4.31	1.28	1.41	0.93	1.24	0.9
Benzo(k)fluoranthene	5.81	1.73	5.77	1.64	5.31	1.39	4.3	1.2	0.61	0.54	0.47	0.47
Benzo(e)pyrene	3.63	0.82	3.62	0.8	3.35	0.69	2.91	0.58	0.26	0.17	0.22	0.16
Benzo(a)pyrene	9.5	2.45	9.43	2.38	8.92	2.11	7.82	1.81	0.49	0.48	0.39	0.42
Perylene	4.48	2.3	4.32	2.27	3.57	2.14	2.93	1.99	0.91	1.62	0.71	1.59
four 6-ring (indeno(1,2,3,cd)pyrene	2	0.87	1.97	0.82	1.9	0.67	1.78	0.53	0.58	0.41	0.35	0.39
dibenzo(a,h)anthrance	4.54	0.76	4.49	0.72	4.22	0.55	3.56	0.5	1.11	0.44	1	0.43
benzo(b)chrycene	6.23	4.94	5.87	4.92	5.3	4.01	3.41	3.94	2.05	3.68	1.79	3.65
benzo(ghi)perylene	6.21	0.79	6.19	0.79	5.74	0.7	4.52	0.66	1.16	0.26	1.02	0.25
one 7-ring (Coronene	3.6	1.39	3.42	1.3	2.96	1.06	2.65	0.94	1.7	0.62	1.53	0.54
MMW-PAHs	80.4	15.2	77.9	14.4	68.7	12.6	57.5	11	12.3	6.36	10.4	5.76
HMW-PAHs	58.7	20.1	57.5	19.6	53.1	16.8	44.3	15.5	11	9.33	9.24	8.94
Total-PAHs	139	35.3	135	34.1	122	29.4	102	26.5	23.3	15.7	19.6	14.7
BbF+BaP+DBA	19.2	4.89	19	4.75	18.1	4.01	15.7	3.6	3.01	1.85	2.62	1.74
Total-BaPeq	16.7	3.99	16.5	3.85	15.6	3.31	13.5	2.9	1.99	1.18	1.69	1.08

Table 10: Concentrations (µg/m^3) of tested 4–7 ring PAHs in DEPs emitted from diesel-engine generator fueled with D100 and S20under 3 kW load

	PM 0.01–18		PM 0.01-10		PM 0.01-25		PM 0.01-1		PM 0.01-1		PM 0.01-0.056	
µg/m^3	D100	S20	D100	S20	D100	S20	D100	S20	D100	S20	D100	S20
Fluorene	60.4	35.6	57.9	33.8	50.8	28.7	43.5	25.1	16.9	12.9	14.3	10.6

Pyrene	51	30.2	49.2	28.8	43.9	24.8	37.6	21.9	12.5	9.86	10.5	8.37
six 5-ring (cyclopenta(c,d)pyrene	14.8	12.7	13.7	12.5	9.61	12.1	6.33	11.8	3.26	1.16	2.69	1
Benzo(a)anthracene	2.57	1.19	2.46	1.14	2.13	1.03	1.83	0.94	0.71	0.39	0.6	0.33
Chrysene	16.8	15.1	16.2	14.5	13.7	12.6	11	11.2	2.95	1.67	2.18	1.48
Benzo(b)fluoranthene	11.4	5.47	11.2	5.28	10.6	4.72	10.1	4.4	7.75	1.45	6.46	1.24
Benzo(k)fluoranthene	16.7	9.3	16.1	8.68	14.9	7.17	12.7	6.39	5.13	3.34	4.31	2.6
Benzo(e)pyrene	3.02	2.49	2.96	2.38	2.68	2.11	2.35	1.91	1.39	0.87	1.2	0.71
Benzo(a)pyrene	9.91	6.72	9.8	6.26	9.24	5.45	7.95	4.9	2.86	1.98	2.43	1.66
Perylene	34.2	5.64	33.2	5.53	25.4	5.22	18.2	4.77	14.8	2.09	11.5	1.95
four 6-ring (indeno(1,2,3,cd)pyrene	12.6	4.28	12.3	4.11	10.3	3.82	9.35	3.72	8.56	1.74	7.69	1.69
dibenzo(a,h)anthrance	22.5	2.79	22.4	2.64	20.7	2.38	19.2	2.23	18.5	0.57	15.5	0.51
benzo(b)chrycene	44.1	8.63	43.5	8.09	42.2	6.93	41.2	6.49	38.7	2.46	32.1	2.1
benzo(ghi)perylene	8.84	2.06	8.74	1.96	8.09	1.51	7.48	1.27	6.67	0.64	6.04	0.53
one 7-ring (Coronene	12.7	8.13	11.8	7.61	10	6.29	8.81	5.52	5.57	3.41	4.72	2.91
MMW-PAHs	131	82.2	126	78.2	111	67.1	93.9	59.1	33	28.8	27.6	23.8
HMW-PAHs	191	68.2	186	65	164	57.7	144	53.4	113	19.7	94.7	16.9
Total-PAHs	321	150	312	143	274	125	238	112	146	48.5	122	40.7
BbF+BaP+DBA	43.8	15	43.4	14.2	40.6	12.6	37.2	11.5	29.1	4	24.4	3.41
Total-BaPeq	38.7	13.1	38.2	12.3	35.1	10.9	31.5	10.1	24.1	3.45	20.3	2.94

Tsai et al. (2011) [Characteristics of particulate emissions from a diesel generator fueled with varying blends of biodiesel and fossil diesel, Journal of Envron Sci and Health Part A] tested diesel fuel and waste cooking oil biodiesel blends at 10, 20, 30, and 50 vol% in a generator operated at a stable energy output (110V/60 Hz, 1800 rpm) under loads of 0, 1.5, and 3 kW. The emissions particle-bound PAHs were evaluated. The diesel generator was a single-cylinder, four-stroke 583 cc engine manufactured by Yanmar Corporation (Japan). The engine was naturally aspirated and water-cooled.

Paper quartz filters (Pall Ltd., USA) were used to sample particle emissions from the generator. Before sampling, the quartz fiber filters were heated for 2.5 h at 900◦C in order to reduce their carbon blank. The Soxhlet-extraction method was used to extract PAHs from the paper filters and glass sleeves used for sampling. The extraction solvent was a mixture of n-hexane and dichloromethane (1:1 volume ratio). The extraction reflux time was 24 h. After extraction, the extract was concentrated to 2 mL using high-purity nitrogen gas. The extract was then poured into a purification tube containing pretreated silica gel (dried at 105◦C for 8 h and then activated with distilled water for 24 h) and n-hexane to remove moisture and highly polar substances. The purified solution was further concentrated to 1 mL with a nitrogen gas stream and then stored in brown sample vials for analysis of 21 PAHs via a gas chromatograph/mass selective detector (GC/MSD; model: GC 6890N/HP 5973; Hewlett-Packard, Wilmington, DE, USA). The GC/MSD, which was equipped with a capillary column (HP Ultra 2, 50 m × 0.32 mm × 0.17 μm) and an automatic sampler (HP-7683), was operated under the following conditions: GC/MSD injection volume of 1 μL, splitless injection temperature of 310◦C, and ion source temperature of 310◦C. Oven temperature was increased from 50◦C to 100◦C at a rate of 20◦C/min then increased from 100◦C to 290◦C at a rate of 3◦C/min then maintained at 290◦C for 40 min. The 21 PAHs were classified by molecular mass as follows: low-molecular-mass PAHs (LMW-PAHs) with 2–3 rings (naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorine (Flu), phenanthrene (PA), and anthracene (Ant)), medium-molecular mass PAHs (MMW-PAHs) with 4 rings (fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), and chrysene (CHR)), and high-molecular-mass PAHs (HMWPAHs) with 5–7 rings (cyclopenta[c,d]pyrene (CYC), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo(a)pyrene (BaP), perylene (PER), dibenzo[a,h]anthracene (DBA), benzo[b]chrycene (BbC), indeno[1,2,3,-cd]pyrene (IND), benzo[ghi]perylene (Bghip), and coronene (COR)).

Table 11: Emission concentrations of PAHs (μg/Nm^3) with corresponding BaPeq from the diesel-engine generator under various loadings.

	0 kW 1,800 rpm					1.5 kW 1800 rpm					3 kW 1,800 rpm				
Concentration (μg/Nm^3)	D100	W10	W20	W30	W50	D100	W10	W20	W30	W50	D100	W10	W20	W30	W50
naphthalene	67.2±23.4	49.1±64.3	39.2±21.3	48.1±22.8	57.2±31.8	73.0±31.5	69.4±35.3	57.9±19.7	64.9±21.1	70.5±1.24	97.7±17.9	82.0±15.3	64.4±12.2	73.7±13.1	97.5±34.0
acenaphthylene	1.04±0.43	0.51±0.88	1.28±0.42	1.56±0.44	2.86±1.51	3.08±1.37	2.77±15.7	3.61±1.92	3.47±2.03	2.28±0.53	6.18±4.38	5.59±1.74	3.21±1.93	4.97±2.05	6.22±2.32
acenaphthene	1.41±0.30	0.52±0.54	0.67±0.34	1.20±0.35	1.61±0.19	1.47±7.35	1.79±27.7	1.22±0.50	1.69±0.52	1.14±0.08	3.86±1.95	2.46±0.35	1.22±0.20	2.89±0.20	5.55±4.21
fluorine	3.86±1.48	3.75±4.77	5.81±5.17	5.86±5.24	7.76±1.12	6.72±5.89	4.61±3.77	3.11±0.78	5.70±0.79	7.19±0.71	6.07±5.33	5.74±1.91	3.88±0.13	12.3±0.13	4.64±1.44
phenanthrene	13.6±0.83	21.3±27.4	10.9±34.6	13.5±35.4	16.0±0.06	27.4±6.65	10.3±3.44	19.2±3.87	17.7±3.96	13.8±3.52	30.7±13.0	30.3±3.99	24.5±3.02	28.2±3.09	21.7±4.29
anthracene	1.37±0.08	1.79±2.92	4.19±4.96	3.72±5.04	4.46±0.48	9.95±5.48	5.92±8.53	1.09±0.30	3.96±0.30	3.86±0.38	11.8±9.62	6.91±0.25	7.20±0.40	7.96±0.40	8.69±0.25
fluoranthene	5.41±1.83	9.81±16.1	2.90±30.1	3.35±31.4	2.53±0.21	7.67±8.88	8.87±4.20	6.57±2.73	7.25±2.85	6.50±5.67	9.53±4.53	20.2±2.49	14.3±1.35	18.4±1.41	18.0±0.78
pyrene	5.30±1.36	4.67±29.5	3.42±39.7	3.21±40.2	2.06±3.60	7.21±10.7	7.14±2.79	5.92±2.68	7.06±2.71	8.12±3.08	18.7±6.52	18.1±1.99	13.9±1.11	18.1±1.12	18.3±1.30
cyclopenta[c,d]pyrene	1.47±0.08	0.92±0.89	1.18±0.96	1.58±0.97	1.22±0.36	1.64±0.10	1.28±0.31	1.42±0.61	2.22±0.62	1.20±0.26	1.24±0.76	1.25±0.36	1.06±0.36	2.74±0.36	1.15±0.05
benzo[a]anthracene	1.38±0.62	0.53±0.52	0.29±0.34	0.42±0.34	0.24±0.10	1.04±0.01	0.60±1.00	0.31±0.07	0.60±0.07	0.24±0.07	1.97±0.86	1.96±1.04	1.64±1.24	0.89±1.24	1.56±0.94
chrysene	2.16±0.95	0.91±0.96	0.68±0.51	0.63±0.55	0.82±0.09	2.19±0.14	2.86±2.69	1.01±0.34	1.00±0.36	1.46±0.14	3.79±2.68	5.54±3.75	2.20±3.14	1.32±3.36	3.66±2.68
benzo[b]fluoranthene	0.64±0.06	0.39±0.42	0.68±0.84	0.84±0.89	1.53±0.18	0.66±0.01	0.63±0.42	0.18±0.08	1.18±0.08	0.62±0.19	0.81±0.03	0.43±0.22	0.49±0.15	1.78±0.16	0.42±0.15
benzo[k]fluoranthene	0.89±0.02	0.78±0.81	0.99±1.01	1.24±1.04	1.14±0.33	1.28±0.22	0.38±0.37	1.06±0.48	1.74±0.49	1.09±0.28	1.79±0.46	1.17±0.66	0.90±0.36	2.55±0.37	1.12±0.15

benzo[e]pyrene	0.94±0.18	0.59±0.49	0.82±0.69	0.77±0.70	0.96±0.18	1.40±0.20	1.49±0.50	1.03±0.34	1.08±0.35	1.18±0.91	1.91±0.58	1.83±0.22	0.84±0.42	1.68±0.42	2.22±0.36
benzo(a)pyrene	1.45±0.32	0.92±1.30	0.31±4.55	0.60±4.65	1.19±0.45	2.39±0.29	2.17±2.13	2.18±0.70	2.11±0.71	3.41±2.56	3.76±1.07	2.57±3.59	2.48±0.17	2.76±0.17	4.37±0.27
perylene	1.36±0.63	0.60±0.95	0.99±1.04	0.82±1.05	1.17±0.29	1.43±0.15	0.69±0.12	0.88±0.40	1.16±0.40	1.04±0.41	1.99±0.62	1.36±1.02	0.94±0.66	1.47±0.67	1.02±0.35
indeno[1,2,3,-cd]pyrene	1.40±0.26	0.63±0.74	0.32±5.84	0.34±6.09	0.19±0.34	1.85±0.04	1.56±1.17	1.87±0.41	0.48±0.43	1.02±0.12	2.27±2.34	2.10±4.42	1.86±1.43	1.57±1.49	1.39±0.70
dibenzo[a,h]anthracene	0.79±0.38	0.67±0.78	0.56±0.79	0.69±0.81	0.21±0.52	0.90±0.01	1.32±2.50	1.26±0.19	1.22±0.19	1.37±0.97	3.76±1.93	2.26±1.76	1.81±2.83	2.80±2.87	4.32±0.13
benzo[b]chrycene	1.69±0.52	1.60±2.30	0.54±3.47	0.58±3.49	0.49±0.62	1.43±0.21	2.37±0.83	2.19±1.10	0.81±1.11	3.54±1.79	4.30±1.30	4.32±3.61	2.87±1.66	2.61±1.67	4.56±1.31
benzo[ghi]perylene	0.66±0.73	0.68±1.26	1.18±1.37	1.07±1.37	1.36±0.30	0.70±0.01	3.11±2.38	0.42±0.27	1.51±0.27	1.03±0.50	0.72±0.63	0.32±0.20	0.25±0.09	0.38±0.09	0.41±0.26
coronene	0.09±0.03	0.41±0.07	0.26±0.52	0.24±0.53	0.21±0.02	0.04±0.03	0.24±0.18	0.06±0.03	0.22±0.03	0.10±0.10	0.30±0.03	0.55±0.02	0.04±0.02	0.13±0.02	0.12±0.03
LMW-PAHs	88.4±26.5	76.9±10.1	62.0±26.7	73.9±21.0	89.9±37.8	122±34.3	94.8±31.4	86.1±32.8	97.4±29.7	98.8±52.5	156±51.8	133±48.4	104±38.8	130±48.3	144±30.7
MMW-PAHs	14.3±4.76	15.9±4.71	7.29±7.07	7.62±5.73	5.66±6.90	18.1±15.9	19.5±8.29	13.8±10.7	15.9±9.04	16.3±15.8	34.0±15.0	45.8±21.8	32.1±15.8	38.6±15.2	41.6±19.2
HMW-PAHs	11.4±3.21	8.18±5.37	7.85±2.11	8.77±6.11	9.67±7.79	13.7±7.29	15.2±7.85	12.6±6.55	13.7±10.3	15.6±9.44	22.8±12.3	18.2±11.2	13.5±8.11	20.5±4.78	21.1±9.03
Total-PAHs	114±34.5	101±51.2	77.2±15.8	90.3±40.2	105±47.4	153±57.2	130±68.7	112±21.2	127±31.6	131±58.4	213±25.3	197±30.8	150±37.8	189±37.33	207±33.8
Total-BaPeq	2.97±1.69	2.04±2.66	1.35±1.19	1.86±1.11	2.00±1.36	4.21±3.66	4.17±3.67	4.06±2.93	4.13±2.00	5.39±3.38	8.68±2.58	5.83±1.91	5.11±2.58	6.78±3.12	9.58±6.21

Table 12: PAH emission factors

	0 kW 1,800 rpm					1.5 kW 1800 rpm					3 kW 1,800 rpm				
Emission Factor (mg/L-fuel)	D100	W10	W20	W30	W50	D100	W10	W20	W30	W50	D100	W10	W20	W30	W50
LMW-PAHs	24.5± 10.8	15.6± 7.61	12.5± 6.17	14.4± 3.16	22.8± 12.1	18.9± 5.21	12.6± 4.95	12.0± 8.81	13.5± 7.77	14.4± 9.82	21.9± 10.5	17.1± 12.2	15.6± 8.13	19.8± 12.0	22.8± 11.9
MMW-PAHs	3.95± 1.40	3.24± 1.55	1.47± 0.68	1.49± 1.36	1.43± 1.02	2.81± 2.34	2.58± 1.24	1.92± 1.58	2.21± 1.88	2.37± 1.41	4.77± 5.51	5.88± 4.75	4.80± 3.18	5.88± 3.19	6.56± 5.71
HMW-PAHs	3.16± 2.31	1.66± 0.50	1.59± 0.71	1.71± 1.59	2.45± 1.74	2.13± 1.02	2.02± 1.47	1.74± 1.20	1.91± 0.80	2.27± 1.27	3.21± 2.56	2.34± 1.76	2.02± 1.18	3.11± 2.18	3.33± 15.6
Total-PAHs	31.6± 14.1	20.5± 16.3	15.6± 11.2	17.6± 9.73	26.6± 11.9	23.8± 13.1	17.2± 10.4	15.6± 7.21	17.7± 5.88	19.0± 10.6	29.9± 10.5	25.3± 10.3	22.4± 12.0	28.7± 21.9	32.7± 19.8

Chen et al. (2017) [Impact of Magnetic Tube on Pollutant Emissions from the Diesel Engine, Aerosol and Air Quality Research] used a magnetic tube fitted on the fuel line for the evaluation of the impact of magnetic field on the energy performance and PAH emissions of a diesel engine generator. The generator (model KX4100D1) used had a maximum power output of 30 kW and a speed of 1800 rpm. Testing was done in triplicate at idling, 25% and 50% load. The exhaust samples for PAH analyses were collected by using isokinetic sampling systems (Fig. 1), which comprised of a glass fiber filter (Whatman International Ltd., 25 × 90 mm), flow meter, condenser, two-stage glass cartridges, and a vacuum pump. The PAHs in the particulate phase were collected by the glass fiber filters. The condenser located before the two-stage glass cartridges was used to lower the exhaust temperature to < 5°C and remove water from the exhaust stream. The PAHs in the gaseous phase were then collected by the two-stage glass cartridges. Specifically, each cartridge, which was previously pretreated via Soxhlet, was packed with a 5.0 cm thick (approximately 15 g) of XAD-16 resin sandwiched between two 2.5 cm-thick polyurethane foam plugs. Each sample was extracted by a Soxhlet extractor using a mixed solvent (n-hexane and dichloromethane; vol/vol, 1:1) for 24 hours. The extracts were concentrated by gently purging to a dimple by ultrapure nitrogen. After that, the solution was cleaned up by passing through a column containing silica gel (15 g with a droplet of deionized water for activation; stored in 105°C), anhydrous sodium sulfate (3 g) and glass wool. The effluents and 200 mL n-hexane used to clean the sample were reconcentrated to exactly 1 mL in vial. PAH contents were detected with gas chromatography/mass spectrometry (GC/MS). The GC/MS (Agilent 5890A and Agilent 5975) for PAH measurement was equipped with a capillary column (HP Ultra 2–50 m × 0.32 mm × 0.17 μm). The 16 PAHs considered in this study were Naphthalene (Nap), Acenaphthylene (AcPy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene(BkF), Benzo[a]pyrene (BaP), Indeno(1,2,3-cd)pyrene (IND), Dibenzo(a,h)anthracene (DBA), and Benzo(ghi)perylene (BghiP). The pertinent operating conditions were as follows: the injection volume of 1 μL; a splitless injection at 300°C; the ion source temperature at 310°C; the oven temperature held at 45°C for 1 min, from 45 to 100°C in 5 min, 100 to 320°C at 8 °C min–1, and held at 320°C for 15 min. The masses of primary and secondary PAHs ions were determined by using the scan mode for pure PAH standards. The PAHs were qualified using the selected ion monitoring (SIM) mode.

Table 13: PAH emissions from the diesel generator with and without the magnetic tube (%)

	Idle State		**25% Load**		**50% Load**	
	Without magnetic tube	With magnetic tube	Without magnetic tube	With magnetic tube	Without magnetic tube	With magnetic tube
Naphthalene (Nap)	97.2	98.6	90.8	93.2	98.6	95.7
Acenaphthylene (AcPy)	N.D.	N.D.	1.11	0.427	N.D.	0.408
Acenaphthene (Acp)	N.D.	1.44	0.77	0.579	N.D.	N.D.
Fluorene (Flu)	0.456	N.D.	1.64	0.84	N.D.	N.D.
Phenanthrene (PA)	1.15	N.D.	3.09	4.97	1.21	3.87
Anthracene (Ant)	0.168	N.D.	0.38	N.D.	N.D.	N.D.
Fluoranthene (FL)	0.257	N.D.	0.531	N.D.	0.174	N.D.
Pyrene (Pyr)	0.738	N.D.	1.68	N.D.	N.D.	N.D.
Benz[a]anthracene (BaA)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Chrysene (CHR)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo[b]fluoranthene (BbF)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo[k]fluoranthene (BkF)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo[a]pyrene (BaP)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Indeno(1,2,3-cd)pyrene (IND)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dibenzo(a,h)anthracene (DBA)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzo(ghi)perylene (BghiP)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Sothea and Oanh (2019) [Characterization of emissions from diesel backup generators in Cambodia] tested two backup diesel generators for particle-bound and gas-phase PAH emissions. the first generator (E1) was a Kubota V2203-KB, 25kVA, four-cylinders, self-ventilation cooling system and a maximum output of 18,4 kW at 1500 rpm. The second generator (E2) was a Cummins 6BT5.9-G2, 110 kVA, six-cylinders, turbocharged cooling system, and a maximum output of 92 kW at 1500 rpm. The engine load was maintained 70-75% during emissions sampling; thus, PAH emission factors represent the stable operating conditions of the generators. Emissions testing was done twice for each generator.

The exhaust samples were collected without dilution with the ambient air. The flue gas sampling was done for 30 min in each test with the same running conditions. Quartz fiber filters (QFF, Advantec QR100, 90 mm, Japan) were used for PM sampling. Before use, the filters were baked at 550 °C for about 5 h to remove organic contaminants. A polyurethane foam (PUF) adsorbent (URG-2000-30-52 PUF, USA) was installed in the URG-3000B sampler to collect gas phase PAHs. Before using the PUF (URG, USA) was cleaned by Soxhlet extraction for 24 h, at about 4 cycles per hour. A mixture of diethyl ether/hexane (10% volume/volume) was used as the cleanup solvent following the US EPA Method TO-13A.

One-fourth (1/4) of the sampled QFF was used to analyze for PAHs in the PM phase (PPAHs). The QFF was ultrasonically extracted twice, each time for 30 min using a 30 mL mixture of n-Hexane:Acetone (1:1 v/v). The gas phase PAHs (GPAHs) collected on PUF (whole PUF used in each sampling) were Soxhlet extracted, following the US EPA Method TO-13A. The extraction was done using the same mixture of solvents (as for PM) for 24 h with 4 cycles per hour. The extract solution (of QFF and PUF sample separately) was evaporated in an evaporator under N2 gas (Biotage TurboVap®II) then filtered through a 0.45 µm polytetrafluoroethylene (PTFE) syringe filter (Lee et al., 2011a) to a volume of 1 mL. A commercial Solid Phase Extraction (SPE) column (Biotage ISOLUTE®SI) was used to clean-up the samples and finally N2 gas was used to concentrate the extract to 0.5 mL. The GC-MS (Agilent 7890A/5975C GC-MS) with Agilent J&W HP-5MS (30 m, 0.25 mm, 0.25 µm) was used for the PAHs quantification. The injection volume was 2 µL in a split mode (2:1) with the injector temperature of 280 °C. The GC oven program was 70 °C for 1.5 min, increased from 70 to 150 °C at 20 °C min−1, and from 150 to 310 °C at 7 °C min−1 and held for 5 min. The MS (mass spectrometry) was operated in the selected ion monitoring (SIM) mode. To quantify the 16 PAHs concentrations, a calibration standard solution from known concentrations of 16 PAHs (Supelco EPA 610 PAHs mixture) was used and the standard curves were constructed using 6 concentration levels yielding linear fit with R2 ranging from 0.998 to 0.999 for each compound.

Table 14: PAHs concentration (average ± SD), µg m^{-3} and share (%, in brackets) of individual compound in the total 16 PAHs in the respective gas (GPAH) and PM (PPAH) phase.

PAH, µg/m^3	E1 (n = 2)			E2 (n = 2)		
	GPAHs	PPAHs	TPAHs	GPAHs	PPAHs	TPAHs
Naphthalene	9.7 ± 1.0 (31)	ND	9.7 ± 1.0	11.6 ± 1.2 (26)	ND	11.6 ± 1.2
Acenaphthene	1.7 ± 0.37 (6)	ND	1.7 ± 0.37	4.1 ± 0.58 (9)	ND	4.05 ± 0.58
Acenaphthylene	1.5 ± 0.26 (5)	ND	1.5 ± 0.26	7.3 ± 0.76 (16)	ND	7.3 ± 0.76
Fluorene	4.2 ± 0.9 (14)	ND	4.2 ± 0.9	5.9 ± 0.2 (13)	ND	5.9 ± 0.2
Phenanthrene	8.7 ± 0.5 (28)	0.07 ± 0.07 (1)	8.8 ± 0.43	9.2 ± 2.3 (20)	0.66 ± 0.13 (8)	9.8 ± 0.4
Anthracene	2.03 ± 0.4 (7)	0.07 ± 0.07 (1)	2.1 ± 0.31	2.1 ± 0.98 (5)	0.58 ± 0.13 (8)	2.7 ± 0.46
Fluoranthene	2.7 ± 0.04 (9)	0.74 ± 0.14(15)	3.4 ± 0.07	2.6 ± 0.14 (6)	0.99 ± 0.24(13)	3.6 ± 0.38
Pyrene	0.46 ± 0.2 (1)	2.0 ± 0.40 (41)	2.5 ± 0.25	2.8 ± 0.44(6)	3.4 ± 0.46 (46)	6.2 ± 0.9

Benz[a]anthracene	ND	0.18 ± 0.03 (4)	0.18 ± 0.02	0.014 ± 0.004	0.20 ± 0.05 (3)	0.22 ± 0.05
Chrysene	ND	0.57 ± 0.10 (12)	0.57 ± 0.05	0.015 ± 0.004	0.63 ± 0.14 (8)	0.64 ± 0.14
Benzo[b]fluoranthene	ND	0.26 ± 0.03 (5)	0.26 ± 0.01	ND	0.19 ± 0.04 (3)	0.19 ± 0.04
Benzo[k]fluoranthene	ND	0.19 ± 0.02 (4)	0.19 ± 0.04	ND	0.22 ± 0.05 (3)	0.22 ± 0.05
Benzo[a]pyrene	ND	0.20 ± 0.02 (4)	0.12 ± 0.03	ND	0.67 ± 0.14 (9)	0.67 ± 0.14
Indeno[1,2,3-c,d]pyrene	ND	0.19 ± 0.03 (4)	0.19 ± 0.01	ND	ND	ND
Dibenzo[a,h]anthracene	ND	0.18 ± 0.02 (4)	0.18 ± 0.01	ND	ND	ND
Benzo[g,h,i,]perylene	ND	0.25 ± 0.04 (5)	0.25 ± 0.10	ND	ND	ND

ND: Not Detected

Zhang and Balasubramanian (2014) [Influence of butanol addition to diesel-biodiesel blend on engine performance and particulate emissions of a stationary diesel engine, Applied Energy] tested diesel-biodiesel-butanol blends to evaluate PAH emissions. Testing was conducted on a single cylinder, four-stroke, air-cooled, direct injection, diesel back-up power generator (L70AE, Yanmar Corporation).

A two-stage Dekati mini-diluter (DI-2000, Dekati Ltd) was used for diluting the exhaust gas for sampling. Only the first stage diluter was used to cool the sampling gas temperature below 52C for particulate sampling. PM2.5 was collected on pre-combusted (650 C for 12 h) 47 mm quartz fiber filters (Whatman, USA) by using two Mini-Vol low volume particulate samplers (Air metrics Ltd.; 5 L min-1 flow rate). Particle-phase PAHs were extracted from the quartz filter samples in 50/50 hexane/acetone (HPLC-grade, Fisher Scientific) mixture using a closed vessel microwave-assisted extraction system (MLS-1200 mega, Milestone, Italy) in accordance with the US EPA method 3546. Each of the eluents was divided into two equal parts, with one part for subsequent PAHs analysis, and the other part for toxicological analysis. The 16 EPA PAHs are separated into three different molecular weight ranges: Low molecular weight (LMW) PAHs are two and three rings PAHs including naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (AcP), fluorine (Flu), phenanthrene (PA) and anthracene (Ant). Middle molecular weight (MMW) PAHs are four rings PAHs including fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA) and chrysene (CHR). High molecular weight (HMW) PAHs are five and six rings PAHs including benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h] anthracene (DBA), indeno [1,2,3,-cd]pyrene (IND) and benzo[ghi] perylene (BghiP).

Table 15: Concentrations of particle-phase PAH emissions (μg/m^3)

	25% engine load			50% engine load			75% engine load		
	LMW-PAHs	MMW-PAHs	HMW-PAHS	LMW-PAHs	MMW-PAHs	HMW-PAHS	LMW-PAHs	MMW-PAHs	HMW-PAHS
USLD	11.77	19.75	21.14	17.44	34.45	35.66	30.57	73.63	75.54
B20	9.13	16.07	17.28	12.88	25.56	27.12	23.59	54.14	55.53
B20Bu5	8.04	14.46	15.50	11.11	22.04	23.26	19.38	42.82	44.21
B20Bu10	7.48	14.08	14.77	9.33	19.75	20.62	15.35	35.84	36.88
B20Bu15	9.18	15.43	16.30	9.64	19.88	20.23	14.62	34.06	34.93

Guarieiro et al. (2014) [Redox activity and PAH content in size-classified nanoparticles emitted by a diesel engine fueled with biodiesel and diesel blends, Fuel] investigated the effect of diesel/biodiesel blends on PAH emissions the redox activity of PM emissions. Emission experiments were carried out with a diesel engine (Agrale, year of fabrication 2005, model M85, 10 HP) coupled to a steady-state dynamometer. PAH samples were collected with a NanoMOUDI and were analyzed for the following PAH compounds: phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BAA), chrysene (CRY), benzo[b]fluoranthene (BBF), benzo[k]fluoranthene (BKF), benzo[a]pyrene (BAP), dibenzo[b]anthracene (DBA), benzo[ghi]perylene (BGP) and indene[1,2,3,cd]pyrene (IND). An HP 1100 series HPLC system (Agilent Technologies, Palo Alto, California, USA) was used for PAH determination. PAH separation was carried out by a Supelco LC-PAH column (Supelco, Bellefonte, Pennsylvania, USA) (5 lm, 15 cm x 4.6 mm) preceded by a Supelcoguard LC-18 precolumn (2 cm x 4 mm).

Table 16: PAH emission factors for the different diesel/biodiesel blends (ng/kg)

PAH	B4	B25	B50	B100
phenanthrene	6.74 (±2.52)	17.6 (±6.63)	6.58 (±4.07)	7.00 (±1.07)
anthracene	2.50 (±0.69)	2.15 (±0.19)	1.30 (±0.83)	1.31 (±0.13)
fluoranthene	14.4 (±3.03)	10.4 (±2.66)	15.5 (±5.30)	24.5 (±7.57)
pyrene	24.0 (±3.82)	14.7 (±5.85)	23.4 (±8.72)	37.2 (±11.9)
benzo[a]anthracene	31.7 (±15.3)	10.6 (±2.04)	20.1 (±5.70)	44.1 (±13.7)
chrysene	24.1 (±5.89)	11.4 (±5.44)	17.7 (±5.57)	28.1 (±9.67)
benzo[b]fluoranthene	45.4 (±10.1)	15.7 (±4.22)	31.1 (±7.11)	47.9 (±13.1)
benzo[k]fluoranthene	14.7 (±1.91)	5.08 (±1.59)	10.7 (±2.74)	18.4 (±5.57)
benzo[a]pyrene	19.7 (±6.23)	14.1 (±2.51)	12.6 (±2.83)	20.8 (±6.15)
dibenzo[b]anthracene	2.73 (±0.51)	0.63 (±0.32)	2.11 (±0.52)	4.09 (±0.78)
benzo[ghi]perylene	32.1 (±9.23)	5.01 (±4.04)	24.2 (±4.79)	47.4 (±11.2)
indene[1,2,3,cd]pyrene	18.8 (±3.13)	4.02 (±2.98)	16.7 (±5.41)	38.3 (±7.14)
Total PAH	237 (±24.7)	111 (±19.4)	182 (±49.9)	319 (±81.3)

Lin et al. (2012) [Reduction in emissions of nitrogen oxides, particulate matter, and polycyclic aromatic hydrocarbon by adding water-containing butanol into a diesel-fueled engine generator, Fuel] studied the effects of nbutanol-diesel blends with 0, 0.5, and 1 wt.% water-content on PAH emissions using a diesel engine generator. The generator was a four-stroke, single horizontal cylinder engine made by Yanmar Corporation. It employed a direct injection system with 196.2 bar injection pressure and injecting at BTDC 19.0 CA. the generator load was controlled by a varied resistance with 100 parallel 50 W bulbs that was equal to maximum 5 kW. The generator loads were fixed at 3.2 kW, 80% of the maximum load of the engine output power (4 kW).

All sampling and analytical processes of PAHs followed the A730.70C method proposed by the National Institute of Environmental Analysis (NIEA) in Taiwan. Particulate-phase PAHs were collected on a glass fiber filter, which was pretreated at 450 _C for 8 h in an oven to remove all organic compounds. The net mass of particles was then determined by subtracting the mass of the initial filter from the final one. Gas-phase PAHs were collected in three-stage glass cartridges in preliminary sampling work. Since the masses of 21 individual PAHs in the third stage were 0.1–2.6% of total three stages, the two-stage glass cartridges were utilized to effectively collect the gaseous PAHs in this study. Specifically, the cartridge was packed with 5.0 cm of XAD-16 resin sandwiched between two 2.5 cm polyurethane foam (PUF) plugs. The new cartridges were pretreated by a Soxhlet extraction process for 24 h with methanol, dichloromethane, and n-hexane for a total of 3 days. All glass fiber filters and packed cartridges were transported to and from the sampling field covered with aluminum foil to avoid PAH photo-dissociation.

After sampling, all samples were extracted using a n-hexane/dichloromethane mixed solvent of 1:1 volume ratio in Soxhlet extractors for 24 h. The total solvent volumes used were 250 and 700 mL for particulate and gaseous samples, respectively. The extract was then purged with ultra-pure nitrogen to 2 mL and passed through the cleanup column packed with silica. The eluents were then re-concentrated by purging with nitrogen to exactly 1 mL in vials. The PAH contents were determined with a gas chromatograph (GC, Agilent 6890 N) with a mass spectrometer detector (MSD, Agilent 5973 N) which was controlled by a computer workstation (Acer Aspire C500). This GC/MSD was equipped with a capillary column (HP Ultra 2; 50 m x 0.32 mm x 0.17 mm) and an automatic sampler (Agilent 7683 series).

Table 17: PAH emission concentration of water-containing butanol–diesel blends.

Conc. (μg/Nm^3)	D100	BT5W0.5	BT10W0.5	BT15W0.5	BT20W0.5	BT25W0.5
	(n = 2)	(n = 2)	(n = 2)	(n = 2)	(n = 2)	Mean
Naphthalene	72.5	69	68.2	66.8	65.8	59.1
acenaphthylene	7.81	7.01	6.81	6.73	6.13	5.82
Acenaphthylene	3.73	3.35	3	2.72	2.36	2.16
fluorine	20.7	19.5	19.3	19.1	18.9	17.2
phenanthrene	249	232	229	216	211	190
anthracene	9.19	8.19	8.57	5.76	5.19	4.74
fluoranthene	12.6	10.9	10.5	10	10.1	8.37
pyrene	31.6	30	29.7	29	27.5	25.3
cyclopenta[c,d]pyrene	0.82	0.78	0.79	0.81	0.76	0.79
benzo[a]anthracene	1.25	1.15	1.16	1.18	1.02	1.07
chrysene	1.26	1.18	1.18	1.22	1.11	1.17
benzo[b]fluoranthene	1.33	1.24	1.25	1.11	1.05	1.06
benzo[k]fluoranthene	1.68	1.6	1.61	1.66	1.56	1.62
benzo[e]pyrene	0.06	0.06	0.05	0.05	0.05	0.04
benzo(a)pyrene	0.17	0.15	0.15	0.16	0.15	0.14
perylene	0.02	0.01	0.02	0.02	0.01	0.01
indeno[1,2,3,-cd]pyrene	0.12	0.11	0.09	0.04	0.03	0.03
dibenzo[a,h]anthracene	0.03	0.02	0.02	0.02	0.02	0.02
B(b)C	0.06	0.06	0.05	0.05	0.04	0.04
B(ghi)Perylene	0.07	0.05	0.05	0.04	0.04	0.04
coronene	0.02	0.02	0.02	0.02	0.02	0.02

Yilmaz and Davis (2016) [Polycyclic aromatic hydrocarbon (PAH) formation in a diesel engine fueled with diesel, biodiesel and biodiesel/n-butanol blends, Fuel] tested different biodiesel blends mixed with 10, 20, and 40% nbutanol on their effects on PAH emissions using an Onan DJC type, four-cylinder diesel engine generator. The engine had a maximum power of 12 kW, naturally aspirated, and air-cooled. Testing was performed at a fixed engine speed of 1800 rpm and four loads of 0, 3, 6, and 9kW.

To collect PAHs, the engine was run for three hours at idle for each fuel and in triplicate. Prior to the start of the PAH collection, the engine was started and run for at least 10 min on neat diesel to minimize cold-starting effects. The undiluted exhaust was sampled at 10 lpm through a set of collection media for the PAHs to condense on. Particle-bound PAHs were collected on a 37 mm diameter, 2 μm pore Pall Corporation (Port Washington, NY) PTFE filter, and semi-volatile PAHs were collected in an adsorbent resin cartridge, and the two collection mediums were connected in series. The resin cartridge was supplied by Sigma Aldrich (St. Louis, MO) and was filled with two stages of Amberlite XAD-2 adsorbent resin (50 mg/100 mg). On average, the temperature across the filter did not exceed 50C.

The filter and cartridge after collection were then spiked with 2000 ng of anthracene-d10 (98%, Sigma Aldrich, St. Louis, MO) as an internal standard. And, the filter and resin cartridges were extracted (separately) into 5 ml of HPLC-grade hexane (Alfa Aesar, Ward Hill, MA). The extracts were naturally aspirated through a cleanup column filled with 500 mg Na2SO4/500 mg alumina (Fisher Scientific, Waltham, MA). The alumina was activated at 120C for 24 h prior to use. The column was washed with 5 ml of n-hexane and the PAHs were recovered by eluting with 5 ml 50/50 (vol%) benzene/acetonitrile (HPLC grade, Alfa Aesar, Ward Hill, MA). The GC–MS analytical conditions were chosen according to the recommendations from EPA for determination of PAHs in ambient air. Prior to GC–MS analysis, the samples were concentrated to 0.5 ml by N2 blowdown under gentle heating. The solutions were then frozen at 80C until the sample could be analyzed. Isotope-dilution mass spectrometry was used to identify and quantify the PAHs in the samples.

Table 18: PAH emissions expressed in μg/m^3

	Diesel		Biodiesel		BBu10		BBu20		BBu40	
	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev	Avg	Stdev
PM-PAH (μg/m^3)										
Naphthalene	0.188	0.099	0.108	0.033	0.129	0.007	0.193	0.104	0.275	0.072
Acenaphthylene	0.062	0.062	0.056	0.031	0.052	0.026	0.093	0.065	0.161	0.055
Fluorene	0.145	0.153	0.051	0.033	0.047	0.024	0.074	0.044	0.098	0.029
Phenanthrene	0.485	0.471	0.229	0.234	0.151	0.097	0.245	0.16	0.366	0.025
Fluoranthene	0.17	0.194	0.069	0.051	0.033	0.023	0.037	0.011	0.054	0.011
Pyrene	0.252	0.281	0.148	0.144	0.069	0.06	0.124	0.104	0.117	0.071
Chrysene	0.065	0.084	0.037	0.036	0.012	0.011	0.017	0.011	0.03	0.014
Semi-volatile PAH (μg/m^3)										
Naphthalene	1.744	0.903	0.655	0.865	0.328	0.23	0.772	0.231	1.003	0.565
Acenaphthylene	0.149	0.082	0.19	0.093	0.291	0.206	0.327	0.078	0.504	0.245
Fluorene	0.449	0.318	0.172	0.104	0.242	0.149	0.205	0.052	0.292	0.091
Phenanthrene	0.709	0.5	0.431	0.31	0.447	0.22	0.462	0.065	0.861	0.367
Fluoranthene	0.118	0.087	0.111	0.108	0.072	0.064	0.058	0.023	0.169	0.147
Pyrene	0.151	0.129	0.157	0.12	0.114	0.082	0.014	0.002	0.316	0.157
Chrysene	0.029	0.016	0.029	0.021	0.024	0.014	0.026	0.011	0.139	0.113
Total PAH emission (μg/m^3)										
Naphthalene	1.932	0.384	0.763	0.893	0.457	0.225	0.965	0.334	1.278	0.592
Acenaphthylene	0.211	0.056	0.246	0.106	0.342	0.198	0.42	0.078	0.665	0.261
Fluorene	0.593	0.295	0.223	0.132	0.29	0.147	0.279	0.095	0.39	0.099
Phenanthrene	1.194	0.636	0.66	0.531	0.598	0.21	0.707	0.199	1.227	0.36
Fluoranthene	0.288	0.153	0.18	0.114	0.105	0.052	0.095	0.014	0.224	0.155
Pyrene	0.403	0.194	0.305	0.255	0.183	0.107	0.138	0.103	0.433	0.225
Chrysene	0.094	0.092	0.065	0.056	0.036	0.012	0.043	0.007	0.169	0.099

Sadiktsis et al. (2014) [Particulate associated polycyclic aromatic hydrocarbon exhaust emissions from a portable power generator fueled with three different fuels – A comparison between petroleum diesel and two biodiesels, Fuel] tested diesel fuel pure biodiesel, and a B30 blend on a SDMO 3-phase portable generating set with a Yanmar L100AE (SDMO Industries, Brest, France) diesel engine (model DX6000TE) with maximum output of 7.4 kW. This is a 435 cm3 single-cylinder, air cooled, naturally aspirated engine with some exhaust gas recirculation as it is sold on the California market. The engine set to run at constant speed to give a constant 50 Hz alternator output at a maximum electrical output of 5.2 kW.

All samples analyzed were inserted into ASE 200 extraction cells followed by the addition of an internal standard mixture, containing the perdeuterated PAHs; PHE-d10, PYR-d10, BaA-d12, BaPd12 and BghiP-d12 in toluene along with a solution of DBaiP-d14 in toluene. Four replicate samples of each SRM with approximately 10 mg (exact mass known) diesel PM was weighed on microfiber filters (Ø = 47 mm, Whatman International Ltd., England) using an analytical balance (d = 0.01 mg). A microfiber filter was used as procedural blank. The filters were inserted into ASE 200 extraction cells, which were cleaned in an ultrasonic bath of ethanol. A mixture of toluene and methanol (9:1; v/v) was used as the extraction solvent operating at maximum instrumental settings (200C and 20.7 MPa). The extraction consisted of five static extraction cycles of 30 min each.

The online HPLC–GC–MS system used for analysis consisted of a Varian 9012 Inert solvent delivery system (Varian Inc., Palo Alto, CA, USA) with a CMA/200 microsampler (CMA Microdialysis AB, Sweden) coupled to an Agilent 6890 N gas chromatograph (Agilent Technologies) with an Agilent 5973 N MSD system (Agilent Technologies).

Table 19: PM-PAH emissions expressed in µg kW^{-1}

Compound (µg kW^{-1})	SD10		B30		B100	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
Phenanthrene	35.6	4.9	12.6	4	9.27	5.16
Anthracene	9.38	0.82	1.66	0.44	0.567	0.263
3-Methylphenanthrene	23.6	6.8	15.4	3.7	4.19	2.15
2-Methylphenanthrene	25.9	7.9	17.2	3.9	5.42	1.89
2-Methylanthracene	5.12	1.92	3.07	0.42	1.25	0.75
9-Methylphenanthrene	29	9	17.6	3.7	5.03	2.41
1-Methylphenanthrene	18.3	5.8	10.6	2.4	4.34	2.37
4H-cyclopenta[def]phenanthrene	8.29	3.61	5.57	0.06	2.66	2.32
2-Phenylnaphthalene	8.86	0.25	6.95	1.41	3.87	0.98
3,6-Dimethylphenanthrene	6.04	0.22	5	0.55	1.09	0.04
9-Methylanthracene	1.98	0.58	1.29	0.1	0.728	0.355
3,9-Dimethylphenanthrene	29.3	3.1	22.2	0.4	8.89	2.71
Fluoranthene	12.2	1.7	12.2	0.9	11.1	2.3
Pyrene	21.6	1.7	15.8	1.5	8.87	2.35
1-Methylfluoranthene	1.38	0.23	1.69	0.07	1.34	0.27
Benzo[a]fluorene	0.464	0.03	0.422	0.01	0.755	0.153
Benzo[b]fluorene	0.2	0.018	0.163	0.001	0.149	0.081
2-Methylpyrene	3.21	0.5	2.11	0	0.511	0.162
4-Methylpyrene	5.22	0.82	3.44	0.04	0.755	0.182
1-Methylpyrene	2.57	0.57	1.73	0.01	0.633	0.195
Benzo[ghi]fluoranthene	2.95	0.45	1.98	0.04	1.39	1.55
Benzo[c]phenanthrene	0.863	0.005	0.595	0.031	0.325	0.375
Benzo[b]naphtho[1,2-d]thiophene	0.0446	0.0003	0.0213	0.0031	N.D.	–
Benz[a]anthracene	3.68	0.43	2.35	0.28	0.96	0.543
Chrysene	3.96	0.86	2.5	0.22	1.36	0.64
Cyclopenta[cd]pyrene	N/A-	–	N/A	–	N/A	–
3-Methylchrysene	0.147	0.008	0.0793	0.0001	0.169	0.065
2-Methylchrysene	0.447	0.027	0.336	0.021	0.152	0.088
6-Methylchrysene	0.426	0.02	0.348	0.005	0.148	0.068
1-Methylchrysene	0.201	0.006	0.145	0.012	0.096	0.075
Benzo[b]fluoranthene	1.65	0.78	1.11	0.42	0.884	0.649
Benzo[k]fluoranthene	0.49	0.248	0.326	0.136	0.297	0.26
Benzo[e]pyrene	1.9	0.6	1.2	0.35	0.92	0.658
Benzo[a]pyrene	0.946	0.262	0.639	0.137	0.492	0.355
Perylene	0.186	0.047	0.138	0.021	0.137	0.121
Indeno[1,2,3-cd]fluoranthene	0.0157	0.0085	0.0163	0.01	0.0724	0.0946
Indeno[1,2,3-cd]pyrene	0.263	0.052	0.363	0.207	0.379	0.34
Dibenzo[a,h]anthracene	0.0191	0.0059	0.0267	0.0175	0.105	0.137

Picene	0.0254	0.0206	0.0199	0.0134	0.117	0.154
Benzo[ghi]perylene	2.09	0.76	1.89	0.58	1.79	1
Dibenzo[a,l]pyrene	N/A	–	N/A	–	N/A	–
Dibenzo[a,e]pyrene	0.112	0.026	0.0683	0.0019	0.0374	0.0205
Coronene	0.345	0.087	0.41	0.197	0.453	0.223
Dibenzo[a,i]pyrene	0.404	0.055	0.193	0.013	0.0207	0.0156
Dibenzo[a,h]pyrene	0.258	0.044	0.116	0.011	0.0126	0.0092

3. Heavy-Duty Diesel Vehicles and Engines

This chapter discusses the PAH and nitro-PAH emissions from heavy-duty on-road diesel vehicles and engines tested either on chassis dynamometers or on engine test cells. Similar to the previous chapter, we summarize the PAH and/or nitro-PAH results in tables for each individual study. The fuel type and aftertreatment impacts on PAH emissions are also shown. Overall, this chapter shows that diesel vehicles or engines without aftertreatment controls can produce significant concentrations of PAH and nitro-PAH emissions. The addition of oxygenated fuels (i.e., biodiesel blends) and DPFs can provide important reductions in PAH emissions.

Jin et al. (2014) [Chemical characteristics of particulate matter emitted from a heavy-duty diesel engine and correlation among inorganic and PAH components, Fuel] investigated the effects of engine speed and load on PAH emissions from an urban bus diesel engine mounted on a bench testing system (AVL, Graz, Austria). The exhaust samples were diluted and collected from the CVS system and FFP4000 particle sampler mounted on a bench testing system. The engine was a Yuchai YC4G180-200 turbocharged 5.2L, four-cylinder diesel engine, complying with China III (equivalent to Euro III). Testing was performed on ‘point’ cycles representing operational data of actual driving cycles of buses in China. The engine speeds were set at 1000 rpm, 1200 rpm, and 1600 rpm, and the engine loads were 60% and 100%. Each sampling process was repeated twice using quartz fiber membranes for PAH analysis.

Concentrations of 16 PM-PAHs (Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene) in the extracts were measured by Gas Chromatography–Mass Spectrometry (GC8000Top-Voyager, Finnigan, US) following USEPA

Method TO-13A. GC (gas chromatography) inject port were keeping 280 °C. GC oven was programmed with an initial temperature of 70 °C, held for 2 min, elevated at rate of 10 °C/min to 260 °C, and then to 300 °C at 5 °C/min and held for 8 min. The transfer line between GC and MSD (mass spectrometer detector) were held 300 °C. The MSD was operated under the following condition: electron impact mode with energy of 70 eV, mass range: 50–300 μm. Selected Ion Mode (SIM) was used for quantitative analysis. When the concentrations of internal standards (Supelco, US) were 0.5 mg L-1, the recovery for each PAH species varied between 86% and 95%, and the relative standard deviation was less than 10%.

Table 20: Proportion of PM-PAHs (wt.% of total PM-PAHs)

PAHs	
Naphthalene	7.4 ± 4.3
Acenaphthylene	1.3 ± 2.8
Fluorene	2.2 ± 2.6
Phenanthrene	22 ± 11
Anthracene	22 ± 7
Fluoranthene	9.5 ± 7.1
Pyrene	17 ± 10
Benzo[a]anthracene	1.0 ± 2.0
Chrysene	1.8 ± 2.5
Benzo[b]fluoranthene	3.7 ± 2.0
Benzo[k]fluoranthene	3.7 ± 2.0
Benzo[a]pyrene	8.8 ± 5.0
Acenaphthene	N.D.
Indeno [1, 2, 3-cd]pyrene	N.D.
Dibenzo[a,h]anthracene	N.D.
Benzo[g,h,i]perylene	N.D.

ND: Not detected

He et al. (2010) [Characteristics of polycyclic aromatic hydrocarbons emissions of diesel engine fueled with biodiesel and diesel, Fuel] characterized the PAH emissions in the exhaust of biodiesel-fueled engine. The authors used three fuels, including a diesel fuel, pure biodiesel from soybean oil, and a B20 blend. Tests were performed on a direct injection turbocharged EURO II diesel engine (FAW-WDEW 4CK, China), with the following characteristics: four-cylinders; bore and stroke of 110 x 125 mm; total displacement of 4.75 L; compression ratio of 16.8; rated power of 117 kW at 2300 r/min; maximum torque of 580 Nm at 1400 r/ min; traditional mechanical injection system; and without EGR (exhaust gas recirculation) or any other after-treatment. The engine was tested on a bench based on an AC dynamometer (Schenck HT350, Germany). PAH emissions were collected over the ISO 8178 Type C1 8-mode steady-state cycle.

PAHs samples of both gas-phase and particle-phase were collected by using a PAHs sampling system at a temperature below 52 °C. Sample gas was drawn from the tailpipe and diluted in an ejection dilutor (Dekati, Finland), which can control the dilution ratio around 8. Particle-phase PAHs were collected on a fiberglass filter, which was pre-cleaned in a muffle at 450 °C for 8 h before sampling. Gas-phase PAHs were collected by a ‘‘PUF/XAD-2/PUF” cartridge (Supelco ORBO-1500, USA). The sampling flow rate of particle-phase and gas-phase PAHs was 35 and 5 L/min, respectively and the sampling time was 30 min.

The sampled filters were extracted in an ultrasonic extractor for 3 times (30 min for each time) and the sampled cartridges were extracted in a Soxhlet extractor for 24 h with dichloromethane. Both the particle-phase and gas-phase PAHs extract was then concentrated, followed by silica gel cleanup procedure using column chromatography to remove potential interferences prior to analysis. The eluent was reconcentrated to exactly 1.0 mL and collected by a volumetric flask for the next analysis. The analytical method for PAHs was based on the EPA method TO-13A. The

PAHs contents were determined by a gas chromatograph/mass spectrometer (GC/MS) (Agilent 6890N/5795C, USA). The GC was equipped with a capillary column (HP-5MS, 30 m x 0.25 mm x 0.25 μm) and the oven was heated from 80 to 160C at 20C/min, and 160–280 °C at 5 °C/min, then held at 280 °C for 10 min. Helium was used as carrier gas at a flow rate of 1 mL/min. The transfer line to MS was at 250 °C and the ion source of MS was electron impact (EI) at 230 °C. The PAHs were qualified by using the selected ion monitoring (SIM).

Table 21: The five most abundant PAHs in gas-phase and particle-phase, and total PAHs

		Gas-phase PAHs		Particle-phase PAHs		Total PAHs	
Fuel	PAH	BSE (μg/kW h)	%	BSE (μg/kW h)	%	BSE (μg/kW h)	%
D	Nap	98.7	59.1	5.7	7.8	76	31.6
	PA	15.5	9.3	37.5	51	76.1	31.6
	Flu	10.8	6.5	NA	NA	10.7	4.4
	Pyr	7.9	4.8	NA	NA	28.7	11.9
	AcPy	6.2	3.7	NA	NA	NA	NA
	Pyr	NA	NA	13.3	18.1	NA	NA
	Ant	NA	NA	3.7	5.1	NA	NA
	FL	NA	NA	6.2	8.4	13.3	5.5
B20	Nap	67.8	42	2.9	6.1	59.9	28.6
	PA	23.1	14.4	15.2	31.8	43.7	20.9
	Pyr	11.9	7.4	11.3	23.6	28.1	13.4
	Flu	9.5	5.9	NA	NA	NA	NA
	CHR	8.9	5.5	2.7	5.6	11.6	5.6
	FL	NA	NA	5.9	12.3	15.6	7.5
B100	Nap	71.8	45.5	5.9	16.2	77	39.7
	Flu	24.9	15.8	1.6	4.4	26.2	13.5
	PA	24.7	15.7	11.7	32.1	36.7	18.9
	Pyr	9.1	5.8	4.9	13.6	14.2	7.3
	AcPy	5.3	3.4	NA	NA	NA	NA
	FL	NA	NA	4	10.9	8.8	4.5

Naphthalene (Nap), Acenaphthylene (AcPy), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Chrysene (CHR)

In an earlier study, **Mi et al. (2000)** [Effect of fuel aromatic content on PAH emission from a heavy-duty diesel engine, Chemosphere] characterized the PAH emissions from four diesel fuels with different levels of aromatics. Testing was conducted on a turbocharged heavy-duty diesel engine (no aftertreatment). The engine was a 6.5L Mitsubishi-6D 14-2AT (manufactured in 1990) with six-cylinders and direct injection. The ECE-R49 procedure was used, which is a five-mode steady-state cycle. These modes, by different weighting, can be simulated to the US-transient cycle. PAH emissions were calculated with different weightings 0.25 (idling), 0.16 (1600 rpm), 0.25 (1600 rpm), and 0.18 (2800 rpm).

Both particle- and gas-phase PAHs emissions were determined with a full flow critical flow venturi (CFV) type dilution tunnel which is 350 mm in diameter. Particulate matter and particle phase PAHs were collected by glass fiber filters (diameter 70 mm) at a temperature below 52 °C. Two sets of filter holders were employed in this system. Back-up filters were used in each holder downstream the sampling filters to check the breakthrough effects at different engine conditions. A glass cartridge holder was installed after the back-up filter holder. This glass cartridge containing polyurethane foam (PUF) plug and XAD-2 resin was used to collect the gas phase PAHs. Before taking the samples, the glass fiber filters were placed in an oven at 450°C for 8 h to burn off any organic compounds that might be present in the filters. The glass cartridge was packed with 2.5 cm of XAD-2 resin sandwiched between a 5-cm upper PUF plug and a 2.5-cm bottom PUF plug. Silicone glue was used to seal and hold these two pieces of PUF to prevent resin from leaking out during sampling and extraction process. After 8 h of adherence, the newly PUF/resin cartridge was cleaned up by Soxhlet extracting for one day each with distilled water, methanol, dichloromethane and finally n-hexane for a total of 4 days and then these PUF/resin cartridges were placed in a vacuum oven at 60°C for 2 h to dry and to evaporate the residual solvent in them.

Each PAH-containing sample including glass cartridge and the glass fiber filters was Soxhlet extracted separately. The extract was then concentrated by purging with ultra-pure nitrogen to 2 ml for the cleanup procedure. The collected eluant from the cleanup procedure was re-concentrated to 0.50 ml with ultra-pure nitrogen. A gas chromatograph (GC) (Hewlett-Packard 5890A) with a mass selective detector (MSD) (Hewlett-Packard 5972) and a computer workstation was used for the PAH analysis. This GC/MS was equipped with a Hewlett-Packard capillary column (HP Ultra 2 - 50 m x0:32 mm x 0:17 µm), and qualification of PAHs was performed by using the selected ion monitoring (SIM) mode.

Table 22: Mean PAH emission factor expressed in mg/l-fuel

PAH	D1 (BF)	D2 (BF + 3% Flu)	D3 (BF + 5% Flu)	D4 (BF + 10% toluene)
Naphthalene	458	525	660	433
Acenaphthylene	18.5	29.1	33.5	21.9
Acenaphthene	16.1	21.6	25.6	15.5
Fluorene	14.7	777	2230	21.4
Anthracene	11.2	14.3	22	8.12
Phenanthrene	1.62	2.98	47.3	1.92
Fluoranthene	1.58	2.21	2.16	1.32
Pyrene	1.55	1.83	1.93	1.16
Cyclopenta(c,d)pyrene	0.2	0.29	0.28	0.19
Benzo[a]anthracene	0.55	0.56	0.54	0.52
Chrysene	0.94	1.01	1.12	0.85
benzo(b)fluoranthene	1.51	0.56	1.86	2.7
benzo(k)fluoranthene	0.71	0.8	0.79	0.55
benzo(e)pyrene	0.3	0.31	0.21	0.43
benzo(a)pyrene	1.03	1.12	1.13	1.28
Perylene	0.4	0.74	0.62	0.87
indeno(1,2,3,-cd)pyrene	3.25	3.7	3.46	4.55
dibenzo(a,h)anthracene	1.17	0.7	0.94	1.45
benzo(b)chrycene	0.89	0.68	0.82	1.27
benzo(ghi)perylene	1.58	1.11	1.64	1.88
Coronene	0.35	0.64	0.21	0.23

Total-PAHs	537	1390	3040	523

Borillo et al. (2018) [Polycyclic Aromatic Hydrocarbons (PAHs) and nitrated analogs associated to particulate matter emission from a Euro V-SCR engine fuelled with diesel/biodiesel blends, Science of the Total Environment] measured PAH and nitro-PAH emissions from a diesel engine used in trucks and buses, compliant with the standard emissions determined in PROCONVE P7/Euro V. The engine was equipped with common-rail direct injection and SCR 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 European Steady Cycle (ESC)was selected as driving cycle for the dynamometer operation to allow PM sampling. The PM emission was 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. 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).

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). Samples and standards were analyzed 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: 1min 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 °Cmin^{-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.

Table 23: PAH concentrations associated to PM exhaust emissions, expressed in µg kWh^{-1}

PAH (µg / kWh)	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	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	0.085 ±0.016	1	0.081 ± 0.016	2	<LoQ		<LoQ	
Benzo[b]fluoranthene	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		3.13 ± 0.40		2.54 ± 0.28		2.12 ± 0.15	
PAHsC - possibly carcinogenic for humans	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

Table 24: Nitro-PAH concentrations associated to PM exhaust, expressed in µg kW^{-1}

Nitro-PAH (µg / kWh)	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	1.339±0.689	5	1.223±0.276	5	1.624±0.596	5	0.624±0.314	2

1-nitropyrene	0.408±0.177	1	0.542±0.177	1	0.360±0.177	1	0.350±0.177	1

u: expanded uncertainties (95% level of confidence); n: number of valid samples; <LoQ: below

Lin et al. (2019) [Characterization and quantification of PM2.5 emissions and PAHs concentration in PM2.5 from the exhausts of diesel vehicles with various accumulated mileages, Science of the Total Environment] evaluated the PAH concentrations in PM2.5 emissions of different heavy-duty and medium-duty diesel vehicles under real-world conditions. The details of each vehicle are shown below.

IS	Manufacturer	Model year	Fuel	Displacement (c.c.)
M1	Mitsubishi	1995	Diesel	4948
M2	Mitsubishi	1992		11149
M3	Toyota	1991		6443
M4	Mitsubishi	1993		11149
M5	Nissan	2002		6925
M6	CMC motor	2012		7545
M7	Toyota	1999		6485
M8	Fuso	1991		4948
M9	Nissan	1990		6925
M10	Mitsubishi	1998		11149
M11	Mitsubishi	1998		11149
M12	Toyota	1987		4009
M13	Scania	1995		11020
M14	Hino	1995		6485
M15	Mitsubishi	1993		11149

Diesel vehicle exhausts were fixed from the tailpipe to a dilution tunnel full-flow, integrating a constant volume sampling (CVS) system. The exhausts were drained from the tunnel of dilution to a manifold of stainless steel, where it gets separated into three streams and directed, via 1/4 in. stainless steel and Teflon lines, to canister, and sorbent backed filter sampling systems used for the collection of PAHs. PAH samples of both the particulate-phase and gas phase were collected by using a PAH sampling system at a temperature below 52 °C with the intention of avoiding desorption of PAH collected by cartridges. Particulate-phase PAHs were collected in glass-fiber filters. Prior sampling, the filters were placed in an oven at 450 °C for 8 h to burn off any organic compounds that might have been present. Lastly, the cleaned filters were stored in a desiccator for at least 8 h to achieve moisture equilibrium before being weighed. Gas-phase PAHs were collected in a three-stage glass cartridge containing a polyurethane foam (PUF) plug followed by XAD-16 resin. The glass cartridge was packed with 5.0 cm of XAD-16 resin sandwiched between a 2.5-cmupper PUF plug and a 2.5-cm bottom PUF plug. Silicone glue was used to seal and hold these two pieces of PUF to prevent resin from leaking out during the sampling and extraction processes. Each and every sample gathered was separated in a Soxhlet extractor with a blended dissolvable (n-hexane and dichloromethane 1:1 (v/v), 750 mL each) for 24 h. These concentrates were awhile later concentrated, cleansed (utilizing a silica segment loaded with silica gel particles (size range = 0.04–0.063 mm) placed under a layer of anhydrous Na_2SO_4 (~1 cm high) and overhead more backup of glass fiber), and reconcentrated by cleansing with ultra-unadulterated nitrogen to precisely 1.0 mL for GC–MS investigation.

Table 25: PAH concentrations in ng/m^3 and PAH emission factors in ng/l-fuel

	PAHs concentration of PM2.5 emitted for diesel engines (ng/m3).		PAHs emission coefficient of PM2.5 particles in the exhaust of diesel engine (ng/L-fuel).	
Compounds	Diesel engine (n=15)		Diesel engine (n=15)	
	Mean	SD	Mean	SD
Naphthalene	990	25.0	315	15.8
Acenaphthylene	48.4	1.35	15	5.74
Acenaphthene	44.3	2.69	14	7.78
Fluorene	204	7.33	50.8	39.8
Phenanthrene	896	28.7	263	16.6
Anthracene	943	7.18	54.5	53
Fluoranthene	229	10.4	249	19
Pyrene	1740	11.2	518	27.7
Benzo(a)Anthracene	29.4	1.61	7.45	5.74
Chrysene	34.9	1.68	10.1	6.24

Benzo(b)Fluoranthene	25.1	1.96	8.01	4.99
Benzo(k)Fluoranthene	31.7	1.77	9.12	8.07
Benzo(a)Pyrene	11.4	2.86	3.24	2.66
Benzo(e)Pyrene	15.0	1.92	4.02	4.19
Cyclopenta(c,d)pyrene	13.1	1.49	3.31	2.66
dibenzo[a,h]anthracene	8.56	1.70	2.44	2.34
Perylene	10.5	1.42	2.38	2.5
indeno[1,2,3,-cd]pyrene	10.9	0.939	3.21	3.11
benzo[b]chrycene	10.3	2.44	3.02	3.15
benzo[ghi]perylene	7.05	1.68	2.01	2.38
Coronene	10.00	1.27	2.92	3.12
ΣLMW	3130	34.2	732	33.6
ΣMMW	2020	13.8	790	45.6
ΣHMW	158	12.7	43.3	31.8
Total PAHs	5310	42.4	1570	77.5
Total-BaPeq	46.8	2.70	11.2	6.9

Liu et al. (2010) [Analysis of C1, C2, and C10 through C33 particle-phase and semi-volatile organic compound emissions from heavy-duty diesel engines, Atmospheric Environment] investigated the PAH and nitro-PAH emissions from two 15L heavy-duty diesel engines, compliant with EPA regulations for the corresponding model year (2004 and 2007). The 2004 engine was equipped with an EGR system. The 2007 engine had an EGR system and a DPF system. The DPF consisted of a DOC and a catalyzed soot filter. The engines were warmed up for 2 h on ISO mode 8, corresponding to 50% load and intermediate speed. For each configuration, the engine was run over the transient Federal Test Procedure (FTP) cycle, which has a duration of 20 min. Each configuration was tested at least three times to determine the measurement variation. Blank substrates were exposed during each step of the process to monitor for contamination from dilution air, background conditions, handling, storage, and transportation.

Engine exhaust samples were collected with a source dilution sampling (SDS) system which consisted of a constant volume primary dilution tunnel, a secondary micro-diluter, a residence time chamber (RTC), isokinetic sampling probes, multiple sampling trains, and control devices. PM-phase PAH species were collected on baked quartz and TIGF filters. Organic species, including PAHs, PAH derivatives, and aromatics were analyzed using gas chromatography/mass spectrometry (GC/MS) in addition to the gaseous samples collected on XAD resins. XAD cartridges were extracted with dichloromethane, combined with TIGF filter extracts, and analyzed for PAHs, and PAH derivatives by GC/MS interfaced with an ion trap operating under electron impact ionization mode (Varian CP-3800 GC equipped with a CP8400 autosampler and interfaced to a Varian Saturn 2000 Ion Trap). Nitro-PAHs were analyzed using negative ion chemical ionization with a triple quadrupole GC/MS/MS system (Varian 1200), which allowed for structural elucidation of unknown compounds with precursor, product and neutral loss scan as well as sensitive analyses of complex mixtures.

Table 26: PAH, nitro-PAH, and oxygenated PAH emissions, expressed in µg/bhp-hr

Compound (carbon number)	2004 Engine	2007 Engine	% Reduced
PAHs			
Naphthalene (10)	719± 79.6	122±129	83.0±29.0
2-Methylnaphthalene (11)	1290±144	82.7±52.1	93.6±15.2
1-Methylnaphthalene (11)	543±52.5	46.1±26.1	91.5±14.5
Dimethylnaphthalenes (12)	1460±113	89.0±18.6	93.9±9.0
Trimethylnaphthalenes (13)	935±45.9	38.8±3.95	95.9±5.3
1-Ethyl-2-methylnaphthalene (13)	115±14.1	4.25±1.18	96.3±13.3
2-Ethyl-1-methylnaphthalene (13)	6.83±1.59	0.673±0.193	90.1±26.1
Anthracene (14)	7.38±1.00	0.862±0.385	88.3±18.8
Phenanthrene (14)	78.6±11.3	12.3±3.62	84.4±19.0
Methylphenanthrenes (15)	85.4±9.49	3.30±0.460	96.1±11.7
Dimethylphenanthrenes (16)	66.9±5.33	1.17±0.239	98.3±8.3
Fluorene (13)	131±20.6	12.9±3.54	90.2±18.4
Methylfluorenes (14)	0.00±0.00	10.9±3.91	-
Fluoranthene (16)	4.31±0.137	1.13±0.564	73.8±16.3
Pyrene (16)	11.7±1.20	0.979±0.649	91.6±15.8
Acenaphthalene (12)	30.5±1.88	2.18±1.42	92.9±10.8

Acenaphthene (12)	45.5±6.55	22.0±21.1	51.6±60.8
Chrysene þ triphenylene (18)	1.05±0.133	0.123±0.109	88.3±23.0
Benz[a]anthracene (18)	0.586±0.0579	0.0632±0.0698	89.2±21.8
Benzo[g,h,i]fluoranthene (18)	0.607±0.593	0.258±0.270	57.5142
Benzo[b+ k + j]fluoranthene (20)	0.240±0.0735	0.0077±0.00715	96.8±33.6
Benzo[a]pyrene (20)	0.0797±0.0378	0.00613±0.00469	92.3±53.3
Benzo[e]pyrene (20)	0.232±0.0575	0.00374±0.0983	98.4±67.2
Benzo[g,h,i]perylene (22)	0.0724±0.0240	0.0168±0.00885	76.8±45.4
Nitro-PAHs			
1-Nitronaphthalene (10)	0.361±0.0701	0.0858±0.0198	76.2±24.9
2-Nitronaphthalene (10)	0.531±0.0896	0.0478±0.00914	91.0±18.6
Methylnitronaphthalenes (11)	0.719±0.110	0.0232±0.00393	96.8±15.8
2-Nitrobiphenyl (12)	0.0228±0.00974	0.00166±0.00087	92.7±46.5
4-Nitrobiphenyl (12)	0.0103±0.00644	0.00012±0.00009	98.9±63.4
1-Nitropyrene (16)	0.0550±0.0154	<0.00025±0.00	99.5±28.0
9-Nitroanthracene (14)	0.192±0.00914	0.0403±0.00931	79.0±9.6
Oxygenated PAHs			
Acenaphthenequinone (12)	29.1±2.68	0.945±1.49	96.8±14.3
9-Fluorenone (13)	13.9±2.29	6.54±1.59	52.9±27.9
Xanthone (13)	8.75±3.94	0.386±0.0908	95.6±46.1
Perinaphthanone (13)	29.7±4.33	1.01±0.288	96.6±15.5
Anthraquinone (14)	5.16±0.886	1.30±0.506	74.8±27.0
9-Anthraaldehyde (15)	1.56±0.829	0.038±0.0291	97.5±55.0
Benzanthrone (17)	1.89±0.109	0.0154±0.00973	99.2±6.3

Alkurdi et al. (2013) [Characterization, concentrations and emission rates of polycyclic aromatic hydrocarbons in the exhaust emissions from in-service vehicles in Damascus, Atmospheric Research] investigated the PAH emissions from six in service vehicles. The vehicles included a conventional gasoline engine, a modern gasoline engine equipped with TWC, a medium-duty diesel engine, an old heavy-duty diesel engine, and modern heavy-duty diesel equipped with catalytic converter. Vehicle details are shown below.

Vehicle type	Manufacturer	Model Year	Fuel type
Car	Hyundai Avante	2008	Gasoline
Car	Hyundai Elantra	1994	Gasoline
Car	Dacia Super Nova	2002	Gasoline

Minibus	Mazda	1996	Diesel
Bus	King Long KLQ6950GQ	2007	Diesel
Bus	Man	1975	Diesel

Engine exhaust samples were collected from the exhaust using a PAH sampling system equipped with a sampling probe with a stainless steel filter holder, a flow meter and a pump. Teflon-coated glass fiber filter (TX40HI20WW Pallflex, Putnam, Connecticut, USA, retention efficiency b99.0% for particles 0.035–1 μm) held in stainless steel filter holder and placed in series with three polyurethane foam plugs (PUF, 10 cm each), were used to ensure the complete collection of particle-associated and vapor phase-PAH, respectively. In order to avoid water condensation in the sampling system, the device was placed as close as possible to the exhaust tailpipe. The sampling point was positioned at the end of the exhaust pipe and engine exhaust samples were collected after ensuring thermal equilibrium between the exhaust and the probe. A vacuum pump (MILLIPORE, 75 mm Hg) was installed behind the flow meter (1–5 L/min) to draw the exhaust gas sample from the tailpipe. During sampling, the exhaust gas was sampled through the sampling train at a sampling flow rate of approximately 3 l/min. Sample extraction and analysis were performed according to EPA method TO-13. After sample collection, the PTFE-coated filters and polyurethane foam plugs were wrapped in aluminum foil to avoid sample degradation from UV light and stored at −17 °C until the extraction. Each sample, including the filter and the three PUF plugs, were extracted together with 300 ml dichloromethane (HPLC grade, purity >99.8%) in a Soxhlet apparatus (500 ml capacity) for about 24 h (5–6 cycles/h). During extraction, the Soxhlet apparatus was wrapped in aluminum foil to protect the samples against UV light. The sample extract volume was reduced to about 5 ml using a rotary evaporator at 36 °C and finally the volume was brought down to about 1 ml under a gentle stream of high purity nitrogen. Following extraction, the extracts were cleaned in order to eliminate interferences from polar compounds and sampling artifacts. The clean-up was performed on a solid phase extraction cartridge (SPE) and entailed removal of water, solid debris and interfering compounds by passing the extract through a column packed with silica SepPak mesh no. 60, topped with 1 cm of anhydrous sodium sulfate. The eluates were transferred to 1.5 ml vials and evaporated to near complete dryness under a gentle flow of high purity nitrogen and re-dissolved with 1 ml of high purity HPLC-grade acetonitrile before analysis. Fifteen PAH compounds were identified and quantified using High Pressure Liquid Chromatography (HPLC) system (Agilent 1100 HPLC System Liquid Chromatograph) equipped with fluorescence and UV detectors connected in series.

Table 27: Emission rates of individual PAHs in µg/m^3 (n=3)

PAH Compound	Hyundai (Avante) 2008		Hyundai (Elantra) 1994		DACIA (Super Nova) 2002		Mazda (minibus) 1996		King Long (minibus) 1996		MAN (old bus) 1975	
	C µg/m^3	SD (%)	C µg/m^3	SD (%)	C µg/m^3	SD (%)	C µg/m^3	SD (%)	C µg/m^3	SD (%)	C µg/m^3	SD (%)
Naphthalene	53.4	4.2	292.67	5.4	97.07	1.4	395.7	3.1	306.8	3.3	1106.46	20.3
Acenaphthene	1.94	0.1	6.95	0.09	3.58	0.09	66	1.2	67.54	1.1	96.92	1.7
Fluorene	3.59	0.2	9.51	0.08	1.09	0.05	14.28	0.8	7.1	0.08	539.56	5.6
Phenanthrene	0.64	0.05	26.99	0.9	0.17	0.01	41.22	1.5	12.37	0.9	153.77	1.2
Anthracene	1.78	0.1	4.25	0.03	24.6	0.2	37.29	0.9	61.99	1.2	107.01	1.2
Fluoranthene	0.63	0.03	2.43	0.03	0.25	0.01	5.07	0.07	4.61	0.03	26.96	0.9
Pyrene	1.2	0.19	2.65	0.02	0.7	0.05	19.05	0.2	6.06	0.08	32.23	0.9
Benz[a]anthracene	0.49	0.03	0.93	0.03	0.32	0.03	7.83	0.07	3.25	0.03	8.82	0.8
Chrysene	0.32	0.04	1.47	0.02	0.16	0.03	4.39	0.08	1.53	0.02	28.18	0.7
Benzo[b]fluoranthene	1.78	0.2	3.29	0.02	1.16	0.08	30.13	1.4	11.88	0.09	18.73	0.4
Benzo[k]fluoranthene	0.56	0.1	0.74	0.01	0.27	0.01	0.68	0.02	2.53	0.01	4.73	0.09
Benzo[a]pyrene	1.1	0.2	3.04	0.03	1.63	0.05	16.84	0.1	10.8	0.09	26.96	0.1
Dibenzo[a,h]anthracene	0.32	0.05	0.6	0.01	0.2	0.01	5.31	0.5	2.11	0.02	3.36	0.09
Benzo[g,h,i]perylene	0.79	0.1	1.57	0.02	0.49	0.01	12.33	0.8	5.18	0.02	8.62	0.06

Indeno[1,2,3-cd]pyrene	0.74	0.1	3.97	0.03	1.43	0.02	15.24	0.9	4.83	0.02	7.1	0.08
Total	69.28	1.06	361.06	1.39	133.12	0.35	671.36	0.82	508.58	0.89	2169.41	5.17

Lin et al. (2011) [Experimental investigation of the performance and emissions of a heavy-duty diesel engine fueled with waste cooking oil biodiesel/ultra-low sulfur diesel blends, Energy] characterized PAH emissions from a heavy-duty diesel engine under the US-HDD transient cycle on five test fuels, including a ULSD, 5, 10, 20, and 30 vol% waste cooking oil biodiesel blends. The engine was a Cummins B5.9-160 with direct injection, injection pressure of 250 bar, injection timing of 12.3 BTDC, bora and stroke with dimensions of 102 mm x 120 mm, a compression ratio of 17.9:1, a maximum power of 118 kW at 2500 rpm, and a maximum torque of 534 Nm at 1600 rpm. The engine was manufactured in 1994. Testing was conducted according to Code of Federal Regulations (CFR) 40 Part 86 Subpart N (the US-HDD transient cycle), with related mild engine loaded conditions, which represents typical urban and freeway driving conditions. A Schenck GS-350 dynamometer was used. A dilution tunnel and a monitoring system were installed downstream of the exhaust to supply dilute air and to facilitate continuous measurement of suspended particles (PM and particulate-phase PAHs).

PAH samples of both particulate-phase and gas-phase were collected by using a PAH sampling system at a temperature below 52C. Particulate-phase PAHs were collected on a glass-fiber filter. Filters were placed in an oven at 450C for 8 h before sampling to burn off any organic compounds that might be present. Gas-phase PAHs were collected on a three-stage glass cartridge containing a polyurethane foam (PUF) plug XAD-16 resin. The glass cartridge was packed with 5.0 cm of XAD-16 resin sandwiched between 2.5 cm top and bottom PUF plugs. Gas-phase PAHs were collected on a three-stage glass cartridge containing a polyurethane foam (PUF) plug XAD-16 resin. The glass cartridge was packed with 5.0 cm of XAD-16 resin sandwiched between 2.5 cm top and bottom PUF plugs.

Table 28: Mean PAH concentrations, expressed in μg/m^3

PAHs	Tested fuel				
	ULSD	WCOB5	WCOB10	WCOB20	WCOB30
naphthalene	1.51	1.42	1.17	1.029	0.968
acenaphthylene	0.198	0.1683	0.145	0.140	0.131
acenaphthene	0.0851	0.0601	0.0547	0.0497	0.0414
Fluorene	0.0858	0.0698	0.0616	0.0466	0.0337
Phenanthrene	0.301	0.275	0.210	0.183	0.163
Anthracene	0.0188	0.0156	0.0140	0.0195	0.0124
Fluoranthene	0.0155	0.0145	0.0128	0.0100	0.0094
Pyrene	0.0141	0.0226	0.0125	0.0131	0.0168
cyclopenta[c,d]pyrene	0.0104	0.0102	0.0101	0.0098	0.0083
benzo[a]anthracene	0.0104	0.0102	0.0098	0.0091	0.0084
Chrysene	0.00621	0.00613	0.00576	0.01172	0.00480
benzo[b]fluoranthene	0.00622	0.00526	0.00516	0.00441	0.00287
benzo[k]fluoranthene	0.0128	0.0123	0.0116	0.0111	0.0103
benzo[e]pyrene	0.0167	0.0165	0.0143	0.0116	0.0098
benzo[a]pyrene	0.00320	0.00301	0.00239	0.00227	0.00201
Perylene	0.0144	0.0134	0.0117	0.0115	0.0101
indeno[1,2,3,-cd]pyrene	0.0190	0.0176	0.0154	0.0152	0.0133
dibenzo[a,h]anthracene	0.0151	0.0140	0.0123	0.0109	0.0105
benzo[b]chrycene	0.0197	0.0182	0.0160	0.0158	0.0137
benzo[ghi]perylene	0.00598	0.00553	0.00483	0.00477	0.00417
Coronene	0.00627	0.00575	0.00505	0.00503	0.00435
Total PAHs	2.37	2.18	1.80	1.61	1.48
Total BaPeq	0.0257	0.0239	0.0208	0.0190	0.0176

Tan et al. (2017) [Size distributions, PAHs and inorganic ions of exhaust particles from a heavy duty diesel engine using B20 biodiesel with different exhaust aftertreatments, Energy] investigated the PAH emissions from a heavy-duty diesel engine using B20 biodiesel fuel and equipped with three aftertreatment devices: DOC, DOC+DPF, and DOC+CDPF (catalyzed DPF). The engine was equipped with a direct injection common-rail fuel system, had a displacement of 8.8 L, turbocharged with intercooler, a compression ratio of 18:1, a maximum power of 184 kW at 2200 rpm, and a maximum torque of 1000 Nm at 1400 rpm. PAH sampling was performed under constant operating conditions (1400 rpm at maximum torque for 3600s). PAHs were measured by gas chromatography-mass spectrometry (GC8000 Top-Voyager, Finnigan, USA) according to USEPA Method TO-13A.

Table 29: PAH emissions, expressed in µg/kW-hr, at 1400 rpm at maximum torque

	After Treatment			
Compound (µg/kW-hr)	None	DOC	DOC+DPF	DOC+CDPF
acenaphthylene	0.061914	0.016916	N/A	N/A
acenaphthene	0.020112	0.019458	N/A	N/A
Fluorene	0.165915	0.410077	N/A	N/A
Phenanthrene	3.851575	3.320754	0.02461	0.0210467
Anthracene	0.162994	0.07146	N/A	N/A
Fluoranthene	0.716173	0.399197	0.028245	0.0253829
Pyrene	2.421948	0.617793	0.0206	0.0184963
benzo[a]anthracene	0.018643	0.055813	N/A	N/A
Chrysene	0.091706	0.091104	0.043118	0.0526462
benzo[b+k]fluoranthene	0.121189	0.295095	0.018065	0.0094212
benzo[a]pyrene	0.092468	0.155784	N/A	N/A
indeno[1,2,3,-cd]pyrene	0.112445	0.114741	0.015866	0.0181211
benzo[ghi]perylene	0.192807	0.184875	0.03297	0.0242997
dibenzo[a,h]anthracene	0.065917	0.055793	N/A	N/A

Topinka et al. (2012) [Genotoxic potential of organic extracts from particle emissions of diesel and rapeseed oil powered engines, Toxicology Letters] studies the health effects and PAH emissions from two nonroad diesel engines when operated on diesel fuel and rapeseed oil biodiesel. Two direct injection, turbocharged, aftercooled, four-cylinder compression ignition (diesel) engines were used for this study. The first was a 4.5-l, 136 kW Cummins ISBe4 engine, model year 2003, with a second-generation electronically controlled Common Rail injection system (Bosch), which is, with various aftertreatment devices, used in smaller buses and trucks. The second was a 4.16-l, 90 kW Zetor 1505 (Zetor, Brno, Czech Republic) tractor engine, model year 2007, with a mechanically controlled inline injection pump (Motorpal, Jihlava, Czech Republic), certified to EU Stage III-A non-road engine standards. Both engines were operated without any exhaust aftertreatment device. Both engines were operated on European highway-grade diesel fuel (EN 590), rapeseed oil methylester (B-100, EN 14214), and locally produced fuel grade (DIN 51605) rapeseed oil. In order to facilitate operation on non-esterified rapeseed oil, both engines were equipped with a heated secondary auxiliary fuel system, consisting of a heated fuel tank, supply pump, heated fuel filter and isolated fuel line, which allows for switching between diesel fuel and heated vegetable oil. Switching between these branches is provided by two three-way valves, one for switching the supply branch and is placed before the in-line injection pump (Zetor) or high-pressure pump for the Common Rail system (Cummins), and the second valve is installed on the fuel return line.

High-volume samplers were used for sampling of diluted exhaust. The exhaust from both engines was directed to the laboratory main exhaust duct, with a nominal flow of 8800 m3/h, serving as an improvised full-flow dilution tunnel with a dilution ratio ranging from approximately 100:1 at idle to 10–15:1 at full load. Both engines were coupled with Schenck Dynabar water-brake dynamometers and run at a series of steady-state operating points. The Cummins engine tests were based on the ESC (European Steady State Cycle; EU directive 2005/55/EC) and WHSC

(World Harmonized Steady State Test Cycle. The Zetor engine tests were based on the ISO-8178 non-road engine test schedules C-1 (also known as the NRSC, Non-Road Steady State Cycle, prescribed for non-road engines). With the exception of the WHSC, which was run as prescribed, the test schedules were modified to allow for continuous, uninterrupted sampling of the diluted exhaust by high-volume samplers for the entire duration of the cycle. The length of each operating point was adjusted according to the weight of this point, with a total cycle length of 1000s for the ESC and 1800s for the ISO-8178 C-1 schedule. Twenty seconds was allowed for gradual transition between two consecutive operating points. Prior to the test, the engines were warmed up and preconditioned according to the customary procedures (a minimum of 10 min at ESC mode 4, WHSC mode 9, C-1 mode 1). For the Cummins engine, each cycle was run at least twice to amass a sufficient amount of sample.

Filters were extracted with dichloromethane (DCM). The concentrations of 12 priority polycyclic aromatic hydrocarbons (PAHs), namely benzo[a]anthracene (B[a]A), chrysene (CHRY), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenzo[a,h]anthracene (DB[ah]A), indeno[1,2,3-cd]pyrene (I[cd]P), benzo[g,h,i]perylene (B[ghi]P), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU) and pyrene (PYR) were analyzed in each EOM sample. The first seven PAHs in this list are regarded as carcinogenic PAHs (c-PAHs) according to IARC. For the in vitro experiments, EOM samples were evaporated under a stream of nitrogen. 1,2-Propandiol (100 µl) was used as a keeper to avoid outflow of c-PAHs in the course of the evaporation. The residues in 100 µl of 1,2-propandiol were stored in a freezer at −80 °C until analysis.

Table 30: Priority PAH emissions, expressed in µg/kWh

Engine	**Test fuel**	**Test Cycle**	**12 PAHs (μg/kWh)**	**7c-PAHs (μg/kWh)**	**B[a]P (μg/kWh)**
Cummins ISBe4, common rail	Diesel	ESC-modified	11	2.1	0.05
	Rapeseed Oil	ESC-modified	5.8	1.8	0.05
	Biodiesel	ESC-modified	3.8	1.6	0.09
	Diesel	WHSC	1.6	0.8	0.04
	Rapeseed Oil	WHSC	1.8	2.1	0.05
Zetor 1505, Inline pump	Diesel	NRSC	54	11	ND
	Rapeseed Oil	NRSC	51	18	0.2

Zhang et al. (2019) [Particle number, size distribution, carbons, polycyclic aromatic hydrocarbons and inorganic ions of exhaust particles from a diesel bus fueled with biodiesel blends, Journal of Cleaner Production] investigated the PAH emissions from a diesel engine operated with waste cooking biodiesel blends at 5, 10, and 20 vol%. Testing was made in a diesel urban bus (type SWB6128V8LF) equipped with a selective catalytic reduction (SCR) system satisfying Euro V emission standards. The 2011 engine had a 9.82L displacement, rated power of 192 kW at 2300 rpm, and a maximum torque of 1100 Nm at 1400 rpm. PAH samples were collected using a MOUDI and Teflon filters, and analyzed with a GC (Agilent-7890GC/5975MSD).

The test cycle used in this study is Chinese city bus cycle (CCBC). The whole CCBC duration is 1314 s, and its mileage is about 5.897 km. The minimum and maximum speed is 0 and 60 km/h, respectively and the average speed is 16.2 km/h. The cycle contains idling, accelerating, cruising, and decelerating conditions, which has a better reflection of the running condition of Chinese urban bus.

Table 31: PAH emissions for the diesel fuel and biodiesel blends, expressed in ng/cm^3

	D100	B5	B15	B20
Naphthalene	0.211	0.219	0.232	0.183
acenaphthylene	0.122	0.133	0.115	0.122
acenaphthene	N/A	N/A	N/A	N/A
Fluorene	0.086	0.067	0.063	0.075
Phenanthrene	0.302	0.265	0.250	0.212
Anthracene	0.449	0.322	0.367	0.393

Fluoranthene	0.114	0.114	0.107	0.084
Pyrene	0.205	0.214	0.188	0.192
Benzo(b)Fluoranthene	0.036	0.036	0.040	0.033
Benzo(a)Anthracene	0.058	0.057	0.049	0.055
Chrysene	0.085	0.095	0.089	0.087
Benzo(k)Fluoranthene	0.036	0.056	0.056	0.069
Benzo(a)Pyrene	0.028	0.025	0.023	0.015
indeno[1,2,3-cd]pyrene	0.088	0.110	0.112	0.114
benzo[g,h,i]perylene	0.095	0.116	0.121	0.116
dibenzo[a,h]anthracene	0.015	0.017	0.013	0.010

Lim et al. (2005) [Effect of fuel composition and engine operating conditions on polycyclic aromatic hydrocarbon emissions from a fleet of heavy-duty diesel buses, Atmospheric Environment] tested the PAH emissions from twelve in-service Volvo and MAN SL200 diesel buses powered by two commercial diesel fuels, LSD and ULSD on a chassis dynamometer. Each of the Volvo buses had an engine capacity of 10L and the engine capacities of the MAN SL200 buses were 9L. None of the tested buses was fitted with a catalyst converter. Measurements were carried out for mode 7 or idle mode (0% power), mode 11 (25% power), mode 10 (50%) and mode 8 (100%). These four modes were selected from the standard thirteen mode SAE test cycle for HDV. Thus, at the start of each test cycle, the engine was allowed to run for a few minutes until the exhaust temperature and CO_2 gas concentrations have attained steady-state values. The buses were then operated for approximately 30 min in mode 7, 20min in modes 11 and 10, and 10 min in mode 8 in order to collect measurable masses of particulate matter for PAH analysis in each mode.

Samples for the PAH analyses were collected from a dilution tunnel at temperatures below 55C by using a high-velocity pump, with a variable flow rate ranging from 0.01 to 0.02 m^3/min. To ensure the complete collection of vapor- and particle-phased PAHs, a Gelman glass fiber filter (47 mm) held in a polycarbonate filter holder and placed in series with a glass cartridge containing 7 g of Amberlite XAD-2 were used to collect particle- and vapor-phased PAHs, respectively. Each sample was extracted three times with a mixture of analytical grade dichloromethane and hexane (2:1) for at least 30 min each time, with a total extraction time of at least 90 min. Following the extraction, the extracts were cleaned up in order to eliminate interferences from sampling artifacts. The clean-up procedure entailed drying of the extract and removal of any solid debris by passing the extract through a column packed with silica SepPak mesh no. 60, topped with 1 cm of anhydrous sodium sulfate. The volume of the solvent in the dry extract was subsequently reduced to about 5 cm^3 on a rotary evaporator at 36C and finally to 1 cm^3 with a stream of high purity nitrogen. PAH analyses were performed on HP 6890 GC FID with an automated injector and fitted with a Restek-5MS capillary column (30.0 m x 0.32 mm x 0.25 mm). The oven temperature was programmed to 80 °C for 4 min and then raised to 320 °C at 10 °C/min, giving a run time of 38 min.

Table 32: Mean emission factors of individual PAHs (mg/km) for the buses

	ULSD buses			LSD buses		
	Mode 11	Mode 10	Mode 8	Mode 11	Mode 10	Mode 8
Naphthalene	46±76	195±251	156±250	7112±2571	28520±47186	16918±15547
acenaphthylene	23±12	44±26	64±66	61±43	114±168	124±82
2-bromo naphthalene	14±10	30±38	21±28	68±68	228±285	212±256
acenaphthene	16±13	41±54	43±48	48±90	133±344	24±55
Fluorene	17±14	19±44	4±6	384±1246	18±35	21±56
Phenanthrene	15±38	48±124	21±49	3607±24	995±1603	3242±6004
Anthracene	60±106	127±296	68±62	32±58	38±63	58±85
Fluoranthene	93±154	322±898	60±81	166±146	344±324	274±310
Pyrene	642±451	763±621	893±889	1567±3846	5092±9322	13231±21126
Chrysene, benzo(a)anthracene	86±128	788±2402	75±64	2283±2558	9902±15240	9898±14100
benzo(b)fluoranthene	202±194	372±406	295±326	58±106	142±453	1488±2366

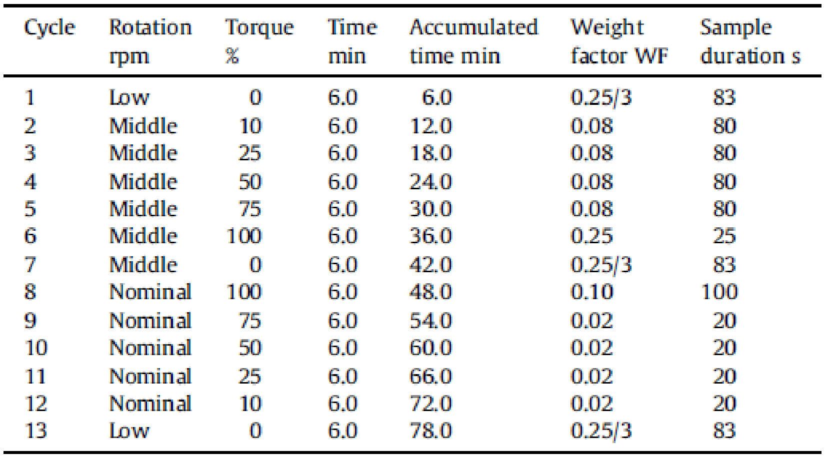
Benzo(a)pyrene	39±37	84±88	108±98	94±58	136±61	171±138
indeno(1,2,3-cd)pyrene, dibenzo(a,-h)anthracene	<0.6	<0.6	<0.6	66±98	136±261	179±304
benzo(g,h,i)perylene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Total	1850±1339	1856±946	1811±424	12301±5529	29726±25936	41788±22626

Correa and Arbilla (2006) [Aromatic hydrocarbons emissions in diesel and biodiesel exhaust, Atmospheric Environment] investigated the PAH emissions from a six-cylinder, in-line MWM heavy-duty engine with direct injection. This was a typical engine used in urban buses in Brazil and had no aftertreatment controls. Testing was made with the engine in a steady-state condition under 1500 rpm. The tests were performed using commercial pure diesel (D) and a blend of diesel and biodiesel (2, 5, and 20% v/v), referred as B2, B5 and B20. The exhausted air was diluted 15–20 times, using a critical orifice to allow 1.0 L/min to be diluted with synthetic air in a PVC tube of 0.10m of diameter and 2.5m of length. All samples were taken at the middle of this tube. Particle- and vapor-phase PAHs were collected. The air was sampled through an air pump (Gast model DOA-141-AA), using Teflon filters (SKC 225-1708, 0.5 mm) for the retention of the PAHs associated to the particulate matter. In series with the Teflon filters, XAD-2 cartridges (SKC 226-30-06, 400/200 mg) were used to retain the PAHs on the vapor phase. The sampling rate was 0.5 L/min and immediately after the samplings the filters and cartridges were extracted with dichloromethane in a sonic bath as reported by the 3550B methodology of USEPA. The identification and quantification of the PAHs were carried using a gas chromatography coupled to a mass spectrometer detector (MSD 5973) and with a flame ionization detector (FID) (Agilent GC 6890).

Table 33: Composition (%) of individual PAHs on the exhaust of D, B2, B5, and B20

	D	B2	B5	B20
Phenanthrene	40.65	40.72	40.90	42.63
Fluorene	15.61	16.20	15.96	14.78
Naphthalene	14.78	14.43	14.54	13.95
Acenaphthene	10.41	9.46	10.05	9.70
Acenaphthylene	9.58	10.29	9.70	9.93
Anthracene	4.49	4.73	4.61	4.85
Benzo[a]pyrene	1.06	0.83	0.71	0.83
Pyrene	0.71	0.59	0.59	0.59
Benzo[b]fluoranthene	0.83	0.59	0.83	0.83
Chrysene	0.47	0.35	0.59	0.47
Fluoranthene	0.24	0.59	0.35	0.71
Benzo[k]fluoranthene	0.24	0.35	0.24	0.00

Casal et al. (2014) [Alkyl polycyclic aromatic hydrocarbons emissions in diesel/biodiesel Exhaust, Atmospheric Environment] investigated PAH emissions and their alkylated homologues from a diesel engine operated with diesel and biodiesel blends. The tests were performed in a dynamometer bench with a six-cylinder in-line heavy-duty diesel engine with a direct injection Euro III standard. This engine is used in many urban buses in Brazilian cities. No after-treatment emission control devices were used. Nine samples were obtained, with three repetitions of the same engine using pure diesel (D), commercial diesel S50 (50 ppm of sulphur with 5% soy biodiesel) and commercial diesel with 20% soy biodiesel (S50B20). The characteristics of the test cycle are shown below:



Cycle	Rotation rpm	Torque %	Time min	Accumulated time min	Weight factor WF	Sample duration s
1	Low	0	6.0	6.0	0.25/3	83
2	Middle	10	6.0	12.0	0.08	80
3	Middle	25	6.0	18.0	0.08	80
4	Middle	50	6.0	24.0	0.08	80
5	Middle	75	6.0	30.0	0.08	80
6	Middle	100	6.0	36.0	0.25	25
7	Middle	0	6.0	42.0	0.25/3	83
8	Nominal	100	6.0	48.0	0.10	100
9	Nominal	75	6.0	54.0	0.02	20
10	Nominal	50	6.0	60.0	0.02	20
11	Nominal	25	6.0	66.0	0.02	20
12	Nominal	10	6.0	72.0	0.02	20
13	Low	0	6.0	78.0	0.25/3	83

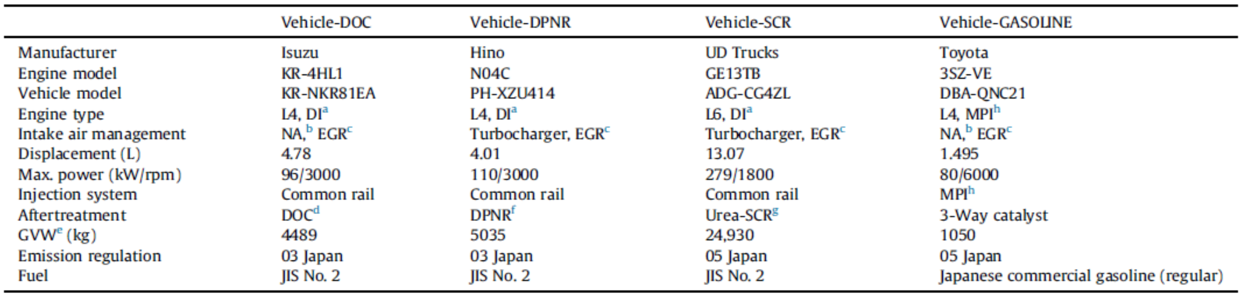
The sampling media used were fiber glass filters with 47mm of diameter and 1.0 mm of porosity (Pall T60A20). Chemical analyses were performed by using a VARIAN CP3800 gas chromatograph with an ion trap mass spectrometer detector (Saturn 2200) operating in electron impact (EI) as the ionization mode.

Table 34: PAH emissions, expressed in ng/mL

PAHs	B20	S50	D
Naphthalene	18.43	21.46	18.27
2-Methylnaphthalene	15.08	15.07	19.00
1-Methylnaphthalene	10.35	7.93	9.29
Acenaphthylene	9.82	1.32	2.08
Fluorene	14.96	5.56	4.19
Phenanthrene	7.21	65.38	74.31
Anthracene	41.88	1.27	2.17
Pyrene	2.33	1.69	1.84

Inomata et al. (2015) [4-Nitrophenol, 1-nitropyrene, and 9-nitroanthracene emissions in exhaust particles from diesel vehicles with different exhaust gas treatments, Atmospheric Environment] used thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) and liquid chromatography/mass spectrometry (LC/MS) to analyze nitro-PAHs and nitrophenols in diesel exhaust particles collected on filters during transient cycles of a chassis dynamometer system with a CVS.

Three diesel trucks, one fitted with an oxidation catalyst (DOC; the vehicle is later called vehicle-DOC), one with a PMeNOx reduction system (DPNR; vehicle-DPNR), and one with a urea-based SCR system (vehicle-SCR), and a compact gasoline passenger car (vehicle-GASOLINE) were tested. Vehicle specifications are show below:



	Vehicle-DOC	Vehicle-DPNR	Vehicle-SCR	Vehicle-GASOLINE
Manufacturer	Isuzu	Hino	UD Trucks	Toyota
Engine model	KR-4HL1	N04C	GE13TB	3SZ-VE
Vehicle model	KR-NKR81EA	PH-XZU414	ADG-CG4ZL	DBA-QNC21
Engine type	L4, DI[a]	L4, DI[a]	L6, DI[a]	L4, MPI[h]
Intake air management	NA,[b] EGR[c]	Turbocharger, EGR[c]	Turbocharger, EGR[c]	NA,[b] EGR[c]
Displacement (L)	4.78	4.01	13.07	1.495
Max. power (kW/rpm)	96/3000	110/3000	279/1800	80/6000
Injection system	Common rail	Common rail	Common rail	MPI[h]
Aftertreatment	DOC[d]	DPNR[f]	Urea-SCR[g]	3-Way catalyst
GVW[e] (kg)	4489	5035	24,930	1050
Emission regulation	03 Japan	03 Japan	05 Japan	05 Japan
Fuel	JIS No. 2	JIS No. 2	JIS No. 2	Japanese commercial gasoline (regular)

The DPNR system consisted of a NOx storage reduction (NSR) catalyst, a wall-flow-type-DPF coated with the NSR catalyst, and a DOC. A fuel injector was mounted upstream of the system. A three-way catalyst was used to control the vehicle-GASOLINE exhaust gas. The exhaust gas from each vehicle was diluted with filtered (through a high-efficiency-particulate-air filter and a charcoal filter) air (later called “background air”) by an average factor of 57 for vehicle-DOC, 15 for vehicle-DPNR, 68 for vehicle-SCR, and 39 for vehicle-GASOLINE.

Each vehicle was set on the chassis dynamometer and driven according to the appropriate Japanese transient emission test cycle, JE05 for the diesel trucks and JC08 for the vehicle-GASOLINE. During a transient driving cycle experiment, automotive exhaust particles in the dilution tunnel were collected on a quartz fiber filter (with a diameter of 47 mm or 70 mm;

2500QAT-UP; Pall, East Hills, NY, USA) with a sampling flow rate of 20-50 L/min. The filter holders (Horiba) for the 47 mm and 70 mm filters were kept at 47 °C and 25 °C, respectively.

The concentrations of 12 unsubstituted PAHs, nine oxy-PAHs, five nitro-PAHs, and three methyl-PAHs in the exhaust particles were determined using TD-GC/MS. The quantification limits (10 times the standard deviation of the analyte concentrations in the blank samples) were 2-18 pg for the unsubstituted PAHs, 9-22 pg for the oxy-PAHs, 59-94 pg for the nitro-PAHs, and 5-23 pg for the methyl-PAHs. The nitrophenols and nitro-PAHs in the automotive exhaust particles were analyzed by LC/MS. Each sample was extracted by sonicating it in 10 mL dichloromethane for 40 min. The extract was concentrated to near dryness under a gentle nitrogen stream. The concentrated extract was then dissolved in 1 mL of a 1:1 (v/v) mixture of methanol and water and sonicated for 5 min. A 50 mL aliquot of the extract was then injected into a sample loop and analyzed by LC/MS (LCMS-8000a; Shimadzu, Kyoto, Japan).

Table 35: Uncorrected emission factors (mg/km) for the unsubstituted PAHs, oxy-PAHs, nitro-PAHs, and methyl-PAHs determined by thermal desorption gas chromatography/mass spectrometry

Compound (mg/km)	DOCb	DOCc	DOC w/o cat.	DOC w/o cat.	DPNR	DPNR	SCR	SCR	GASOLINE	GASOLINE
	JE05H	JE05C	JE05H	JE05C	JE05H	JE05C	JE05H	JE05C	JC08H × 3	JC08C
Phenanthrene	0.90±0.40	1.1 ± 0.3	0.65	0.51	0.51	0.45	1.1	1	<QL	<QL
Anthracene	0.19±0.07	0.20±0.02	0.16	0.12	0.068	0.075	0.11	0.089	<QL	<QL
Fluoranthene	0.89±0.34	0.96±0.25	1	0.53	0.18	0.17	0.49	0.55	<QL	<QL
Pyrene	1.6 ± 1.3	1.3 ± 0.8	0.5	0.52	0.53	0.6	0.52	0.49	<QL	0.0022
Benzo(a)Anthracene	0.43±0.41	0.75±0.60	0.32	0.34	0.025	0.012	0.19	0.2	0.00017	0.0031
Chrysene	1.3 ± 0.9	2.0 ± 1.3	0.79	0.8	0.19	0.088	0.27	0.23	0.00059	0.0044
Benzo(b)Fluoranthene	0.69±0.55	1.0 ± 0.9	0.47	0.45	0.037	0.016	0.45	0.44	0.0011	0.015
Benzo(k)Fluoranthene	0.04±0.01	0.05±0.02	0.037	0.045	0.0018	0.0015	0.083	0.062	<QL	0.0032
Benzo(a)Pyrene	0.17±0.07	0.16±0.05	0.16	0.12	0.0081	0.0055	0.66	0.4	0.00014	0.0094
indeno(1,2,3-cd)pyrene,	0.30±0.23	0.29±0.14	0.23	0.22	0.011	<QL	1	0.45	0.00051	0.023
dibenzo(a,-h)anthracene	0.04±0.01	0.09±0.02	0.073	0.062	0.014	<QL	0.31	0.061	<QL	0.0016
Benzo(ghi)Perylene	0.70±0.79	0.66±0.57	0.3	0.32	0.02	0.0074	1.5	0.85	0.00052	0.025
oxy-PAHs										
9-Fluorenone	0.42±0.17	0.63±0.13	0.22	0.26	0.12	0.13	0.17	0.2	<QL	<QL
Perinaphthenone	17 ± 3	20 ± 6	9.4	6.7	1.4	1.3	0.21	0.2	0.057	0.086
Anthrone	0.10±0.13	0.11±0.08	0.15	0.066	0.016	0.021	<QL	0.12	<QL	<QL
9,10-Anthraquinone	2.8 ± 1.9	4.6 ± 1.7	0.55	0.24	0.058	0.064	0.33	0.28	<QL	<QL
Cyclopenta[def]phenanthrenone	1.5 ± 0.6	1.9 ± 0.3	0.71	0.42	0.091	0.088	0.23	0.17	0.00061	0.0019
Benzo[*a*]fluoren-11-one	1.4 ± 0.8	1.6 ± 1.3	0.26	0.27	0.0057	0.0053	0.029	0.04	0.0029	0.0073
Benzo[*b*]fluoren-11-one	0.97±0.94	2.0 ± 1.8	0.24	0.33	0.0042	<QL	<QL	0.013	0.0035	0.0052
Benzanthrone	2.2 ± 1.4	3.9 ± 2.2	1.5	1.6	0.0057	0.0082	0.14	0.21	0.0064	0.01

Benz[*a*]anthracene-7,12-dione	0.34±0.23	0.61±0.54	0.075	0.091	<QL	<QL	0.01	0.018	0.0036	0.0048
nitro-PAHs										
9-Nitroanthracene	1.4 ± 1.1	2.0 ± 1.3	0.97	0.31	0.022	<QL	<QL	<QL	<QL	<QL
2&3-Nitrofluoranthene	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
4-Nitropyrene	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
1-Nitropyrene	1.3 ± 0.8	1.8 ± 1.6	0.18	0.14	<QL	<QL	<QL	<QL	0.01	0.017
2-Nitropyrene	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL	<QL
methyl-PAHs										
2-Methylphenathrene	0.94±0.55	1.1 ± 0.7	0.51	0.46	1	0.94	0.91	0.64	<QL	<QL
1-Methylphenathrene	0.08±0.04	0.07±0.03	<QL	<QL	0.11	0.1	<QL	<QL	<QL	<QL
1-Methylpyrene	0.08±0.07	0.05±0.02	0.1	0.14	0.038	0.049	0.038	0.033	<QL	<QL

bThe mean and standard deviation of three tests are shown; cThe mean and standard deviation of two tests are shown.

Cao et al. (2017) [Emission characteristics of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons from diesel trucks based on on-road measurements, Atmospheric Environment] studied the real emissions of gaseous- and particle-phase PAHs and nitro-PAHs from nine China III and nine China IV diesel trucks of different sizes (light, medium, and heavy duty) in Beijing.

Both the gaseous- and particulate-phase PAHs and NPAHs were collected and then quantified by high-performance liquid chromatography (HPLC). Emissions were measured with a SEMTECH-DS (Sensors Inc., USA), exhaust flow meter (EFM-2, Sensors Inc., USA), micro-proportional sampling system (MPS, Sensors Inc., USA) and PAH-collection unit. The MPS was applied to dilute the exhaust sample before it was passed through the PAH-collection unit. The dilution ratios were approximately 8:1. The PAH-collection unit included quartz filters (QFs, 47 mm in diameter) followed by two-stage polyurethane foam (PUF) cartridges. Particle-phase PAHs and NPAHs were collected on a 47 mm QF (2500QAT-UP, PALL Corp., USA). Gas-phase PAHs were sampled by two-stage PUF cartridges. The flow rate of the sampling was controlled at approximately 3 L/min.

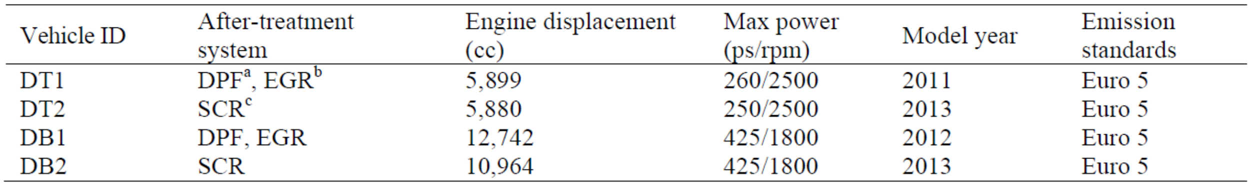
The samples were collected when the tested trucks were driven on highway and non-highway roads, respectively. Each type of road was tested twice. The sampling time for each test was approximately 30-40 min. Before sampling, a PUF was pre-cleaned in an ultrasonic cleaner with dichloromethane three times, with each time lasting 30 min. The QFs were pre-combusted at 550C for 12 h in a muffle furnace. Samples were ultrasonically extracted for 30 min with 10 mL of a mixed solvent (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) and dichloromethane (15 mL for QF and 150 mL for PUF) three times. The extracts were then concentrated to approximately 1 mL and subsequently solvent exchanged to hexane.

The concentrated extracts were then transferred to a silica/alumina chromatography column (20 cm of silica gel and 10 cm of alumina) and eluted with 40 mL n-hexane/dichloromethane (3:2) and 35 mL dichloromethane. The eluate was concentrated to 1 mL and converted to an acetonitrile solution. The solutions were analyzed for PAHs and NPAHs using an HPLC system (Agilent 1200, Santa Clara, CA, USA) equipped with a UV detector (Agilent G1314A, Santa Clara, CA, USA), detected at 220 nm, 230 nm, 254 nm and 290 nm, and an Agilent HC-C18 chromatographic column (5 mm, 250 x 4.6 mm2) (Agilent, USA) operated at 30C. A linear binary gradient composed of acetonitrile (A) and water (B) was employed using the following scheme: 50% A for 81 min, 50-85% A for 10 min, 85% A for 19 min, and 85-50% A for 5 min. When the initial conditions were restored, the column was re-equilibrated for 5 min. The flow rate of the eluent was controlled at 0.8 mL/min.

Table 36: Mean emission factors and standard deviations of PAHs and nitro-PAHs for the LDDTs, MDDTs and HDDTs

	LDDTs (mg/km)	MDDTs (mg/km)	HDDTs (mg/km)
PAHs			
Naphthalene	2194.34 ± 1247.66	1747.64 ± 1112.70	3057.44 ± 1397.73
Acenaphthylene	66.25 ± 22.82	41.40 ± 32.88	112.59 ± 71.12
Fluorene	7552.49 ± 2917.83	5589.10 ± 2488.39	8134.24 ± 2389.60
acenaphthene	19209.08 ± 10591.10	11614.87 ± 5764.24	28295.68 ± 8033.49
Phenanthrene	1226.43 ± 549.90	727.99 ± 855.69	2076.70 ± 723.18
Anthracene	13624.77 ± 7421.41	9463.86 ± 5697.43	16461.67 ± 5639.52
Fluoranthene	189.65 ± 185.00	87.76 ± 82.97	366.13 ± 257.65
Pyrene	2703.88 ± 1529.65	1447.67 ± 1104.47	4325.02 ± 1337.82
Chrysene	92.80 ± 48.49	59.59 ± 38.17	145.41 ± 35.05
Benzo(a)Anthracene	1026.23 ± 914.82	495.71 ± 255.93	1601.82 ± 1081.41
benzo[b]fluoranthene	1409.70 ± 1062.45	764.63 ± 483.68	1027.79 ± 1081.55
benzo[k]fluoranthene	3115.96 ± 2247.35	2297.52 ± 1259.07	3089.23 ± 1911.98
Benzo(a)Pyrene	3651.96 ± 1944.47	2077.26 ± 1279.88	3234.35 ± 1328.37
dibenzo[a,h]pyrene	22752.12 ± 16438.66	14271.72 ± 6848.33	19163.10 ± 17528.95
benzo[g,h,i]perylene	3111.70 ± 2883.71	2053.89 ± 440.57	1976.36 ± 1252.00
indeno[1,2,3-cd]pyrene	301.72 ± 369.96	126.82 ± 103.15	769.83 ± 499.55
Total PAHs	82229.11 ± 41906.06	52867.43 ± 18946.47	93837.35 ± 32193.14
Nitro-PAHs			
5-nitroacenaphthene	77.06 ± 43.31	76.60 ± 42.62	124.87 ± 97.46
9-nitroanthracene	4.76 ± 3.44	2.92 ± 2.49	5.81 ± 2.49
3-nitrophenanthrene	720.41 ± 389.25	516.69 ± 269.41	861.37 ± 325.91
1,3-nitropyrene	48.68 ± 24.63	43.72 ± 38.35	96.22 ± 44.44
1-Nitropyrene	135.66 ± 46.75	84.88 ± 48.83	184.65 ± 84.11
3-nitrofluoranthene	38.87 ± 25.01	27.18 ± 14.84	47.65 ± 19.71
6-nitrochrysene	27.10 ± 24.16	23.81 ± 19.52	33.41 ± 23.62
7-nitrobenz[a]anthracene	54.16 ± 30.04	30.61 ± 22.89	90.38 ± 48.23
6-nitrobenz[a]pyrene	17.29 ± 18.44	35.96 ± 39.83	21.74 ± 24.67
Total nitro-PAHs	1123.98 ± 528.19	842.38 ± 345.70	1466.09 ± 481.48

Jung et al. (2019) [Emission Characteristics of Regulated and Unregulated Air Pollutants from Heavy Duty Diesel Trucks and Buses, Aerosol and Air Quality Research] studied PAH emissions from heavy duty diesel trucks and buses under urban driving conditions in the Seoul Metropolitan Area. Four heavy duty diesel trucks and buses, which represent the majority of in-use trucks and buses in Korea, were selected for investigation of their PAH emission characteristics. The tested vehicles were model year 2011–2013, all of which met the Euro 5 emission standards. These vehicles were equipped with two different after-treatment systems (DPF + EGR and SCR). Vehicle specifications are shown below:



Vehicle ID	After-treatment system	Engine displacement (cc)	Max power (ps/rpm)	Model year	Emission standards
DT1	DPF[a], EGR[b]	5,899	260/2500	2011	Euro 5
DT2	SCR[c]	5,880	250/2500	2013	Euro 5
DB1	DPF, EGR	12,742	425/1800	2012	Euro 5
DB2	SCR	10,964	425/1800	2013	Euro 5

The heavy-duty diesel trucks and buses were tested on a chassis dynamometer (AVL Zöllner) following the National Institute of Environment Research (NIER)-9 mode according to vehicle type and considering the operating speed for heavy duty trucks and buses in the study area. The NIER-9 mode (average speed: 34–35 km/h) is one of the 15 driving cycles developed by the NIER to simulate actual vehicle operating conditions on various urban roads in Korea. The effects of cold and hot start conditions were also investigated in the test cycles considering a 50% load.

The PAHs were collected in quartz filters that had been placed in an 11 mL extraction cell of the accelerated solvent extractor. The accelerated solvent extractor was then extracted using 20 mL dichloromethane for 15 min at a pressure of 13,789.5 kPa and temperature of 100 °C. GC/MS was used to analyze the PAHs according to the 16 EPA PAH compounds present in the 16 component PAH mixture (PAHs Mix, Supelco Inc.).

Table 37: PAH emissions (μg/km) according to vehicle type over cold-start and hot-start conditions

	Cold Start (μg/km)			
	DT1 (DPF+EGR)	DT2 (SCR)	DB1 (DPF+EGR)	DB2 (SCR)
Naphthalene	1.638	1.396	1.517	2.000
Phenanthrene	1.168	0.846	0.980	N/A
	Hot Start (μg/km)			
Naphthalene	1.128	1.450	1.047	N/A
Phenanthrene	0.913	0.993	0.604	N/A

Lea-Langton et al. (2008) [Comparison of Particulate PAH Emissions for Diesel, Biodiesel and Cooking Oil using a Heavy Duty DI Diesel Engine, SAE Technical Paper] investigated the PAH emissions from a Perkins Phaser 180 Ti, 6-cylinder, 6 L, direct injection, turbocharged inter-cooled, heavy-duty diesel engine fitted with an oxidation catalyst. The engine was manufactured in 1999 to Euro 2 emissions standards. The test was conducted under steady state, 23kW and 47kW power output conditions. Testing was conducted on three fuels: a low sulfur petroleum diesel (PD), 100% methyl ester made from a mixture of waste cooking oils (WCOB100), and 100% rapeseed oil (FCO).

PAH exhaust samples were taken at 1.3m from the turbocharger upstream (US) of the catalyst and at 2.05m, downstream (DS) of the catalyst. The particulate samples were taken simultaneously at upstream and downstream of the catalyst. A constant temperature sampling (CTS) technique was used with a 6.3mm stainless steel pipe inserted with a curved bend onto the center line of the exhaust pipe. The sample for particulate collection was passed through a heated sample line to a heated filter in an oven at 50 °C.

Chemical characterization of the particulate in terms of the 16 EPA priority list PAH was achieved using GCMS. Due to the low levels of PAH expected, multiple filter paper samples were required for each extraction, equivalent to at least 500l of exhaust sample. The solvent organic fraction (SOF) of the particulate was extracted using Accelerated Solvent Extraction (ASE) into toluene. The extractor specification was a Dionex 3000 series, temperature set to 100°C, pressure 1500psi. The temperature program involved a 5 min heat up time followed by two static cycles of 10 minutes each in order to achieve maximum extraction. Validation of the extraction efficiency was achieved using a PAH standard mix, giving efficiency of over 90% for all species except for dibenzo(a,h)anthracene and indeno(1,2,3-c,d)pyrene, which had an efficiency of 86% each. The solvent was removed by rotary evaporation then N2 blowdown, before dissolving in dichloromethane for GCMS injection. The samples were injected using Selected Ion Monitoring (SIM) to identify the PAH. PAH mass spectra give an intense molecular ion peak with very little further fragmentation. The SIM mode was programmed to identify all major ions associated with the PAH within the specific retention times that each species is expected. The GCMS used was a Trace 2000 series GC by Thermoquest attached to a MD800 MS by Fisons Instruments with DB5 column. The temperature program was 60 °C for 5 minutes followed by ramp up to 300 °C at 5 °C per minute, then dwell for 8 minutes.

Table 38: Particulate PAH specific emissions (mg/kWh) measured upstream and downstream the oxidation catalyst

diesel fuel, mg/kWh	**23kW US**	**23kW DS**	**47kW US**	**47kW DS**
Naphthalene	0.021	0.051	0.018	0.013
Acenaphthylene	nd	0.101	0.01	nd
Fluorene	nd	0.045	0.006	0.006
Phenanthrene	0.045	0.074	0.026	0.025
Anthracene	0.027	nd	0.006	nd
Fluoranthene	0.186	0.066	0.042	0.015
Pyrene	0.172	0.066	0.044	0.016
Benzo(a)anthracene	0.038	0.047	0.01	nd
Chrysene	0.037	0.035	0.01	0.005
Benzo(b)fluoranthene	0.03	0.03	0.006	nd
Benzo(k)fluoranthene	nd	0.029	0.004	nd
Benzo(a)pyrene	nd	nd	0.005	nd
WCOB100, mg/kWh				
Naphthalene	0.012	0.011	0.016	nd
Acenaphthylene	nd	nd	0.016	nd
Fluorene	nd	nd	0.009	nd
Phenanthrene	0.04	0.041	0.026	0.018
Anthracene	nd	nd	nd	nd
Fluoranthene	0.295	0.05	0.039	0.017
Pyrene	0.295	0.059	0.049	0.015
Benzo(a)anthracene	0.029	0.02	0.011	nd
Chrysene	0.04	0.021	0.01	0.006
Benzo(b)fluoranthene	0.017	nd	0.006	nd
Benzo(k)fluoranthene	0.009	nd	0.004	0.002
Benzo(a)pyrene	nd	nd	0.005	nd
FCO, mg/kWh				
Naphthalene	0.013	nd	0.034	0.018
Acenaphthylene	nd	nd	0.013	nd
Fluorene	nd	nd	0.003	nd
Phenanthrene	0.044	0.062	0.02	0.023
Anthracene	nd	nd	0.005	nd
Fluoranthene	0.21	0.056	0.026	0.014
Pyrene	0.207	0.055	0.043	0.018
Benzo(a)anthracene	0.024	0.027	0.014	0.005
Chrysene	0.032	0.029	0.016	nd

Benzo(b)fluoranthene	0.015	0.025	0.009	0.001
Benzo(k)fluoranthene	0.008	0.009	0.006	0.003
Benzo(a)pyrene	nd	nd	0.006	nd

Sandstroem-Dahl et al. (2012) [Fuel Impact on Exhaust Emissions - Comparison of Two Diesel Fuels, SAE Technical Paper] investigated the PAH emissions differences between Swedish Environmental Class 1 (EC1) and European EN590 diesel fuel. Tests were carried out on a chassis dynamometer over the Worldwide Harmonized Vehicle Cycle (WHVC) test cycle. The vehicle tested was a 2011 Volvo truck (FH 6*2) certified according to Euro V. The vehicle was equipped with SCR (Selective Catalytic Reduction) exhaust aftertreatment. The SCR system includes an SCR catalyst, oxidation catalyst and urea injection system.

The vehicle was tested according to the WHVC hot start test procedure. To ascertain comparable results, the vehicle was preconditioned prior to each test by driving on the chassis dynamometer until the engine oil reach a stabilized temperature of approximately 90 °C. The vehicle was then idling for two minutes in order to prepare and load necessary data parameters. Triplicate tests were performed for each fuel.

The particle associated compounds were collected on a large filter and the PAH in gaseous phase were collected in polyurethane foam (PUF) plugs. The filters and foam plugs were extracted and analyzed separately to distinguish between the different phases. The extracts were chemically characterized and different types of PAH could be identified. The filters used for collection of particulate emission samples (Pallflex T60A20) had a diameter of 240 mm diameter. Before sampling, the filters were washed with ethanol, acetone and dichloromethane and dried at 200 °C. A specially designed sampling device with polyurethane foam (PUF) plugs (50 mm height × 70 mm diameter, 60 PPI) was used for sampling the semivolatile compounds and was situated downstream from the particulate filter. The PUF plugs were washed ten at a time in a washing machine for one hour at 85 °C and then centrifuged to near dryness. The PUF and filter samples were extracted with pressurized fluid extraction using an accelerated solvent extraction system (ASE 200) (Dionex Corporation, Sunnyvale, CA, USA). The filter samples were extracted in 5 ml extraction cells with an ASE method recently developed and validated for analysis of PAHs in diesel particulate matter using standard reference materials from the US National Institute of Standards and Technology (NIST). Extractions were performed with a mixture of toluene and methanol (9:1; v/v) at elevated temperature and pressure (200 °C and 3000 psi). The extraction consisted of five 30 min extraction cycles. The analysis of PAHs was performed using a hyphenated High-Performance Liquid Chromatography- Gas Chromatography/Mass Spectrometry (HPLC-GC/MS) System. The HPLC system consisted of an autosampler (CMA/200 Microsampler; CMA Microdialysis AB, Sweden), a Varian 9012 Inert solvent delivery system (Varian Inc., Palo Alto, CA, USA), a UV detector (SPD-6A; Shimadzu, Japan) and a nitrophenylpropylsilica column (4.0 mm i.d. ×125 mm, 5 μm particle size; Phenomenex, Torrance, CA, USA). Isocratic separation was performed using hexane with 0.1% dodecane (v/v) as the mobile phase. The HPLC part was connected to a GC (6890N; Agilent Technologies, Palo Alto, CA, USA) through a fused silica capillary inserted into the Programmed Temperature Vaporizer injector (CIS-3; Gerstel, Germany), which was operated in the solvent vent mode. The GC separation was carried out on a DB-17MS capillary column (60 m × 0.25 mm i.d. with 0.15 μm film thickness; J & W Scientific, Folsom, CA, USA) equipped with a retention gap (5 m × 250 μm i.d., J&W Scientific). Mass selective detection was performed using a quadrupole mass spectrometer (MSD 5973N; Agilent Technologies) operated in the electron ionization (EI) mode.

Table 39: PAH emissions for both fuels divided between filter and semivolatile phase

PAH (pg/m)	Filter phase, averaged		Semivolatile phase	
	EC1	EN590	EC1	EN590
Phenanthrene	426	521	64	124
Anthracene	114	181	10	0
3-Methylphenathrene	103	194	31	39
2-Methylphenathrene	146	260	23	30
2-Methylphenthracene	29	180	0	0
9-Methylphenathrene	72	122	16	27
1-Methylphenathrene	83	145	13	23
Fluoranthene	238	308	30	31
Pyrene	302	394	35	21
Benzo(b)fluoranthene	186	310		
Benzo(k)fluoranthene	85	152		
Benzo(a)pyrene	227	391		
Dibenzo(a,l)pyrene	4	7		
Dibenzo(a,e)pyrene	5	12		
Dibenzo(a,i)pyrene	2	3		
Dibenzo(a,h)pyrene	1	1		
Sum PAH (pg/m)	2022	3178	222	295

Fanick and Kroll, (2018) [Polycyclic Aromatic Hydrocarbons in Diesel Engine Exhaust Both with and without Aftertreatment, SAE Technical Paper] investigated the effect of aftertreatment system from a modern technology engine on PAH emissions under transient conditions. Testing was made on a 2012 Ford 6.7 L diesel engine (engine family: CFMXH06.7A24) that was mounted in a transient capable test cell. This engine had a V-8-cylinder configuration rated for 224 kW (300 hp) at 2800 rpm. This engine was turbocharged with a stock aftertreatment configuration that included a DOC, DPF, and SCR catalyst in series. Emissions sampling for PAH was performed on the engine-out emissions (aftertreatment removed) and aftertreatment-out emissions to compare the SVOC in the exhaust. When the engine was operated with the aftertreatment removed, the exhaust backpressure was set to simulate the aftertreatment, and a breakout electronic control module was used to operate the engine in a similar manner as if the aftertreatment was in place.

The PAH samples were collected in a manner similar to the sampling of particulate matter in 40 CFR Part 1065 using a secondary dilution tunnel. The secondary dilution tunnel and flow volumes across the filters were increased to collect a much larger sample. The dilute exhaust sample was taken from the main dilution tunnel and further diluted with filtered ambient air through a high-efficiency particulate air (HEPA) filter. The dilute exhaust from the secondary dilution tunnel passed through a 203X254 mm filter for the particulate-phase PAH, and semi-volatile PAH were collected on four XAD-2 traps located after the filter. Zefluor™ filter media was used to collect the particulate-phase PAH, and cleaned XAD-2 resin was used to collect the semivolatile-phase PAH. Each XAD sample was comprised of five traps (four sample and one ambient background). In addition, a field blank was also analyzed with each set of traps for a given test day. Before testing, the XAD-2 sample media was cleaned with a multiple solvent extraction technique. Each trap holder was loaded with 100 g of XAD-2, and the traps were spiked with a two-component sampling surrogate (9-methylanthracene-d12 and 1,8-dimethylnaphthalened12) to establish if there were any losses during sample collection and provided sample recovery data. After sample collection, the XAD-2 samples were extracted with toluene/methylene chloride using a Soxhlet extraction technique. The samples were then concentrated and a clean-up step was used to remove sample interferences.

The analyses for PAH were separated on either a 30-meter Restek Rxi-5Sil MS analytical column, a 30-meter Phenomenex XLB analytical column, or a 30-meter Rxi-PAH analytical column. The Rxi-5Sil MS and Phenomenex XLB columns both had a 0.25 mm internal diameter and 0.25 μm film thickness. The Rxi-PAH analytical column had a 0.25 mm internal diameter and

0.1 µm film thickness. Samples were quantified using gas chromatography/mass spectrometry (GC/MS). The GC/MS systems were either an Agilent 7890 N gas chromatograph coupled to a 5975 inert MSD with a triple-axis detector or a 7890 N gas chromatograph coupled to a 5975 inert mass selective detector mass spectrometer (MS) system in Selected Ion Monitoring (SIM) mode. The molecular ion or characteristic ion of each compound and each deuterated compound from the internal standard were used to determine the sample concentrations.

Table 40: PAH emissions (ng/kW-hr) with and without aftertreatment

	Without Aftertreatment		With Aftertreatment	
Compound	Particulate Phase ng/kW-hr	Semi-Volatile Phase ng/kW-hr	Particulate Phase ng/kW-hr	Semi-Volatile Phase ng/kW-hr
Naphthalene	4.91	5.96	3.80	3.99
2-Methylnaphthalene	4.92	5.93	3.79	N/A
1-Methylnaphthalene	4.87	5.91	3.69	N/A
Biphenyl	4.84	5.85	3.64	N/A
Acenaphthylene	4.83	5.83	N/A	N/A
Acenaphthene	4.75	N/A	3.54	N/A
Fluorene	4.83	N/A	3.09	N/A
Phenanthrene	4.88	5.81	3.56	N/A
Anthracene	4.76	5.71	3.19	N/A
Fluoranthene	4.75	5.69	2.91	N/A
Pyrene	4.81	5.76	N/A	N/A
Benzo(a)anthracene	4.61	5.56	N/A	N/A
Chrysene	4.64	5.53	N/A	N/A
Benzo(b,j)fluoranthene	4.50	5.45	N/A	N/A
Benzo(k)fluoranthene	4.40	5.27	N/A	N/A
Benzo(e)pyrene	4.59	5.55	N/A	N/A
Benzo(a)pyrene	4.59	N/A	N/A	N/A
Perylene	4.37	5.31	N/A	N/A
Indeno(123-cd)pyrene	4.44	5.50	N/A	N/A
Benzo(ghi)perylene	4.66	5.65	N/A	N/A

Hu et al. (2013) [Emissions of polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs from heavy-duty diesel vehicles with DPF and SCR, Journal of the Air & Waste Management Association] assessed the effect of aftertreatment on total (gas and particle phase) PAH emissions and on particle-phase nitro-PAHs from four heavy-duty vehicles in seven configurations. These configurations refereed as Veh1-baseline, Veh1-DPF1, Veh1-DPF1+SCR1, Veh1-DPF1+SCR2, Veh2-DPF2, Veh3-DPF3, and Veh4-DPF4, respectively. Veh1 was a class 8 tractor with a 1998 Cummins M11 diesel engine (11 L), operated without an after-treatment device as the baseline vehicle. This vehicle was then tested in three configurations including with a continuously regenerating trap (CRT, DPF1), which consisted of a DOC followed by an uncatalyzed DPF; the same CRT in combination with a vanadium-based SCR (SCR1); and the same CRT in combination with a zeolite-based SCR (SCR2). Veh2 was a medium heavy-duty stake truck with a 2000 International DT466 (7.8 L) engine equipped with an Engelhard DPX filter (catalyzed filter, DPF2). Veh3 was a school bus with a 2003 Cummins Interact System B (ISB) engine (5.9 L), which was equipped with a Horizon electrically regenerated particle filter (DPF3). DPF3 consisted of an uncatalyzed silicon carbide substrate for PM control coupled with an electric heating element and a small blower for regeneration. Veh4 was an urban transit bus with a 2006 Cummins ISB engine (5.9 L) with Allison Parallel Drive electric hybrid drive train, equipped with catalyzed continuously regenerating technology (CCRT, DPF4).

Three driving cycles were selected: a steady-state cruise at 50 mph, the transient Urban Dynamometer Driving Schedule (UDDS) (40 CFR 86), and idle operation. The CVS was operated at a nominal flow rate of 73.6 m^3/min for the cruise and UDDS cases (except Veh2-DPF2, and Veh3-DPF3 and Veh4-DPF4 at UDDS cycles) or 45.3 m^3/min for the other testing, which provided nominal dilution factors from 9 (cruise) to 130 (idle).

A two-stage sampler consisting of two 70-mm Pallflex Teflon filters (front and back filter, respectively) and XAD adsorbents were used to collect samples during a single testing cycle for analysis of particle- and gas-phase PAHs, respectively. Accumulated samples over several testing cycles were also collected using a parallel secondary sampling system (identical to the primary two-stage sampler).

Prior to extraction, the following deuterated internal standards are added to each filter sample: 1-nitronaphthalene-d7, 2-nitrobiphenyl-d9, 1-nitrofluorene-d9, 9-nitroanthracene-d9, 3-nitrofluoranthene-d9, 1-nitropyrene-d9, 9-nitrochrysene-d11, 6-nitrobenzo[a]pyrene-d11. Filters are extracted with dichloromethane using the Dionex ASE300. All extracts are then concentrated by rotary evaporation at 35 °C under gentle vacuum to ~1 mL and filtered through 0.2 μm PTFE disposal filter devise (Whatman Pura discTM 25TF), rinsing the flask 3 times with 1 ml dichloromethane each time. The extracts are further precleaned by the solid-phase extraction technique, using Aminopropyl (NH2) SPE cartridges (Waters), with sequential elution with hexane/DCM, 98/2 v/v and hexane/DCM 80/20 v/v as described by Bamford et al. (2003). For nitro- and dinitro-PAH analysis, these fractions are combined and analyzed by negative ion chemical ionization (NICI) gas chromatography – mass spectrometry (GC/MS) Varian 1200 triple quadrupole gas chromatograph/mass spectrometer (GC/MS/MS) system with CP-8400 autosampler is used for these analyses. Negative chemical ionization (CI) offers a superior sensitivity for the analysis of nitro-PAH (approximately 100 times higher than EI or positive CI) The MDLs for nitro-PAHs are generally in the range of 0.5-1 pg/µl. The sample extracts are usually concentrated down to 100 µl for analysis; thus, the MDLs in ng/µl, are multiplied by 100 to obtain the MDLs in ng/sample (0.05 - 0.1 ng/sample).

Table 41: Particle-phase PAHs in mg/mile for the UDDS and Cruise, in mg/hr for idle operation

PAH mg/mile for cruise and UDDS mg/hr for idle	Vehicle 1									
	Baseline			DPF1		DPF1+SCR1			DPF1+SCR2	
	Cruise (n=3)	UDDS (n=4)	Idle (n=2)	Cruise (n=3)	UDDS (n=4)	Cruise (n=2)	UDDS (n=2)	Idle (n=2)	Cruise (n=2)	UDDS (n=2)
Naphthalene	bdl	bdl	bdl	bdl	bdl	bdl	2.7E-05	bdl	bdl	bdl
							3.8E-05			
2-Methylnaphthalene	bdl	6.8E-04	7.2E-02	bdl	bdl	bdl	bdl	bdl	bdl	bdl
		1.4E-03	*1.7E-02*							
1-Methylnaphthalene	bdl	2.9E-04	4.3E-02	bdl	bdl	bdl	8.3E-06	bdl	bdl	Bdl
		5.8E-04	*7.1E-03*				*1.2E-05*			
2,6-Dimethylnaphthalene	bdl	2.1E-04	2.9E-02	bdl	bdl	1.5E-05	3.4E-05	bdl	bdl	8.1E-06
		4.1E-04	*4.7E-04*			*2.1E-05*	*4.8E-05*			*1.1E-05*
Acenaphthylene	8.5E-05	8.5E-04	7.8E-03	bdl	bdl	2.3E-06	4.9E-06	7.1E-05	1.2E-06	bdl
	1.5E-06	*4.7E-05*	*3.4E-03*			*1.7E-06*	*3.3E-06*	*1.0E-04*	*1.7E-06*	
Acenaphthene	bdl	3.3E-05	2.5E-03	bdl	9.3E-06	1.1E-06	1.2E-06	5.9E-05	1.5E-06	bdl
		6.6E-05	*4.1E-05*		*1.6E-05*	*1.5E-06*	*1.7E-06*	*8.3E-05*	*2.1E-06*	
2,3,5-Trimethylnaphthalene	1.3E-05	3.9E-04	4.9E-02	bdl	bdl		bdl	bdl	bdl	bdl
	2.3E-05	*9.1E-05*	*1.6E-02*							
Fluorene	1.2E-04	1.3E-03	4.9E-02	bdl	bdl	1.2E-06	2.9E-06	1.1E-04	4.8E-06	1.9E-05
	9.0E-06	*9.8E-05*	*1.0E-02*			*1.7E-06*	*4.1E-06*	*1.6E-04*	*1.5E-06*	*1.8E-05*
Phenanthrene	1.7E-03	1.2E-02	1.7E-01	bdl	bdl		6.6E-06	1.7E-03	1.2E-05	4.5E-05
	3.3E-04	*7.7E-04*	*8.3E-02*				*9.3E-06*	*2.4E-03*	*3.9E-06*	*4.1E-05*
Anthracene	5.6E-04	3.9E-03	1.8E-02	bdl	bdl		bdl	bdl	bdl	4.6E-06
	4.1E-05	*2.7E-04*	*4.6E-03*							*6.6E-06*
1-Methylphenanthrene	1.3E-03	8.5E-03	3.3E-01	bdl	bdl	1.6E-06	1.3E-05	bdl	bdl	bdl
	7.2E-05	*2.4E-03*	*9.5E-02*			*2.3E-06*	*1.9E-05*			
Fluoranthene	5.3E-03	2.5E-02	2.2E-01	2.6E-06	1.3E-05	2.5E-06	1.5E-05	3.1E-04	8.8E-06	6.7E-05
	4.7E-05	*7.2E-03*	*1.1E-01*	*2.4E-06*	*1.2E-05*	*1.2E-06*	*8.2E-06*	*1.1E-04*	*6.3E-06*	*6.8E-05*
Pyrene	1.5E-02	8.1E-02	9.5E-01	bdl	1.4E-05	2.4E-06	1.6E-05	2.5E-04	7.7E-06	5.4E-05
	1.9E-04	*1.9E-02*	*3.8E-01*		*1.2E-05*	*9.4E-07*	*8.8E-06*	*1.0E-04*	*5.4E-06*	*5.4E-05*
Benz[a]anthracene	3.8E-03	2.5E-02	9.8E-02	1.3E-06	bdl	4.6E-07	8.6E-07	bdl	2.8E-06	9.5E-07
	3.6E-04	*6.6E-03*	*6.0E-02*	*2.2E-06*		*6.5E-07*	*1.2E-06*		*7.2E-08*	*1.3E-06*
Chrysene	3.4E-03	2.2E-02	8.9E-02	4.8E-06	1.7E-05	7.0E-07	1.9E-06	bdl	6.7E-06	5.8E-06
	3.4E-04	*5.4E-03*	*5.5E-02*	*5.1E-07*	*1.6E-06*	*9.9E-07*	*2.7E-06*		*9.5E-07*	*1.1E-06*
Benzo[b]fluoranthene	3.3E-03	2.8E-02	1.1E-01	2.2E-06	bdl	6.7E-07	2.4E-06	4.2E-05	3.4E-06	9.9E-07
	2.5E-04	*6.7E-03*	*7.5E-02*	*1.9E-06*		*9.5E-07*	*1.4E-06*	*5.9E-05*	*4.9E-07*	*1.4E-06*
Benzo[k]fluoranthene	7.9E-04	8.7E-03	3.5E-02	bdl	bdl	bdl	bdl	bdl	bdl	bdl
	1.9E-04	*2.3E-03*	*2.4E-02*							
Benzo[e]pyrene	2.0E-03	1.4E-02	3.9E-02	bdl	bdl	4.7E-07	bdl	bdl	1.0E-06	bdl
	2.4E-04	*2.1E-03*	*2.5E-02*			*6.6E-07*			*1.4E-06*	
Benzo[a]pyrene	2.2E-03	2.3E-02	1.2E-01	bdl	bdl	bdl	bdl	3.9E-05	bdl	bdl
	5.0E-04	*6.7E-03*	*8.5E-02*					*5.5E-05*		
Perylene	3.7E-04	3.8E-03	1.7E-02	bdl	bdl	bdl	bdl	bdl	bdl	bdl
	5.3E-05	*7.0E-04*	*1.2E-02*							
Indeno[1,2,3-cd]pyrene	8.1E-04	9.3E-03	8.6E-02	bdl	bdl	bdl	bdl	7.7E-05	bdl	bdl
	2.4E-04	*5.3E-03*	*5.5E-02*					*1.1E-04*		
Dibenz[a,h]anthracene	1.9E-04	1.7E-03	1.3E-02	bdl	bdl	bdl	bdl	bdl	bdl	bdl
	4.2E-05	*5.1E-04*	*1.0E-02*							
Benzo[ghi]perylene	1.8E-03	1.5E-02	8.8E-02	bdl	bdl	4.1E-07	1.9E-06	8.3E-05	1.6E-06	8.3E-07
	4.0E-04	*5.9E-03*	*5.6E-02*			*5.8E-07*	*2.7E-06*	*1.2E-04*	*4.0E-07*	*1.2E-06*
Total PAHs	4.2E-02	2.9E-01	2.6E+00	1.1E-05	5.3E-05	2.9E-05	1.4E-04	2.7E-03	5.2E-05	2.1E-04

Bdl: below detection limit; value in *Italics* is one standard deviation

Table 42: Particle-phase PAHs in mg/mile for the UDDS and Cruise, in mg/hr for idle operation

PAH mg/mile for cruise and UDDS mg/hr for idle	Vehicle 2			Vehicle 3			Vehicle 4
	DPF2			DPF3			DPF4
	Cruise (n=2)	UDDS (n=2)	Idle (n=2)	Cruise (n=2)	UDDS (n=2)	Idle (n=2)	UDDS (n=3)
Naphthalene	bdl	bdl	1.7E-03	bdl	bdl	bdl	bdl
			2.4E-03				
2-Methylnaphthalene	bdl	bdl		bdl	bdl	bdl	bdl
1-Methylnaphthalene	bdl	bdl	4.2E-04	bdl	bdl	bdl	bdl
			5.9E-04				
2,6-Dimethylnaphthalene	5.0E-06	1.1E-05	3.4E-04	bdl	1.7E-05	4.4E-04	1.9E-05
	2.2E-06	*1.5E-05*	*4.8E-04*		*2.4E-05*	*6.2E-04*	*2.6E-05*
Acenaphthylene	bdl	bdl	9.6E-05	bdl	bdl	bdl	bdl
			1.4E-04				
Acenaphthene	bdl	2.9E-06	7.4E-05	bdl	3.7E-06	bdl	2.9E-06
		1.2E-06	*2.1E-05*		*2.2E-06*		*4.1E-06*
2,3,5-Trimethylnaphthalene	bdl	bdl	bdl	bdl	bdl	bdl	Bdl
Fluorene	1.9E-06	6.0E-06	2.6E-04	bdl	3.7E-06	bdl	4.6E-06
	9.5E-07	*2.7E-06*	*9.4E-05*		*5.3E-06*		*6.5E-06*
Phenanthrene	8.0E-06	bdl	bdl	bdl	bdl	bdl	bdl
	1.1E-05						
Anthracene	bdl	bdl	4.9E-05	1.2E-06	1.5E-06	bdl	bdl
			6.9E-05	*1.2E-07*	*2.1E-06*		
1-Methylphenanthrene	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Fluoranthene	1.3E-06	8.1E-06	1.3E-04	1.2E-06	7.2E-06	8.7E-05	1.8E-05
	1.3E-07	*3.7E-06*	*8.6E-05*	*1.6E-06*	*4.8E-06*	*5.4E-05*	*5.8E-06*
Pyrene	9.3E-07	7.2E-06	8.2E-05	1.6E-06	6.4E-06	7.1E-05	1.7E-05
	2.0E-07	*3.1E-06*	*4.4E-05*	*1.3E-06*	*7.6E-08*	*3.5E-05*	*5.6E-06*
Benz[a]anthracene	bdl	bdl	bdl	4.3E-06	1.1E-05	bdl	3.5E-06
				2.1E-06	*9.2E-06*		*1.9E-06*
Chrysene	1.9E-06	3.4E-06	9.8E-05	1.1E-06	1.1E-05	8.3E-05	8.5E-06
	2.4E-07	*2.7E-07*	*7.6E-05*	*3.5E-07*	*1.1E-05*	*3.0E-06*	*3.5E-06*
Benzo[b]fluoranthene	1.1E-06	bdl	bdl	2.3E-06	4.8E-06	bdl	9.1E-07
	9.6E-08			*4.0E-07*	*1.2E-06*		*1.3E-06*
Benzo[k]fluoranthene	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Benzo[e]pyrene	2.9E-07	bdl	bdl	1.2E-06	2.4E-06	bdl	bdl
	4.1E-07			*1.9E-07*	*3.1E-07*		
Benzo[a]pyrene	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Perylene	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Indeno[1,2,3-cd]pyrene	bdl	bdl	bdl	2.7E-07	bdl	bdl	bdl
				3.8E-07			
Dibenz[a,h]anthracene	bdl	bdl	bdl	2.9E-07	bdl	bdl	bdl
				4.0E-07			
Benzo[ghi]perylene	bdl	bdl	bdl	5.7E-07	3.9E-07	bdl	bdl
				1.8E-07	*5.6E-07*		
Total PAHs	2.0E-05	3.8E-05	3.2E-03	1.4E-05	6.9E-05	6.8E-04	7.4E-05

Bdl: below detection limit; value in *Italics* is one standard deviation

Table 43: Summary of gas-phase PAHs emissions in mg/mile for the Cruise cycle

PAH Components	**Veh1**				**Veh2**	**Veh3**
	Baseline	**DPF1**	**DPF1+SCR1**	**DPF1+SCR2**	**DPF2**	**DPF3**
mg/mile	**Cruise**	**Cruise**	**Cruise**	**Cruise**	**Cruise**	**Cruise**
Naphthalene	4.7E-01	3.5E-02	6.9E-02	bdl	1.1E-02	1.6E-01
2-Methylnaphthalene	4.5E-01	3.9E-03	1.8E-03	2.0E-04	1.2E-03	8.6E-02
1-Methylnaphthalene	3.4E-01	2.0E-03	1.4E-03	1.2E-04	6.6E-04	5.1E-02
2,6-Dimethylnaphthalene	1.9E-01	1.8E-03	1.2E-03	1.1E-04	4.4E-04	1.3E-02
Acenaphthylene	1.0E-01	bdl	bdl	bdl	bdl	5.0E-03
2,3,5-Trimethylnaphthalene	1.5E-01	2.9E-04	3.0E-04	5.5E-05	5.3E-05	2.1E-03
Fluorene	6.9E-02	5.3E-04	9.3E-05	3.3E-05	1.7E-04	2.5E-03
Phenanthrene	1.3E-01	1.2E-03	3.9E-04	1.4E-04	4.5E-04	1.5E-02
Anthracene	2.4E-02	3.0E-05	1.2E-04	bdl	bdl	5.2E-04
1-Methylphenanthrene	2.7E-02	2.4E-04	3.2E-04	2.8E-05	2.8E-04	3.6E-04
Fluoranthene	1.5E-02	1.1E-04	bdl	bdl	3.8E-05	9.8E-04
Pyrene	2.4E-02	1.2E-06	bdl	7.7E-06	7.2E-05	5.1E-04

Bdl: below detection limit

Table 44: Summary of gas-phase PAHs emissions in mg/mile for the UDDS

PAH Components	**Veh1**				**Veh2**	**Veh3**	**Veh4**
(mg/mile)	**Baseline**	**DPF1**	**DPF1+SCR1**	**DPF1+SCR2**	**DPF2**	**DPF3**	**DPF4**
	UDDS	**UDDS**	**UDDS**	**UDDS**	**UDDS**	**UDDS**	**UDDS**
Naphthalene	2.9E+00	2.0E-01	3.8E-02	2.7E-02	1.2E-01	4.7E-01	2.0E-02
	3.5E-01	*na*	*3.6E-02*	*6.6E-03*	*2.1E-03*	*1.7E-01*	*9.9E-03*
2-Methylnaphthalene	3.0E+00	7.0E-02	1.1E-02	1.4E-02	9.2E-02	1.1E-01	1.6E-04
	3.6E-02	*na*	*1.8E-02*	*5.9E-03*	*3.2E-02*	*5.9E-02*	*2.0E-03*
1-Methylnaphthalene	2.2E+00	4.1E-02	6.7E-03	7.4E-03	3.2E-02	7.8E-02	2.5E-04
	1.2E-01	*na*	*1.0E-02*	*2.6E-03*	*1.2E-02*	*4.0E-02*	*1.0E-03*
2,6-Dimethylnaphthalene	1.2E+00	1.1E-02	2.1E-03	2.4E-03	1.2E-02	1.6E-02	5.7E-04
	4.7E-01	*na*	*2.8E-03*	*1.1E-03*	*6.6E-03*	*5.4E-03*	*4.2E-04*
Acenaphthylene	8.1E-01	bdl	4.1E-03	5.6E-04	bdl	7.4E-03	bdl
	6.0E-02	*na*	*4.5E-03*	*4.5E-04*		*1.4E-03*	
2,3,5-Trimethylnaphthalene	1.0E+00	2.5E-03	7.4E-04	9.2E-04	3.6E-04	2.4E-03	1.4E-04
	1.2E-01	*na*	*8.5E-04*	*3.5E-04*	*3.7E-04*	*8.1E-04*	*1.0E-04*
Fluorene	4.6E-01	3.8E-03	1.9E-04	1.2E-03	2.2E-03	2.5E-03	4.4E-04
	8.9E-02	*na*	*6.9E-04*	*9.2E-05*	*2.0E-03*	*5.2E-04*	*3.5E-04*
Phenanthrene	7.9E-01	1.6E-02	4.5E-04	1.8E-03	2.9E-03	2.9E-02	1.3E-03
	1.3E-01	*na*	*4.8E-04*	*9.7E-04*	*2.9E-03*	*2.4E-03*	*5.7E-04*

Anthracene	1.5E-01	bdl	8.3E-05	1.2E-05	bdl	1.1E-03	7.1E-05
	4.3E-02	*na*		*6.2E-06*		*1.6E-04*	*1.8E-05*
1-Methylphenanthrene	2.0E-01	1.1E-03	bdl	2.0E-04	4.3E-04	2.2E-04	1.8E-04
	3.5E-02	*na*		*4.3E-05*	*3.3E-04*	*1.3E-05*	*1.1E-04*
Fluoranthene	9.3E-02	1.1E-03	bdl	bdl	bdl	1.4E-03	1.2E-04
	3.0E-02	*na*				*6.7E-05*	*1.5E-04*
Pyrene	1.6E-01	bdl	bdl	1.1E-04	3.8E-05	6.4E-04	1.6E-04
	5.9E-02	*na*		*1.7E-06*	*4.7E-06*	*8.2E-05*	*8.5E-05*

Bdl: below detection limit; value in *Italics* is one standard deviation

Table 45: Summary of gas-phase PAHs emissions in mg/hr for the idle operation

PAH Components	**Veh1**		**Veh2**	**Veh3**
	Baseline	**DPF1+SCR1**	**DPF2**	**DPF3**
mg/hr	**Idle**	**Idle**	**Idle**	**Idle**
Naphthalene	2.9E+01	1.7E+01	9.2E+00	6.8E-01
2-Methylnaphthalene	5.6E+01	bdl	9.3E+00	7.0E-01
1-Methylnaphthalene	3.8E+01	bdl	4.4E+00	5.9E-01
2,6-Dimethylnaphthalene	1.9E+01	bdl	9.9E-01	3.3E-01
Acenaphthylene	7.8E+00	1.1E-03	1.8E-01	bdl
2,3,5-Trimethylnaphthalene	1.9E+01	bdl	8.4E-02	3.6E-02
Fluorene	6.5E+00	6.7E-04	2.1E-01	3.4E-02
Phenanthrene	6.8E+00	1.4E-03	1.1E-01	1.4E-02
Anthracene	1.0E+00	bdl	bdl	2.1E-03
1-Methylphenanthrene	1.9E+00	bdl	7.9E-03	bdl
Fluoranthene	2.2E-01	bdl	1.3E-04	1.3E-03
Pyrene	6.1E-01	bdl	1.0E-03	bdl

Bdl: below detection limit

Table 46: Selected particle-phase nitro-PAHs, expressed in ng/mile, during steady-state highway cruise cycle

ng/mile	**Baseline**	**DPF1+SCR1**	**DPF1+SCR2**	**DPF2**	**DPF3**
1-nitropyrene	131.286	0.025	0.030	11.000	6.100
3-nitrophenanthrene	0.144	0.000	0.010	0.363	0.427
9-nitrophenanthrene	0.000	0.000	0.566	1.516	0.000

An early study by **Rogge et al. (1993)** [Sources of Fine Organic Aerosol. 2. Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks, Environ. Sci. Technol.] measured PAH emissions from light-duty vehicles and diesel trucks that were in use in the Los Angeles area.

The reason this older study made the list of papers suitable for the literature review, was to provide perspective and historical data on the PAH emissions evolution between the early 90's and today's more advanced and cleaner engines.

The authors used six vehicles without catalytic converters, seven catalyst-equipped vehicles, and two heavy-duty diesel trucks. The passenger cars were tested over the FTP cycle, while the diesel trucks were tested over a drive cycle including idle modes, constant driving speed at 40 and 70 km/h, plus abrupt acceleration and deceleration modes.

Table 47: Emissions from noncatalyst and catalyst vehicles and from heavy-duty diesel

	Noncatalyst	Catalyst	Heavy Duty Diesel Trucks
Polycyclic Aromatic Hydrocarbons			
phenanthrene	17.3	0.88	12.2
anthracene	5.1	0.11	1.6
methylphenanthrenes-anthracenes	42.2	1.9	31.3
dimethylphenanthrenes-anthracenes	75.5	3.0	56.9
fluoranthene	48.3	2.0	13.0
pyrene	31.0	2.5	22.6
benzacenaphthylene	16.5	0.77	2.9
2-phenylnaphthalene	11.9	0.57	3.5
2-benzylnaphthalene	4.3	0.72	nd
methylfluoranthenes-pyrenes	106.9	4.2	12.8
benzo[a]fluorene/benzo[b]fluorene	31	0.72	1.9
benzo[ghi]fluoranthene	24.7	1.3	6.9
cyclopenta[cd]pyrene	49.3	1.7	1.4
benzo[a]anthracene	73.8	1.9	3.6
chrysene/triphenylene	55.8	3.8	9.9
methylbenz[o]anthracenes,-chrysenes,-triphenylenes	143.5	3.4	2.7
dimethylfluoranthenes,-pyrenes	161.1	4.1	14.6
benzo[fe]fluoranthene	40.7	2.0	2.7
benzo[b]fluoranthene	37.9	2.9	2.9
benzo[j]fluoranthene	6.0	0.54	nd
benzo[e]pyrene	45.8	2.0	2.6
benzo[a]pyrene	43.5	1.9	1.3
perylene	14.0	0.60	1.0
methylbenzofluoranthenes,-benzopyrenes,-perylenes	6.4	0.47	nd

indeno[l,2,3-cd]pyrene	6.4	0.47	nd
indeno[1,2,3-cd]fluoranthene	32.6	1.7	nd
benzo[g/u]perylene	145.4	4.7	1.6
anthanthrene	9.4	0.08	nd
benzo[b]triphenylene	4.0	0.09	nd
dibenzo[o,h]anthracene	8.3	0.33	nd
benzo[b]chrysene	2.3	0.02	nd
coronene	104.6	1.1	nd
total class emission rate	1405.5	52.47	209.9
Polycyclic Aromatic Carboxaldehydes			
1-naphthalenecarboxaldehyde(1-formylnaphthalene)	13.5	5.5	nd
2-naphthalenecarboxaldehyde(2-formylnaphthalene)	68.0	22.2	nd
total class emission rate	81.5	27.7	
Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ)			
9Ãf-fluoren-9-one (fluorenone)	113.4	24.3	65.0
2-methylfluoren-9-one	9.7	1.9	17.2
9,10-phenanthrenedione(phenanthrenequinone)	31.6	3.8	63.1
9,10-anthracenedione(anthraquinone)	24.3	4.4	23.5
phenanthrone/enthrone	19.4	2.8	20.9
9H-xanthen-9-one(xanthone)	29.4	2.6	2.7
4-cyclopenta[de/]phenanthren-4-one	7.9	1.0	5.1
lH-benz[de]anthracen-1-one	26.3	1.2	2.7
7fi-benz[de]anthracen-7-one	27.9	1.3	5.6
6H-benzo[cd]pyren-6-one (benzo[cd]pyrenone)	20.0	0.78	1.2
total class emission rate	309.9	44.08	207.0

Okamoto et al. (2006) [Unregulated Emissions from Compressed Natural Gas (CNG) Transit Buses Configured with and without Oxidation Catalyst, Environ. Sci. Technol.] measured the PAH emissions from CNG-powered heavy-duty vehicles using a chassis dynamometer. A 2001 Cummins Westport C Gas Plus 8.3-L bus (CWest) was tested, which met the 2002 California Air Resources Board (CARB) optional NOx standard (2.0 g/bhp-hr). This was a lean-burn, spark-ignited, 6-cylinder, turbocharged engine with a compression ratio of 10:1 and electronic engine management with full control of air/fuel handling. The second engine was a 2000 New Flyer 40-passenger low-floor bus powered by a DDCs50G engine with and without an OxiCat. The

DDCs50G engine was an 8.5-L, 4-cylinder, turbocharged engine with closed loop fuel control, electronic spark ignition, and a compression ratio of 10:1. Emissions testing was conducted at the CARB Heavy-Duty Emissions Testing Laboratory (HDETL) using the CBD test cycle and a steady-state (SS) 55-mph cruise condition. Test sequences were composed of multiple individual cycles run consecutively to ensure collection of sufficient samples for subsequent chemical analyses. The SS test cycle sequences were approximately 30 min long to coincide with the approximate duration of three consecutive CBD cycles.

The filters used for collecting PAH samples were standard 70-mm Teflon-coated glass fiber filters (T60A20, Pall-Gelman, Ann Arbor, MI). PAH samples were collected from a secondary dilution tunnel using two filters in series, followed by polyurethane foam (PUF) and XAD-4. PAH samples were collected at a nominal flow rate of ap proximately 3.5 standard cubic feet per minute (scfm).

Internal deuterated standards were added directly onto the filters before extraction and the filters were extracted with DCM three times by sonication (Bransonic model 5210R, Branson Ultrasonics Corp., Danbury, CT) for 15 min each time. Each filter extract was further purified by silica gel chromatography. The hexane/DCM (9:2) fraction was collected for PAH analysis and concentrated to approximately 50 μL. PUF samples were extracted using acetone. XAD samples were transferred to separatory funnels and extracted four times with DCM. The XAD extracts were filtered and concentrated to 1 mL. The sample extracts were analyzed for PAHs using a Hewlett-Packard model 5890 Series II gas chromatograph interfaced to a HP 5972 mass selective detector. The GC was equipped with a 30 m × 0.25 mm i.d. DB-5MS fused silica capillary column (0.25-μm film thickness; Agilent Technologies; Palo Alto, CA).

Table 48: Emission rates of PM-associated PAHs (µg/mi) from CNG transit buses configured with and without oxidation catalyst

	CBD test cycle			SS test cycle		
PAH	DDC w/oOxiCat	DDC wOxiCat	CWest wOxiCat	DDC w/oOxiCat	DDC wOxiCat	CWest wOxiCat
naphthalene	77	29	36	49	7.5	6.6
2-methyl naphthalene	18	7.2	7.3	10	1.9	1.7
1-methyl naphthalene	9.6	3.8	3.8	5.5	1.0	0.84
biphenyl	3.4	2.2	1.7	1.5	0.65	0.40
2,6-dimethyl naphthalene	3.3	2.4	2.1	0.88	0.61	0.54
acenaphthylene	2.8	0.97	0.96	1.0	0.28	0.36
acenaphthene	1.4	1.2	0.75	0.51	0.26	0.057
2,3,5-trimethyl naphthalene	1.7	1.6	0.97	0.70	0.46	0.29
fluorene	2.1	1.5	1.2	0.91	0.40	0.21
phenanthrene	7.4	5.2	6.0	4.0	2.0	2.1
anthracene	0.32	0.17	0.21	0.48	ND	0.10
1-methyl phenanthrene	1.5	1.9	2.1	0.92	0.89	0.76
fluoranthene	3.7	3.5	2.3	2.2	1.4	1.7
pyrene	7.4	5.6	4.3	4.4	2.6	3.2
total PAH mw 128-202	141	67	70	82	20	19
benzo[a]anthracene	0.13	0.11	0.17	0.071	0.042	0.027
chrysene	0.20	0.13	0.36	0.16	0.094	0.025
benzo[b]fluoranthene	0.12	ND	0.14	0.035	0.032	0.029
benzo[k]fluoranthene	ND	ND	ND	0.024	ND	ND
benzo[e]pyrene	0.074	0.064	0.094	0.028	ND	0.017
benzo[a]pyrene	ND	ND	ND	ND	ND	ND
perylene	ND	ND	ND	ND	ND	ND
indeno(1,2,3-cd)pyrene	0.13	0.13	ND	0.013	ND	0.031
dibenzo(a,h)anthracene	ND	ND	ND	ND	ND	ND

benzo(g,h,i)perylene	0.12	0.10	0.12	0.031	0.02	0.028
total PAH mw 228-278	0.77	0.53	0.87	0.37	0.18	0.16

Shah et al. (2005) [On-Road Emission Rates of PAH and n-Alkane Compounds from Heavy-Duty Diesel Vehicles, Environ. Sci. Technol.] characterized the mass emission rates of PAHs from nine heavy-duty diesel (HDD) engines as they were operated on the road. Testing was performed on on-road with the vehicle following the speed trace of the ARB Four Phase HDDT Cycle. This cycle consists of four phases simulating four distinct operating conditions: Cold-Start/Idle, Creep, Transient, and Cruise.

PM samples for chemical analysis were collected on Pall Gelman (Ann Arbor, MI) 47 mm Tissuequartz fiber filters. Prior to sampling, filters were cleaned by baking in a furnace oven at 600 °C for 5 h. Sorbent cartridges consisting of XAD-4 resin in a glass tube, sandwiched by 1.5" polyurethane foam plugs were used to collect SVOC samples. Polyurethane foam plugs, obtained from URG (Chapel Hill, NC), were cleaned by triple sonication in a mixture of hexane, acetonitrile, and methylene chloride (50:30:20) and dried in a vacuum oven. Supelco (Bellefonte, PA) XAD-4 resin was cleaned by methylene chloride extraction in a Dionex (Sunnyvale, CA) Automated Solvent Extractor (ASE 200). Prior to extraction, collected sample media were spiked with an internal recovery standard consisting of several deuterated species (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12, hexadecane-d34, and tetracosane-d50). Samples were solvent extracted in methylene chloride using the ASE 200.

Extracted samples were concentrated to a volume of approximately 5 mL through rotary evaporation using a Buchi Roto-Evaporator. Samples were further concentrated to a volume of 1.5

mL through gentle blowing with purified nitrogen. Extracted, concentrated samples were transferred to amber autoinjector vials for injection into an Agilent 6890N GC equipped with a 5973N MS detector. The GC-MS is equipped with a 0.32 mm i.d., 60 m DB-5ms column, and an Agilent Programmable Temperature Vaporizer (PTV) inlet. The PTV inlet allows for the introduction of a large volume of sample through successive sample injections. Aliquots of sample are injected onto a cooled inlet liner at 35 °C (∼100 °C below the lowest boiling point of our compounds of interest), and excess solvent is evaporated in helium. In our current configuration, three successive injections of 20 μL each are made onto a deactivated single baffle liner. This yields a total injection volume of 60 μL, far above the traditional injection volume of 1−2 μL used in most other systems.

After sample injection, the PTV inlet temperature is ramped to 325 °C at a rate of 720 °C min-1, while the GC oven temperature is maintained at 38 °C. This transfers the entire sample from the inlet liner onto the front of the column. The GC-MS was operated with a temperature profile of the following: hold 5 min at 38 °C, 10 °C min-1 to 180 °C, 6 °C min-1 to 230 °C, 3 °C min-1 to 325 °C, hold 5 min. Column pressure was initially held at 10 psi for 10 min. Following this, the pressure was ramped at a rate of 0.20 psi min-1 to 18 psi and held constant until analysis was complete. The MS was operated in scan mode with an 18 min solvent delay. Quantification was performed using a five-point calibration and target ion extraction. The entire method of analysis is based on a modified version of those outlined in EPA Method TO-13A guidelines

Table 49: PAH emission rates for the 1997 DDC Series 60 engine

	1997 DDC Series 60			
PAH	Idle (ug /min)	Creep (ug/mi)	Transient (ug/mi)	Cruise (ug/mi)
Naphthalene	34400±5600	2530000±995000	1370000±700000	181±6.57
Acenaphthylene	17.1±3.45	560±145	164±4.24	5.55±0.252
Acenaphthene	99.9±51.8	3370±972	1810±18.2	12.9±0.889
Fluorene	104±70.7	3540±1689	1810±126	5.79±0.668
Phenanthrene	22±11.6	584±140	248±31.4	31.4±0.49
Anthracene	29.6±12.7	623±363	245±2.63	2.63±0.199
Fluoranthene	4.16±0.659	104±25	53.2±18.4	7.77±1.6
Pyrene	6.95±3.11	184±70.5	81.1±7.73	18.8±6.49
Benz(a)anthracene	1±0.705	9.42±1.1	1.41±0.448	0.659±0.355
Chrysene	0.995±0.532	3.95±0.837	0.966±0.048	0.346±0.158
Benzo(b)fluoranthene	1.24±0.603	5.51±1.5	1.58±0.226	0.422±0.243
Benzo(k)fluoranthene	1.18±0.739	5.35±1.77	0.834±0.083	0.16±0.043
Benzo(a)pyrene	0.681±0.498	13.7±2.64	0.354±0.148	0.241±0.075
Indeno[1,2,3-cd]pyrene	0.977±0.409	1.95±0.301	BDL	0.247±0.117
Dibenzo[a,h]anthracene	1.4±0.915	2.21±0.486	BDL	0.266±0.18
Benzo[ghi]perylene	0.267±0.087	2.54±0.056	BDL	BDL

Table 50: PAH emission rates for the 1997 Cummins N14 engine

	1997 Cummins N14			
PAH	Idle (ug /min)	Creep (ug/mi)	Transient (ug/mi)	Cruise (ug/mi)
Naphthalene	435±117	33900±8950	18200±1670	1230±133
Acenaphthylene	4.22±1.42	1120±82.9	390±91.7	14.8±5
Acenaphthene	4.39±1.69	1020±101	900±303	12.3±1.92
Fluorene	5.7±2.21	951±377	1200±646	288±135
Phenanthrene	5.87±1.96	11300±5110	7920±814	67.2±35.1
Anthracene	3.98±1.3	431±163	188±10.9	9.71±6.79
Fluoranthene	1.23±0.16	1360±301	836±52	17.1±7.44
Pyrene	2.03±0.66	1650±752	1040±108	62±11.5
Benz(a)anthracene	0.319±0.124	39.6±11.3	8.98±4.93	2.01±0.405
Chrysene	0.275±0.102	47.9±13.6	9.72±3.89	2.8±1.15
Benzo(b)fluoranthene	0.405±0.211	34±17.5	3.14±1.68	2.3±1.1

Benzo(k)fluoranthene	0.189±0.128	43.4±18.6	5.43±0.82	3.45±0.942
Benzo(a)pyrene	0.619±0.068	57.2±24.8	7.17±3.45	5.02±1.12
Indeno[1,2,3-cd]pyrene	0.743±0.132	162±58.2	32.5±11.6	18.2±9.81
Dibenzo[a,h]anthracene	0.963±0.096	172±37.5	23.8±11.5	19.1±12.8
Benzo[ghi]perylene	BDL	207±64.8	19.7±5.64	21.6±15.6

Table 51: PAH emission rates for the 1998 DDC Series 60 engine

	1998 DDC Series 60			
PAH	Idle (ug /min)	Creep (ug/mi)	Transient (ug/mi)	Cruise (ug/mi)
Naphthalene	1100±73.1	13600±7870	12300±2380	2060±607
Acenaphthylene	81.7±22.2	908±245	438±77.4	98.4±44.8
Acenaphthene	26.5±6.50	316±155	232±27.5	28.7±4.13
Fluorene	186±46.1	1640±1100	631±117	105±27.2
Phenanthrene	353±133	2510±1380	1420±391	256±83.5
Anthracene	5.95±2.97	67.6±2.87	20.1±0.85	1.34±0.242
Fluoranthene	8.67±5.69	146±66.6	59.9±23.4	23.8±10.8
Pyrene	23.2±10.8	354±211	144±50.5	31.3±11.1
Benz(a)anthracene	0.808±0.243	15.0±8.63	8.62±0.62	0.706±0.380
Chrysene	1.26±0.62	16.0±9.60	7.06±0.22	0.623±0.469
Benzo(b)fluoranthene	0.458±0.135	9.85±5.84	6.52±0.32	0.265±0.119
Benzo(k)fluoranthene	0.0845±0.0417	3.70±1.71	2.70±0.12	0.198±0.0580
Benzo(a)pyrene	0.238±0.0853	6.81±2.41	4.06±1.74	0.157±0.105
Indeno[1,2,3-cd]pyrene	0.409±0.272	5.64±1.35	0.741±0.277	0.0598±0.0375
Dibenzo[a,h]anthracene	0.394±0.208	7.25±2.19	0.851±0.489	0.0444±0.0291
Benzo[ghi]perylene	0.352±0.128	4.74±2.82	0.571±0.311	0.0204±0.0116

Table 52: PAH emission rates for the 1998 DDC Series engine

	1998 DDC Series 60		
PAH	Idle (ug /min)	Transient (ug/mi)	Cruise (ug/mi)
Naphthalene	11700±537	184000±10900	33700±1040
Acenaphthylene	13.2±3.58	92.5±68.7	39.4±2.98
Acenaphthene	74.6±2.11	638±343	195±3.36
Fluorene	217±24	1420±667	577±19.9
Phenanthrene	687±57.1	5010±1420	1750±32.2
Anthracene	38.9±6.05	593±86.4	97.3±9.97
Fluoranthene	17.5±1.14	163±127	841±392

Pyrene	37.9±5.05	326±244	101±7.99
Benz(a)anthracene	0.941±0.206	14.1±0.378	2.81±0.117
Chrysene	1.11±0.357	14.2±0.41	2.95±0.279
Benzo(b)fluoranthene	0.0856±0.0553	0.59±	0.228±0.0271
Benzo(k)fluoranthene	0.0507±0.0161	0.56±0.357	0.0766±0.0367
Benzo(a)pyrene	0.0783±0.0438	BDL	0.0461±0.0051
Indeno[1,2,3-cd]pyrene	0.0891±0.0561	BDL	0.0548±0.016
Dibenzo[a,h]anthracene	0.313±0.232	1.51±0.691	0.116±0.0298
Benzo[ghi]perylene	0.196±0.109	BDL±0.0569	0.0569±0.0329

Table 53: PAH emission rates for the 1998 DDC Series engine

	1998 DDC Series 60			
PAH	Idle (ug /min)	Creep (ug/mi)	Transient (ug/mi)	Cruise (ug/mi)
Naphthalene	2030±757	28900±6094	45700±89.4	12200±176
Acenaphthylene	15.3±6.22	343±16.3	150±2.42	31.5±3.02
Acenaphthene	25.8±11.4	140±19.1	52.6±1.08	13.4±5.32
Fluorene	184±94.3	1400±184	994±5.82	420±82.9
Phenanthrene	991±437	6290±877	5620±401	1870±302
Anthracene	48.4±8.5	355±20.6	298±45.2	95.5±8.06
Fluoranthene	39.1±15.9	278±35.8	225±42.6	62.2±8.11
Pyrene	93.6±34.1	601±94.2	477±17.5	140±21.9
Benz(a)anthracene	1.8±0.769	16.3±1.93	10.9±0.612	3.37±0.563
Chrysene	2.74±1.39	17.7±3.24	12.2±0.237	4.42±0.715
Benzo(b)fluoranthene	0.131±0.0746	3.42±0.648	0.479±0.155	0.197±0.0482
Benzo(k)fluoranthene	0.067±0.0298	1.23±0.646	0.097±0.06	0.119±0.0397
Benzo(a)pyrene	0.167±0.0385	2.82±1.01	0.486±0.08	0.106±0.0219
Indeno[1,2,3-cd]pyrene	0.255±0.0537	2.61±0.701	BDL	0.0486±0.0358
Dibenzo[a,h]anthracene	0.563±0.302	5.49±0.744	BDL	0.12±0.0749
Benzo[ghi]perylene	BDL	0.54±0.0801	BDL	0.0187±0.00204

Table 54: PAH emission rates for the 1998 CAT C-12 engine

	1998 CAT C-12			
PAH	Idle (ug /min)	Creep (ug/mi)	Cruise (ug/mi)	Cruise (ug/mi)
Naphthalene	5420±2340	19300±4970	164000±8000	28400±7910
Acenaphthylene	155±108	2230±24.5	833±59.3	176±23
Acenaphthene	280±114	16100±6630	8830±187	1070±133

Fluorene	1610±892	71000±5440	60300±7176	8650±1730
Phenanthrene	5710±2140	236000±38000	227000±52600	29300±3980
Anthracene	166±69.1	5930±663	6090±647	665±116
Fluoranthene	121±42.5	4560±752	4380±1120	602±113
Pyrene	231±81	8100±1433	7780±2050	1070±222
Benz(a)anthracene	3.62±0.896	81.6±12.9	79.7±23.8	10.6±2.22
Chrysene	4.32±1.92	115±36.6	116±34.2	15.4±3.09
Benzo(b)fluoranthene	4.38±1.39	21.1±7.12	8.4±4	0.752±0.147
Benzo(k)fluoranthene	1.18±0.51	17.5±4.31	7.3±5.51	0.874±0.104
Benzo(a)pyrene	3.89±1.48	12±2.55	3.56±0.403	1.03±0.224
Indeno[1,2,3-cd]pyrene	2.98±1.89	33.3±5.84	8.27±3.8	4.47±0.144
Dibenzo[a,h]anthracene	0.359±0.174	36±8.44	8.02±3.9	4.93±0.171
Benzo[ghi]perylene	0.377±0.133	31.5±7.87	6.57±3.58	4.12±1.83

Table 55: PAH emission rates for the 1999 CAT C-12 engine

	1999 CAT C-12			
PAH	Idle (ug /min)	Creep (ug/mi)	Cruise (ug/mi)	Cruise (ug/mi)
Naphthalene	14100±4750	247000±63600	236000±48000	26000±11200
Acenaphthylene	98.2±29.4	1022±452	417±286	50.7±5.74
Acenaphthene	762±335	2570±822	1020±354	418±122
Fluorene	15.5±6.99	2620±1780	34.4±17.7	636±54.7
Phenanthrene	1330±152	25300±1550	21000±1250	2480±242
Anthracene	4070±545	67100±10700	34800±19000	5630±281
Fluoranthene	0.85±0.239	BDL	2249±197	228±30.5
Pyrene	1.95±0.743	BDL	4609±1317	452±65.8
Benz(a)anthracene	0.299±0.098	BDL	45±6.79	1.4±0.482
Chrysene	0.318±0.216	BDL	85.2±15.4	1.21±0.38
Benzo(b)fluoranthene	2.48±1.43	3.67±1.37	15.2±5.06	7.44±2.26
Benzo(k)fluoranthene	2.08±0.0911	BDL	14.5±4.19	10.7±1.39
Benzo(a)pyrene	5.5±0.0995	91.3±12	18.3±5.84	8.57±4.35
Indeno[1,2,3-cd]pyrene	0.743±0.463	22.1±9.73	27.7±13.8	BDL
Dibenzo[a,h]anthracene	1.22±0.533	16.4±8.92	26.2±20.2	BDL
Benzo[ghi]perylene	0.0365±0.0214	40.5±7.49	38.1±24.4	7.14±2.86

Kado et al. (2005) [Emissions of Toxic Pollutants from Compressed Natural Gas and Low Sulfur Diesel-Fueled Heavy-Duty, Environ. Sci. Technol.] measured the PAH emissions from two transit buses: one fueled with CNG and one fueled with ultralow sulfur diesel (ECD-1) equipped with either an oxidation catalyst or CRT. The buses were tested in three configurations. These configurations included the following: (1) a CNG 40-passenger New Flyer bus equipped with a 2000 DDC Series 50G engine (CNG.1 and CNG.2), (2) a diesel 40-passenger New Flyer bus equipped with a 1998 DDC Series 50 engine and a Nelson Exhaust System catalyzed muffler (ECD.OC), and (3) the same New Flyer diesel bus retrofitted with a Johnson Matthey Continuously Regenerating Trap (CRT) in place of the muffler (ECD.CR). The CNG bus had no after-treatment system. Testing was performed over the Urban Dynamometer Driving Schedule (UDDS), the New York City Bus (NYB), and the Central Business District (CBD) cycles. The Steady-State (SS) 55 mph cruise was 20-min in duration for the “baseline” diesel ECD.OC and 40-min for both CNG.1 and CNG.2 and for ECD.CR. Dynamometer test sequences were composed of multiple equivalent cycles to ensure collection of sufficient sample for analyses. For the SS runs, the chassis dynamometer applied road load and additional vehicle-specific load corresponding to approximately 60% of the available engine power.

Filters used for PAH and bioassay analyses were 70 mm Teflon-coated glass fiber filters (T60A20, Pall-Gelman, Ann Arbor, MI) that were precleaned in methanol (3 times) followed by dichloromethane (3 times). Polyurethane foam (PUF) media were precleaned by sonication in hexane (3 times) followed by acetone (3 times). Filters were pre-weighed in a temperature and humidity-controlled room as per the CFR. The XAD-4 resin (precleaned; Altech Associates, Inc., Deerfield, IL) was cleaned by sonication in methanol (3 times) and in dichloromethane (3 times) and dried under vacuum for 5 days. Samples for PAH analyses were collected from the secondary dilution tunnel with a sampling train (flow rate ∼ 3.5 scfm) that consisted of precleaned filters (two 70 mm T60A20 filters placed in series), PUF, and XAD-4.

Internal deuterated standards were added to the filters before extraction, and the filters were extracted with DCM three times using sonication for 15 min each time period. The temperature of the sonication bath was maintained between 25 °C and 30 °C. Internal deuterated standards were added to the filters, the filters were extracted, and the extract was filtered through a 0.45 μm filter (Acrodisc CR, Gelman Sciences, Ann Arbor, MI) and concentrated to 1 mL with nitrogen. Selected filter extracts were either further concentrated or pooled with other filter extracts and further concentrated to a final volume of 50 or 100 μL prior to analyses. The PUF samples were extracted with acetone. XAD samples were transferred to precleaned separatory funnels and extracted with DCM four times. The XAD extracts were filtered and concentrated to1 mL using the same procedure described for the filter extracts.

The PAH present on the filter, PUF, and XAD were analyzed by gas chromatography/mass spectrometry (GC/MS) using a Hewlett-Packard (HP) model 5890 series II gas chromatograph interfaced to a HP 5972 mass selective detector (MSD). The injector was run in splitless mode and an electronic pressure controller was programmed for vacuum compensation and constant flow. The GC was equipped with a DB-5ms fused silica capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness; Agilent Technologies, Palo Alto, CA). The MSD was run in selective ion monitoring (SIM) mode.

Table 56: Particle-associated PAHs for each test cycle, expressed in µg/mile

vehicle configuration	CNG.1				ECD.OC				ECD.CR				CNG.2		
test cycle	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	UDDS	CBD	NYB
naphthalene	0.12	0.13	0.65	1.6	ND	1.2	0.70	16	0.30	0.11	0.14	1.0	0.14	0.22	2.0
2-methylnaphthalene	0.14	0.29	0.57	1.3	0.10	1.4	1.8	16	0.10	0.16	0.23	1.1	0.17	ND	ND
1-methylnaphthalene	ND	ND	0.28	0.66	ND	ND	1.8	4.8	ND	ND	0.17	0.58	0.06	ND	ND
biphenyl	ND	ND	0.21	0.40	0.10	0.71	0.60	8.7	ND	ND	0.17	0.041	0.042	ND	0.68
2,6-dimethylnaphthalene	ND	0.09	ND	0.36	0.10	0.68	0.84	6.3	ND	0.040	0.054	ND	ND	ND	ND
acenaphthylene	ND	0.10	ND	0.68	ND	ND	0.75	2.0	ND	ND	ND	ND	ND	ND	2.2
acenaphthene	ND	ND	0.36	0.50		ND	ND	ND	ND	ND	ND	ND	ND	ND	2.2
2,3,5-trimethylnaphthalene	0.09	0.18	ND	1.2	ND	ND	ND	ND	ND	ND	ND	0.54	ND	ND	
fluorene	0.19	0.31	0.63	1.1	0.50	0.32	0.97	6.3	ND	0.22	1.1	0.51	0.085	ND	ND
phenanthrene	0.074	0.17	0.68	1.5	0.40	7.5	9.7	80	0.20	0.15	0.19	1.3	0.085	0.14	1.6
anthracene	ND	ND	ND	ND		0.34	0.75	5.0	ND	ND	ND	ND	ND	0.044	ND
1-methylphenanthrene	0.16	0.61	1.09	1.0	0.50	6.1	4.6	27	0.10	0.055	0.20	1.2	0.041	0.09	0.65
fluoranthene	0.13	0.26	0.94	1.9	1.50	6.5	6.5	39	0.20	0.26	0.27	1.5	0.14	0.22	2.0
pyrene	0.33	0.49	1.65	3.1	6.3	13	12	93	0.50	0.68	0.56	3.5	0.37	0.55	4.9
benz(a)anthracene	0.06	0.15	0.28	D	0.10	0.26	0.27	1.1	NDe	0.029	0.034	0.20	0.051	0.11	0.62
chrysene/triphenylene	0.19	0.20	0.53	0.94	0.30	0.39	0.36	2.1	ND	0.11	0.053	0.31	0.24	0.28	1.9
benzo(b)fluoranthene	ND	ND	ND	ND	ND	2.5c	0.42	3.0c	ND	NDe	ND	ND	0.066	ND	0.7
benzo(k)fluoranthene	ND	ND	ND	ND		ND	0.20	c	NDe	ND	ND	ND	0.029	ND	ND
benzo(e)pyrene	ND	0.05	ND	ND		0.32	0.44	1.7	ND	NDe	ND	ND	0.043	0.047	0.36
benzo(a)pyrene	ND	0.012	ND	0.75	ND	0.31	0.49	1.4	ND	ND	ND	ND	ND	ND	0.41
perylene	ND	ND	ND	0.95	ND	NDe	NDe	NDe	ND	ND	ND	ND	ND	ND	ND
indeno(1,2,3-cd)pyrene	0.06	ND	ND	ND	ND	0.36	0.54	1.5	ND	ND	ND	ND	0.032	ND	0.5
dibenz(a,h)anthracene	ND	0.11	ND	ND		ND	0.35	1.3	ND	ND	ND	ND	ND	ND	ND
benzo(g,h,i)perylene	0.045	0.077	0.105	0.81	0.10	0.57	0.74	3.2	ND	0.019	ND	ND	0.034	D	0.47

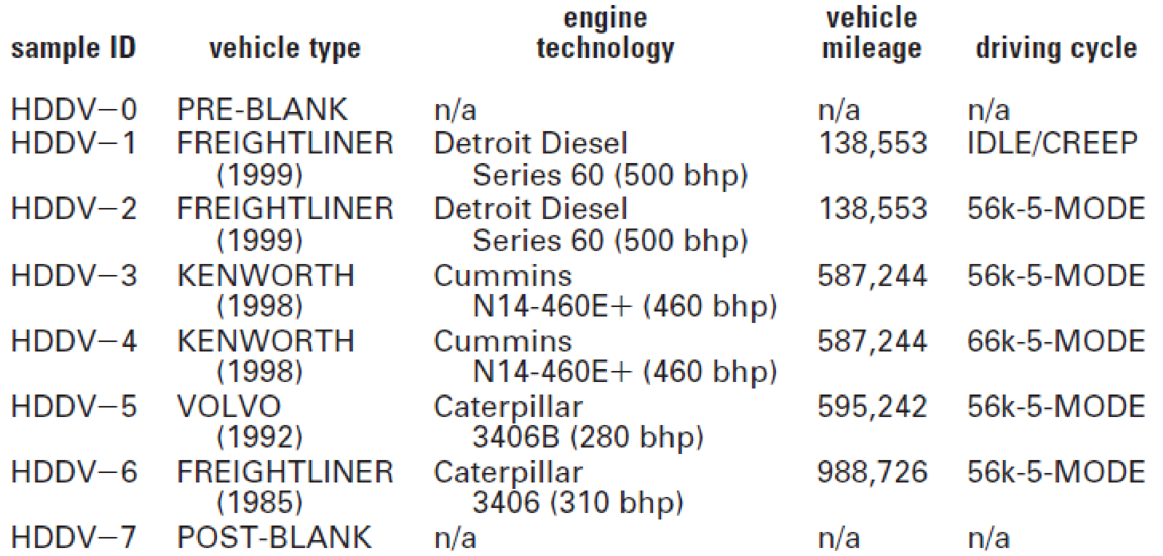
total	1.58	3.21	7.97	18.2	10.5	40.9	45.2	317.2	1.40	1.83	3.15	11.9	1.64	3.15	21.2

Table 57: Semivolatile PAHs for each test cycle, expressed in µg/mile

	CNG.1				ECD.OC				ECD.CR				CNG.2		
test cycle	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	SS	UDDS	CBD	NYB	UDDS	CBD	NYB
naphthalene	0.34	3.9	31	87	4.0	32	43	103	1.9	1.9	9.1	33	2.8	6.7	31
2-methylnaphthalene	0.38	5.6	40	110	5.7	110	70	129	3.7	2.0	15	62	3.1	5.1	28
1-methylnaphthalene	0.25	4.0	25	70	2.8	57	31	62	1.9	0.8	7.6	29	2.4	3.4	19
biphenyl	ND	1.9	9.3	45	3.1	75	42	150	3.0	3.5	5.8	36	1.6	2.0	13
2,6-dimethylnaphthalene	0.11	2.8	14	46	3.6	55	23	89	4.2	1.2	8.7	48	1.5	2.3	14
acenaphthylene	0.12	4.6	12	33	1.0	ND	25	37	2.1	0.4	4.3	25	5.2	5.7	37
acenaphthene	0.044	1.1	3.7	21	ND	11	5.7	ND	2.0	ND	5.9	30	0.75	1.4	9.0
2,3,5-trimethylnaphthalene	0.26	5.6	8.2	28	3.4	8.6	7.6	24	3.1	2.0	8.3	54	2.1	4.3	17
fluorene	1.8	4.4	7.1	26	1.8	ND	4.3	ND	1.6	3.2	4.7	28	3.1	6.2	18
phenanthrene	3.3	9.4	17	44	22	9.6	9.5	67	3.9	8.1	8.6	61	9.9	21.9	44
anthracene	0.64	1.3	2.4	7.4	ND	ND	ND	ND	ND	ND	ND		1.4	3.0	6.4
1-methylphenanthrene	0.82	1.8	4.0	7.6	8.0	1.8	1.7	18	0.60	2.0	2.4	8.3	1.7	7.0	9.1
fluoranthene	0.99	1.8	4.3	9.6	2.2	0.79	0.81	5.9	0.70	2.8	1.6	7.0	1.7	4.5	9.4
pyrene	2.6	3.8	8.0	18	3.5	0.89	0.83	7.4	1.4	6.7	3.1	16	3.3	9.2	19
benzo(a)anthracene	ND	ND	0.31	ND		0.20	ND	ND	ND	ND	ND	ND	ND	ND	ND
chrysene/triphenylene	ND	ND	0.45	ND	ND	0.20	ND	ND	ND	ND	ND	ND	ND	ND	ND
total	11.6	52.0	187.5	552.3	61.0	362.8	264.9	694.1	30.1	34.6	85.5	437.3	40.7	82.7	273.7

Riddle et al. (2007) [Size Distribution of Trace Organic Species Emitted from Heavy-Duty Diesel Vehicles, Environ. Sci. Technol.] measured the size distribution of PAH emissions contained in airborne particles released from on-road heavy-duty diesel vehicles. All vehicles were operated under realistic driving cycles and dilution conditions were adjusted to achieve a balance between sample collection times and the need to simulate the high dilution rates that are experienced in the atmosphere.

Samples of particulate matter were collected using a chassis dynamometer combined with a dilution sampling system that was equipped with Micro Orifice Uniform Deposit Impactors (MOUDIs) (MSP Corporation, Shoreview MN) and Reference Ambient Air Samplers (RAAS) (Andersen Instruments, Smyra GA). Information of the four test vehicles is shown below:



sample ID	vehicle type	engine technology	vehicle mileage	driving cycle
HDDV−0	PRE-BLANK	n/a	n/a	n/a
HDDV−1	FREIGHTLINER (1999)	Detroit Diesel Series 60 (500 bhp)	138,553	IDLE/CREEP
HDDV−2	FREIGHTLINER (1999)	Detroit Diesel Series 60 (500 bhp)	138,553	56k-5-MODE
HDDV−3	KENWORTH (1998)	Cummins N14-460E+ (460 bhp)	587,244	56k-5-MODE
HDDV−4	KENWORTH (1998)	Cummins N14-460E+ (460 bhp)	587,244	66k-5-MODE
HDDV−5	VOLVO (1992)	Caterpillar 3406B (280 bhp)	595,242	56k-5-MODE
HDDV−6	FREIGHTLINER (1985)	Caterpillar 3406 (310 bhp)	988,726	56k-5-MODE
HDDV−7	POST-BLANK	n/a	n/a	n/a

The basic driving cycle used for all tests was the California Air Resources Board (CARB) Heavy Heavy Duty Diesel Test (HHDDT). HDDV-1 focused on the first two modes (idle and creep), and all other tests used the full five modes of the HHDDT. Test no. HDDV-4 used an inertial weight of 66 000 lbs, and all other tests used an inertial weight of 56 000 lbs. The truck used in test no. HDDV-5 had an engine governor that limited the maximum speed to 60 miles/hr.

Aluminum substrates from three MOUDIs were composited by size for each test and extracted as one sample. Quartz filter PM1.8 samples were extracted individually. Sampling substrates were spiked with an isotopically labeled sterane (ααα-20R-cholesatne-d4) and two isotopically labeled PAHs (chrysene-d12 and dibenzo[ah]anthracene-d14) then allowed to dry. Substrates were then placed into screw-cap centrifuge tubes for organic solvent extraction. Each tube was filled with ~15 mL of dichloromethane then suspended in an ultrasonic cleaning bath for 15 min. The sonication procedure was then repeated and the two extractions were combined before evaporation under Nitrogen to a final volume of 200 µL.

PAH analysis was done using a Varian 3400 gas chromatograph (GC) coupled with a Varian 2000 ion-trap mass spectrometer (ITMS) (GC−ITMS). The separation of the analytes was performed on an Agilent J&W DB-XLBMSD capillary GC column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) with a stationary phase consisting of a 5% phenyl/95% methyl substituted polysiloxane. GC−ITMS was operated in electron impact (EI) ionization mass spectrometry/selected ion monitoring (SIM) mode.

Table 58: Ratio of analyte mass (µg) to organic carbon mass (g) for the filter measurements emitted from HDDVs in the PM1.8 size fraction

	1999 Freightliner, idle/creep		1999 Freightliner, 56K		1998 Kenworth, 56K		1998 Kenworth 66K		1992 Volvo, 56K		1985 Freightliner, 56K	
	ratio	error	ratio	error	ratio	error	ratio	error	ratio	error	ratio	error
phenanthrene	6.7	2.1	84.5	10.3	90.1	11.2	22.8	6.5	49.0	7.0	358.5	33.3
anthracene	ND		ND		ND		ND		ND		20.8	14.0
A-methylphenanthrene	7.1	10.9	52.4	22.4	50.8	20.6	120.5	44.5	27.0	22.9	318.5	60.3
B-methylphenanthrene	8.8	10.9	123.2	25.4	102.9	23.0	149.3	45.6	68.6	23.9	418.8	67.2
C-methylphenanthrene	ND		45.1	22.2	49.2	20.6	83.2	43.6	44.4	23.2	233.7	54.0
D-methylphenanthrene	ND		36.5	22.0	41.4	20.4	60.2	43.2	37.4	23.1	171.3	50.8
fluoranthene	16.3	2.5	101.0	11.9	65.9	8.4	52.0	8.7	203.2	23.3	389.2	49.5
pyrene	35.2	4.8	219.1	25.2	203.3	24.3	114.0	15.6	454.9	51.6	662.8	77.6
benzo[ghi]fluoranthene	9.6	1.9	13.5	3.5	40.5	5.6	30.4	4.8	52.8	6.9	89.9	13.8
chrysene	3.7	2.1	ND		17.4	4.4	22.5	8.6	13.6	4.6	31.6	10.3
benzo[b]fluoranthene	8.7	5.8	ND		18.1	10.8	37.7	40.6	15.6	12.2	52.8	45.3
benzo[k]fluoranthene	3.2	1.3	ND		3.1	2.2	3.1	20.4	ND		5.1	8.5
benzo[e]pyrene	7.6	2.5	ND		13.3	4.6	11.2	6.2	21.0	5.5	35.4	33.2
benzo[a]pyrene	6.1	2.9	ND		13.5	5.4	1.5	6.9	ND		11.4	10.4
indeno[1,2,3-cd]pyrene	6.2	5.4	ND		ND		ND		ND		ND	
benzo[ghi]perylene	26.8	3.9	ND		14.9	5.9	9.2	17.1	ND		ND	
coronene	11.9	2.1	ND		ND		ND		ND		ND	

Table 59: Ratio of analyte mass (µg) to organic carbon mass (g) for the filter measurements emitted from HDDVs in the PM0.1 size fraction

	1999 Freightliner, idle/creep		1999 Freightliner, 56K		1998 Kenworth, 56K		1998 Kenworth 66K		1992 Volvo, 56K		1985 Freightliner, 56K	
	ratio	error	ratio	error	ratio	error	ratio	error	ratio	error	ratio	error
phenanthrene	23.7	3.4	170.3	20.1	55.0	10.7	70.2	14.7	171.3	21.2	320.8	33.3
anthracene	ND		ND		ND		ND		ND		107.9	14.0
A-methylphenanthrene	ND		178.2	41.0	40.4	45.9	ND		123.8	43.5	392.9	60.3
B-methylphenanthrene	ND		251.2	45.2	58.4	46.1	ND		260.9	50.5	496.7	67.2
C-methylphenanthrene	ND		106.7	38.0	23.1	45.8	ND		157.1	44.8	280.0	54.0
D-methylphenanthrene	ND		97.5	37.7	18.4	45.8	ND		123.6	43.5	202.0	50.8
fluoranthene	7.4	2.3	264.6	29.9	58.1	10.1	71.4	15.0	517.9	59.8	483.7	49.5
pyrene	12.0	3.6	584.4	65.3	147.3	21.2	229.3	31.3	1298.8	149.2	761.1	77.6
benzo[ghi]fluoranthene	3.3	2.0	26.2	6.0	68.0	10.6	56.4	9.3	109.9	14.2	129.2	13.8
chrysene	2.7	2.6	ND		36.1	9.8	31.2	16.9	26.4	8.5	44.9	10.3
benzo[b]fluoranthene	6.6	7.2	ND		35.1	24.6	42.1	82.3	ND		70.6	45.3
benzo[k]fluoranthene	2.1	1.5	ND		ND		ND		ND		ND	
benzo[e]pyrene	6.7	3.0	ND		12.7	9.9	30.4	12.9	ND		ND	
benzo[a]pyrene	5.2	3.5	ND		11.4	11.8	ND		ND		ND	
indeno[1,2,3-cd]pyrene	2.9	6.7	ND		ND		ND		ND		ND	
benzo[ghi]perylene	14.8	4.1	ND		ND		ND		ND		ND	
coronene	ND		ND		ND		ND		ND		ND	

Tang et al. (2007) [Unregulated Emissions from a Heavy-Duty Diesel Engine with Various Fuels and Emission Control, Environ. Sci. Technol.] investigated the PAH emissions from 10 diesel fuels in conjunction with three commercially available diesel emission control technologies including diesel oxidation catalyst (DOC), CRDPF, and CRDPF coupled with an exhaust gas recirculation system (EGRT). Ten different fuels were studied in twenty four combinations of fuel and aftertreatment configurations. 10 diesel fuels in conjunction with three commercially available diesel emission control technologies including diesel oxidation catalyst (DOC), CRDPF, and CRDPF coupled with an exhaust gas recirculation system (EGRT). Ten different fuels were studied in twenty four combinations of fuel and aftertreatment configurations. Pretest engine and dynamometer preparation as well as the engine emission testing were conducted in accordance with the respective sections of the U.S. Code of Federal Regulation (CFR).

The sampling system was preconditioned by operating the engine at the rated-speed and 100% torque for a period of 20 min. The constant volume sampling (CVS) and secondary dilution system temperatures were verified to establish conformance with CFR. Emission measurements were performed on diluted exhaust from the CVS system, which diluted the engine exhaust during the test with dilution air filtered through a set of filters (bag, activated carbon, and HEPA).

The collection of both PM-phase and gas-phase PAHs and n-PAHs was achieved with a 70 mm precleaned Pallflex Emfab filter followed by a PUF plug. The filter and PUF plug were treated as one sample and extracted with a precleaned Soxhlet extraction apparatus. The analyses for PAHs and n-PAHs were performed on the extracts using a high-resolution GC/MS. Over forty-five PAH/n-PAHs compounds were analyzed.

Table 60: PAH speciation (mg/nh-hr)

	LSD		Equilon-ULSD				Tosco-ULSD			Fischer-Tropsch		
PAH (mg/hp-hr)	EO	DOC	EO	DOC	CRT	EGRT	DOC	CRT	EGRT	DOC	CRT	EGRT
Naphthalene	-	0.0350	0.4610	0.0383	0.020	0.0187	0.0605	0.0308	0.0274	0.0118	0.0078	0.0132
Acenaphthylene	-	0.0032	0.0407	0.0023	0.000	0.0002	0.0019	0.0002	0.0002	0.0009	<ql	<ql
Acenaphthene	-	0.0021	0.0194	0.0012	0.000	0.0004	0.0011	0.0005	0.0004	0.0004	0.0003	0.0003
Fluorene	-	0.0052	0.0351	0.0024	0.001	0.0005	0.0030	0.0007	0.0006	0.0008	0.0005	0.0005
2-Me-Fluorene	-	0.0025	0.0099	0.0009	0.000	0.0002	0.0009	0.0004	0.0003	0.0005	<ql	0.0002
Phenanthrene	-	0.0086	0.0219	0.0024	0.001	0.0010	0.0026	0.0012	0.0010	0.0022	0.0008	0.0007
Anthracene	-	0.0009	0.0037	0.0008	0.001	0.0005	0.0003	<ql	0.0005	0.0006	<ql	0.0007
Fluoranthene	-	0.0003	0.0032	0.0007	<ql	<ql	0.0004	<ql	<ql	0.0006	<ql	<ql
Pyrene	-	0.0004	0.0043	0.0009	0.000	<ql	0.0005	0.0002	<ql	0.0002	0.0002	<ql
RET	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(a)Fluorene	-	<ql	0.0001	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(b)Fluorene	-	<ql	0.0007	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
1-Me-Pyrene	-	0.0001	0.0005	0.0001	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(g,h,i)Fluoranthene	-	<ql	0.0004	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(a)Anthracene	-	<ql	0.0004	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Triphenylene	-	<ql	0.0002	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Chrysene	-	<ql	0.0003	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
coeluting Triphenylene&Chrysene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
7-Me-Benzo(a)Anthracene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(b)Fluoranthene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(k)Fluoranthene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
coeluting B(b)F & B(k)F	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(e)Pyrene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(a)Pyrene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Perylene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Indeno(1,2,3-cd)flooranthene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql

2-Me-Cholanthrene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Indeno(1,2,3-cd)Pyrene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Dibenzo(a,c)&(a,h)Anthracene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(b)Chrysene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Benzo(g,h,i)Perylene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Anthanthrene	-	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql	<ql
Total	-	0.0583	0.6019	0.0500	0.023	0.0216	0.0712	0.0339	0.0305	0.0179	0.0095	0.0157

Table 61: PAH speciation (mg/nh-hr)

	Bio-Diesel			PuriNOx		#1 Diesel		#1 E-Diesel		#2 Diesel		#2 E-Diesel	
PAH (mg/hp-hr)	DOC	CRT	EGRT	DOC	CRT	EO	DOC	EO	DOC	EO	DOC	EO	DOC
Naphthalene	0.0299	0.0158	0.0201	0.3693	0.0882	0.6586	0.0513	0.7355	0.1542	0.4829	0.0389	0.7355	0.1542
Acenaphthylene	0.0023	0.0001	<ql	0.0115	0.0012	0.0495	0.0026	0.0719	0.0075	0.0524	0.0025	0.0719	0.0075
Acenaphthene	0.0010	0.0003	0.0003	0.0091	0.0011	0.0317	0.0017	0.0545	0.0048	0.0215	0.0010	0.0545	0.0048
Fluorene	0.0022	0.0005	0.0006	0.0180	0.0020	0.0918	0.0056	0.0839	0.0107	0.0425	0.0021	0.0839	0.0107
2-Me-Fluorene	0.0009	0.0002	0.0003	0.0054	0.0007	0.0365	0.0024	0.0560	0.0057	0.0203	0.0010	0.0560	0.0057
Phenanthrene	0.0027	0.0009	0.0008	0.0096	0.0019	0.0983	0.0085	0.0820	0.0116	0.0500	0.0044	0.0820	0.0116
Anthracene	0.0006	0.0005	0.0009	0.0015	0.0005	0.0073	0.0011	0.0220	0.0022	0.0121	0.0008	0.0220	0.0022
Fluoranthene	0.0005	<ql	<ql	0.0008	0.0003	0.0040	0.0009	0.0062	0.0010	0.0041	0.0010	0.0062	0.0010
Pyrene	0.0005	0.0002	<ql	0.0012	0.0003	0.0041	0.0005	0.0186	0.0020	0.0101	0.0013	0.0186	0.0020
RET	<ql	<ql	<ql	<ql	<ql <ql	<ql		0.0015	<ql	0.0007	<ql	0.0015	<ql
Benzo(a)Fluorene	<ql	<ql	<ql	<ql	<ql	0.0003	<ql	0.0008	0.0001	0.0004	0.0001	0.0008	0.0001
Benzo(b)Fluorene	<ql	<ql	<ql	<ql	<ql	0.0001	<ql	0.0004	<ql	0.0002	<ql	0.0004	<ql
1-Me-Pyrene	0.0001	<ql	<ql	0.0002	<ql	0.0005	<ql	0.0030	0.0003	0.0012	0.0001	0.0030	0.0003
Benzo(g,h,i)Fluoranthene	<ql	<ql	<ql	<ql	<ql	0.0004	<ql	0.0008	<ql	0.0005	<ql	0.0008	<ql
Benzo(a)Anthracene	<ql	<ql	<ql	<ql	<ql <ql	<ql		0.0006	<ql	0.0004	<ql	0.0006	<ql
Triphenylene	<ql	<ql	<ql	<ql	<ql <ql	<ql		0.0003	<ql	0.0003	<ql	0.0003	<ql
Chrysene	<ql	<ql	<ql	<ql	<ql <ql	<ql		0.0006	<ql	0.0004	<ql	0.0006	<ql

coeluting Triphenylene&Chrysene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
7-Me-Benzo(a)Anthracene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Benzo(b)Fluoranthene	<ql	<ql	<ql	<ql	<ql <ql	<ql		0.0005	<ql	<ql	<ql	0.0005	<ql
Benzo(k)Fluoranthene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
coeluting B(b)F & B(k)F	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Benzo(e)Pyrene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Benzo(a)Pyrene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Perylene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Indeno(1,2,3-cd)flooranthene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
2-Me-Cholanthrene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Indeno(1,2,3-cd)Pyrene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Dibenzo(a,c)&(a,h)Anthracene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Benzo(b)Chrysene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Benzo(g,h,i)Perylene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Anthanthrene	<ql	<ql	<ql	<ql	<ql <ql	<ql		<ql	<ql	<ql	<ql	<ql	<ql
Total	0.0407	0.0186	0.0229	0.4265	0.0963	0.9831	0.0745	1.1390	0.2000	0.7001	0.0533	1.1390	0.2000

Table 62: nitro-PAH speciation (ng/bhp-hr)

	LSD		Equilon-ULSD				Tosco-ULSD			Fischer-Tropsch		
N-PAH (ng/bhp-hr)	EO	DOC	EO	DOC	CRT	EGRT	DOC	CRT	EGRT	DOC	CRT	EGRT
2- Nitrofluorene	-	8.4	44.6	30.2	2.2	2.0	57.6	5.1	2.9	80.7	2.5	2.0
Total Nitro-C13*	-	123.5	164.9	127.9	18.9	21.2	83.1	12.7	26.9	138.2	26.4	15.3
9-Nitroanthracene	-	18.0	87.1	44.5	4.7	3.4	37.3	6.5	3.4	155.1	<DL	2.6
2-Nitroanthracene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
9-Nitrophenanthrene	-	36.0	58.6	79.0	15.3	17.5	89.1	24.9	17.4	462.2	1.1	8.5
Total Nitro-C14*	-	742.0	1480.4	513.2	356.6	473.0	372.6	822.0	631.0	1086.4	1172.9	2275.0
2-Nitrofluoranthene	-	<DL	3.3	<DL	<DL	<DL	2.6	<DL	<DL	<DL	<DL	<DL
3-Nitorfluoranthene	-	1.2	<DL	3.5	<DL	<DL	3.7	<DL	<DL	9.2	<DL	<DL

4-Nitropyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
1-Nitropyrene	-	8.7	49.5	31.6	4.5	3.7	20.9	6.5	3.7	161.4	5.0	2.6
2-Nitropyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Total Nitro-C16*	-	9.9	93.5	35.1	5.6	4.5	32.1	13.0	3.7	172.9	5.0	2.6
7-Nitrobenz(a)anthracene	-	<DL	<DL	<DL	<DL	<DL	1.7	<DL	<DL	5.5	<DL	<DL
6-Nitrochrysene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.0	<DL	<DL
Total Nitro-C18*	-	0.0	0.0	0.0	0.0	0.0	1.7	0.0	0.0	7.5	0.0	0.0
1-Nitrobenzo(e)pyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
6-Nitrobenzo(a)pyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.9	<DL	<DL
4-Nitrobenzo(e)pyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
3-Nitrobenzo(e)pyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
3-Nitrobenzo(a)pyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
1-Nitrobenzo(a)pyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
2-Nitrobenzo(a)pyrene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Total Nitro-C20*	-	0	0	0	0	0	0	0	0	0.1	0	0
9-Nitrodibenzo(a,c)anthracene	-	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Total Nitro-C22*	-	0	0	0	0	0	0	0	0	0	0	0
Total Nitro-PAH (C13 to C22)	-	875.4	1738.8	676.3	381.1	498.7	489.6	847.8	661.6	1407.8	1211.9	2292.8

Table 63: nitro-PAH speciation (ng/bhp-hr)

	Bio-Diesel			PuriNOx		#1 Diesel		#1 E-Diesel		#2 Diesel		#2 E-Diesel	
N-PAH (ng/bhp-hr)	DOC	CRT	EGRT	DOC	CRT	EO	DOC	EO	DOC	EO	DOC	EO	DOC
2- Nitrofluorene	52.0	14.4	1.5	105.9	54.2	193.4	93.5	189.9	101.4	65.0	49.7	153.7	73.7
Total Nitro-C13*	78.8	35.3	16.1	128.8	130.1	257.0	130.2	477.8	169.7	74.3	94.2	197.9	123.2
9-Nitroanthracene	34.2	13.8	2.9	139.4	52.8	2.6	210.9	769.4	221.9	781.7	225.0	709.3	305.5
2-Nitroanthracene	<DL	<DL	<DL	<DL	<DL	<DL		4.8	<DL	6.7	<DL	9.5	<DL
9-Nitrophenanthrene	72.1	33.2	7.3	50.4	91.6	4.9	244.2	199.8	209.5	194.5	160.6	157.6	125.4

Total Nitro-C14*	594.3	524.8	886.0	731.5	1148.5	1132.0	637.4	2309.4	704.7	4246.7	1202.6	3194.3	1050.4
2-Nitrofluoranthene	<DL	<DL	<DL	<DL	<DL	<DL		6.1	<DL	<DL	<DL	8.3	<DL
3-Nitorfluoranthene	4.1	<DL	<DL	4.0	<DL		7.4	<DL	7.7	<DL	3.8	<DL	12.4
4-Nitropyrene	<DL	<DL	<DL	<DL	<DL	<DL		13.5	1.5	21.6	3.2	35.6	8.9
1-Nitropyrene	25.4	7.4	2.6	108.4	15.8	2.6	90.1	315.9	97	631.8	144.2	602.9	303.6
2-Nitropyrene	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Total Nitro-C16*	29.5	7.4	3.8	116.8	37.0	2.6	108.6	335.5	110.3	665.1	151.5	646.4	324.8
7-Nitrobenz(a)anthracene	<DL	<DL	<DL	4.0	<DL		6.3	12.2	3.4	15.2	3.5	12.1	8.9
6-Nitrochrysene	<DL	<DL	<DL	2.2	<DL		2.0	<DL	0.9	2.3	<DL	<DL	4.4
Total Nitro-C18*	7.3	0	0	8.0	0.0	0.0	12.5	12.2	4.3	17.5	3.5	12.1	13.3
1-Nitrobenzo(e)pyrene	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
6-Nitrobenzo(a)pyrene	<DL	<DL	<DL	<DL	<DL		2.6	9.9	2.2	3.8	1.8	<DL	2.9
4-Nitrobenzo(e)pyrene	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
3-Nitrobenzo(e)pyrene	<DL	<DL	<DL	<DL	<DL	<DL	<DL		0.6	<DL	<DL	<DL	<DL
3-Nitrobenzo(a)pyrene	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
1-Nitrobenzo(a)pyrene	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
2-Nitrobenzo(a)pyrene	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Total Nitro-C20*	0	0	0	0	0	0	2.6	9.9	2.8	3.8	1.8	0	2.9
9-Nitrodibenzo(a,c)anthracene	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Total Nitro-C22*	0	0	0	0	0	0	0	0	0	1.73	0	0	0
Total Nitro-PAH													
(C13 to C22)	709.9	567.4	905.8	985.1	1315.6	1159.8	891.2	3144.8	991.8	5057.8	1453.6	3852.7	1514.7

Ratcliff et al. (2010) [Diesel Particle Filter and Fuel Effects on Heavy-Duty Diesel Engine Emissions, Environ. Sci. Technol.] measured gas-phase and particle-phase PAH and nitro-PAH emissions from a heavy-duty engine operating both with and without a catalyzed DPF (intended for passive regeneration at moderate temperatures), and operating on biodiesel fuel. Emissions were measured from three fuels: certification ultra-low-sulfur diesel (ULSD), neat soy biodiesel (B100), and a 20% blend (B20).

The engine test setup consisted of a 2002 model year 5.9 L 300 hp Cummins ISB (serial number: 56993170), retrofitted with a diesel particulate filter. The engine had a rated power of 224 kW at 2500 rpm, a rated torque of 895 Nm at 1600 rpm, and a compression ratio of 16.5:1. The engine was equipped with cooled high-pressure exhaust gas recirculation (EGR), a variable geometry turbocharger, and high-pressure common rail direct fuel injection. It was engineered and calibrated to meet the 2004 U.S. heavy-duty emissions standards. The DPF (12 L capacity) was a catalyzed continuously regenerating technology (CCRT) manufactured by Johnson Matthey. This DPF included a diesel oxidation catalyst to convert NO to NO2, followed by a catalyzed wall-flow soot filter.

The dynamometer test cell conforms to the requirements of the Code of Federal Regulations (CFR) 40, part 86, subpart N. Engine intake air temperature, pressure and humidity were controlled. Engine testing was conducted over an 8-mode test cycle that captures a wide range of operating conditions. The test cycle was based on the AVL 8-mode test, a steady-state test procedure designed to closely correlate with the exhaust emission results obtained from the U.S. Federal Test Procedure heavy-duty engine transient cycle. Some modes were slightly modified for greater test repeatability with this engine.

The PM samples were collected from the dilution tunnel using a conventional PM sampling system comprising a sample probe, a stainless steel filter holder loaded with a pre-weighed Tissuquartz filter (Pall Corp. No. 7202, 47 mm diameter), a sample pump, and mass flow controller. The PM samples were collected at a flow rate of 60 L/min. The PM samples were obtained with either the DPF removed (engine-out) or installed (DPF-out). Engine-out test cycles were run in triplicate using a new, pre-weighed Tissuquartz filter for each test. However, because the PM emissions were expected to be very low with the DPF installed, a single Tissuquartz filter was used to collect all the PM from the triplicate runs for the DPF-out samples. In this case, the final PAH and nitro-PAH levels were calculated by dividing the total value by 3 to determine the per-test value.

Filters were spiked with solutions of deuterated PAH and deuterated nitro-PAH internal standards, then Soxhlet extracted with dichloromethane (DCM) a minimum of 200 cycles. The DCM solutions were placed in an ice bath and evaporated under flowing nitrogen to 10 mL. The DCM concentrates were diluted with pentane and purified by solid-phase extraction. Toluene was added to the extracted solutions and the solutions were again placed in an ice bath and evaporated to a final volume of 200 μL (173 mg).

A four-sector MStation JMS-700T gas chromatograph-mass spectrometer (JEOL USA, Inc., Peabody, Massachusetts) equipped with an experimental JEOL trochoidal electron monochromator ionization source was used for the PAH and nitro-PAH analyses. One μL of each sample was injected onto a Hewlett Packard 6890 Series GC system, equipped with an on-column injection port (Agilent Technologies, Palo Alto, California) maintained at the GC oven temperature. A 0.25 mm i.d. x 30 m RTX-5Sil MS column (Restek Corp, Bellefonte, Pennsylvania), with an intermediate polarity guard column (Supelco Inc., Bellefonte, Pennsylvania) connected on the front end, was used to separate the various analytes. The GC was temperature-programmed using the following parameters: 100°C, hold 1 min; 10°C/min to 190°C, hold 2 min; 5°C/min to 240°C, hold 1 min; 10°C/min to 310°C, hold 3 min. The NO2- containing compounds were detected using selected ion monitoring (SIM) at 3.5 eV for m/z 46, allowing identification of each compound by retention time. SIM monitoring of the molecular ions at near 0 eV allowed confirmation of the molecular weights and quantification of the individual compounds. Nitrobenzene was used as the calibration standard to set the electron energies, while nitrobenzene, hexafluorobenzene, and perfluoro-kerosene standards (Sigma-Aldrich) were used to calibrate the masses monitored in SIM mode. Analyses for PAH were performed using positive ion electron ionization (EI+, ~25 eV), and the molecular ion chromatograms were used to quantify the amounts of each PAH. The MS conditions were as follows: two-sector operation, 6.0 kV accelerating voltage, 1000 resolution, and 100 ms switching rate (magnetic field control). The source temperature was 280°C.

Table 64: Engine-out PAH emissions, expressed in pg/bhp-hr, from 8-Mode composite PM samples

	ULSD (pg/bhp-hr)	B20 (pg/bhp-hr)	B100 (pg/bhp-hr)	ratio ULSD/B20	ratio ULSD/B100
naphthalene	2137.0	1612.4	4421.2	1.3	0.48
biphenyl	423.8	428.9	565.9	1.0	0.75
acenaphthylene	51.7	49.1	46.5	1.1	1.1
fluorene	333.3	217.1	69.8	1.5	4.8
phenanthrene	23018.1	13692.5	2310.1	1.7	10
anthracene	1491.0	917.3	51.7	1.6	29
fluoranthene	21242.9	15372.1	4,829.50	1.4	4.4
pyrene	13863.0	8578.8	3379.8	1.6	4.1
benzo[c]-phenanthrene	341.1	232.6	108.5	1.5	3.1
chrysene	496.1	457.4	237.7	1.1	2.1
total PAH	63398	41558	16021	1.5	4.0

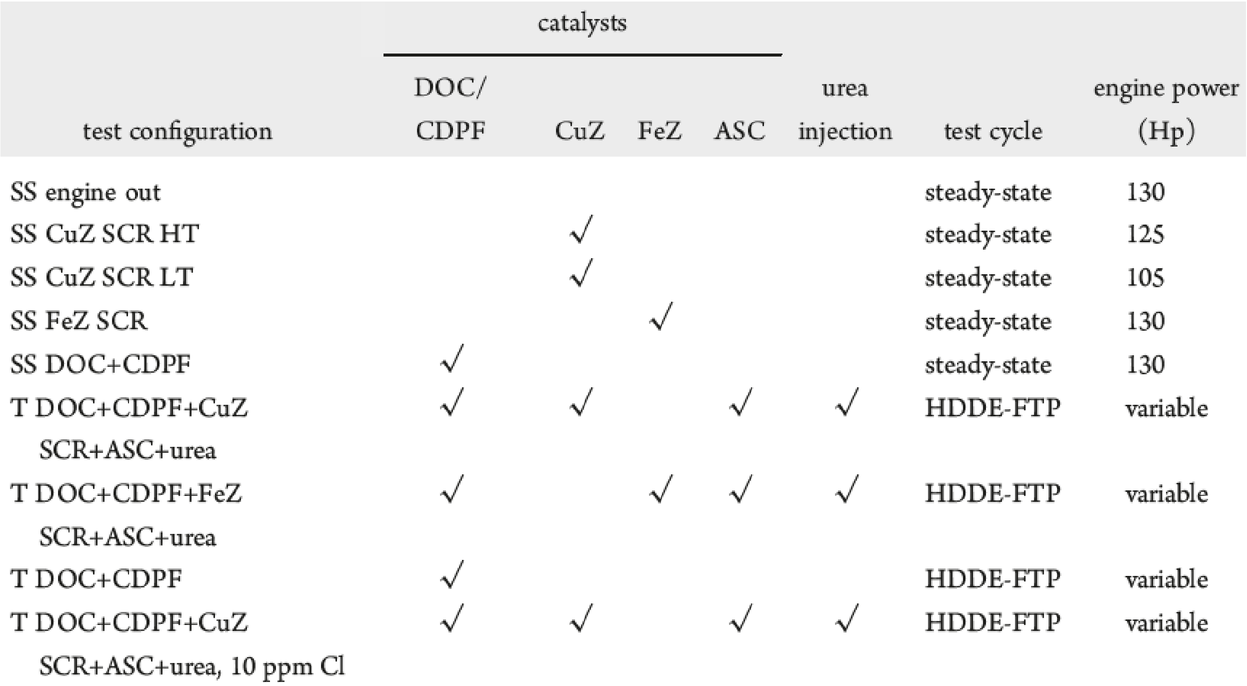
Table 65: Engine-out nitro-PAH emissions, expressed in pg/bhp-hr, from 8-Mode composite PM samples

	ULSD (pg/bhp h)	B20 (pg/bhp h)	B100 (pg/bhp h)	ratio ULSD/B20	ratio ULSD/B100
1-nitronaphthalene	24.5	12.7	5.9	1.9	4.2
2-nitronaphthalene	111.9	77.8	18.9	1.4	5.9
9-nitroanthracene	777.8	480.6	190.4	1.6	4.1
9-nitrophenanthrene	304.9	224.5	133.9	1.4	2.3
3-nitrophenanthrene	62.3	39.0	26.6	1.6	2.3
3-nitrofluoranthene	63.0	29.2	17.1	2.2	3.7
1-nitropyrene	3188.6	1563.3	692.5	2.0	4.6
total nitro-PAH	4533	2427	1085	1.9	4.2

Laroo et al. (2011) [Emissions of PCDD/Fs, PCBs, and PAHs from a Modern Diesel Engine Equipped with Catalyzed Emission Control Systems, Environ. Sci. Technol.] measured PAH emissions from a modern diesel engine utilizing various catalyst configurations representing baseline, model year 2008, and various model year 2010 configurations.

Testing was performed at the U.S. EPA National Vehicle and Fuel Emissions Laboratory (NVFEL) in Ann Arbor, MI using a Schenck AC dynamometer and STARS control system. The engine used to generate exhaust gas was a 280 hp, turbocharged, 2008 MY 6.7 L Cummins ISB equipped with electronically controlled high pressure common rail fuel injection, high pressure loop EGR, and a DOC/CDPF for PM control.

Steady-state testing was performed at 2275 rpm and engine power was adjusted as necessary from configuration to configuration to maintain a target exhaust gas or catalyst temperature. An overview of the conditions can be found below:



	catalysts						
test configuration	DOC/ CDPF	CuZ	FeZ	ASC	urea injection	test cycle	engine power (Hp)
SS engine out						steady-state	130
SS CuZ SCR HT		√				steady-state	125
SS CuZ SCR LT		√				steady-state	105
SS FeZ SCR			√			steady-state	130
SS DOC+CDPF	√					steady-state	130
T DOC+CDPF+CuZ SCR+ASC+urea	√	√		√	√	HDDE-FTP	variable
T DOC+CDPF+FeZ SCR+ASC+urea	√		√	√	√	HDDE-FTP	variable
T DOC+CDPF	√					HDDE-FTP	variable
T DOC+CDPF+CuZ SCR+ASC+urea, 10 ppm Cl	√	√		√	√	HDDE-FTP	variable

Steady-state tests that included CuZ and FeZ SCR catalysts were run without urea injection to worst case PCDD/F emissions. Transient testing was performed over the Heavy-Duty Diesel Engine Federal Test Procedure (HDDE-FTP). For the transient testing performed here, 2 cold start and 46 hot start HDDE-FTPs were run for each sample taken affording a 1:23 ratio of cold to hot start tests.

PAH emissions were collected using a sampling system based on EPA method 23A. The system differs from Method 23A in that it uses a larger sorbent module design similar to that used by Method 20 to allow up to 50 g of XAD-2 resin; as well as a titanium (Ti) sample probe, filter holder, and condenser along with a nickel (Ni) sample module per EN 1948-1. The larger sorbent module permits a higher sampled exhaust volume to ensure that there is no breakthrough due to the potential for high hydrocarbon concentrations.

Samples were taken from the center of the dilution tunnel or exhaust pipe. Proportional sampling was maintained for both transient and steady-state testing, according to 40 CFR part 1065.545. Exhaust flow was calculated from the intake air and fuel flow measurement. Sample flow was calculated by taking the difference between the total flow through the sampler and makeup flow, taking into account the water that condensed and was removed from the sample flow when passing through the condenser. The sampler total flow was controlled with a positive displacement pump while the makeup flow was measured with a laminar flow element and controlled using a proportional valve. Each test required 16 h of sampling.

Particulate Matter was collected onto a 110 mm Pall Tissuquartz filter (7 mil thickness) supported by a perforated titanium disk. Filters were precleaned via Soxhlet extraction with methylene chloride for 24 h and dried over dry nitrogen. The sample probe and filter holder maintained a temperature of 191 °C over the test. The inlet and outlet cones were sealed with a Ti gasket. Non-CDPF tests required multiple filter changes (up to 45) to prevent loss of sample flow due to an increase in back pressure (60 kPa limit) from the PM collected.

Gaseous phase PAHs were collected on 40–50 g of XAD-2 located in between 3 in. diameter polyurethane foam (PUF) plugs. A perforated Teflon disk held the downstream PUF plug in place. The module was located downstream of the condenser and both were submersed in a water bath controlled to achieve a sample gas temperature of 5 ± 1 °C at the module outlet. A leak check was performed between the inlet of the sample probe and the outlet of the sample flow control hardware before each test. The target sample flow rate through the module was 200 slpm for the steady-state tests and 1.35% of the exhaust flow for transient testing, averaging 70 slpm. Target total sample volumes were 192 m^3 for the steady-state and 65 m3 for transient tests. These volumes represent a 64- and 21-fold increase in total sample volume targeted by Method 23A.

PUF and XAD-2 were cleaned via a series of Soxhlet extractions: 8 h water, 22 h methanol, 22 h methylene chloride, and 22 h toluene followed by drying over nitrogen. Sample preparation was carried out according to an enhanced version of EPA method 8290a, taking into consideration ARB methods 428 and 429. Briefly, the sample train wetted surfaces were rinsed with acetone followed by toluene post test. The volumes were reduced as needed using a Kuderna-Danish concentrator and added to the extraction solvents before extraction was initiated. To accommodate the Soxhlet extractions of PAHs from a single sample, two 16 h extractions were employed; the first using hexane and the second using toluene. For all tests that incorporated the use of a DOC+CDPF, the PUF, XAD-2, rinse, and PM filter were extracted together. For all other tests, due to the number of PM filters used over the 16 h test (up to 45), the PM filters were extracted and analyzed in a single batch, separate from the PUF and XAD-2. The results were then combined with the results from PUF/XAD-2/rinse and reported as a single value for each congener.

Table 66: PAH emission factor results for steady-state engine-out and CuZ SCR HT tests

	SS engine out (n=17)				SS CuZ SCR HT (n=9)			
	ng/L		ng/m3		ng/L		ng/m3	
analyte	average	standard deviation	average	standard deviation	average	standard deviation	average	standard deviation
Naphthalene	1,084,405	398,586	52,283	19,137	1,299,934	78,195	55,590	6,829
2-Methylnaphthalene	815,442	250,816	39,338	12,204	410,175	141,400	16,946	3,511
Acenaphthylene	67,988	6,108	3,275	284.5	32,966	8,773	1,373	174.2
Acenaphthene	18,605	5,535	896.9	266.1	2,475	839.6	102.5	21.3
Fluorene	68,149	27,840	3,281	1,339	16,737	6,890	686.6	176.7
Phenanthrene	186,268	25,928	8,989	1,363	210,057	33,673	8,872	852.6
Anthracene	14,707	2,111	708.4	99.4	4,017	1,674	164.6	45.2
Fluoranthene	10,345	1,555	498.7	77.2	8,497	1,003	360.1	27.2
Pyrene	22,980	5,249	1,107	252.1	5,778	1,238	243.6	37.3
Benzo(a)Anthracene	1,214	100.4	58.5	5.1	493.2	42.7	21.2	3.9
Chrysene	1,299	148.4	62.6	7.1	734.4	41.6	31.3	3.1

Benzo(b)Fluoranthene	699.7	176.8	33.6	8.1	600.7	55.8	25.9	4.9
Benzo(k)Fluoranthene	261.1	87.7	12.5	4.0	182.6	30.2	7.9	1.9
Benzo(e)Pyrene	589.9	68.2	28.4	2.9	302.1	27.5	13.0	2.5
Benzo(a)Pyrene	586.6	108.0	28.2	4.8	404.1	59.5	17.5	4.0
Perylene	108.1	10.9	5.2	0.5	59.4	11.8	2.6	0.8
Indeno(1,2,3-c,d)Pyrene	509.1	330.4	24.5	15.7	540.9	190.3	23.5	10.0
Dibenzo(a,h)Anthracene	88.3	61.2	4.2	2.9	72.0	10.4	3.1	0.7
Benzo(g,h,i)Perylene	846.1	979.5	40.5	46.2	658.5	226.8	28.9	12.3

Table 67: PAH emissions factor results for steady-state CuZ SCR LT and FeZ SCR tests

	SS CuZ SCR LT (n=5)				SS FeZ SCR (n=5)			
	ng/L		ng/m3		ng/L		ng/m3	
analyte	average	standard deviation	average	standard deviation	average	standard deviation	average	standard deviation
Naphthalene	2,399,417	271,776	109,326	12,777	13,732	4,233	619.9	231.1
2-Methylnaphthalene	630,964	84,075	28,742	3,841	6,610	1,433	297.9	85.1
Acenaphthylene	43,746	6,013	1,993	277.2	1,105	124.0	49.7	10.1
Acenaphthene	3,698	2,422	168.1	109.3	249.3	81.3	11.1	4.0
Fluorene	20,472	4,775	932.8	218.8	586.4	147.0	26.1	7.0
Phenanthrene	361,051	35,615	16,444	1,590	3,295	711.2	145.7	27.6
Anthracene	8,667	2,043	395.0	94.0	275.9	23.3	12.4	2.4
Fluoranthene	13,959	1,753	635.7	78.4	640.7	74.0	28.8	5.5
Pyrene	10,369	2,197	472.1	98.9	790.9	98.8	35.5	6.7
Benzo(a)Anthracene	803.8	133.7	36.6	5.9	350.5	47.4	15.7	3.0
Chrysene	1,099	163.1	50.0	7.3	323.9	45.0	14.5	2.7
Benzo(b)Fluoranthene	547.3	87.7	24.9	4.0	567.1	199.6	25.3	9.7
Benzo(k)Fluoranthene	202.7	19.5	9.2	0.9	185.0	65.1	8.2	2.9
Benzo(e)Pyrene	386.0	67.7	17.6	3.0	299.3	112.3	13.2	5.1
Benzo(a)Pyrene	435.9	59.7	19.8	2.6	553.9	229.5	23.6	6.1
Perylene	80.0	12.4	3.6	0.5	120.6	40.4	5.3	1.4
Indeno(1,2,3-c,d)Pyrene	498.6	38.7	22.7	1.7	337.3	230.0	13.4	3.8
Dibenzo(a,h)Anthracene	73.2	7.1	3.3	0.3	71.7	43.3	2.9	0.7
Benzo(g,h,i)Perylene	797.8	159.3	36.3	7.0	569.3	395.3	22.6	7.2

Table 68: PAH Emission Factor Results for Steady-state DOC+CDPF and Tunnel Blank Tests

	SS DOC+CDPF (n=5)				tunnel blank (n=5)			
	ng/L		ng/m3		ng/L		ng/m3	
analyte	average	standard deviation	average	standard deviation	average	standard deviation	average	standard deviation
Naphthalene	1,644	1,836	81.3	91.8	44.3	10.7	63.9	14.4
2-Methylnaphthalene	76.8	58.2	3.8	2.9	22.3	3.8	32.2	4.8
Acenaphthylene	3.4	4.3	0.2	0.2	0.083	0.01	0.1	0.02
Acenaphthene	2.9	0.2	0.1	0.009	2.3	1.0	3.3	1.5
Fluorene	13.3	2.3	0.7	0.12	3.3	1.4	4.8	2.1
Phenanthrene	78.8	59.8	3.9	3.0	7.9	3.4	11.4	5.2
Anthracene	2.8	2.4	0.1	0.12	0.080	0.02	0.1	0.03
Fluoranthene	15.9	6.0	0.8	0.3	1.004	0.2	1.4	0.2
Pyrene	10.8	5.1	0.5	0.2	0.344	0.1	0.5	0.10
Benzo(a)Anthracene	0.9	1.1	0.05	0.05	0.008	0.003	0.012	0.004
Chrysene	0.8	0.9	0.04	0.04	0.014	0.003	0.021	0.005
Benzo(b)Fluoranthene	2.3	3.5	0.1	0.2	0.017	0.005	0.024	0.007
Benzo(k)Fluoranthene	0.9	1.6	0.04	0.08	0.006	0.002	0.009	0.003
Benzo(e)Pyrene	1.5	1.8	0.1	0.09	0.011	0.003	0.016	0.004
Benzo(a)Pyrene	0.4	0.8	0.02	0.04	0.007	0.002	0.010	0.003
Perylene	0.1	0.2	0.004	0.01	0.011	0.01	0.016	0.013
Indeno(1,2,3-c,d)Pyrene	1.0	1.6	0.05	0.1	0.008	0.002	0.012	0.003
Dibenzo(a,h)Anthracene	0.2	0.3	0.01	0.02	ND	-	ND	-
Benzo(g,h,i)Perylene	1.6	1.8	0.1	0.1	0.012	0.003	0.018	0.004

Table 69: PAH Emission Factor Results for Transient DOC+CDPF+CuZ SCR+ASC+urea and DOC+CDPF+FeZ SCR+ASC+urea tests

	FTP DOC+CDPF+CuZ SCR+ASC+urea (n=5)				FTP DOC+CDPF+FeZ SCR+ASC+urea (n=5)			
	ng/L		ng/m3		ng/L		ng/m3	
analyte	average	standard deviation	average	standard deviation	average	standard deviation	average	standard deviation

Naphthalene	846.5	207.5	34.1	8.1	2,323	1,503	95.6	62.2
2-Methylnaphthalene	171.3	41.5	6.9	1.7	522.1	549.2	21.4	22.4
Acenaphthylene	5.7	0.9	0.2	0.04	8.6	11.3	0.4	0.5
Acenaphthene	23.1	1.4	0.9	0.1	31.2	7.7	1.3	0.3
Fluorene	59.3	19.9	2.4	0.8	61.8	24.7	2.5	1.0
Phenanthrene	223.8	34.7	9.0	1.4	220.9	66.8	9.1	2.7
Anthracene	9.5	5.0	0.4	0.2	7.8	9.4	0.3	0.4
Fluoranthene	52.4	5.9	2.1	0.3	52.9	13.3	2.2	0.6
Pyrene	60.9	47.9	2.5	1.9	34.0	11.7	1.4	0.5
Benzo(a)Anthracene	1.4	0.4	0.1	0.02	1.6	1.8	0.1	0.07
Chrysene	2.5	0.9	0.1	0.04	1.5	0.3	0.1	0.01
Benzo(b)Fluoranthene	3.0	1.0	0.1	0.04	2.2	1.0	0.1	0.04
Benzo(k)Fluoranthene	0.8	0.2	0.03	0.007	0.6	0.3	0.02	0.01
Benzo(e)Pyrene	2.1	0.9	0.1	0.04	1.3	0.3	0.1	0.01
Benzo(a)Pyrene	0.8	0.3	0.03	0.01	0.4	0.2	0.02	0.01
Perylene	0.4	0.1	0.02	0.004	0.1	0.1	0.004	0.004
Indeno(1,2,3-c,d)Pyrene	0.9	0.3	0.04	0.01	0.5	0.3	0.02	0.01
Dibenzo(a,h)Anthracene	ND	-	ND	-	ND	-	ND	-
Benzo(g,h,i)Perylene	1.7	0.6	0.1	0.02	0.9	0.5	0.04	0.02

Table 70: PAH Emission Factor Results for Transient DOC+CDPF and DOC+CDPF+CuZ SCR+ASC+urea, 10 ppm Cl Tests

	FTP DOC+CDPF (n=5)				FTP DOC+CDPF+CuZ SCR+ASC+urea, 10 ppm Cl (n=5)			
	ng/L		ng/m^3		ng/L		ng/m^3	
analyte	average	standard deviation	average	standard deviation	average	standard deviation	average	standard deviation
Naphthalene	2,103	503.2	85.9	20.8	1,487	2,468	61.2	101.7
2-Methylnaphthalene	556.1	270.4	22.8	11.2	535.9	847.8	22.0	34.9
Acenaphthylene	5.7	1.6	0.2	0.06	6.3	7.5	0.3	0.3
Acenaphthene	28.0	11.9	1.1	0.5	33.1	23.3	1.4	1.0
Fluorene	65.3	30.9	2.7	1.3	59.7	32.0	2.5	1.3

Phenanthrene	251.5	74.7	10.3	3.1	195.3	69.1	8.0	2.9
Anthracene	5.5	1.8	0.2	0.07	7.1	2.3	0.3	0.09
Fluoranthene	55.9	11.1	2.3	0.5	48.3	11.2	2.0	0.5
Pyrene	40.1	26.6	1.6	1.1	29.6	8.1	1.2	0.3
Benzo(a)Anthracene	0.9	0.2	0.04	0.009	1.2	1.3	0.05	0.05
Chrysene	2.6	0.5	0.1	0.02	1.9	1.2	0.1	0.05
Benzo(b)Fluoranthene	3.0	0.4	0.1	0.02	2.9	2.5	0.1	0.10
Benzo(k)Fluoranthene	1.0	0.2	0.04	0.006	1.3	1.2	0.1	0.05
Benzo(e)Pyrene	2.0	0.2	0.1	0.01	1.8	1.4	0.1	0.06
Benzo(a)Pyrene	0.8	0.5	0.03	0.02	1.1	1.4	0.05	0.06
Perylene	0.2	0.2	0.01	0.01	0.9	1.5	0.04	0.06
Indeno(1,2,3-c,d)Pyrene	1.0	0.6	0.04	0.02	1.3	1.4	0.1	0.06
Dibenzo(a,h)Anthracene	0.1	0.1	0.002	0.005	0.2	0.3	0.01	0.01
Benzo(g,h,i)Perylene	2.3	0.9	0.1	0.04	1.9	1.5	0.1	0.1

Heeb et al. (2008) [Secondary Effects of Catalytic Diesel Particulate Filters: Conversion of PAHs versus Formation of Nitro-PAHs, Environ. Sci. Technol.] investigated the PAH and nitro-PAH emissions from a heavy-duty diesel engine with direct injection (Liebherr, type 914 T, 6.11 L, 4 cylinders, 105 kW, Bulle, Switzerland). The engine was operated in the eight-stage ISO 8178/4 C1 test cycle, which consists of four load stages at maximum revolutions-per-minute (RPM), three load stages at intermediate RPM (60% of max. RPM), an idling phase, and eight transients. Each stage is held for 10 or 15 min, resulting in a total cycle time of 100 min. The base fuel for all experiments was a commercial diesel (class D, SN 181190–1:2000).

Two new, uncoated, cordierite-based, monolithic, wall-flow DPFs (Greentop, 100 cells per square inch, 22.8 L, Grävenwiesbach, Germany) were used in combination with an iron- and a copper/iron-based fuel additive. Both additives were diluted with reference fuel to final iron- and copper/iron-concentrations of 4.5 and 9.0 ± 0.5/7.5 ± 0.7 µg/g, respectively. Four additional fuel blends were mixed with 1,6-dichlorohexane as chlorine dopant.

For the analysis of non- and semivolatile trace compounds such as PAHs and nitro-PAHs, 5–7 m^3 of undiluted exhaust were collected through an all-glass sampling arrangement consisting of a sampling probe, a cooler, a condensate separator, a glass fiber filter, and a two-stage adsorber unit (XAD-2). A water/isopropyl-alcohol cooling bath was used to keep the condensate below 4 °C during sampling, and exhaust temperatures remained below 30 °C all the time. Mass flow proportional aliquots of the exhaust were taken during two consecutive runs (200 min) covering both, steady-state and transient operation modes. Prior to sampling, the employed glass apparatus was intensively cleaned and heated to 450 °C.

Aliquots of a mixture of perdeuterated-PAHs containing naphthalene, phenanthrene, pyrene, fluoranthene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and d9-1-nitropyrene (CIL, Andover, MA) were added to the samples as quantification standards. A mixture of unlabeled nitro-PAHs containing 1-nitronaphthalene, 2-nitronaphthalene, 3-nitrophenanthrene, 9-nitrophenanthrene, 9-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, and 4-nitropyrene (Dr. Ehrenstorfer AG, Augsburg, Germany) were mixed with an aliquot of d9-1-nitropyrene and used as quantification standard. Separation of PAHs and nitro-PAHs was obtained by gas chromatography (Fisons Instruments HRGC Mega 2, Rodano, Italy) on a capillary column (PS086, 20 m × 0.28 mm, 0.15 µm) and detection and identification was achieved by high resolution mass spectrometry (Thermo Finnigan MAT 95, Bremen, Germany) in electron ionization mode (GC/EI-HRMS).

PAH and nitro-PAH emissions from the 6.11 L heavy duty diesel engine that was operated with reference fuel (ref) or with iron- (Fe) or copper/iron-doped (Cu) fuels with (F) or without DPFs are shown below.

Table 71: Effects of DPFs and Catalysts on PAH and nitro-PAH Emissions Emission factors (µg/L fuel)

PAH	**Ref**	**Fe**	**FeF**	**Cu**	**CuF**	**Cl**	**ClFe**	**ClFeF**	**ClCuF**	**xClCuF**
Pyrene	82	85	16	72	12	95	92	24	15	14
Fluoranthene	26	23	15	21	10	28	30	17	14	13
Chrysene	4.1	4.6	1.3	3.6	0.8	4.7	5.3	1.6	1	0.9
Benz(a)anthracene	2.6	2.6	0.3	2	0.2	2.9	3.2	0.5	0.2	0.3
Benzo(b)fluoranthene	0.45	0.62	0.13	0.52	0.08	0.58	0.92	0.14	0.1	0.09
Benzo(b)fluoranthene	0.34	0.46	0.07	0.42	0.05	0.4	0.68	0.07	0.06	0.04
Benzo(a)pyrene	0.27	0.36	0.09	0.33	0.06	0.26	0.53	0.09	0.07	0.09
Indeno(1,2,3-cd)-pyrene	0.1	0.18	0.11	0.24	0.06	0.14	0.3	0.08	0.07	0.07
1-Nitro-naphthalene	15	20	37	16	15	15	22	23	26	17
2-Nitro-naphthalene	25	34	77	36	35	30	44	76	54	43
3-Nitro-phenanthrene	nd	0.73	0.4	0.57	0.32	0.91	1.05	0.79	0.48	0.35
9-Nitro-phenanthrene	nd	nd	0.1	nd	0.16	nd	nd	0.21	nd	0.12
9-Nitro-anthracene	nd	nd	0.6	nd	0.47	nd	nd	1.12	0.91	0.64
3-Nitro-fluoranthene	0.13	0.19	0.03	0.16	nd	0.15	0.2	0.14	0.1	0.08
1-Nitro-pyrene	0.68	0.64	0.22	0.59	0.2	0.64	0.86	0.39	0.27	0.3
4-Nitro-pyrene	0.07	0.08	0.07	0.06	nd	0.07	0.14	0.04	nd	nd

Pakbin et al. (2009) [Characterization of Particle Bound Organic Carbon from Diesel Vehicles Equipped with Advanced Emission Control Technologies, Environ. Sci. Technol.] studied the PAH emissions from heavy-duty diesel vehicles equipped with advanced emission control technologies on a chassis dynamometer. The chassis dynamometer experiments were carried out at California Air Resources Board's (CARB) Heavy-Duty Diesel Emission Testing Laboratory (HDETL) facility. Two different driving cycles were tested to emulate real-world driving conditions, including steady state cruise (80 km/h) and transient EPA urban chassis dynamometer driving schedule (UDDS) which represents city driving conditions. The exhaust emissions were diluted with filtered air, using activated carbon and high-efficiency particulate air (HEPA) filters through the CVS. The USC high volume sampler was placed approximately 18 diameter lengths downstream of the exhaust introduction in the CVS.

A 1998 Kenworth truck with an 11 L engine without any after-treatment emission control devices was tested as the baseline vehicle. The same truck was also tested with three different emission control technologies: a continuously regenerating technology (CRT) which consists of a diesel oxidation catalyst (DOC) followed by an uncatalyzed trap; CRT systems in combination with selective catalytic reduction system (SCRT) using zeolite and vanadium as catalysts. The test vehicles are referred to as baseline, CRT, V-SCRT and Z-SCRT. The nominal dilution air flow rate in the CVS was 2600 cfm (74 m^3/min) for both cruise and UDDS driving cycles. As result, dilution ratios were 6−9 for cruise and 5−80 for UDDS. The exhaust temperature at the sampling inlets of the CVS varied between 35 and 40 °C, which was very consistent during the experiments.

Particulate matter was collected on Teflon coated glass fiber filters (20 × 25 cm) (Pallflex Fiberfilm T60A20-8x10, Pall Corp., East Hills, NY) using a high-volume sampler operating at 450 Lpm. Samples were extracted in dichloromethane and methanol and were combined and reduced in volume to approximately 1 mL by rotary evaporation, followed by pure nitrogen evaporation. The underivatized samples were analyzed by auto injection into a GC/MSD system (GC model 5890, MSD model 5973, Agilent). A 30 m × 0.25 mm DB-5MS capillary column (Agilent) was used with a splitless injection. Along with the samples, a set of authentic quantification standard solutions were also injected and used to determine response factors for the compounds of interest. All the results were blank-corrected prior to data analysis and converted to mass of analyte per distance traveled.

Table 72: PAH emission factors (µg/km) at cruise driving cycle

Compound	V-SCRT µg/km	Z-SCRT µg/km	CRT µg/km	Baseline µg/km
Phenanthrene	N/A	0.0169	0.01	1.6
Anthracene	0.008	N/A	N/A	0.42
Fluoranthene	N/A	0.0025	0.003	3.17
Acephenanthrene	0.0111	N/A	N/A	1.68
Pyrene	0.0043	0.0029	0.011	8.99
Benzo(ghi)fluoranthene	N/A	0.0045	N/A	3.52
Cyclopenta(cd)pyrene	N/A	N/A	N/A	2.87
Benz(a)anthracene	N/A	0.0029	N/A	2.36
Chrysene	N/A	0.0083	0.018	3.43
Benzo(b)fluoranthene	N/A	N/A	N/A	1.2
Benzo(k)fluoranthene	N/A	N/A	N/A	0.86
Benzo(e)pyrene	N/A	N/A	N/A	1.59
Benzo(a)pyrene	N/A	N/A	N/A	3.82
Benzo(ghi)perylene	N/A	N/A	N/A	1.78

Table 73: PAH emission factors (µg/km) at UDDS driving cycle

Compound	V-SCRT µg/km	Z-SCRT µg/km	CRT µg/km	Baseline µg/km
Phenanthrene	N/A	0.0054	0.04	9.56
Anthracene	N/A	N/A	N/A	2.36
Fluoranthene	0.0023	0.0046	0.023	14.2
Acephenanthrene	N/A	0.0095	N/A	7.71
Pyrene	0.0013	0.0054	0.05	49.41
Benzo(ghi)fluoranthene	N/A	0.006	N/A	19.98
Cyclopenta(cd)pyrene	N/A	N/A	N/A	18.94
Benz(a)anthracene	N/A	0.0035	N/A	15.96
Chrysene	N/A	0.0066	0.082	20.44
Benzo(b)fluoranthene	N/A	N/A	N/A	12.58
Benzo(k)fluoranthene	N/A	N/A	N/A	7.94
Benzo(j)fluoranthene	N/A	N/A	N/A	3.5
Benzo(e)pyrene	N/A	N/A	N/A	17.72
Benzo(a)pyrene	N/A	N/A	N/A	17.1
Perylene	N/A	N/A	N/A	15.6
Indeno(1,2,3-cd)pyrene	N/A	N/A	N/A	2.65
Benzo(ghi)perylene	N/A	N/A	N/A	11.03

Mabilia et al. (2004) [Characterization of polycyclic aromatic hydrocarbons and carbonyl compounds in diesel exhaust emissions, Annali di Chimica] investigated the particle-phase PAH emissions collected from a recent model heavy duty diesel vehicle equipped with a catalytic converter. The vehicle was one of the city bus fleet used for public transportation in Milan.

An IVECO city bus provided by ATM (Milan) equipped with an 8.26 L diesel engine, giving a maximum effect of 165 kW at 1800 rpm, was tested in a fully instrumented chassis dynamometer. The engine was representative for heavy duty diesel vehicles in Europe and complied with the EURO-2 requirements. The driving cycle, developed by ATM, was a bus cycle simulating urban driving conditions. The duration of the cycle was 20 min and the covered distance was 4.9 km with average speed of 13.9 km/h and a top speed not exceeding 50 km/h.

Vehicle exhaust was sampled using a CVS system. A portion of the diluted exhaust cooled at 30°C was pulled through a cyclone separator and an ambient temperature Teflon-coated glass fiber filter (Pallflex T60A20), porosity 1μ m and 47 mm diameter, for collection of PM10 or PM2.5 in alternate runs. A sampling flow rate of 12 L min-1 was used corresponding to a face velocity of 20 cm s-1, so as to achieve a volume sampled of 240 L in each test. Sampling protocol comprised 30 repeated runs (15 for each particle size fraction).

The filters were Soxhlet extracted for 12 h with a dichloromethane-methanol (9:1) mixture. Before extraction, they were spiked with a perdeuterated PAH standard solution [fluoranthene, chrysene, perylene and benzo(ghi)perylene] to account for any losses of analytes during sample treatment. Each filter extract was concentrated to 5 mL using a Kuderna-Danish evaporator, added with 0.5 mL of cyclohexane and finally drawn to close dryness (~100 μ L) under nitrogen flow. PAHs were separated, identified and quantified using a HP-5890 gas chromatograph coupled to a

HP-5971A mass selective detector, both supplied by Hewlett Packard (Palo Alto, CA, USA). 1-μ L volume samples were injected in hot split-less mode, with the partitioning valve closed for 60 s. The separation capillary column was a DB-5S type (L = 30 m, i.d. = 250 μ m, film thickness = 0.25 μ m). Carrier gas was helium (0.5 mL min-1). The oven temperature was held at 90°C for 1 min, then programmed at 20°C min-1 up to 170°C, held for 2 min, raised to 280°C at 4°C min-1 and finally held for 25.5 min. Both injection port and liner of MS detector temperatures were set equal to 280°C. MS detection was operated in SIM mode; for each target PAH four ion current traces were selected, i.e. those corresponding to M/Z ratios equal to [M], [M-1], [M-2] and [M/2]. For quantitative determinations a set of standard mixtures of PAHs were spiked with the same perdeuterated solution used for samples and average response factors were calculated for all analytes with respect to the closest deuterated internal standards eluted in the chromatogram. Background contents of PAH in blank filters were negligible.

Table 74: Emission rates of PAHs (μg/km) found in respirable PM10 and fine PM2.5

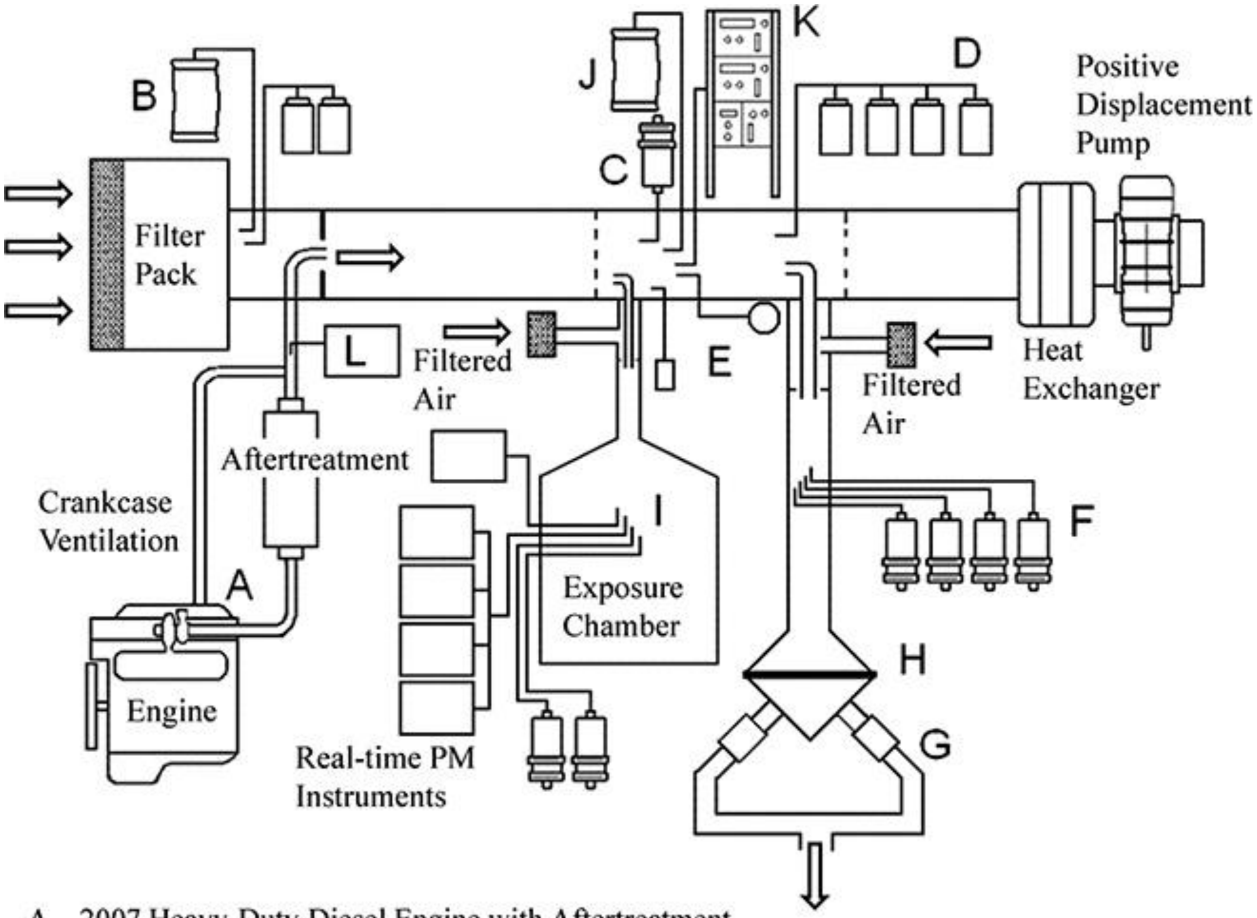
Compound (μg/km)	PM10	PM2.5
fluoranthene	44.4 ± 5.1	36.1 ± 3.5
pyrene	134.9 ± 13.4	120.8 ± 11.4
benzo(a)anthracene	6.2 ± 2.7	7.1 ± 1.4
chrysene	7.2 ±1.4	8.0 ± 2.0
benzo(b)fluoranthene	6.0 ± 2.4	7.3 ± 2.4
benzo(k)fluoranthene	1.4 ± 0.7	1.4 ± 0.4
benzo(e)pyrene	3.5 ± 0.6	5.4 ± 1.3
benzo(a)pyrene	0.9 ± 0.3	1.3 ± 0.5
indeno(1,2,3-cd)pyrene	0.5 ± 0.2	0.6 ± 0.3
dibenzo(a,h)anthracene	0.6 ± 0.5	0.7 ± 0.6
benzo(ghi)perylene	0.7 ± 0.3	1.2 ± 0.3

Khalek et al. (2011) [Regulated and Unregulated Emissions from Highway Heavy-Duty Diesel Engines Complying with U.S. Environmental Protection Agency 2007 Emissions Standards, Journal of the Air & Waste Management Association] investigated PAH, nitro-PAH, and oxygenated PAH emissions from heavy-duty diesel vehicles as part of the Advanced Collaborative Emissions Study (ACES) that was launched to fully characterize the emissions from four 2007 heavy-duty diesel engines.

The 2007 heavy-duty highway engines evaluated in the phase 1 ACES work were a Caterpillar C13 (430 hp), a Cummins ISX (455 hp), a Detroit Diesel Corporation series 60 (455 hp), and a Mack MP7 (395 hp) manufactured by Volvo. All engines were equipped with variable geometry turbochargers with water-cooled intake air systems. Three of the four engines were equipped with water-cooled high-pressure loop EGR systems in which the exhaust gas is routed from the exhaust manifold to the high-pressure side of the intake air compressor. The remaining engine was equipped with a low-pressure loop water-cooled EGR system in which the exhaust gas is routed from downstream of the C-DPF to the inlet side of the intake air compressor. Three of the four engines were equipped with a DOC followed by a C-DPF in the exhaust system. The C-DPF for each of these engines was actively regenerated or cleaned using diesel fuel injection into the exhaust stream upstream of the DOC. The fuel injected into the exhaust stream reacts with oxygen over the surface of the DOC, leading to an increase in exhaust temperature at the outlet of the DOC/inlet of C-DPF. One of the four engines was equipped with an exhaust diesel fuel burner that supplies a stream of hot exhaust. The burner stream is mixed with the main exhaust stream to elevate the temperature before entering the C-DPF to achieve soot oxidation similar to that of the other three engines. Testing was performed over the FTP cycle and over the 16-hr transient cycle developed by West Virginia University. The 16-hr cycle represents a more complete engine operation that includes C-DPF active regenerations. The 16-hr cycle consists of four 4-hr segments that are repeated 4 times. Each 4-hr segment is composed of three FTP transient cycles and several

California Air Resources Board (CARB) steady-state modes, including three creeps, four transients, two cruises, and four high-speed cruises.

The figure below shows the experimental setup:



A 2007 Heavy-Duty Diesel Engine with Aftertreatment

B Background bag sample of dilution air for CO, CO_2, NO_X, NO, THC, CH_4, and C_2-C_{12} speciation

C Regulated PM following CFR Part 1065 using 47 mm Teflo filter

D Impingers for carbonyls, alcohols, ions, and cyanide ion

E Sorbent traps for nitrosamines and Summa canister for SVOC

F Auxiliary PM samples on 47mm filters for inorganic ions (Fluoropore Filter), XRF (Teflo Filter), and ICP-MS (Fluoropore Filter), DFI/GC (TX-40 filter)

G XAD traps for gas phase semi-volatile compounds: PAH, oxyPAH, nitroPAH, hopanes, steranes, carpanes, polar organics, high molecular weight alkanes and cycloalkanes, dioxins, furans

H Filter (8x10 inch Zefluor) for particulate-phase semi-volatile compounds: PAH, oxyPAH, nitroPAH, dioxins, furans, hopanes, steranes, carpanes, polar organics, high molecular weight alkanes, and cycloalkanes, dioxins, furans

I Animal Exposure chamber (unoccupied) PM mass using Teflo filter, OC/EC collection using a pair of quartz filters, size and number using EEPS, real time total PM using DMM-230, real-time soot using MSS

J Proportional bag sample for hydrocarbon speciation of C_2 through C_{12} compounds

K Horiba MEXA 7200 for THC, CO, CO_2, NO_X , NO analyzer, and CH_4 analyzer

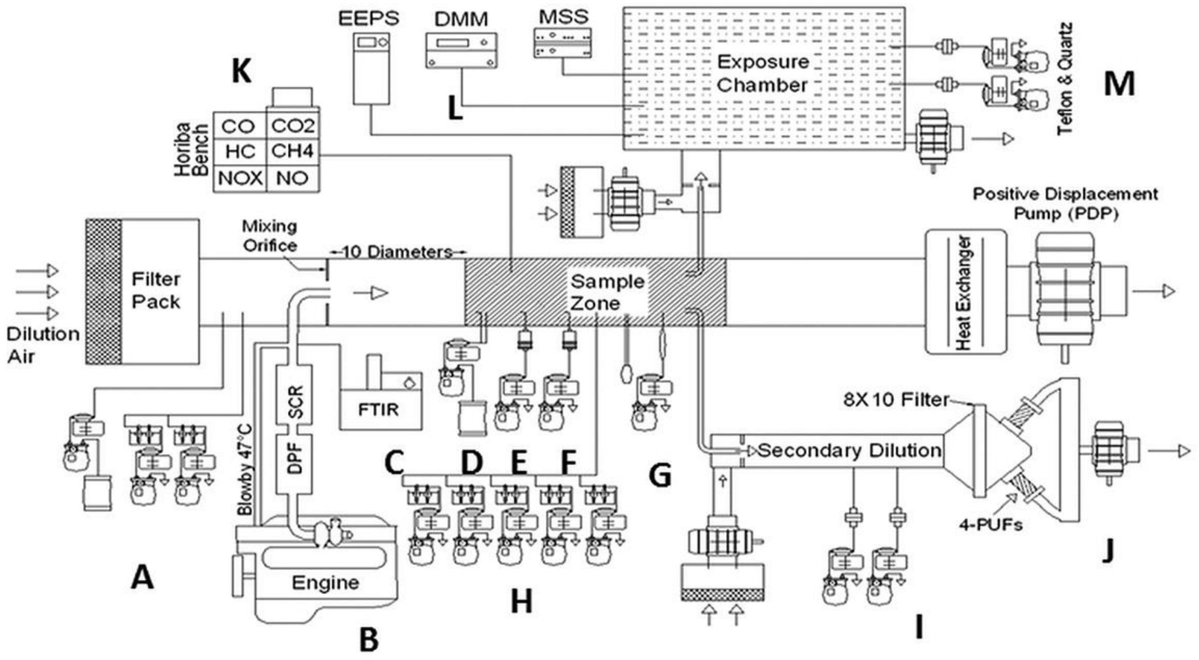
L FTIR for N_2O

Table 75: PAH and nitro-PAH average emissions (mg/bhp-hr) for all 12 repeats of the 16-hr cycles for all four engines

PAH and Nitro-PAH Compounds	2007 Engines (mg/bhp-hr)
Naphthalene	0.0982000±0.0423000
Acenaphthylene	0.0005000±0.0005000
Acenaphthene	0.0004000±0.0001000
Fluorene	0.0015000±0.0009000
Phenanthrene	0.0077000±0.0025000
Anthracene	0.0003000±0.0001000
Fluoranthene	0.0006000±0.0006000
Pyrene	0.0005000±0.000400
Benzo(a)anthracene	<0.0000001
Chrysene	<0.0000001
Benzo(b)fluoranthene	<0.0000001
Benzo(k)fluoranthene	<0.0000001
Benzo(e)pyrene	<0.0000001
Benzo(a)pyrene	<0.0000001
Perylene	<0.0000001
Indeno(123-cd)pyrene	<0.0000001
Dibenzo(ah)anthracene	<0.0000001
Benzo(ghi)perylene	<0.0000001
2-Nitrofluorene	0.00000360±0.00000410
9-Nitroanthracene	0.0000148±0.0000213
2-Nitroanthracene	0.00000040±0.00000090
9-Nitrophenanthrene	0.00002110±0.00002090
4-Nitropyrene	<0.0000001
1-Nitropyrene	0.00001970±0.00002430
7-Nitrobenz(a)anthracene	0.00000020±0.00000020
6-Nitrochrysene	<0.0000001
6-Nitrobenzo(a)pyrene	<0.0000001

Khalek et al. (2015) [Regulated and unregulated emissions from modern 2010 emissions-compliant heavy-duty on highway diesel engines, Journal of the Air & Waste Management Association] investigated the PAH and nitro-PAH emissions from three 2011 model-year heavy-duty on-highway diesel engines operated on an engine dynamometer. The engines used in this work were 2011 model-year six-cylinder in-line diesel engines that included a Cummins ISX (500 hp), a Detroit Diesel DD15 (455 hp), and a Mack MP8 (415 hp). All three engines are considered to be heavy heavy-duty on-highway diesel engines that are currently being marketed in the United States as compliant with the EPA 2010 emissions standards. All engines were equipped with turbochargers and water-cooled high-pressure loop exhaust gas recirculation (EGR) systems in which the exhaust is routed from the exhaust manifold to the high-pressure side of the intake air compressor. The induction system is air-to-air-cooled in truck operation, but was water-cooled in the laboratory setting used for this project. All three engines were equipped with exhaust NOX sensors for active NOX emissions control. Each of the three engines was equipped with an exhaust DOC followed by a catalyzed DPF followed by an SCR catalyst and an AMOX catalyst.

The exhaust sampling system was identical to that described by Khalek et al. (2011) for the 2007 technology engines. The experimental setup for the engine and sampling system is shown below:



A	Background bag sample of dilution air for CO, CO_2, Nox, No, total hydrocarbon, CH_4, and C_2-C_{12} speciation. Impingers for Carbon & Alcohol
B	2010 Heavy-Duty Diesel Engine with DPF-SCR
C	FTIR for NH_3 and N_2O measurements
D	Proportional bag sample for hydrocarbon speciation of C_2-C_{12} compounds
E	Regulated PM followed CFR Part 1065 using 47mm Teflo filter
F	90mm Zefluor filter system will be used for particle phase urea-related compounds (Urea, melamine, cyanuric acid, ammelide and ammeline
G	Sorbent traps for nitrosamines and Summa canister for SVOC
H	Impingers for carbonyls, alcohols, ions, and cyanide ion
I	Auxiliary PM samples on 47mm filters for inorganic ions (Floropore Filter), ICP-MS (Floropore Filter), DFI GC (TX-40 filter)
J	Filter (8"x10" Zefluor) for particulate-phase semi-volatile compounds: PAH, oxyPAH, nitroPAH, dioxins, furans, hopanes, steranes, carpanes, polar organics, high molecular weight alkines and cycloalkanes, dioxins, furans. XAD traps for gas phase semi-volatile compounds: PAH, oxyPAH, nitroPAH, hopanes, steranes, carpanes, polar organics, high molecular weight alkanes and cycloalkanes, dioxins, furans
K	Horiba MEXA 7200 for total hydrocarbon, CH_4, CO, CO_2, Nox, and NO measurements
L	PM mass size and number using EEPS, real time total PM using DMM-230, real time soot using MSS
M	PM mass using Teflo filter, OC/EC collection using a pair of quartz filters

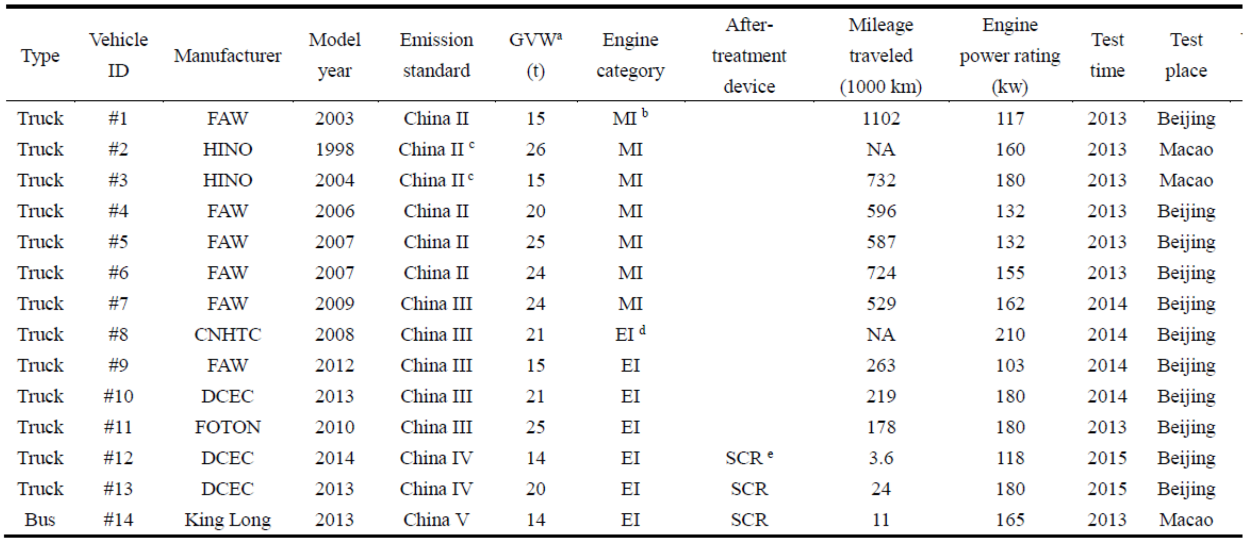
The three 2010-compliant engines were tested for regulated and unregulated emissions using the hot-start Federal Test Procedure (FTP) and the 16-hr transient cycle.

Table 76: PAH and nitro-PAH average emissions for all 12 repeats of the 16-hr cycles for all three 2010 engines

PAH and nitro-PAH compounds	2010-Technology engines, mg/bhp-hr
Naphthalene	0.0019050 ± 0.0013350
Acenaphthylene	0.0000397 ± 0.0000413
Acenaphthene	0.0000529 ± 0.0000349
Fluorene	0.0001217 ± 0.0000637
Phenanthrene	0.0004535 ± 0.0001218
Anthracene	0.0000207 ± 0.0000150
Fluoranthene	0.0000339 ± 0.0000053
Pyrene	0.0000233 ± 0.0000078
Benz[a]anthracene	0.0000030 ± 0.0000027
Chrysene	<0.0000001
Benzo[b + j + k] fluoranthene	0.0000004 ± 0.0000003
Dibenzo[a,e]pyrene	<0.0000001
Perylene	<0.0000001
Indeno[123-cd]pyrene	<0.0000001
Dibenzo[ah + ac] anthracene	<0.0000001
Benzo[ghi]perylene	0.0000002 ± 0.0000001
2- Nitrofluorene	<0.00000001
9-Nitroanthracene	0.00000050 ± 0.0000002
2-Nitroanthracene	<0.00000001
9-Nitrophenanthrene	0.00000020 ± 0.0000002
4-Nitropyrene	<0.00000001
1-Nitropyrene	<0.00000001
7-Nitrobenz[a]	<0.00000001
anthracene	
6-Nitrochrysene	<0.00000001
6-Nitrobenzo[a]pyrene	<0.00000001

Zheng et al. (2017) [Characterizing particulate polycyclic aromatic hydrocarbon emissions from diesel vehicles using a portable emissions measurement system, Scientific Reports] employed a PEMS system to collect real-world particle samples from diesel vehicles and characterize p-PAH emissions by gas chromatography-mass spectrometry (GC-MS). Fourteen in-use heavy-duty diesel vehicles (HDDVs) were recruited to measure the species-resolved p-PAH emissions under real-world driving conditions. These HDDVs were declared to comply with China I to China V standards and supposed to use improved engine and after-treatment technologies to meet the increasingly stringent emission limits.

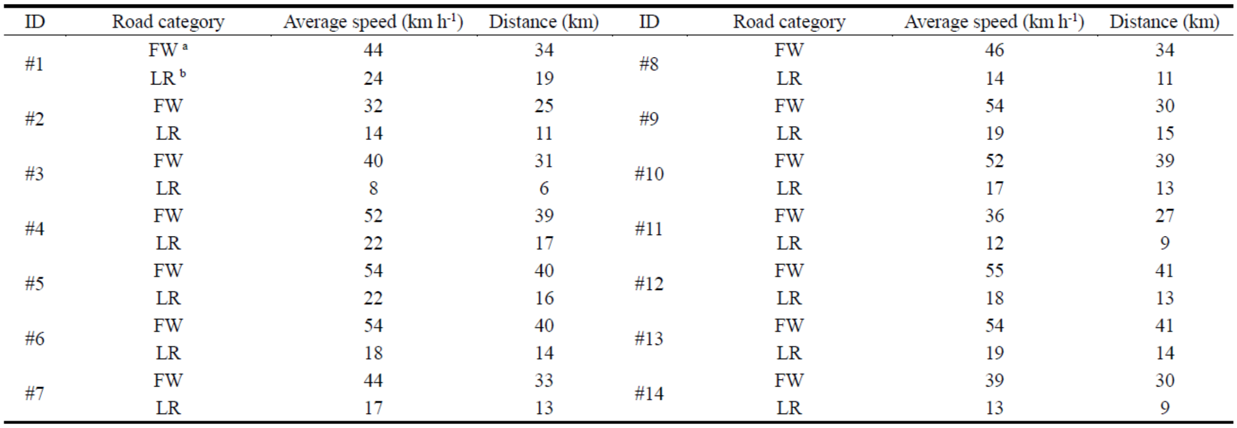
Fourteen in-use HDDVs, including 13 diesel trucks and 1 diesel transit bus were tested. These HDDVs covered a wide range of production years (1998 to 2014) and were declared by their manufacturers to comply with emission standards from China II to China V (equivalent to Euro II through Euro V). Thus, these vehicles could represent both older and modern generations of HDDVs in China. China IV and China V HDDVs are rapidly penetrating the diesel fleet in China and are required to use improved engine technologies (e.g., electronically controlled, high-pressure common rail fuel injection) to reduce DPM emissions and selective catalyst reduction (SCR) systems to control NOx emissions. Importantly, none of the HDDVs was equipped with a diesel particle filter (DPF) since the DPF is not a mandatory requirement for most HDDVs until the China VI stage. All six China II HDDVs (#1 to #6) and one China III HDDV (#7) were equipped with mechanical pump fuel injection engines (MI engines), which cannot control fuel injection as precisely as electronically controlled fuel injection engines (EI engines). The other seven HDDV samples (#8 to #14) were EI engines. The specifications of each vehicle are summarized below:



Type	Vehicle ID	Manufacturer	Model year	Emission standard	GVW[a] (t)	Engine category	After-treatment device	Mileage traveled (1000 km)	Engine power rating (kw)	Test time	Test place
Truck	#1	FAW	2003	China II	15	MI [b]		1102	117	2013	Beijing
Truck	#2	HINO	1998	China II [c]	26	MI		NA	160	2013	Macao
Truck	#3	HINO	2004	China II [c]	15	MI		732	180	2013	Macao
Truck	#4	FAW	2006	China II	20	MI		596	132	2013	Beijing
Truck	#5	FAW	2007	China II	25	MI		587	132	2013	Beijing
Truck	#6	FAW	2007	China II	24	MI		724	155	2013	Beijing
Truck	#7	FAW	2009	China III	24	MI		529	162	2014	Beijing
Truck	#8	CNHTC	2008	China III	21	EI [d]		NA	210	2014	Beijing
Truck	#9	FAW	2012	China III	15	EI		263	103	2014	Beijing
Truck	#10	DCEC	2013	China III	21	EI		219	180	2014	Beijing
Truck	#11	FOTON	2010	China III	25	EI		178	180	2013	Beijing
Truck	#12	DCEC	2014	China IV	14	EI	SCR [e]	3.6	118	2015	Beijing
Truck	#13	DCEC	2013	China IV	20	EI	SCR	24	180	2015	Beijing
Bus	#14	King Long	2013	China V	14	EI	SCR	11	165	2013	Macao

Note: [a]Gross vehicle weight; [b]Mechanical fuel injection system; [c]Approximate to the China II level; [d]Electronically-controlled fuel injection; eSelective catalytic reduction

The on-road tests were conducted in Beijing and Macao, China. The testing routes in the two cities both consisted of two road types with distinctive traffic conditions: local roads representing congested traffic conditions and urban freeways representing relatively medium and high-speed traffic conditions. Below is a summary of the average speed and distance (i.e., effective sampling distance) of each trip during which particle sampling was conducted:



ID	Road category	Average speed (km h^{-1})	Distance (km)	ID	Road category	Average speed (km h^{-1})	Distance (km)
#1	FW [a]	44	34	#8	FW	46	34
	LR [b]	24	19		LR	14	11
#2	FW	32	25	#9	FW	54	30
	LR	14	11		LR	19	15
#3	FW	40	31	#10	FW	52	39
	LR	8	6		LR	17	13
#4	FW	52	39	#11	FW	36	27
	LR	22	17		LR	12	9
#5	FW	54	40	#12	FW	55	41
	LR	22	16		LR	18	13
#6	FW	54	40	#13	FW	54	41
	LR	18	14		LR	19	14
#7	FW	44	33	#14	FW	39	30
	LR	17	13		LR	13	9

Note: [a]Freeways (no intersection or traffic signal light); [b] Local roads

The URG-2000-30FVT filter impactor was placed in the sampling system, which was heated to 47 ± 5 °C for the entire testing duration. For each vehicle, we used 47 mm quartz fiber filters (Pall

Corp., NY, U.S.) to separately collect the DPM samples on freeways and local roads. Prior to use, all the quartz fiber filters were baked in a muffle furnace (550 °C, 5 h). Before extraction, each filter was spiked with 50 ng of the internal standards (acenaphthylene-d8, phenanthrene-d10, fluoranthene-d10, pyrene-d10, benzo[a]anthracene-d10, benzo[a]pyrene-d12 and benzo[ghi]perylene-d12) and extracted in a Soxhlet extractor with 300 ml of a mixture of hexane and dichloromethane (1/1, v/v). The extracts were concentrated by rotary evaporation at 30 °C under vacuum to approximately 1–2 ml, followed by solvent exchange to hexane. Silica gel solid-phase extraction (SPE) cartridges (500 mg, 6 ml−1, Agilent Technologies) were employed to clean and fractionate the PAH compounds66. The SPE cartridges were eluted three times with 5 ml of a C6H12-CH2Cl2 mixture (85/15, v/v) at a flow rate of 2 ml/min. The eluate was concentrated to 2 ml by rotary evaporation and dried to 0.5 ml under a gentle stream of nitrogen.

An Agilent 7890 A/5975 C GC-MS system equipped with a DB-5MS column (30 m × 0.25 mm i.d. × 0.25 mm film thickness) was used to analyze the p-PAH contents. 50 ng of benzo[a]anthracene-d12 (AccuStandard) was added to the concentrates, of which 1 microliter was then injected into the GC-MS system. The oven temperature program was as follows: 50 °C for 5 min; increased to 200 °C at 19.5 °C min−1; increased to 240 °C at 4.5 °C min−1; and increased to 290 °C at 2.5 °C min−1, followed by a hold of 5 min. Electron impact ionization (EI) was used at 70 eV. Selected ion monitoring (SIM) mode was used for qualitative analysis. The ion source temperature was 250 °C, and the quadrupole temperature was 150 °C. The solvent delay was 4 mins. A series of certified standard mixtures (0.5–125 ng/mL, 15 priority PAHs) were used to quantify the PAH levels. The linear correlation coefficients (R) of the calibration were 0.9945 to 0.9999, and the recovery percentages of the internal standards were 79% to 89%. Finally, 15 U.S.

EPA priority PAHs, except for naphthalene, were analyzed in this study. Naphthalene was not analyzed because of its high volatility and difficult preservation.

Table 77: The detailed distance-based p-PAH emissions for each compound, unit in µg/km

ID	Road type	Ace	Acy	Fl	Phe	Ant	Flu	Pyr	BaA	Chr	BbF	BkF	BaP	DaA	InP	BghiP	Total
	FW	2.45	8.46	10.8	16.0	1.60	21.1	32.7	2.55	4.99	3.22	1.44	1.52	ND	0.79	2.08	110
1#	LR	4.09	19.8	26.5	25.2	2.82	22.0	32.1	2.51	6.89	6.50	2.77	ND	ND	ND	6.17	157
	FW	0.13	1.77	3.18	7.09	0.59	11.3	30.4	3.96	7.21	4.38	1.38	0.15	ND	1.48	2.48	75.6
2#	LR	1.49	6.80	10.5	18.9	2.08	13.8	22.9	5.37	8.99	8.81	3.50	6.86	ND	4.15	7.01	121
	FW	0.38	2.71	3.97	16.7	3.01	8.49	22.9	3.75	5.43	1.84	0.52	0.72	ND	ND	2.13	72.6
3#	LR	3.56	31.0	41.8	63.3	5.79	19.9	18.4	4.03	4.96	2.17	1.90	ND	ND	ND	3.29	200
	FW	3.78	1.74	1.68	12.1	0.65	6.37	6.74	0.63	1.64	2.11	0.83	ND	ND	ND	2.66	41.0
4#	LR	10.5	2.35	0.025	67.5	2.07	101	138	3.46	6.83	7.66	4.52	ND	ND	ND	8.35	352
5#	FW	0.34	0.44	2.20	19.4	2.81	19.5	46.4	1.48	2.44	ND	ND	0.31	ND	ND	0.77	96.1
	LR	1.38	1.23	10.9	63.5	8.19	71.6	134	10.1	15.2	12.3	5.04	3.52	ND	7.12	20.8	364
	FW	0.51	1.11	1.30	5.93	1.40	4.11	7.00	1.06	1.17	1.39	0.53	0.73	ND	ND	1.67	27.9
6#	LR	3.34	2.91	19.6	92.3	21.6	50.9	72.6	3.38	5.30	3.35	0.78	1.30	ND	ND	2.78	281
	FW	1.11	0.55	5.54	43.1	7.00	28.1	58.9	0.92	1.18	ND	ND	ND	ND	ND	ND	146
7#	LR	3.30	0.09	8.23	81.2	13.8	38.7	86.3	0.99	1.43	0.72	0.14	ND	ND	ND	ND	235
	FW	1.37	10.1	6.01	2.38	0.17	2.19	3.33	0.43	0.73	ND	ND	ND	ND	ND	ND	26.7
8#	LR	1.18	5.93	6.77	5.66	0.65	5.94	10.9	0.61	0.90	0.52	0.25	0.18	ND	ND	0.54	40.1
	FW	0.49	1.66	3.18	3.97	0.43	1.73	3.59	0.26	0.33	ND	ND	ND	ND	ND	0.72	16.4
9#	LR	1.63	6.67	11.1	12.9	1.50	5.32	5.99	0.46	1.06	1.60	0.56	ND	ND	ND	2.40	51.1
	FW	0.073	0.027	0.0053	3.19	0.43	2.14	4.03	0.27	0.42	0.41	0.07	ND	ND	ND	ND	11.0
10#	LR	2.49	4.04	7.78	5.73	0.81	2.25	3.09	0.48	0.52	1.49	1.60	ND	ND	ND	ND	30.3
	FW	0.62	0.44	3.76	5.29	1.29	3.61	6.78	0.11	0.10	ND	ND	ND	ND	ND	ND	22.0
11#	LR	0.65	1.49	6.13	8.04	1.14	6.23	11.3	0.12	0.19	ND	ND	ND	ND	ND	ND	35.3
	FW	0.14	0.63	0.98	2.30	0.26	2.93	10.4	0.14	0.31	ND	ND	ND	ND	ND	ND	18.1
12#	LR	1.14	5.62	6.72	6.13	0.58	2.19	5.08	0.17	0.45	ND	ND	ND	ND	ND	ND	28.1
	FW	0.38	2.39	2.57	4.63	0.43	2.32	5.64	0.26	0.45	ND	ND	ND	ND	ND	ND	19.1
13#	LR	0.95	8.07	7.55	8.13	0.68	5.39	14.6	0.52	0.71	ND	ND	ND	ND	ND	ND	46.6
	FW	0.071	0.50	0.69	3.23	0.39	2.52	3.28	0.03	0.05	ND	ND	ND	ND	ND	0.09	10.9

14#	LR	0.74	3.27	5.78	11.7	1.64	6.46	8.44	0.18	0.26	ND	ND	ND	ND	ND	ND	38.4

Note: Acenaphthylene (Acy); Acenaphthene (Ace); Fuorene (Fl); Phenanthrene (Phe); Anthracene (Ant); Fluoranthene (Flu); Pyrene (Pyr); Benzo[a]anthracene (BaA); Chrysene (Chr); Benzo[b]fluoranthene (BbF); Benzo[k]fluoranthene (BkF); Benzo[a]pyrene (BaP); Dibenzo[ah]anthracene (DaA); Indeno[123cd]pyrene (InP); Benzo[ghi)perylene (BghiP)

Table 78: The detailed fuel-based p-PAH emissions for each compound, unit in µg/kg

ID	Road type	Ace	Acy	Fl	Phe	Ant	Flu	Pyr	BaA	Chr	BbF	BkF	BaP	DaA	InP	BghiP	Total
	FW	20.1	69.7	89.2	132	13.2	174	269	21.0	41.1	26.5	11.8	12.5	ND	6.51	17.2	903
1#																	
	LR	51.4	249	332	317	35.5	276	403	31.5	86.4	81.6	34.8	ND	ND	ND	77.5	1975
	FW	0.51	7.12	12.8	28.5	2.37	45.5	122	15.9	29.0	17.6	5.56	0.62	ND	5.96	10.0	304
2#																	
	LR	4.40	20.0	31.0	55.7	6.12	40.5	67.6	15.8	26.5	26.0	10.3	20.2	ND	12.2	20.6	357
	FW	1.72	12.3	18.1	76.2	13.7	38.7	104	17.1	24.7	8.40	2.36	3.26	ND	ND	9.7	330
3#																	
	LR	12.0	105	141	214	19.6	67.1	62.1	13.6	16.8	7.34	6.42	ND	ND	ND	11.1	676
	FW	13.9	6.36	6.14	44.4	2.38	23.3	24.7	2.32	5.99	7.74	3.02	ND	ND	ND	9.7	150
4#																	
	LR	38.4	8.59	0.09	247	7.58	368	506	12.7	25.0	28.0	16.5	ND	ND	ND	30.6	1288
	FW	1.25	1.62	8.06	71.1	10.3	71.3	170	5.41	8.94	ND	ND	1.13	ND	ND	2.82	352
5#																	
	LR	5.03	4.52	40.0	232	30.0	261.9	489	36.9	55.6	45.1	18.5	12.9	ND	26.07	76.1	1334
	FW	1.85	4.07	4.75	21.7	5.12	15.0	25.6	3.88	4.28	5.08	1.92	2.69	ND	ND	6.12	102
6#																	
	LR	12.2	10.6	71.6	338	79.0	186	266	12.4	19.4	12.3	2.84	4.75	ND	ND	10.2	1025
	FW	7.11	3.50	35.3	275	44.7	180	376	5.85	7.51	ND	ND	ND	ND	ND	ND	934
7#																	
	LR	17.1	0.49	42.7	422	71.6	201	448	5.15	7.45	3.75	0.74	ND	ND	ND	ND	1220
	FW	12.6	92.0	55.0	21.7	1.60	20.1	30.5	3.95	6.65	ND	ND	ND	ND	ND	ND	244
8#																	
	LR	10.0	50.4	57.6	48.2	5.54	50.5	92.9	5.23	7.65	4.44	2.13	1.51	ND	ND	4.63	341
	FW	3.61	12.1	23.3	29.1	3.18	12.7	26.3	1.87	2.42	ND	ND	ND	ND	ND	5.27	129
9#																	
	LR	8.54	34.9	57.9	67.4	7.85	27.8	31.4	2.41	5.55	8.36	2.95	ND	ND	ND	12.6	268

	FW	0.05	0.18	0.04	21.5	2.90	14.4	27.1	1.81	2.80	2.76	0.44	ND	ND	ND	ND	74
10#																	
	LR	15.1	24.5	47.1	34.7	4.88	13.6	18.7	2.90	3.17	9.01	9.68	ND	ND	ND	ND	183
	FW	2.28	1.62	13.8	19.4	4.73	13.2	24.8	0.41	0.35	ND	ND	ND	ND	ND	ND	81
11#																	
	LR	2.37	5.45	22.4	29.4	4.16	22.8	41.4	0.43	0.70	ND	ND	ND	ND	ND	ND	129
	FW	1.92	8.47	13.2	31.0	3.54	39.4	139	1.93	4.20	ND	ND	ND	ND	ND	ND	243
12#																	
	LR	14.0	69.2	82.8	75.5	7.11	27.0	62.6	2.05	5.53	ND	ND	ND	ND	ND	ND	346
	FW	2.62	16.4	17.6	31.7	2.92	15.9	38.6	1.79	3.05	ND	ND	ND	ND	ND	ND	131
13#																	
	LR	4.81	40.8	38.2	41.1	3.44	27.3	74.0	2.63	3.59	ND	ND	ND	ND	ND	ND	236
	FW	0.30	2.14	2.94	13.7	1.65	10.7	13.9	0.11	0.22	ND	ND	ND	ND	ND	0.37	46
14#																	
	LR	3.48	15.4	27.2	54.8	7.73	30.4	39.7	0.86	1.22	ND	ND	ND	ND	ND	ND	181

Note: Acenaphthylene (Acy); Acenaphthene (Ace); Fuorene (Fl); Phenanthrene (Phe); Anthracene (Ant); Fluoranthene (Flu); Pyrene (Pyr); Benzo[a]anthracene (BaA); Chrysene (Chr); Benzo[b]fluoranthene (BbF); Benzo[k]fluoranthene (BkF); Benzo[a]pyrene (BaP); Dibenzo[ah]anthracene (DaA); Indeno[123cd]pyrene (InP); Benzo[ghi)perylene (BghiP)

Karavalakis et al. (2017) [Impact of biodiesel on regulated and unregulated emissions, and redox and proinflammatory properties of PM emitted from heavy-duty vehicles, Science of the Total Environment] investigated the particle-phase PAH emissions and toxicological properties of PM from two heavy-duty diesel vehicles operated on CARB ULSD and three biodiesel blends over the EPA Urban Dynamometer Driving Schedule (UDDS). The fuels used were a CARB ULSD, a 50% blend of waste cooking oil biodiesel (WCO-50), a 50% blend of soybean oil biodiesel (SME-50), and a 50% of animal fat biodiesel (AFME-50). Testing was conducted on a 2010 model year Cummins ISX-15 engine with cooled exhaust gas recirculation (EGR) and a turbocharger, at a rated horsepower of 344 kW at 1700 rpm, and on a 2002 model year Cummins ISX-450 engine with EGR at a rated horsepower of 336 kW at 1700 rpm. The vehicle with the Cummins ISX-450 engine was not equipped with aftertreatment control devices. The vehicle with the Cummins ISX-15 engine was equipped with SCR for NOx removal, and a diesel oxidation catalyst (DOC)/DPF for PM, CO, and THC removal.

Both vehicles on each fuel were tested over the EPA UDDS in triplicate. A double UDDS cycle was conducted for each of the three tests for the Cummins ISX-15 truck to obtain sufficient PM mass for gravimetric analysis. The vehicles were preconditioned at the start of each test day by performing a power map to bring the vehicle up to its operational temperature. A preconditioning UDDS was then performed on each fuel prior to beginning testing on each fuel. The preconditioning cycle warmed up both the vehicle and dynamometer to the conditions of the test configuration, thus reducing the emissions variability between tests. Between tests, there was a ‘hot soak’, where the engine was turned off for about 20 min. All tests were conducted as ‘hot running’ tests and the UDDS cycle was run on triplicate for each fuel.

PM chemical speciation was performed on samples collected in pre-weighed Zefluor reinforced Teflon filters (Pallflex, 8 x 10-inch, Pall Corp., East Hills, NY) using a high-volume sampler developed by USC (HI-Q Environmental Products Co., CA; flow rate = 450 L/min). PAHs were quantified by gas chromatography-mass spectrometry (GC-MS). Samples were extracted in dichloromethane and methanol and were combined and reduced in volume to approximately 1 mL by rotary evaporation, followed by pure nitrogen evaporation. The underivatized samples were analyzed by auto injection into a GC-MSD system (GC model 5890, MSD model 5973, Agilent). A 30 m x0.25 mm DB-5MS capillary column (Agilent) was used with a split-less injection. Along with the samples, a set of authentic quantification standard solutions were also injected and used to determine response factors for the compounds of interest.

Table 79: Emission rates of individual PAH compounds, expressed in mg/mile, of CARB ULSD and the biodiesel blends for both test vehicles

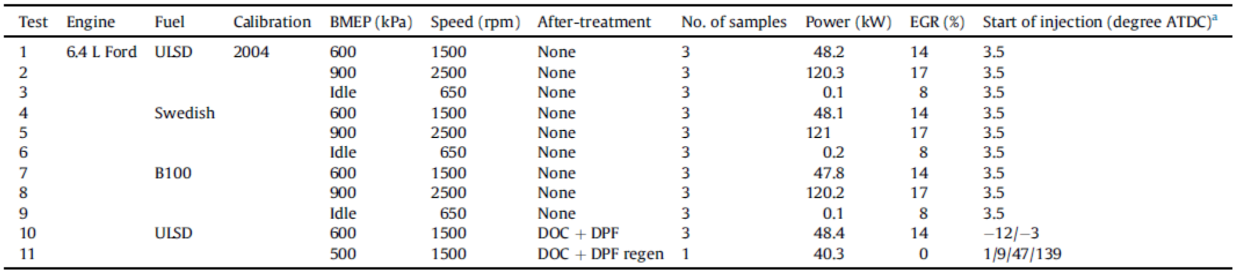
	CARB ULSD	SME-50	AFME-50	WCO-50
PAHs (mg/mile)	2002 Cummins ISX-450			
Phenanthrene	0.154±0.021	0.045±0.019	0.052±0.022	0.025±0.002
Anthracene	0.011±0.002	0.005±0.007	0.000±0.000	0.000±0.000
Fluoranthene	0.386±0.017	0.280±0.081	0.365±0.108	0.158±0.021
Acephenanthrene	0.021±0.004	0.019±0.012	0.000±0.000	0.000±0.000
Pyrene	0.610±0.046	0.431±0.205	0.383±0.046	0.223±0.053
Benzo(ghi)fluoranthene	0.124±0.019	0.128±0.039	0.225±0.039	0.090±0.011
Benz(a)anthracene	0.055±0.005	0.060±0.003	0.050±0.008	0.038±0.009
Chrysene	0.092±0.010	0.125±0.046	0.173±0.030	0.089±0.008

1-Methylchrysene	0.000±0.000	0.003±0.004	0.000±0.000	0.000±0.000
Retene	0.039±0.023	0.000±0.000	0.000±0.000	0.000±0.000
Benzo(b)fluoranthene	0.062±0.020	0.094±0.039	0.124±0.018	0.088±0.009
Benzo(k)fluoranthene	0.046±0.010	0.066±0.021	0.069±0.004	0.043±0.011
Benzo(j)fluoranthene	0.000±0.000	0.011±0.000	0.015±0.002	0.008±0.001
Benzo(e)pyrene	0.087±0.015	0.101±0.021	0.105±0.014	0.072±0.004
Benzo(a)pyrene	0.010±0.001	0.015±0.021	0.000±0.000	0.005±0.006
Perylene	0.013±0.003	0.018±0.003	0.022±0.003	0.010±0.001
Indeno(1,2,3-cd)pyrene	0.042±0.003	0.040±0.015	0.033±0.005	0.028±0.011
Benzo(ghi)perylene	0.103±0.028	0.064±0.048	0.047±0.010	0.038±0.024
Coronene	0.018±0.003	0.022±0.004	0.022±0.010	0.018±0.007
	2010 Cummins ISX-15			
Phenanthrene	0.0007±0.0010	0.0017±0.0025	0.0024±0.0021	0.0027±0.0014
Fluoranthene	0.0029±0.0016	0.0058±0.0064	0.0073±0.0053	0.0047±0.0015
Pyrene	0.0040±0.0030	0.0057±0.0067	0.0072±0.0040	0.0028±0.0039

Huang et al. (2015) [Effects of fuels, engine load and exhaust after-treatment on diesel engine SVOC emissions and development of SVOC profiles for receptor modeling, Atmospheric Environment] investigated the PAH and nitro-PAH emissions from a well-controlled bench test of a heavy-duty diesel engine. Emissions were tested at idle and two loaded conditions with three types of fuels, and with and without a DOC+DPF control.

The test engine is a Ford 2008 6.4 L “Power Stroke” engine manufactured by Navistar International Corporation (Lisle, IL) used in pick-up trucks, SUVs, vans, and school buses. This 8-cylinder, 32 valve common rail direct-injection engine is equipped with dual sequential turbocharging, cooled exhaust gas recirculation (EGR), and an EGR oxidation catalyst. Bore, stroke and compression ratio are 98.0 mm, 104.9 mm, and 16.7:1, respectively. Maximum power and torque are 261 kW at 3000 rpm and 880 Nm at 2000 rpm. Three fuels tested were mid-cetane U.S. specification ultralow sulfur conventional diesel (sulfur content <15 ppm), Swedish Environmental Class 1 (MK1) low sulfur and low aromatic diesel fuel (Swedish, sulfur content <10 ppm, aromatics <5% volume), and neat soy-based biodiesel (B100, 100% soy methyl ester).

For tests with aftertreatment, the engine was equipped with a 2008 Ford F250 production DOC (cordierite substrate) and catalyzed DPF system (silicon carbide substrate, 31 cells/cm2 (200 cpsi), wall thickness of 0.457mm (18 MIL), 42% porosity, 11 ± 2 mm pore size). Experiments used 11 test conditions described below. Tests 1-9 operated the engine without after-treatment using each fuel at idle, low-load (600 kPa BMEP at 1500 rpm), and high-load (900 kPa BMEP at 2500 rpm). Injection timing was set as at 3.5 degrees after top dead center (ATDC). Test 10 sampled tailpipe PM during DPF loading, and test 11 sampled tailpipe PM during DPF regeneration. DPF regeneration used four injections, including two very late injections that elevated engine-out hydrocarbon concentration to boost the temperature rise across the DOC. Except for condition 11, each test was run in triplicate, and three filter samples were collected sequentially.



Test	Engine	Fuel	Calibration	BMEP (kPa)	Speed (rpm)	After-treatment	No. of samples	Power (kW)	EGR (%)	Start of injection (degree ATDC)[a]
1	6.4 L Ford	ULSD	2004	600	1500	None	3	48.2	14	3.5
2				900	2500	None	3	120.3	17	3.5
3				Idle	650	None	3	0.1	8	3.5
4		Swedish		600	1500	None	3	48.1	14	3.5
5				900	2500	None	3	121	17	3.5
6				Idle	650	None	3	0.2	8	3.5
7		B100		600	1500	None	3	47.8	14	3.5
8				900	2500	None	3	120.2	17	3.5
9				Idle	650	None	3	0.1	8	3.5
10		ULSD		600	1500	DOC + DPF	3	48.4	14	−12/−3
11				500	1500	DOC + DPF regen	1	40.3	0	1/9/47/139

Exhaust PM was sampled using a partial flow dilution tunnel (BG-2, Sierra Instruments Inc., Monterey, CA, USA) at a flow rate of 10 L/min through a heated (191C) stainless steel sample probe (0.95-cm dia., 40-cm length) inserted into the center of a straight section of exhaust pipe, facing upstream, and 2 m downstream of the engine's turbine. The dilution tunnel, at the probe's end, mixed raw exhaust with filtered air (dilution ratio ¼ 6:1). The mixture then passed through a transfer tube (16 mm dia., 40 cm length) to a 2.5-mm cyclone separator (Sierra Instruments Inc., Monterey, CA, USA), a second transfer tube (16 mm i.d., 20 cm length), and to a Teflon filter cassette holder (Sierra Instruments Inc., Monterey, CA, USA) supporting a 47 mm PTFE-bonded glass fiber filter (Emfab™ TX40-HI20WW; Pall Corporation, Port Washington, NY, USA) on a perforated stainless steel backing plate. The exposed area of the filter was 39 mm in diameter. The transfer tubes, cyclone separator, and filter were maintained at 47 ± 5C, and the filter flow rate was 60 L/min (face velocity ¼ 91 cm/s).

Filters were extracted by placing each in a 50 mL centrifuge tube, adding 15 mL of the surrogate standard, adding 25 mL of dichloromethane/hexane (4:1, v/v) immersing the entire filter, and sonicating for 30 min (1510R-MTH, Branson Ultrasonics Corporation, Danbury, CT). The filter was then removed using a cotton stick and discarded. Extracts were passed through an activated Florisil column and fractionated into two portions: fraction A with 15 mL of hexane/acetone (1:1, v/v); and fraction B with 30 mL of methanol. Each fraction was evaporated under nitrogen gas to

0.25 mL. Fractions A and B were analyzed for PAHs and NPAHs, respectively. No additional cleaning of each fraction was necessary.15 mL of the IS was added to extracts using a 25 mL syringe prior to analysis. Target compounds were measured using a gas chromatography mass spectrometer (GC-MS; HP 6890/5973, Agilent Industries, Palo Alto, CA, USA), splitless 2 mL injections, and a capillary column (DB-5: 30 m x 0.25 mm id; film thickness 0.25 mm; J&W Scientific, Folsom, CA, USA). Injector and detector temperatures were 275C and 280C, respectively. The carrier gas was helium (flow of 1.5 mL/min, pressure of 37.4 kPa, average velocity of 31 cm/s), and the reagent gas for the MS detector, operated in the negative chemical ionization (NCI) mode for NPAHs, was ultra-high purity methane. The MS detector was operated in the electron impact (EI) mode for PAHs, hopanes and steranes. Each compound was quantified against authentic standards.

Table 80: Effect of fuel on PAH and nitro-PAH emissions

		Idle condition			Low-load condition			High-load condition		
		ULSD	**Swedish**	**B100**	**ULSD**	**Swedish**	**B100**	**ULSD**	**Swedish**	**B100**
PAHs	**NAP**	1.814	0.460	0.039	3.373	1.959	0.661	53.295	17.554	2.208
	ACY	0.133	0.036	0.003	0.397	0.148	0.036	3.708	1.015	0.185
	ACT	0.163	0.044	0.003	0.371	0.121	0.045	6.705	0.978	0.185
	FLU	0.011	0.006	0.000	0.034	0.013	0.007	0.701	0.172	0.022
	PHE	0.288	0.099	0.006	0.661	0.303	0.125	11.258	2.969	0.374
	ANT	0.193	0.092	0.006	0.384	0.255	0.125	6.957	2.757	0.334
	FLA	0.199	0.092	0.006	0.455	0.303	0.125	6.705	2.969	0.374
	PYR	0.252	0.099	0.006	0.539	0.347	0.129	6.226	3.573	0.334
	BAA	0.138	0.052	0.004	0.347	0.201	0.078	6.226	1.835	0.231
	CHR	0.143	0.056	0.004	0.359	0.195	0.078	6.705	1.768	0.222
	BBF	0.036	0.022	0.002	0.109	0.066	0.032	1.177	0.675	0.088
	BKF	0.007	0.008	0.001	0.026	0.017	0.009	0.402	0.199	0.022
	BAP	0.014	0.012	0.001	0.050	0.044	0.021	0.783	0.627	0.066
	IcdP	0.054	0.011	0.001	0.095	0.037	0.014	1.642	0.388	0.047
	DBA	0.056	0.022	0.001	0.106	0.066	0.029	1.704	0.727	0.088
	BghiP	0.044	0.019	0.001	0.063	0.024	0.025	2.561	0.651	0.076
NPAHs	**1-NNAP**	0.025	0.010	0.002	0.054	0.025	0.001	0.582	0.322	0.008
	2-NNAP	0.049	0.028	0.002	0.134	0.070	0.003	1.315	0.675	0.017
	2-NBPL	0.003	0.001	0.000	0.008	0.004	0.000	0.079	0.038	0.002
	3-NBPL	0.003	0.001	0.000	0.009	0.007	0.000	0.082	0.042	0.002
	4-NBPL	0.002	0.001	0.000	0.006	0.003	0.000	0.099	0.022	0.002
	5-NACT	<IDL	<IDL	0.008	<IDL	<IDL	<IDL	<IDL	<IDL	<IDL
	2-NFLU	0.012	0.004	0.001	0.023	0.007	0.003	0.240	0.073	0.017
	9-NANT	0.017	0.023	0.002	0.083	0.055	0.003	0.908	0.582	0.015
	9-NPHE	0.009	0.009	0.004	0.054	0.025	0.001	0.521	0.258	0.008

	1-NPYR	0.102	0.039	0.003	0.231	0.083	0.004	2.561	0.727	0.017
	6-NCHR	0.008	0.004	0.000	0.015	0.007	0.000	0.178	0.088	0.002

Note: Naphthalene (NAP); Acenaphthylene (Acy); Acenaphthene (Act); Fluorene (Flu); Phenanthrene (Phe); Anthracene (Ant); Fluoranthene (Fla); Pyrene (Pyr); Benzo[a]anthracene (BaA); Chrysene (Chr); Benzo[b]fluoranthene (BbF); Benzo[k]fluoranthene (BkF); Benzo[a]pyrene (BaP); Dibenzo[ah]anthracene (DaA); Indeno[123cd]pyrene (IcdP); Benzo[ghi)perylene (BghiP); 1-nitronaphthalene (1-nnap); 2- nitronaphthalene (2-nnap); 2-nitrobiphenyl (2-nbpl); 3-nitrobiphenyl (3-nbpl); 4-nitrobiphenyl (4-nbpl); 5-nitroacenaphthene (5-nact); 2-nitrofluorene (2nflu); 9-nitroanthracene (9-nant); 9-nitrophenanthrene (9-nphe); 1-nitropyrene (1-npyr); 6-nitrochrysene (6-nchr)

4. Light-Duty Gasoline and Diesel Vehicles and Engines

This chapter discusses the PAH and nitro-PAH emissions from light-duty diesel and light-duty gasoline vehicles and engines. The majority of peer-reviewed papers have been conducted on diesel engines or vehicles with and without aftertreatment emission controls. Most of these studies have been conducted on engines and vehicles operated on alternative fuel formulations, such as biodiesel blends. The gasoline studies have been conducted on current GDI engines when operated on conventional gasoline fuels or on alcohol blends. The findings presented here reveal that gasoline engines produce higher concentrations of PAH emissions compared to diesel engines. Also, GDI engines form substantially higher concentrations of PAH emissions compared to the traditional PFI engines. Finally, this chapter shows that the use of aftertreatment controls (i.e., DPF or GPF) provides significant PAH emissions reductions.

Ballesteros et al. (2009) [Determination of PAHs in diesel particulate matter using thermal extraction and solid phase micro-extraction, Atmospheric Environment] measured PM-associated PAH emissions generated by a 4-cylinder, 4-stroke, turbocharged, intercooled, 2.2 L Nissan diesel engine connected to an asynchronous electric brake from Schenck. The operating modes were selected among the collection of steady stages which reproduce the transient cycle that the vehicles with this type of engine must follow according to the European Emission Directive 70/220, amendment 2001/C 240 E/01. Two extreme modes were chosen, an urban mode (U) and an extra-urban mode (EU).

Table 81: Specific PAH emissions of the diesel fuel for an urban and an extra-urban operating mode

PAH (μg/kWh)	Mode	
	Urban	Extra-Urban
Naphthalene	223.404	131.206
Acenaphthylene	4.409	1.527
Acenaphthene	3.161	2.043
Fluorene	6.366	2.301
Phenanthrene	4.624	1.892
Anthracene	2.430	0.602
Fluoranthene	1.226	0.473
Pyrene	328.369	146.809
Benzo[a]anthracene	229.078	81.560
Chrysene	186.525	48.936
Benzo[b]fluoranthene + Benzo[k]fluoranthene	234.752	67.376
Benzo[a]pyrene	214.894	29.078
Dibenzo[ah]anthracene + Indeno[123cd]pyrene	187.943	115.603
Benzo[ghi)perylene	159.574	254.610

Ballesteros et al. (2010) [An experimental study of the influence of biofuel origin on particle-associated PAH emissions, Atmospheric Environment] evaluated PAH emissions from different biodiesel fuels and their blends with conventional diesel using a 4-cylinder, 4-stroke, turbocharged, intercooled, 2.2l Nissan diesel engine without any after treatment system. The operating modes were selected among the collection of steady stages which reproduce the transient cycle that the vehicles with this type of engine must follow according to the European Emission Directive 70/220, amendment 2001/C 240 E/01. Fuels tested included methyl esters of rapeseed oil (RSM) and waste cooking oil (WCOM), and ethyl esters of waste cooking oil (WCOE). Additionally, a reference fuel (REF) was tested to evaluate the difference in PAHs emissions between these alternative fuels and those coming from conventional diesel fuel.

The method used for PAH speciation combined thermal extraction of particle matter with solid phase micro-extraction (SPME) before analysis by means of gas chromatography–mass spectrometry (GC–MS). Filters used in this study (glass microfiber filters, 70 mm diameter, Whatman) were stored in a climatic chamber (Minitest CCM 0/81, Dicometal) at 22 °C and 45% relative humidity and weighed before sampling in a microbalance. For the particles collection, the filters were introduced, one at a time, into the partial dilution minitunnel (Nova Mess-Technik). After sampling, filters were weighed again and stored at −15 °C protected from light until thermal extraction.

Then a fraction of the filter is cut with scissors, folded with tweezers and placed into the thermogravimetric analyzer (TGA) pan (TGA Q5000, TA Instruments). Afterward, a solution of internal standards (Semivolatile Internal Standards mix, Supelco), used for quantification purposes, is added and the thermal program of the TGA is started. When the initial temperature of 170 °C is reached, the exhaust gas outlet of the TGA furnace is connected to the inlet port of a Tedlar® bag (18 in × 18 in, Alltech) by means of a transfer line. The transfer line and Tedlar® bag are disconnected once the test is finished. Subsequently, the needle containing the coated fibre of SPME (SPME fibre PDMS 100 μm, Supelco) is injected in the septum port of the Tedlar® bag, the fibre is exposed and PAHs are distributed between the gas in the bag and the coating.

Following the SPME, the fibre is retracted in the needle and introduced into the injection port of the GC (GC–MS QP5000, Shimadzu), where it is immediately exposed. The desorption temperature, which is the GC injector temperature, is set within the range recommended by the manufacturer (270 °C), needle exposure depth is held constant and adjusted to place the fibre in the center of the hot zone of the injector. Desorption time was adjusted to 20 min to guarantee complete extraction of the compounds. The GC–MS analytical conditions were chosen according to the recommendations for determination of PAHs in ambient air, as specified in US EPA, 1999. All analyses were conducted on a Supelco SLB™-5ms column of 30 m × 0.25 mm × 0.25 µm film thickness (bonded and highly crosslinked, silphenylene polymer virtually equivalent in polarity to poly (5% diphenyl/95% (dimethyl) siloxane phase). Since there are many interfering compounds in the DPM which could add considerable noise to the results, all analysis was performed in the selected ion monitoring mode (SIM) of the MS in order to enhance the selectivity and sensitivity of the method.

Table 82: PAH emissions in urban mode for RSM fuels (µg/kWh)

PAH (µg/kWh)	REF	RSM30	RSM70	RSM100
Naphthalene	226.54	125.45	184.54	49.52
Acenaphthylene	4.67	4.55	3.83	1.64
Acenaphthene	3.40	1.53	1.34	0.98
Fluorene	6.92	7.17	6.26	1.53
Phenanthrene	4.87	3.05	2.38	2.45
Anthracene	2.69	4.21	4.45	1.18
Fluoranthene	1.42	N/A	N/A	N/A
Pyrene	340.56	72.56	N/A	N/A
Benzo[a]anthracene	240.90	153.23	128.75	66.03
Chrysene	204.24	168.55	171.19	56.51
Benzo[b]fluoranthene + Benzo[k]fluoranthene	251.12	152.29	105.25	71.82
Benzo[a]pyrene	234.90	97.62	98.01	78.04
Dibenzo[ah]anthracene + Indeno[123cd]pyrene	209.58	67.83	N/A	N/A
Benzo[ghi)perylene	182.12	103.51	N/A	N/A

Table 83: PAH emissions in extra-urban mode for RSM fuels (µg/kWh)

PAH (µg/kWh)	REF	RSM30	RSM70	RSM100
Naphthalene	137.21	245.57	257.63	23.66
Acenaphthylene	2.11	1.98	1.88	0.46
Acenaphthene	2.71	0.84	0.80	0.57
Fluorene	2.57	2.07	2.11	0.40
Phenanthrene	2.24	0.90	0.76	0.36

Anthracene	1.05	1.26	1.18	0.36
Fluoranthene	0.49	N/A	N/A	N/A
Pyrene	151.25	24.07	24.27	12.53
Benzo[a]anthracene	87.01	35.40	23.69	N/A
Chrysene	55.37	25.94	N/A	11.52
Benzo[b]fluoranthene + Benzo[k]fluoranthene	77.09	62.48	24.14	31.68
Benzo[a]pyrene	41.01	21.95	22.14	22.27
Dibenzo[ah]anthracene + Indeno[123cd]pyrene	126.41	62.92	N/A	N/A
Benzo[ghi)perylene	174.78	46.07	N/A	N/A

Table 84: PAH emissions in urban mode for WCOM fuels (µg/kWh)

PAH (µg/kWh)	REF	RSM30	RSM70	RSM100
Naphthalene	227.64	804.34	784.49	430.06
Acenaphthylene	4.83	8.95	9.49	18.26
Acenaphthene	3.27	5.48	3.69	55.54
Fluorene	6.85	8.22	5.24	22.37
Phenanthrene	5.00	55.29	31.04	15.60
Anthracene	2.60	55.12	35.28	24.25
Fluoranthene	1.17	7.08	8.45	9.28
Pyrene	330.00	259.53	70.19	63.55
Benzo[a]anthracene	228.58	74.46	59.03	125.04
Chrysene	191.00	109.53	74.28	162.30
Benzo[b]fluoranthene + Benzo[k]fluoranthene	234.87	102.78	87.33	76.30
Benzo[a]pyrene	214.91	60.80	111.38	51.92
Dibenzo[ah]anthracene + Indeno[123cd]pyrene	192.75	98.06	190.47	42.96
Benzo[ghi)perylene	163.97	97.89	298.17	36.20

Table 85: PAH emissions in extra-urban mode for WCOM fuels (µg/kWh)

PAH (µg/kWh)	REF	RSM30	RSM70	RSM100
Naphthalene	141.62	137.47	467.81	288.09
Acenaphthylene	2.05	8.66	12.10	9.53
Acenaphthene	2.68	7.68	1.04	0.53
Fluorene	2.58	14.97	10.68	0.42
Phenanthrene	2.15	24.83	22.26	1.08
Anthracene	1.08	28.82	36.94	3.13
Fluoranthene	0.53	15.92	20.98	1.71

Pyrene	165.98	71.78	52.37	39.25
Benzo[a]anthracene	98.00	46.71	70.05	36.84
Chrysene	71.50	42.97	49.56	31.82
Benzo[b]fluoranthene + Benzo[k]fluoranthene	90.67	86.43	74.89	32.61
Benzo[a]pyrene	51.81	65.99	97.16	38.08
Dibenzo[ah]anthracene + Indeno[123cd]pyrene	139.69	N/A	68.94	46.66
Benzo[ghi)perylene	189.45	81.61	112.68	45.88

Table 86: PAH emissions in urban mode for WCOE fuels (μg/kWh)

PAH (μg/kWh)	REF	RSM30	RSM70	RSM100
Naphthalene	223.25	863.13	346.91	896.68
Acenaphthylene	4.76	31.57	18.90	7.35
Acenaphthene	3.23	24.15	4.22	9.11
Fluorene	6.87	23.41	6.57	19.57
Phenanthrene	4.86	66.55	16.36	25.37
Anthracene	2.51	5.62	2.27	N/A
Fluoranthene	1.39	1.86	0.80	1.68
Pyrene	340.84	154.35	218.39	N/A
Benzo[a]anthracene	239.03	43.66	151.71	206.88
Chrysene	196.42	7.49	111.27	131.41
Benzo[b]fluoranthene + Benzo[k]fluoranthene	250.65	46.49	132.54	42.68
Benzo[a]pyrene	232.25	45.67	81.17	N/A
Dibenzo[ah]anthracene + Indeno[123cd]pyrene	205.11	N/A	111.12	N/A
Benzo[ghi)perylene	177.94	246.35	257.65	244.76

Table 87: PAH emissions in extra-urban mode for WCOE fuels (μg/kWh)

PAH (μg/kWh)	REF	RSM30	RSM70	RSM100
Naphthalene	146.21	292.15	139.01	100.41
Acenaphthylene	2.08	20.37	3.01	10.16
Acenaphthene	2.73	11.94	3.08	2.49
Fluorene	2.54	12.52	3.04	2.61
Phenanthrene	2.24	13.04	1.81	3.45
Anthracene	1.08	0.97	0.46	0.61
Fluoranthene	0.48	0.85	0.10	0.16
Pyrene	152.94	77.13	31.11	16.32
Benzo[a]anthracene	83.50	52.37	24.19	15.38

Chrysene	57.25	20.15	20.28	18.89
Benzo[b]fluoranthene + Benzo[k]fluoranthene	72.65	N/A	53.54	N/A
Benzo[a]pyrene	38.97	N/A	18.35	N/A
Dibenzo[ah]anthracene + Indeno[123cd]pyrene	121.34	N/A	26.31	N/A
Benzo[ghi)perylene	170.98	267.83	65.56	144.55

Chiang et al. (2012) [Pollutant constituents of exhuast emitted from light-duty diesel vehicles, Atmospheric Environment] measured the PAH and nitro-PAH emission factors from six in-use light-duty diesel vehicles. All vehicles were without catalyst and mileage ranged from 56,000 to 160,000 km. All vehicles were tested over the FTP-75 cycle.

A dilution tunnel and a monitoring system were installed downstream of the diesel exhaust to supply air for dilution and to measure particles and gas pollutants. A cascade impactor (Graseby Anderson Mark III) with quartz filters (with diameters of 64 mm, Pallflex, Pall Corporation, USA) was installed downstream of the dilution tunnel to collect size-resolved samples. These impactors can effectively separate the particulate matter into eight size ranges with the following equivalent cut-off diameters: 6.6–10.5 (stage 8), 4.4–6.6 (stage 7), 3.1–4.4 (stage 6), 1.9–3.1 (stage 5), 1.0–1.9 (stage 4), 0.6–1.0 (stage 3), 0.4–0.6 (stage 2), and <0.4 μm (stage 1). A linear interpolation method was employed to determine the mass concentration of PM2.5 and PM10. All quartz filters were baked at 900 °C for 3 h before use to ensure low concentrations of organic compounds on the blank filter materials. In addition, polyurethane foam (PUF) and an XAD-16 resin backup cartridge were utilized to collect PAHs in the vapor phase, which is connected after the particle sampling system.

Combination samples of PUF and XAD-16 resin were extracted in an all-glass Soxhlet system combined with an electro-thermal heating plate. The samples were extracted for 16 h with 300 ml of mixed solvent (dichloromethane-acetonitrile 3:1, by volume) in a 500-ml flat-bottom flask. The filters (cut size was larger than 1.9 μm) were mixed as one sample for consideration of low PAH content in large particles to ensure that the concentration was higher than the method detection limitation. Samples of quartz filter were extracted using sonication with the above solvent three times (3 × 40 = 120 ml) for periods of 15 min. The temperature of the sonication bath was maintained between 25 and 30 °C. The extracts from the various procedures were concentrated on a rotary evaporator (EYELA, Japan) equipped with a water bath held at 40 °C, and the solution volume was reduced to 1–2 ml. In the cleanup process, the residual solution was introduced into a silica column (1 cm internal diameter and 25 cm length), and the column was first eluted with 10 ml of n-hexane. About 2 cm height of anhydrous sodium sulfate was packed at the fore-end of the cleanup column to exclude water. The n-hexane fraction was discarded, and the available fractions were then obtained by elution with 20 ml of dichloromethane-hexane 1:2 and 30 ml of acetone-hexane 1:2. The last two fractions were combined and concentrated just to dryness, then quantified to 2 ml (PUF+XAD-16) or 1 ml (quartz filter) with solvent acetone-hexane 1:2. The final solutions were analyzed with the gas chromatography (GC) method.

PAHs were analyzed by GC–MS. The GC apparatus consisted of a Hewlett–Packard GC 6890 equipped with a mass (5973 N) and split/splitless injector. An HP-5MS capillary column (5% phenyl methyl siloxane, 30 m, internal diameter 0.32 mm, and film thickness 0.25 μm) was used. The injector program was set to 280 °C at the pulsed splitless mode (12 psi for 1 min). The oven temperature program was 60 °C for 1 min, 35 °C min^{-1} to 170 °C, 8 °C min^{-1} to 210 °C, 4 °C min^{-1} to 300 °C, and 15 °C min^{-1} to 320, which was held for 3 min. The carrier gas (99.9995% nitrogen) flow rate was held at 1.5 ml min−1. A mass selective detector (MSD) was operated in selected ion monitoring (SIM) mode, with the electron energy at 70 eV, the electron ionization (EI) source held at 175 °C and the interface temperature at 300 °C.

To analyze the nitro-PAHs, a 63Ni electron-capture detector (ECD) was used for GC-ECD analysis under the same conditions as the PAH analyses. The ECD temperature was 300 °C, and the total gas flow rate was 30 ml min^{-1} (makeup plus column). In a preliminary investigation for the above conditions, these PAHs and nitro-PAHs have a completely isolated chromatogram with retention time ranging from 4.66 to 27.39 min. The mixed stock solution was used to make five concentrations of mixed standard solution, which was required to establish calibration curves for PAH and nitro-PAH measurement. The injection volume was 1 μl for all samples. The spike was added to the blank sampling PUF+XAD-16 and quartz filter prior to extraction for recovery analysis. The average recovery of PAHs based on QA/QC ranged from 68% (naphthalene) to 93% (pyrene) and 71% (naphthalene) to 94% (Benzo(g,h,i)perylene) for the PUF+XAD-16 and quartz filter samples, respectively. The nitro-PAHs had lower average recoveries for the PUF+XAD-16 and quartz filter samples, which ranged from 59% (1,3-Dinitropyrene) to 87% (2-Nitrofluorene) and 61% (1,8-Dinitropyrene) to 89% (3-Nitrofluoranthene), respectively.

Table 88: PAH emission factors of light-duty diesel vehicle exhaust in mg/km

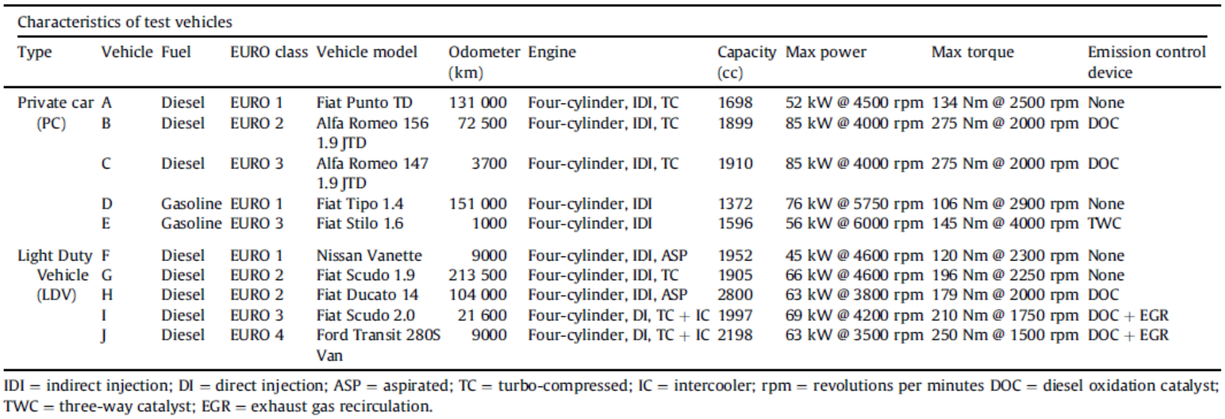
PAH (mg/km)	Gas-phase	PM 2.5	Pm 2.5-10
Naphthalene	0.015	0.294	0.730
Acenaphthylene	0.160	0.321	0.202
Acenaphthene	0.020	0.087	0.066
Fluorene	0.120	0.113	0.036
Phenanthrene	0.014	0.096	0.017
Anthracene	0.016	0.091	0.089
Fluoranthene	0.055	0.302	0.013
Pyrene	0.034	0.087	0.074
Benzo[a]anthracene	n/a	n/a	n/a
Chrysene	n/a	n/a	n/a

Benzo[b]fluoranthene	0.018	0.006	0.011
Benzo[k]fluoranthene	0.016	0.015	0.013
Benzo[a]pyrene	0.025	0.017	n/a
Indeno[123cd]pyrene	0.023	0.074	n/a
Dibenzo[ah]anthracene	0.025	0.017	n/a
Benzo[ghi)perylene	0.028	0.015	n/a

Table 89: Nitro-PAH emission factors of light-duty diesel vehicle exhaust in mg/km

PAH (mg/km)	Gas-phase	PM 2.5	Pm 2.5-10
2-Nitrofluorene	0.0039	0.0336	0.0022
9-Nitroanthracene	N/A	0.0010	0.0007
3-Nitrofluoranthene	N/A	0.0021	0.0007
1-Nitropyrene	N/A	0.0056	0.0003
7-Nitrobenzo(a)anthracene	0.0034	0.0033	0.0063
6-Nitrochrysene	N/A	0.0015	0.0007
1,3-Dinitropyrene	N/A	0.0015	0.0007
1,6-Dinitropyrene	0.0055	0.0337	0.0007
1,8-Dinitropyrene	N/A	0.0170	0.0021
6-Nitrobenzo(a)pyrene	N/A	0.0070	0.0008

Perrone et al. (2014) [Exhaust emissions of polycyclic aromatic hydrocarbons, n-alkanes and phenols from vehicles coming within different European classes, Atmospheric Environment] measured PM-phased PAH emissions from vehicles of different Euro class and fuel type using a chassis dynamometer. The types of vehicles are shown below.



Characteristics of test vehicles

Type	Vehicle	Fuel	EURO class	Vehicle model	Odometer (km)	Engine	Capacity (cc)	Max power	Max torque	Emission control device
Private car (PC)	A	Diesel	EURO 1	Fiat Punto TD	131 000	Four-cylinder, IDI, TC	1698	52 kW @ 4500 rpm	134 Nm @ 2500 rpm	None
	B	Diesel	EURO 2	Alfa Romeo 156 1.9 JTD	72 500	Four-cylinder, IDI, TC	1899	85 kW @ 4000 rpm	275 Nm @ 2000 rpm	DOC
	C	Diesel	EURO 3	Alfa Romeo 147 1.9 JTD	3700	Four-cylinder, IDI, TC	1910	85 kW @ 4000 rpm	275 Nm @ 2000 rpm	DOC
	D	Gasoline	EURO 1	Fiat Tipo 1.4	151 000	Four-cylinder, IDI	1372	76 kW @ 5750 rpm	106 Nm @ 2900 rpm	None
	E	Gasoline	EURO 3	Fiat Stilo 1.6	1000	Four-cylinder, IDI	1596	56 kW @ 6000 rpm	145 Nm @ 4000 rpm	TWC
Light Duty Vehicle (LDV)	F	Diesel	EURO 1	Nissan Vanette	9000	Four-cylinder, IDI, ASP	1952	45 kW @ 4600 rpm	120 Nm @ 2300 rpm	None
	G	Diesel	EURO 2	Fiat Scudo 1.9	213 500	Four-cylinder, IDI, TC	1905	66 kW @ 4600 rpm	196 Nm @ 2250 rpm	None
	H	Diesel	EURO 2	Fiat Ducato 14	104 000	Four-cylinder, IDI, ASP	2800	63 kW @ 3800 rpm	179 Nm @ 2000 rpm	DOC
	I	Diesel	EURO 3	Fiat Scudo 2.0	21 600	Four-cylinder, DI, TC + IC	1997	69 kW @ 4200 rpm	210 Nm @ 1750 rpm	DOC + EGR
	J	Diesel	EURO 4	Ford Transit 280S Van	9000	Four-cylinder, DI, TC + IC	2198	63 kW @ 3500 rpm	250 Nm @ 1500 rpm	DOC + EGR

IDI = indirect injection; DI = direct injection; ASP = aspirated; TC = turbo-compressed; IC = intercooler; rpm = revolutions per minutes DOC = diesel oxidation catalyst; TWC = three-way catalyst; EGR = exhaust gas recirculation.

Each vehicle was tested following the same standardized format, involving three separated driving cycles: the non-conventional Intense Traffic (IT) mode, designed to simulate congested urban traffic; the conventional EU standard Urban Driving Cycle (UDC), for flowing, less intense urban traffic; the conventional EU standard Extra-Urban Driving Cycle (EUDC), simulating extra urban traffic characterized by the highest mean and maximum drive speeds. All vehicles (PCs and LDVs) were tested under warm start conditions for the IT, UDC and EUDC cycles, while the LDVs were also tested under cold start conditions for the UDC and EUDC cycles.

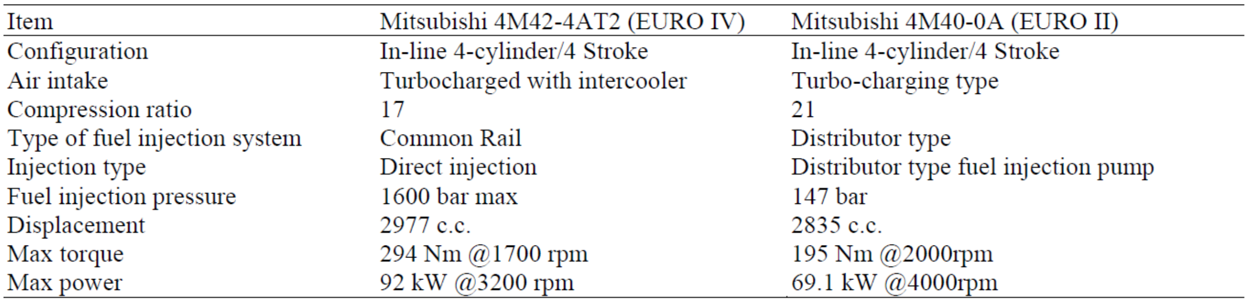
Vehicle exhaust emissions were mixed with clean filtered air in a dilution tunnel, with a dilution ratio (DR) of 1:10. Exhaust samples were collected downstream of the dilution tunnel, under isokinetic sampling conditions, with air temperature of around 40 °C at the sampling point. Particles were sampled with a 10 µm cut-size cyclone to determine the PM10 fraction. The sampling flow rate was constant (15 L min^{-1}), and PM10 was collected on PTFE filters (Ø = 47 mm, 2 µm pore size; Pall Gelman), using two filters in series: a front filter and a backup filter. The backup filter was used to control for particle sampling efficiency.

PAHs were determined by extracting filters in dichloromethane using an ultrasonic bath (Sonica®, Soltec): the extract was then filtered, evaporated (under N2) and dissolved in isooctane for GC–MS analysis (GC 6850; MS 5973, Agilent).

Table 90: PAH emission factors (mg/km) for diesel and gasoline passenger cars and diesel light duty vehicles belonging to different Euro classes. Results are reported for each vehicle as the average (A) and the standard deviation (SD) of the n tests performed.

PAH EFs		Passenger Cars (PC)										Light Duty Vehicles (LDVS)									
Vehicle		A		B		C		D		E		F		G		H		I		J	
Species	Abb.	Diesel						Gasoline				Diesel									
		Euro 1	(n=6)	Euro 2	(n=9)	Euro 3	(n=6)	Euro 1	(n=3)	Euro 3	(n=3)	Euro 1	(n=5)	Euro 2	(n=5)	Euro 2	(n=9)	Euro 3	(n=3)	Euro 4	(n=5)
		A	SD	A	SD	A	SD	A	SD	A	SD	A	SD	A	SD	A	SD	A	SD	A	SD
Pyrene	PY	19.19	7.42	1.00	1.12	0.74	0.3	0.24	0.16	0.14	0.03	11.45	6.73	8.08	5.73	1.22	0.44	1.81	0.57	1.07	0.56
Benzo[a]anthracene	BaA	3.78	2.07	0.75	0.84	0.26	0.13	0.65	0.82	0.05	0.01	0.94	0.33	0.48	0.34	0.4	0.17	0.20	0.08	0.21	0.07
Chrysene	CHR	1.13	0.47	1.00	1.11	0.25	0.11	0.59	0.77	0.07	0.01	1.01	0.40	0.38	0.29	0.45	0.26	0.12	0.07	0.07	0.03
Benzo[b]fluoranthene	BbF	0.08	0.03	0.18	0.17	0.03	0	1.22	1.64	0.03	0.02	0.70	0.21	0.68	0.49	0.03	0	0.27	0	0.19	0.09
Benzo[k]fluoranthene	BkF	<0.03		0.06	0.04	<0.03		0.47	0.55	<0.03		0.12	0	0.18	0.12	<0.03		0.11	0	0.05	0.02
Benzo[e]pyrene	BeP	2.47	1.49	0.42	0.40	0.07	0.02	0.10	0.12	0.04	0.01	0.55	0.14	0.58	0.45	0.11	0.04	0.15	0.03	0.07	0.03
Benzo[a]pyrene	BaP	0.09	0.06	0.07	0.04	<0.03		0.65	0.97	<0.03		0.24	0.09	0.44	0.19	0.04	0.01	0.12	0.01	nd	
Dibenzo[a,h]anthracene	dBahA	<0.03		0.04	0.03	<0.03		0.23	0.17	<0.03		0.13	0.04	nd		<0.03		nd		nd	
Benzo[g,h,i]perylene	BghiP	0.08	0.04	0.06	0.02	0.06	0.01	1.70	2.30	0.02	0.00	0.29	0.04	0.62	0.14	0.06	0.01	0.34	0.02	nd	
Indeno[1,2,3-c,d]pyrene	IcdP	<0.05		<0.05		<0.05		<0.05		<0.05		0.37	0.11	0.52	0.33	<0.05		nd		nd	

Redfern et al. (2017) [Influences of Waste Cooking Oil-Based Biodiesel Blends on PAH and PCDD/F Emissions from Diesel Engines in Durability Testing Cycle, Aerosol and Air Quality Research] measured PAH emissions from a diesel engine by a series of durability tests, with the objective to determine the long-term effects on PAH emissions from waste cooking oil (WCO)-based biodiesel fuels. Testing was made on a Mitsubishi 4M42-4AT2 (EURO IV) engine and Mitsubishi 4M40-0A (EURO II) engine. The technical specifications of the engines are shown below.



Item	Mitsubishi 4M42-4AT2 (EURO IV)	Mitsubishi 4M40-0A (EURO II)
Configuration	In-line 4-cylinder/4 Stroke	In-line 4-cylinder/4 Stroke
Air intake	Turbocharged with intercooler	Turbo-charging type
Compression ratio	17	21
Type of fuel injection system	Common Rail	Distributor type
Injection type	Direct injection	Distributor type fuel injection pump
Fuel injection pressure	1600 bar max	147 bar
Displacement	2977 c.c.	2835 c.c.
Max torque	294 Nm @1700 rpm	195 Nm @2000rpm
Max power	92 kW @3200 rpm	69.1 kW @4000rpm

The sampling was conducted at 0, 125, 250, 375, and 500 hours. At every selected accumulated mileage, the exhaust gas samples were collected from the test engines by an isokinetic sampling system, which was specified by the U.S. EPA, modified Method 5 for PAH analysis. A heated sampling probe (120 ± 14°C) was employed to collect PAH samples.

The PAH samples were analyzed in accordance with the US EPA modified Method 23. The samples for PAH were extracted with a Soxhlet extractor using a mixture of n-hexane and dichloromethane (v:v = 1:1; each 250 mL) for 24 hours. The extracts were then concentrated by gently purging a stream of ultra-pure Nitrogen followed by passing through a silica gel column to be cleaned. The effluents were then re-concentrated to precisely 1 mL and moved to vial. There were 16 USEPA priority PAHs detected with gas chromatography/mass spectrometry (GC/MS) (HP 5890A/5972) equipped with a capillary column (HP Ultra 2, 50 m × 0.32 mm × 0.17 µm).

Table 91: PAH emissions (μg Nm^{-3}) from the Euro IV engine fueled with B10

PAHs (μg Nm^{-3})	0 hr	125 hr	*Increase %*	250 hr	*Increase %*	375 hr	*Increase %*	500 hr	*Increase %*
	(0 km)	(20,000 km) *%*		(40,000 km)		(60,000 km)		(80,000 km)	
Naphthalene	34.2	29.0	*– 15*	21.9	*– 36*	14.7	*– 57*	11.5	*– 66*
Acenaphthylene	0.0610	0.0570	*– 7*	0.0110	*– 82*	0.0847	*+39*	0.0110	*– 82*
Acenaphthene	0.0439	0.0504	*+15*	0.0193	*– 56*	0.0626	*+43*	0.100	*+128*
Fluorene	0.167	0.161	*– 4*	0.128	*+23*	0.217	*+30*	0.191	*+14*
Phenanthrene	1.14	1.04	*– 9*	1.73	*+52*	1.55	*+36*	0.968	*– 15*
Anthracene	0.0889	0.157	*+77*	0.189	*+111*	0.118	*+33*	0.0919	*+3*
Fluoranthene	0.513	0.486	*– 5*	0.201	*– 61*	0.194	*– 62*	0.293	*– 43*
Pyrene	1.67	1.81	*+8*	1.74	*+4*	1.40	*– 16*	0.754	*– 55*
Benzo[a]anthracene	0.0877	0.210	*+139*	0.0990	*+13*	0.110	*+25*	0.0784	*– 11*
Chrysene	0.105	0.113	*+8*	0.0835	*– 20*	0.163	*+55*	0.112	*+7*
Benzo[b]fluoranthene	0.0392	0.0444	*+13*	0.00924	*– 76*	0.0552	*+4*	0.0362	*– 8*
Benzo[k]fluoranthene	0.0191	0.0329	*+72*	0.00987	*– 48*	0.0364	*+91*	0.0222	*+16*
Benzo[a]pyrene	0.0253	0.0304	*+20*	0.0749	*+196*	0.103	*+307*	0.114	*+351*
Indeno[123cd]pyrene	0.00909	0.00909	*+0*	0.00909	*+0*	0.00909	*+0*	0.0284	*+212*
Dibenzo[ah]anthracene	0.00874	0.00874	*+0*	0.00874	*+0*	0.00874	*+0*	0.0139	*+59*
Benzo[ghi)perylene	0.00901	0.0126	*+40*	0.00901	*+0*	0.00901	*+0*	0.0189	*+110*

Table 92: PAH emissions (μg Nm^{-3}) from the Euro II diesel engine fueled with B10

PAHs (μg Nm^{-3})	0 hr	*Increase %*	125 hr	*Increase %*	250 hr	*Increase %*	375 hr	*Increase %*
	(0 km)		(20,000 km)		(40,000 km)		(60,000 km)	
Naphthalene	12.3	*Base*	12.3	*+0*	12.1	*– 2*	6.19	*– 50*
Acenaphthylene	0.0649	*Base*	0.0608	*– 6*	0.0315	*– 51*	0.0217	*– 67*
Acenaphthene	0.0570	*Base*	0.0581	*+2*	0.0263	*– 54*	0.0182	*– 68*
Fluorene	0.179	*Base*	0.179	*+0*	0.0831	*– 54*	0.0400	*– 78*
Phenanthrene	1.41	*Base*	0.901	*– 36*	0.680	*– 52*	0.584	*– 59*
Anthracene	0.137	*Base*	0.108	*– 21*	0.0598	*– 56*	0.0459	*– 66*
Fluoranthene	3.41	*Base*	1.71	*– 50*	1.12	*– 67*	1.17	*– 66*
Pyrene	4.98	*Base*	2.66	*– 47*	1.86	*– 63*	2.00	*– 60*
Benzo[a]anthracene	0.541	*Base*	0.266	*– 51*	0.177	*– 67*	0.205	*– 62*
Chrysene	0.694	*Base*	0.350	*– 50*	0.250	*– 64*	0.275	*– 60*
Benzo[b]fluoranthene	0.674	*Base*	0.363	*– 46*	0.270	*– 60*	0.303	*– 55*
Benzo[k]fluoranthene	0.140	*Base*	0.0866	*– 38*	0.0685	*– 51*	0.0845	*– 40*
Benzo[a]pyrene	0.568	*Base*	0.327	*– 42*	0.249	*– 56*	0.262	*– 54*
Indeno[123cd]pyrene	0.145	*Base*	0.100	*– 31*	0.0634	*– 56*	0.0773	*– 47*

Dibenzo[ah]anthracene	0.0161	*Base*	0.0300	*+86*	0.00893	*– 45*	0.00965	*– 40*
Benzo[ghi)perylene	0.274	*Base*	0.197	*– 28*	0.139	*– 49*	0.161	*– 41*

Merritt et al. (2006) [Unregulated Exhaust Emissions from Alternate Diesel Combustion Modes, SAE Technical Paper] measured PAH and nitro-PAH emissions for the following alternate diesel combustion modes: premixed charge compression ignition (PCCI) and low-temperature combustion (LTC). PCCI and LTC were studied on a PSA DW10 light-duty 2L diesel engine. Sampling was conducted while the engine operated in PCCI, LTC, and standard diesel mode. PCCI and LTC were operated in modes under "lean" and "rich" conditions – which are not necessarily lean or rich by the standard definition of flame stoichiometry – rather, these modes were simply lean or rich within the boundaries of PCCI or LTC. The engine was fitted with a DOC, DPF and LNT.

For PCCI and LTC, engine combustion characteristics were investigated at five speed/load conditions selected to be representative of the FTP-75 cycle for light-duty vehicles. A partial flow dilution tunnel with a constant volume blower was used. A portion of the raw exhaust was diverted to the tunnel to dilute and cool the exhaust, allowing bag samples to be collected for detailed analysis. Particulate filters (Pallflex T60A20) and PUF/XAD-2 traps were used for sample collection. Both media were extracted and analyzed by GC/MS for PAH and nitro-PAH species. The media extracts were combined into one proportioned sample which represented both gas- and particulate-phases. Methodology was based on California Air Resources Board (CARB) Method 429. The GC/MS system used included an Agilent 6890N GC, G2613A Auto-sampler, and 5973N MS detector. Injections (1 μL) were made in the splitless mode onto a 30 m (0.32 mm id, and 0.25 um film thickness), 5 percent phenylmethylsilicone fused-silica capillary column. Analysis of the PAH compounds was performed by GC/MS in positive ion/electron impact selective ion monitoring (PI/EI/SIM) mode. The NPAH and deuterated NPAH (internal standards) were quantified using the same GC/MS described above. However, the GC/MS was operated in negative ion/chemical ionization/selective ion monitoring (NI/CI/SIM) mode. This technique has proven to be much more sensitive for the NPAH than using the PI/EI/SIM technique.

Table 93: PAH emissions for the baseline diesel operation

PAH Compound	Emission Rate, ng/hr				
	Point 1	Point 2	Point 3	Point 4	Point 5
Naphthalene	119440	118667	77489	97387	31634
2-Methylnaphthalene	18430	13501	4454	6234	1608
Acenaphthylene	4158	4987	3673	2691	9780
Acenaphthene	853	359			1103
Fluorene	2504	1251	38		8873
Phenanthrene	3734	3387	7096	11190	37385
Anthracene	641	520	735	1186	2218
Fluoranthene	526	1305	2755	4889	14845
Pyrene	2005	3285	5602	8589	15260
Benzo(a)anthracene	100	141	62	138	146
Chrysene	183	277	147	277	370
Benzo(b+j+k)fluoranthene	62	94	29	37	30
Benzo(e)pyrene	46	74	43	29	21
Benzo(a)pyrene	46	52	21	13	
Perylene	19	29	30	16	8
Ideno(1,2,3-cd)pyrene	19	23	10	10	2
Dibenzo(a,h)anthracene	2				
Benzo(g,h,i)perylene	34	74	58	33	

Table 94: PAH emissions for the low-temperature combustion (LTC) mode

PAH Compound	LTC LEAN ENGINE OUT,ng/hr			LTC LEAN TAILPIPE OUT,ng/hr			LTC RICH ENGINE OUT, ng/hr			LTC RICH TAILPIPE OUT, ng/hr			LTC LEAN, Point 1	
	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3	DOC Out	DOC + DPF
Naphthalene	293648	1016341	473314	3452	8635	9418	462214	1017559	1326733	250794	2286274	1281752	14799	
2-Methylnaphthalene	73833	244073	108296	867	2133	4025	58273	201257	166721	15343	103170	131875	1012	
Acenaphthylene	44276	209245	97485	385	2528	19640	59195	206339	343562	920	161325	268980	997	
Acenaphthene	5422	21386	8822	77	441	2478	3523	17114	17263	510	6934	9555	227	
Fluorene	11403	48017	25070	684	2766	8605	11259	39992	70305	2033	43196	49005	885	
Phenanthrene	14251	69693	41651	2788	9282	24074	21417	41800	76781	818	62747	79429	1301	
Anthracene	2614	10027	5922	252	1006	2557	3224	6563	14112	110	10652	13482	54	
Fluoranthene	1364	14752	7678	457	1703	3687	4642	11823	26054	174	14003	16212	154	
Pyrene	4294	38983	21318	1100	3482	7987	7147	28249	50212	330	23126	24940	256	
Benzo(a)anthracene	250	2558	1018		10	21	960	2087	4855	5	686	6609	4	
Chrysene	307	3401	1558		8	26	1336	2699	5840	6	695	7041	11	
Benzo(b+j+k)fluoranthene	226	5062	2287	1	1	19	2132	3175	10433	3	852	8273	3	1
Benzo(e)pyrene	109	2816	1655				867	1457	5999	1	511	2714	2	0
Benzo(a)pyrene	241	6485	3085			2	2574	4030	15676	1	646	4941	2	
Perylene	54	1557	821	6			612	875	4007	0	69	802	1	1
Ideno(1,2,3-cd)pyrene	130	3952	2065		1	2	1480	2093	9409	0	234	1917	2	0
Dibenzo(a,h)anthracene	7	100	46				47	79	228		38	815		1
Benzo(g,h,i)perylene	280	9406	7403			8	2168	4660	23629	1	716	3807	4	2

Table 95: PAH emissions for the premixed charge compression ignition (PCCI) mode

PAH Compound ng/hr	PCCI LEAN				PCCI RICH			
	Engine Out Point 4	Tailpipe Out Point 4	Engine Out Point 5	Tailpipe Out Point 5	Engine Out Point 4	Tailpipe Out Point 4	Engine Out Point 5	Tailpipe Out Point 5
Naphthalene	320420	12049	62401	1753	159493	135156		
2-Methylnaphthalene	57382	2304	8251	925	14012	5368		
Acenaphthylene	97614	3990	4049		17224	18011		
Acenaphthene	6929	513	419		1194	751		
Fluorene	158500	11425	6205	2031	3842	2350		
Phenanthrene	484222	208619	132665	30541	7787	22168		1176
Anthracene	110470	34879	10948	3828	1191	3010		
Fluoranthene	100547	34305	42909	10909	3377	14696	481	2421
Pyrene	217163	65978	106897	24642	8837	32596	4126	5448
Benzo(a)anthracene	9770	387	9252	266	153	409	37	36
Chrysene	11119	422	12307	321	247	819	58	53
Benzo(b+j+k)fluoranthene	4986	442	6119	127	210	158	10	3
Benzo(e)pyrene	2284	249	2887	65	281	312	6	1
Benzo(a)pyrene	3845	233	2346	51	229	90	4	1
Perylene	1121	81	561	28	122	77	1	3
Ideno(1,2,3-cd)pyrene	2025	215	686	45	299	68	6	3
Dibenzo(a,h)anthracene	125	19	56	6	9	2		3
Benzo(g,h,i)perylene	3761	375	1427	81	1786	743	23	15

Table 96: Nitro-PAH emissions for baseline diesel operation

NPAH Compound, ng/hr	**Baseline Diesel**				
	Point 1	**Point 2**	**Point 3**	**Point 4**	**Point 5**
1-Nitronaphthalene	11.7	4.2	1.2	9.5	42.2
2-Methyl-1-nitronaphthalene	1.6				7.1
2-Nitronaphthalene	14.6	2.9	2.1	15.7	68.2
2-Nitrofluorene	0.3				1.2
9-Nitroanthracene	14.3	25.1	24.0	95.1	613
3-Nitrofluoranthene					7.1
4-Nitropyrene	12.6	5.4			9.1
1-Nitropyrene	12.6	38.1	14.0	92.2	1403
7-Nitrobenzo(a)anthracene					16.2

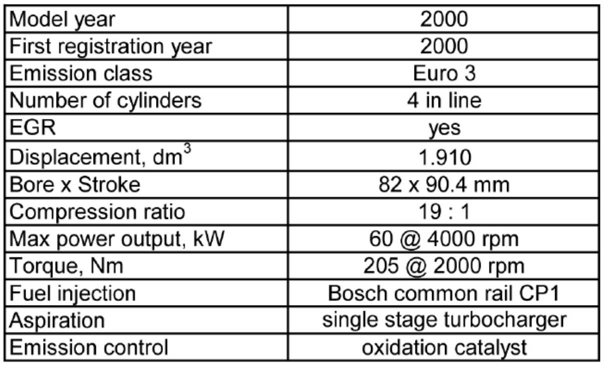
Table 97: Nitro-PAH emissions for the low-temperature combustion (LTC) mode

NPAH Compound ng/hr	LTC LEAN						LTC RICH						LTC LEAN	
	ENGINE-OUT			TAILPIPE-OUT			ENGINE-OUT			TAILPIPE-OUT			DOC Out	DOC + DPF
	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3	Point 1	Point 2	Point 3	Point 1	Point 1
1-Nitronaphthalene	8.8	76.3	21.0	4.2	9.4	6.6	1.9	6.9	15.3	0.3	0.6	3.0	4.5	
2-Methyl-1-nitronaphthalene	2.2	0.5	4.9		0.3	1.2	1.6			0.5				
2-Nitronaphthalene	8.8		42.2	1.3	17.8	10.0	3.4	8.2	21.5		9.9	10.2	2.7	1.1
2-Nitrobiphenyl														
4-Nitrobiphenyl														
5-Nitroacenaphthene	24.6	42.0												
2-Nitrofluorene										0.9				
9-Nitroanthracene				1.7	3.8				6.2	5.2	2.6	1.0	5.9	
3-Nitrofluoranthene														
4-Nitropyrene		16.0	16.4						14.4					
1-Nitropyrene	4.7	58.4	20.0				7.9	32.1	38.5	1.9	3.6	5.4	19.4	2.9

Table 98: Nitro- PAH emissions for the premixed charge compression ignition (PCCI) mode

NPAH Compound ng/hr	PCCI LEAN				PCCI RICH			
	Engine Out Point 4	Tailpipe Out Point 4	Engine Out Point 5	Tailpipe Out Point 5	Engine Out Point 4	Tailpipe Out Point 4	Engine Out Point 5	Tailpipe Out Point 5
1-Nitronaphthalene	68.0	32.5	58.4	20.8	9.6	6.1	9.5	
2-Methyl-1-nitronaphthalen			3.5				1.8	
2-Nitronaphthalene	257	70.4	86.8		28.9	9.7	35.2	
2-Nitrobiphenyl	16.2		6.6		2.6		2.6	
4-Nitrobiphenyl	321				46.0		150	
5-Nitroacenaphthene	13.7							
2-Nitrofluorene	10.6						3.0	20.9
9-Nitroanthracene	42.3	19.2	81.9	20.9	34.7	3.7	51.2	
3-Nitrofluoranthene	47.4	9.2						
4-Nitropyrene	58.5	8.1	61.2		5.1		7.3	
1-Nitropyrene	118		565	23.8	23.2		48.1	
7-Nitrobenzo(a)anthracene	44.6	9.8	66.3		23.6		5.9	
6-Nitrochrysene		13.8						
1,3-Dinitropyrene								
1,6-Dinitropyrene								
1,8-Dinitropyrene								
6-Nitrobenzo(a)pyrene	9.5		81.6		2.4			

Pellegrini et al. (2014) [Effect of POMDME Blend on PAH Emissions and Particulate Size Distribution from an In-Use Light-Duty Diesel Engine, SAE Technical Paper] measure PAH emissions from polyoxymethylene dimethyl ether (POMDME) from a Euro 3 diesel engine. The engine was fueled with a 7.5% blend of POMDME in commercial diesel fuel. The diesel engine was removed from in in-use vehicle and had the following technical characteristic.



Model year	2000
First registration year	2000
Emission class	Euro 3
Number of cylinders	4 in line
EGR	yes
Displacement, dm^3	1.910
Bore x Stroke	82 x 90.4 mm
Compression ratio	19 : 1
Max power output, kW	60 @ 4000 rpm
Torque, Nm	205 @ 2000 rpm
Fuel injection	Bosch common rail CP1
Aspiration	single stage turbocharger
Emission control	oxidation catalyst

PAH were sampled out of a diluted exhaust stream using an AVL “Smart sampler”. Dilution ratio was kept constant for all tests at 5:1. The diluted exhaust gas was first sucked over a particulate filter (Pallflex TX40-HI20, 70 mm Ø) at a flow rate of 68.4 l/min. Then, downstream of the PM filter, a trap filled with 2 g of toluene-prewashed Tenax as adsorbing material was placed for gaseous PAH sampling. The flow over the Tenax trap was 16.7 l/min. The lower flow through the trap was necessary due to its high resistance. Sampling time was at least 30 min for each point. Each Tenax trap with the adsorbed gaseous PAH was extracted with 30 ml toluene. Each PM filter was refluxed with 50 ml toluene for 1 h and the hot toluene filtered. Trap and filter extracts were first concentrated in a 100 ml Erlenmeyer bulb to a few µl, then transferred without any other cleaning steps to a 1 ml volumetric flask. The Erlenmeyer bulb was washed 2-3 times with a few µl of toluene. These washings were added to the volumetric flask and the total volume made up to the mark with toluene.

2 µl of each sample were injected into a gas chromatograph (GC) and the compounds separated on a 5% phenyl 95% dimethylpolysiloxane fused silica column, (30 m × 0.25 mm, 0.25 µm film thickness; CP-Sil 8 CB Low Bleed MS, Varian). Splitless injection at 350°C injector temperature was adjusted. The GC oven program began at 100°C for 5 min, and then the temperature was ramped at a 3°C/min rate to a final temperature of 319°C, and held constant for 2 min. A mass selective detector (MSD) was used for sample identification and for quantification the mass ion of each PAH compound was used.

Table 99: PAH emissions (µg/km) for the base diesel fuel

Base Diesel Fuel	Mode 2: 1000 rpm and .92 bar						50 km/h					
PAH (µg/km)	Gaseous PAH		Particulate PAH		Total PAH		Gaseous PAH		Particulate PAH		Total PAH	
	Before cat	After cat	Before cat	After cat	Before cat	After cat	Before cat	After cat	Before cat	After cat	Before cat	After cat
Acenaphthylene	23	0.49	0.24	0.21	23.24	0.7	11.05	0.14	0.08	0.02	11.13	0.16
Fluorene	49.28	0.54	0.32	0.15	49.6	0.69	15.31	0.45	0.14	0.07	15.45	0.52
Phenanthrene	53.63	2.45	2.18	1.69	55.81	4.14	13.09	5.82	2.57	0.54	15.66	6.36
Anthracene	2.53	0.16	0.27	0.1	2.8	0.26	1.34	0.2	0.4	0.07	1.74	0.27
Fluoranthene	1.06	0.62	2.08	0.85	3.14	1.47	0.53	0.48	2.04	0.4	2.57	0.88
Pyrene	2.01	0.43	3.33	0.88	5.34	1.31	0.55	0.38	3.02	0.49	3.57	0.87
Benzo(g,h,i)fluoranthene	0	0	0.37	0.11	0.37	0.11	0	0	0.32	0.08	0.32	0.08
Benzo(c)phenanthrene	0	0	0.13	0.06	0.13	0.06	0	0	0.17	0.04	0.17	0.04
Cyclopentane(c,d)pyrene	0	0	0.07	0.05	0.07	0.05	0	0	0.16	0.04	0.16	0.04
Benz(a) anthracene	0	0	0.48	0.14	0.48	0.14	0	0	0.32	0.13	0.32	0.13
Triphenylene + Chrysene	0	0	0.21	0.12	0.21	0.12	0	0	0.23	0.09	0.23	0.09
Benzo(b) + (j) fluoranthene	0	0	0.29	0.14	0.29	0.14	0	0	0.18	0.08	0.18	0.08
Benzo(k)fluoranthene	0	0	0.12	0.05	0.12	0.05	0	0	0.08	0.03	0.08	0.03
Benzo(e) pyrene	0	0	0.3	0.16	0.3	0.16	0	0	0.23	0.08	0.23	0.08
Benzo(a) pyrene	0	0	0.25	0.14	0.25	0.14	0	0	0.17	0.05	0.17	0.05
Perylene	0	0	0	0	0	0	0	0	0.05	0	0.05	0
Indeno(1,2,3-c,d)pyrene	0	0	0.09	0.05	0.09	0.05	0	0	0.09	0.03	0.09	0.03
Dibenza(a,c)+ (a,h)anthracene	0	0	0	0.02	0	0.02	0	0	0.02	0	0.02	0
Benz(b)chrysene	0	0	0	0	0	0	0	0	0.03	0	0.03	0
Picene	0	0	0	0	0	0	0	0	0.11	0.03	0.11	0.03
Benzo(g,h,i)perylene	0	0	0.14	0.1	0.14	0.1	0	0	0.03	0	0.03	0
Anthanthrene	0	0	0	0	0	0	0	0	0	0	0	0

Table 100: PAH emissions for the POMDME blend

POMDME Blend	Mode 2: 1000 rpm and .92 bar						50 km/h					
	Gaseous PAH		Particulate PAH		Total PAH		Gaseous PAH		Particulate PAH		Total PAH	
PAH (µg/km)	Before cat	After cat	Before cat	After cat	Before cat	After cat	Before cat	After cat	Before cat	After cat	Before cat	After cat
Acenaphthylene	36.71	0.49	0.54	0.16	37.25	0.65	10.62	0.23	0.28	0.12	10.9	0.35
Fluorene	43.73	1.52	0.56	0.41	44.29	1.94	10.8	1.44	0.22	0.15	11.02	1.59
Phenanthrene	68.37	18.42	3.78	3.34	72.15	21.76	19.07	9.8	3.26	0.92	22.33	10.72
Anthracene	3.91	0.94	0.63	0.25	4.54	1.19	1.07	0.38	0.45	0.12	1.52	0.5
Fluoranthene	3.23	2.3	5.23	1.35	8.46	3.65	0.65	0.66	2.96	0.54	3.61	1.2
Pyrene	3.29	2.19	7.29	1.33	10.58	3.52	0.7	0.63	4.17	0.55	4.87	1.18
Benzo(g,h,i)fluoranthene	0	0	1.13	0.31	1.13	0.31	0	0	0.46	0.07	0.46	0.07
Benzo(c)phenanthrene	0	0	0.28	0.06	0.28	0.06	0	0	0.11	0.03	0.11	0.03
Cyclopentane(c,d)pyrene	0	0	0.23	0.19	0.23	0.19	0	0	0.14	0.08	0.14	0.08
Benz(a) anthracene	0	0	0.91	0.53	0.91	0.53	0	0	0.36	0.16	0.36	0.16
Triphenylene + Chrysene	0	0	0.76	0.32	0.76	0.32	0	0	0.23	0.1	0.23	0.1
Benzo(b)+(j) fluoranthene	0	0	0.71	0.31	0.71	0.31	0	0	0.2	0.15	0.2	0.15
Benzo(k)fluoranthene	0	0	0.39	0.11	0.39	0.11	0	0	0.09	0.08	0.09	0.08
Benzo(e) pyrene	0	0	0.83	0.4	0.83	0.4	0	0	0.22	0.17	0.22	0.17
Benzo(a) pyrene	0	0	0.71	0.32	0.71	0.32	0	0	0.17	0.11	0.17	0.11
Perylene	0	0	0.16	0.03	0.16	0.03	0	0	0.07	0.02	0.07	0.02
Indeno(1,2,3-c,d)pyrene	0	0	0.64	0.21	0.64	0.21	0	0	0.09	0.07	0.09	0.07
Dibenza(a,c)+ (a,h)anthracene	0	0	0.08	0.06	0.08	0.06	0	0	0.02	0	0.02	0
Benz(b)chrysene	0	0	0.14	0.09	0.14	0.09	0	0	0.01	0	0.01	0
Picene	0	0	0.11	0.08	0.11	0.08	0	0	0	0	0	0
Benzo(g,h,i)perylene	0	0	0.86	0.29	0.86	0.29	0	0	0.14	0.08	0.14	0.08
Anthanthrene	0	0	0.12	0.09	0.12	0.09	0	0	0.04	0.03	0.04	0.03

Pacenti et al. (2009) [Physicochemical Characterization of Exhaust Particulates from Gasoline and Diesel Engines by Solid-Phase Micro Extraction Sampling and Combined Raman Microstroscopic/Fast Gas-Chromatography Mass Spectrometry Analysis, European Journal of Inflammation] measured PAH emissions from gasoline and diesel-powered vehicles. Eight different vehicles were used: four diesel cars (A: Euro 1, B: Euro 3, C: Euro 4 without DPF, and D: Euro 4 with DPF) a Euro 3 gasoline car with TWC, one heavy-duty Euro 3 diesel truck, and two motorcycles (G: two-stroke engine Euro 0 without catalysts and H: four-stroke Euro 2 catalyst-equipped). Testing and sample collection was conducted when the engines were operated at 2000 rpm with no load.

PAH analysis was performed with a fast GC/MS on a Shimadzu GC 2010 using a SLB5-MS column (5m x 0.10 mm x 0.4 μm film thickness), with a Shimadzu QP 2010 series mass selective detector operating in the EI, methane negative chemical ionization (NCI), and methane positive chemical ionization (PCI) mode.

Table 101: Source composition normalized (%) to the sum of 26 PAHs selected in the exhaust emissions

	A	B	C	D	E	F	G	H
Naphthalene	1.4	0.5	0.2	0.1	83.9	0.5	17.6	71.1
2-Mehtylnapthalene	bd	bd	bd	bd	bd	bd	bd	bd
1-Mehtylnapthalene	bd	bd	bd	bd	bd	bd	bd	bd
Biphenyl	bd	bd	bd	bd	bd	bd	bd	bd
2,3 Dimethylnapthalene	bd	bd	bd	bd	bd	bd	bd	bd
Acenaphthylene	1.3	1.0	0.3	0.6	1.0	2.0	37.3	18.8
Acenaphthene	bd	bd	bd	bd	bd	bd	0.1	bd
Fluorene	2.0	1.4	0.5	0.6	1.8	3.1	12.1	10.1
1-Nitronaphthalene	bd	bd	bd	bd	bd	bd	bd	bd
2-Nitronaphthalene	bd	bd	bd	bd	bd	bd	bd	bd
Phenanthrene	26.8	16.8	18.4	20.1	9.3	20.5	8.2	bd
Anthracene	2.1	2.7	1.2	1.2	bd	3.7	3.4	bd

3-Nitrobiphenyl	bd	bd	bd	bd	bd	bd	bd	bd
2-Methylphenanthrene	12.1	6.6	7.4	7.1	1.6	10.1	3.8	bd
1-Methylphenanthrene	11.4	10.7	11.5	11.5	2.4	8.9	4.5	bd
Fluoranthene	16.9	17.9	19.7	21.8	bd	22.4	3.1	bd
Pyrene	21.2	36.9	36.4	30.8	bd	25.4	9.3	bd
Benzo(a)anthracene	1.2	2.0	1.7	2.1	bd	1.0	0.9	bd
Chrysene	0.8	1.4	0.9	1.7	bd	0.4	0.9	bd
1-Nitropyrene	bd	bd	bd	bd	bd	bd	bd	bd
Benzo(b)fluoranthene	0.9	0.6	1.0	1.2	bd	0.8	bd	bd
Benzo(k)fluoranthene	0.8	1.4	0.8	1.2	bd	1.1	bd	bd
Benzo(a)pyrene	1.1	0.1	bd	bd	bd	0.1	bd	bd
Indeno(1,2.3,cd)pyrene	bd	bd	bd	bd	bd	bd	bd	bd
Dibenzo(ah)anthracene	bd	bd	bd	bd	bd	bd	bd	bd
Benzo(ghi)perylene	bd	bd	bd	bd	bd	bd	bd	bd

Prokopowicz et al. (2015) [The Effects of Neat Biodiesel and Biodiesel and HVO Blends in Diesel Fuel in Exhaust Emissions from a Light Duty Vehicle with a Diesel Engine, Environmental Science and Technology] measured PAH and nitro-PAH emissions from fuels containing different proportions of biodiesel and HVO in diesel fuel. Testing was performed on a chassis dynamometer over the European legislative NEDC cycle. A midsized passenger car produced in 2009 with a compression ignition engine of displacement 1920 cm^3 was used. The vehicle's engine also featured typical technology for a Euro 4 diesel passenger car: a turbocharger, cooled exhaust gas recirculation controlled by an air flow meter, and a common-rail fuel injection system with high-pressure injectors. A diesel particulate filter was not present, but an oxidation catalyst was fitted.

Particle bound PAHs and nitro-PAH collected onto Pallflex (T60A20) filters were extracted with dichloromethane in Soxhlet apparatus over an 8-hour period. The extracts were concentrated and fractionated on a silica gel column using the following procedure: the sample was placed onto the column, which was then eluted successively by cyclohexane (I fraction), 25% dichloromethane in cyclohexane (II fraction) and dichloromethane (III fraction). The second fraction, which contained

PAH compounds, was analyzed by HPLC with fluorescence detection (AT1200 Agilent Technologies). Zorbax Eclipse PAH 5.0 µm; 150x4.6 mm (Agilent Technologies) column and gradient elution with acetonitrile/H2O were used for PAH separation. Nitro-PAHs were measured in the third fraction of the purified extract and were determined by gas chromatography (Varian 450 GC) with a mass detector (320 MS) and electrospray ionization, using VF 5 MS; 30mx0.25mmx0.25mm capillary column (Varian).

Table 102: PAH emissions (µg/km) for the test fuels over the UDC, EUDC, and complete NEDC

PAH [µg/km]	B0			B7			B15			B30			B100			HVO30		
	NEDC	UDC	EUDC	NEDC	UDC	EUDC	NEDC	UDC	EUDC	NEDC	UDC	EUDC	NEDC	UDC	EUDC	NEDC	UDC	EUDC
Acenaphthene + Fluorene	2.993	4.357	2.203	1.572	1.9	1.383	2.073	2.261	1.964	2.744	2.47	2.902	1.669	2.537	1.166	4.223	5.079	3.727
Phenanthrene	0.044	0.121	-	0.018	0.05	-	0.321	0.876	-	1.131	1.458	0.942	0.539	0.318	0.667	1.23	1.986	0.793
Anthracene	0.006	0.016	-	0.004	0.012	-	0.028	0.077	-	0.064	0.131	0.024	0.015	0.016	0.014	0.081	0.168	0.031
Fluoranthene	0.578	1.577	-	0.322	0.64	0.138	0.762	1.664	0.24	0.963	0.581	1.184	0.401	1.094	-	0.805	0.529	0.965
Pyrene	0.685	1.442	0.247	0.488	1.24	0.054	0.627	1.559	0.087	1.177	2.689	0.302	0.298	0.528	0.164	1.012	2.243	0.3
Benzo(a)anthracene	0.732	1.553	0.257	0.506	1.217	0.094	0.562	1.345	0.108	0.733	1.94	0.034	0.277	0.713	0.024	0.62	1.617	0.043
Chrysene	1.119	2.296	0.437	0.661	1.606	0.113	0.833	1.947	0.187	1.228	2.664	0.396	0.142	0.297	0.052	1.11	2.456	0.33
Benzo(b)fluoranthene	0.084	0.101	0.074	0.297	0.759	0.029	0.073	0.122	0.044	0.196	0.327	0.12	0.202	0.363	0.109	0.169	0.186	0.159
Benzo(k)fluoranthene	0.055	0.118	0.018	0.091	0.235	0.008	0.054	0.128	0.01	0.103	0.253	0.016	0.115	0.294	0.011	0.038	0.065	0.023
Benzo(a)pyrene	0.061	0.147	0.012	0.156	0.406	0.011	0.068	0.184	-	0.18	0.469	0.013	0.354	0.927	0.023	0.021	0.028	0.016
Dibenzo(a,h)anthracene	-	-	-	0.02	0.055	-	0.007	0.02	-	0.013	0.035	-	0.017	0.046	-	-	-	-
Benzo(g,h,i)perylene	0.079	0.217	-	0.322	0.877	-	0.14	0.383	-	0.377	0.973	0.033	0.915	2.425	0.042	0.025	0.067	-
Indeno(1,2,3-c,d)pyrene	0.201	0.263	0.166	0.281	0.549	0.125	0.23	0.36	0.154	0.351	0.631	0.189	0.831	1.535	0.424	0.187	0.235	0.159

Table 103: Nitro-PAH emissions for the test fuels over the UDC cycle

Nitro-PAH, [µg/km]	B0	B7	B15	B30	B100	HVO30
7-nitrobenzo(a)anthracene	0.035	0.048	-	-	0.021	0.039
2-nitrofluorene	0.058	0.019	-	-	0.032	0.039
9-nitroanthracene	0.081	0.048	-	-	0.021	0.026
3-nitrofluoranthene	0.058	0.01	-	-	0.011	0.013
1-nitropyrene	0.046	0.048	-	-	0.011	0.026
6-nitrochryzene	0.104	-	-	-	0.011	0.013
Total nitro-PAHs	0.382	0.173	-	-	0.106	0.157

Zou and Atkinson (2003) [Characterising vehicle emissions from the burning of biodiesel made from vegetable oil, Environmental Technology] measured PAH emissions from diesel vehicles when operated on 100% biodiesel to 100% diesel fuel. The vehicle used was a 1979 model VW Golf with a 1.6L engine and no catalyst. Testing was made on the ECE (Euro 2) drive test cycle, consisting of 4 urban driving cycles with a maximum speed of 50 km/h.

Accumulative samples were collected on both filter media and XAD sorbent tubes. The PAHs were determined using the US EPA standard method 8270C Determination of semivolatile organic compounds by gas chromatography/mass spectrometry. Filters and XAD sorbent were extracted using dichloromethane for two hours, and the extract and internal standard were then injected on a GC/MS (HP 6890 GC and 5973 MS), which was fitted with a BD-5ms 30m x 0.25 cm column.

Table 104: Gaseous PAH emissions of biodiesel/diesel blends (µg/m^3)

	100% Biodiesel	80% Biodiesel	60% Biodiesel	40% Biodiesel	20% Biodiesel	100% Diesel
Naphthalene	364.459	388.341	456.223	448.226	571.154	681.912
Acenaphthylene	38.418	40.606	57.505	48.814	71.420	86.672
Acenaphthene	4.983	5.713	6.187	5.650	5.202	6.161
Fluorene	12.756	14.157	17.183	19.225	30.506	37.026
Phenanthrene	11.081	10.887	14.331	15.398	22.167	28.244

Anthracene	2.468	1.869	2.343	3.135	6.297	6.186

Table 105: Particulate PAH emissions of biodiesel/diesel blends (μg/m^3)

	100% Biodiesel	80% Biodiesel	60% Biodiesel	40% Biodiesel	20% Biodiesel	100% Diesel
Phenanthrene	20.466	20.611	22.300	18.232	14.600	11.985
Fluoranthene	12.276	11.477	15.327	14.165	15.182	16.126
Pyrene	13.656	12.203	15.617	15.617	17.361	18.814
Benz(a)anthracene	1.689	1.435	2.088	2.052	2.597	3.033
chrysene	2.016	1.762	2.161	1.907	2.343	2.706
Benzo(b)fluoranthene	1.834	1.435	1.943	1.580	2.306	2.996
Benzo(k)fluoranthene	1.653	1.507	1.798	1.689	2.016	2.524
Benzo(a)pyrene	1.870	1.689	2.052	1.471	1.326	1.326
Benzo(ghi)perylene	2.815	1.979	1.979	1.762	2.343	2.615

Bikas and Zervas (2007) [Regulated and Non-Regulated Pollutants Emitted during the Regeneration of a Diesel Particulate Filter, Energy and Fuels] measured PAH emissions during the regeneration of a DPF from a Euro 4 passenger car. The car was equipped with a 1.9 L diesel Euro 4 engine and a commercial oxidation catalyst of 1.6 L with 50 /ft3 of Pt and a noncatalyzed DPF of 2.5 L made of SiC. The DPF was retrofitted to this vehicle, which was initially not equipped with DPF, and thus not optimized to treat eventually increased emissions occurring during DPF regeneration. The test protocol comprised of a cold NEDC with 20 g of soot charge on the DPF. At the end of this cycle, the soot charge remained approximately at 20 g as a very small quantity of soot was added. During this cycle, there was only soot collection without DPF regeneration. After this first, cold NEDC, a second, hot NEDC with a regeneration started at 980 s from the beginning of the cycle, at the extra-urban part of the cycle (extra-urban driving cycle, EUDC), was performed. The DPF regeneration was achieved using delayed injection, which increased the exhaust temperature and thus regenerated the DPF, over 130 s. The regeneration stopped when 80% of the accumulated soot mass was oxidized, leaving 4 g of soot on the DPF. At this cycle, PAHs were analyzed over the entire NEDC. A third, hot NEDC, using the DPF with 4 g of soot charge, where there was no regeneration, was performed after the second NEDC. A last measurement of PAHs was performed on a hot NEDC upstream of the DPF, which corresponded to the emissions of this vehicle without DPF.

Table 106: PAH emissions during filtration and regeneration, and comparison with the same emissions upstream of DPF (μg/km)

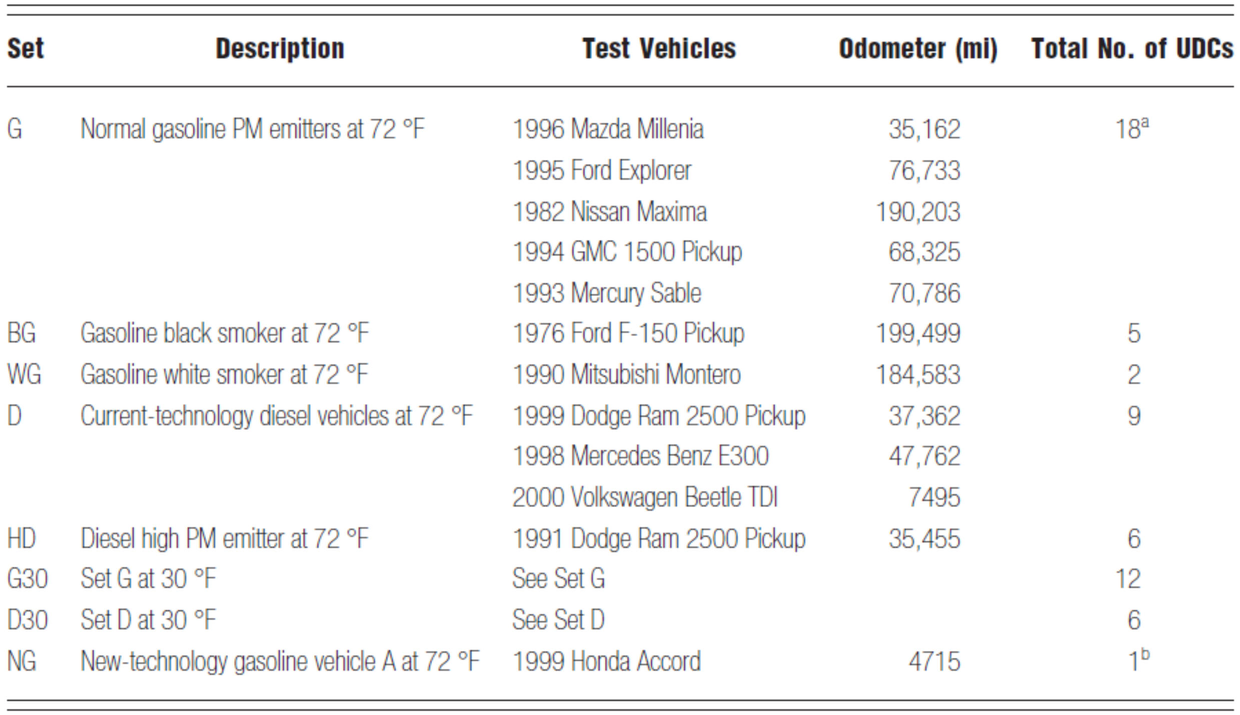
PAHs, μg/km	DPF, hot NEDC, DI, 20g, regeneration, PM: 0.015 g/km	Upstream DPF, PM: 0.030 g/km	DPF, hot NEDC, without DI, 20g, filtration, PM: 0.015 g/km
Fluoranthene	1.020	1.110	0.041
Pyrene	0.765	0.508	0.001
Benzo(a)Anthracene	0.038	0.083	0.005
Chrysene	0.111	0.070	0.013
Benzo(b)Fluoranthene	0.086	0.144	0.004
Benzo(k)Fluoranthene	0.010	0.055	0.003
Benzo(a)Pyrene	0.007	0.132	0.001
Indeno(1,2,3,cd)pyrene	0.007	0.101	0.015
Dibenzo(ah)anthracene	0.002	0.016	0.004
Benzo(ghi)Perylene	0.005	0.150	0.002

Bikas and Zervas (2007) [Nonregulated Pollutants Emitted from Euro 3 Diesel Vehicles as a Function of Their Mileage, Energy and Fuels] studied the mileage accumulation effect, from 4000 to 96000 km, on PAH emissions from a Euro 3, 1.9L diesel engine. This car was tested at 4000 and 75000 km. testing was performed over the NEDC. PAH emissions were analyzed using high-performance liquid chromatography (HPLC) with fluorescence detection.

Table 107: Exhaust emissions of PAHs as a function of the mileage at the NEDC (µg/km)

PAHs, µg/km	4000km	75000km
Fluoranthene	2.396	2.883
Pyrene	1.456	2.192
Benzo (a) anthracene	0.35	0.532
Chrysene	0.342	0.604
Benzo (e) pyrene	0.947	0.983
Benzo (j) fluoranthene	0.328	0.109
Benzo (b) fluoranthene + perylene	0.444	0.379
Benzo (k) fluoranthene	0.131	0.138
Benzo (a) pyrene	0.393	0.379
Dibenzo (a,h) anthracene	0.058	0.073
Benzo (ghi) perylene	0.663	0.269
Benzo (b) chrysene	0.087	0.058
Anthanthrene	0.087	0.073
Indeno(1,2,3,cd)pyrene	0.291	0.182
Coronene	0.087	0.087

Zielinska et al. (2004) [Emission Rates and Comparative Chemical Composition from Selected In-Use Diesel and Gasoline-Fueled Vehicles, Journal of the Air & Waste Management Association] measured PAH emissions from a variety of gasoline and diesel in-use vehicles operated on the LA92 cycle or the California Unified Driving Cycle (UDC) on a chassis dynamometer. Passenger cars, sport utility vehicle, and pickup trucks ranging from 1976 to 200 models were selected for this study, as shown below.



Set	Description	Test Vehicles	Odometer (mi)	Total No. of UDCs
G	Normal gasoline PM emitters at 72 °F	1996 Mazda Millenia	35,162	18[a]
		1995 Ford Explorer	76,733	
		1982 Nissan Maxima	190,203	
		1994 GMC 1500 Pickup	68,325	
		1993 Mercury Sable	70,786	
BG	Gasoline black smoker at 72 °F	1976 Ford F-150 Pickup	199,499	5
WG	Gasoline white smoker at 72 °F	1990 Mitsubishi Montero	184,583	2
D	Current-technology diesel vehicles at 72 °F	1999 Dodge Ram 2500 Pickup	37,362	9
		1998 Mercedes Benz E300	47,762	
		2000 Volkswagen Beetle TDI	7495	
HD	Diesel high PM emitter at 72 °F	1991 Dodge Ram 2500 Pickup	35,455	6
G30	Set G at 30 °F	See Set G		12
D30	Set D at 30 °F	See Set D		6
NG	New-technology gasoline vehicle A at 72 °F	1999 Honda Accord	4715	1[b]

For PAH analysis, samples were collected on Teflon-impregnated glass fiber (TIGF; Pallflex, 100 mm) backed by a polyurethane foam (PUF)/XAD-4 resin/PUF sandwich cartridge. PUF/XAD/PUF cartridges and TIGF filters were extracted and analyzed separately. Before extraction, the following deuterated internal standards were added to each filter and cartridge pair: naphthalene-d8, acenaphthylene-d8, phenanthrene-d10,anthracene-d10, chrysene-d12, pyrene-d10, benzo[a]anthra-cene-d12, benzo[a]pyrene-d12, benzo[e]pyrene-d12, benzo[k]fluoranthene-d-12,benzo[g,h,i]perylene-d12, coronene-d12, cholestane-d50, 1-nitropyrene-d11, and tetrocosane-d50.The PUF plugs and XAD resins were Soxhlet-extracted with acetone and the filters were microwave-extracted (CEM 1000) with acetone. The extracts then were concentrated by rotary evaporation at 20°C under gentle vacuum to1mL and filtered through 0.45-mm Acrodiscs (Gelman Scientific), rinsing the sample flask twice with 1mL dichloromethane each time. Approximately 100L of acetonitrile was added to the sample and dichloromethane was evaporated under a gentle stream of nitrogen. For the nitro-PAH, samples were cleaned before analysis using a solid-phase extraction (SPE) technique. The samples were cleaned on 6-mL Supelco SPE cartridges packed with 0.5 g of SiOH. For nitro-PAH quantification, the hexane/benzene fraction was precleaned further using semi-preparative high-performance liquid chromatography method.

Samples were analyzed on a Varian Star 3400CX gas chromatograph equipped with an 8200CX Automatic Sampler interfaced to a Saturn 2000 Ion Trap operated in electron impact ionization and selective ion storage analysis mode. Splitless injections (1μL) were made onto a phenylmethylsilicone fused-silica capillary column (30m, 0.25mm x 0.25μm; DB-5 ms, J&W Scientific).

Table 108: PAH emissions (µg/mile) in the samples with filter (F) and PUF/XAD/PUF (P)

Compounds	G		BG		WG		D		HD		G30		D30		NG	
	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P
Naphthalene		816.327	653.061	979.592		2775.51	244.898	816.327	326.531	408.163	897.959	408.163	244.898	4979.592	244.898	1469.388
Methylnaphthalenes		816.327		816.327		3591.837		897.959		1306.122		653.061		3428.571		163.265
Dimethylnaphthalenes		2285.714		3918.367	489.796	9142.857		1061.224		1551.02		3510.204		2122.449		
Methylbiphenyls						1306.122		244.898		489.796		408.163		979.592		
Trimethylnaphthalenes		5551.02		5551.02		6938.776		1224.49		1469.388		6693.878		3591.837		
Acenaphthylene				816.327	1469.388	3183.673						3510.204		979.592		
Acenaphthene		326.531				326.531										
Fluorene				326.531	326.531	2612.245						1224.49		1551.02		
Phenanthrene				326.531	489.796	816.327				326.531		1061.224		816.327		
Methylfluorenes					163.265	653.061				326.531				653.061		
9-fluorenone				2775.51	816.327	734.694		326.531				2857.143				
Xanthone		1469.388														
Methylphenanthrenes					1306.122	653.061				326.531		408.163		979.592		
Anthraquinone					326.531											
Dimethylphenanthrenes					1469.388	326.531				326.531			244.898	571.429		
Anthracene						163.265						326.531				
Fluoranthene					489.796							326.531		408.163		
Pyrene					326.531							326.531				

Mepyrene/mefluoranthene					1142.857											
Benzo(c)phenanthrene (BaA)																
Benz(a)anthracene																
Chrysene/triphenylene					326.531											
Benzo(b+j+k)fluoranthene																
Benzo(e)pyrene																
Benzo(a)pyrene																
Indeno[123-cd]pyrene																
Benzo(ghi)perylene																
Dibenzo(ah+ac)anthracene																
Coronene																

Table 109: PAH emissions (µg/mile) in the samples on filter only

Compounds	**G**	**BG**	**WG**	**D**	**HD**	**G30**	**D30**	**NG**
Naphthalene	11.111111	40.740741	170.64846	22.222222		18.518519	214.81481	29.6296296
Methylnaphthalenes		18.518519	119.45392				48.148148	14.8148148
Dimethylnaphthalenes			273.03754				22.222222	
Methylbiphenyls			51.194539					
Trimethylnaphthalenes		11.111111	1313.9932			48.148148	70.37037	
Acenaphthylene			51.194539					
Acenaphthene			51.194539				55.555556	33.3333333
Fluorene			255.9727					
Phenanthrene		25.925926	460.75085		18.518519	22.222222	18.518519	
Methylfluorenes			255.9727					
9-fluorenone			802.04778			29.62963	14.814815	

Xanthone						11.111111		
Methylphenanthrenes		62.962963	1211.6041	14.814815	85.185185	29.62963	48.148148	
Anthraquinone			392.49147			51.851852	37.037037	
Dimethylphenanthrenes		66.666667	1313.9932	37.037037	114.81481	51.851852	222.22222	
Anthracene			153.58362					
Fluoranthene		62.962963	529.01024	14.814815		107.40741	118.51852	
Pyrene		66.666667	273.03754		29.62963	77.777778	100	
Mepyrene/mefluoranthene		44.444444	1399.3174			103.7037	159.25926	
Benzo(c)phenanthrene (BaA)		29.62963	85.324232		14.814815			
Benz(a)anthracene		18.518519	136.51877			33.333333	29.62963	
Chrysene/triphenylene			187.71331			66.666667	100	
Benzo(b+j+k)fluoranthene		18.518519	102.38908			40.740741	51.851852	
Benzo(e)pyrene		11.111111	51.194539			18.518519	29.62963	
Benzo(a)pyrene		11.111111	85.324232			29.62963	14.814815	
Indeno[123-cd]pyrene			68.259386				22.222222	
Benzo(ghi)perylene		25.925926	102.38908			37.037037	29.62963	
Dibenzo(ah+ac)anthracene		22.222222				18.518519	18.518519	
Coronene								

Table 110: Nitro-PAH emissions (µg/mile) for the gasoline and diesel vehicles

Compound	**G**	**BG**	**WG**	**D**	**HD**	**G30**	**D30**
1-nitronaphthalene	0.152	0.696	0.109	0.348	2.022	-	2.978
2-methylnitronaphthalene	-	-	-	-	-	-	0.130
methylnitronaphthalenes	-	-	0.717	0.717	0.304	-	0.630
9-nitroanthracene	-	-	0.239	0.283	0.109	-	0.848
3-nitrofluoranthene	-	-	0.217	-	0.130	-	-
1-nitropyrene	-	-	-	1.978	1.065	-	3.935

7-nitrobenz(a)anthracene	-	-	0.326	-	0.130	-	0.261
6-nitrochrysene	-	0.348	-	0.109	0.761	-	1.304
6-nitrobenzo(a)pyrene	-	-	-	0.109	0.543	-	2.457

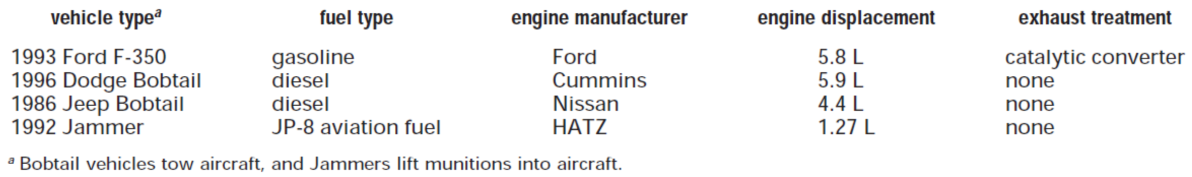
Cheung et al. (2009) [Emissions of Particulate Trace Elements, Metals and Organic Species from Gasoline, Diesel, and Biodiesel Passenger Vehicles and Their Relation to Oxidative Potential, Aerosol Science and Technology] tested three light-duty vehicles in five configurations in a chassis dynamometer to determine PAH emissions. The first vehicle was a diesel Honda with a three-stage oxidation system. Its main catalyst was replaced with a diesel particulate filter (DPF) and tested as a second configuration. The second vehicle was a gasoline-fueled Toyota Corolla with a three-way catalytic converter. The last vehicle was an older Volkswagen Golf, tested using petro-diesel in its original configuration, and biodiesel with an oxidation catalyst as an alternative configuration.

Each vehicle/configuration was driven on the chassis dynamometer using the same protocol: a variety of real-world driving cycles (Artemis Cycles) and the certification test (New European Driving Cycle). The three Artemis driving cycles (urban, rural road, and motorway) consist of frequent speed variation and stronger acceleration compared to the NEDC, and were designed to simulate typical driving conditions in Europe. The vehicle and the sampling system were pre-conditioned by running three extra urban driving cycles (EUDC), according to the specifications of the UNECE R83 regulation. PAH emissions were quantified by gas chromatography/mass spectrometry (GC/MS). Filters were extracted with methanol and methylene chloride using Soxhlet for PAH compounds. The extracts were combined then concentrated using a rotary evaporator then a nitrogen evaporator.

Table 111: Emission factors (ng/km) of 12 priority PAHs classified by the US EPA

	Accord Diesel	DPF-Accord	Corolla Gas	Golf Diesel	Golf Biodiesel
Phenanthrene	1885.863	9.654	48.840	3473.892	1098.541
Anthracene	98.832	NA	NA	238.534	207.170
Fluoranthene	152.642	NA	15.086	4291.934	3598.508
Pyrene	186.384	NA	11.650	3861.310	858.368
Benz(a)anthracene	70.297	NA	26.827	390.694	294.705
Chrysene	184.207	NA	67.863	1192.698	617.755
Benzo(b)fluoranthene	NA	NA	91.030	429.193	511.898
Benzo(k)fluoranthene	NA	NA	29.819	127.980	212.095
Benzo(a)pyrene	NA	NA	15.445	NA	154.446
Indeno(1,2,3-cd)pyrene	NA	NA	46.598	NA	241.353
Benzo(ghi)perylene	NA	NA	112.466	NA	828.643
Dibenz(ah)anthracene	NA	NA	21.460	NA	NA

Zielinska et al. (2009) [Phase and Size Distribution of Polycyclic Aromatic Hydrocarbons in Diesel and Gasoline Vehicle Emissions, Environmental Science and Technology] measured PAH emissions for a variety of military vehicles on a chassis dynamometer, including aircraft ground support equipment vehicles using gasoline, diesel, and JP8 fuels. The exhaust from the tested vehicle was passed to a dilution tunnel where it was diluted 30−40 times and collected using Micro-Orifice Uniform Deposit Impactor (MOUDI) fitted with aluminum substrates, an XAD-coated annular denuder, and a filter followed by a solid adsorbent. All MOUDI substrates were analyzed for polycyclic aromatic hydrocarbons (PAHs) by GC/MS. The test vehicles are shown below.



vehicle type[a]	fuel type	engine manufacturer	engine displacement	exhaust treatment
1993 Ford F-350	gasoline	Ford	5.8 L	catalytic converter
1996 Dodge Bobtail	diesel	Cummins	5.9 L	none
1986 Jeep Bobtail	diesel	Nissan	4.4 L	none
1992 Jammer	JP-8 aviation fuel	HATZ	1.27 L	none

[a] Bobtail vehicles tow aircraft, and Jammers lift munitions into aircraft.

The gas-phase components of the semivolatile PAHs were collected using a sorbent-coated annular denuder. The denuder sampler consisted of three stages; the first stage was an 8-channel denuder section (52 mm o.d., 600 mm length) coated with polystyrene−divinylbenzene resin XAD-4, which strips the gas-phase species from the airstream before collection of the particles on a second stage, consisting of a 47-mm Teflon-impregnated glass fiber (TIGF, T60X20) filter. The third stage consisted of polyurethane foam plugs (1 in. diameter) in combination with the 5 g of adsorbent resin XAD-4 (PUF/XAD/PUF “sandwich” cartridge) that was placed downstream of the filter to assess “blow off” or volatilization loss of semivolatile PAHs from the particles. In parallel, a medium-volume DRI fine particulate/semivolatile organic compound (FP/SVOC) sampler, using 90 mm TIGF (T60X40) filters backed by the PUF/XAD/PUF “sandwich” cartridge (10 g of XAD-4 resin between two 2-in. PUF plugs) was employed. The flow was set at approximately 90 L/min for the denuder and at 100 L/min for the FP/SVOC sampler.

Prior to sampling, the XAD-4 resin was cleaned by Soxhlet extraction with methanol followed by dichloromethane (CH2Cl2), each for 48 h. The cleaned resin was then dried in a vacuum oven heated at 40 °C and stored in sealed glass containers in a clean freezer. The PUF plugs were cleaned by Soxhlet extraction with acetone followed by extraction with 10% diethyl ether in hexane, as described in U.S. EPA Method TO-13. Prior to sampling, XAD-4 resin and PUF plugs were loaded into the glass sampling cartridges. The TIGF filters were cleaned by sonication in methanol for 10 min (twice), followed by two more 10-min sonications in CH_2Cl_2.

The SVOCs collected on each denuder-filter-PUF/XAD/PUF sampling train were extracted separately with high-purity, HPLC grade solvents. The denuder portion was extracted with cyclohexane immediately following the sample collection. Approximately 200 mL of cyclohexane was poured into the denuder section, which had been capped at one end. The other end was capped, and the denuder was manually inverted about 10 times. The solvent was drained and the procedure repeated two more times, using n-hexane for the last extraction. The PUF/XAD plugs were microwave-extracted with 10% diethyl ether in hexane, and the filters were microwave-extracted with dichloromethane.

The extracts were concentrated by rotary evaporation at 20 °C under gentle vacuum to ~1 mL and filtered through 0.20 μm of Anatop (Whatman International, Ltd.), rinsing the sample flask twice with 1 mL of CH_2Cl_2 each time. Approximately 50 μL of acetonitrile was added to the sample, and CH_2Cl_2 was evaporated under a gentle stream of nitrogen. The final volume was adjusted to 1 mL with acetonitrile. The sample was then analyzed by electron impact (EI) GC/MS technique, using an Ion Trap Varian Saturn 2000, operating in the selected ion storage (SIS) mode. Injections (1 μL) were made in the splitless mode onto a 30 m × 0.25 mm i.d. CPSil 8 fused-silica capillary column (Varian, Inc.).

Table 112: Distribution of PAH (ng/m^3) over MOUDI stages for 1996 Dodge Bobtail runs. (A-C) variable (95, 81, 54, and 27%) load; (D-F) low (27% load)

(A)									
Compound	**<.05**	**.05-.10**	**.10-.18**	**.18-.32**	**0.32-0.53**	**0.53-1.0**	**1.0-1.8**	**1.8-3.2**	**3.2-5.6**
Naphthalene	5.752	6.932	11.799	8.702	6.637	6.932	5.457	7.670	9.145
Methylnaphthalenes	6.342	5.162	8.997	12.537	8.702	3.687	4.277	3.982	6.195
Dimethylnaphthalenes	6.932	8.997	17.404	16.077	11.947	9.882	6.047	17.257	10.619
Trimethylnaphthalenes	44.100	6.932	8.702	12.537	11.062	8.112	9.292	30.531	14.454
Acenaphthylene	1.622	0.737	2.950	1.622	0.885	0.885	1.032	3.245	1.032
Acenaphthene	3.392	0.737	1.622	1.475	0.885	1.917	1.032	1.622	1.032
Fluorene		0.737	3.687	7.522	3.097	1.622	1.032	1.180	2.065
(B)									
Compound	**<.05**	**.05-.10**	**.10-.18**	**.18-.32**	**0.32-0.53**	**0.53-1.0**	**1.0-1.8**	**1.8-3.2**	**3.2-5.6**
phenanthrene	18.913	3.783	9.456	20.804	18.913	7.565		3.783	3.783

Methylphenanthrenes	68.085		34.043	160.757	90.780			3.783	3.783
Dimethylphenanthrenes	155.083	9.456	211.820	724.350	342.317	7.565		3.783	11.348
Fluoranthene	7.565		18.913	49.173	26.478			3.783	3.783
pyrene	18.913	11.348	60.520	153.191	75.650	9.456	9.456	9.456	11.348
methyl pyrene/methyl fluoranthene	30.260	24.586	132.388	308.274	124.823	15.130	13.239	17.021	15.130
(C)									
Compound	**<.05**	**.05-.10**	**.10-.18**	**.18-.32**	**0.32-0.53**	**0.53-1.0**	**1.0-1.8**	**1.8-3.2**	**3.2-5.6**
benzo[a]anthracene	0.957	2.154	11.011	14.601	7.899	0.718	1.197	1.676	1.676
chrysene	4.548	8.856	44.282	84.016	33.032	1.915	1.676	2.633	1.676
benzo[b+j+k]fluoranthene	1.676	2.394	16.516	30.399	15.080	1.436	1.197	1.676	1.676
benzo[e]pyrene	1.676	1.915	6.702	13.404	6.463	1.197	1.197	1.436	0.718
benzo[a]pyrene	0.718	0.718	2.154	4.548	1.676	1.197	0.718	1.197	1.676
benzo[ghi]perylene	2.154	0.718	1.676	4.548	2.154	1.197	0.718	1.915	1.676
coronene	2.154	0.000	1.197	2.633	1.676	0.718	1.197	1.436	1.676
(D)									
Compound	**<.05**	**.05-.10**	**.10-.18**	**.18-.32**	**0.32-0.53**	**0.53-1.0**	**1.0-1.8**	**1.8-3.2**	**3.2-5.6**
Naphthalene	3.805	5.929	8.761	1.593	3.009	3.805	3.628	3.628	4.867
Methylnaphthalenes	4.336	5.044	5.929	2.212	1.681	1.858	2.920	4.159	3.982
dimethylnaphthalene	4.159	5.929	11.416	4.336	2.832	28.584	4.690	3.628	5.221
trimethylnaphthalenes	11.416	6.903	7.168	1.593	5.487	2.389	7.168	8.053	9.115
Acenaphthylene	0.531	0.442	1.770	1.327	0.619	3.097	1.504	0.973	0.796
Acenaphthene	0.442	0.619	0.708	0.708	0.619	2.566	1.327	0.796	1.327
fluorene	1.770	0.442	1.062	0.708	-0.177	-1.504	0.973	0.796	0.973
(E)									
Compound	**<.05**	**.05-.10**	**.10-.18**	**.18-.32**	**0.32-0.53**	**0.53-1.0**	**1.0-1.8**	**1.8-3.2**	**3.2-5.6**
phenanthrene	6.052	1.702	2.459	1.135	0.946	0.946	1.135	1.324	2.080
Methylphenanthrenes	28.558	3.215	6.241	3.593	2.080	1.135	1.135	0.757	1.135
dimethylnaphthalene	69.976	8.132	36.312	14.563	1.702	1.135	3.026	1.324	2.648
fluoranthene	3.215		3.215	2.080	0.757	0.757	1.324	1.324	1.324
pyrene	10.213	3.783	12.671	8.511	0.946	1.135	1.891	1.324	2.459
methyl pyrene/methyl fluoranthene	30.827	26.288	61.655	45.012	5.296	5.106	5.485	5.296	5.296
(F)									
Compound	**<.05**	**.05-.10**	**.10-.18**	**.18-.32**	**0.32-0.53**	**0.53-1.0**	**1.0-1.8**	**1.8-3.2**	**3.2-5.6**
benzo[a]anthracene	1.120	1.707	4.747	1.813	0.480	0.107	0.747		0.587
chrysene	4.320	12.053	17.760	11.253	0.053	0.480		0.587	1.173
benzo[b+j+k]fluoranthene	1.493	3.787	3.253	1.813	0.480	0.480	0.587	0.587	0.800
benzo[e]pyrene	0.960	2.293	2.720	1.547	0.480	0.480	0.533		0.587

benzo[a]pyrene	0.373	1.547	1.547	0.693		0.480			0.267
benzo[ghi]perylene	0.373	0.907	0.640	0.693	0.480	0.480	0.800		0.907
coronene	0.587	0.907	0.427	0.053	0.693		0.800	0.587	1.227

Table 113: Comparison of samples collected with the denuder with samples collected in parallel with FP/SVOC sampler. (A) 1996 Dodge Bobtail, idle, denuder filter + denuder PUF/XAD/PUF vs FP/SVOC filter; (B) 1996 Dodge Bobtail, idle, denuder XAD portion vs. FP/SVOC PUF/XAD/PUF cartridge; (C) 1996 Dodge Bobtail, variable load, denuder filter + denuder PUF/XAD/PUF vs FP/SVOC filter; (D) 1996 Dodge Bobtail, high load, denuder XAD portion vs. FP/SVOC PUF/XAD/PUF cartridge (ng/m^3).

	(A) Dodge Bobtail, Idle		**(B) Dodge Bobtail, Idle**		**(C) Dodge Bobtail, 95-27% Load**		**(D) Dodge Bobtail, 95-27% Load**	
Compound, ng/m^3	**DF+DP**	**FP/SVOC/ Filter**	**XAD Denude**	**FP/SVOC/ Filter**	**DF+DP**	**FP/SVOC/ Filter**	**XAD Denude**	**FP/SVOC/ Filter**
Acenaphthylene	1.514	2.946	500.000	891.892	N/A	N/A	526.316	754.386
Acenaphthene	10.892	0.730	54.054	729.730	65.217	N/A	70.175	596.491
fluorene	1.432	0.703	1797.297	1418.919	117.391	26.087	1614.035	1192.982
phenanthrene	N/A	0.676	2121.622	2581.081	247.826	78.261	2964.912	2877.193
methylfluorenes	N/A	0.649	1081.081	2635.135	65.217	26.087	1052.632	2000.000
xanthone	0.676	2.946	189.189	783.784	65.217	39.130	192.982	385.965
methylphenanthrene	11.568	2.135	2364.865	2108.108	913.043	234.783	3456.140	1859.649
dimethylphenanthrene	2.135	0.622	1959.459	959.459	2543.478	1239.130	3385.965	964.912
anthracene	0.676	N/A	135.135	270.270	91.304	117.391	210.526	192.982
fluoranthene	N/A	1.432	121.622	135.135	182.609	104.348	140.351	87.719
pyrene	N/A	2.892	189.189	202.703	495.652	313.043	280.702	122.807
benzonaphthothiophene	13.757	0.676	N/A	27.027	169.565	195.652	52.632	N/A
methyl pyrene/methyl fluoranthene	1.432	0.676	162.162	67.568	795.652	821.739	175.439	70.175
benzo[c]phenanthrene	0.622	N/A	N/A	N/A	26.087	26.087	N/A	N/A
benzo[a]anthracene	0.622	N/A	N/A	N/A	39.130	52.174	N/A	N/A

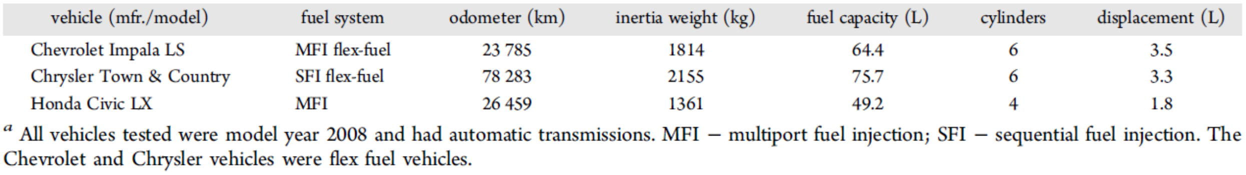
chrysene	N/A	2.135	27.027	N/A	208.696	208.696	52.632	N/A
benzo[b+j+k]fluoranthene	12.243	0.649	N/A	N/A	65.217	52.174	N/A	N/A
benzo[e]pyrene	1.405	0.622	N/A	N/A	26.087	39.130	N/A	N/A
benzo[a]pyrene	N/A	N/A	N/A	N/A	26.087	26.087	N/A	N/A
indeno[1,2,3-cd]pyrene	0.622	0.676	N/A	N/A	26.087	N/A	N/A	N/A
benzo[ghi]perylene	0.676	3.595	N/A	N/A	26.087	N/A	N/A	N/A
dibenz[ah+ac]anthracene	13.000	0.676	N/A	N/A	N/A	N/A	N/A	N/A
coronene	0.622	0.676	N/A	N/A	N/A	N/A	N/A	N/A
Naphthalene	1881.443	N/A	5309.735	10088.496	986.047	18.605	8258.929	8482.143
Methylnaphthalenes	2216.495	N/A	15929.204	20707.965	855.814	18.605	14285.714	15848.214
biphenyl	103.093	N/A	2389.381	3185.841	46.512	N/A	2678.571	2678.571
dimethylnaphthalene	979.381	N/A	18318.584	25752.212	409.302	46.512	17410.714	19866.071
methylbiphenyls	77.320	N/A	5044.248	5840.708	251.163	18.605	4241.071	4687.500
trimethylnaphthalenes	541.237	N/A	13539.823	21238.938	241.860	139.535	11830.357	16741.071

Table 114: Comparison of samples collected with the denuder with samples collected in parallel with FP/SVOC sampler. (A) Ford F350, high load, denuder filter+denuder PUF/XAD/PUF vs FP/SVOC filter; (B) Ford F350, high load, denuder XAD portion vs. FP/SVOC PUF/XAD/PUF cartridge; (C) Ford F350, variable load, denuder filter + denuder PUF/XAD/PUF vs FP/SVOC filter; (D) Ford F350, variable load, denuder XAD portion FP/SVOC vs. PUF/XAD/PUF cartridge (ng/m^3).

	(A) Ford F350, 53% Load		**(B) Ford F350, 53% Load**		**(C) Ford F350, 53-11% Load**		**(D) Ford F350, 53-11% Load**	
Compound, ng/m^3	**DF+DP**	**FP/SVOC/ Filter**	**XAD Denude**	**FP/SVOC/ Filter**	**DF+ DP**	**FP/SVOC/ Filter**	**XAD Denude**	**FP/SVOC/ Filter**
phenanthrene	3.266	2.177	344.531	847.266	N/A	1.575	342.412	428.016
methylfluorenes	1.452	2.903	94.922	112.500	4.134	0.886	17.510	31.128
xanthone	N/A	3.629	158.203	14.062	0.295	3.642	15.564	11.673

methylphenanthrene	13.065	2.177	225.000	112.500	13.091	4.724	66.148	171.206
dimethylphenanthrene	16.331	N/A	63.281	28.125	12.795	1.181	11.673	17.510
anthracene	6.169	1.815	66.797	210.937	N/A	N/A	27.237	60.311
fluoranthene	5.806	1.452	42.187	63.281	N/A	1.575	60.311	42.802
pyrene	10.524	3.266	35.156	56.250	1.575	2.165	46.693	38.911
benzonaphthothiophene	2.903	N/A	N/A	N/A	0.787	N/A	N/A	N/A
methyl pyrene/methyl fluoranthene	26.855	4.718	N/A	17.578	19.783	2.953	7.782	11.673
benzo[c]phenanthrene	1.815	N/A	N/A	N/A	0.394	0.591	N/A	N/A
benzo[a]anthracene	7.258	4.718	N/A	N/A	N/A	N/A	5.837	N/A
chrysene	19.960	14.879	17.578	14.062	N/A	1.280	5.837	N/A
benzo[b+j+k]fluoranthene	77.298	68.589	N/A	N/A	2.461	2.165	N/A	N/A
benzo[e]pyrene	50.081	53.347	17.578	14.062	4.528	2.362	N/A	N/A
benzo[a]pyrene	80.565	86.008	N/A	14.062	3.248	1.575	N/A	N/A
indeno[1,2,3-cd]pyrene	27.218	38.468	N/A	N/A	1.280	0.492	5.837	N/A
benzo[ghi]perylene	38.105	45.000	N/A	N/A	1.870	N/A	N/A	N/A
dibenz[ah+ac]anthracene	13.427	7.984	N/A	N/A	0.591	N/A	N/A	3.891
coronene	18.145	14.879	N/A	N/A	2.264	0.591	N/A	N/A
Naphthalene	2530.120	N/A	55841.584	42178.218	39.796	5.102	9469.697	9621.212
Methylnaphthalenes	253.012	N/A	47524.752	10099.010	30.612	2.041	1969.697	1363.636
dimethylnaphthalene	72.289	N/A	8316.832	1782.178	32.653	3.061	151.515	303.030
trimethylnaphthalenes	N/A	N/A	9504.950	594.059	94.898	10.204	75.758	75.758

Hays et al. (2013) [Carbonaceous Aerosols Emitted from Light-Duty Vehicles Operating on Gasoline and Ethanol Fuel Blends, Environmental Science and Technology] examined the effects of fuel ethanol content (e0 versus e10 versus e85), operating conditions, and ambient temperature (−7 and 24 °C) on the PAH composition of the carbonaceous PM emitted from a set of three modern LDVs meeting U.S. Tier 2 emissions standards. Technical characteristics of the vehicles are shown below.



vehicle (mfr./model)	fuel system	odometer (km)	inertia weight (kg)	fuel capacity (L)	cylinders	displacement (L)
Chevrolet Impala LS	MFI flex-fuel	23 785	1814	64.4	6	3.5
Chrysler Town & Country	SFI flex-fuel	78 283	2155	75.7	6	3.3
Honda Civic LX	MFI	26 459	1361	49.2	4	1.8

[a] All vehicles tested were model year 2008 and had automatic transmissions. MFI − multiport fuel injection; SFI − sequential fuel injection. The Chevrolet and Chrysler vehicles were flex fuel vehicles.

Test vehicles were operated over the three-phase LA-92 unified driving cycle (UDC). Each LDV-fuel-temperature combination was tested in duplicate sequentially. LDV exhaust was directed to a dilution tunnel and constant volume sampling (CVS) system using an insulated transfer tube. Briefly, dilution air (21 m3/min; 21 °C) passed through a charcoal bed to stabilize hydrocarbons and then through a HEPA-filter to remove PM before mixing with the LDV raw exhaust. Particle emissions were collected on Teflon (R2PJ047, Pall Corporation, Ann Arbor, MI) positioned downstream of a PM2.5 cyclone (93 L/min; URG-2000–30-EP, URG, Chapel Hill, NC). Multiple four-point isokinetic probe assemblies were used that allowed separate and proportional PM2.5 sampling of each UDC phase.

Due to its sensitivity, thermal extraction gas chromatography–mass spectroscopy (TE-GC-MS) was selected to further examine the PM PAH composition. Briefly, filters were introduced to a glass TE tube and spiked with internal standard solution. After tube insertion, the TE unit (TDS2, Gerstel Inc., Germany) temperature was ramped from 25 to 300 °C at 10 °C/min and held constant at 300 °C for 5 min. A splitless-mode extraction was performed with He flowing continuously (50 mL/min) over the sample. Extract was directed through a heated (300 °C) capillary transfer line to a cryo-cooled (−100 °C) PTV inlet also operating in splitless mode. Following the TE step, the inlet was flash-heated to 300 °C at a rate of 702 °C/min. Sample was chromatographed on an ultralow bleed capillary column (DB5, Agilent Technologies, 30 m length, 0.25 μm film thickness and 0.25 mm i.d.). Helium was used as the carrier gas (1 mL/min). The GC oven temperature was programmed at 65 °C for 10 min and then ramped to 300 °C at 10 °C/min and held fixed for 41.5 min. The MS (5973, Agilent Technologies) was operated in scan mode (50–500 amu, 3 scans/s).

Table 115: PAH emissions

Compound	Phase	Temp.		concentration (ng/km)					
		(C)	Fuel	N	N Miss	Mean	Minimum	Median	Maximum
1-Methylchrysene	1	-7	E0	3	0	448.3	363.6	463.7	517.6
			E10	3	0	400.1	122.5	372.0	705.8
			E85	2	0	38.9	0.0	38.9	77.8
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
1-Methylnaphthalene	1	-7	E0	3	0	2011.0	1290.8	1447.1	3295.2
			E10	3	0	1533.6	352.2	1333.7	2915.0
			E85	2	0	577.5	0.0	577.5	1154.9
		24	E0	4	0	132.8	0.0	102.8	325.6
			E10	3	0	94.7	0.0	0.0	284.2
			E85	2	0	118.6	0.0	118.6	237.2
	2	-7	E0	3	0	87.5	0.0	71.0	191.5
			E10	3	0	83.9	0.0	115.6	136.2
			E85	2	0	82.0	0.0	82.0	164.1
		24	E0	4	0	24.8	0.0	25.7	47.8
			E10	3	0	25.7	0.0	36.1	41.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	41.4	0.0	0.0	124.2
			E10	3	0	42.5	0.0	0.0	127.5
			E85	2	0	14.4	0.0	14.4	28.7
		24	E0	4	0	5.7	0.0	0.0	23.0
			E10	3	0	11.5	0.0	0.0	34.5
			E85	2	0	8.1	0.0	8.1	16.2
2,6-Dmethylnaphthalene	1	-7	E0	3	0	263.6	0.0	205.5	585.1

			E10	3	0	238.5	0.0	256.1	459.3
			E85	2	0	79.8	0.0	79.8	159.5
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	43.8	0.0	43.8	87.5
	2	-7	E0	3	0	9.9	0.0	0.0	29.6
			E10	3	0	5.0	0.0	0.0	14.9
			E85	2	0	8.6	0.0	8.6	17.3
		24	E0	4	0	3.7	0.0	0.0	14.9
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	7.3	0.0	0.0	22.0
			E10	3	0	5.8	0.0	0.0	17.5
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
2-Methylnaphthalene	1	-7	E0	3	0	72.5	0.0	0.0	217.5
			E10	3	0	69.9	0.0	0.0	209.6
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	8.5	0.0	0.0	25.5
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	11.7	0.0	11.7	23.5
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
2-Methylnonadecane/Interference	1	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0

	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
3-Methylnonadecane/Interference	1	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
9-Methylanthracene	1	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Acenaphthene	1	-7	E0	3	0	557.6	278.2	312.3	1082.2
			E10	3	0	621.2	0.0	496.0	1367.6
			E85	2	0	147.7	0.0	147.7	295.3
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	46.7	0.0	0.0	140.2

			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	2.9	0.0	0.0	8.6
			E10	3	0	19.0	0.0	8.4	48.5
			E85	2	0	12.7	0.0	12.7	25.4
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	6.3	0.0	0.0	19.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Acenaphthylene	1	-7	E0	3	0	397.1	0.0	391.4	799.9
			E10	3	0	443.1	0.0	542.5	786.7
			E85	2	0	264.4	0.0	264.4	528.8
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	12.8	0.0	0.0	38.3
			E10	3	0	11.1	0.0	0.0	33.4
			E85	2	0	35.1	0.0	35.1	70.2
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Anthracene	1	-7	E0	3	0	2342.0	1007.8	3003.8	3014.3
			E10	3	0	1258.6	288.3	1584.5	1902.9
			E85	2	0	165.3	0.0	165.3	330.5
		24	E0	4	0	30.0	0.0	0.0	120.1
			E10	3	0	77.9	0.0	0.0	233.7
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	109.0	62.6	122.3	142.1
			E10	3	0	78.4	26.2	70.8	138.2
			E85	2	0	17.1	0.0	17.1	34.2
		24	E0	4	0	10.7	0.0	0.0	42.6
			E10	3	0	12.0	4.2	6.3	25.4
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	40.3	0.0	38.8	82.1
			E10	3	0	27.1	0.0	0.0	81.3
			E85	2	0	2.2	0.0	2.2	4.4
		24	E0	4	0	4.9	0.0	0.0	19.8

			E10	3	0	0.9	0.0	0.0	2.7
			E85	2	0	0.0	0.0	0.0	0.0
Benz(a)anthracene	1	-7	E0	3	0	11753.2	8813.1	11100.6	15345.8
			E10	3	0	7905.9	2051.9	10331.6	11334.2
			E85	2	0	1576.8	1498.0	1576.8	1655.6
		24	E0	4	0	49.3	23.2	48.5	76.7
			E10	3	0	104.4	61.0	61.5	190.7
			E85	2	0	5.8	0.0	5.8	11.7
	2	-7	E0	3	0	200.8	111.6	142.3	348.4
			E10	3	0	56.2	19.0	40.5	109.0
			E85	2	0	14.8	12.4	14.8	17.2
		24	E0	4	0	9.1	0.0	2.2	32.0
			E10	3	0	9.9	4.1	4.2	21.3
			E85	2	0	1.0	0.0	1.0	2.0
	3	-7	E0	3	0	79.1	46.4	63.4	127.3
			E10	3	0	22.6	1.8	3.0	62.8
			E85	2	0	3.2	1.1	3.2	5.3
		24	E0	4	0	4.9	0.0	1.8	16.1
			E10	3	0	2.4	0.0	3.5	3.6
			E85	2	0	0.9	0.0	0.9	1.7
Benzo(a)pyrene	1	-7	E0	3	0	8065.1	4375.9	7141.5	12677.9
			E10	3	0	8978.6	1316.9	9207.5	16411.3
			E85	2	0	2647.4	2574.6	2647.4	2720.3
		24	E0	4	0	11.6	0.0	0.0	46.5
			E10	3	0	36.0	0.0	45.8	62.3
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	32.2	21.2	31.6	43.8
			E10	3	0	16.5	0.0	18.1	31.4
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	3.7	0.0	0.0	14.9
			E10	3	0	2.1	0.0	0.0	6.3
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	30.1	0.0	14.7	75.6
			E10	3	0	4.8	0.0	0.0	14.5
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	1.4	0.0	0.0	5.5
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Benzo(b)fluoranthene	1	-7	E0	3	0	6549.9	3807.5	7558.9	8283.3
			E10	3	0	5436.9	1301.6	5130.8	9878.4
			E85	2	0	1564.9	1404.3	1564.9	1725.4
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	67.1	27.5	54.8	118.9
			E10	3	0	10.5	0.0	0.0	31.4
			E85	2	0	0.0	0.0	0.0	0.0

		24	E0	4	0	5.8	0.0	0.0	23.4
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	94.2	0.0	20.1	262.4
			E10	3	0	6.7	0.0	0.0	20.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Benzo(e)pyrene	1	-7	E0	3	0	5568.2	2537.0	5959.5	8208.1
			E10	3	0	4276.0	1209.7	4030.2	7588.0
			E85	2	0	2351.4	2200.1	2351.4	2502.7
		24	E0	4	0	11.6	0.0	0.0	46.5
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	67.7	23.3	42.2	137.7
			E10	3	0	19.2	6.3	24.2	27.2
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	3.7	0.0	0.0	14.9
			E10	3	0	2.1	0.0	0.0	6.3
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	30.5	12.8	21.6	57.2
			E10	3	0	4.2	0.0	0.0	12.7
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	1.4	0.0	0.0	5.5
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Benzo(ghi)fluoranthene	1	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Benzo(ghi)perylene	1	-7	E0	3	0	11436.8	6446.2	11587.1	16277.1
			E10	3	0	12851.3	3261.7	13454.8	21837.5

			E85	2	0	12272.7	8379.0	12272.7	16166.3
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	31.6	0.0	0.0	94.7
			E10	3	0	11.9	0.0	0.0	35.6
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	28.8	0.0	0.0	86.4
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Benzo(k)fluoranthene	1	-7	E0	3	0	7359.2	5030.8	8115.4	8931.5
			E10	3	0	7323.7	1470.0	6122.9	14378.2
			E85	2	0	1783.4	1694.3	1783.4	1872.4
		24	E0	4	0	15.5	0.0	0.0	62.0
			E10	3	0	20.3	0.0	0.0	61.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	57.4	29.6	54.8	87.6
			E10	3	0	11.1	0.0	0.0	33.4
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	5.8	0.0	0.0	23.4
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	64.8	18.3	21.6	154.4
			E10	3	0	6.0	0.0	0.0	18.1
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Chrysene	1	-7	E0	3	0	14233.3	9398.4	10473.8	22827.8
			E10	3	0	8021.3	3057.8	10496.0	10510.2
			E85	2	0	1757.6	1494.1	1757.6	2021.1
		24	E0	4	0	64.7	34.9	60.2	103.4
			E10	3	0	149.3	76.3	76.8	294.8
			E85	2	0	24.8	10.9	24.8	38.7
	2	-7	E0	3	0	351.3	178.8	211.1	664.0
			E10	3	0	72.8	35.6	52.6	130.2
			E85	2	0	20.2	16.7	20.2	23.7
		24	E0	4	0	12.4	0.0	7.6	34.3
			E10	3	0	6.1	3.8	6.3	8.1
			E85	2	0	4.4	0.1	4.4	8.8
	3	-7	E0	3	0	157.3	82.0	91.6	298.4

			E10	3	0	32.2	2.6	8.3	85.7
			E85	2	0	2.6	2.1	2.6	3.1
		24	E0	4	0	7.0	0.0	6.1	15.7
			E10	3	0	6.6	5.5	7.1	7.2
			E85	2	0	3.1	1.3	3.1	4.8
Coronene	1	-7	E0	3	0	9036.5	6863.3	8251.7	11994.6
			E10	3	0	8961.3	1653.8	10804.1	14426.0
			E85	2	0	8914.1	5844.8	8914.1	11983.3
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	14.1	0.0	0.0	42.2
			E10	3	0	25.8	0.0	0.0	77.4
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	8.3	0.0	0.0	24.8
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Cyclopentane(cd)pyrene	1	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Dibenzo(a,e)pyrene	1	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0

	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Dibenzo(a,h)anthracene	1	-7	E0	3	0	610.3	517.6	649.2	664.0
			E10	3	0	538.1	0.0	290.9	1323.5
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	30.6	0.0	0.0	91.8
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Dibenzofuran	1	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0

			E85	2	0	0.0	0.0	0.0	0.0
Fluoranthene	1	-7	E0	3	0	25608.1	11889.9	28838.7	36095.7
			E10	3	0	10817.0	2100.7	15060.5	15289.8
			E85	2	0	2675.9	2667.2	2675.9	2684.5
		24	E0	4	0	275.3	0.0	250.0	601.3
			E10	3	0	775.8	316.8	376.4	1634.2
			E85	2	0	222.2	127.6	222.2	316.8
	2	-7	E0	3	0	1775.5	842.4	899.4	3584.7
			E10	3	0	683.2	287.6	741.7	1020.2
			E85	2	0	154.4	133.4	154.4	175.5
		24	E0	4	0	45.7	0.0	21.8	139.2
			E10	3	0	114.5	32.7	131.6	179.3
			E85	2	0	31.5	24.2	31.5	38.8
	3	-7	E0	3	0	805.6	295.5	434.5	1687.0
			E10	3	0	246.0	26.9	250.2	461.0
			E85	2	0	34.5	30.3	34.5	38.8
		24	E0	4	0	36.8	0.0	33.5	80.0
			E10	3	0	137.0	27.8	40.8	342.4
			E85	2	0	12.9	7.1	12.9	18.8
Fluorene	1	-7	E0	3	0	1108.4	413.5	557.6	2354.1
			E10	3	0	912.9	73.6	922.6	1742.4
			E85	2	0	118.6	0.0	118.6	237.3
		24	E0	4	0	40.3	0.0	27.2	107.0
			E10	3	0	71.2	0.0	46.1	167.4
			E85	2	0	25.5	0.0	25.5	51.0
	2	-7	E0	3	0	9.1	0.0	7.8	19.5
			E10	3	0	22.0	0.0	17.0	49.0
			E85	2	0	5.5	0.0	5.5	10.9
		24	E0	4	0	1.1	0.0	0.0	4.5
			E10	3	0	7.1	0.0	0.0	21.2
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	3.9	0.0	0.0	11.7
			E10	3	0	7.2	0.0	7.9	13.8
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.7	0.0	0.0	2.9
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	1.3	0.0	1.3	2.6
Indeno(1,2,3-cd)pyrene	1	-7	E0	3	0	10278.1	5128.7	11083.2	14622.3
			E10	3	0	13835.5	1868.2	14183.3	25455.1
			E85	2	0	6909.1	3885.2	6909.1	9932.9
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	16.8	0.0	0.0	50.5
			E10	3	0	8.4	0.0	0.0	25.1
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0

			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	19.8	0.0	0.0	59.4
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Methyl-fluorene	1	-7	E0	3	0	841.8	498.7	822.4	1204.4
			E10	3	0	504.9	0.0	518.3	996.4
			E85	2	0	81.8	0.0	81.8	163.6
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	51.9	0.0	0.0	155.6
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	10.8	0.0	0.0	32.3
			E10	3	0	9.9	0.0	0.0	29.7
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	2.8	0.0	0.0	11.2
			E10	3	0	10.0	0.0	15.0	15.1
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	8.7	0.0	0.0	26.0
			E10	3	0	9.3	0.0	0.0	28.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	1.9	0.0	0.0	7.6
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Naphthalene	1	-7	E0	3	0	2437.3	1746.9	1885.8	3679.2
			E10	3	0	1955.2	479.5	1717.5	3668.7
			E85	2	0	723.2	0.0	723.2	1446.5
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	58.9	0.0	0.0	176.8
			E10	3	0	34.4	0.0	0.0	103.2
			E85	2	0	78.9	0.0	78.9	157.9
		24	E0	4	0	13.5	0.0	0.0	54.0
			E10	3	0	17.8	0.0	0.0	53.4
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	38.8	0.0	0.0	116.5
			E10	3	0	39.9	0.0	0.0	119.8
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	14.6	0.0	0.0	43.8
			E85	2	0	0.0	0.0	0.0	0.0
Perylene	1	-7	E0	3	0	1717.1	1223.4	1762.2	2165.7
			E10	3	0	2345.6	336.9	1891.1	4808.7
			E85	2	0	420.6	373.1	420.6	468.1

		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	2	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
	3	-7	E0	3	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
		24	E0	4	0	0.0	0.0	0.0	0.0
			E10	3	0	0.0	0.0	0.0	0.0
			E85	2	0	0.0	0.0	0.0	0.0
Phenanthrene	1	-7	E0	3	0	15020.3	6296.6	14117.2	24647.2
			E10	3	0	7105.3	1277.8	9627.2	10411.1
			E85	2	0	1649.0	1303.1	1649.0	1995.0
		24	E0	4	0	414.7	54.7	294.6	1015.0
			E10	3	0	1203.5	336.0	595.4	2679.0
			E85	2	0	406.0	383.3	406.0	428.7
	2	-7	E0	3	0	558.2	167.4	569.4	937.7
			E10	3	0	688.7	152.1	574.1	1339.8
			E85	2	0	192.2	145.3	192.2	239.0
		24	E0	4	0	24.7	0.0	13.6	71.6
			E10	3	0	147.3	22.7	68.1	351.1
			E85	2	0	27.4	20.4	27.4	34.5
	3	-7	E0	3	0	175.6	27.5	237.5	261.7
			E10	3	0	195.5	7.6	265.8	313.3
			E85	2	0	34.7	31.0	34.7	38.3
		24	E0	4	0	12.8	0.0	10.2	31.0
			E10	3	0	21.3	3.9	17.8	42.1
			E85	2	0	9.9	3.7	9.9	16.2
Pyrene	1	-7	E0	3	0	27768.2	12335.2	30832.3	40137.1
			E10	3	0	14157.6	2957.4	18788.2	20727.2
			E85	2	0	5083.2	3721.9	5083.2	6444.5
		24	E0	4	0	205.0	27.3	137.6	517.5
			E10	3	0	978.6	198.4	203.6	2533.8
			E85	2	0	157.6	91.2	157.6	223.9
	2	-7	E0	3	0	1286.8	858.7	967.8	2033.8
			E10	3	0	801.7	344.4	931.7	1129.0
			E85	2	0	232.5	143.6	232.5	321.4
		24	E0	4	0	43.7	0.0	37.2	100.5
			E10	3	0	136.0	28.5	79.6	299.8
			E85	2	0	33.4	20.1	33.4	46.7
	3	-7	E0	3	0	502.7	299.8	542.1	666.0
			E10	3	0	313.9	37.3	361.0	543.4

			E85	2	0	57.8	40.1	57.8	75.5
		24	E0	4	0	34.6	0.0	34.2	70.0
			E10	3	0	30.8	18.7	24.7	49.0
			E85	2	0	10.5	4.8	10.5	16.2

Devos et al. (2006) [Exhaust Emissions of PAHS of Passenger Cars, Polycyclic Aromatic Compounds] tested 13 gasoline and 17 diesel cars of different categories depending on European directives for exhaust emissions (ECE 1504, Euro 1, Euro 2, and Euro 3) for PAH emissions. testing was conducted on two type of driving cycles using a chassis dynamometer. The first two cycles were representative of the actual driving conditions in Europe, called urban and motorway VP low/high motorization (18.3/19.3 km/h, 945 s and 119.0/121.8 km/h, 729 s), under hot engine start conditions. The second type of driving cycle was a short cycle, called INRETS short urban free-flow, which was repeated 15 times (19.0 km/h, 2835 s) and carried out under cold or hot engine start conditions.

A Constant Volume Sampling (CVS) system was used for collecting exhaust emissions of the 16 PAHs listed by the U.S. Environmental Protection Agency (USEPA). PAHs were collected at the end of the dilution tunnel at room temperature using a filter and an absorber. The system consisted of two stainless steel cartridges separated by a stainless steel grid and filled respectively with 15 g of Teflon wool and 20 g of XAD2 Amberlite resin. PAHs on Teflon wool and XAD2 were extracted separately in cyclohexane by an ultrasonic method performed over 30 min at 37°C. After evaporation near to dryness, extracts were dissolved in n-octane. To eliminate polar compounds a clean-up was performed on silica cartridges with an elution by n-hexane. After evaporation, residues were dissolved in acetonitrile. All solvents used were of spectrometric grade.

PAH analysis was performed on a Merck-Hitachi chromatograph equipped with a LiChroCART 250-4 LiChrospher PAH column fed by an injection loop of 20 µ L and coupled with absorption and fluorescence spectrometers. Elution was performed using ACN/H_2O mobile phase at a flow rate of 1 mL/min.

Table 116: Mean distribution of PAHs for Euro 2 vehicles (gasoline and diesel)

PAH (ug/km)	Gasoline	Diesel
Naphthalene	0.736	1.625
Acenaphthene	0.074	0.148
Fluorene	0.035	0.094
Phenanthrene	0.702	2.278
Anthracene	0.025	0.054
Fluoranthene	0.119	0.563
Pyrene	0.124	0.435
Benz[a]anthracene	0.049	0.163
Chrysene	0.015	0.084
Benzo[b]fluoranthene	0.138	0.361
Benzo[k]fluoranthene	0.054	0.124
Benzo[a]pyrene	0.054	0.282
Indeno[1,2,3-cd]pyrene	0.336	0.534
Benzo[ghi]perylene	0.173	0.509
Dibenzo[ah]anthracene	0.049	0.094

Table 117: Average sums of the twelve less volatile PAHs according to the segmentation for gasoline (G) and diesel (D) cars

	Gasoline EURO 1	**Gasoline EURO 2**	**Gasoline EURO 3**	**Diesel 1504**	**Diesel EURO 1**	**Diesel EURO 2**	**Diesel EURO 3**
Cold short urban INRETS	1.299	1.286	0.758	3.695	0.460	0.379	0.054
Hot short urban INRETS	0.027	0.041	0.014	1.245	0.284	0.162	0.014
Urban VP I/h motorization	0.068	0.068	0.054	2.179	0.298	0.352	0.122
Motorway VP I/h motorization	0.041	0.068	0.230	1.435	0.541	0.108	0.027

Table 118: Average sums of the six carcinogenic PAHs according to the segmentation for gasoline (G) and diesel (D) cars

	Gasoline EURO 1	**Gasoline EURO 2**	**Gasoline EURO 3**	**Diesel 1504**	**Diesel EURO 1**	**Diesel EURO 2**	**Diesel EURO 3**
Cold short urban INRETS	7.841	4.300	4.132	26.138	4.806	5.143	1.096
Hot short urban INRETS	0.506	1.518	1.686	15.936	8.853	2.867	0.422
Urban VP I/h motorization	1.265	1.012	1.939	19.393	6.239	3.794	2.024
Motorway VP I/h motorization	0.422	0.843	1.096	22.681	7.167	3.457	0.927

Louis et al. (2016) [PAH, BTEX, carbonyl compound, black-carbon, NO2 and ultrafine particle dynamometer bench emissions for Euro 4 and Euro 5 diesel and gasoline passenger cars, Atmospheric Environment] examined PAH emissions from Euro 4 and Euro 5 vehicles equipped with different aftertreatment devices and technologies (Diesel vehicles with catalyzed or additive DPF and direct-injection gasoline vehicles).

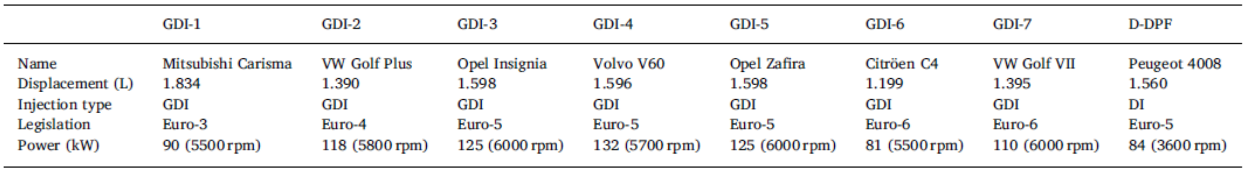
Six in-use vehicles were studied: one Euro 5 gasoline vehicle with direct injection system (G-DI); two Euro 5 Diesel vehicles with additive particulate filter (DPF add); one Euro 5 Diesel vehicle with catalyzed particulate filter (DPF cat); one Euro 4 gasoline vehicle (G); and one Euro 4 Diesel vehicle with catalyzed particulate filter (DPF cat). Experiments were conducted using the real-world Artemis driving cycles.

Gas-phase PAHs were collected into ORBO 43 cartridges at flow rates up to 0.5 L/min. Particulate-phase PAHs were collected on quartz filters at flow rates up to 50 L/min. PAH analysis was performed using High Performance Liquid Chromatography/Fluorescence Detector. For the gas-phase species the NIOSH 5506 methods was used, while for the PM-phase species the NF x 43-025 methods was used.

Table 119: PAH emission factors

Driving cycle	Artemis urban hot start	Artemis urban cold start	Artemis road hot start	Artemis motorway hot start
Vehicle 1	Euro 5 Diesel additive DPF			
Naphthalene (gas) (mg/km)	< LQ	< LQ	< LQ	2 ± 0.3
Anthracene (ng/km)	15 ± 0.2	15 ± 0.4	30 ± 3	8 ± 2
Pyrene (ng/km)	109 ± 19	129 ± 2	40 ± 3	23 ± 2
Benz[a]anthracene (ng/km)	101 ± 22	93 ± 30	38 ± 11	12 ± 1
Vehicle 2	Euro 5 Diesel additive DPF			
Naphthalene (gas) (mg/km)	21 ± 6	29 ± 9	< LQ	7 ± 3
Anthracene (ng/km)	49 ± 17	153 ± 16	60 ± 4	23 ± 9
Pyrene (ng/km)	54 ± 30	147 ± 6	22 ± 12	8 ± 5
Benz[a]anthracene (ng/km)	116 ± 20	112 ± 2	41 ± 3	23 ± 6
Vehicle 3	Euro 4 Diesel catalyzed DPF			
Phenanthrene (ng/km)	709 ± 284	146 ± 37	124 ± 44	85 ± 20
Vehicle 4	Euro 5 Diesel catalyzed DPF			
Naphthalene (gas) (mg/km)	< LQ	36 ± 3	19 ± 14	1 ± 0.7
Phenanthrene (ng/km)	< LQ	< LQ	63 ± 10	46 ± 22
Vehicle 5	Euro 4 gasoline			
Naphthalene (gas) (mg/km)	35 ± 7	144 ± 26	7 ± 2	5 ± 1
Naphthalene (ng/km)	< LQ	< LQ	< LQ	151 ± 5
Phenanthrene (ng/km)	2 ± 0.2	943 ± 94	< LQ	22 ± 2
Anthracene (ng/km)	< LQ	137 ± 14	< LQ	9 ± 5
Pyrene (ng/km)	2 ± 0.2	63 ± 6	< LQ	14 ± 0.1
Benz[a]anthracene (ng/km)	< LQ	80 ± 8	< LQ	9 ± 6
Benzo[obj]fluoranthene (ng/km)	< LQ	< LQ	< LQ	53 ± 5
Vehicle 6	Euro 5 gasoline DI			
Naphthalene (gas) (mg/km)	38 ± 4	47 ± 25	28 ± 13	19 ± 13
Phenanthrene (ng/km)	< LQ	< LQ	< LQ	66 ± 34

Munoz et al. (2018) [Co-formation and co-release of genotoxic PAHs, alkyl-PAHs and soot nanoparticles from gasoline direct injection vehicles, Atmospheric Environment] examined PAH emissions from a fleet of 7 GDI vehicles representing Euro-3, -4, -5 and -6 technologies, as well as a Euro-5 diesel vehicle with integrated diesel particle filter (DPF). The vehicle characteristics are shown below.



	GDI-1	GDI-2	GDI-3	GDI-4	GDI-5	GDI-6	GDI-7	D-DPF
Name	Mitsubishi Carisma	VW Golf Plus	Opel Insignia	Volvo V60	Opel Zafira	Citröen C4	VW Golf VII	Peugeot 4008
Displacement (L)	1.834	1.390	1.598	1.596	1.598	1.199	1.395	1.560
Injection type	GDI	GDI	GDI	GDI	GDI	GDI	GDI	DI
Legislation	Euro-3	Euro-4	Euro-5	Euro-5	Euro-5	Euro-6	Euro-6	Euro-5
Power (kW)	90 (5500 rpm)	118 (5800 rpm)	125 (6000 rpm)	132 (5700 rpm)	125 (6000 rpm)	81 (5500 rpm)	110 (6000 rpm)	84 (3600 rpm)

Testing was performed on the world harmonized light vehicle test cycle (WLTC). The WLTC was driven under cold-start (cWLTC) and hot engine/catalyst conditions (hWLTC). It includes urban, extra-urban, highway and motorway driving at mean velocities of 26, 45, 61 and 94 km/ h with a total cycle time of 30 min. The steady-state cycle (SSC), represents steady driving at mean velocities of the four WLTC phases and an idling phase. Each phase is driven for 20 min. During SSC runs, the cruise control of the vehicle was used to keep the speed constant.

Diluted exhausts were sampled from a constant volume sampling (CVS) tunnel with an all-glass sampling device including filter-, condenser- and absorber units (XAD2) according to the filter/condenser method described in the European standard EN-1948-1. This allows quantitative sampling of complete exhausts including particle-bound, liquid and gaseous fractions. Analysis of PAHs is performed by gas chromatography (Fisons Instruments HRGC Mega 2, Rodano, Italy) on a 30 m × 0.25 µm x 0.10 µm capillary column (Restek, Bellefonte, USA). Detection and identification of compounds were achieved by high resolution mass spectrometry (Thermo Finnigan MAT 95, Bremen, Germany) in electron-impact ionization mode (GC/EI-HRMS).

Table 120: Emission factors (ng/km) for detected PAHs and alkyl-PAHs in all vehicles in the cold-start WLTC.

	GDI-1	**GDI-2**	**GDI-3**	**GDI-4**	**GDI-5**	**GDI-6**	**GDI-7**	**GDI**	**D-DPF**
	Mitsubishi Carisma	VW Golf	Opel Insignia	Volvo V60	Opel Zafira	Citröen C4	VW Golf VII	Mean	Peugeot 4008
PAH, ng/km	Euro-3	Euro-4	Euro-5	Euro-5	Euro-5	Euro-6	Euro-6		Euro-5
Naphthalene	163000	448000	429300	78800	92100	56500	96100	194800 ± 158000	5700
2-methyl-naphthalene	31700	58800	22000	16000	6400	8400	14100	22500 ± 16800	1500
1-methyl-naphthalene	21700	30300	16100	8720	4000	7700	11400	14300 ± 8480	900
2,6-dimethyl-naphthalene	3940	3810	640	3240	380	510	1500	2000 ± 1490	260
1,6-dimethyl-naphthalene	2490	7470	360	1840	400	590	1580	2104 ± 2310	310
1,2-dimethyl-naphthalene	1000	1690	190	500	59	190	790	630 ± 540	120
Acenaphthylene	3400	80100	4980	5920	1140	7640	7380	15800 ± 26300	3.7
Acenaphthene	1190	20600	1180	390	490	440	1140	3640 ± 6950	100
Fluorene	1110	8520	1020	2080	88	1360	2210	2340 ± 2600	270
Phenanthrene	6300	56800	400	14800	1860	20510	15900	16700 ± 17800	3020
Anthracene	1370	4680	490	1770	180	1400	1560	1640 ± 1360	370
3-methyl-phenanthrene	380	1310	290	1060	100	860	1310	760 ± 470	930
2-methyl-phenanthrene	420	1280	220	1370	130	1000	1670	870 ± 570	990
9-methyl-phenanthrene	310	561	93	500	15	430	540	350 ± 203	460
1-methyl-phenanthrene	260	634	100	610	9.1	520	670	400 ± 250	470
1,7-dimethyl-phenanthrene	250	115	7940	300	*6.9*	210	160	1280 ± 2720	150
2-methyl-anthracene	210	527	810	560	46	410	810	480 ± 270	250
retene	330	67	230	250	17	190	500	230 ± 150	78
Fluoranthene	3220	4860	1440	2280	270	760	1410	2030 ± 1460	4760
3-methylfluoranthene	28	66	44	47	2.8	1.5	56	35 ± 20	*0.9*
1-methyl-fluoranthene	15	73	31	23	2.5	*0.7*	28	25 ± 20	5.3
Pyrene	13750	3692	390	1600	*220*	1510	148	3240 ± 4420	3760

4-methyl-pyrene	110	67	45	83	*2*	46	72	61 ± 30	30
1-methyl-pyrene	50	36	36	38	*1.3*	21	40	32 ± 15	11
Benzo[a]anthracene	82	284	250	71	35	81	47	122 ± 90	6.7
Chrysene	180	408	310	130	50	130	88	186 ± 120	12.4
3-methyl-chrysene	110	30	30	27	*1.5*	46	160	60 ± 50	0.1
6-methyl-chrysene	28	*0.5*	-	7	*0.3*	*0.8*	25	8.9 ± 10	8
Benzo[b]fluoranthene	360	374	240	100	19	54	48	170 ± 140	8
Benzo[k]fluoranthene	86	122	110	38	25	18	22	60 ± 40	*1.3*
Benzo[a]pyrene	830	178	250	75	5	103	47	210 ± 260	5.5
Indeno[1,2,3-cd]pyrene	380	231	41	32	26	37	22	110 ± 130	*4.5*
Dibenzo[ah]anthracene	17	35	16	9	86	*0.7*	12	25 ± 30	*9.1*
Benzo[ghi]perylene	2040	285	*38*	92	*34*	87	65	377 ± 680	12

Table 121: Emission factors (ng km-1) for detected PAHs and alkyl-PAHs in all vehicles in the hot-start WLTC.

	GDI-1	**GDI-2**	**GDI-3**	**GDI-4**	**GDI-5**	**GDI-6**	**GDI-7**	**GDI**	**D-DPF**
PAH, ng/km	Mitsubishi Carisma	VW Golf	Opel Insignia	Volvo V60	Opel Zafira	Citröen C4	VW Golf VII	Mean	Peugeot 4008
	Euro-3	**Euro-4**	**Euro-5**	**Euro-5**	**Euro-5**	**Euro-6**	**Euro-6**		**Euro-5**
Naphthalene	138600	204300	15900	43800	12400	3066	25300	63300 ± 71600	1000
2-methyl-naphthalene	24300	23200	1700	12300	2900	217	6700	10200 ± 9300	500
1-methyl-naphthalene	15600	10500	900	6230	1800	*14*	2500	5400 ± 5360	300
2,6-dimethyl-naphthalene	6060	1143	10	3220	340	530	450	1680 ± 2040	42
1,6-dimethyl-naphthalene	4430	2753	190	1820	340	40	450	1430 ± 1530	46
1,2-dimethyl-naphthalene	1790	602	150	530	58	10	170	470 ± 580	16
Acenaphthylene	9760	15229	1170	4900	300	470	3400	5030 ± 5170	*0.6*
Acenaphthene	820	4403	56	290	160	*4.3*	230	850 ± 1470	13
Fluorene	1830	2518	540	2140	250	510	2050	1400 ± 870	60

Phenanthrene	26880	26318	260	11900	5880	8450	16260	13710 ± 9350	2700
Anthracene	2030	2955	350	2400	420	420	1160	1390 ± 990	210
3-methyl-phenanthrene	1250	540	180	1600	380	410	610	710 ± 780	160
2-methyl-phenanthrene	1540	547	200	1900	410	540	810	850 ± 580	150
9-methyl-phenanthrene	790	242	120	910	240	240	380	420 ± 280	54
1-methyl-phenanthrene	880	287	53	1060	210	290	480	470 ± 340	61
1,7-dimethyl-phenanthrene	580	47	4500	500	100	170	220	870 ± 1490	14
2-methyl-anthracene	210	224	450	920	100	110	570	390 ± 270	*2.6*
retene	720	77	83	180	130	110	90	200 ± 210	1.1
Fluoranthene	9150	1924	1590	2330	474	860	1020	2480 ± 2780	300
3-methylfluoranthene	130	29	0	53	10	1.6	*1.2*	32 ± 40	*0.9*
1-methyl-fluoranthene	46	9	0	50	2	1	2.9	16 ± 20	*0.2*
Pyrene	30850	1500	3610	2320	*200*	880	380	5680 ± 1030	*290*
4-methyl-pyrene	300	27	55	210	51	23	40	100 ± 100	9.8
1-methyl-pyrene	130	10	30	89	11	8.7	30	40 ± 40	3.9
Benzo[a]anthracene	210	37	50	150	18	9.4	30	70 ± 70	5.7
Chrysene	540	74	88	300	46	41.2	90	170 ± 170	6.4
3-methyl-chrysene	260	8	38	43	*1.4*	38	50	60 ± 80	*0.4*
6-methyl-chrysene	64	5	37	11	*0.3*	*0.9*	*1*	17 ± 20	9.6
Benzo[b]fluoranthene	930	60	9	200	*3.7*	17.2	34	180 ± 310	24
Benzo[k]fluoranthene	130	16	74	59	11	18.8	12	45 ± 40	*1.2*
Benzo[a]pyrene	1590	22	42	112	5	12.5	27	259 ± 540	10
Indeno[1,2,3-cd]pyrene	760	25	*15*	63	10	38.9	21	134 ± 250	*4.2*
Dibenzo[ah]anthracene	19	5	*250*	6	178	*0.8*	19	68 ± 90	*8.4*
Benzo[ghi]perylene	4480	46	*39*	151	*31*	308.7	46	729 ± 1530	*6.6*

Table 122: Emission factors (ng/km) for detected PAHs and alkyl-PAHs in all vehicles in the SSC.

	GDI-1	**GDI-2**	**GDI-3**	**GDI-4**	**GDI-5**	**GDI**	**D-DPF**
PAH, ng/km	Mitsubishi Carisma	VW Golf	Opel Insignia	Volvo V60	Opel Zafira	Mean	Peugeot 4008
	Euro-3	**Euro-4**	**Euro-5**	**Euro-5**	**Euro-5**		**Euro-5**
Naphthalene	40250	49300	8290	*110*	7340	21100 ± 19700	*100*
2-methyl-naphthalene	6300	4663	1030	*33*	*130*	2400 ± 2570	*100*
1-methyl-naphthalene	4050	1922	600	*18*	*100*	1300 ± 1520	*43*
2,6-dimethyl-naphthalene	690	325	*28*	*13*	*35*	200 ± 260	*14*
1,6-dimethyl-naphthalene	650	665	*24*	*10*	*37*	277 ± 310	*16*
1,2-dimethyl-naphthalene	490	132	*1.7*	*5*	*14*	130 ± 190	*4.6*
Acenaphthylene	650	4208	*6.6*	60	280	1040 ± 1600	*1.1*
Acenaphthene	310	986	87	*4.3*	*24*	280 ± 370	*6.5*
Fluorene	53	738	67	90	*74*	200 ± 270	*21*
Phenanthrene	900	7451	35	2720	*770*	2380 ± 2690	*170*
Anthracene	660	881	42	280	*64*	380 ± 330	*19*
3-methyl-phenanthrene	18.5	195	18	360	*53*	130 ± 130	*13*
2-methyl-phenanthrene	47.1	171	19	430	*56*	140 ± 150	*14*
9-methyl-phenanthrene	*9*	87	9	230	*33*	70 ± 80	*7.3*
1-methyl-phenanthrene	17.73	107	*2.7*	230	*29*	80 ± 80	*6.4*
1,7-dimethyl-phenanthrene	*6.5*	7	720	90	*15*	170 ± 280	*3.7*
2-methyl-anthracene	20	76	170	140	*15*	80 ± 60	*4.8*
retene	5.59	21	43	20	39	30 ± 10	*10*
Fluoranthene	*49*	606	*19*	360	*243*	250 ± 210	*62*
3-methylfluoranthene	*1*	4	0	10	*1*	3.5 ± 4.0	*1.6*
1-methyl-fluoranthene	*0.6*	*0.3*	0	4	*1*	1.2 ± 1	*0.3*
Pyrene	293	528	*55*	320	*488*	340 ± 170	*430*
4-methyl-pyrene	*2*	4	6	24	*4*	8.1 ± 8.0	*5.2*
1-methyl-pyrene	*1.2*	*0.4*	*0.4*	8	*3*	2.6 ± 3.0	*0.3*

Benzo[a]anthracene	*1.2*	*0.4*	3	3	14	4.3 ± 5.1	*1.1*
Chrysene	3	*1.7*	*1.3*	15	*5.5*	5.3 ± 5.1	*2.4*
3-methyl-chrysene	*1.2*	*0.3*	*0.8*	*0.4*	*3.4*	-	*0.7*
6-methyl-chrysene	*0.6*	*0.3*	-	*0.3*	*0.8*	0.4 ± 0.2	*4.4*
Benzo[b]fluoranthene	10	*0.8*	*4*	1	*9.2*	4.9 ± 3.8	*11*
Benzo[k]fluoranthene	*1.2*	*0.6*	*0.5*	*0.3*	6	1.6 ± 2.0	*2.2*
Benzo[a]pyrene	1	*0.5*	*3.9*	*0.5*	*12*	3.6 ± 4.3	*3*
Indeno[1,2,3-cd]pyrene	6	*0.9*	*8.9*	*0.6*	*15*	6.1 ± 5.2	*7.8*
Dibenzo[ah]anthracene	*0.4*	*0.7*	-	*0.2*	136	27 ± 54	*16*
Benzo[ghi]perylene	15	*1*	*24*	*2.2*	*75*	23 ± 27	*99*

Munoz et al. (2016) [Bioethanol Blending Reduces Nanoparticle, PAH, and Alkyl- and Nitro-PAH Emissions and the Genotoxic Potential of Exhaust from a Gasoline Direct Injection Flex-Fuel Vehicle, Environmental Science and Technology] examined the PAH and nitro-PAH emissions from a flex-fuel Euro-5 GDI vehicle operated with gasoline (E0) and two ethanol/gasoline blends (E10 and E85) under transient and steady driving conditions.

A Euro-5 flex-fuel GDI vehicle (Volvo V60) with a 1.6 L engine was used. Two driving cycles simulating transient and steady driving were applied. The worldwide harmonized light-duty vehicle test cycle (WLTC) was used, which includes urban, extra-urban, highway, and motorway driving. The cycle was investigated under cold- (cWLTC) and hot-start conditions (hWLTC). Furthermore, a steady-state cycle (SSC) representing mean velocities of the WLTC and idle was applied.

Diluted exhausts were sampled from a constant volume sampling (CVS) tunnel. Aliquots were collected in all-glass sampling devices including filter, condenser, and adsorber units (XAD2) according to the filter/condenser method described in the European standard EN-1948-1. This allows quantitative sampling of semivolatile compounds in combined samples, including particle-bound, liquid, and gaseous fractions.

The combined sample is extracted in a Soxhlet apparatus with dichloromethane. An aliquot of a mixture of those16 perdeuterated PAHs, and D10-2-methylnaphthalene (CIL, Andover, MA, USA), D12-9-methylanthracene, D12-2,6-dimethylnaphthalene and D9-1-methylpyrene is added to the samples as quantification standards. Furthermore, aliquots of a mixture containing D7-1-nitronaphthalene, D9-9-nitrophenanthrene, D9-2-methyl-1-nitronaphthalene and D9-1-nitropyrene and D11-6-nitrochrysene are added as quantification standards for nitro-PAHs. The extraction is followed by a multistep cleanup procedure with silica which allows the fractionation of PAHs and nitro-PAHs. Analyses of PAHs and nitro-PAHs are performed by gas chromatography (Fisons Instruments HRGC Mega 2, Rodano, Italy) on 30 m and 15 m capillary columns (Restek, Bellefonte, USA) for PAHs and nitro-PAHs, respectively.

Table 123: Emission factors (µg/km) for detected PAHs, alkyl-PAHs in complete Euro-5 vehicle exhausts (VOLVO V60, 1.6 L, 132 kW). Levels found in dilution air are reported as detection limits (Bold)

Compound, µg/km	WLTC (cold)	WLTC (hot)	SSC (hot)	WLTC (cold)	WLTC (hot)	SSC (hot)	WLTC (cold)	WLTC (hot)	SSC (hot)
Naphthalene	79	44	***0.1***	60	15	0.64	44	17	0.32
2-methyl-naphthalene	16	12	***0.033***	12	6.4	0.7	8.4	3.4	0.31
1-methyl-naphthalene	8.7	6.2	***0.018***	6.9	3.3	0.33	4.3	1.7	0.1
2,6-dimethyl-naphthalene	3.2	3.2	***0.013***	1.8	1.2	0.047	0.92	0.25	***0.014***
1,6-dimethyl-naphthalene	1.8	1.8	*0.01*	1	0.7	**0.013**	0.56	0.19	***0.011***
1,2-dimethyl-naphthalene	0.5	0.53	***0.005***	0.25	0.12	**0.006**	0.13	0.047	***0.005***
Acenaphthylene	5.9	4.9	0.058	2.5	0.89	0.013	2.1	0.046	0.009
Acenaphthene	0.39	0.29	***0.0043***	0.32	0.11	**0.005**	0.25	0.064	**0.0044**
Fluorene	2.1	2.1	0.087	0.63	0.49	**0.017**	0.69	0.28	**0.014**
Phenanthrene	15	12	2.7	3.2	4.6	**0.1**	14	3.5	0.54
Anthracene	1.8	2.4	0.28	**0.025**	**0.029**	**0.019**	**0.025**	**0.024**	**0.015**
3-methyl-phenanthrene	1.1	1.6	0.36	0.24	0.3	**0.008**	1.3	0.22	0.025
2-methyl-phenanthrene	1.4	1.9	0.43	0.26	0.35	**0.01**	1.3	0.3	0.035
9-methyl-phenanthrene	0.5	0.91	0.23	0.12	0.14	**0.006**	0.5	0.11	**0.0049**
1-methyl-phenanthrene	0.61	1.1	0.23	0.14	0.18	**0.005**	0.56	0.15	0.01
1,7-dimethyl-phenanthrene	0.3	0.5	0.086	0.041	0.063	**0.0033**	0.056	0.056	**0.0027**
2-methyl-anthracene	0.56	0.92	0.14	0.15	0.13	0.011	0.33	0.073	0.032
Retene	0.25	0.18	0.024	0.04	0.1	0.073	0.07	0.087	0.11
Fluoranthene	2.3	2.3	0.36	0.6	1.2	0.34	2.3	0.56	0.14
3-methylfluoranthene	0.047	0.053	0.01	**0.0004**	**0.0005**	**0.0003**	**0.00045**	**0.00043**	**0.00027**
1-methyl-fluoranthene	0.023	0.05	0.004	**0.0003**	**0.0004**	**0.0002**	**0.00034**	**0.00032**	**0.0002**
Pyrene	1.6	2.3	0.32	0.5	0.79	1.1	1.1	0.46	0.1
4-methyl-pyrene	0.083	0.21	0.024	0.037	0.035	**0.0012**	0.028	0.012	**0.001**
1-methyl-pyrene	0.038	0.089	0.0084	0.013	0.012	**0.0007**	0.014	0.0063	**0.0006**
Benzo(a)anthracene	0.07	0.15	0.0025	0.033	0.016	**0.0007**	0.021	0.0065	**0.0006**

Chrysene	0.13	0.3	0.015	0.046	0.041	0.003	0.046	0.027	0.001
3-methyl-chrysene	0.03	0.04	0.00043	0.002	0.005	**0.0005**	0.008	0.0066	**0.0004**
6-methyl-chrysene	0.01	0.01	0.00034	**0.001**	**0.001**	**0.0004**	**0.001**	**0**	**0.0003**
Benzo(b)fluoranthene	0.1	0.2	0.0009	0.048	0.009	**0.001**	0.02	0.0154	**0.001**
Benzo(k)fluoranthene	0.038	0.059	0.00032	0.009	**0.001**	**0.0004**	0.004	0.0002	**0.0003**
Benzo(a)pyrene	0.075	0.11	0.0005	0.11	0.024	0.014	0.022	0.011	**0.001**
Indeno(1,2,3-cd)pyrene	0.032	0.063	**0.0006**	0.023	**0.001**	**0.001**	0.002	**0**	**0.001**
Dibenzo(ah)anthracene	0.01	0.006	**0.00015**	**0.003**	**0.0003**	**0.0002**	**0.0003**	**0**	**0.0002**
Benzo(ghi)perylene	0.092	0.15	**0.0022**	**3.73**	**0.004**	**0.003**	**0.004**	**0**	**0.002**

Table 124: Emission factors (ng/km) for detected nitro-PAHs PAHs in complete Euro-5 vehicle exhausts (VOLVO V60, 1.6 L, 132 kW). Levels found in dilution air are reported as detection limits (bold).

Compound, ng/km	WLTC (cold)	WLTC (hot)	SSC (hot)	WLTC (cold)	WLTC (hot)	SSC (hot)	WLTC (cold)	WLTC (hot)	SSC (hot)
1-nitro-naphthalene	250	480	**4.8**	26	15	6.1	58	57	5.1
2-nitro-naphthalene	180	460	**2.6**	4.6	3.3	0.55	8.4	194	2.8
9-nitro-phenanthrene	3.8	13	**0.028**	0.4	2.7	0.04	**0.05**	**0.046**	**0.029**
3-nitro-phenanthrene	4.2	14	**0.042**	2.5	2.07	0.05	**0.5**	1.1	0
2-nitro-phenanthrene	2.4	9.6	**0.072**	5.7	1.7	0.09	**0.12**	1.5	1.1
2-nitro-anthracene	0.39	1.8	**0.025**	0	**0.81**	**0.03**	**0.04**	3.9	1.5
9-nitro-anthracene	5.7	10	**0.2**	2.4	3.3	0.25	**1.8**	14	0.2
1-nitro-fluoranthene	**0.0001**	1	**0.047**	0.1	**0.09**	**0.53**	0.08	2.8	2.2
2-nitro-fluoranthene	**0.0001**	**0.0001**	**0**	0.1	**0.16**	**0.11**	**0.14**	**0.1**	**4.2**
4-nitro-pyrene	**0.061**	**0.0001**	**0**	1.2	0.32	0.06	**0.08**	1.6	0.6
1-nitro-pyrene	11	39	**0.049**	0.9	0.4	0.06	1.26	5	0.1
2-nitro-pyrene	**0.0004**	**0.0004**	**0.2**	0.34	0.4	1.5	0.35	**0.3**	**14**
1,3-dinitro-pyrene	**0.0004**	**0.0004**	**0.2**	0.38	1.05	0.29	0.39	**0.4**	18

1,6-dinitro-pyrene	**0.006**	**0.0004**	**0.2**	6.5	0.46	0.3	**0.41**	**6.6**	14
6-nitro-chrysene	**0.0003**	**0.0003**	**0.2**	**0.26**	**0.31**	**0.2**	**0.27**	**0.3**	**4.9**

Munoz et al. (2018) [Effects of Four Prototype Gasoline Particle Filters (GPFs) on Nanoparticle and Genotoxic PAH Emissions of a Gasoline Direct Injection (GDI) Vehicle, Environmental Science and Technology] examined PAH emissions from a 1.6L Euro 5 GDI vehicle equipped with four prototype gasoline particle filters (GPFs).

The worldwide harmonized light-duty vehicle test cycle was used. The WLTC including urban, extra-urban, highway, and motorway driving was driven under cold (cWLTC) and hot-start conditions (hWLTC). Furthermore, a steady-state cycle (SSC) representing mean velocities of the four WLTC phases and an idle phase was applied. Four prototype ceramic wall-flow filters (GPFs) were tested on the reference vehicle and installed approximately 60 cm downstream of the three-way catalyst. Two filters were coated with noble metals to support oxidation (GPF-2, GPF-3); and two were noncoated filters (GPF-1, GPF-4).

An all-glass sampling device including filter-, condenser- and adsorber units (XAD2) was used to sample PAHs and alkyl-PAHs of diluted exhausts from a constant volume sampling (CVS) tunnel, according to the filter/condenser method described in the European standard EN-1948–1. Analysis of individual PAHs is performed by gas chromatography (Fisons Instruments HRGC Mega 2, Rodano, Italy) on a 30 m × 0.25 μm × 0.10 μm capillary column (Restek, Bellefonte, U.S.A.). Detection and identification were achieved by high resolution mass spectrometry (Thermo Finnigan MAT 95, Bremen, Germany) in electron-impact ionization mode (GC/EI-HRMS).

The internal standard method is used to quantify PAHs. Five concentrations containing deuterated PAHs, 16 native PAHs (Supelco, Bellefonte, U.S.A.) and a standard reference material (SRM) mix of 18 methyl-substituted PAHs from methyl-naphthalene to methyl-chrysene (LGC

Standards, Switzerland) were analyzed to determine respective calibration curves and response factors. For compounds identified by mass spectrometry but not present in labeled form, quantification was performed with relative response factors of PAHs or alkyl-PAHs with closest chromatographic retention time. Aliquots of $^{13}C_6$-naphthalene, $^{13}C_6$-phenanthrene and $^{13}C_3$-pyrene were placed on quartz swab and given to the condensate separator prior to each sampling. These compounds were used to calculate losses during sampling and workup. CVS blank samples were also collected to determine background air concentrations and with it detection limits of the methodology.

Table 125: Emission factors (ng/km) for detected PAHs and alkyl-PAHs in the reference vehicle without filter (GDI-R), with filters (GPF-1-4) and in the diesel vehicle with DPF (DPF) in the cWLTC. Levels found in dilution air are reported as detection limits (italics).

	GDI-R	GPF-1	GPF-2	GPF-3	GPF-4	GDI Mean (n=7)	DPF
Naphthalene	47770	14070	50270	69240	79670	194800 ± 158000	5700
2-methylnaphthalene	17010	2470	7610	4930	11230	22500 ± 16800	1500
1-methylnaphthalene	9630	1660	5200	3370	6980	14300 ± 8480	900
2,6-dimethylnaphthalene	4390	290	800	360	1960	2000 ± 1490	260
1,6-dimethylnaphthalene	2200	190	400	220	1120	2104 ± 2310	310
1,2-dimethylnaphthalene	1140	30	250	70	350	630 ± 540	120
Acenaphthylene	9990	1620	4070	1470	4390	15790 ± 26300	3.7
Acenaphthene	570	310	170	190	370	3640 ± 6950	100
Fluorene	2470	560	740	470	1140	2340 ± 2600	270
Phenanthrene	10820	4380	2830	9490	4970	16650 ± 17800	3020
Anthracene	1830	190	440	760	510	1640 ± 1360	370
3-methylphenanthrene	1900	130	130	1370	410	760 ± 470	930
2-methylphenanthrene	1980	160	120	1820	440	870 ± 570	990
9-methylphenanthrene	710	100	52.4	650	190	350 ± 203	460
1-methylphenanthrene	1240	*70*	86.3	860	330	400 ± 250	470
1,7-dimethylphenanthrene	350	70	53.6	860	150	1280 ± 2720	150
2-methylanthracene	1950	21.8	89.6	620	310	480 ± 270	250
Retene	15.3	16.6	20	91	190	230 ± 150	78
Fluoranthene	2580	1290	380	18770	730	2030 ± 1460	4760

3-methylfluoranthene	57.4	0.8	17.7	210	36.3	35 ± 20	0.9
1-methylfluoranthene	85	0	11.6	120	19.9	25 ± 20	5.3
Pyrene	4020	6510	1330	10580	880	3240 ± 4420	3760
4-methylpyrene	220	17.3	13.4	135.2	30.7	61 ± 30	30
1-methylpyrene	140	10.6	10.4	72.5	25.6	32 ± 15	11
Benzo(a)anthracene	290	1.1	41	56.7	76.4	122 ± 90	6.7
Chrysene	420	36.8	74.1	78.9	140	186 ± 120	12.4
3-methylchrysene	43.1	13.8	20.8	0.8	10	60 ± 50	0.1
6-methylchrysene	0	0	5	0.2	0	8.9 ± 10	8
Benzo(b)fluoranthene	250	39.7	140	52.6	120	170 ± 140	8
Benzo(k)fluoranthene	52.2	2.1	2	14.8	20.8	60 ± 40	1.3
Benzo(a)pyrene	210	21.6	34.3	24.4	100	210 ± 260	5.5
Indeno(1,2,3-cd)pyrene	8.4	10.1	12.7	11.9	11.3	110 ± 130	4.5
Dibenzo(ah)anthracene	13.1	28.5	28.9	33.7	32	25 ± 30	9.1
Benzo(ghi)perylene	190	84.2	170	10.2	63.2	377 ± 680	12

Table 126: Emission factors (ng/km) for detected PAHs and alkyl-PAHs in the reference vehicle without filter (GDI-R), with filters (GPF-1-4) and in the diesel vehicle with DPF (DPF) in the hWLTC. Levels found in dilution air are reported as detection limits (italics).

	GDI-1	**GPF-1**	**GPF-2**	**GPF-3**	**GPF-4**	**GDI Mean (n=7)**	**DPF**
Naphthalene	120	13650	13610	3040	10090	63300 ± 71600	1000
2-methylnaphthalene	1530	1730	4140	240	3700	10200 ± 9300	500
1-methylnaphthalene	1070	700	2120	170	1770	5400 ± 5360	300
2,6-dimethylnaphthalene	910	240	920	9	930	1680 ± 2040	42
1,6-dimethylnaphthalene	500	180	520	15.3	550	1430 ± 1530	46
1,2-dimethylnaphthalene	260	30	170	3.4	160	470 ± 580	16
Acenaphthylene	1620	590	1420	150	1390	5030 ± 5170	0.6
Acenaphthene	100	340	310	58.9	110	850 ± 1470	13
Fluorene	970	520	860	210	920	1400 ± 870	60
Phenanthrene	6450	4090	4470	4580	4480	13710 ± 9350	2700
Anthracene	540	230	340	390	450	1390 ± 990	210
3-methylphenanthrene	770	90	310	650	440	710 ± 780	160
2-methylphenanthrene	800	110	390	760	560	850 ± 580	150
9-methylphenanthrene	280	26.8	130	370	340	420 ± 280	54
1-methylphenanthrene	440	52	140	400	340	470 ± 340	61
1,7-dimethylphenanthrene	160	21.3	130	190	240	870 ± 1490	14
2-methylanthracene	470	26	120	190	160	390 ± 270	2.6

Retene	31.9	16.1	20	210	290	200 ± 210	1.1
Fluoranthene	1170	510	1260	840	2710	2480 ± 2780	300
3-methylfluoranthene	30.2	1.2	18.7	10.3	12.3	32 ± 40	0.9
1-methylfluoranthene	41.5	5	19.7	17.3	19.1	16 ± 20	0.2
Pyrene	1620	420	1160	940	14880	5680 ± 1030	290
4-methylpyrene	100	1.1	27	40.5	100	100 ± 100	9.8
1-methylpyrene	54.2	1.1	17.4	34.1	61.6	40 ± 40	3.9
Benzo(a)anthracene	87.5	1.1	18.3	24	51.8	70 ± 70	5.7
Chrysene	140	15	51.1	58.3	230	170 ± 170	6.4
3-methylchrysene	19.5	3.2	21.5	5.8	170	60 ± 80	0.4
6-methylchrysene	0	0.2	5.3	0.2	30	17 ± 20	9.6
Benzo(b)fluoranthene	86.4	2.7	27.7	18.3	580	180 ± 310	24
Benzo(k)fluoranthene	8.3	2.1	2.1	6.1	43	45 ± 40	1.2
Benzo(a)pyrene	190	2.1	1.1	42	360	259 ± 540	10
Indeno(1,2,3-cd)pyrene	5.8	9.8	9.9	11.6	600	134 ± 250	4.2
Dibenzo(ah)anthracene	14.3	27.6	27.9	32.8	31	68 ± 90	8.4
Benzo(ghi)perylene	52.1	8.3	8.4	43.5	2420	729 ± 1530	6.6

Table 127: Emission factors (ng/km) for detected PAHs and alkyl-PAHs in the reference vehicle without filter (GDI-R), with filters (GPF-1-4) and in the diesel vehicle with DPF (DPF) in the SSC. Levels found in dilution air are reported as detection limits (italics). SSC values in GPF-2 are not reported.

	GDI-R	GPF-1	GPF-3	GPF-4	GDI Mean	DPF
Naphthalene	630	800	*56.1*	370	21100 ± 19700	100
2-methylnaphthalene	320	20.7	*23.2*	58.2	2400 ± 2570	100
1-methylnaphthalene					1300 ± 1520	43
2,6-dimethylnaphthalene	130	12.5	*14*	13.6	200 ± 260	14
1,6-dimethylnaphthalene	50	10.8	*12.1*	11.8	277 ± 310	16
1,2-dimethylnaphthalene	0	7.1	*7.9*	7.7	130 ± 190	4.6
Acenaphthylene	10	*4.1*	0	0	1040 ± 1600	1.1
Acenaphthene	260	13.8	10	110	280 ± 370	6.5
Fluorene	*0*	12.5	*4.2*	0	200 ± 270	21
Phenanthrene	80	9.9	*11*	44.2	2380 ± 2690	170
Anthracene	300	110	130	120	380 ± 330	19
3-methylphenanthrene	150	6.6	50	48.7	130 ± 130	13
2-methylphenanthrene	91	10.4	*11.6*	11.3	140 ± 150	14
9-methylphenanthrene	76	12.9	*14.4*	14	70 ± 80	7.3

1-methylphenanthrene	0	6.3	*7*	6.9	80 ± 80	6.4
1,7-dimethylphenanthrene	47	6.9	*7.7*	7.5	170 ± 280	3.7
2-methylanthracene	2.7	*2.9*	10	0	80 ± 60	4.8
Retene	4	11	12.4	12	30 ± 10	10
Fluoranthene	12.4	29.6	100	32.2	250 ± 210	62
3-methylfluoranthene	9	0.6	0	0	3.5 ± 4.0	1.6
1-methylfluoranthene	10.7	1.6	0	0	1.2 ± 1	0.3
Pyrene	260	18.1	1500	130	340 ± 170	430
4-methylpyrene	20	0.8	9.3	10	8.1 ± 8.0	5.2
1-methylpyrene	10.6	0.4	7.4	0	2.6 ± 3.0	0.3
Benzo(a)anthracene	29.4	0.8	0.9	0	4.3 ± 5.1	1.1
Chrysene	40.5	1.5	4.8	0	5.3 ± 5.1	2.4
3-methylchrysene	0.1	0.5	0.5	0	-	0.7
6-methylchrysene	0	0.1	0.2	0	0.4 ± 0.2	4.4
Benzo(b)fluoranthene	1.2	1.9	2.1	0	4.9 ± 3.8	11
Benzo(k)fluoranthene	0.5	1.4	1.6	0	1.6 ± 2.0	2.2
Benzo(a)pyrene	1.3	1.5	33.8	0	3.6 ± 4.3	3
Indeno(1,2,3-cd)pyrene	0.9	6.7	7.5	7.3	6.1 ± 5.2	7.8
Dibenzo(ah)anthracene	3.6	19	21.2	20.6	27 ± 54	16
Benzo(ghi)perylene	1.3	5.7	6.4	10	23 ± 27	99

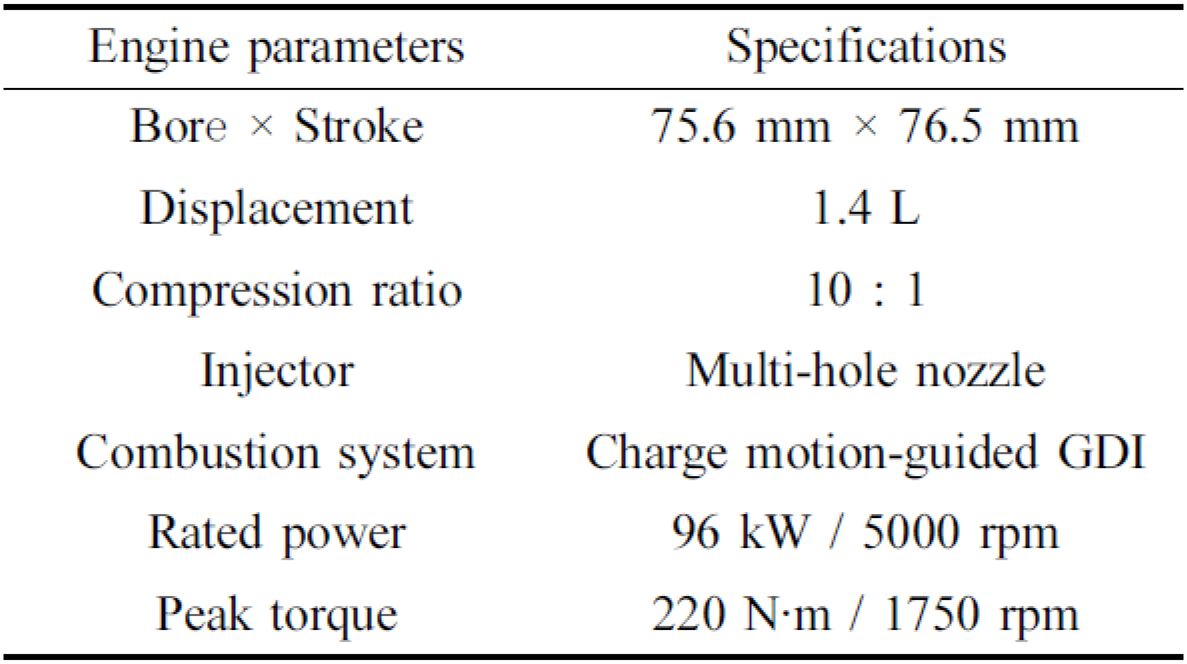
Li et al. (2018) [Effect of biodiesel on PAH, OPAH, and NPAH emissions from a direct injection diesel engine, Environmental Science and Pollution Research] examined PAH, oxy-PAH, and nitro-PAH emissions from a direct injection diesel engine fueled with diesel fuel, waste cooking oil biodiesel (B100) and their two blends (B20 and B50). Experiments were conducted at a steady engine speed of 1800 rpm and at 20%, 50%, and 80% loads, corresponding to the brake mean effective pressures (BMEP) of 0.16, 0.41, and 0.56 MPa, respectively.

Samples were analyzed by using a gas-chromatography mass-spectrometry (GC/MS, 7890C/5975A, Agilent) to determine the concentration of PAH, OPAH, and NPAH compounds in PM.

Table 128: Brake-specific emissions of individual PAH, OPAH, and NPAH for the tested fuels at different loads (µg/kWh)

	20% Load				50% Load				80% Load			
Compound	D	B20	B50	B100	D	B20	B50	B100	D	B20	B50	B100
Naphthalene	82.828	51.515	30.303	13.131	51.675	26.794	21.053	11.483	44.231	53.846	40.385	12.500
Acenaphthylene	42.424	29.293	29.293	33.333	34.450	27.751	23.923	24.880	61.538	55.769	49.038	32.692
Acenaphthene	86.869	62.626	47.475	8.081	65.072	29.665	27.751	8.612	78.846	69.231	53.846	11.538
Fluorene	62.626	57.576	35.354	16.162	72.727	33.493	28.708	17.225	73.077	66.346	53.846	25.000
Phenanthrene	153.535	107.071	57.576	28.283	158.852	65.072	46.890	27.751	193.269	125.962	92.308	50.962
Anthracene	61.616	43.434	39.394	48.485	49.761	36.364	30.622	43.062	79.808	76.923	65.385	51.923
Fluoranthene	57.576	42.424	37.374	35.354	48.804	34.450	26.794	26.794	80.769	67.308	63.462	38.462
Pyrene	91.919	67.677	43.434	67.677	78.469	40.191	34.450	21.053	104.808	96.154	75.000	31.731
Benzo[a]anthracene	36.364	26.263	18.182	5.051	46.890	17.225	13.397	1.914	45.192	40.385	30.769	4.808
Chrysene	41.414	28.283	25.253	3.030	35.407	22.967	17.225	1.914	46.154	40.385	40.385	3.846
Benzo[b]fluoranthene	52.525	29.293	16.162	20.202	28.708	14.354	12.440	20.096	25.962	22.115	11.538	23.077
Benzo[k]fluoranthene	57.576	35.354	23.232	37.374	36.364	21.053	19.139	27.751	45.192	42.308	32.692	42.308
Ben=o[a]pyrene	34.343	20.202	15.152	15.152	18.182	N/A	13.397	13.397	23.077	22.115	26.923	17.308
1,4-Naphthoquinone	16.162	10.101	23.232	23.232	17.225	13.397	20.096	17.225	23.077	22.115	25.000	22.115
1-Naphthaldehyde	4.040	6.061	9.091	8.081	4.785	10.526	18.182	5.742	22.115	33.654	37.500	15.385
9-Fluorenone	37.374	50.505	55.556	53.535	36.364	57.416	64.115	47.847	57.692	69.231	81.731	61.538
9,10-Anthraquinone	39.394	56.566	65.657	50.505	48.804	59.330	71.770	43.062	53.846	75.962	105.769	70.192
Benzanthrone	24.242	29.293	29.293	26.263	33.493	24.880	34.450	25.837	38.462	46.154	57.692	40.385
Benz[a]anthracene-7,12-dione	26.263	26.263	37.374	26.263	24.880	39.234	44.019	11.483	25.000	44.231	53.846	31.731
9-Nitrophenanthrene	4.242	2.929	2.323	2.929	3.062	2.488	2.584	2.201	3.846	5.096	4.038	3.654
3-Nitrophenanthrene	2.424	1.414	1.313	2.121	1.914	2.105	1.435	1.435	7.212	3.365	2.788	2.692
3-Nitrofluoranthene	13.131	9.091	8.384	8.687	9.665	7.751	6.794	7.081	11.442	12.115	11.635	11.538
1-Nitropyrene	14.949	10.707	9.495	7.778	11.196	9.282	8.230	8.230	15.385	14.712	13.942	12.212

Su et al. (2019) [Experimental study of particulate emission characteristics from a gasoline direct injection engine during starting process, International Journal of Automotive Technology] examined the PM-phase PAH emissions from a GDI engine during starting period. The engine used in this investigation was an in-line four cylinders, turbo-charged VW1.4L GDI engine. Technical characteristics of the engine are shown below.



Engine parameters	Specifications
Bore × Stroke	75.6 mm × 76.5 mm
Displacement	1.4 L
Compression ratio	10 : 1
Injector	Multi-hole nozzle
Combustion system	Charge motion-guided GDI
Rated power	96 kW / 5000 rpm
Peak torque	220 N·m / 1750 rpm

Soluble organic fraction (SOF) was extracted from the filter with methylene chloride by a Soxhlet extraction system. Then it was condensed to 1ml. GC-MS (7000B GC-QQQ, Agilent) was used to analyze PAHs qualitatively and quantitatively. Temperature programming was that GC temperature began from 70 °C (held for 3 minutes), then increased at the speed of 15 °C/min to 200 °C (held for 4 minutes), then continued at the speed of 5 °C/min to 250 °C (held for 4 minutes), and finally ramped up at the speed of 8 °C/min to 300 °C (held for 8 minutes). In order to carry out quantitative analysis of PAHs, GC–MS was calibrated with a standard solution containing 16

EPA-PAH compounds in acetonitrile solvent. 7 concentrations were selected for the standard solution: 10 ng/mL, 20 ng/mL, 50 ng/mL, 100 ng/mL, 200 ng/mL, 500 ng/mL, 1000 ng/mL.

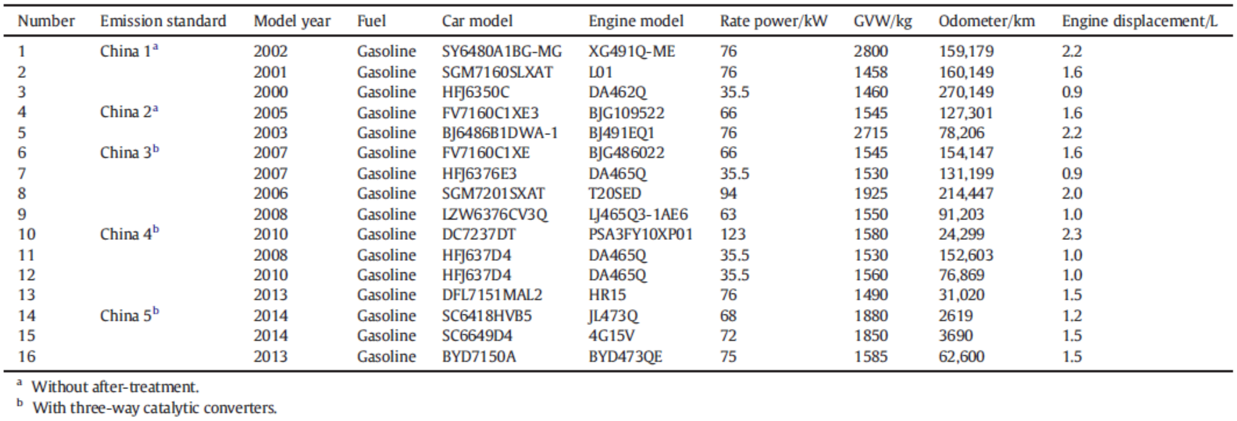
PAH emissions were investigated as a function of the effect of the coolant temperature on PM emissions over the first 40 seconds after engine started. Under warm start conditions, coolant was heated up to the required temperature by a heating system before engine started. The coolant was heated with a heater and circulated by a pump between the external cooling system and the engine's internal coolant system. When the temperature reached the set temperature, the heating was stopped and the engine was started. This method was more effective than running the engine to a fixed warm start condition. All experiments were carried out at ambient temperature of 20oC.

Table 129: Effect of coolant's temperature on specific PAHs (ppb)

	20 °C		80 ° C	
PAHs	0-40s	0-13s	0-40s	0-13s
Naphthalene	234.7694	229.3199	232.4619	168.5608
Acenaphthene	121.1519	138.5174	115.9772	95.05225
Acenaphthylene	30.33246	30.56977	15.69721	16.28117
Fluorene	174.0621	139.9412	157.6534	158.3625
Phenanthrene	1450.35	1036.288	1565.835	1478.511
Anthracene	182.6688	124.2805	189.3758	200.6932
Pyrene	714.8916	374.2228	530.6484	372.3832
Fluoranthene	711.9429	389.6127	440.8393	317.8445
Chrysene	1174.564	826.531	739.771	362.3203
Benzo[a]Anthracene	903.9747	720.8923	579.3117	392.6003
Benzo[b]Fluoranthene	2242.059	1451.373	1125.684	546.5593
Benzo[a]Pyrene	522.5437	369.6014	282.7292	138.5229
Benzo[k]Fluoranthene	508.4908	360.389	288.2625	140.603
Dibenzo[a,h]Anthracene	88.98867	123.8099	113.58	68.25127
Indeno[1,2,3-cd]Pyrene	1834.64	1029.154	628.1894	282.3369
Benzo[g,h,i]Perylene	1751.326	930.9953	594.698	259.6976

Hao et al. (2018) [Characterization and carcinogenic risk assessment of polycyclic aromatic and nitro-polycyclic aromatic hydrocarbons in exhaust emission from gasoline passenger cars using on-road measurements in Beijing, China, Science of the Total Environment] investigated PAH and nitro-PAH emissions from 16 gasoline passenger cars encompassing five emission standards and two driving conditions. Experiments were conducted on-road in Beijing.

In total, 16 vehicles were selected from the most common in-use gasoline passenger cars, including vehicles that met five different emission standards (China 1 to China 5). The specifications of the vehicles are shown below.



Number	Emission standard	Model year	Fuel	Car model	Engine model	Rate power/kW	GVW/kg	Odometer/km	Engine displacement/L
1	China 1[a]	2002	Gasoline	SY6480A1BG-MG	XG491Q-ME	76	2800	159,179	2.2
2		2001	Gasoline	SGM7160SLXAT	L01	76	1458	160,149	1.6
3		2000	Gasoline	HFJ6350C	DA462Q	35.5	1460	270,149	0.9
4	China 2[a]	2005	Gasoline	FV7160C1XE3	BJG109522	66	1545	127,301	1.6
5		2003	Gasoline	BJ6486B1DWA-1	BJ491EQ1	76	2715	78,206	2.2
6	China 3[b]	2007	Gasoline	FV7160C1XE	BJG486022	66	1545	154,147	1.6
7		2007	Gasoline	HFJ6376E3	DA465Q	35.5	1530	131,199	0.9
8		2006	Gasoline	SGM7201SXAT	T20SED	94	1925	214,447	2.0
9		2008	Gasoline	LZW6376CV3Q	LJ465Q3-1AE6	63	1550	91,203	1.0
10	China 4[b]	2010	Gasoline	DC7237DT	PSA3FY10XP01	123	1580	24,299	2.3
11		2008	Gasoline	HFJ637D4	DA465Q	35.5	1530	152,603	1.0
12		2010	Gasoline	HFJ637D4	DA465Q	35.5	1560	76,869	1.0
13		2013	Gasoline	DFL7151MAL2	HR15	76	1490	31,020	1.5
14	China 5[b]	2014	Gasoline	SC6418HVB5	JL473Q	68	1880	2619	1.2
15		2014	Gasoline	SC6649D4	4G15V	72	1850	3690	1.5
16		2013	Gasoline	BYD7150A	BYD473QE	75	1585	62,600	1.5

[a] Without after-treatment.
[b] With three-way catalytic converters.

The driving route for the onboard measurement was designed to simulate real traffic conditions in Beijing and included highway and nonhighway roads. The total length of the route was approximately 35 km, consisting of 15 km of nonhighway roads and 20 km of highways in northwest Beijing, mainly Lianhuachi Road, west 5th Ring Road and Fushi Road. All of the tested vehicles were tested in parallel two times on the two types of roads.

The particulate phase was collected on a 47 mm quartz filter (QF, 2500QAT-UP, PALL Corp., USA), and the gas phase was sampled by three-stage polyurethane foam (PUF) cartridges. The exhaust was first passed through the QF, followed by passage through the three-stage PUF. The dilution ratios were approximately 8:1. The flow rate of the sampling was controlled at approximately 3 L/min, and the flow meter used in this work was calibrated with a BIOS Defender 530 (Drycal Technology Inc., USA) before each test. To ensure that the PAH and NPAH contents measured in the laboratory were within the detection limits of the instruments, the sampling time was set at 30–40 min. All samples were collected under hot, stabilized conditions. The PAHs and NPAHs were analyzed using an HPLC system (Agilent 1200, Santa Clara, CA, USA) equipped with a UV detector (Agilent G1314A, Santa Clara, CA, USA) to detect at 220 nm, 230 nm, 254 nm and 290 nm. In total, 16 PAHs and 9 NPAHs were quantified.

Table 130: PAH and nitro-PAH emissions

Compounds (µg/km)			Nap	Act	Flr	Acl	Phe	Ant	Flu	Pyr	Chr	BaA	BbF	BkF	BaP	DBahA	BghiP	IP	5-NAcp	1-Npyr	6-NChr
China 1	NHW	Gas	3.9±0.4	0.3±0.1	2.2±0.8	11.9±3.9	0.2±0.1	48.9±15.2	0.1±0.04	0.5±0.3	0.2±0.1	6±5.8	6.9±6.2	4.3±3	521.5±384.6	104.2±46	4.8±1.7	0.6±0.7	5.8±4.7	1.4±0.9	101.7±65.8
		Particulate	0.1±0.03	0.1±0.002	0.1±0.02	ND	0.1±0.025	ND	0.1±0.02	0.1±0.02	0.3±0.4	1.6±1.4	11±8.1	129.7±124.8	3.1±4.2	5425.4±647.9	ND	0.8±1.1	0.1±0.01	ND	9.3±13.1
		Total TEQBaP	3.9±0.3	0.3±0.1	2.2±0.8	11.9±3.9	0.2±0.1	48.9±15.2	0.1±0.1	0.5±0.3	0.5±0.2	7.5±5.1	17.9±14.1	134±121.7	524.5±380.5	5529.6±650.9	4.8±1.7	1.4±0.9	5.8±4.7	1.4±0.9	110.9±72.7
	HW	Gas	2.3±0.6	0.3±0.2	1.8±0.3	10.3±2.9	0.1±0.1	44.6±15	0.1±0.01	0.4±0.05	0.2±0.05	4.9±3	3.8±2.7	18.5±16.2	457.7±309.8	1295.4±20.2	4.6±1.6	0.3±0.2	3.8±3.6	0.9±0.7	80.3±19.1
		Particulate	0.1±0.01	0.1±0.001	0.1±0.003	0.1±0.006	ND	ND	ND	0.1±0.001	0.1±0.01	0.7±1	13±9.2	69.1±18.7	0.2±0.2	3269.5±484	ND	0.8±1.1	0.1±0.005	0.1±0.04	ND
		Total TEQBaP	2.3±0.6	0.3±0.2	1.8±0.2	10.3±2.9	0.1±0.1	44.6±15	0.1±0.01	0.4±0.05	0.2±0.04	5.6±2	16.8±11.8	87.5±33.5	457.8±309.9	4564.8±348.5	4.6±1.6	1.1±0.9	3.8±3.6	1±0.8	80.3±19.1
China 2	NHW	Gas	3.7±3.4	0.3±0.3	3±4.7	13.3±20.4	0.3±0.3	106.2±40.5	0.1±0.2	0.6±1.1	0.3±0.6	7.7±3.8	9.9±6	10.6±7.4	1026±765.1	136.3±189.1	5.8±7.6	0.2±6.2	8.9±0.8	2.2±1.5	128.3±290.1
		Particulate	0.2±0.1	0.1±0.003	0.1±0.04	ND	0.2±0.1	ND	0.1±0.1	0.2±0.1	0.1±0.0003	3.5±3.5	56.4±29.5	117.5±62.3	ND	6805.3±1865.2	ND	ND	ND	ND	ND
		Total TEQBaP	3.8±3.5	0.3±0.3	3±4.8	13.3±20.4	0.4±0.5	106.2±40.5	0.2±0.2	0.7±1.2	0.3±0.6	11.2±0.4	66.3±35.5	128.1±69.8	1026±765.1	6941.6±1933.3	5.8±7.6	0.2±6.2	8.9±0.8	2.2±1.8	128.3±331.1
	HW	Gas	2.9±0.2	0.2±0.04	2.2±0.2	8.7±4.2	0.7±0.5	67.1±31	0.1±0.02	0.5±0.002	0.3±0.001	5.3±5.2	8.1±0.9	8.2±0.3	565.8±3.8	109±3.9	4.9±0.4	1.2±0.9	7.3±2.2	1.1±0.1	111.1±4.2
		Particulate	0.1±0.04	0.1±0.001	0.1±0.02	ND	0.8±0.8	ND	0.1±0.02	0.1±0.1	0.1±0.001	2±1.4	17.1±17.1	38.7±38.7	ND	2932.7±2932.6	ND	ND	0.1±0	0.1±0.1	17.8±17.7
		Total TEQBaP	3±0.2	0.2±0.04	2.2±0.2	8.7±4.2	1.5±1.3	67.1±31	0.2±0.04	0.6±0.1	0.3±0.002	7.2±3.8	25.1±16.1	46.8±39	565.8±3.8	3041.7±56.4	4.9±0.4	1.2±0.9	7.4±2.2	1.2±0.2	128.9±21.9
China 3	NHW	Gas	1±0.2	0.1±0.03	2.5±1.7	10±5.6	0.4±0.3	32±17.1	0.1±0.1	1.4±1.2	0.7±0.6	21.3±18.5	11.8±14.3	9.2±10	582.7±280.4	331.2±314.8	16.6±17.1	1.6±1.7	1.5±1.3	2.2±1.8	267.3±280.7
		Particulate	0.1±0.02	0.1±0.007	0.1±0.1	0.1±0.1	0.1±0.1	2.3±4	0.1±0.002	ND	0.1±0.03	0.4±0.5	68.2±60.6	186.5±616.9	113.3±253.3	3691.6±2973.9	ND	3±2.6	0.1±0.2	0.4±0.6	ND

		Total TEQBaP	1.1±0.2	0.1±0.04	2.6±1.7	10±5.5	0.5±0.3	34.3±17.3	0.1±0.1	1.4±1.2	0.7±0.6	21.6±18.4	80±55.7	195.7±612.9	696±393.4	4022.8±2976.1	16.6±17.1	4.5±2.2	1.6±1.3	2.5±1.9	267.3±280.7
	HW	Gas	0.6±0.2	0.1±0.02	2.2±1.5	8±5	0.3±0.3	24.6±15.6	0.1±0.04	0.9±0.8	0.5±0.4	14.2±13.8	7±10.7	5.2±6.4	663.8±1081.4	240±250.8	13.1±13.8	2.5±3.8	0.8±0.8	1.5±1.3	192.8±207.7
		Particulate	0.1±0.004	0.1±0.0001	0.1±0.01	ND	ND	ND	ND	ND	0.1±0.01	0.9±1.2	40.7±62.2	92.7±81.6	5.5±158.6	2796.4±1647.1	ND	1.4±0.8	0.1±0	0.1±0.1	ND
		Total TEQBaP	0.6±0.2	0.1±0.023	2.2±1.5	8±5	0.3±0.3	24.6±15.6	0.1±0.04	0.9±0.8	0.5±0.4	15±13.5	47.7±73	97.8±86.6	669.2±1233.9	3036.3±1375.1	13.1±13.8	3.8±4.3	0.8±0.8	1.5±1.3	192.8±207.7
China 4	NHW	Gas	0.9±0.3	0.2±0.1	2.4±0.9	8.7±3.3	0.5±0.3	30.9±11.3	0.2±0.1	1±0.4	0.4±0.1	14.8±8.2	5±1.3	6.8±2.9	739.1±219.8	112.7±24.1	5.9±1.6	0.4±0.4	2±1.6	1.4±0.5	67.7±8.3
		Particulate	0.1±0.01	0.1±0.0002	0.1±0.03	ND	0.1±0.003	ND	0.4±0.4	ND	0.1±0.01	0.1±0.03	53.9±31.3	34.2±32.2	124.9±117.7	4576.2±835.1	ND	3.1±1.8	ND	0.3±0.3	0.5±0.7
		Total TEQBaP	0.9±0.3	0.2±0.1	2.5±0.9	8.7±3.3	0.5±0.3	30.9±11.3	0.5±0.5	1±0.4	0.4±0.1	14.8±8.2	58.9±31.8	40.9±34.9	864±285.3	4688.8±835.5	5.9±1.6	3.5±1.8	2±1.6	1.6±0.8	68.2±9
	HW	Gas	1.1±0.9	0.2±0.1	2.1±1.1	8.6±5.4	0.3±0.2	29.7±17.9	0.1±0.005	0.8±0.6	0.3±0.2	5.3±3.4	7.2±4.7	4.3±1.6	588.6±224.2	152.8±112.8	8.9±7.3	0.2±0.2	0.9±0.7	1.3±0.8	61±93.6
		Particulate	0.1±0.001	0.1±0.002	0.2±0.1	0.1±0.01	0.1±0.04	1.2±1.1	ND	ND	ND	ND	ND	93.7±135.2	ND	2920.7±1167.5	ND	7.7±5.6	0.1±0.1	0.2±0.5	ND
		Total TEQBaP	1.1±0.9	0.2±0.1	2.2±1.04	8.6±5.4	0.4±0.1	30.8±17.5	0.1±0.01	0.8±0.6	0.3±0.2	5.3±3.3	7.2±4.4	98±135.5	588.6±224.2	3073.5±1169.6	8.9±7.3	7.8±5.5	1±0.6	1.5±0.9	61±93.6
China 5	NHW	Gas	1.4±1.9	0.1±0.7	1.6±2.6	6.9±4.5	0.3±0.1	26.7±37.9	0.1±0.01	0.5±0.6	0.2±0.2	3.9±2.2	5±3.9	5.6±3	426.7±579.2	65±108.4	5.3±5.8	1.4±1.2	1.4±0.8	1.5±0.4	66.8±73
		Particulate	0.1±0.01	0.1±0.003	0.1±0.1	ND	0.1±0.04	1.5±1.5	ND	ND	ND	ND	66±13.1	ND	ND	3423.2±1011.6	ND	2.2±2.1	ND	ND	ND
		Total TEQBaP	1.4±0.1	0.1±0.04	1.7±0.2	6.9±0.3	0.3±0.1	28.2±3.3	0.1±0.01	0.5±0.04	0.2±0.02	3.9±2.6	70.9±9.3	5.6±1.7	426.7±69.8	3488.2±946.6	5.3±0.3	3.5±0.8	1.4±0.9	1.5±1.3	66.8±0.7
	HW	Gas	1.2±0.7	0.2±0.1	1.1±0.97	6.7±3.3	0.2±0.1	23.4±8.7	0.1±0.004	0.7±0.4	0.2±0.1	6.8±6.5	20.6±22.3	7.9±6.3	278.4±675.2	160.2±101.1	8.1±6.1	ND	1.5±1.6	1±1.2	75.6±99.1
		Particulate	ND	0.1±0.003	0.1±0.1	ND	ND	0.1±0.05	ND	ND	ND	ND	ND	93.9±93.9	ND	2184.4±2184.4	10±9.9	0.8±0.8	0.1±0	ND	ND
		Total TEQBaP	1.2±0.2	0.2±0.1	1.2±0.5	6.7±3.5	0.2±0.1	23.5±10.4	0.1±0.001	0.7±0.5	0.2±0.2	6.8±6	20.6±4.3	101.8±94.9	278.4±630.1	2344.6±2285.4	18±3.2	0.8±0.8	1.6±0.1	0.93±0.7	75.6±116.6

Nap: Naphthalene; Act: Acenaphthene; Flr: Fuorene; Acl: Acenaphthylene; Phe: Phenanthrene; Ant: Anthracene; Flu: Fluoranthene; Pyr: Pyrene; Chr: Chrysene; BaA: Benzo[a]anthracene; BbF: Benzo[*b*]fluoranthene; BkF: Benzo[*k*]fluoranthene; BaP: Benzo[a]pyrene; DBahA: Dibenz[*a*,*h*]anthracene; BghiP: Benzo[*ghi*]perylene; IP: Indeno[1,2,3-*cd*]pyrene; 5-NAcp: 5-Nitroacenaphthene; 9-NAnt: 9-Nitroanthracene; 3-Nphe: 3-Nitrophenanthrene; 1,3-Npyr: 1,3-Nitropyrene; 3-Nflu: 3-Nitrofluoranthene; 6-NChr: 6-Nitrochrysene; 7-NBaA: 7-Nitrobenz[*a*]anthracene; 6-NBaP: 6-Nitrobenzo[*a*]pyrene

He et al (2010) [Characteristics of polycyclic aromatic hydrocarbons emissions of diesel engine fueled with biodiesel and diesel, Fuel] examined gas- and PM-phase PAH emissions from a diesel engine fueled with diesel fuel and B100 (100% soybean oil biodiesel), B20 (20% soybean oil biodiesel + 80% fossil diesel).

Tests were performed on a direct injection, turbocharged EURO II diesel engine (FAW-WDEW 4CK, China), with the following characteristics: four-cylinders; bore and stroke of 110 × 125 mm; total displacement of 4.75 L; compression ratio of 16.8; rated power of 117 kW at 2300 r/min; maximum torque of 580 Nm at 1400 r/min; traditional mechanical injection system; and without EGR (exhaust gas recirculation) or any other after-treatments. Testing was performed on the ISO 8178 C18-mode steady state cycle.

PAHs samples of both gas-phase and particle-phase were collected by using a PAHs sampling system at a temperature below 52 °C. Sample gas was drawn from the tailpipe and diluted in an ejection dilutor (Dekati, Finland), which can control the dilution ratio around 8. Particle-phase PAHs were collected on a fiberglass filter, which was pre-cleaned in a muffle at 450 °C for 8 h before sampling. Gas-phase PAHs were collected by a “PUF/XAD-2/PUF” cartridge (Supelco ORBO-1500, USA), as recommended by the manufacturer. The sampling flow rate of particle-phase and gas-phase PAHs was 35 and 5 L/min, respectively and the sampling time was 30 min.

The sampled filters were extracted in an ultrasonic extractor for 3 times (30 min for each time) and the sampled cartridges were extracted in a Soxhlet extractor for 24 h with dichloromethane. Both the particle-phase and gas-phase PAHs extract was then concentrated, followed by silica gel cleanup procedure using column chromatography to remove potential interferences prior to analysis. The eluent was reconcentrated to exactly 1.0 mL and collected by a volumetric flask for the next analysis.

The analytical method for PAHs was based on the EPA method TO-13A. The PAHs contents were determined by a gas chromatograph/mass spectrometer (GC/MS) (Agilent 6890N/5795C, USA). The GC was equipped with a capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 μm) and the oven was heated from 80 to 160 °C at 20 °C/min, and 160–280 °C at 5 °C/min, then held at 280 °C for 10 min. Helium was used as carrier gas at a flow rate of 1 mL/min. The transfer line to MS was at 250 °C and the ion source of MS was electron impact (EI) at 230 °C. The PAHs were qualified by using the selected ion monitoring (SIM).

In order to quantify the samples, the GC/MS was calibrated with a commercial standard mixture (Supelco EPA 610 PAH MIX, USA), which contains 16 PAH compounds, that are Naphthalene (Nap), Acenaphthylene (AcPy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benzo[*a*]anthracene (BaA), Chrysene (CHR), Benzo[b]Fluoranthene (BbF), Benzo[k]Fluoranthene (BkF), Benzo[*a*]Pyrene (BaP), Indeno[1,2,3-cd]Pyrene (IND), Dibenzo[a,h]Anthracene (DBA) and Benzo[g,h,i]Perylene (BghiP). Five-point calibration curves were constructed and the correlation coefficient was more than 0.999.

Table 131: The five most abundant PAHs in gas-phase and particle-phase for D, B20, and B100 fuels

Fuel	Gas-phase PAHs			Particle-phase PAHs		
	PAH	BSE (μg/kW h)	Percentage (%)	PAH	BSE (μg/kW h)	Percent-age (%)
D	Naphthalene	98.7	59.1	Phenanthrene	37.5	51
	Phenanthrene	15.5	9.3	Pyrene	13.3	18.1
	Fluorene	10.8	6.5	Fluoranthene	6.2	8.4

	Pyrene	7.9	4.8	Naphthalene	5.7	7.8
	Acenaphthylene	6.2	3.7	Anthracene	3.7	5.1
B20	Nap	67.8	42	Phenanthrene	15.2	31.8
	Phenanthrene	23.1	14.4	Pyrene	11.3	23.6
	Pyrene	11.9	7.4	Fluoranthene	5.9	12.3
	Fluorene	9.5	5.9	Naphthalene	2.9	6.1
	Chrysene	8.9	5.5	Chrysene	2.7	5.6
B100	Naphthalene	71.8	45.5	Phenanthrene	11.7	32.1
	Fluorene	24.9	15.8	Naphthalene	5.9	16.2
	Phenanthrene	24.7	15.7	Pyrene	4.9	13.6
	Pyrene	9.1	5.8	Fluoranthene	4	10.9
	Acenaphthylene	5.3	3.4	Fluorene	1.6	4.4

Table 132: Total PAH emissions at different engine conditions (µg/m^3)

Engine Condition	**PAH**	**D**	**B20**	**B100**
Mode 1	Gas-phase	43.565	22.043	18.913
	Particle-phase	16.565	11.739	6.261
	Total	60.130	33.783	25.174
Mode 2	Gas-phase	40.957	34.957	33.000
	Particle-phase	11.870	7.565	7.304
	Total	52.826	42.522	40.304
Mode 3	Gas-phase	24.652	25.174	24.130
	Particle-phase	7.826	7.304	5.217
	Total	32.478	32.478	29.348
Mode 4	Gas-phase	14.478	9.130	8.348
	Particle-phase	3.652	3.652	4.174
	Total	18.130	12.783	12.522
Mode 5	Gas-phase	4.826	8.870	15.391
	Particle-phase	10.565	3.783	3.913
	Total	15.391	12.652	19.304
Mode 6	Gas-phase	10.826	21.652	22.565
	Particle-phase	7.696	4.565	3.000
	Total	18.522	26.217	25.565
Mode 7	Gas-phase	20.478	13.696	13.957
	Particle-phase	8.348	7.174	5.087

	Total	28.826	20.870	19.043
Mode 8	Gas-phase	19.696	7.304	14.348
	Particle-phase	10.957	1.696	1.957
	Total	30.652	9.000	16.304

Vojtisek-Lom et al (2017) [Blends of butanol and hydrotreated vegetable oils as drop-in replacement for diesel engines: Effects on combustion and emissions, Fuel] examined PAH emissions from a diesel engine with different alcohol and diesel fuels.

A water-cooled inline six-cylinder turbocharged 2001 model year 5.9-liter Iveco Tector F4a E0681B C109 diesel engine with intercooler, bore 102 mm, stroke 120 mm, compression ratio 17:1, max power 176 kW @ 2700 min−1, max torque 810 Nm @ 1250–2100 min−1, common rail, Euro3 compliant, ECU Iveco RDC7 ELT 3.1 was used. The engine operated without any exhaust aftertreatment devices, with approximately 1900 operating hours accumulated, was operated on a four-quadrant transient heavy-duty engine dynamometer (DynoExact 220 kW, AVL), in the following test sequence: WHTC as preconditioning, cold WHTC, subsequent WHTC (warm but not a fully stabilized warm), multiple hot-start WHTC, and WHSC (World Harmonized Steady-State Cycle).

Several renewable fuels were tested: a market-grade biodiesel (methyl esters of primarily rapeseed oil), a paraffinic diesel fuel made from renewable sources (NExBTL, Neste Oil, Finland, provided directly by Neste Oil), and two isomers of butanol, n-butanol and isobutanol. Biodiesel (further referred to as B100) and NExBTL (further referred to as HVO) were used both neat (B100 and HVO100) and blended at 30% by volume with diesel fuel (B30 and HVO30). NExBTL was also used in blends of 30% n-butanol with 70% HVO (referred to as nBu30), and 30% isobutanol with 70% HVO (referred to as iBu30). Neat diesel fuel used as a reference (referred to as B0).

The diluted exhaust was sampled with a standard gravimetric sampling system on 47 mm diameter quartz fiber (Tissuquartz, Pall) at a nominal flow rate of 40 dm3/min. Prior to extraction, recovery standards, deuterated PAHs (1,4-dichlorbenzene-D8, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12), 6-nitrochrysene-D11 and ααα (20R)-cholestane-D2, were added to filters. The filters were extracted three times for 30 min under ultrasonic agitation; once with 20 mL of mixture of dichloromethane with hexane (v/v 1:1) and then twice with 20 mL of dichloromethane. The extracts were pooled and then dried under a stream of nitrogen to 1 mL.

The extracts were then fractionated by flash chromatography in a glass column filled with 10 g of Al2O3 (Aluminum oxide 90 standardized, for column chromatographic adsorption analysis according to Brockmann, activity II - III). Analysis was carried out by GC–MS (Agilent, 7890A, 5975C). A capillary column HP5-MS, 1 µm film thickness, 0.32 mm i.d., 30 m length was used. A sample volume of 2 µL was injected into a split/splitless injector, operated in the splitless mode at a temperature of 280 °C for non-polar compounds and at 260 °C for other compounds. The carrier gas was helium at a flow rate of 4 ml min−1. For analysis of nitrated PAHs, the temperature program was started at 70 °C for 2 min, a gradient of 20 °C min−1 was used up to 150 °C, then a gradient of 5 °C min-1 was used up to 300 °C and then the temperature was held for 14 min. The MS was operated in SIM mode with *m*/*z* 173, 211, 223, 247, 273, 275, 284, 292 and 297.

Table 133: Emissions of individual PAHs across different fuels for the hot-start WHTC (µg/kWh)

PAH, µg/kWh	**B0, PM2.5**	**B30, PM2.5**	**B100, PM2.5**	**HVO30, PM2.5**	**HVO100, PM2.5**	**iBu30-HVO70, PM2.5**	**nBu30-HVO70, PM2.5**
Fluorene	0.151	0.120	0.090	0.211	0.181	0.060	0.060
Phenanthrene	7.500	2.982	1.506	15.934	7.560	1.536	1.446
Anthracene	0.873	0.542	0.181	1.928	1.054	0.241	0.151
Fluoranthene	8.404	21.084	3.584	13.373	4.518	2.952	2.018
Pyrene	14.247	27.560	5.030	17.711	5.361	3.494	2.349
Benz[a]anthracene	1.114	1.054	0.843	0.512	0.211	0.361	0.331
Chrysene+triphenylene	0.873	0.783	0.572	0.542	0.181	0.241	0.181
Benzo[b+j+k]fluoranthene	0.151	0.211	0.211	0.090	0.271		
Benzo[e]pyrene	0.301	0.392	0.301	0.211	0.060	0.060	0.060
Benzo[a]pyrene	0.120	0.151	0.181	0.120			
Indeno[1,2,3-c,d]pyrene	0.090	0.060	0.060	0.090			
Dibenzo[a,h]anthracene							
Benzo[g,h,i]perylene	0.090	0.060	0.090	0.151			

Ahmed et al. (2018) [Emissions of particulate associated oxygenated and native polycyclic aromatic hydrocarbons from vehicles powered by ethanol/gasoline fuel blends, Fuel] characterized emission factors for oxygenated polycyclic aromatic hydrocarbons (OPAHs) and PAHs determined from two different fuel flexible light duty vehicles operated at −7 °C in the New European Driving Cycle (NEDC) and at +22 °C in the Artemis Driving Cycle (ADC).

Testing was made on two flex fuel passenger cars a Saab 95 (FFV1) and a Volvo V50 (FFV2) (both Euro 4). Three gasoline/ethanol fuel blends were tested: Swedish commercial petrol (5% ethanol in gasoline (E5) and ethanol fuels (E85 and winter quality E70 with 85% and 70%) ethanol in gasoline, respectively. The sampling was performed using a constant volume sampling system (CVS) with a dilution of the exhaust applied. Particulate exhaust samples were collected on Teflon coated glass fiber filters (Pallflex Inc T60A20, Putnam, USA).

Filter parts (about one quarter of each filter) were spiked with a mixture of six perdeuterated surrogate internal standards: phenanthrene-D10, pyrene-D10, benzo[a]anthracene-D12, B[a]P-D12, benzo[ghi]perylene-D12 and anthraquinone-D8 prior to extraction. The samples were extracted using an accelerated solvent extraction system (ASE 200, Dionex Corporation, Sunnyvale, CA, USA) with toluene: methanol (Tol: MeOH, 9:1) as extraction solvent. The extract was evaporated to approximately 5 ml under a gentle gas stream of nitrogen in a water bath heated to about 60 °C. The extracts were then transferred to disposable test tubes and further evaporated to 0.5 ml. Clean-up was performed using silica solid phase extraction (SPE) cartridges (100 mg, Isolute, IST, UK) with toluene as mobile phase.

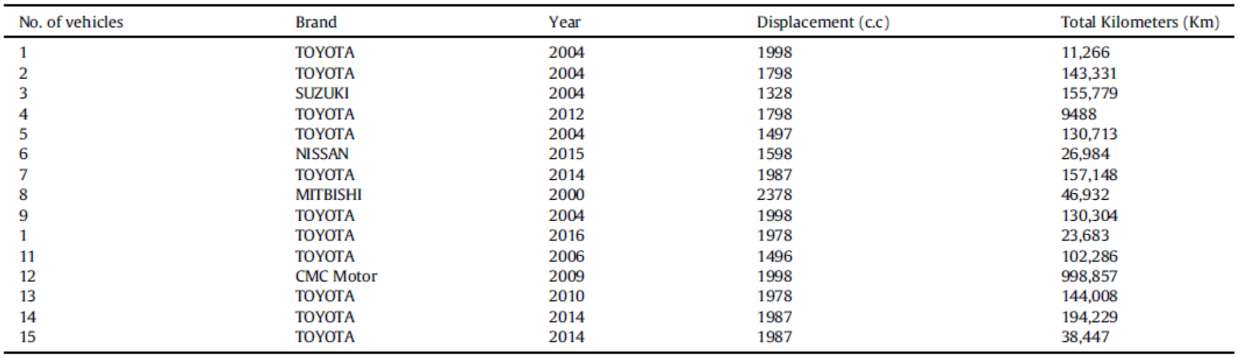
A hyphenated High Performance Liquid Chromatography Gas Chromatography/Mass Spectrometry (LC-GC/MS) system was used for the analysis of OPAHs and PAHs. This system consists of an auto sampler (CMA/200 micro sampler, CMA Microdialysis AB, Sweden), a HPLC pump (Varian Inc, Palo Alto, CA, USA), an UV detector (SPD-6A, Shimadzu, Japan) and a normal phase LC column (Nucleosil 100-5NO2 124 × 4.6 mm, 5 μm) which was coupled to an Agilent 6890 N gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) fitted with a DB-17MS column (60 m × 0.25 mm i.d. x 0.1 μm film thickness) and interfaced with an Agilent 5973 N MSD (Agilent Technologies).

Table 134: Average PAH emission factors in ng/km

Compound	NEDC E5 −7 °C		NEDC E70 −7 °C		NEDC E85 −7 °C		ADC E5 +22 °C		ADC E85 +22 °C	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Phenanthrene	1340	389	2770	569	2590	1390	47	23	45	43
Anthracene	176	26	545	107	550	356	20	5	15	15
cyclopentaphenanthrene	42	9	325	124	209	176	2	1	2	2
Fluoranthene	1600	297	7030	1340	3020	3830	30	13	32	28
Pyrene	1690	993	9590	1810	4290	4130	46	24	38	34
Benz[a]fluorene	177	213	1080	921	142	107	3	2	2	2
Benz[b]fluorene	257	188	1120	955	212	242	3	1	1	1
Benzo[ghi]fluoranthene	951	608	1230	352	3340	745	20	4	24	18
Benz[a]anthracene	483	354	1540	1850	930	373	17	5	15	13
Chrysene	2290	1320	7600	8920	4380	2190	99	33	74	65
Benzo[b]fluoranthene	1900	1650	5770	6780	4107	843	116	15	116	100
Benzo[k]fluoranthene	1270	1260	3500	4220	2290	488	47	9	44	39
Benzo[e]pyrene	1450	1120	6780	7340	6280	2020	88	15	87	73
Benzo[a]pyrene	2760	2570	11600	13500	10100	2990	92	23	74	62
Perylene	430	453	1930	2350	1320	460	10	4	8	7
Indeno[1,2,3-cd]fluoranthene	63	63	63	67	61	14	4	3	2	2
Indeno[1,2,3-cd]pyrene	1020	1030	2660	2530	3530	816	84	67	38	28
Dibenzo[a,h]anthracene	44	41	77	80	65	38	3	3	1	1
Benzo[ghi]perylene	1070	1190	3660	2680	6570	1830	114	85	55	43
Dibenzo[a,l]pyrene	18	6	63	75	51	30	2	1	1	0.3
Dibenzo[a,e]pyrene	72	33	95	74	98	95	16	13	3	2
Coronene	1090	1410	2220	426	5800	3200	332	271	42	45
Dibenzo[a,i]pyrene	64	56	203	201	194	156	28	17	2	1

Dibenzo[a,h]pyrene	15	10	21	20	22	14	1	1	1	

Lin et al. (2019) [Assessment of PM2.5 and PAH content in PM2.5 emitted from mobile source gasoline-fueled vehicles in concomitant with the vehicle model and mileages, Chemosphere] examined the PAH emissions from gasoline vehicles with different model years and mileage. Three vehicles were tested for Euro 3 and Euro 4, five vehicles for Euro 5, and four vehicles for Euro 6. A list of the test vehicles is shown below.



No. of vehicles	Brand	Year	Displacement (c.c)	Total Kilometers (Km)
1	TOYOTA	2004	1998	11,266
2	TOYOTA	2004	1798	143,331
3	SUZUKI	2004	1328	155,779
4	TOYOTA	2012	1798	9488
5	TOYOTA	2004	1497	130,713
6	NISSAN	2015	1598	26,984
7	TOYOTA	2014	1987	157,148
8	MITBISHI	2000	2378	46,932
9	TOYOTA	2004	1998	130,304
1	TOYOTA	2016	1978	23,683
11	TOYOTA	2006	1496	102,286
12	CMC Motor	2009	1998	998,857
13	TOYOTA	2010	1978	144,008
14	TOYOTA	2014	1987	194,229
15	TOYOTA	2014	1987	38,447

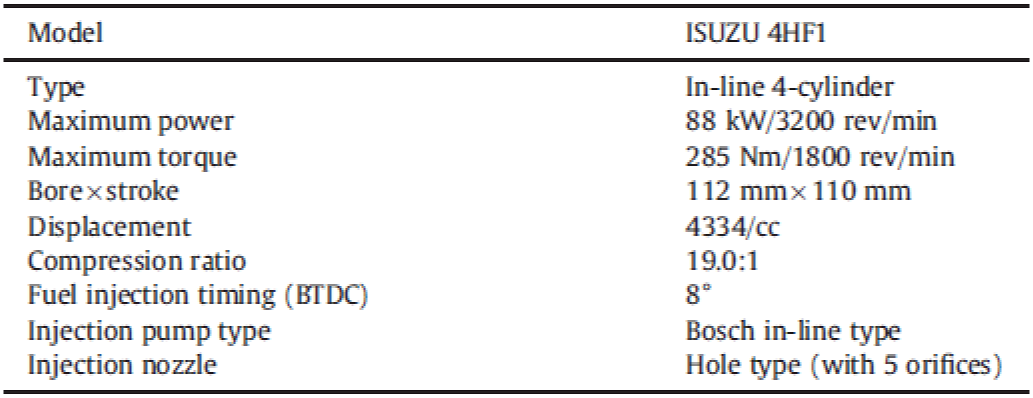
For analyzing PAH, the sample was separated in a Soxhlet extractor with a blended dissolvable (n-hexane and dichloromethane; vol/vol, 1:1; 500ml each) for 24 h. The PAH substance was regulated by HP gas chromatograph (GC) (HP 5890A; Hewlett Packard, Wilmington, DE, USA), a mass selective detector (MSD) (HP 5972), and a PC workstation (Aspire C500; Acer, Taipei, Taiwan). The extract was concentrated and cleaned up by utilizing a silica segment loaded with silica gel particles positioned under a layer of Na_2SO_4 and specifically reconcentrated with ultra-pure nitrogen to precisely 0.2 mL for GC/MS analysis.

Table 135: PAH emission factors of PM2.5 in the exhaust of gasoline vehicles (ng/L-Fuel)

Compounds, ng/L-Fuel	Mean	SD	RSD (%)
naphthalene	0.111	0.0752	53.3
acenaphthylene	0.00592	0.00422	47.6
acenaphthene	0.00532	0.00389	37.2

Fluorene	0.0135	0.0126	51.8
Phenanthrene	0.103	0.0765	51.5
Anthracene	0.0145	0.0131	48.3
Fluoranthene	0.035	0.0198	48.4
Pyrene	0.0198	0.0209	37.6
benzo(a)anthracene	0.00502	0.00258	53.2
Chrysene	0.00582	0.00258	46
benzo(b)fluoranthene	0.00546	0.0057	53.6
benzo(k)fluoranthene	0.00498	0.00514	51.8
benzo (a) pyrene	0.00527	0.00558	55.2
benzo (e) pyrene	0.0131	0.03987	43.7
cyclopenta[cd]pyrene	0.00256	0.0032	47.7
dibenzo(a,h)anthracene	0.00207	0.00243	40.1
Perylene	0.00326	0.00233	50.4
indeno(1,2,3,-cd)pyrene	0.00487	0.00206	36.5
benzo[b]chrycene	0.00349	0.00397	52.9
benzo[ghi]perylene	0.00697	0.00356	48
Coronene	0.00584	0.00322	57

Lu et al. (2012) [Size distribution of EC, OC and particle-phase PAHs emissions from a diesel engine fueled with three fuels, Science of the Total Environment] examined the particle-phase PAHs emission from a direct injection diesel engine fueled with a waste cooking biodiesel, ultra-low sulfur diesel (ULSD, 10-ppm-wt), and low sulfur diesel (LSD, 400-ppm-wt). testing was performed on a pre-Euro standard naturally-aspirated, water cooled, 4-cylinder direct-injection diesel engine (ISUZU 4HF1). Technical parameters of the engine are shown below.



Model	ISUZU 4HF1
Type	In-line 4-cylinder
Maximum power	88 kW/3200 rev/min
Maximum torque	285 Nm/1800 rev/min
Bore × stroke	112 mm × 110 mm
Displacement	4334/cc
Compression ratio	19.0:1
Fuel injection timing (BTDC)	8°
Injection pump type	Bosch in-line type
Injection nozzle	Hole type (with 5 orifices)

Particulate samples were collected at a steady engine speed of 1800 rev/min and at a high and a low engine load, corresponding to the brake mean effective pressure (BMEP) of 0.08 and 0.7 MPa. A micro-orifice uniform deposit impactor (MOUDI-110R, MSP) with 10 cut-point sizes of 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1 and 0.056 μm was used to classify particulate samples. Before particulate sampling, the exhaust gas was diluted by a Dekati ejector diluter (Dekati Limited). The transfer line from the exhaust to the diluter and the diluter were heated to avoid volatile hydrocarbon condensation loss. The transfer line from the diluter to the MOUDI was a 1.5 m long PTFE lined flexible pipe. The exhaust gas was naturally cooled to below 50 °C in the transfer line before going through the MOUDI. The overall dilution ratio was found to be 11.7 and 8.6 for high and low engine load, respectively.

Particle-phase PAHs were analyzed by GC/MS (Shimadzu GCMS 2010). Samples on the quartz filters were extracted by Dionex accelerated solvent extraction (ASE150) at 130 psi, 80 °C using a mixture of dichloromethane (DCM) and n-hexane (3:1, v/v). The extract was concentrated to 4 mL and five deuterated internal standards (PAH-Mix 31 deuterated, Dr. Inc. Germany, Acenaphthene-D10, Chrysene-D12, Perylene-D12, Phenanthrene-D10 and Naphthalene-D8) were added to all extracts for quantification purpose. The concentrated extracts were purified, and fractionated using activated silica gel column (2 g) chromatography. The silica gel column was prewashed with 50 mL of *n*-hexane, and the target compounds PAHs were eluted with 20 mL of 20% DCM in *n*-hexane after passage of 5 mL of *n*-hexane. The fraction contained PAHs were reconcentrated to 200 μL for GC/MS analysis. The MS was operated in selected ion monitoring (SIM) mode and GC was equipped with an Rtx-5MS capillary column (30 m × 0.25 mm, film thickness 0.25 μm), with helium as carrier gas at a flow rate of 1.0 mL min− 1. Splitless injection volume was 2 μL at 280 °C. Ion source temperature was 280 °C. The column oven temperature was programmed from 80 (1 min) to 140 °C at a rate of 15 °C min− 1, and to 300 °C at 5 °C min− 1, and then held at 300 °C for 5 min.

Table 136: Specific emissions of particle-phase PAHs (μg/kW-h) in PM1.8

PAHs	**ULSD**		**Biodiesel**		**LSD**	
	High load	**Low load**	**High load**	**Low load**	**High load**	**Low load**
naphthalene	2.39	7.03	1.29	9.94	2.71	8.61
acenaphthylene	0.39	0.74	0.21	0.62	0.46	0.78
acenaphthene	1.24	5.37	0.61	3.34	1.4	5.3
Fluorene	8.67	29.33	5.02	16.79	9.54	28.5
Phenanthrene	31.93	54.23	16.17	43.32	33.83	56.38
Anthracene	3.26	1.48	0.72	0.99	3.12	1.48
Fluoranthene	14.14	12.75	7.89	11.5	15.22	13.65
Pyrene	22.06	11.95	15.32	13.84	26.1	13.71
benzo(a)anthracene	0.99	3.47	1.02	1.18	1.45	4.17
Chrysene	3	6.41	2.96	3.19	4.23	8.01
benzo(b)fluoranthene	0.25	5.12	0.33	1.22	0.44	6
benzo(k)fluoranthene	0.22	4.61	0.25	1.09	0.38	5.4
benzo (a) pyrene	0.1	2.52	0.06	0.67	0.18	2.97
indeno(1,2,3,-cd)pyrene	0.12	3.5	0.07	0.56	0.19	4.02
benzo[ghi]perylene	0.08	1.32	0.05	0.89	0.15	1.72

Table 137: Distribution of the individual PAHs over MOUDI stages for ULSD (ng/kW-h)

PAH	**High engine load**							**Low engine load**						
	<0.056	**0.056-0.1**	**0.1-0.18**	**0.18-0.32**	**0.32-0.56**	**0.56-1**	**1-1.8 (μm)**	**<0.056**	**0.056-0.1**	**0.1-0.18**	**0.18-0.32**	**0.32-0.56**	**0.56-1**	**1-1.8 (μm)**
acenaphthylene	59.478	34.435	117.913	52.174	52.696	38.609	39.130	197.080	65.693	111.679	111.679	78.832	91.971	131.387
benzo(b)fluoranthene	34.435	41.739	44.348	43.826	32.348	28.696	21.913	354.745	919.708	1747.445	965.693	512.409	381.022	236.496
benzo(k)fluoranthene	31.826	28.174	36.522	33.391	33.913	29.217	29.217	374.453	781.752	1491.241	900.000	499.270	302.190	262.774
benzo (a) pyrene	13.043	32.348	13.565	11.478	9.913	7.826	18.783	98.540	302.190	610.949	308.759	696.350	446.715	52.555
indeno(1,2,3,-cd)pyrene	15.130	14.609	18.261	19.826	18.783	18.783	14.609	223.358	637.226	1011.679	696.350	348.175	341.606	223.358
benzo[ghi]perylene	9.913	10.435	15.130	14.609	13.043	12.522	8.348	26.277	39.416	45.985	39.416	486.131	472.993	249.635
naphthalene	434.363	93.822	253.668	368.340	413.514	448.263	385.714	1705.776	356.318	841.516	1902.888	659.567	667.148	947.653
acenaphthene	295.367	52.124	142.471	135.521	163.320	184.170	257.143	1326.715	280.505	659.567	894.585	492.780	629.242	1053.791
Anthracene	486.486	371.815	833.977	531.660	552.510	274.517	191.120	227.437	113.718	310.830	288.087	204.693	144.043	144.043
benzo(a)anthracene	138.996	163.320	260.618	163.320	135.521	79.923	45.174	257.762	538.267	1190.253	629.242	386.643	250.181	189.531
Chrysene	392.664	587.259	781.853	483.012	392.664	208.494	135.521	614.079	1053.791	2024.188	1068.953	689.892	538.267	447.292
Fluorene	1446.494	856.089	1564.576	1239.852	1269.373	1269.373	1151.292	7265.625	3890.625	3328.125	3515.625	2109.375	3234.375	6046.875
Phenanthrene	4693.727	3217.712	6878.229	4811.808	5490.775	3690.037	3040.590	12515.625	5390.625	7640.625	8015.625	5109.375	5906.250	9703.125
Fluoranthene	2036.900	2420.664	3926.199	2095.941	1859.779	1092.251	678.967	2578.125	1734.375	1921.875	1640.625	1265.625	1265.625	2109.375
Pyrene	3601.476	3394.834	6464.945	3158.672	3040.590	1564.576	944.649	1359.375	796.875	3046.875	2484.375	2062.500	1078.125	1078.125

Table 138: Distribution of the individual PAHs over MOUDI stages for biodiesel (ng/kW-h)

PAH	**High engine load**							**Low engine load**						
	<0.056	**0.056-0.1**	**0.1-0.18**	**0.18-0.32**	**0.32-0.56**	**0.56-1**	**1-1.8 (µm)**	**<0.056**	**0.056-0.1**	**0.1-0.18**	**0.18-0.32**	**0.32-0.56**	**0.56-1**	**1-1.8 (µm)**
acenaphthylene	19.048	40.774	57.738	18.750	25.595	24.405	23.512	44.291	13.841	59.516	60.900	196.540	155.017	94.118
benzo(b)fluoranthene	-	-	-	-	-	-	-	81.661	146.713	308.651	207.612	202.076	148.097	123.183
benzo(k)fluoranthene	21.429	44.048	51.786	43.452	33.333	25.000	27.679	96.886	127.336	251.903	196.540	211.765	91.349	116.263
benzo (a) pyrene	5.357	10.119	14.286	10.714	7.738	5.952	7.738	35.986	76.125	157.785	119.031	123.183	110.727	44.291
indeno(1,2,3,-cd)pyrene	5.357	9.524	11.310	8.929	10.714	7.738	11.905	52.595	71.972	88.581	66.436	99.654	105.190	71.972
benzo[ghi]perylene	3.571	8.631	10.714	8.333	7.738	4.762	8.333	58.131	123.183	196.540	127.336	159.170	143.945	77.509
naphthalene	163.320	281.467	246.718	69.498	149.421	135.521	225.869	1338.843	502.066	1260.744	1204.959	2510.331	2287.190	792.149
acenaphthene	69.498	121.622	107.722	41.699	86.873	76.448	93.822	368.182	33.471	301.240	256.612	870.248	1026.446	435.124
Anthracene	62.548	145.946	198.069	79.923	107.722	62.548	38.224	55.785	11.157	167.355	145.041	234.298	211.983	122.727
benzo(a)anthracene	76.448	184.170	295.367	201.544	114.672	76.448	52.124	78.099	145.041	256.612	178.512	189.669	211.983	78.099
Chrysene	222.394	569.884	865.251	569.884	333.591	232.819	149.421	256.612	368.182	680.579	479.752	513.223	468.595	357.025
Fluorene	479.167	937.500	854.167	625.000	791.667	562.500	666.667	1776.173	606.498	1342.960	996.390	4072.202	3335.740	2729.242
Phenanthrene	1354.167	2833.333	3854.167	2062.500	2333.333	1979.167	1708.333	3552.347	1039.711	4592.058	4245.487	9703.971	8750.903	6671.480
Fluoranthene	583.333	1520.833	2416.667	1250.000	916.667	708.333	500.000	866.426	519.856	1819.495	1559.567	2122.744	1949.458	1429.603
Pyrene	1000.000	3020.833	5229.167	2208.333	1708.333	1375.000	791.667	519.856	346.570	2859.206	2685.921	2512.635	2079.422	1299.639

Table 139: Distribution of the individual PAHs over MOUDI stages for LSD (ng/kW-h)

PAH	High engine load							Low engine load						
	<0.056	0.056-0.1	0.1-0.18	0.18-0.32	0.32-0.56	0.56-1	1-1.8 (µm)	<0.056	0.056-0.1	0.1-0.18	0.18-0.32	0.32-0.56	0.56-1	1-1.8 (µm)
acenaphthylene	94.957	48.000	124.174	56.348	54.261	42.783	46.435	164.198	60.494	103.704	103.704	120.988	120.988	120.988
benzo(b)fluoranthene	76.696	62.609	102.261	70.957	50.609	42.783	37.565	423.457	1054.321	2013.580	1123.457	622.222	475.309	276.543
benzo(k)fluoranthene	71.478	46.957	80.348	52.174	47.478	38.609	40.696	432.099	898.765	1711.111	1037.037	622.222	354.321	328.395
benzo (a) pyrene	46.435	34.435	40.174	14.609	12.522	9.913	20.348	112.346	362.963	725.926	380.247	812.346	501.235	77.778
indeno(1,2,3,-cd)pyrene	49.043	18.783	43.826	21.913	21.913	19.826	19.304	259.259	725.926	1140.741	777.778	414.815	397.531	276.543
benzo[ghi]perylene	42.261	12.522	40.696	17.217	15.130	12.522	12.000	51.852	69.136	120.988	69.136	579.012	570.370	285.185
naphthalene	512.903	222.581	329.032	372.581	411.290	430.645	459.677	1768.966	444.828	1065.517	1882.759	1293.103	1231.034	1003.448
acenaphthene	338.710	111.290	179.032	145.161	179.032	188.710	285.484	1189.655	237.931	631.034	796.552	672.414	817.241	972.414
Anthracene	508.065	372.581	774.194	527.419	508.065	256.452	198.387	217.241	113.793	300.000	300.000	248.276	196.552	155.172
benzo(a)anthracene	198.387	246.774	411.290	246.774	188.710	111.290	72.581	320.690	651.724	1386.207	744.828	496.552	362.069	258.621
Chrysene	503.226	822.581	1166.129	725.806	527.419	309.677	208.065	755.172	1282.759	2431.034	1334.483	920.690	744.828	610.345
Fluorene	1563.830	1021.277	1531.915	1404.255	1308.511	1276.596	1340.426	6387.097	3290.323	3193.548	3096.774	3096.774	3677.419	5709.677
Phenanthrene	4946.809	3702.128	7085.106	5361.702	5329.787	3734.043	3574.468	11225.806	4645.161	7645.161	7838.710	7354.839	7645.161	10064.516
Fluoranthene	2106.383	2553.191	4085.106	2521.277	1851.064	1148.936	893.617	2419.355	1596.774	2129.032	1935.484	1645.161	1741.935	2129.032
Pyrene	3734.043	4212.766	7755.319	3957.447	3223.404	1914.894	1244.681	1258.065	870.968	3387.097	2806.452	2516.129	1548.387	1354.839

Wu et al. (2017) [Chemical characterization and toxicity assessment of fine particulate matters emitted from the combustion of petrol and diesel fuels, Science of the Total Environment] examined the PAH emissions produced by the combustion of four typical petrol and diesel fuels widely-used in China.

The particles were sampled with a wick burner under a semi-enclosed cylindrical glass cover with a sufficient particle-free air supply and a stainless-steel environmental chamber equipped with magnetic fans fixed at the bottom of the chamber ensured mixing of the chamber contents. Each combustion experiment lasted for 10 min and the combustion experiments for each fuel type were conducted at least in triplicate.

After sampling, 16 PAHs, namely, naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Acp), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InP), dibenzo[*a*,*h*]anthracene (DahA), and benzo[*g*,*h*,*i*]perylene (BghiP) were extracted and identified with gas chromatography/mass spectrometry. The extraction and analytical procedures used for the PAHs were those used in a previous study in our laboratory (Zhang et al., 2011). One quarter of the filter was ultrasonicated twice with 25 mL (15 + 10 mL) of dichloromethane in a Branson™ Ultrasonic Cleaner for 30 min. The solution of each sample was evaporated to 2–3 mL on a rotary evaporator (Buchi, Switzerland) and was blow down to 1 mL under a gentle stream of nitrogen. To ensure high-quality data, quality assurance procedures were conducted. First, the recoveries of the PAHs were determined to test the availability of the analytical method. The average recovery efficiencies ranged from 85% to 99%, and the PAH concentrations were calculated from the recovery efficiencies. In general, laboratory blanks detection showed that no PAHs have been detected and the method detection limit (MDL) for PAH analysis by GC–MS was about 0.005 mg/L.

Table 140: Emission factors of 16 priority polycyclic aromatic hydrocarbons (PAHs) in mg/kg fuel from fuel combustion.

PAHs	Light diesel oil	Marine heavy diesel oil	93 octane petrol	97 octane petrol
Naphthalene	1.10 ± 0.25	0.16 ± 0.04	0.14 ± 0.05	0.23 ± 0.07
Acenaphthylene	0.02 ± 0.00	0.29 ± 0.13	ND	ND
Acenaphthene	ND	1.32 ± 0.21	ND	ND
Fluorene	0.01 ± 0.00	0.03 ± 0.01	0.07 ± 0.03	0.05 ± 0.02
Anthracene	0.11 ± 0.02	0.06 ± 0.02	0.24 ± 0.08	0.18 ± 0.01
Phenanthrene	0.05 ± 0.01	0.03 ± 0.00	0.07 ± 0.05	0.14 ± 0.03
Fluoranthene	0.03 ± 0.02	0.06 ± 0.01	0.59 ± 0.23	0.73 ± 0.19
Pyrene	0.08 ± 0.03	0.10 ± 0.00	0.78 ± 0.16	0.66 ± 0.07
Benz[a]anthracene	ND	ND	0.05 ± 0.00	0.02 ± 0.01
Chrysene	ND	ND	0.09 ± 0.02	0.05 ± 0.04
Benzo[a]pyrene	ND	0.06 ± 0.04	0.12 ± 0.06	0.16 ± 0.05
Benzo[b]fluoranthene (	ND	0.45 ± 0.10	0.07 ± 0.01	0.05 ± 0.00
Benzo[k]fluoranthene	ND	ND	0.02 ± 0.00	0.09 ± 0.02
Benzo[g,h,i]pyrene	ND	ND	0.05 ± 0.04	0.02 ± 0.01
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND
Dibenz[a,h]anthracene	ND	ND	0.07 ± 0.03	0.02 ± 0.00

Zimmerman et al. (2019) [Carbonaceous aerosol sampling of gasoline direct injection engine exhaust with an integrated organic gas and particle samples, Science of the Total Environment] examined the PAH emissions in GDI engine exhaust PM using an integrated organic gas and particle sampler (IOGAPS). Three configurations (denuder+sorbent impregnated filters (SIFs), upstream Zefluor filter + denuder + SIFs, and standard filter pack + SIFs) were used to collect GDI exhaust samples at cold start and highway cruise operating conditions with no aftertreatment.

Sampling was conducted on light-duty GDI engine exhaust (2012 Ford Focus, 2.0 L displacement) mounted on a laboratory engine dynamometer. The engine was not fitted with exhaust aftertreatment; all measurements were taken from engine-out exhaust. The engine was fueled with commercially-available premium gasoline containing no ethanol. The engine was operated under two conditions: (1) cold start (no load and 12–24 h soak time) and (2) steady-state highway cruise condition (2600 rpm, 56 N-m) representative of highway driving at approximately 100 km/h. The raw engine exhaust was diluted by a Dekati Fine Particle Sampler (FPS-4000), which supplied the IOGAPS. Briefly, the IOGAPS is composed of a 2.5 μm cyclone (URG, Chapel Hill, NC, USA), a 60 cm eight-channel XAD-4-coated denuder, and a multistage filter pack containing XAD-4-coated quartz filters known as sorbent-impregnated filters (SIFs). The XAD-4 resin powder was finely ground in a Tema mill using tungsten carbide rings for 6 min, and the ground XAD-4 was cleaned using a mixture of dichloromethane: hexane: methanol (1:1:1) in an ultrasonic bath. Subsequently, the XAD was separated from the solvent by ultracentrifugation at 3200 rpm for 5 min, and dried in an oven (100°C) overnight. Once dry, the XAD was stored in a clean, airtight bottle in a dry place. Pre-fired 47 mm quartz filters (Pall Corporation) and the eight-channel denuder were weighed before coating with XAD-4. Filters were immersed in a slurry of XAD-4, acetone and hexane (Caledon, pesticide grade) for 30 s and then dried under a gentle stream of nitrogen. This coating procedure was repeated three times. Dried SIFs were then weighed to determine XAD-4 loading and stored in pre-fired, acetone washed aluminum foil at −4 °C. SIFs were loaded in the IOGAPS for sample collection and a selection of filters were analyzed as laboratory blanks. Prior to coating the denuder, the glass apparatus was washed with acetone, followed by hexane. The XAD-4 slurry was then applied to the denuder's annuli. Once excess slurry was removed, the denuder was dried under a low flow of nitrogen. This coating procedure was repeated a total of three times.

Before extraction, each filter sample was spiked with an isotopically labeled internal standard mixture, and the samples were then extracted using 15mL of dichloromethane under mild sonication at 25 °C using an ultrasonic bath. The extracts were then filtered through pre-cleaned glass wool and sodium sulphate columns and the samples were then concentrated to 50 µL under a gentle stream of oxygen-free nitrogen. Analysis was undertaken by direct injection of the sample into the GC–MS system (Agilent GC-6890 N plus MSD-5973 N) fitted with a HP-5MS (30 m, 0.25 mm diameter, 0.25 µm thickness) column. All analytes were quantified in the single ion monitoring mode covering specific masses ranging from 122 to 302 amu. The sample was injected using an Agilent 7683 auto-liquid sampler (1 µL), in a splitless and non-pulsed injection mode at 300 °C. The initial temperature was held at 70 °C for 2min and then ramped at 4 °C/min to a final temperature of 300 °C held for 10 min. The carrier gas was helium flowing at a constant rate of 1 mL/min. The analysis time per sample was 59.5 min. Five-point calibration graphs were prepared using pure natural compound standards in the concentration range of 20–1000 pg/µL for each PAH congener, and the samples were quantified using the concentration ratio of the analyte to the internal standard against corresponding peak area ratios.

Table 141: PAH emission factors (µg/kg fuel)

PAHs	**Denuded Quartz Filter**		**Highway Cruise**	
	Cold Start	**Highway Cruise**	**Quartz Filter**	**Denuded Quartz Filter**
Acenaphthylene	203.658	16.592	6.637	17.412
Acenaphthene	29.594	2.298	2.411	2.411
Fluorene	98.802	9.762	7.309	10.750

Phenanthrene	55.393	7.670	45.676	8.049
Anthracene	29.594	4.098	25.608	4.098
Fluoranthene	194.070	5.743	89.718	5.743
pyrene	194.070	8.864	119.821	8.864
Benzo(a)anthracene	314.327	29.594	50.300	29.594
Chrysene	285.429	21.116	32.590	21.116
Benzo(b)fluoranthene	299.530	21.116	19.174	21.116
Benzo(k)fluoranthene	246.985	15.811	13.681	16.592
Benzo(a)pyrene	381.199	21.116	19.174	21.116
Indeno(123-cd)pyrene	299.530	16.592	16.592	15.811
Dibenzo(ah)anthracene	45.676	2.655	2.411	2.655
Benzo(ghi)perylene	314.327	19.174	22.159	19.174

Table 142: Combined Denuder+Quartz+SIF PAH concentrations measured in engine-out exhaust

PAHs	**Highway Cruise (µg/kg fuel)**
Acenaphthylene	1575.319
Acenaphthene	415.357
Fluorene	833.782
Phenanthrene	784.760
Anthracene	1095.150
Fluoranthene	316.228
pyrene	9.702
Benzo(a)anthracene	59.747
Chrysene	37.927
Benzo(b)fluoranthene	24.076
Benzo(k)fluoranthene	20.074
Benzo(a)pyrene	29.764
Indeno(123-cd)pyrene	17.252
Dibenzo(ah)anthracene	2.718
Benzo(ghi)perylene	25.580

Table 143: Fraction of total PAH extracted from the denuder, the denuded quartz filters, and the SIFs for highway cruise and cold start operation.

	Highway Cruise			**Cold Start**		
PAHs	**Denude**	**Quartz**	**SIF**	**Denude**	**Quartz**	**SIF**
Acenaphthylene	95.5%	3.2%	1.3%	98.5%	1.0%	0.5%
Acenaphthene	95.8%	2.6%	1.6%	98.9%	0.6%	0.5%
Fluorene	95.8%	2.4%	1.8%	98.4%	1.3%	0.3%
Phenanthrene	99.2%	0.5%	0.3%	98.2%	1.1%	0.6%
Anthracene	97.9%	1.0%	1.1%	99.4%	0.6%	0.0%
Fluoranthene	83.0%	16.3%	0.6%	98.1%	1.6%	0.3%
pyrene	76.4%	21.7%	1.9%	-5.7%	0.0%	0.0%
Benzo(a)anthracene	23.3%	76.1%	0.6%	49.0%	50.2%	0.8%
Chrysene	23.1%	76.2%	0.6%	43.4%	55.5%	1.1%
Benzo(b)fluoranthene	6.1%	93.2%	0.6%	12.5%	85.8%	1.8%
Benzo(k)fluoranthene	2.8%	96.8%	0.5%	18.6%	80.3%	1.1%
Benzo(a)pyrene	8.7%	90.1%	1.1%	26.5%	71.5%	1.9%
Indeno(123-cd)pyrene	11.0%	88.2%	0.8%	8.1%	90.1%	1.8%
Dibenzo(ah)anthracene	11.8%	46.1%	42.1%	-2.8%	0.0%	0.0%
Benzo(ghi)perylene	11.7%	87.7%	0.6%	22.5%	76.1%	1.5%

Lin et al. (2019) [Characterization and quantification of PM2.5 emissions and PAHs concentration in PM2.5 from the exhausts of diesel vehicles with various accumulated mileages, Science of the Total Environment] investigated PAH emissions from the exhausts of diesel vehicles with various accumulated mileages.

Diesel vehicle exhausts were fixed from the tailpipe to a dilution tunnel full-flow, integrating a constant volume sampling (CVS) system. The diesel vehicle exhausts' samples from all the 15 tested vehicles were collected at a steady, measured flow rate, appropriate to the specific sampling system, for the period parallel to the period of each mode of the drive phase. The samples from the exhaust were collected from the ignition of the diesel vehicle engines in consistent with the US EPA method 21 to quantity PAHs. All PAHs were then captured in the cartridge and converted to equivalent hydrazone derivatives. Every cartridge is then eluted with acetonitrile. The eluted solutions are studied with a GC–MS/MS system (Gas Chromatography-Mass Spectrometry).

PAH samples of both the particulate-phase and gas-phase were collected by using a PAH sampling system at a temperature below 52 ° with the intention of avoiding desorption of PAH collected by cartridges. Particulate-phase PAHs were collected in glass-fiber filters. Prior sampling, the filters were placed in an oven at 450 °C for 8 h to burn off any organic compounds that might have been present. Lastly, the cleaned filters were stored in a desiccator for at least 8 h to achieve moisture equilibrium before being weighed. Gas-phase PAHs were collected in a three-stage glass cartridge containing a polyurethane foam (PUF) plug followed by XAD-16 resin. The glass cartridge was packed with 5.0 cm of XAD-16 resin sandwiched between a 2.5-cmupper PUF plug and a 2.5-cm bottom PUF plug. Silicone glue was used to seal and hold these two pieces of PUF to prevent resin from leaking out during the sampling and extraction processes. The new PUF/resin cartridge was cleaned up by Soxhlet extracting for one day each with distilled water, methanol, dichloromethane and finally n-hexane for a total of 4 days and then these PUF/resin cartridges were placed in a vacuum oven at 60 °C for 2 h to dry and to evaporate the residual solvent in them.

Samples were separated in a Soxhlet extractor with a blended dissolvable (n-hexane and dichloromethane 1:1 (v/v), 750mL each) for 24 h. These concentrates were awhile later concentrated, cleansed (utilizing a silica segment loaded with silica gel particles (size range = 0.04–0.063 mm) placed under a layer of anhydrous Na2SO4 (~1 cm high) and overhead more backup of glass fiber), and reconcentrated by cleansing with ultra-unadulterated nitrogen to precisely 1.0 mL for GC–MS investigation.

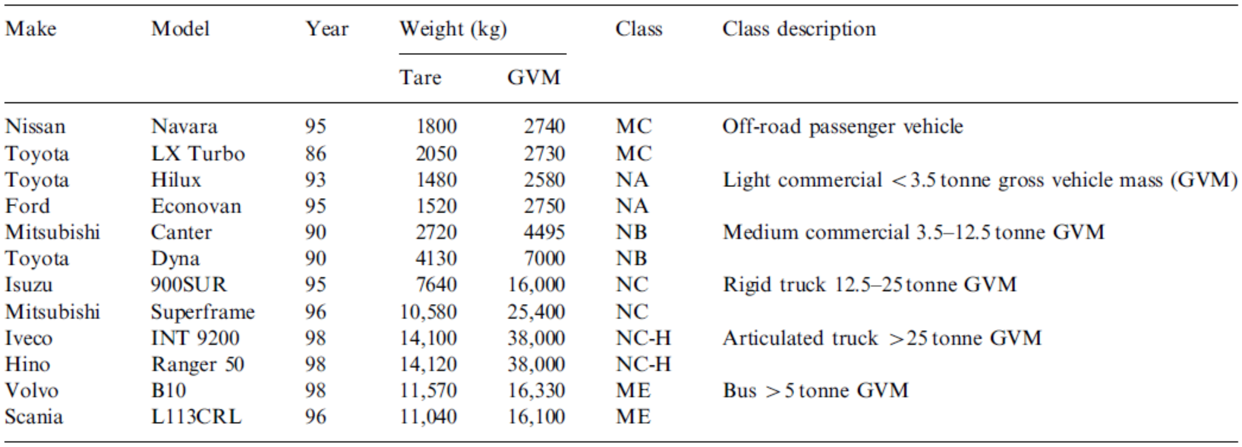
Table 144: PAH emission factors of PM2.5 particles in the exhaust of diesel engine (ng/L-fuel)

Compounds	Diesel engine (n = 15)	
	Mean	SD
Naphthalene	315	15.8
Acenaphthylene	15	5.74
Acenaphthene	14	7.78
Fluorene	50.8	39.8
Phenanthrene	263	16.6
Anthracene	54.5	53
Fluoranthene	249	19
pyrene	518	27.7
Benzo(a)anthracene	7.45	5.74
Chrysene	10.1	6.24
Benzo(b)fluoranthene	8.01	4.99
Benzo(k)fluoranthene	9.12	8.07
Benzo(a)pyrene	3.24	2.66
Benzo(e)pyrene	4.02	4.19
Cyclopentane[c,d]pyrene	3.31	2.66
Dibenzo(ah)anthracene	2.44	2.34
Perylene	2.38	2.5
Indeno(123-cd)pyrene	3.21	3.11
benzo[b]chrycene	3.02	3.15
Benzo(ghi)perylene	2.01	2.38
Coronene	2.92	3.12

Table 145: Total PAH emission factors with model year and various mileages

Model Year	**Total PAH EF ng/km**
<1987	87.605
1992-1997	62.053
1998-2004	75.741
2005-2012	62.966
Mileage	**Total PAH EF ng/km**
10001-20000	64.457
20001-30000	71.455
30001-50000	68.140

Nelson et al. (2008) [Effects of vehicle type and fuel quality on real world toxic emissions from diesel vehicles, Atmospheric Environment] examined the PAH emissions from diesel exhaust using twelve vehicles. Vehicle details are shown below.



Make	Model	Year	Weight (kg)		Class	Class description
			Tare	GVM		
Nissan	Navara	95	1800	2740	MC	Off-road passenger vehicle
Toyota	LX Turbo	86	2050	2730	MC	
Toyota	Hilux	93	1480	2580	NA	Light commercial <3.5 tonne gross vehicle mass (GVM)
Ford	Econovan	95	1520	2750	NA	
Mitsubishi	Canter	90	2720	4495	NB	Medium commercial 3.5–12.5 tonne GVM
Toyota	Dyna	90	4130	7000	NB	
Isuzu	900SUR	95	7640	16,000	NC	Rigid truck 12.5–25 tonne GVM
Mitsubishi	Superframe	96	10,580	25,400	NC	
Iveco	INT 9200	98	14,100	38,000	NC-H	Articulated truck >25 tonne GVM
Hino	Ranger 50	98	14,120	38,000	NC-H	
Volvo	B10	98	11,570	16,330	ME	Bus >5 tonne GVM
Scania	L113CRL	96	11,040	16,100	ME	

Vehicles were driven according to a composite urban emission drive cycle (CUEDC), specific to each class of vehicle, and which comprised four separate modes designed to simulate a range of traffic conditions. The modes were congested traffic, minor roads, arterial roads and freeway operation.

Vehicle exhaust was directed from the tailpipe to a full-flow dilution tunnel, incorporating a constant volume sampling (CVS) system. The exhaust sample was collected at a constant, controlled flow rate, applicable to the particular sampling system, for the time period corresponding to the duration of each mode of the drive cycle. In this way, a time-averaged emissions rate (g km^{-1}) for each mode of the cycle was obtained.

PAH compounds were collected onto resin-backed filter cartridges (Supelco Inc.). The cartridges and filters used were cleaned by solvent extraction. Analysis of a field blank was performed with each vehicle tested to check for cartridge background and/or environmental contamination and the sample results were corrected for any analyte background obtained. The glass cartridges were packed with a bed of cleaned Amberlite XAD-2™ resin, to capture vapor phase PAH components, and a glass fibre filter preceded the resin to collect components associated with the PM. The diluted exhaust was sampled from the manifold with a small diaphragm pump and passed through the cartridge at a constant flow rate of around 10 L min^{-1}. The flow rate was controlled using a needle valve and calibrated rotameter installed downstream of the pump. On completion of the test, the samples were protected from light and refrigerated until analysis.

PAH compounds were analyzed using gas chromatography and mass spectrometry (GC/MS; HP 5890 Series II GC and a HP 5971A quadrupole mass spectrometer) for the determination of the 16 US EPA priority PAHs namely: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c*,*d*]pyrene, dibenzo[*a*,*h*]anthracene, benzo[*g*,*h*,*i*]perylene. The combined sample filter and resin were Soxhlet extracted, using dichloromethane, and the extract was concentrated to 5 mL volume using the Kuderna–Danish concentration technique. Prior to extraction, each sample was spiked with a standard mixture of five deuterated PAH compounds to determine the extraction efficiency of the method. The extract was introduced to a gas chromatograph using splitless injection onto a 5% phenylmethylsilicone column. Detection, using a quadrupole mass spectrometer, was in the selected ion monitoring (SIM) mode. The PAH compounds present in the sample were identified by comparing their retention times to those in external standards prepared from a certified 16 component PAH mixture (Supelco Inc.). They were quantified using ion peak areas entered into a linear regression equation obtained from a multi-point calibration curve.

Table 146: Emission rates of PAHs (µg/km) from two test vehicles. Results are for mode 2 (minor roads) of the CUEDC

Fuel	**Commercial base**		**Euro 2**		**Euro 3**		**Euro 4**		**WW Cat 3**		**CARB**	
Vehicle class	**NA**	**NC**	**NA**	**NC**	**NA**	**NC**	**NA**	**NC**	**NA**	**NC**	**NA**	**NC**
Emission rate (µg/km)												
Naphthalene	2000	4790	933	3240	814	5130	562	2720	890	2980	1540	3720
Acenaphthylene	38	278	32	162	24.5	208	15.7	103	33.3	68.4	21.1	78.1
Acenaphthene	13	154	8.2	56.8	4.3	110	2.8	35.7	9.2	17	3.2	26.8
Fluorene	34	247	16	106	8	159	5.2	51.6	24.3	25	6.9	33.4
Phenanthrene	120	167	95	59.6	57	71.8	33	110	117	63.4	58.4	34
Anthracene	6	7.5	4.3	2.3	2.5	1.2	1.5	6.3	5.6	3.4	3.4	1.2
Fluoranthene	18	20.2	12	8.5	10.3	9	5.6	8.1	8.7	7.1	9.1	7.1
Pyrene	17	43.1	12.7	17	10.1	16.8	5.6	13.8	10.8	13.3	10.9	11.9
Benz[a]anthracene	1.8	7.5	0.9	1.7	0.55	1.8	0.6	0.6	0.5	0.8	0.7	1.8
Chrysene	2.7	1.3	2.1	8.5	1.7	6.6	0.9	1.6	0.8	1.7	1.3	2.4
Benzo[b]fluoranthene	1.5	5.9	1.9	2.3	1.8	4.2	0.6	1.6	1	1.7	0.8	1.2
Benzo[k]fluoranthene	1.5	4.8	0.9	2.3	0.97	1.8	0.6	1.6	0.8	0.8	0.8	1.8
Benzo[a]pyrene	2.1	4.3	1.6	2.3	1.5	3	0.6	1.6	1	1.7	1.3	1.8
Indeno[1,2,3-c,d]pyrene		1.6	0.5	0.6	0.13	0.6	0.3		0.5	0	0.4	
Benzo[g,h,i]perylene	0.9	2.7	1	2.3	1.4	1.8	0.6	1.3	1	1.7	0.8	0.6

Borras et al. (2009) [Polycyclic aromatic hydrocarbon exhaust emissions from different reformulated diesel fuels and engine operating conditions, Atmospheric Environment] characterized the PAH exhaust emissions from modified fuels using light-duty diesel vehicles. Two different models of light-duty diesel engines were selected. The diesel engine supplied by Renault (Boulogne-Billancourt Cedex, France), model DTI 19.l, was used to collect the exhaust particulate matter from the synthesized diesel fuels – different types of reformulated diesel fuels with different percentages of aromatic hydrocarbons. The diesel engine was mounted on a home-made test bed and placed in a test cell. The other diesel engine – the Ford model – a light-duty diesel engine model A 90PS Stage 3, Delphi Fuel System, Fixed Geometry Turbo Transit Connect, supplied by the Ford Motor Company (Dearborn MI, USA), was employed to check the differences in exhaust emissions according to the engine operation conditions. The Ford diesel engine was installed in an engine test bed (braking dynamometer), model MP 100 S built by Weinlich Steuerungen (Reilingen, Germany).

Three synthesized fuels with 5%, 15% or 25% aromatic content and a biodiesel (rape oil methyl ester) were used. Diesel particulates were collected from the exhaust emission of the Renault diesel engine. Engine conditions during particle collection were in the following range: speed 2000 rpm, 3 bar break mean effective pressure, fuel temperature 26–30 °C, specific fuel consumption 0.8–0.9 g s^{-1}, air mass 71.5–86 kg h^{-1}, load at 25% and torque 44–51 Nm. For each diesel fuel, the particles generated were sampled by a particle collection system composed of a home-made cyclone and a filter holder. The cut size of the cyclone was 10 μm. The cyclone eliminated artifacts by extracting large particles from the flow before they passed through the glass fiber filter that was used to collect the particles. The selected probe sampling conditions were a dilution ratio of 3.3, cooling at 22 °C with filtered air to avoid condensation processes and 180 s of sampling time.

To study the effect of different engine operating conditions on the exhaust composition, a Ford light-duty diesel engine was used. Several engine cycles, such as cold start, idling, accelerating and steady-state conditions, were evaluated as they were considered the four stages in diesel vehicle activity. Cold start at 298 ± 5 K was defined as starting-up the engine without a warm-up period and turning it off few seconds later. During idling, the engine speed parameter was around 900 ± 10 rpm, with no load, and engine water, air and oil temperatures stable. Accelerating consisted of increasing the speed from 2000 rpm to 2500 rpm from 2 to 9 times and then immediately returning to 2000 rpm. Finally, an engine was considered to be in steady-state conditions when the speed parameter was 2000 rpm, and the load was constant during the whole test.

The particles were collected directly on glass microfiber binder free filter GF/A (47 mm diameter, Whatman, Brentford, England) from the hot part of the exhaust pipe (see filter holder in Fig. 1), using a constant volume sampler. The air dilution ratio employed was 17.8. The filters were pre-baked at 450 °C for 12 h prior to sampling to avoid organic artifacts. These kinds of filters were selected to permit high volume sampling and they are tolerant to high temperatures for PAH sampling.

The particles were extracted ultrasonically in 15 mL of CH2Cl2 in two 15-minute cycles. For particles from the Ford engine at different engine cycles, PAH compounds were extracted from microfiber filters ultrasonically with two cycles of 15 mL of CH2Cl2 for 15 min.

Both kinds of particulate samples were analyzed by triplicate to study their PAH composition. The extracts were concentrated using the rotavapor and dissolved in 1 mL of CH2Cl2. Open-column chromatography (silica gel C60) was employed to fractionate the compounds. The column was eluted with CH2Cl2 and five aliquots of 1.4 mL were collected at 0.9 mL min−1 flow rate. A fraction collector model CF-1 supplied by Spectra/Chrom (Houston, TX, USA) was used. Each aliquot was dried under a gentle stream of N2. Extracts were dissolved in 150 μL of cyclohexane. One microliter of this solution was injected into the GC–MS system.

A 5890 SERIES II Plus gas chromatograph coupled to a HP 5989 mass spectrometer, supplied by Hewlett-Packard Co. (Wilmington, DE, USA), was used. All analyses were conducted on a HP-5MS column of 30 m × 0.25 mm I.D × 0.25 μm film thickness (Crosslinked 5% Ph Me Siloxane) supplied by J & W Scientific (Albany, NY, USA).

The gas chromatograph was held at 90 °C for 1 min, ramped at a rate of 10 °C min−1–120 °C, 4 °C min−1–280 °C and then held at 280 °C for 10 min. Total chromatogram run time was 54 min. The injection port was held at 280 °C and the transfer line from the GC to MS was held at 300 °C. Samples were injected in splitless injection mode (t = 0.75 min) using helium as the carrier gas, with a total flow of 50 mL min−1 and an on-column flow of 1 mL min−1.

Electron impact ionization (EI) at 70 eV was used in the analysis. For the qualitative analysis, we used the full-scan mode (SCAN), with the detector recording an m/z range of 50–650. For the quantitative analysis, we used the selected ion monitoring (SIM) mode. The ion source temperature was 200 °C and the quadrupole temperature was 100 °C. Other MS conditions were 2268 V for the electron multiplier and 5 min for the solvent delay.

To quantify the PAH content, a certified standard mixture of 10 ng μL^{-1} in cyclohexane PAH-Mix 9 – Reference Material ref. 20950900CY (16 EPA PAH compounds) was used. The mixture composition was: low molecular weight (LMW): naphthalene (NaP), acenaphthylene (AcPy), acenaphthene (AcP), fluorene (Flu), phenanthrene (PA), anthracene (Ant); medium molecular weight (MMW): fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (CHR); and high molecular weight (HMW): benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indene[1,2,3-c,d]pyrene (IND), benzo[g,h,i]perylene (BghiP), dibenzo[a,h]anthracene (DBA).

Table 147: Total PAH emissions in g/mg in four diesel exhaust particle emissions from Renault engine at steady-state condition

Priority compound	**Diesel 5%**	**Diesel 15%**	**Diesel 25%**	**Biodiesel**
Naphthalene	–	–	–	–
Acenaphthylene	0.183 ± 0.009	0.25 ± 0.03	0.21 ± 0.03	0.11 ± 0.02
Acenaphthene	0.81 ± 0.14	0.73 ± 0.03	0.4 ± 0.01	0.46 ± 0.05
Fluorene	0.46 ± 0.04	0.27 ± 0.03	0.26 ± 0.07	0.10 ± 0.01
Phenanthrene	1.4 ± 0.3	1.11 ± 0.09	2.3 ± 0.3	0.40 ± 0.02
Anthracene	0.12 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.03
Fluoranthene	0.2 ± 0.07	0.24 ± 0.01	0.14 ± 0.03	0.020 ± 0.003
Pyrene	0.23 ± 0.11	0.9 ± 0.3	0.15 ± 0.05	0.18 ± 0.10
Benzo[a]anthracene	0.12 ± 0.07	0.24 ± 0.05	n.d	0.018 ± 0.008
Chrysene	n.d	n.d	n.d	0.010 ± 0.007
Benzo[b]fluoranthene	n.d	n.d	n.d	0.032 ± 0.006
Benzo[k]fluoranthene	n.d	n.d	n.d	0.018 ± 0.004
Benzo[a]pyrene	0.13 ± 0.10	0.23 ± 0.04	n.d	0.04 ± 0.01
Indene[l,2,3-cd]pyrene	n.d	n.d	n.d	0.039 ± 0.007
Benzo[g,h,i]perylene	0.37 ± 0.05	n.d	0.24 ± 0.06	0.07 ± 0.01
Dibenzo[a,h]anthracene	0.30 ± 0.05	n.d	n.d	0.05 ± 0.01
Methylnaphthalene isomer 1-2	–	–	–	–
Dimethylnaphthalene isomer 1-7	–	–	–	–
Trimethylnaphthalene isomer 1-2	–	–	–	–
Methylfluorene isomer 1	0.14 ± 0.06	0.15 ± 0.02	0.2 ± 0.1	0.09 ± 0.02
Methylfluorene isomer 2	0.8 ± 0.2	0.13 ± 0.07	0.04 ± 0.01	0.06 ± 0.04
Methylphenanthrene isomer 1/Methylanthracene isomer 1	0.20 ± 0.08	0.18 ± 0.01	0.16 ± 0.05	0.3 ± 0.2
Methylphenanthrene isomer 2/Methylanthracene isomer 2	n.d	n.d	n.d	0.12 ± 0.6
Methylphenanthrene isomer 3/Methylanthracene isomer 3	0.5 ± 0.2	0.27 ± 0.13	0.5 ± 0.2	0.3 ± 0.1
Methylphenanthrene isomer 4/Methylanthracene isomer 4	n.d	0.07 ± 0.02	n.d	0.3 ± 0.1
Methylphenanthrene isomer 5/Methylanthracene isomer 5	0.18 ± 0.06	0.07 ± 0.03	0.11 ± 0.02	0.3 ± 0.2
Methylphenanthrene isomer 6/Methylanthracene isomer 6	0.23 ± 0.09	0.38 ± 0.04	0.20 ± 0.07	0.17 ± 0.12

Methylphenanthrene isomer 7/Methylanthracene isomer 7	1.2 ± 0.5	0.25 ± 0.08	n.d	0.047 ± 0.002
Dimethylphenanthrene isomer 1/Dimethylanthracene isomer 1	0.08 ± 0.03	0.06 ± 0.02	0.03 ± 0.01	0.03 ± 0.01
Dimethylphenanthrene isomer 2/Dimethylanthracene isomer 2	1.3 ± 0.7	1.11 ± 0.15	1.4 ± 0.6	6 ± 1
Dimethylphenanthrene isomer 3/Dimethylanthracene isomer 3	0.03 ± 0.01	n.d	n.d	0.05 ± 0.02
Dimethylphenanthrene isomer 4/Dimethylanthracene isomer 4	0.9 ± 0.3	0.24 ± 0.05	0.036 ± 0.007	0.07 ± 0.02
Dimethylphenanthrene isomer 5/Dimethylanthracene isomer 5	0.6 ± 0.2	0.17 ± 0.03	0.032 ± 0.006	0.046 ± 0.008
Dimethylphenanthrene isomer 6/Dimethylanthracene isomer 6	0.06 ± 0.02	0.024 ± 0.005	0.010 ± 0.002	0.017 ± 0.012
Benzoanthracene isomer 1	0.6 ± 0.2	0.17 ± 0.03	0.031 ± 0.006	0.047 ± 0.008
Benzopyrene isomer 1/Benzofluoranthene isomer 1	0.06 ± 0.02	0.024 ± 0.005	0.010 ± 0.002	0.017 ± 0.011
Benzopyrene isomer 2/Benzofluoranthene isomer 2	n.d	n.d	n.d	n.d

Table 148: Concentrations in ng PAH mg-1 during cold start (II.1–II.2) – idling engine cycles (II.3–II.8) from a Ford engine exhaust.

	II.1	II.2	II.3	II.4	II.5	II.6	II.7	II.8
Priority compounds								
Naphthalene	–	–	–	–	–	–	–	–
Acenaphthylene	n.d	n.d	0.21 ± 0.04	0.6 ± 0.1	0.32 ± 0.06	n.d	0.42 ± 0.08	0.28 ± 0.05
Acenaphthene	0.05 ± 0.01	n.d	0.24 ± 0.05	0.30 ± 0.06	1.1 ± 0.2	0.32 ± 0.06	0.48 ± 0.09	n.d
Fluorene	n.d	n.d	0.30 ± 0.06	0.35 ± 0.07	0.9 ± 0.2	0.5 ± 0.1	0.38 ± 0.07	n.d
Phenanthrene	3.5 ± 0.7	9 ± 2	27 ± 5	17 ± 3	10 ± 2	6 ± 1	7 ± 1	n.d
Anthracene	0.24 ± 0.05	n.d	1.3 ± 0.3	2.5 ± 0.5	n.d	n.d	0.9 ± 0.2	n.d
Fluoranthene	5 ± 1	13 ± 2	19 ± 4	18 ± 3	8 ± 2	15 ± 3	9 ± 1	6 ± 1
Pyrene	9 ± 2	17 ± 3	40 ± 8	36 ± 7	36 ± 7	28 ± 6	19 ± 4	11 ± 2
Benzo[a]anthracene	6 ± 1	3.1 ± 0.6	2.4 ± 0.5	7 ± 1	n.d	12 ± 2	13 ± 3	n.d
Chrysene	50 ± 10	22 ± 4	10 ± 2	16 ± 3	14 ± 3	31 ± 6	29 ± 6	6 ± 1
Benzo[b]fluoranthene	1.1 ± 0.2	n.d	n.d	6 ± 2	n.d	n.d	37 ± 7	n.d
Benzo[k]fluoranthene	69 ± 14	60 ± 12	13 ± 3	70 ± 8	55 ± 11	28 ± 6	118 ± 23	30 ± 6

Benzo[a]pyrene	148 ± 29	11 ± 2	n.d	0.04 ± 0.01	77 ± 15	14 ± 3	25 ± 5	n.d
Indene[l,2,3-cd]pyrene	15 ± 3	n.d	n.d	n.d	n.d	14 ± 3	n.d	n.d
Benzo[g,h,i]perylene	23 ± 5	n.d	n.d	12 ± 2	17 ± 3	14 ± 3	8 ± 1	n.d
Dibenzo[a,h]anthracene	57 ± 6	8 ± 1	n.d	31 ± 6	33 ± 6	36 ± 7	12 ± 2	n.d

Table 149: Priority PAH concentrations (ng PAH mg-1) in accelerating-steady-state engine regimes from a Ford engine exhaust.

Priority PAH	Max		Q3		Median		Q1		Min	
	acceleration cycles	steady state	acceleration cycles	steady state	acceleration cycles	steady state	acceleration cycles	steady state	acceleration cycles	steady state
Naphthalene	3.893	5.787	2.710	4.982	1.195	2.639	0.840	0.840	0.840	0.556
Acenaphthylene	4.059	3.846	3.089	3.538	2.379	3.207	1.183	2.331	0.201	1.148
Acenaphthene	1.527	2.426	0.935	1.787	0.272	1.124	0.154	0.982	0.095	0.817
Fluorene	0.462	1.574	0.343	1.574	0.272	0.864	0.201	0.769	0.154	0.651
Phenanthrene	1.444	11.917	0.888	8.982	0.331	4.367	0.320	2.237	0.249	1.669
Anthracene	0.675	7.207	0.367	5.006	0.249	4.556	0.201	2.828	0.107	1.148
Fluoranthene	0.805	11.633	0.698	8.272	0.438	3.751	0.249	2.260	0.201	2.000
Pyrene	0.840	7.444	0.556	5.527	0.272	4.462	0.178	3.254	0.178	1.527
Benzo[a]anthracene	16.300	24.340	14.807	23.536	12.510	21.698	9.869	20.205	7.112	19.171
Chrysene	18.712	16.760	11.936	14.578	9.869	11.017	4.815	6.998	2.518	-0.008
Benzo[b]fluoranthene	7.457	4.471	5.964	3.208	3.322	1.600	1.944	0.911	1.255	0.451
Benzo[k]fluoranthene	5.734	2.404	3.322	2.404	2.289	1.829	1.600	-0.008	0.336	-0.008
Benzo[a]pyrene	45.070	10.443	34.561	6.653	21.468	2.978	17.793	2.059	15.554	1.140

Indene[l,2,3-cd]pyrene	37.662	7.457	25.144	4.586	11.132	2.174	8.261	-0.008	4.701	-0.008
Benzo[g,h,i]perylene	21.813	11.936	16.530	6.998	10.098	1.485	7.572	0.681	5.275	0.681
Dibenzo[a,h]anthracene	6.596	2.059	5.964	1.715	5.734	0.681	4.356	-0.008	3.897	-0.008

Vouitsis et al. (2009) [An investigation on the physical, chemical and ecotoxicological characteristics of particulate matter emitted from light-duty vehicles, Environmental Pollution] examined the PAH emissions from two Euro 4 vehicles.

The diesel car (Honda Accord 2.2i-CTDi) was equipped with high-pressure -rail fuel injection, an oxidation pre-catalyst and a two-stage oxidation underfloor catalyst with $DeNO_x$ characteristics (the so-called “4-way catalyst”). This vehicle was first tested in this original exhaust aftertreatment (Diesel OEA) configuration. The same vehicle was also tested by replacing the underfloor catalyst with a silicon-carbide catalyzed diesel particle filter (CDPF). The gasoline vehicle (Ford Mondeo 1.8) was equipped with electronic fuel injection and a closed-loop three-way catalyst.

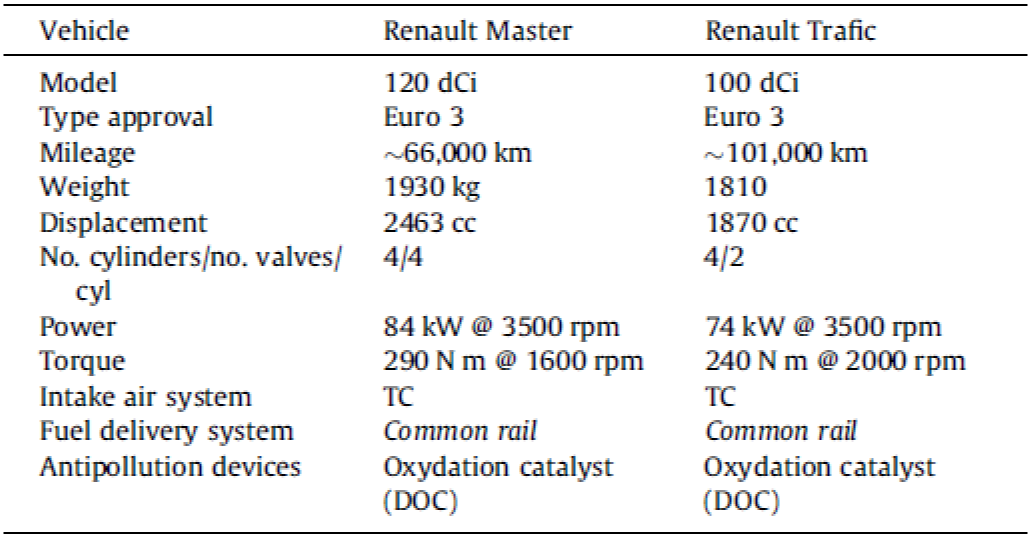
The vehicles were tested on a transient vehicle dynamometer, simulating drag, inertia and rolling resistances, as specified by EU Directive 98/69/EC. The exhaust was primarily diluted and conditioned by means of Constant Volume Sampling (CVS). A 6 m long corrugated stainless steel tube transferred the exhaust from the tailpipe to the CVS tunnel inlet. The tube was insulated to minimize heat losses and particle thermophoresis and was clamped onto the vehicle exhaust pipe with a metal-to-metal connection to avoid exposing the hot exhaust gas to any synthetic material connectors. A flowrate of 500 Nm^3/h was maintained in the CVS tunnel by a positive displacement pump. The dilution air was filtered through a HEPA class H13/EN1822 filter at the inlet of the dilution tunnel.

Each measurement day started with a New European Driving Cycle (NEDC) which was followed by three real-time driving cycles, developed in the framework of the European “Artemis” Project. PM was collected on 47 mm PTFE-coated fibre filters (Pallflex TX40H120-WW) after 24 h conditioning of the filters in controlled temperature and humidity. PAHs were determined by high-pressure liquid chromatography with programmable fluorescence detection (HPLC/FD). The system was calibrated with the 16 PAH NIST 1647a standard mixture.

Table 150: Average PAH emission rates (mg/km)

PAH	**NEDC**			**Urban**			**Road**			**Motorway**		
	Diesel OEA	**CDPF**	**Gasol.**	**Diesel OEA**	**CDPF**	**Gasol.**	**Diesel OEA**	**CDPF**	**Gasol.**	**Diesel OEA**	**CDPF**	**Gasol.**
Naphthalene	23.9 ± 0.6	ND	0.4	4.5 ± 0.07	ND	ND	2.3 ± 0.6	ND		4.7 ± 0.7	0.6 ± 0.2	1.0 ± 0.6
Acenaphthene	8.5	1.9 ± 0.3	0.8	8.2	4.2 ± 0.4	3.8 ± 0.001	1.2 ± 0.1	2	1.2 ± 0.2	1.0 ± 0.2	0.8 ± 0.3	0.8 ± 0.1
Fluoranthene	6	ND	ND	ND	ND	ND	0.9 ± 0.2	ND		0.59 ± 0.1	0.3	0.3
Phenanthrene	8.4 ± 2.9	0.4 ± 0.04	0.3	3.7	2.6 ± 1.4	0.8 ± 0.001	1 ± 0.3	0.45 ± 0.1	0.4 ± 0.1	0.9 ± 0.2	0.2 ± 0.03	0.9 ± 0.8
Anthracene	0.1 ± 0.03	ND	ND	0.2 ± 0.005	ND	ND	0.02	ND	0.04 ± 0.03	0.1 ± 0.10	ND	0.04 ± 0.04
Fluorene	0.29	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.17
Pyrene	0.8 ± 0.8	ND	0.3	ND	ND	ND	ND	ND	ND	ND	0.04	0.7 ± 0.5
TBP[a]	2.8 ± 1.5	ND	0.3	0.8	0.9 ± 0.4	0.7 ± 0.2	ND	0.4 ± 0.1	ND	0.14	ND	0.3 ± 0.1
Benz[a]anthracene	0.7 ± 0.3	ND	ND	1.8	ND	0.2 ± 0.06	ND	0.1 ± 0.01	ND	ND	ND	0.1 ± 0.04
Chrysene	0.2 ± 0.1	ND	ND	ND	ND	0.1	ND	0.04 ± 0.01	ND	0.02 ± 0.01	ND	0.1 ± 0.08
Benzo[e]pyrene	1.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.6
Benzo[b]fluoranthene	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1 ± 0.1
Benzo[k]fluoranthene		ND	ND	ND	ND	ND	ND	ND	0.02	ND	ND	0.04 ± 0.04
Benzo[a]pyrene		ND	ND	ND	ND	ND	ND	ND	0.02	ND	0.01	0.06
dibenzo[a,h]anthracene		ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01	0.06
Benzo[ghi]perylene		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.2

Macor et al. (2011) [Effects of 30% v/v biodiesel/diesel fuel blend on regulated and unregulated pollutant emissions from diesel engines, Applied Energy] examined the PAH emissions from two Euro 3 vehicles fueled with a 30% v/v biodiesel/diesel fuel blend (B30) and pure diesel fuel. The main characteristics of the vehicles are shown below.



Vehicle	Renault Master	Renault Trafic
Model	120 dCi	100 dCi
Type approval	Euro 3	Euro 3
Mileage	~66,000 km	~101,000 km
Weight	1930 kg	1810
Displacement	2463 cc	1870 cc
No. cylinders/no. valves/cyl	4/4	4/2
Power	84 kW @ 3500 rpm	74 kW @ 3500 rpm
Torque	290 N m @ 1600 rpm	240 N m @ 2000 rpm
Intake air system	TC	TC
Fuel delivery system	*Common rail*	*Common rail*
Antipollution devices	Oxydation catalyst (DOC)	Oxydation catalyst (DOC)

The vehicles were tested on a chassis dynamometer using at first the diesel fuel, then the B30 blend; each test was repeated 4 times. Testing was performed on the European Urban Driving Cycle (UDC), the Extra Urban Driving Cycle (EUDC) and the Common Artemis Driving Cycles (CADC) Urban Cycle (URBAN). The PM was sampled by deriving part of the exhaust emissions by means of the CVS system from dilution tunnel, and collecting the particles on conditioned Pallflex T60A20 membranes.

The PAHs emission was obtained summing the light fractions (2–3 aromatic rings) contained in the gaseous phase with the heavy fraction (3–5 rings) contained in the soluble organic fraction (SOF) of the particulate. A quote of the exhausts was direct to the vials containing adsorbent resin XAD2 for trapping the chemical species in gaseous phase. The resin and the membranes were treated with toluene following ASE. (Soxhlet Warm) indications for 12 h at 7 cycle/h, in order to extract the polyaromatic species using solid phase extraction Silica columns (Restek 24038). The purification of the analytes was carried out by means of repeated washings with toluene and N-hexane leaving evaporate the solvent excess. Finally, the samples were analyzed by a gas chromatograph-mass spectrometer (GC–MS).

Table 151: Average values of PAH emissions (µg/km) of the Renault Master 120 dCI vehicle fueled with both fuels

PAH (µg/km)	UDC					EUDC					URBAN				
	Diesel fuel		B30 blend			Diesel fuel		B30 blend			Diesel fuel		B30 blend		
	Aver	VC (%)	Aver	VC (%)	D (%)	Aver	VC (%)	Aver	VC (%)	D (%)	Aver	VC (%)	Aver	VC (%)	D (%)
Test vehicle: Renault Master 120 dCI															
Phenanthrene	0.93	98.6	0.85	95.7	8.4	0.25	74.2	0.49	91.2	95.7	0.87	57.8	0.29	96.5	66.8
Anthracene	1.11	92.6	0.95	97.8	14.9	0.28	77.6	0.44	123.3	61.3	1.01	59	0.31	103.8	69.0
Fluoranthene	0.63	36.2	1.1	17.1	73.7	0.4	42.2	0.72	38.4	80.5	0.78	36.3	0.93	47.4	20
Pyrene	0.83	55	1.37	22	65.6	0.5	35.8	0.7	34.5	39.1	0.96	40.8	1.07	39.1	12.2
Benzo(a)anthracene	0.15	0	0.15	0	0	0.1	0	0.1	0	0	0.15	0	0.15	0	0
Chrysene	0.44	45.6	0.26	84.2	41.2	0.19	57.4	0.1	0	46.9	0.3	37	0.15	0	50.7
Benzo(b) + (k)fluoranthene	0.51	34.6	0.36	72.2	29.8	0.14	58.9	0.1	0	29.5	0.31	47.5	0.25	77.8	21.5
Benzo(a)pyrene	0.46	59	0.32	61.6	30.6	0.13	49.8	0.1	0	24.9	0.4	17.6	0.15	0	62.8
lndeno(1,2,3-cd)pyrene	0.38	54.9	0.43	81.6	14.2	0.1	0	0.1	0	0	0.22	61.6	0.15	0	30.8
Dibenzo(a,h)anthracene	0.15	0	0.15	0	0	0.1	0	0.1	0	0	0.15	0	0.15	0	0
Benzo(g,h,i)perylene	0.53	94.4	0.77	83	44.4	0.1	0	0.1	0	0	0.47	36.6	0.29	62.4	38.0

Table 152: Table 149: Average values of PAH emissions (µg/km) of the Renault Trafic 100 dCI vehicle fueled with both fuels

PAH (µg/km)	UDC					EUDC					URBAN				
	Diesel fuel		B30 blend			Diesel fuel		B30 blend			Diesel fuel		B30 blend		
	Aver	VC (%)	Aver	VC (%)	D (%)	Aver	VC (%)	Aver	VC (%)	D (%)	Aver	VC (%)	Aver	VC (%)	D (%)
Test vehicle: Renault Trafic 100 dCi															

Phenanthrene	0.45	133.3	0.61	87.1	35.3	0.28	129.5	0.55	77	93.6	0.15	0	0.48	93.3	223
Anthracene	0.5	140.2	0.76	71.7	50.7	0.31	135.1	0.63	78.4	104	0.15	0	0.51	97.2	237
Fluoranthene	0.75	94.1	1.14	21.2	52.7	0.36	97.2	0.6	37.3	66.5	0.62	54.4	1	31	62
Pyrene	1.2	79.8	1.38	10.3	14.8	0.35	94.1	0.69	39.4	99.9	0.84	30	1.19	33	42
Benzo(a)anthracene	0.29	98	0.15	0	49.0	0.1	0	0.1	0	0	0.15	0	0.15	0	0
Chrysene	0.5	140.2	0.15	0	70.1	0.1	0	0.1	0	0	0.19	37.9	0.15	0	18.9
Benzo(b) + (k)fluoranthene	0.32	106.3	0.34	64.7	6.4	0.1	0	0.1	0	0	0.22	64.4	0.24	75.4	8.8
Benzo(a)pyrene	0.42	129.3	0.34	64.2	20.6	0.1	0	0.1	0	0	0.2	52.3	0.2	53	0.5
lndeno(1,2,3-cd)pyrene	0.27	88.2	0.29	98	9.6	0.1	0	0.1	0	0	0.2	52.3	0.15	0	26.2
Dibenzo(a,h)anthracene	0.15	0	0.15	0	0	0.1	0	0.1	0	0	0.15	0	0.15	0	0
Benzo(g,h,i)perylene	0.45	47.5	0.46	51.4	3.3	0.1	0	0.1	0	0	0.24	74.7	0.2	53	14.7
Total	5.31	97.2	5.77	16.7	8.7	1.99	71.4	3.16	44	58.5	3.1	29.1	4.43	31	42.5

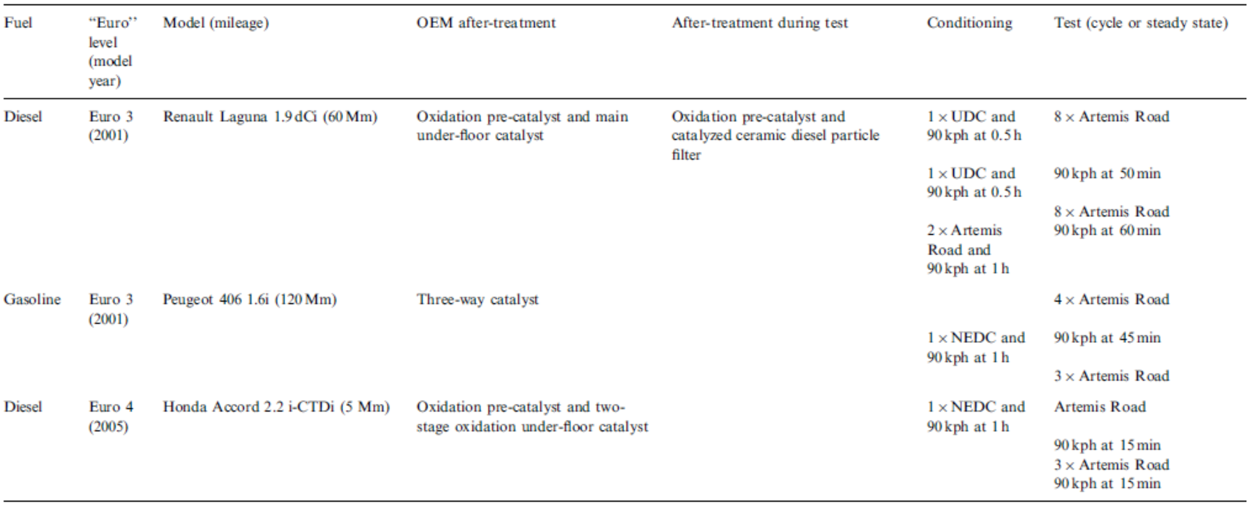
Zheng et al. (2018) [Measurement of particulate polycyclic aromatic hydrocarbon emissions from gasoline light-duty passenger vehicles, Journal of Cleaner Production] examined PM-PAH emissions from gasoline vehicles. The fleet of tested vehicles is in compliance with typical emission standards, and uses various engine technologies (e.g., port-fuel injection, PFI, vs. GDI). Five in-use gasoline LDGVs manufactured during 2007–2015 were tested. The tested vehicles were in compliance with emission standards from China 3 to China 5, representing a major part of in-use LDPVs in China according to emission certification level. All these vehicles were equipped with three-way catalytic converters (TWCs). Three vehicle samples (#1 to #3) used PFI engines, and the other two samples (# 4 and #5) were equipped with GDI engines. Two regulatory cycles were applied in this study. First, all the LDPVs were tested under the WLTC (version 5.3) over the chassis dynamometer. In addition, the NEDC cycle was also used.

First, 50 ng internal standards were added in each filter sample before extraction, and then a Soxhlet extractor was employed to extract PAH compounds with a hexane-dichloromethane mixture. The extracts were carefully concentrated at 30 °C under vacuum by rotary evaporation. After concentration, silica gel solid-phase extraction (SPE) cartridges (500 mg, 6 ml, Agilent Technologies) were employed to clean and fractionate the PAH compounds. The SPE cartridges were eluted three times with a hexane-dichloromethane mixture, and the eluate was concentrated and dried to 0.5 ml for following chemical analysis. PAHs were analyzed by a GC-MS (Agilent, Model 7890A/5975, U.S.) which was equipped with DB-5MS column. 50 ng of benzo [a]anthracene-d12 was added to the concentrates as accustandard, of which 1 μL was then injected into the GC-MS system.

Table 153: Distance-based PAH emissions (µg/km) from gasoline vehicles

ID	Driving cycle	Acenaphthene	Acenaphthylene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz[a]anthracene	Chrysene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	dibenzo[a,h]anthracene	Indene[l,2,3-cd]pyrene	Benzo[ghi]perylene
#1	WLTC	0.03	0.02	0.05	0.22	0.07	0.55	0.63	0.87	1.25	1.85	0.6	1.6	0.3	1.67	1.56
	NEDC	0.03	0.04	0.09	0.2	0.08	0.73	0.62	0.61	0.89	1.24	0.4	0.96	1.16	0.25	1.07
#2	WLTC P1	0.06	0.11	0.37	0.25	0.05	0.07	0.06	0.4	0.47	0.41	0.17	0.27	0.55	0.19	0.52
	WLTC P2	0.05	0.16	0.33	0.16	0.02	0.06	0.04	0.07	0.09	0.05	0.02	0.03	0.11	0.09	0.03
	WLTC P3	0	0.05	0.11	0.05	0.01	0.04	0.06	0.23	0.34	0.37	0.12	0.15	0.52	0.07	0.4
	WLTC	0.02	0.08	0.19	0.1	0.01	0.05	0.05	0.22	0.31	0.31	0.11	0.14	0.09	0.44	0.34
#3	WLTC P1	0.06	0.19	0.44	0.27	0.03	0.11	0.07	0.09	0.1	0.08	0.09	0.1	0.3	0.17	0.19
	WLTC P2	0.03	0.1	0.21	0.33	0.03	0.06	0.05	0.03	0.02	0.02	0.02	0.01	0.09	0.09	0.02
	WLTC P3	0.01	0.04	0.1	0.04	0	0.01	0.01	0.02	0.04	0.02	0.03	0.01	0.03	0.03	0.01
	WLTC	0.02	0.07	0.17	0.13	0.01	0.04	0.03	0.03	0.04	0.03	0.03	0.02	0.06	0.08	0.04
#4	WLTC P1	0.1	0.01	0.2	0.52	0.22	0.61	0.61	3.58	4.02	5.75	2.29	4.34	5.15	0.72	5.66
	WLTC P2	0.07	0.09	0.29	0.29	0.08	0.29	0.37	0.06	0.07	0.04	0.02	0.02	0.1	0.09	0.04
	WLTC P3	0.02	0.02	0.08	0.13	0.03	0.17	0.26	0.12	0.18	0.09	0.02	0.04	0.06	0.03	0.06
	WLTC	0.04	0.04	0.14	0.22	0.07	0.26	0.33	0.57	0.67	0.84	0.32	0.61	0.14	0.75	0.8
#5	WLTC	0.05	0.06	0.04	0.28	0.08	0.52	0.56	0.26	0.32	0.35	0.13	0.26	0.09	0.36	0.52
	NEDC	0.06	0	0.04	0.36	0.07	0.42	0.42	0.19	0.24	0.21	0.08	0.15	0.23	0.09	0.17

Geller et al. (2006) [Physicochemical and redox characteristics of particulate matter (PM) emitted from gasoline and diesel passenger cars, Atmospheric Environment] studied PAH emissions with respect to vehicle type and driving cycle. The vehicle sample set included three passenger cars. The first vehicle was a 1.9 l Euro 3 diesel (Renault Laguna 1.9 dCi) retrofitted with a catalyzed DPF (NGK SiC 300 cpsi), which replaced a main oxidation catalyst with which the vehicle was originally equipped. The catalyzed DPF was nearly new and aged 10, 000 km. The second vehicle tested was a Euro 3 port fuel injection spark ignition vehicle (Peugeot 406), and the last one was a new Euro 4 compliant diesel passenger car (Honda Accord 2.2 i-CTDi) equipped with a three-stage oxidation after treatment system. The characteristics of the different vehicles, including their model year and total mileage is shown below.



Fuel	"Euro" level (model year)	Model (mileage)	OEM after-treatment	After-treatment during test	Conditioning	Test (cycle or steady state)
Diesel	Euro 3 (2001)	Renault Laguna 1.9 dCi (60 Mm)	Oxidation pre-catalyst and main under-floor catalyst	Oxidation pre-catalyst and catalyzed ceramic diesel particle filter	1 × UDC and 90 kph at 0.5 h	8 × Artemis Road
					1 × UDC and 90 kph at 0.5 h	90 kph at 50 min
					2 × Artemis Road and 90 kph at 1 h	8 × Artemis Road 90 kph at 60 min
Gasoline	Euro 3 (2001)	Peugeot 406 1.6i (120 Mm)	Three-way catalyst			4 × Artemis Road
					1 × NEDC and 90 kph at 1 h	90 kph at 45 min
						3 × Artemis Road
Diesel	Euro 4 (2005)	Honda Accord 2.2 i-CTDi (5 Mm)	Oxidation pre-catalyst and two-stage oxidation under-floor catalyst		1 × NEDC and 90 kph at 1 h	Artemis Road
						90 kph at 15 min 3 × Artemis Road 90 kph at 15 min

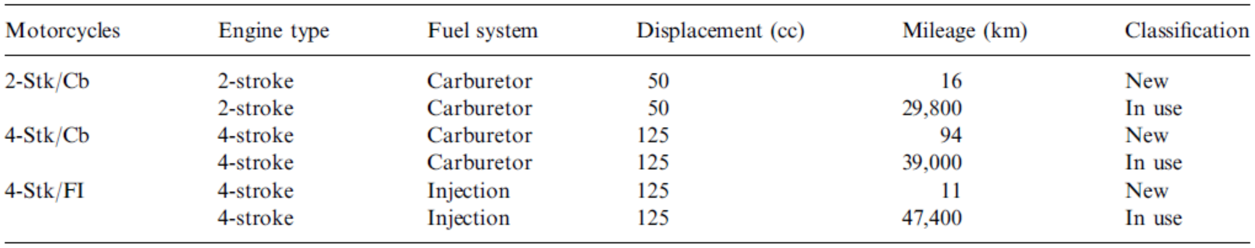
The vehicle exhaust was primarily diluted and conditioned according to the constant volume sampling (CVS) procedure. Exhaust was transported to the tunnel through an insulated 6 m long corrugated stainless steel tube, and it was introduced along the tunnel axis near an orifice plate, ensuring rapid mixing with the dilution air. A positive displacement pump controlled the nominal flow rate, 500 m3 h−1, of dilute exhaust gas through the tunnel. The vehicles were driven on a chassis dynamometer under both transient and steady-state operation. The cycles employed were the New European Driving Cycle (NEDC), the urban part of the NEDC (UDC) and the Artemis Road cycle. In addition, the vehicles were tested at a constant cruising speed of 90 km per hour (kph) under road load in order to sample under typical freeway cruising conditions. PAHs were quantified by HPLC with selective fluorescence detection.

Table 154: Emission rates (ng/km) for selected PAH emissions

Component, ng/km	Diesel transient	Diesel Steady-state	Gasoline	Gasoline Steady-state	Cat DPF transient	Cat DPF Steady-state
Naphthalene	217773	201	1575	1.9	1.771.4	ND
Phenanthrene	285788	61	39716	3.4	7.371.7	4.070.2
Anthracene	7.672.4	5.1	5.471.9	0.4	0.370.3	ND
Fluoranthene	1275.4	ND	43712	5.3	1271.7	5.873.2
Pyrene	161721	107	48712	5.4	2673.2	9.676.6
Benz(a)anthracene	5.070.8	1.2	2374.2	17	1375	6.471.0
Chrysene	6.170.4	1.7	3174.4	27.7	1774.3	1171.2
Benzo(b)fluoranthene	0.770.2	ND	6.770.5	1.2	7.075.4	1.870.8
Benzo(k)fluoranthene	ND	ND	1.670.4	0.5	ND	ND
Benzo(a)pyrene	ND	ND	4.270.4	0.3	0.270.2	ND
Benzo(g)perylene	ND	ND	7.772.9	0.3	ND	ND

Yang et al. (2005) [Polycyclic aromatic hydrocarbon emissions from motorcycles, Atmospheric Environment] examined PAH emissions from 2-stroke carburetor (2-Stk/Cb), 4-stroke carburetor

(4-Stk/Cb) and 4-stroke fuel injection (4-Stk/FI) motorcycles using a chassis dynamometer. Technical characteristics of the motorcycles are shown below.



Motorcycles	Engine type	Fuel system	Displacement (cc)	Mileage (km)	Classification
2-Stk/Cb	2-stroke	Carburetor	50	16	New
	2-stroke	Carburetor	50	29,800	In use
4-Stk/Cb	4-stroke	Carburetor	125	94	New
	4-stroke	Carburetor	125	39,000	In use
4-Stk/FI	4-stroke	Injection	125	11	New
	4-stroke	Injection	125	47,400	In use

The European driving cycle (ECE) is the type approval cycle used for automotive emission certification in Taiwan (CNS 11386). One complete test cycle (780 s) included the term of idle (240 s), acceleration (168 s), cruising (228 s) and deceleration (144 s), and four different cruising speeds (15, 32, 35 and 50 km h−1) are applied in the test (Tsai et al., 2003). Both cold-start and hot-start tests were performed in this study.

Particulate PAHs were collected by Pallflex filters at temperature approximately 25–30 °C. Two sets of filter holders were employed in this system. Back-up filters were used in each holder downstream the sampling filters to check the breakthrough effects. Two glass cartridges containing polyurethane foam (PUF) plug and XAD-16 resin were used to collect the gaseous PAHs. Before taking the samples, the filters were placed in an oven at 450 °C for 8 h to burn up any organic compounds that might be present in the filters.

PAH-containing sample was Soxhlet extracted with a mixed solvent (n-hexane and dichloromethane, 500 mL/L each) for 24 h. The extract was then concentrated by purging with ultra-pure nitrogen to 2 mL for the cleanup procedure and then reconcentrated to 0.5 mL with ultra-pure nitrogen.

The concentrations of the following PAHs were determined: naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), cyclopenta[c,d]pyrene (CYC), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (PER), indeno[1,2,3,-cd]pyrene (IND), dibenz[a,h]anthracene (DBA), benzo[b]chrysene (BbC), benzo[ghi]perylene (BghiP) and coronene (COR).

A gas chromatography (GC) (Agilent 6890) with a mass selective detector (MSD) (Agilent 5973N) and a computer workstation was used for the PAH analysis. This GC/MS was equipped with an Agilent capillary column (Agilent Ultra 2–50 m×0.32 mm×0.17 μm), an Agilent 7673A automatic sampler, injection volume 1 μL, splitless injection at 310 °C, ion source temperature at 310 °C, oven, from 50 °C to 100 °C at 20 °C min^{-1}, 100 °C–290 °C at 3 °C min^{-1}, hold at 290 °C for 40 min. The masses of primary and secondary ions of PAHs were determined by using the scan mode for pure PAH standards. Qualification of PAHs was performed by using the selected ion monitoring (SIM) mode.

Table 155: PAH emission factors for cold-start driving cycle test (mg/km)

PAHs	2-Stk/Cb		4-Stk/Cb		4-Stk/FI	
	In use	New	In use	New	In use	New
naphthalene	8130±1560	4170±1390	5930±1170	4360±1190	3340±704	1074±590
acenaphthylene	14.5±4.8	27.3±7.60	58.9±12.1	14.6±5.80	16.6±4.7	12.6±3.60
acenaphthene	1.75±1.28	2.40±0.28	2.84±0.92	4.97±2.48	3.17±1.07	2.59±1.06
Fluorene	52.4±21.4	6.43±1.93	7.38±1.91	14.0±5.32	21.1±5.60	9.97±2.60
Phenanthrene	49.4±14.0	6.60±2.21	4.47±1.23	9.59±3.06	7.68±2.53	7.94±2.59
Anthracene	10.2±3.20	2.86±1.03	1.30±0.49	3.60±1.28	2.11±1.22	1.85±0.47
Fluoranthene	8.44±3.70	2.44±1.05	0.95±0.23	1.72±1.00	1.34±0.37	1.68±0.26
Pyrene	6.17±2.22	2.90±0.89	0.65±0.17	1.46±0.76	0.97±0.23	1.36±0.49
cyclopenta[c,d]pyrene	5.99±1.87	7.49±2.92	0.12±0.053	0.50±0.14	0.19±0.012	0.46±0.19

benzo[a]anthracene	0.87±0.30	0.014±0.022	0.044±0.01	0.080±0.052	0.024±0.010	0.15±0.14
Chrysene	1.31±0.64	0.50±0.28	0.06±0.014	0.060±0.026	0.022±0.005	0.13±0.081
benzo[b]fluoranthene	1.42±0.19	0.44±0.13	0.17±0.10	0.076±0.014	0.174±0.044	0.51±0.17
benzo[k]fluoranthene	0.32±0.14	0.10±0.055	0.058±0.10	0.063±0.021	0.070±0.026	0.026±0.020
benzo[e]pyrene	4.13±1.94	2.29±1.07	0.105±0.095	0.42±0.15	0.258±0.087	0.57±0.084
benzo[a]pyrene	1.22±0.48	1.25±0.71	0.066±0.016	0.050±0.042	0.050±0.018	0.19±0.052
Perylene	1.10±0.43	0.53±0.24	0.093±0.017	0.14±0.041	0.15±0.018	0.098±0.042
indeno[1,2,3,-cd]pyrene	5.07±1.20	1.39±1.03	0.12±0.058	0.21±0.061	0.29±0.17	0.38±0.10
dibenzo[a,h]anthracene	4.38±1.27	1.67±0.59	0.013±0.010	0.087±0.086	0.011±0.010	0.028±0.008
benzo[b]chrysene	5.48±2.64	1.78±0.79	0.108±0.040	0.12±0.034	0.12±0.030	0.10±0.016
benzo[ghi]perylene	2.69±0.55	1.66±0.70	0.052±0.006	0.053±0.003	0.054±0.025	0.166±0.034
Coronene	6.78±1.29	1.11±0.79	0.25±0.020	0.14±0.27	0.161±0.020	0.359±0.110

Lim et al. (2007) [Influence of fuel composition on polycyclic aromatic hydrocarbon emissions from a fleet of in-service passenger cars, Atmospheric Environment] examined PAH emissions from eight in-service passenger cars powered by liquefied petroleum gas (LPG) and unleaded petrol (ULP) using a chassis dynamometer.

Measurements were based on variable volume sampling which involved diluting the exhaust gases by passing clean air through a HEPA filter into a dilution tunnel at a temperature below 52 °C and using a high velocity pump (0.01–0.02 m^3 min^{-1}) to draw particle-phased and vapor-phased PAHs into a Gelman glass fibre filter (47 mm) held in a polycarbonate filter holder and connected in tandem with a glass cartridge containing 7 g of Amberlite XAD-2. Each sampling cycle lasted approximately 10 min.

Exhaust emissions from a vehicle fleet that consisted of eight new Ford Falcon Forte passenger cars (six LPG-powered cars and two ULP-powered cars) were measured on a chassis dynamometer during three repetitive tests. wo steady-state cycle modes adapted from the US EPA Final ASM Test Procedure Documentation and defined as 60 km h^{-1} (mode 2) and 80 km h^{-1} (mode 3) were employed for the emission measurements.

Immediately after the sampling, the filters and XAD samples were wrapped in aluminum foil and stored at −15 °C prior to sample pretreatment and chemical analysis. Sample pre-treatment involved an extraction procedure, which is summarized as follows. Each filter was extracted three times with a 2:1 (vol/vol) mixture of dichloromethane and hexane in an ultrasonic bath. Each extraction cycle lasted thirty minutes and after the extraction, each extract was cleaned by passing it through a column packed with silica SepPak mesh no. 60, topped with 1 cm of anhydrous sodium sulphate to remove sampling artifacts. The volume of the resulting eluant was reduced to about 5 cm^3 on a rotary evaporator maintained at 36 °C and then further reduced to 1 cm^3 by using a gentle flow of high purity nitrogen.

Chromatographic analyses of the extracts were carried out on a HP 6890 GC FID fitted with a Restek-5MS capillary column (30.0 m×0.32 mm×0.25 μm) using guidelines from NIOSH method 5515 and the California Environmental Protection Agency Method 429. The following oven temperature program was used: initial temperature was set to 80 °C for 4 min, then increased to 320 °C at a rate of 10 °C min^{-1} and kept at 320 °C for 10 min. QTM standard PAH mix in dichloromethane was used as supplied by Supelco for the quantification of 2-bromonaphthalene (BNAP) and the following US EPA Priority PAHs: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), benzo(*a*)anthracene (BAA), chrysene (CHR), pyrene (PYR) and fluoranthene (FLT), benzo(a)pyrene (BAP), dibenzo(*a*,*h*)anthracene (DBA), benzo(*b*)fluoranthene (BBF), indeno(1,2,3-cd)pyrene (IND) and benzo(*g*,*h*,*i*)perylene (BGP). Under the conditions used for the analysis, CHR and BAA eluted together while IND and DBA also co-eluted.

Table 156: PAH emission factors in µg/km

	LPG		ULP or gasoline	
	Mode 2	Mode 3	Mode 2	Mode 3
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
naphthalene	60769	57748	6067852	4947688
acenaphthylene	271	372	371	672
2-BNAP	372	373	26722	672
acenaphthene	272	271	671	370
Fluorene	13711	8712	878	22727
Phenanthrene	1157119	1087110	124721	149726
Anthracene	44776	1379	37724	31718
Fluoranthene	574	14728	54767	475
Pyrene	28745	15722	78753	8710
Chrysene, benzo(*a*)anthracene	48737	27735	60748	29740
benzo(*b*)fluoranthene	35729	21718	22733	18718
benzo(a)pyrene	10710	777	13717	14712
indeno(1,2,3-cd)pyrene, dibenzo(*a*,*h*)anthracene	677	10719	578	374
benzo(*g*,*h*,*i*)perylene	5710	8711	8711	778

Riddle et al. (2007) [Large PAHs detected in fine particulate matter emitted from light-duty gasoline vehicles, Atmospheric Environment] examined large PAHs with 6–8 aromatic rings with molecular weights (MW) of 300–374 from 16 light-duty gasoline-powered vehicles (LDGV) and one heavy-duty diesel-powered vehicle (HDDV) operated under realistic driving conditions.

LDGV emission samples were collected at the Haagen-Smit Laboratory in El Monte, CA. Vehicles were operated on a stationary chassis dynamometer using the Federal Test Procedure (FTP) driving cycle. Information on the test vehicles are shown below.

Category [a]	**Make**	**Model**	**Production Year**	**Number of Cylinders**	**Fuel Delivery [b]**	**Mileage**
LDGV's						
LEV PC	Chevrolet	Monte Carlo	2002	6	FI	20,230
LEV PC	Toyota	Camry	1999	6	SFI	43,160
LEV PC	Nissan	Sentra	1999	4	SFI	52,630
LEV PC	Honda	**Accord**	1998	4	SFI	97,811
LEV PC	Honda	Civic	1996	4	SFI	77,703
LEV LDT/SUV	Chevrolet	Silverado	2003	8	SFI	1,264
LEV LDT/SUV	Nissan	Pathfinder	2002	6	SFI	8,169
LEV LDT/SUV	Toyota	Tacoma	2000	6	SFI	51,554
LEV LDT/SUV	Jeep	Grand Cherokee	2000	6	SFI	31,751
LEV LDT/SUV	Ford	Explorer	1998	8	SFI	82,513
TWC PC	Cadillac	Sedan de Ville	1999	8	FI	35,320
TWC PC	Ford	Mustang	1998	6	SFI	10,697
TWC PC	Honda	Acura	1994	4	SFI	104,441
TWC PC	Ford	Taurus	1991	6	MPFI	136,983
TWC PC	Toyota	Camry	1991	4	MPFI	95, 532
TWC PC	Chrysler	Plymouth	1988	4	EPFI	32, 097
HDDV						
	Freightliner	Detroit Diesel Series 60 (500 bhp)	1999	6		138,553

[a] LEV=low emission vehicle, TWC=three-way catalyst equipped vehicle, PC=passenger car, LDT=light-duty truck, SUV = sports-utility vehicle [b] FI=fuel injection, SFI=sequential fuel injection, MPFI = multi-port fuel injection, EPFI=electronic port fuel injection

HDDV emissions were collected from a 1999 Freightliner truck using the 5-mode heavy heavy-duty diesel truck (HHDDT) transient driving cycle consisting of a 30 min idle, 17 min creep, 11 min transient stage and two cruise stages of 34 and 31 min, with a top speed of 65 mile h^{-1} for the second cruise. In addition to the full HHDDT test cycle, emissions were sampled while the truck was operating under only the idle and creep modes of the HHDDT cycle, hereafter referred to as idle+creep.

Quartz filter PM2.5 samples were extracted individually. Filters were spiked with isotopically labeled PAHs and the solvent was allowed to dry before proceeding. Substrates were then placed into screw-cap centrifuge tubes for organic solvent extraction. Each tube was filled with ∼15 mL of a 1:1 mixture of hexane (Burdick and Jackson trace analysis grade) and dichloromethane (Burdick and Jackson trace analysis grade) then suspended in an ultrasonic cleaning bath for 15 min. The sonication extraction procedure was repeated three times and all of the extracts were combined. Samples were concentrated by nitrogen evaporation to a final volume of 200 μL.

PAHs were analyzed with a Varian 3400 gas chromatograph (GC) coupled with a Varian 2000 ion-trap mass spectrometer (GC–ITMS). Chemical separation of PAHs was performed on a J&W DB-5HT high-temperature capillary column (30 m×0.25 mm i.d., 0.1 μm film thickness, 5% phenyl-substituted polysiloxane, Agilent Technologies, Palo Alto, CA) with helium as the carrier gas at a linear velocity of 37 cm s^{-1}. Samples were introduced through a temperature programmable injection port that was held at the initial temperature of 64 °C for 1 min, then ramped at a rate of 20 °C min^{-1} to a temperature of 120 °C, the rate of heating was then increased to 100 °C min^{-1} to a final injector temperature of 375 °C where it was held until the end of the column program. The column was initially at a temperature of 64 °C for the first 7 min to allow the analytes to pass through the injection port and become cryo-focused on the front-end of the analytical column. The column oven temperature was then increased at a rate of 5 °C min^{-1} to a final temperature of 400 °C where it was held for 5 min for a total run time of 79.2 min. The ion trap oven, manifold, and transfer line were operated at 220, 80, and 300 °C, respectively. Analyte identification and quantification was conducted by electron ionization mass spectrometry–mass spectrometry (EI–MS^2) analysis.

Table 157: PAH emission factors normalized by total PM emission rates (mgPAH/gPM) for gasoline-powered low emission vehicles (LEVs), three-way catalyst vehicles (TWC), heavy-duty diesel vehicles operated under idle+creep driving conditions (HDDV Idle/Creep) and heavy-duty diesel vehicles operated under the full HHDDT 5-mode driving cycle

	LEV FTP	TWC FTP	HDDV Idle/Creep	HDDV 5-mode
Light PAHs				
Phenanthrene	320737	240728	4075	150717
Anthracene	3975			
Fluoranthene	110711	8178	670.6	7877
Pyrene	230723	160717	1572	110711
Cyclopenta[c,d]pyrene	3874	3774		
MW 228 isomers		350726	det	9577
Heavy PAHs				
Benzofluoranthene isomers	170716	700765	170.1	detected
Benzo[e]pyrene	8778	190717	670.6	1071
Benzo[a]pyrene	300727	600755	2172	1872
Perylene	1071	2172		
Indeno[1,2,3-c,d]pyrene	140713	320730	871	871
Dibenz[a,h]anthracene	870.3	2070.7		
Benzo[g,h,i]perylene	180715	470738	270.1	detected
Large PAHs				
Coronene	9478	260721	570.4	
MW 302 isomers	190716	1100788		
MW 326 isomers	10078	200716		
MW 350 isomers	130711	460737		
MW 374 isomers	det	det		

Table 158: PAH emissions factors (mg/L fuel burned) for low emission gasoline-powered vehicles (LEV), three-way catalyst gasoline powered vehicles (TWC), heavy-duty diesel vehicle operated under idle+creep (99 Frtlnr Idle/Creep) and heavy-duty diesel vehicle operated under 5-mode transient cycle (99 Frtlnr 56 K).

	LEV FTP	**TWC**	**99 Frtlnr Idle/Creep**	**99 Frtlnr 56 K**
Light PAHs				
Phenanthrene	1.240	1.930	29.908	72.910
Fluoranthene	0.689	0.965	4.548	39.005
Pyrene	0.965	1.240	11.853	56.095
MW 228 isomers	0.000	3.170	0.000	46.861
Heavy PAHs				
Benzofluoranthene isomers	0.636	6.608	1.134	0.000
Benzo[e]pyrene	0.359	1.853	4.673	4.673
Benzo[a]pyrene	0.968	5.613	15.982	8.820
Indeno[1,2,3-c,d]pyrene	0.470	2.986	6.415	3.982
Benzo[g,h,i]perylene	0.664	4.452	1.244	0.000
Large PAHs				
Coronene	0.359	2.406	4.065	0.000
MW 302 isomers	0.664	10.037	0.000	0.000
MW 326 isomers	0.359	1.935	0.000	0.000
MW 350 isomers	0.470	4.286	0.000	0.000

Karavalakis et al. (2011) [Biodiesel emissions profile in modern diesel vehicles. Part 2: Effect of biodiesel origin on carbonyl, PAH, nitro-PAH and oxy-PAH emissions, Science of the Total Environment] examined PAH emissions from a Euro 4 diesel vehicle fueled with biodiesel blends. Testing was performed on the NEDC and Artemis driving cycles.

PAH samples were collected on a glass-fiber filter. Each collected sample was extracted with dichloromethane in ultrasonic bath for 20 min. The extraction was repeated three times using

80 mL of the solvent each time. The extract was then concentrated by rotary evaporation to nearly 2 mL for further cleanup. The cleanup column (inner diameter, 1 cm) was filled with glass wool, 3 g of 6% deactivated silica gel, 2 g of 5% deactivated alumina and 0.5 g of anhydrous sodium sulphate. After loading the sample in the cleanup column, the column was washed firstly with 20 mL of n-hexane and then with 25 mL of the 30% CH_2Cl_2 in cyclohexane. Both fractions were reduced to 1 mL under a gentle stream of nitrogen for the analysis. The fraction of CH_2Cl_2/cyclohexane was analyzed for PAHs and their products. A gas chromatograph (Agilent 6890) with a mass spectrometric (MS) detector (Agilent 5975B) was used for the PAHs (Electron Ionization, EI) and nitro-PAHs analysis (Negative Chemical Ionization, NCI). The GC–MS was equipped with a capillary column (HP 5 MS, 30 m × 0.25 μm × 0.25 mm, Agilent); an auto sampler (Agilent 7673A), with an injection volume of 1 μL, pulsed splitless injection. For PAHs analysis the injector temperature was set at 310 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 55 to 325 °C at 20 °C min^{-1}. For nitro-PAH and oxy-PAH analyses the injector temperature was set at 280 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 60 to 200 °C at 20 °C min^{-1}, and from 200 °C to 300 °C at 5 °C min^{-1}. The oven remained at this temperature for 10 min. The masses of primary and secondary PAH, nitro-PAH and oxy-PAH ions were determined by using the scan mode for pure standards of these compounds. Quantification was performed by using the selected ion monitoring (SIM) mode. The efficiencies of the studied PAHs ranged from 85.0% to 105.0%. For the studied nitro-PAHs the efficiencies ranged from 75.0% to 93.0% and for the oxy-PAHs from 66.5% to 89.5%. The repeatability of PAHs ranged from 2.7% to 5.4%. For the nitro-PAHs the repeatability ranged from 3.2% to 8.4% and for the oxy-PAHs from 8.7% to 11.1%. The combined uncertainty

for the overall emission measurements was calculated to be: PAHs (4.1–8.3%), nitro-PAHs (4.7–12.4%) and oxy-PAHs (10.4%–14.7%).

Table 159: Emissions of PAH, nitro-PAH, ad oxy-PAH for diesel fuel and UFOME blends

	Diesel				**UFOME-10**				**UFOME-20**				**UFOME-30**			
	NEDC	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**
PAH, µg km^{-1}																
Phenanthrene	9.03	10.677	7.963	5.828	12.851	14.574	8.823	5.471	13.859	15.07	8.809	5.738	15.35	17.251	9.822	6.196
Anthracene	7.725	9.984	4.787	1.498	9.4	14.973	9.944	5.393	12.489	15.217	7.118	4.121	13.754	18.988	8.204	5.976
Fluoranthene	9.35	10.702	5.625	2.36	13.091	16.442	7.494	4.476	14.997	16.923	7.682	5.326	16.31	20.406	9.043	5.932
Pyrene	9.047	9.801	6.059	4.74	9.758	13.131	7.775	4.151	10.272	15.181	8.288	4.753	12.47	14.464	8.72	4.144
Chrysene	9.102	8.21	4.179	2.606	5.756	6.996	3.522	2.566	3.895	7.469	3.118	1.935	3.191	4.217	2.967	1.417
Benzo[a]anthracene	4.341	7.831	3.334	2.258	4.012	7.494	5.213	2.044	3.075	7.015	3.033	1.556	2.564	8.89	2.823	1.881
Benzo[b,k]fluoranthenes	5.911	8.627	4.038	1.54	5.919	9.4	4.912	2.081	5.595	9.773	5.223	2.098	6.972	9.961	5.799	2.399
Benzo[a]pyrene	3.898	4.492	3.633	3.194	3.944	4.575	3.729	3.208	3.605	4.355	3.582	2.984	3.318	3.707	2.961	2.371
Indeno[1,2,3-c,d]pyrene	–	–	–	–	–	–	–	–	–	–	–	–	1.675	1.991	1.242	0.847
Dibenzo[a,h]anthracene	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Benzo[g,h,i]perylene	–	–	–	–	–	–	–	–	–	–	–	–	1.347	1.883	1.036	0.669
Nitro-PAH, ng km^{-1}																
3-Nitro-fluoranthene	1.882	3.96	1.639	0.59	1.386	3.8	1.002	0.795	1.403	3.816	0.978	0.679	1.146	3.592	0.96	0.673
1-Nitro-pyrene	4.45	17.177	10.69	7.54	6.32	11.383	7.05	13.52	8.123	13.626	10.021	9.895	8.448	14.693	10.777	8.887
7-Nitro-benzo[a]anthracene	1.448	2.957	1.109	0.856	1.434	2.397	1.72	0.834	1.409	2.402	1.661	0.974	1.478	2.56	1.285	0.811
6-Nitro-benzo[a]pyrene	3.364	5.047	1.589	1.23	1.882	6.437	1.787	1.834	1.889	6.558	2.686	0.376	0.763	8.133	2.574	0.389
Oxy-PAH, ng km^{-1}																
1-Naphthaldehyde	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
9-Fluorenone	4.749	9.34	6.363	2.422	5.684	7.959	4.11	2.295	5.677	7.728	4.197	2.444	6.009	8.067	4.38	2.989

Anthraquinone	3.52	6.776	4.604	2.294	6.41	8.356	5.567	3.88	6.954	9.103	6.307	3.273	7.348	9.287	6.08	2.542
9-Phenanthrenecarboxaldehyde	2.44	2.973	1.787	0.859	1.356	2.799	0.868	0.521	1.257	3.017	0.624	0.553	1.209	3.245	0.939	0.75
Benzanthrone	3.821	5.327	3.52	2.923	4.49	6.804	3.498	3.635	5.978	9.751	4.077	4.177	6.993	13.166	5.556	5.169
Benz[a]anthracene-7,12-dione	2.63	4.49	2.35	1.92	3.294	6.171	2.296	1.339	3.017	6.538	2.036	1.484	3.691	6.925	2.002	1.345

Table 160: Emissions of PAH, nitro-PAH, ad oxy-PAH for OME blends

	OME-10				**OME-20**				**OME-30**			
	NEDC	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**
PAH, μg km^{-1}												
Phenanthrene	11.769	13.672	8.203	5.888	12.548	14.089	9.06	6.254	14.739	15.069	9.538	6.566
Anthracene	9.446	13.324	8.724	4.341	10.479	13.708	8.667	4.149	11.789	15.033	8.528	3.746
Fluoranthene	10.276	15.12	9.001	3.541	7.815	13.573	7.526	2.544	7.803	11.938	3.511	2.703
Pyrene	10.909	12.763	9.327	3.117	10.638	12.306	8.387	2.507	10.528	11.381	7.953	4.669
Chrysene	5.557	7.744	4.534	2.052	5.772	6.687	4.672	1.872	5.476	5.235	2.233	1.278
Benzo[a]anthracene	4.531	7.35	3.778	2.679	4.647	6.934	3.697	2.536	4.433	6.067	3.219	2.05
Benzo[b,k]fluoranthenes	6.106	8.721	5.017	2.315	6.088	8.967	5.151	2.173	6.625	9.198	5.495	2.795
Benzo[a]pyrene	3.886	4.618	3.522	3.103	3.497	4.25	3.437	2.955	3.186	3.609	2.846	2.311
Indeno[1,2,3-c,d]pyrene	–	–	–	–	–	–	–	–	–	–	–	–
Dibenzo[a,h]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
Benzo[g,h,i]perylene	–	–	–	–	–	–	–	–	–	–	–	–
Nitro-PAH, ng km^{-1}												
3-Nitro-fluoranthene	–	–	–	–	–	–	–	–	–	–	–	–
1-Nitro-pyrene	1.913	5.009	1.053	1.047	1.429	3.907	0.967	0.978	1.402	3.567	0.833	0.884
7-Nitro-benzo[a]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
6-Nitro-benzo[a]pyrene	1.177	2.184	1.244	0.913	1.035	1.883	1.153	0.896	0.984	1.549	1.107	0.89

Oxy-PAH, ng km^{-1}												
1-Naphthaldehyde	–	–	–	–	–	–	–	–	–	–	–	–
9-Fluorenone	0.486	1.9	0.785	0.381	0.643	1.827	0.655	0.266	0.764	1.597	0.44	0.204
Anthraquinone	4.811	6.063	3.565	2.168	4.96	6.92	3.329	2.943	5.285	7.5	3.4	2.048
9-Phenanthrenecarboxaldehyde	1.176	2.875	0.802	0.582	1.167	2.906	0.796	0.543	1.169	2.883	0.772	0.547
Benzanthrone	2.745	4.113	2.107	1.651	2.68	4.161	2.068	1.234	2.585	3.901	1.971	1.097
Benz[a]anthracene-7,12-dione	2.718	4.237	2.171	1.298	2.911	4.291	2.166	1.4	3.713	4.343	2.639	1.817

Table 161: Emissions of PAH, nitro-PAH, ad oxy-PAH for AFME blends

	AFME-10				**AFME-20**				**AFME-30**			
	NEDC	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**
PAH, µg km^{-1}												
Phenanthrene	9.665	9.966	7.865	4.847	9.155	10.525	5.886	3.634	9.063	10.128	4.565	2.281
Anthracene	8.315	8.55	6.023	2.277	7.965	9.758	5.394	2.058	7.899	7.448	6.671	2.427
Fluoranthene	9.871	10.338	6.268	3.477	8.958	9.267	5.864	3.14	9.388	8.817	5.29	2.828
Pyrene	9.135	11.327	8.012	5.501	8.247	9.952	5.182	4.126	7.346	9.02	4.28	2.691
Chrysene	4.183	4.939	3.17	2.985	3.794	4.477	3.502	2.772	3.092	3.803	2.786	1.515
Benzo[a]anthracene	3.941	4.343	2.699	2.446	3.475	4.013	2.263	1.276	3.163	3.724	2.239	1.407
Benzo[b,k]fluoranthenes	5.99	6.433	3.66	2.107	5.228	5.88	3.461	1.93	4.98	35.65	2.655	1.448
Benzo[a]pyrene	2.477	3.142	2.501	2.118	2.132	2.895	2.306	1.966	1.954	2.372	1.607	1.201
Indeno[1,2,3-c,d]pyrene	–a	–	–	–	–	–	–	–	–	–	–	–
Dibenzo[a,h]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
Benzo[g,h,i]perylene	–	–	–	–	–	–	–	–	–	–	–	–
Nitro-PAH, ng km^{-1}												
3-Nitro-fluoranthene	–	–	–	–	–	–	–	–	–	–	–	–
1-Nitro-pyrene	3.202	2.06	1.34	1.18	3.33	2.28	1.111	0.624	3.17	2.15	0.907	0.674
7-Nitro-benzo[a]anthracene	–	–	–	–	–	–	–	–	–	–	–	–

6-Nitro-benzo[a]pyrene	1.397	2.408	1.106	0.773	1.215	2.077	1.005	0.824	1.246	1.983	0.927	0.704
Oxy-PAH, ng km^{-1}												
1-Naphthaldehyde	–	–	–	–	–	–	–	–	–	–	–	–
9-Fluorenone	2.97	2.751	1.96	1.44	2.55	1.741	1.45	1.15	2.06	2.292	1.55	0.99
Anthraquinone	2.69	5.79	2.314	1.99	2.83	4.98	2.296	2.275	6.559	8.095	2.51	2.85
9-Phenanthrenecarboxaldehyde	2.16	3.07	1.88	1.04	2.22	3.19	2.12	1.22	2.38	2.95	1.75	1.25
Benzanthrone	4.88	4.023	2.16	2.73	4.629	3.949	2.08	2.79	4.06	3.33	2.1	2.16
Benz[a]anthracene-7,12-dione	2.7	4.465	2.17	1.79	2.51	4.217	2.15	1.9	2.12	4.307	2.44	1.5

Table 162: Emissions of PAH, nitro-PAH, ad oxy-PAH for SMEP blends

	SMEP-10				**SMEP-20**				**SMEP-30**			
	NEDC	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**
PAH, μg km^{-1}												
Phenanthrene	9.451	10.904	7.388	5.211	9.606	11.51	7.643	5.062	10.427	12.419	8.131	4.837
Anthracene	8.982	10.432	6.694	3.865	9.346	10.14	6.28	3.531	9.626	10.854	6.565	5.968
Fluoranthene	9.765	11.731	7.207	4.879	9.975	10.851	7.258	4.82	10.248	11.093	5.031	3.432
Pyrene	10.911	12.079	6.321	4.935	11.551	12.246	6.707	4.83	11.873	12.965	6.895	3.723
Chrysene	5.209	6.878	4.798	3.19	4.101	5.726	3.38	2.948	2.875	4.743	2.809	4.74
Benzo[a]anthracene	3.994	5.873	3.106	2.572	3.517	5.442	2.968	2.166	2.975	3.885	2.418	1.562
Benzo[b,k]fluoranthenes	5.788	7.267	4.637	2.433	5.851	7.209	4.142	3.475	3.936	6.173	3.659	1.747
Benzo[a]pyrene	3.559	3.881	3.148	3.107	3.209	3.225	2.996	2.47	2.822	2.794	2.136	4.461
Indeno[1,2,3-c,d]pyrene	–a	–	–	–	–	–	–	–	–	–	–	–
Dibenzo[a,h]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
Benzo[g,h,i]perylene	–	–	–	–	–	–	–	–	–	–	–	–
Nitro-PAH, ng km^{-1}												
3-Nitro-fluoranthene	–	–	–	–	–	–	–	–	–	–	–	–
1-Nitro-pyrene	1.45	3.29	1.09	0.82	1.575	3.617	1.325	1.063	1.83	3.894	1.52	1.209

7-Nitro-benzo[a]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
6-Nitro-benzo[a]pyrene	1.398	2.705	1.306	1.051	1.155	2.147	1.109	0.911	1.062	1.588	0.974	1.018
Oxy-PAH, ng km^{-1}												
1-Naphthaldehyde	–	–	–	–	–	–	–	–	–	–	–	–
9-Fluorenone	2.31	1.87	1.36	1.12	1.97	1.97	1.18	0.89	1.55	1.48	1.23	0.97
Anthraquinone	5.923	4.446	2.372	1.85	5.14	3.89	2.87	1.72	3.67	3.85	3.36	1.8
9-Phenanthrenecarboxaldehyde	2.24	2.901	1.66	0.96	2.02	2.55	1.54	0.83	1.93	2.16	1.3	0.64
Benzanthrone	3.97	3.933	2.08	2.75	3.61	3.89	1.96	2.22	3.1	3.18	1.33	1.67
Benz[a]anthracene-7,12-dione	2.89	3.98	2.66	1.64	2.66	4.13	2.14	1.44	2.74	4.2	2.28	0.99

Karavalakis et al. (2010) [The impact of soy-based biodiesel on PAH, nitro-PAH and oxy-PAH emissions from a passenger car operated over regulated and nonregulated driving cycles, Fuel] examined PAH emissions from a Euro 2 compliant VW Golf 1.9 TDi equipped with a turbocharged direct injection diesel engine and an oxidation catalyst. Three fuels were evaluated in this study. Methyl ester obtained from soya seed oil was used pure (B100) and as a blending feedstock to create a 50% v/v blend (B50) with diesel fuel. Testing was performed on the NED and Artemis driving cycles.

Each collected sample was extracted with dichloromethane in ultrasonic bath for 20 min. The extraction was repeated three times using 80 mL of the solvent each time. The extract was then concentrated by rotary evaporation to nearly 2 mL for further cleanup. The cleanup column (inner diameter, 1 cm) was filled with glass wool, 3 g of 6% deactivated silica gel, 2 g of 5% deactivated alumina and 0.5 g of anhydrous sodium sulphate . The column was conditioned by passing 10 mL of 30% CH_2Cl_2 in cyclohexane and 15 mL of n-pentane. After loading the sample in the cleanup column, the column was washed initially with 20 mL of n-pentane, which was discarded, and then with 25 mL of the 30% CH_2Cl_2 in cyclohexane. This fraction was collected and the volume was reduced to 1 mL under a gentle stream of nitrogen for the analysis. A gas chromatograph (GC) (Agilent 6890) with a mass spectrometric (MS) detector (Agilent 5975B) was used for the PAHs (Electron Ionization, EI) and nitro-PAHs analysis (Negative Chemical Ionization, NCI). The GC–MS was equipped with a capillary column (HP 5 MS, 30 m × 0.25 μm × 0.25 mm, Agilent); an auto sampler (Agilent 7673A), with an injection volume of 1 μL, pulsed splitless injection. For PAHs analysis the injector temperature was set at 310 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 55 to 325 °C at 20 °C min^{-1}. For nitro-PAHs and oxy-PAHs analysis the injector temperature was set at 280 °C and the ion source temperature at 280 °C.

Oven operating temperature ranged from 60 to 200 °C at 20 °C min^{-1}, and from 200 to 300 °C at 5 °C min^{-1}. The oven remained at this temperature for 10 min. The masses of primary and secondary PAH, nitro-PAHs and oxy-PAHs ions were determined by using the scan mode for pure PAH and nitro-PAHs standards (Supelco). Quantification of PAHs, nitro- and oxy-PAHs was performed by using the selected ion monitoring (SIM) mode. The recovery efficiencies of the studied PAHs ranged from 85.0% to 105.0%. For the studied nitro-PAHs the recovery efficiencies ranged from 75.0% to 93.0% and for the oxy-PAHs from 66.5% to 89.5%. The recovery efficiency (R) is defined as $R = (X_a/X_{ca})\times 100$, where R is the recovery efficiency of the studied compound in %, X_a is the measured fraction of the studied compound and $X_{ca}$is the certified mass fraction of the studied compound. The recovery efficiency is used when the external or internal standard method for quantification is used. The recovery efficiency is calculated other using a certified reference material or spiked filters using a standard solution of the studied compounds.

Table 163: PAH, nitro-PAH, and oxy-PAH emissions in the vehicle exhaust with automotive diesel fuel

	UDC	EUDC	NEDC	UDC (hot-start)	Art. Urban	Art. Road	Art. Motorway
PAH emissions, µ*g km*$^{-1}$							
Phenanthrene	8.23	11.07	10.03	4.95	12.28	11.08	4.63
Anthracene	5.65	3.16	4.07	5.15	4.83	1.42	1.12
Fluoranthene	25.6	4.74	12.36	5.78	5.15	2.13	2.78
Pyrene	22.4	2.98	10.07	1.97	3.87	2.24	2.85
Chrysene	5.95	3.45	4.36	4.85	3.56	1.34	1.39
Benzo[*a*]anthracene	2.65	1.23	1.74	2.47	2.46	0.51	0.42
Benzo[b]fluoranthene	3.17	1.47	2.09	2.01	1.15	0.72	0.38
Benzo[k]fluoranthene	2.48	1.67	1.96	1.65	0.87	0.59	0.4
Benzo[*a*]pyrene	2.83	2.87	2.85	2.48	3.01	1.25	1.25
Indeno[1,2,3-*c*,*d*]pyrene	3.14	0.45	1.43	–a	–	–	–
Benzo[*g*,*h*,*i*]perylene	–	–		–	–	–	–
Dibenzo[*a*,*h*]anthracene	1.65	–	0.6	–	–	0.34	–
nitro-PAH emissions, ng km^{-1}							
3-nitro-fluoranthene	–	2	1.26	–	–	–	0.63
1-nitro-pyrene	3.34	1.9	2.42	3.2	2.9	0.9	0.58
7-nitro-benzo[*a*]anthracene	3.5	–	1.28	–	–	–	0.61
6-nitro-benzo[*a*]pyrene	5.2	3	3.8	5.1	4.6	1.3	0.89
oxy-PAH emissions, ng km^{-1}							
1-naphthaldehyde	2	1.3	1.55	1.9	1.8	0.6	0.44
9-fluorenone	1.33	1.2	1.31	1	2.7	1.3	1.26
Anthraquinone	1.54	6.5	4.68	8.57	19.4	6.6	8.1
9-phenanthrenecarboxaldehyde	3.7	2.52	2.95	3.18	3.1	1.1	0.7
Benzanthrone	5.56	2.68	3.73	4.55	4.2	1.2	0.78
Benz[*a*]anthracene-7,12-dione	4.83	2.74	3.5	4.8	4.4	1.2	0.96

Table 164: PAH, nitro-PAH, and oxy-PAH emissions in the vehicle exhaust with B50

	UDC	EUDC	NEDC	UDC (hot-start)	Art. Urban	Art. Road	Art. Motorway
PAH emissions, µ*g km*$^{-1}$							
Phenanthrene	–	1.63	1.03	–	–	6.1	1.26
Anthracene	4.97	3.17	3.82	5.43	4.92	1.22	0.84
Fluoranthene	10.2	6.34	7.75	2.37	5.04	2.44	2.85
Pyrene	7.46	4.75	5.74	2.41	2.24	2.57	2.11
Chrysene	4.83	3.38	3.91	5.67	4.98	1.22	1.26
Benzo[*a*]anthracene	2.74	1.55	1.98	2.13	2.31	0.53	0.38
Benzo[b]fluoranthene	2.43	1.39	1.77	2.38	–	0.72	0.49
Benzo[k]fluoranthene	2.52	1.42	1.82	2.62	–	0.61	0.56
Benzo[*a*]pyrene	2.25	–	0.82	–	–	–	–
Indeno[1,2,3-*c*,*d*]pyrene	2.36	1.28	1.67	–	–	–	–
Benzo[*g*,*h*,*i*]perylene	2.17	–	0.79	–	–	–	–
Dibenzo[*a*,*h*]anthracene	–	–	–	–	–	0.65	–
nitro-PAH emissions, ng km^{-1}							
3-nitro-fluoranthene	–	2.03	1.28	–	–	–	0.6
1-nitro-pyrene	3.94	2.48	3.01	3.13	2.92	0.96	0.7
7-nitro-benzo[*a*]anthracene	–	2.04	1.29	–	–	0.86	0.61
6-nitro-benzo[*a*]pyrene	5.18	2.99	3.79	5.12	4.61	1.28	0.9
oxy-PAH emissions, ng km^{-1}							
1-naphthaldehyde	1.97	1.12	1.43	2.1	1.67	0.5	0.34
9-fluorenone	1.58	1.16	1.31	0.52	1.5	0.5	0.3
Anthraquinone	36.06	32.72	33.94	13.38	4.5	8	2.91
9-phenanthrenecarboxaldehyde	3.54	2.33	2.77	3.23	3.09	0.9	0.81
Benzanthrone	4.45	2.73	3.35	4.35	4.1	1.1	0.73
Benz[*a*]anthracene-7,12-dione	7.03	2.93	4.43	5.13	4.32	1.5	0.97

Table 165: PAH, nitro-PAH, and oxy-PAH emissions in the vehicle exhaust with B100

	UDC	EUDC	NEDC	UDC (hot-start)	Art. Urban	Art. Road	Art. Motorway
PAH emissions, μ*g km*$^{-1}$							
Phenanthrene	9.97	2.75	5.39	1.95	2.21	3.05	2.53
Anthracene	5.15	8.36	3.67	4.96	4.77	1.03	0.77
Fluoranthene	17.4	8.53	11.66	5.14	4.32	2.14	2.67
Pyrene	17.4	8.53	11.66	5.14	4.32	2.14	2.67
Chrysene	7.47	1.26	4.55	4.65	4.59	1.37	1.31
Benzo[*a*]anthracene	4.72	1.48	2.52	2.48	2.36	0.45	0.43
Benzo[b]fluoranthene	2.14	1.54	1.72	–	2.41	0.37	0.52
Benzo[k]fluoranthene	2.38	–	1.84	–	2.15	0.67	0.47
Benzo[*a*]pyrene	2.25	–	0.92	–	–	–	–
Indeno[1,2,3-*c*,*d*]pyrene	2.57	–	0.94	–	–	0.64	–
Benzo[*g*,*h*,*i*]perylene	2.04	–	–	–	–	–	–
Dibenzo[*a*,*h*]anthracene	–	–	–	–		–	–
nitro-PAH emissions, ng km^{-1}							
3-nitro-fluoranthene	–	–	–	–	–	–	–
1-nitro-pyrene	4.16	2.02	2.8	3.24	2.95	0.94	0.72
7-nitro-benzo[*a*]anthracene	–	–	–	–	–	–	0.52
6-nitro-benzo[*a*]pyrene	5.16	2.78	3.77	5.24	–	1.26	0.88
oxy-PAH emissions, ng km^{-1}							
1-naphthaldehyde	1.96	–	0.71	1.93	1.73	0.47	0.33
9-fluorenone	1.04	0.4	0.63	0.82	0.85	0.33	0.26
Anthraquinone	32.21	16.59	22.3	10.03	18.4	5.38	3.27
9-phenanthrenecarboxaldehyde	3.26	1.92	2.41	3.41	3.15	0.95	0.58
Benzanthrone	4.4	–	1.61	–	3.95	1.13	0.76
Benz[*a*]anthracene-7,12-dione	5.15	2.79	3.65	6.02	4.74	1.3	0.95

Karavalakis et al. (2010) [Influence of Oxidized Biodiesel Blends on Regulated and Unregulated Emissions from a Diesel Passenger Car, Environmental Science and Technology] evaluated the effects of biodiesel source material on PAH, nitro-PAH, and oxy-PAH emissions from a Euro 4 diesel vehicle. Seven fuels were used, including an ultra-low sulfur diesel with two types of methyl esters. Soy-based methyl ester (SME) and used frying oil methyl ester (UFOME) were blended with the reference diesel at proportions of 20, 30, and 50% v/v. A 2007 model year Subaru Forester 2.0D XS (SUV type), equipped with a common-rail direct injection diesel engine and meeting Euro 4 emission standards, was used in this study. Emissions in this vehicle were controlled by a diesel oxidation catalyst (DOC) and a silicon carbide (SiC) diesel particulate filter (DPF). Testing was performed over the NEDC and Artemis cycles using a chassis dynamometer.

Each collected sample was extracted with dichloromethane in ultrasonic bath for 20 min. The extraction was repeated three times using 80 mL of the solvent each time. The extract was then concentrated by rotary evaporation to nearly 2 mL for further cleanup. The cleanup column (inner diameter, 1 cm) was filled with glass wool, 3 g of 6% deactivated silica gel, 2 g of 5% deactivated alumina and 0.5 g of anhydrous sodium sulphate . The column was conditioned by passing 10 mL of 30% CH_2Cl_2 in cyclohexane and 15 mL of n-pentane. After loading the sample in the cleanup column, the column was washed initially with 20 mL of n-pentane, which was discarded, and then with 25 mL of the 30% CH_2Cl_2 in cyclohexane. This fraction was collected and the volume was reduced to 1 mL under a gentle stream of nitrogen for the analysis. A gas chromatograph (GC) (Agilent 6890) with a mass spectrometric (MS) detector (Agilent 5975B) was used for the PAHs (Electron Ionization, EI) and nitro-PAHs analysis (Negative Chemical Ionization, NCI). The GC–MS was equipped with a capillary column (HP 5 MS, 30 m × 0.25 μm × 0.25 mm, Agilent); an auto sampler (Agilent 7673A), with an injection volume of 1 μL, pulsed splitless injection. For

PAHs analysis the injector temperature was set at 310 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 55 to 325 °C at 20 °C min^{-1}. For nitro-PAHs and oxy-PAHs analysis the injector temperature was set at 280 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 60 to 200 °C at 20 °C min^{-1}, and from 200 to 300 °C at 5 °C min^{-1}. The oven remained at this temperature for 10 min. The masses of primary and secondary PAH, nitro-PAHs and oxy-PAHs ions were determined by using the scan mode for pure PAH and nitro-PAHs standards (Supelco). Quantification of PAHs, nitro- and oxy-PAHs was performed by using the selected ion monitoring (SIM) mode. The recovery efficiencies of the studied PAHs ranged from 85.0% to 105.0%. For the studied nitro-PAHs the recovery efficiencies ranged from 75.0% to 93.0% and for the oxy-PAHs from 66.5% to 89.5%. The recovery efficiency (R) is defined as $R = (X_a/X_{ca})\times 100$, where R is the recovery efficiency of the studied compound in %, X_a is the measured fraction of the studied compound and X_{ca} is the certified mass fraction of the studied compound. The recovery efficiency is used when the external or internal standard method for quantification is used. The recovery efficiency is calculated other using a certified reference material or spiked filters using a standard solution of the studied compounds.

Table 166: PAH, nitro-PAH, and oxy-PAH emissions from the diesel fuel and UFOME blends

PAH, µg/km	Diesel				UFOME-20				UFOME-30				UFOME-50			
	NEDC	Urban	Road	Motorway	NEDC	Urban	Road	Motorway	NEDC	Urban	Road	Motorway	NEDC	Urban	Road	Motorway
Phenanthrene	1.746	3.38	1.262	0.745	1.807	3.63	1.084	1.103	1.624	4.601	1.162	0.717	2.022	7.97	1.184	0.937
Anthracene	1.942	3.837	1.571	0.938	1.308	3.015	0.708	0.769	3.783	4.529	0.989	0.485	3.901	6.194	1.05	0.628
Fluoranthene	1.521	3.647	1.083	0.818	1.776	3.884	1.265	0.919	1.976	5.354	1.596	1.15	2.227	6.12	1.604	0.936
Pyrene	1.47	2.273	1.075	0.849	1.702	3.857	1.296	1.052	2.009	4.01	1.334	0.968	2.082	7.515	1.845	0.88
Chrysene	1.16	2.396	0.86	0.489	1.715	3.16	0.799	0.894	2.243	3.698	1.14	0.722	2.365	3.445	1.223	0.598
Benzo[a]anthracene	0.901	1.882	0.519	0.335	1.363	3.313	0.648	0.712	1.784	3.75	0.903	0.46	1.86	4.947	1.196	0.879
Benzo[b,k]fluoranthenes	1.539	2.049	0.637	0.408	1.47	3.474	1.15	0.911	1.9	4.017	1.588	0.643	1.94	4.393	1.196	0.761
Benzo[a]pyrene	1.431	2.093	1.305	0.953	1.486	2.959	0.966	0.539	1.775	3.508	0.573	0.416	1.841	3.969	0.642	0.355
Indeno[1,2,3-c,d]pyrene	0.947	1.482	0.886	0.463	0.679	1.494	0.503	0.458	0.753	2.558	0.461	0.27	0.85	3.11	0.579	0.391
Dibenzo[a,h]anthracene	-[a]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	0.555	1.25	0.401	0.291	0.604	1.879	0.276	0.179	0.682	2.506	0.43	0.3
nitro-PAH, ng/km																
3-nitro-fluoranthene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1-nitro-pyrene	1.533	3.213	1.083	4.354	1.481	5.302	1.56	2.758	1.948	6.087	2.401	4.384	2.435	8.862	5.184	8.701
7-nitro-benzo[a]anthracene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6-nitro-benzo[a]pyrene	1.717	3.966	1.852	0.905	1.886	2.979	1.27	0.917	1.557	2.484	1.285	0.878	1.196	2.109	1.214	0.869
oxy-PAH, ng/km																
1-Naphthaldehyde	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
9-Fluorenone	0.194	0.519	0.117	0.096	0.213	0.542	0.506	0.158	0.209	0.592	0.119	0.108	0.182	0.612	0.104	0.345

Anthraquinone	1.459	4.98	1.009	0.651	1.633	5.047	1.185	0.942	1.894	5.188	1.307	1.029	2.106	5.315	1.512	1.174
9-Phenanthrenecarboxaldehyde	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzanthrone	1.62	4.093	1.469	0.931	1.594	4.107	1.385	0.946	1.728	4.347	1.419	1.088	1.969	4.393	1.448	1.114
Benz[a]anthracene-7,12-dione	1.701	4.177	1.181	0.82	1.971	4.192	1.237	0.945	2.022	4.486	1.298	1.102	2.235	4.513	1.474	1.196

Table 167: PAH, nitro-PAH, and oxy-PAH emissions from the SME blends

PAH, µg/km	**SME-20**				**SME-30**				**SME-50**			
	NEDC	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**	**NEDC**	**Urban**	**Road**	**Motorway**
Phenanthrene	1.09	2.27	0.789	0.588	1.249	2.665	1.225	1.34	1.393	4.628	1.091	1.774
Anthracene	1.179	1.537	0.675	0.289	0.627	1.333	0.442	0.271	0.646	2.336	0.417	0.223
Fluoranthene	1.433	2.323	1.252	0.978	1.388	2.573	1.089	0.985	1.117	2.155	0.895	0.615
Pyrene	1.229	1.849	1.061	0.94	0.934	1.542	0.746	0.69	0.705	1.428	0.493	0.622
Chrysene	1.131	1.965	0.514	0.314	0.747	1.625	0.486	0.35	0.793	1.049	0.707	0.272
Benzo[a]anthracene	0.903	1.552	0.756	0.443	0.588	1.288	0.552	0.269	0.625	1.43	0.376	0.244
Benzo[b,k]fluoranthenes	0.874	1.689	1.137	0.299	0.796	1.488	0.685	0.328	0.709	1.217	0.465	0.23
Benzo[a]pyrene	0.859	1.874	0.746	0.76	0.66	1.438	0.671	0.523	0.702	1.224	0.457	0.412
Indeno[1,2,3-c,d]pyrene	-a	-	-	-	-	-	-	-	-	-	-	-
Dibenzo[a,h]anthracene	-	-	-	-	-	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-	-	-	-	-	-
nitro-PAH, ng/km												
3-nitro-fluoranthene	-	-	-	-	-	-	-	-	-	-	-	-
1-nitro-pyrene	1.442	3.178	1.106	1.974	1.361	3.077	1.229	1.483	1.188	2.895	1.131	1.558
7-nitro-benzo[a]anthracene	-	-	-	-	-	-	-	-	-	-	-	-
6-nitro-benzo[a]pyrene	1.998	4.096	1.794	1.157	1.675	3.778	1.467	1.241	1.429	3.522	1.185	1.066
oxy-PAH, ng/km												

1-Naphthaldehyde	-	-	-	-	-	-	-	-	-	-	-	-
9-Fluorenone	0.299	0.668	0.169	0.152	0.319	0.656	0.342	0.235	0.53	1.005	0.436	0.277
Anthraquinone	1.14	3.787	1.028	0.822	1.505	3.872	1.154	0.773	1.687	3.953	1.13	0.968
9-Phenanthrenecarboxaldehyde	-	-	-	-	-	-	-	-	-	-	-	-
Benzanthrone	1.337	3.951	1.173	0.907	1.592	3.957	1.125	0.959	1.625	4.108	1.168	1.129
Benz[a]anthracene-7,12-dione	1.745	4.201	1.177	0.916	1.809	4.275	1.237	1.094	1.719	4.072	1.205	0.958

Yang et al. (2018) [Gasoline Particulate Filters as an Effective Tool to Reduce Particulate and Polycyclic Aromatic Hydrocarbon Emissions from Gasoline Direct Injection (GDI) Vehicles: A Case Study with Two GDI Vehicles, Environmental Science and Technology] investigated the gas-phase and PM-phase PAH emissions from two GDI vehicles with and without gasoline particle filters (GPFs) using a chassis dynamometer. This study utilized two 2016 model year passenger cars. GDI_1 was equipped with a 2.0 L wall-guided direct injection SI Atkinson cycle engine, and GDI_2 was equipped with a 1.5 L downsized turbocharged centrally mounted direct injection engine. Both vehicles were operated stoichiometrically and were equipped with three-way catalysts (TWCs). GDI_1 and GDI_2 were certified to meet LEV III SULEV30 (PZEV) and LEV II emissions standards and had 14 780 and 24 600 miles at the start of the campaign, respectively. Both vehicles were tested over duplicate LA92s cycles on typical California E10 fuel.

PAH and nitro-PAH samples were collected on precleaned Teflon-impregnated glass fiber (TIGF) filters (100 mm). Semivolatile organic compounds were collected on cleaned Amberlite XAD-4 polyaromatic absorbent resin (Aldrich Chemical Co., Inc.) that was packed into a glass cartridge. The samples collected on each filter-XAD sampling train were extracted separately with high-purity dichloromethane and then acetone, followed by an accelerated solvent extraction (ASE). A Varian 4000 Ion Trap in electron impact (EI) mode was used for PAH analysis, and a Varian 1200 triple quadrupole GC/MS operating in negative chemical ionization (CI) mode was used for nitro-PAH compounds. Negative CI offers superior sensitivity for the analysis of nitro-PAHs (approximately 100 times higher than EI or positive CI) and other compounds with electron-withdrawing substituents, but not for regular PAH and hydrocarbons.

Table 168: Individual particle-phase PAH compounds, expressed in ng/mile, for both test vehicles over the LA92 cycle

Compounds	**GDI_1**		**GDI_2**	
ng/mile	**Without GPF**	**With GPF**	**Without GPF**	**With GPF**
Non-substituted PAHs				
Naphthalene	507.41±404.8	26.86±25.33	227.03±62.22	1.95±2.67
Acenaphthylene	36.77±20.4	0±0	24.79±12.8	0±0
Acenaphthene	0±0	0±0	0±0	0±0.02
Fluorene	29.76±4.5	0±0	0±0	0±0
Phenanthrene	248.73±180.9	4.38±0.25	84.75±5.16	0±0
Anthracene	50.82±29.4	0±0	26.06±0.46	0±0
Fluoranthene	129.51±52	3.12±1.56	113.71±17.25	0±0
Pyrene	135.91±56.5	2.07±0.06	126.13±13.05	0±0
Benzo(a)fluorene	9.59±4.5	0±0	20.21±1.87	0±0
Benzo(b)fluorene	7.99±2.3	0±0	18.67±0.3	0±0
benzo(c)phenanthrene	3.2±0	0±0	20.21±1.87	0±0
Benzo(ghi)fluoranthene	76.75±18.1	1.06±1.49	264.45±4.5	0±0
Cyclopenta(c,d)pyrene	33.58±6.8	0±0	141.33±30.71	0±0
Benz(a)anthracene	22.38±4.5	0±0	125.88±17.76	0±0
Chrysene-Triphenylene	17.59±6.8	0±0	112±2.58	0±0
Benzo(b+j+k)fluoranthene	30.38±6.8	2.07±0.06	233.01±44.62	0±0
Benzo(a)fluoranthene	0±0	0±0	12.45±0.2	0±0
Benzo[e]pyrene	9.59±0	0±0	62.17±7.79	0±0
Benzo[a]pyrene	14.39±2.3	0±0	114.97±20.13	0±0
Perylene	1.6±2.3	9.11±12.88	21.75±4.05	0±0
Indeno[123-cd]fluoranthene	0±0	0±0	3.11±0.05	0±0
dibenzo(a,h)acridine	0±0	0±0	0±0	0±0
dibenzo(a,j)acridine	0±0	0±0	0±0	0±0
Indeno[123-cd]pyrene	11.19±2.3	0±0	93.18±20.49	0±0
Dibenzo(ah+ac)anthracene	0±0	1.01±1.43	10.87±2.02	0±0
Dibenzo(a,j)anthracene	0±0	0±0	7.76±2.07	0±0
Benzo(b)chrysene	0±0	0±0	7.76±2.07	0±0
Picene	0±0	0±0	9.3±4.25	0±0
Benzo(ghi)perylene	31.98±9	0±0	181.71±38.85	0±0
Anthanthrene	0±0	0±0	20.21±1.87	0±0
Dibenzo(a,l)pyrene	0±0	0±0	0±0	0±0
Coronene	8±2.3	0±0	62.17±7.79	0±0
Dibenzo(a,e)pyrene	0±0	0±0	6.22±0.1	0±0
Dibenzo(a,i)pyrene	0±0	0±0	0±0	0±0
Dibenzo(a,h)pyrene	0±0	0±0	0±0	0±0

Dibenzo(b,k)fluoranthene	0±0	0±0	18.64±4.1	0±0
Substituted PAHs				
2-methylnaphthalene	390.69±366.31	7.41±12.76	228.67±51.19	0±0
1-methylnaphthalene	116.37±117.58	3.16±4.23	58.61±14.42	0±0
2,6+2,7-dimethylnaphthalene	54.02±56.53	0±0	19.84±0.35	0±0
1,3+1,6+1,7dimethylnaphth	41.57±49.75	0±0	18.6±8.5	0±0
1,4+1,5+2,3-dimethylnaphth	9.59±13.57	0±0	0±0	0±0
1,2-dimethylnaphthalene	0±0	0±0	0±0	0±0
1,8-dimethylnaphthalene	0±0	0±0	0±0	0±0
1-ethyl-2-methylnaphthalene	0±0	0±0	0±0	0±0
2,3,5+I-trimethylnaphthalene	0±0	0±0	0±0	0±0
B-trimethylnaphthalene	4.45±4.52	0±0	0±0	0±0
A-trimethylnaphthalene	18.84±15.83	0±0	2.7±2.13	0±0
C-trimethylnaphthalene	4.45±4.52	0±0	0±0	0±0
1+2ethylnaphthalene	43.17±56.53	0±0	23.29±6.22	0.97±1.37
2-ethyl-1-methylnaphthalene	1.6±2.26	0±0	0±0	0±0
E-trimethylnaphthalene	1.6±2.26	0±0	1.57±2.23	0±0
2,4,5-trimethylnaphthalene	0±0	0±0	0±0	0±0
F-trimethylnaphthalene	6.4±4.52	0±0	1.57±2.23	0±0
1,4,5-trimethylnaphthalene	0±0	0±0	0±0	0±0
J-trimethylnaphthalene	0±0	0±0	0±0	0±0
A-Methylfluorene	12.79±9.04	0±0	0±0	0±0
B-Methylfluorene	0±0	0±0	0±0	0±0
1-Methylfluorene	6.4±4.52	0±0	3.11±0.05	0±0
2-methylphenanthrene	25.58±13.57	1.06±1.49	7.8±2.33	0±0
3-methylphenanthrene	38.03±20.35	1.18±1.56	22.91±4	1.96±0.04
2-methylanthracene	17.59±2.26	0±0	15.56±0.25	0±0
4,5-methylenephenanthrene	28.78±18.09	0±0	1.54±2.17	0±0
9-methylphenanthrene	27.18±20.35	0±0	4.65±2.13	0±0
1-methylphenanthrene	31.63±15.83	0.12±0.06	10.54±4.6	0±0
9-methylanthracene	0±0	0±0	0±0	0±0
A-dimethylphenanthrene	6.4±0	0±0	7.76±2.07	0±0
B-dimethylphenanthrene	4.8±2.26	0±0	3.11±0.05	0±0
1,7-dimethylphenanthrene	7.99±6.78	0±0	4.69±2.28	0±0
3,6-dimethylphenanthrene	4.8±6.78	0±0	4.69±2.28	0±0
D-dimethylphenanthrene	4.8±2.26	0±0	3.08±4.35	0±0
E-dimethylphenanthrene	4.45±0	0±0	1.17±0.05	0±0
C-dimethylphenanthrene	22.39±22.61	1.01±1.43	21.82±4.75	0±0
B-MePy/MeFl	17.59±2.26	0±0	32.66±1.67	0±0
1-MeFl+C-MeFl/Py	1.6±2.26	0±0	7.8±2.33	0±0
1+3-methylfluoranthene	7.99±6.78	0±0	9.3±4.25	0±0
4-methylpyrene	11.19±2.26	0±0	20.28±6.93	0±0
C-MePy/MeFl	14.39±6.78	0±0	35.81±2.78	0±0

D-MePy/MeFl	6.4±0	0±0	18.71±4.7	0±0
1-methylpyrene	6.4±0	0±0	12.48±4.6	0±0
3-methylchrysene	0±0	0±0	13.99±1.97	0±0
5+6-methylchrysene	0±0	0±0	3.11±0.05	0±0
7-methylbenzo(a)pyrene	0±0	0±0	1.54±2.17	0±0
Oxygenated PAHs				
Dibenzofuran	75.01±65.58	0±0	5.79±4.15	0±0
9-fluorenone	108.38±101.75	0.12±0.06	38.51±0.66	0±0
Xanthone	12.79±18.09	5.19±1.62	9.34±0.15	0±0
Acenaphthenequinone	0±0	0±0	0±0	0±0
Perinaphthenone	57.21±38.44	0.08±2.86	193.08±66.98	0±0
Anthraquinone	24.89±18.09	5.35±4.11	47.55±11.84	0±0
9-Anthraaldehyde	1.6±2.26	0±0	3.15±4.45	0±0
Benzanthrone	0±0	0±0	63.78±1.16	0±0
Benz(a)anthracene-7,12-dione	3.2±0	0±0	12.38±8.6	0±0
Phenyl PAHs				
3-methylbiphenyl	23.78±4.52	0±0	0±0	0±0
4-methylbiphenyl	18.15±6.78	0.32±2.74	5±6.42	2.95±1.48
2-phenylnaphthalene	20.79±11.31	0±0	24.9±0.4	0±0
Biphenyl	66.81±61.05	1.13±1.37	13.62±0.25	0±0
2-methylbiphenyl	10.15±18.09	0±0	0±0	10.69±9.47

Table 169: Individual gas-phase PAH compounds, expressed in ng/mile, for both test vehicles over the LA92 cycle

Compounds	**GDI_1**		**GDI_2**	
ng/mile	**Without GPF**	**With GPF**	**Without GPF**	**With GPF**
Non-substituted PAHs				
naphthalene	32881±18908	17010±8564	339292±184527	229738±172108
Acenaphthylene	262±140	16±5	10229±7255	801±663
Acenaphthene	172±104	39±47	852±67	346±383
Fluorene	210±127	23±21	1121±68	22±29
Phenanthrene	212±88	76±17	2572±597	98±12
Anthracene	22±5	6±0	418±79	9±1
Fluoranthene	0±0	0±0	337±43	0±0
Pyrene	4±0	6±2	436±38	17±4
Retene	0±0	0±0	0±0	3±1
benzo(a)fluorene	0±0	0±0	20±11	0±0
benzo(b)fluorene	0±0	0±0	14±2	0±0
benzo(c)phenanthrene	0±0	0±0	8±2	1±1

Benzo(ghi)fluoranthene	0±0	0±0	73±32	0±0
Cyclopenta(c,d)pyrene	0±0	0±0	12±17	0±0
Benz(a)anthracene	2±2	0±0	16±4	1±1
Chrysene-Triphenylene	0±0	0±0	5±2	0±0
Benzo(b+j+k)fluoranthene	2±2	0±0	3±0	1±1
Benzo(a)fluoranthene	0±0	0±0	0±0	0±0
Benzo[e]pyrene	0±0	0±0	0±0	0±0
Benzo[a]pyrene	0±0	0±0	0±0	0±0
Dibenzothiophene	5±2	4±3	14±6	2±0
Dibutyl phthalate	125±213	0±0	264±44	138±362
Substituted PAHs				
2-methylnaphthalene	8618±5479	15471511	390402±290615	157967±187511
1-methylnaphthalene	4725±2921	1110±1051	177406±118496	76477±81765
2,6+2,7-dimethylnaphthalene	680±402	14±23	25868±15530	3915±4876
1,3+1,6+1,7dimethylnaphth	1126±642	37±59	45875±28110	7461±9131
1,4+1,5+2,3-dimethylnaphth	332±206	18±3	11972±7127	1908±2311
1,2-dimethylnaphthalene	139±104	5±1	13285±12941	845±1047
1,8-dimethylnaphthalene	0±0	0±0	0±0	0±0
1-ethyl-2-methylnaphthalene	66±29	16±15	1573±1231	122±123
2,3,5+I-trimethylnaphthalene	112±45	0±0	2548±1271	207±158
B-trimethylnaphthalene	210±102	0±0	4395±2361	450±471
A-trimethylnaphthalene	249±54	0±0	6602±3779	682±740
C-trimethylnaphthalene	159±79	1±2	3600±2015	293±258
1+2ethylnaphthalene	693±387	76±104	24031±14764	8259±10185
2-ethyl-1-methylnaphthalene	4±5	0±0	206±80	29±38
E-trimethylnaphthalene	101±32	0±0	2023±1080	179±163
2,4,5-trimethylnaphthalene	129±45	19±0	1236±639	165±141
F-trimethylnaphthalene	65±45	0±0	1495±716	110±99
1,4,5-trimethylnaphthalene	4±5	4±3	303±196	7±7
J-trimethylnaphthalene	34±5	12±7	505±267	75±47
A-Methylfluorene	30±25	4±4	242±48	0±0
B-Methylfluorene	11±0	2±3	53±29	3±1
1-Methylfluorene	21±2	0±0	157±32	3±12
2-methylphenanthrene	5±2	1±1	126±9	4±0
3-methylphenanthrene	1±0	0±0	111±22	0±3
2-methylanthracene	0±0	0±0	81±12	0±0
4,5-methylenephenanthrene	17±5	3±1	179±25	5±1
9-methylphenanthrene	4±7	8±2	108±33	8±5
1-methylphenanthrene	0±0	2±2	129±42	9±1
9-methylanthracene	0±0	0±0	9±0	0±0
A-dimethylphenanthrene	0±0	0±0	42±7	0±0
B-dimethylphenanthrene	0±0	0±0	22±14	1±1
1,7-dimethylphenanthrene	0±0	0±0	34±25	0±0

3,6-dimethylphenanthrene	0±0	0±0	23±16	0±0
D-dimethylphenanthrene	0±0	0±0	26±2	6±3
E-dimethylphenanthrene	0±0	0±0	26±3	0±0
C-dimethylphenanthrene	0±0	0±0	82±23	2±3
B-MePy/MeFl	0±0	0±0	36±2	0±0
1-MeFl+C-MeFl/Py	0±0	0±0	14±2	0±0
1+3-methylfluoranthene	0±0	0±0	11±2	0±0
4-methylpyrene	2±2	1±1	16±4	0±0
C-MePy/MeFl	0±0	0±0	26±6	0±0
D-MePy/MeFl	0±0	1±1	5±2	0±0
1-methylpyrene	0±0	0±0	11±2	0±0
3-methylchrysene	0±0	0±0	0±0	0±0
5+6-methylchrysene	0±0	0±0	0±0	0±0
7-methylbenz(a)anthracene	0±0	0±0	0±0	0±0
7,12-dimethylbenz(a)anthracene	0±0	0±0	0±0	0±0
3-methylcholanthrene	0±0	0±0	0±0	0±0
7-methylbenzo(a)pyrene	0±0	0±0	0±0	0±0
Oxygenated PAHs				
Dibenzofuran	369±310	150±62	1426±220	314±303
9-fluorenone	38±11	86±22	655±130	46±8
Xanthone	2±2	31±10	73±8	16±5
Perinaphthenone	2±2	0±0	80±69	6±8
Anthraquinone	0±0	0±0	19±6	7±1
9-Anthraaldehyde	2±2	0±0	5±2	1±1
Phenyl PAHs				
Biphenyl	541±405	90±81	3882±57	2649±2415
3-methylbiphenyl	0±0	0±0	731±103	170±300
4-methylbiphenyl	0±0	0±0	684±62	83±77
Bibenzyl	0±0	0±0	0±0	0±0
2-phenylnaphthalene	2±2	5±2	106±11	6±0

Table 170: Individual particle-phase nitrated PAH compounds, expressed in ng/mile, for both test vehicles over the LA92 cycle

Compounds	**GDI_1**		**GDI_2**	
ng/mile	**Without GPF**	**With GPF**	**Without GPF**	**With GPF**
1-Nitronaphthalene	0.195±0.122	0±0	0.058±0.005	0±0
5-Methyl-1-nitronaphthalene	0.015±0.016	0.002±0.003	0.014±0.003	0.005±0.007
2-Nitronaphthalene	1.006±0.914	0±0	0.287±0.033	0±0
2-Nitrobiphenyl	0.07±0.046	0.001±0.002	0.016±0.005	0±0

2-Methyl-4-nitronaphthalene	0.049±0.07	0±0	0±0	0.014±0.019
1-Methyl-4-nitronaphthalene	0.035±0.023	0±0	0.005±0.01	0±0
1-Methyl-6-nitronaphthalene	0.101±0.065	0.008±0.012	0.041±0.001	0±0
3-Nitrobiphenyl	0.079±0.052	0±0	0.017±0.016	0±0
4-Nitrobiphenyl	0.075±0.076	0±0	0.136±0.245	0.033±0.099
1,3-Dinitronaphthalene	0±0	0.049±0.069	0±0	0.142±0.019
1,5-Dinitronaphthalene	0±0	0.004±0.006	0±0	0.003±0.004
5-Nitroacenaphthene	0.062±0.007	0.015±0.022	0.086±0.017	0.02±0.008
2-Nitrofluorene	0±0	0±0	0±0	0±0
4-Nitrophenanthrene	0±0	0±0	0±0	0±0
9-Nitroanthracene	0.218±0.041	0±0	0±0	0.086±0.122
9-Nitrophenanthrene	0.011±0.016	0±0	0.034±0.012	0±0
1,8-Dinitronaphthalene	0±0	0±0	0.013±0.018	0±0
3-Nitrophenanthrene	0.003±0.004	0±0	0.026±0.009	0±0
2-Nitrophenanthrene	0±0	0±0	0.01±0.014	0±0
2-Nitroanthracene	0±0	0±0	0±0	0±0
1-Nitrofluoranthene	0±0	0±0	0±0	0±0
7-Nitrofluoranthene	0±0	0±0	0±0	0±0
2-Nitrofluoranthene	0.02±0.058	0.073±0.133	0.173±0.125	0±0
3-Nitrofluoranthene	0±0	0±0	0±0	0±0
4-Nitropyrene	0.021±0.03	0±0	0.092±0.025	0.011±0.015
8-Nitrofluoranthene	0±0	0±0	0±0	0±0
1-Nitropyrene	0.118±0.042	0.041±0.034	0.222±0.016	0.068±0.016
2-Nitropyrene	0±0	0±0	0±0	0±0
2,7-Dinitrofluorene	0±0	0±0	0.352±0.228	0±0
2,7-Dinitrofluoen-9-one	0±0	0±0	0±0	0±0
7-Nitrobenz(a)anthracene	0±0	0±0	0.084±0.119	0±0
6-Nitrochrysene	0±0	0±0	0±0	0±0
3-Nitrobenzanthrone	0±0	0±0	0±0	0±0
1,3-Dinitropyrene	0±0	0±0	0±0	0±0
1,6-Dinitropyrene	0±0	0±0	0±0	0±0
1,8-Dinitropyrene	0±0	0±0	0±0	0±0
6a+1e-nitrobenzo(e)pyrene	0±0	0±0	0±0	0±0
3-Nitrobenz(e)pyrene	0±0	0±0	0±0	0±0

Table 171: Individual gas-phase nitrated PAH compounds, expressed in ng/mile, for both test vehicles over the LA92 cycle

Compounds	**GDI_1**		**GDI_2**	
ng/mile	**Without GPF**	**With GPF**	**Without GPF**	**With GPF**

1-Nitronaphthalene	0.9±0.078	0.489±0.309	5.372±1.256	0.582±0.113
5-Methyl-1-nitronaphthalene	0.117±0.035	0.033±0.014	0.263±0.073	0.052±0.031
2-Nitronaphthalene	2.127±1.529	0.737±0.825	7.326±0.63	0±0
2-Nitrobiphenyl	0.292±0.113	0.228±0.031	0.952±0.104	0.277±0.031
2-Methyl-4-nitronaphthalene	0±0	0±0	0±0	0±0
1-Methyl-4-nitronaphthalene	0.097±0.366	0±0	0±0	0±0
1-Methyl-6-nitronaphthalene	0.139±0.06	0.085±0.063	0.333±0.345	0.084±0.051
3-Nitrobiphenyl	0.036±0.142	0.062±0.022	0.235±0.159	0±0
4-Nitrobiphenyl	0.063±0.089	0±0	0.16±0.227	0.088±0.051
1,3-Dinitronaphthalene	0±0	0±0	0±0	0±0
1,5-Dinitronaphthalene	0±0	0±0	0.033±0.046	0±0
5-Nitroacenaphthene	0±0	0±0	0±0	0±0
2-Nitrofluorene	0.001±0.007	0±0	0.035±0.008	0.007±0.007
4-Nitrophenanthrene	0±0	0±0	0±0	0.025±0.036
9-Nitroanthracene	0.405±0.572	0.185±0.262	0.488±0.483	0.137±0.193
9-Nitrophenanthrene	0±0	0±0	0.017±0.024	0.018±0.025
1,8-Dinitronaphthalene	0±0	0±0	0.016±0.022	0±0
3-Nitrophenanthrene	0±0	0±0	0.011±0.015	0±0
2-Nitrophenanthrene	0±0	0±0	0±0	0±0
2-Nitroanthracene	0±0	0±0	0±0	0±0
1-Nitrofluoranthene	0±0	0±0	0±0	0±0
7-Nitrofluoranthene	0±0	0±0	0±0	0±0
2-Nitrofluoranthene	0±0	0±0	0.013±0.018	0±0
3-Nitrofluoranthene	0±0	0±0	0±0	0±0
4-Nitropyrene	0.043±0.061	0.012±0.017	0.029±0.041	0.017±0.024
8-Nitrofluoranthene	0±0	0±0	0±0	0±0
1-Nitropyrene	0±0	0.015±0.022	0.08±0.113	0.018±0.025
2-Nitropyrene	0±0	0±0	0±0	0±0
2,7-Dinitrofluorene	0±0	0±0	0±0	0±0
2,7-Dinitrofluoen-9-one	0±0	0±0	0±0	0±0
7-Nitrobenz(a)anthracene	0±0	0±0	0±0	0±0
6-Nitrochrysene	0±0	0±0	0±0	0±0
3-Nitrobenzanthrone	0±0	0±0	0±0	0±0
1,3-Dinitropyrene	0±0	0±0	0±0	0±0
1,6-Dinitropyrene	0±0	0±0	0±0	0±0
1,8-Dinitropyrene	0±0	0±0	0±0	0±0
6a+1e-nitrobenzo(e)pyrene	0±0	0±0	0±0	0±0
3-Nitrobenz(e)pyrene	0±0	0±0	0±0	0±0

Karavalakis et al. (2010) [Effects of low concentration biodiesel blends application on modern passenger cars. Part 3: Impact on PAH, nitro-PAH, and oxy-PAH emissions, Environmental Pollution] examined the PAH, nitro-PAH, and oxy-PAH emissions from a Euro 3 compliant, Renault Laguna 1.9 dCi passenger car when operated on diesel fuel and 5 different B10 blends. The vehicle was equipped with a common-rail diesel engine with exhaust gas recirculation (EGR). The exhaust aftertreatment comprised of a closed-coupled pre-catalyst and an underfloor main oxidation catalyst. The methyl esters were derived from soybean oil, used frying oil, palm oil, sunflower oil, and rapeseed oil and their blends tested in this study will be hereafter referred to as SME-10, UFOME-10, PME-10, SUME-10 and RME-10 respectively. Testing was conducted on the NEDC and the Artemis driving cycles (Urban, Road and Motorway cycles).

Each collected sample was extracted with dichloromethane in ultrasonic bath for 20 min. The extraction was repeated three times using 80 mL of the solvent each time. The extract was then concentrated by rotary evaporation to nearly 2 mL for further cleanup. The cleanup column (inner diameter, 1 cm) was filled with glass wool, 3 g of 6% deactivated silica gel, 2 g of 5% deactivated alumina and 0.5 g of anhydrous sodium sulphate. After loading the sample in the cleanup column, the column was washed firstly with 20 mL of n-hexane and then with 25 mL of the 30% CH_2Cl_2 in cyclohexane. Both fractions were reduced to 1 mL under a gentle stream of nitrogen for the analysis. The fraction of n-hexane was analyzed for the determination of CH_2Cl_2/cyclohexane for PAHs and their products. A gas chromatograph (GC) (Agilent 6890) with a mass spectrometric (MS) detector (Agilent 5975B) was used for the PAHs (Electron Ionization, EI) and nitro-PAHs analysis (Negative Chemical Ionization, NCI). The GC–MS was equipped with a capillary column (HP 5 MS, 30 m × 0.25μm × 0.25 mm, Agilent); an auto sampler (Agilent 7673A), with an injection volume of 1 μL, pulsed splitless injection. For PAHs analysis, the injector temperature was set at 310 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 55 to 325 °C at 20 °C min^{-1}. For nitro-PAHs and oxy-PAHs analysis the injector temperature was set at 280 °C and the ion source temperature at 280 °C. Oven operating temperature ranged from 60 to 200 °C at 20 °C min^{-1}, and from 200 °C to 300 °C at 5 °C min^{-1}. The oven remained at this temperature for 10 min. The masses of PAH, nitro-PAHs and oxy-PAHs ions were determined by using the scan mode for pure standards of these compounds. Quantification was performed by using the selected ion monitoring (SIM) mode. The efficiencies of the studied PAHs ranged from 85.0% to 105.0%. For the studied nitro-PAHs the efficiencies ranged from 75.0% to 93.0% and for the oxy-PAHs from 66.5% to 89.5%. The repeatability of the PAHs ranged from 2.7% to 5.4%. For the n-PAHs the repeatability ranged from 3.2% to 8.4% and for the oxy-PAHs from 8.7% to 11.1%.

Table 172: Individual PAH, nitro-PAH, and oxy-PAH emissions for the test fuels over the cold-start UDC and EUDC

PAH emissions, µg/km	**UDC (cold-start)**						**EUDC**					
	Diesel	**SME-10**	**UFOME-10**	**PME-10**	**SUME-10**	**RME-10**	**Diesel**	**SME-10**	**UFOME-10**	**PME-10**	**SUME-10**	**RME-10**
Phenanthrene	9.42	12.2	10.58	9.86	11.43	10.73	6.31	7.75	5.33	5.76	5.33	4.71
Anthracene	9.19	11.65	9.54	9.4	10.96	9.91	5.86	6.38	5.31	5.13	5.18	4.67
Fluoranthene	8.48	9.89	9.54	9.92	9.58	9.49	5.44	3.69	2.86	3.88	4.96	3.7
Pyrene	7.28	8.78	7.49	7.78	7.78	8.51	4.74	4.18	3.3	2.88	3.78	3.54
Chrysene	4.86	4.27	3.12	4.96	4.17	3.79	2.88	2.77	2.55	3.35	2.95	2.59
Benzo[*b*,*k*]fluoranthenes	2.77	2.45	2.38	2.48	2.42	2.5	1.76	1.69	1.44	1.53	1.55	1.75
Indeno[1,2,3-*c*,*d*]pyrene	1.82	1.07	1.03	0.97	1.11	1.22	–	–	–	–	–	–
Dibenzo[*a*,*h*]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
Benzo[*g*,*h*,*i*]perylene	1.57	0.87	0.81	0.92	0.94	1.23	–	–	–	–	–	–
nitro-PAH emissions, ng/km												
3-nitro-fluoranthene	–	–	–	–	–	–	–	–	–	–	–	–
1-nitro-pyrene	3.52	3.21	3.13	3.28	3.46	3.4	1.36	1.22	1.13	1.05	1.27	1.18
7-nitro-benzo[*a*]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
6-nitro-benzo[*a*]pyrene	5.19	5.08	4.96	4.82	5.13	5.02	2.18	2.06	1.92	1.83	2.14	1.95
Oxy-PAH emissions, ng/km												
1-Naphthaldehyde	–	–	–	–	–	–	–	–	–	–	–	–
9-Fluorenone	1.92	1.62	1.47	1.37	1.46	1.29	0.73	0.59	0.32	0.28	0.41	0.36
9-Phenanthrenecarboxaldehyde	3.31	3.12	3.09	3.22	3.17	3.2	2.41	2.08	1.72	1.91	2.01	1.82
Benzanthrone	3.67	4.49	4.31	4.17	4.52	4.4	1.96	2.52	2.59	2.32	2.22	2.61

Table 173: Individual PAH, nitro-PAH, and oxy-PAH emissions for the test fuels over the hot-start UDC and Artemis Urban

PAH emissions, µg/km	**UDC (hot-start)**						**Artemis urban**					
	Diesel	**SME-10**	**UFOME-10**	**PME-10**	**SUME-10**	**RME-10**	**Diesel**	**SME-10**	**UFOME-10**	**PME-10**	**SUME-10**	**RME-10**
Phenanthrene	5.96	6.19	6.16	6.21	6.64	6.53	9.34	10.75	8.68	8.37	8.6	8.56
Anthracene	4.95	5.78	5.24	5.98	5.69	5.42	8.55	9.24	7.97	6.79	8.62	7.81
Fluoranthene	4.47	5.05	4.88	4.64	4.71	4.5	8.02	9.58	6.67	4.53	6.73	7.55
Pyrene	3.87	5.35	4.21	3.44	4.19	4.25	5.09	6.18	5.2	4.23	5.46	5.66
Chrysene	4.15	2.93	2.79	2.75	2.98	2.83	3.75	2.5	2.46	3.86	3.48	2.78
Benzo[*b*,*k*]fluoranthenes	2.38	2.23	1.77	1.98	2.09	2.02	2.33	2.3	2.23	2.17	2.26	2.15
Indeno[1,2,3-*c*,*d*]pyrene	–	–	–	–	–	–	–	–	–	–	–	–
Dibenzo[*a*,*h*]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
Benzo[*g*,*h*,*i*]perylene	–	–	–	–	–	–	–	–	–	–	–	–
nitro-PAH emissions, ng/km												
3-nitro-fluoranthene	–	–	–	–	–	–	–	–	–	–	–	–
1-nitro-pyrene	2.69	2.41	2.32	2.27	2.48	2.33	3.15	2.87	2.71	2.58	2.82	2.76
7-nitro-benzo[*a*]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
6-nitro-benzo[*a*]pyrene	4.12	3.81	3.56	3.47	3.52	3.48	4.21	4.07	3.52	3.28	3.91	3.73
Oxy-PAH emissions, ng/km												
1-Naphthaldehyde	–	–	–	–	–	–	–	–	–	–	–	–
9-Fluorenone	0.86	0.77	0.53	0.45	0.73	0.48	0.52	0.65	0.71	0.83	0.54	0.79
9-Phenanthrenecarboxaldehyde	3.38	2.92	3.21	2.82	3.27	3.11	3.7	3.53	2.96	3	2.92	3.41
Benzanthrone	3.12	4.01	3.77	3.82	4.12	4.17	3.67	3.21	3.09	3.14	3.26	3.19

Table 174: Individual PAH, nitro-PAH, and oxy-PAH emissions for the test fuels over Artemis Road and Artemis Motorway cycles

PAH emissions, µg/km	**Artemis road**						**Artemis motorway**					
	Diesel	**SME-10**	**UFOME-10**	**PME-10**	**SUME-10**	**RME-10**	**Diesel**	**SME-10**	**UFOME-10**	**PME-10**	**SUME-10**	**RME-10**
Phenanthrene	5.94	5.39	4.22	4.91	5.25	4.32	3.43	3.84	2.91	2.11	2.95	2.47
Anthracene	5.76	6.96	4.09	3.53	4.61	4.12	3.33	3.34	2.61	1.93	3.09	1.98
Fluoranthene	4.85	3.06	3.7	2.84	3.72	3.13	2.52	2.1	2.98	1.66	1.54	1.96
Pyrene	3.64	3.85	2.62	2.28	2.1	2.97	2.61	2.77	1.33	1.19	1.43	1.85
Chrysene	2.67	1.78	1.7	1.13	1.66	1.42	1.12	0.84	0.58	0.46	0.56	0.66
Benzo[*b*,*k*]fluoranthenes	0.86	0.61	0.59	0.62	0.48	0.52	0.42	0.31	0.35	0.29	0.23	0.28
Indeno[1,2,3-*c*,*d*]pyrene	–	–	–	–	–	–	–	–	–	–	–	–
Dibenzo[*a*,*h*]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
Benzo[*g*,*h*,*i*]perylene	–	–	–	–	–	–	–	–	–	–	–	–
nitro-PAH emissions. ng/km												
3-nitro-fluoranthene	–	–	–	–	–	–	–	–	–	–	–	–
1-nitro-pyrene	1.52	1.21	1.17	1.11	1.32	1.28	1.07	0.93	0.52	0.47	0.86	0.71
7-nitro-benzo[*a*]anthracene	–	–	–	–	–	–	–	–	–	–	–	–
6-nitro-benzo[*a*]pyrene	2.78	2.12	2.01	1.94	2.23	2.18	1.2	0.88	0.71	0.67	0.79	0.81
Oxy-PAH emissions. ng/km												
1-Naphthaldehyde	–	–	–	–	–	–	–	–	–	–	–	–
9-Fluorenone	0.26	0.14	0.21	0.32	0.29	0.3	0.19	0.32	0.41	0.27	0.44	0.52
9-Phenanthrenecarboxaldehyde	1.38	1.26	0.97	0.82	1.03	0.9	0.77	0.65	0.51	0.6	0.59	0.63
Benzanthrone	1.19	1.01	0.96	0.87	1.12	0.79	0.87	0.71	0.52	0.62	0.72	0.68

Aakko-Saksa et al. (2014) [Ethanol, Isobutanol, and Biohydrocarbons as Gasoline Components in Relation to Gaseous Emissions and Particulate Matter, Environmental Science and Technology] studied PAH emissions from three cars using different biofuels at a temperature of -7 °C. Five fuels were used, including a fossil gasoline fuel, a E10 fuel, a E22 blend (E10 and renewable gasoline), an iso-butanol blend (iBu14), a E30, and a E85. The vehicles used were a multipoint fuel injection (MPFI), a direct injection spark ignition (DISI), and flex fuel vehicles (FFV). The MPFI and DISI cars were model year 2010, whereas the FFV was model year 2006. Tests were conducted on a chassis dynamometer in a climatic test cell at −7 °C using a driving cycle according to the Directive 70/220/EEC and its amendments. The driving cycle was 11.007 km in total.

PM was collected with a high-capacity collection system. This includes a dilution tunnel (i.d. = 265 mm), a sample probe (i.d. = 80 mm), two filter holders in parallel (i.d. = 142 mm), a blower (Siemens ELMO-G), a flow meter (Bronkhorst F-106C1-HD-V-12), and a controller (Stafsjö MV-E-80-P-TY-AC100-PN10). The sample flow in these measurements was 700–850 L/min. The filter type was Fluoropore 3.0 μm FSLW. The microbalance was a Sartorius SE2-F.

Soxhlet extraction with dichloromethane was conducted for the filter samples. Several filters were combined for each extraction batch, and an equivalent number of filters was used for the control sample. Filters were protected from light during and after the Soxhlet treatment. The Soxhlet apparatus was cleaned by solvent extraction (6 h). An internal standard was added, and samples were Soxhlet-extracted for 16 h.

A total of 30 individual PAHs were analyzed from the Soxhlet-extracted PM samples using GC/SIM-MS following purification of the extract by liquid chromatography. An EPA 610 PAH mixture from Supelco and PAH-MIX 63 from Ehrensdorf were used to check the calibration standard, which was made from pure solid substances of each PAH compound determined. The detection limit was 0.1 μg of component/sample, which represents approximately 0.04 μg/km for the MPFI car and 0.08 μg/km for the DISI and FFV cars over the European test. Focus was placed on seven PAHs defined in a list of mobile-source air toxics by the U.S. EPA (2007): benzo(a)anthracene (BaA, group 2B), chrysene (Chr, group 2B), benzo(b)fluoranthene (BbF, group 2B), benzo(k)fluoranthene (BbF, group 2B), benzo[a]pyrene (BaP, group 1), 7,12-dimethylbenz[a]anthracene, and indeno(1,2,3-cd)pyrene (IP, group 2B).

Table 175: PAH emissions (µg/km) for the test vehicles on all fuels

	Benzo[a]anthracene	7,12-dimethylbenz[a]anthracene	Chrysene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	Indeno[1,2,3-cd]pyrene
MPFI Car							
Base	1.1	0.3	0.5	1.2	0.4	1.2	0.6
E10	1.4	0.2	0.8	1.5	0.4	1.6	0.9
E10+R	1.3	0.2	0.7	1.9	0.5	2.0	0.9
iBu	2.1	0.3	1.3	2.6	0.7	2.4	1.0
DISI Car							
Base	16.1±0.2	0.4±0.4	9.2±0.2	22.3±0.6	6.1±0.3	20.4±0.3	11.5±0.9
E10	11.1±1	0.7±0.1	6.6±0.8	17±1.9	5±0.4	14.1±0.6	8.9±1.3
E10+R	11.4±1.5	0.7±0	6.7±0.7	18±2.6	4.7±0.5	14.7±1.2	8.4±0.8
iBu	10.2±0.7	0.6±0	5.8±0.3	15.1±1.1	4±0.3	13.4±1.6	8.4±0.3
FFV							
Base							
E10	1.7	0	0.9	2.3	0.6	1.9	0.9
E10+R	2.3	0	1.3	3.1	0.8	2.5	1.3
iBu	2.7	0	1.4	3.4	1	3	1.3
E30	2.2	0	1.1	2.5	0.7	2.6	1.4
E85	2.7	0	1.4	4	1.1	7	2.9

Wei et al. (2015) [Emission of polycyclic aromatic hydrocarbons from different types of motor vehicles' exhaust, Environmental Earth Sciences] characterized the vapor- and particle-phase PAH emissions from a gasoline and a diesel passenger car. A 2000 model year Nanjing Iveco (4 cylinders, 76 kW maximum power at 3600 rpm, 245 Nm maximum torque at 1900 rpm, and 4000 kg weight), and a 2002 model year Chang'an minibus (4 cylinders, 29 kW maximum power at 6000 rpm, 57 Nm maximum torque at 3500 rpm, and 870 kg weight) were employed in chassis dynamometer test. All emission tests were performed with the original configuration of the vehicle's exhaust system. To simulate the real-world vehicle running condition, the chassis dynamometer was used to simulate vehicle acceleration, deceleration, uniform speed and idle conditions.

Sample extraction and cleanup were carried out according to Method 3540C and Method 3630C published by US EPA. After extraction and cleanup, samples were concentrated and adjusted to 1 mL volume for analysis. PAHs analysis was performed by reversed-phase high-performance liquid chromatography (HPLC, Waters). The HPLC system was equipped with two model Waters515 pumps, a model LC-1250 GBC fluorescence spectrophotometer and a Waters temperature controller to maintain the column temperature at 30 °C. For the separation of the PAHs a NUCLEOSILR 100-5 C18 PAH column was used (MACHREY-NAGEL, Germany).

The mobile phase used in this study was consisted of two solvent mixtures: Mixture A—100 % water; and Mixture B—100 % acetonitrile. The gradient program was operated at 50 % A/50 % B mixture for 25 min, followed by a linear gradient to 100 % mixture B for 20 min and held in 100 % acetonitrile for 5 min. All analysis was kept at a constant flow of 1.0 mL min^{-1}. The UV detector was set at the wavelength of 260 nm throughout the run. Identification of PAHs was based on retention time and the ultraviolet spectra of PAH standards and the quantification was performed by the external standard method.

Table 176: PAH emissions from the gasoline and diesel vehicles

PAHs species	**Concentrations (μg m^{-3})**							
	Acceleration		**Deceleration**		**Uniform speed**		**Idle**	
	Diesel vehicle	**Gasoline vehicle**	**Diesel vehicle**	**Gasoline vehicle**	**Diesel vehicle**	**Gasoline vehicle**	**Diesel vehicle**	**Gasoline vehicle**
Gaseous-phase PAHs								
Naphthalene	9.485	6.842	5.340	2.836	6.473	1.843	4.824	6.935
Acenaphthylene	7.915	2.637	9.840	2.196	9.818	1.676	8.833	1.624
Acenaphthene	12.612	3.601	3.165	1.646	2.027	2.179	5.909	2.166
Fluorene	13.368	2.806	12.567	2.460	8.310	1.921	10.137	2.218
Phenanthrene	8.901	6.152	3.722	4.462	7.301	2.583	14.136	4.031
Anthracene	10.343	1.474	2.498	2.403	4.740	1.943	8.952	3.718
Fluoranthene	12.339	2.975	2.067	1.689	3.295	1.143	14.189	2.006
Pyrene	2.822	0.222	0.634	0.278	6.109	0.303	3.783	0.381
Chrysene	4.711	3.311	0.854	2.946	2.684	1.889	3.154	0.921
Benzo[a]anthracene	7.014	0.531	0.621	0.269	0.838	0.762	6.806	1.189
Benzo[b]fluoranthene	1.297	0.498	2.631	0.217	1.211	0.349	1.972	0.266
Benzo[k]fluoranthene	1.573	2.758	0.477	0.971	1.233	1.182	1.914	0.853
Benzo[a]pyrene	0.595	0.169	0.132	0.135	0.215	0.213	0.612	0.092
Dibenz[a,h]anthracene	0.617	1.060	0.303	0.789	1.096	1.274	0.700	0.485
Indeno[1,2,3-cd]pyrene	0.729	0.781	0.205	0.578	0.563	0.658	0.592	0.317
Benzo[ghi]perylene	0.622	0.737	0.293	0.381	0.539	1.162	0.559	0.257
Total gaseous PAHs	94.943	36.554	45.349	24.256	56.452	21.08	87.072	27.459
Solid-phase PAHs								
Naphthalene	8.836	6.142	3.526	0.808	1.053	0.537	3.080	3.070
Acenaphthylene	7.697	2.152	8.782	1.258	6.358	0.824	8.140	0.776
Acenaphthene	9.838	1.762	2.388	1.026	1.660	0.696	3.998	0.830
Fluorene	5.091	1.948	8.870	2.052	4.807	1.606	8.449	1.069
Phenanthrene	10.968	4.666	8.112	4.352	4.135	2.279	11.513	3.761

Anthracene	5.302	0.941	1.525	4.968	1.301	0.361	2.672	0.727
Fluoranthene	9.465	2.599	3.217	0.943	2.441	0.898	10.763	1.184
Pyrene	2.473	0.202	4.324	0.148	0.419	0.244	1.735	0.781
Chrysene	9.139	2.637	4.092	1.753	1.141	1.174	2.752	1.474
Benzo[a]anthracene	9.759	2.441	3.808	0.827	1.304	1.162	4.570	1.618
Benzo[b]fluoranthene	9.766	0.829	3.082	0.528	1.909	0.499	2.330	0.438
Benzo[k]fluoranthene	6.591	2.599	3.072	1.066	1.324	1.286	2.489	1.286
Benzo[a]pyrene	1.244	0.182	0.526	0.212	0.279	0.234	0.679	0.678
Dibenz[a,h]anthracene	4.156	1.489	1.417	1.136	0.747	0.646	0.782	0.710
Indeno[1,2,3-cd]pyrene	2.693	0.866	1.125	0.523	0.599	0.739	0.604	0.677
Benzo[ghi]perylene	2.608	0.815	0.818	0.401	0.596	1.425	0.632	0.498

Maikawa et al. (2016) [Murine precision-cut lung slices exhibit acute responses following exposure to gasoline direct injection engine emissions, Science of the Total Environment] investigated the gas-phase and particle-phase PAH emissions from a gasoline direct injection (GDI) engine (2012 Ford Focus, 2.0L displacement) operated at conditions equivalent to vehicle highway cruise conditions.

Particulate matter from the GDI engine exhaust was diluted by a Dekati Fine Particle Sampler (FPS-4000, Dekati Inc., dilution ratio = 15) and sampled through a PM2.5 cyclone onto a filter pack. Briefly, the filter pack consisted of a pre-fired 47 mm quartz filter (Pall Corporation) and a XAD-4 coated quartz filter known as a sorbent-impregnated filter (SIF). Flow through the filter pack was 26 L/min over a 20 min sampling time. Immediately following collection, all quartz filters and SIFs were stored in 47 mm petri dishes (Pall Analyslide), placed in an airtight container, and kept in a freezer (< -4 °C).

Prior to extraction, all filters were spiked with an isotopically-labelled internal standard mixture. Samples were extracted within two weeks of collection using high-pressure liquid chromatography grade dichloromethane under mild sonication in an ultrasonic bath maintained at room temperature. Extracts were filtered through pre-cleaned glass wool and sodium sulphate and then concentrated under a gentle stream of nitrogen. Concentrated extracts were analyzed by a gas chromatography mass spectrometry system (Agilent GC-6890 N plus MSD-5973 N) fitted with a HP-5MS column (30 m, 0.25 mm diameter, 0.25 μm thickness). Concentrations were assessed using a five-point standard curve of pure national compound standards, ranging from 20 to 1000 pg/μL for each PAH congener. PAH molecular geometry was extracted from the NIST Polycyclic Aromatic Hydrocarbon Index.

Table 177: GDI engine exhaust PAH emissions

PAH phase	***Particle phase***		***Gas phase***		**Particle & gas phases**	
Sampling media	***Quartz filter***		***Backup sorbent impregnated filter***		***Quartz and backup filter total***	
PAH concentration (ng m^{-3})	***Mean***	***SD***	***Mean***	***SD***	***Mean***	***SD***
Low molecular weight PAHs						
Acenaphthylene	4.2	0.1	228	78.9	232	78.9
Acenaphthene	1.1	0.6	60.4	27.1	61.6	27.1
Fluorene	3.2	0.2	23.4	14.9	26.6	14.9
Phenanthrene	18.7	3.4	547	120	565	120
Anthracene	11.4	3.4	299	51.1	310	51.2
High molecular weight PAHs						
Fluoranthene	39.1	16.3	48.3	22.8	87.4	28.0
Pyrene	50.9	8.1	73.4	34.7	124	35.6
Benzo[*a*]anthracene	24.9	6.5	0.2	0.0	25.2	6.5
Chrysene	16.3	4.2	0.2	0.0	16.4	4.2
Benzo[*b*]fluoranthene	10.8	2.7	0.2	0.0	11.0	2.7
Benzo[*k*]fluoranthene	7.7	1.9	0.1	0.0	7.8	1.9
Benzo[*a*]pyrene	10.2	3.1	0.3	0.1	10.4	3.1
Indeno[1,2,3-*cd*]pyrene	8.4	3.2	0.1	0.0	8.5	3.2
Dibenz[*a*,*h*]anthracene	1.2	0.4	0.0	0.0	1.3	0.4
Benzo[*ghi*]perylene	11.6	4.6	0.2	0.0	11.7	4.6

Luo et al. (2015) [Size distribution, chemical composition and oxidation reactivity of particulate matter from gasoline direct injection (GDI) engine fueled with ethanol-gasoline fuel, Applied Thermal Engineering] studied the PAH emissions from a GDI engine fuelled with gasoline and E10 fuels. The engine tests were conducted on a 2.0-L, four-cylinder, turbocharged GDI engine with a wall-guided injection system and an underfloor TWC. Experiments were conducted at low speed (1500 rpm) and high speed (3000 rpm) at four engine loads (corresponding to BMEP of 2.1 bar, 5.3 bar, 10.6 bar and 14.2 bar, respectively).

A two-stage ejection dilutor manufactured by Dekati was adopted to dilute the exhaust samples. The PM samples were collected downstream of primary dilutor with a quartz filter (Whatman Model 1851-047). Each sampling proceeded for 20 min, with a sampling flow rate of 40 L min^{-1}. The filters were dried at 550 °C for 8 h before use. For PAH analysis, PM samples were extracted ultrasonically in dichloromethane. The solution was then filtered and concentrated with N-EVAP. The organic extracts were analyzed using gas chromatography (GC, Agilent 7890A system) with an Agilent 19091S-433 column (30 m, 250 μm, 0.25 μm) and mass spectrometer (MS, Agilent 5975C) operated in electron impact (EI) mode. For the GC–MS analyses, the column temperature was held at 50 °C for 2 min, raised to 200 °C at 20 °C min^{-1}, and then raised to 320 °C at 8 °C min^{-1}. The carrier gas was helium with a flow rate of 1 mL min^{-1}.

Table 178: PAH mass concentrations in different operation conditions with gasoline and E10

PAH compounds	**1500 rpm, ng/mL**			**3000 rpm, ng/mL**		
	Gasoline	**E10**	**Changes, %**	**Gasoline**	**E10**	**Changes, %**
Naphthalene	126.49	142.57	12.70	222.69	262.93	18.07
Acenaphthylene	55.62	60.62	8.99	104.45	135.96	30.16
Acenaphthene	51.84	49.96	−3.61	79.37	90.13	13.57
Fluorene	77.45	64.04	−17.32	99.35	94.12	−5.26
Phenanthrene	110.89	103.51	−6.65	136.29	158.80	16.51

Anthracene	47.47	49.12	3.47	47.99	53.63	11.76
Fluoranthene	105.72	106.13	0.38	161.86	48.42	−70.09
Pyrene	248.67	266.69	7.25	536.87	501.63	−6.56
Benz[a]anthracene	52.26	50.27	−3.82	52.60	48.49	−7.81
Chrysene	49.06	48.33	−1.48	50.69	49.70	−1.95
Benzo[b]fluoranthene	43.03	41.10	−4.47	41.78	59.09	41.42
Benzo[k]fluoranthene	39.50	38.91	−1.49	42.52	39.86	−6.24
Benzo[a]pyrene	44.34	43.60	−1.65	44.85	46.18	2.98
Dibenz[a,h]anthracene	0.00	0.00	-	0.00	45.63	-
Benzo[g,h,i]perylene	0.00	0.00	-	0.00	58.02	-
Indeno[1,2,3-cd]pyrene	40.36	39.26	−2.74	39.59	37.85	−4.40

5. Critical Review on the Sampling and Analysis of PAH

The first requirement of any sampling protocol is that the sample taken is representative of the matrix from which it has been taken and remains unchanged prior to its analysis. For PAH analysis, the situation is very complicated because a wide range of individual compounds is being samples, each exhibiting unique chemical and physical properties and each of which has the possibility of undergoing further reactions over time.

There are, at present, no standard procedures or methodologies for the sampling of PAHs from vehicle or engine exhaust. There are, however, recommended procedures available for the collection of gas-phase and particulate-phase PAHs, which can be used to address exhaust PAH emissions. Historically, the analysis of PAH emissions is based on chromatographic techniques, with an overall analytical approach of extraction, fractionation, and end analysis. A wide range of techniques is available for all three phases of this approach. To complicate matters further, fractionation and isolation techniques are dependent on the PAH of interest and the end analysis being used.

Sampling methods for PAH are generally divided between filters (for particulate-phase PAHs) and adsorbents (gas-phase PAHs), or a combination of both. Filters are widely used for all types of particulate analysis and have historically been the first approach for PAH analysis. For exhaust sampling, legislation for diesel and gasoline particulate measurement has provided a convenient sampling point for particulate-bound PAHs. Some of the filters used to collect the particulate phases include glass fiber filters, quartz fiber filters, cellulose filters or Teflon filters. Glass fiber filters are the most frequently employed collection devices for particle-phase PAHs. The target PAHs mainly include the 16 priority PAHs and their nitrated and oxygenated derivatives but are occasionally extended to additional PAHs. In a typical sampling train, the particulate phase is first trapped on a filter and the gaseous phase in trapped on a solid adsorbent located downstream from the filter. For the gaseous phase PAHs, sampling is performed with XAD resins and/or polyurethane foams. The sampling system is equipped with glass cartridges containing either XAD resin only or XAD resin sandwiched between two polyurethane foam (PUF) plugs. Other methods of collection, such as denuders or cryogenic samplers are also possible, but less popular for on-road and off-road engine exhaust sampling.

These sampling procedures have also been shown to be affected by several sampling artifacts (McMurry, 2000). In the particulate phase, positive artifacts (over-estimation of the particle phase concentrations) are mainly due to sorption of gaseous compounds on the filter, while negative artifacts (underestimation of the particle phase concentrations) result from the volatilization of particulate PAH from the filter (McMurry, 2000; Goriaux et al., 2006). Moreover, PAH trapped on the filter medium may undergo continuing chemical reactions on the filter surface, including chemical degradations of PAHs by oxidizing compounds such as nitrogen oxides, hydroxyl radicals, halogens, nitric acid, hydrogen peroxide, and ozone may occur during sampling (Ravindra et al., 2008; Tsapakis and Stephanou, 2003; Schauer et al., 2003). To reduce artifacts induced by conventional samplers employed in the vast majority of vehicle/engine exhaust studies, denuder sampling devices are used. The denuder sampler systems are designed to trap the gas-phase on a solid sorbent coated on the surface of the trap prior to collecting the particulate-phase on a filter (Goriaux et al., 2006; Liu et al., 2014). This methodology avoids the phenomenon of adsorption of the gas-phase on the filter and reduces the desorption artifact by collecting the volatilized fraction on a sorbent cartridge placed downstream from the filter.

Prior to emissions sampling, the filters and the glass cartridges are pre-cleaned and pre-dried and wrapped with aluminum foil to minimize any interferences and contamination. Usually, this process involves using distilled water, methanol, dichloromethane, and a mixture of acetone plus normal hexane. The extraction process can be performed either using a self-acting Soxhlet apparatus, microwave extraction, an ultrasonic extractor or an accelerated solvent extraction system. The most common (and cheaper) method is the Soxhlet extraction, where the cartridges and filters are placed in a Soxhlet extractor with a mixture of n-hexane and dichloromethane in a 1:1 v/v ratio. The extraction process takes about 24 hours. Following the extraction on process is the concentration process, whereby the extract is purged to about 2 mL using pure nitrogen then undergoes cleanup process. On the other hand, microwave extraction uses hexane: acetone (1:1), while accelerated extraction uses toluene, dichloromethane or a 1:1 mixture of hexane: dichloromethane, and ultrasonic extraction uses toluene and dichloromethane as the solvents (Pandey et al., 2011; Cheruiyot et al., 2015).

For PAH analysis process, there is a cleanup process involved, where pollutants that might co-elute with PAHs are removed. Deactivated silica is placed in a cleanup column with glass wool placed at the bottom to hold it in place. Usually the silica is wet using deionized water then topped up with a few grams of anhydrous sodium sulfate. The elution solvent is hexane and the eluate is concentrated using nitrogen (Cheruiyot et al., 2015).

Typically, high-performance liquid chromatography (HPLC) with fluorescence detection and gas chromatography (GC) coupled with mass spectroscopy (MS) techniques are used for the successful quantification of PAHs. Other methods include thin layer chromatography (TLC), gel permeation chromatography (GPS), or liquid chromatography (LC). Detectors used with these methods include fluorescence, ultra-violet (UV), photoionization detector (PID), flame ionization detector (FID), or MS. The GC/MS technique has been the most common analytical separation mechanism for the analysis of PAHs in engine exhaust. The preference for GC over other systems (e.g., HPLC) has been demonstrated by such factors as its greater selectivity, resolution, and sensitivity (Poster et al., 2006). For the GC/MS method, scan mode is employed to determine the primary and secondary ions for PAHs, while the actual quantification is done using selective ion monitoring mode. The selective ion monitoring mode offers discrete monitoring and lower detection limits compared to full scan modes (Poster et al., 2006).

References

Cheruiyot et al., An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient air. Aerosol and Air Quality Research 2015, 15, 2730-2762.

Goriaux, et al. Field comparison of PAH measurements using a low flow denuder device and conventional sampling systems. Environmental Science and Technology 2006, 40, 6398-6404.

McMurry P.H. A review of atmospheric aerosol measurements. Atmospheric Environment 2000, 34, 1959-1999.

Liu et al. Investigation on sampling artifacts of particle associated PAHs using ozone denuder systems. Front. Environ. Sci. Eng. 2014, 8, 284-292.

Pandey et al. Review of techniques for the determination of polycyclic aromatic hydrocarbons in air. Trends Anal. Chem. 2011, 30, 1716-1739.

Poster et al. Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: A critical review of gas chromatographic (GC) methods. Analytical and Bioanalytical Chemistry 2006, 386, 859-881.

Ravindra et al. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment 2008, 42, 2895-2921.

Schauer et al. Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation and sampling artifacts. Environmental Science and Technology 2003, 37, 2861-2868.

Tsapakis, M., Stephanou, E.G. Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling. Atmospheric Environment 2003, 37, 4935-4944.