

evaluation of automotive polycyclic aromatic hydrocarbon emissions

Prepared for the CONCAWE Automotive Emissions Management Group by its
Special Task Force FE/STF-12:

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Brussels
June 2005

ABSTRACT

CONCAWE has measured PAH emissions from a range of vehicles and fuels. For diesel vehicles, the relationship between fuel poly-aromatics content and PAH in exhaust emissions has been examined. The programme focused on the US EPA's Priority Pollutant list of 16 polycyclic aromatic hydrocarbons (PAH) and both particulate-bound and vapour phase PAH were measured.

In older technology diesel vehicles, reducing fuel poly-aromatics content gave lower PAH emissions, although reducing fuel poly-aromatics content even to zero would not eliminate PAH emissions, as a significant proportion of the total PAH emissions is combustion derived.

The improvements with advanced emissions control systems were impressive. Modern three-way catalyst (TWC) gasoline cars all gave very low PAH emissions. In the newer technology diesel vehicles with effective exhaust after-treatment, either oxidation catalysts or diesel particulate filters, PAH emissions were so low that there was no longer any sensitivity to fuel poly-aromatics content. The advances in exhaust after-treatment, which are being implemented for the control of total hydrocarbon and particulate emissions, are clearly effective in also controlling PAH emissions.

KEYWORDS

Automotive polycyclic aromatic hydrocarbons, PAH, aromatics content, benzo(a)pyrene (BaP), mono-aromatics, poly-aromatics, di-aromatics, tri-aromatics, gasoline, diesel, light-duty vehicles, heavy-duty engines, emissions, 16 EPA PAH species, exhaust PAH, fuel poly-aromatics

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SUMMARY

The 16 polycyclic aromatic hydrocarbons (PAH) defined by the US Environmental Protection Agency (EPA), have been measured in automotive exhaust emissions from a range of vehicles and fuels in a 2-phase programme. Both particulate-bound and vapour phase PAH species were investigated. The vehicles chosen for Phase 1 covered a range of Euro 1-2 technologies (light-duty diesel, heavy-duty diesel and gasoline). The diesel test fuels were blended in order to study the relationship between fuel poly-aromatics content and exhaust PAH emissions. The vehicles tested in Phase 2 surpassed Euro-3 emissions standards and were fitted with more advanced exhaust after-treatment, including a diesel vehicle with a particulate filter. A separate matrix of fuels was used during this Phase.

The total EPA-16 PAH exhaust emissions measured (particulate-bound and vapour phase) was found to be a very small percentage of the total emitted hydrocarbons.

Older diesel vehicles showed relatively high exhaust PAH emissions, which increased linearly with higher diesel fuel poly-aromatics content. However, reducing diesel fuel poly-aromatics, even to zero, would not eliminate exhaust PAH emissions, as a significant proportion is combustion derived.

Gasoline vehicles with three-way catalysts or other advanced exhaust after-treatment showed very low PAH emissions compared to the older diesel vehicles. Advanced diesel vehicles with state-of-the-art exhaust after-treatment systems showed very low PAH emissions, close to or below the gasoline vehicles. In these advanced diesel vehicles PAH emissions were so low that there was no longer any sensitivity to diesel fuel aromatics content.

Overall, it is clear that advanced exhaust after-treatment systems, which are being implemented for the control of total hydrocarbon and particulate emissions, are also effective in controlling PAH emissions.

1. INTRODUCTION

Certain individual polycyclic aromatic hydrocarbons (PAH) have been classified by the International Agency for Research on Cancer (IARC [1]) as carcinogenic to animals and probably carcinogenic to humans. The general public are exposed to PAH from various sources. In particular, wood burning is forecast to make by far the largest contribution to total PAH emissions by 2010 [2]. In view of the discussions relating to the transport sector, it is important for CONCAWE to understand the factors that influence automotive PAH emissions and their contribution to ambient PAH levels.

In July 1999, the UK published a proposal from EPAQS¹ for an air quality standard for PAH using benzo(a)pyrene (BaP) as a marker [3]. BaP is classified "2A" by IARC - probably carcinogenic to humans. The European Commission's Air Quality Framework Directive [4] has addressed a range of pollutants under a series of Daughter Directives. The fourth in this series addresses both heavy metals and PAH concentrations in ambient atmospheres [5]. It establishes an Air Quality target value for BaP at max 1ng/m³ annual mean and also requires monitoring of the levels of other PAHs, including at least benz(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene.

The first step in CONCAWE's work in this area was to undertake a literature review [6], collating information on the occurrence and analysis of PAH both in automotive exhaust emissions and in fuels. This review showed that despite extensive literature on automotive PAH emissions, there was a surprising lack of definitive investigations into the link between diesel fuel poly-aromatics content and exhaust PAH emissions. There had also been limited work investigating total PAH emissions i.e. particulate-bound PAH plus vapour phase PAH emissions, with most work concentrating only on particulate-bound PAH. This was especially true for diesel emissions; gasoline emissions (by their nature) have been more extensively studied in the vapour phase.

Following the literature review, two phases of test work were run using both gasoline and diesel vehicles. In phase 1, Euro 1-2 vehicles were tested and in Phase 2 more advanced vehicles meeting Euro 3 standards or better were tested.

For gasoline, there was sufficient literature to understand the nature of current vehicle PAH emissions. Thus, in Phase 1, the exercise undertaken by CONCAWE was by way of demonstration that a current gasoline vehicle, equipped with a state-of-the-art TWC would emit very low levels of PAH emissions. Two fuels were tested, covering a wide range of aromatics and sulphur content (within the limits of the EN228:1998 gasoline standard).

For diesel emissions, existing knowledge was less complete. Not only was there a general lack of data on vapour phase PAH emissions, it was also considered essential to investigate the relationship between fuel poly-aromatics content and PAH exhaust emissions. In Phase 1, a matrix of fuels was blended to assess the effects from a range of poly-aromatics and total aromatics content. Tests were

¹ A glossary of terms used in this report is given in **Section 11**.

carried out on Euro 1-2 generation light-duty vehicles and on a heavy-duty engine.

Following the completion of Phase 1 and the analysis of the data, a subsequent test programme (Phase 2) was undertaken to extend the investigation to include more advanced light-duty vehicle technologies. In Phase 2, two light-duty diesel vehicles, with advanced exhaust after-treatment, were tested on a new matrix of test fuels (**See Section 5.1**). Two advanced gasoline vehicles, including one lean DI system, were also tested on a single gasoline.

1.1. DEFINITION OF PAH MEASURED IN THIS PROGRAMME

Multi-ring organic species (i.e. those with two or more rings) are called "Polycyclic Aromatic Compounds" (PAC). Within this wide range of compounds are species containing heteroatoms (S, N and O), as well as those containing only carbon and hydrogen. This report addresses the latter i.e. "Polycyclic Aromatic Hydrocarbons" (PAH), identified in automotive emissions. A more comprehensive definition of PAH can be found in the report on the CONCAWE literature review [6].

1.2. SELECTION OF PAH TO BE MEASURED

The term "total" PAH is used extensively throughout the literature but has no firm definition. It usually refers to the sum of the species that a particular researcher has analysed. It may or may not include both particulate-bound and vapour phase emissions and generally only includes parent PAH, omitting any alkylated species. In this programme, the US EPA's "Priority Pollutants" list of 16 PAHs was used as the selection criterion (see **Table 1**).

Table 1 List of PAHs measured

EPA 16 PAH	"2+ ring"	"3+ ring"	Carcinogenicity Category	
			IARC ⁽ⁱⁱⁱ⁾	European ^(iv)
Naphthalene	Y		Not assessed	3
Acenaphthene + Acenaphthylene ⁽ⁱ⁾	Y		Not assessed	Not classified
Fluorene	Y		3	Not classified
Phenanthrene	Y	Y	3	Not classified
Anthracene	Y	Y	3	Not classified
Fluoranthene	Y	Y	3	Not classified
Pyrene	Y	Y	3	Not classified
Benz(a)anthracene	Y	Y	2A	2
Chrysene	Y	Y	3	2
Benzo(b)fluoranthene ⁽ⁱⁱ⁾	Y	Y	2B	2
Benzo(k)fluoranthene ⁽ⁱⁱ⁾	Y	Y	2B	2
Benzo(a)pyrene	Y	Y	2A	2
Dibenz(a,h)anthracene	Y	Y	2A	2
Benzo(g,h,i)perylene	Y	Y	3	Not classified
Indeno(1,2,3-cd)pyrene	Y	Y	Not assessed	Not classified

(i) Acenaphthene / acenaphthylene cannot be separated using HPLC technique.

(ii) Benzo(j)fluoranthene is also included in the list of PAHs to be monitored under the EU Directive [5], however, this PAH is not included in EPA-16 list and so was not measured in this programme.

(iii) <http://www-cie.iarc.fr/monoeval/crthall.html> Category 2A = probably carcinogenic to humans;
Category 2B = possibly carcinogenic to humans; Category 3 = Not classifiable as to carcinogenicity to humans.

(iv) <http://ecb.jrc.it/esis> Category 2 = Substances which should be regarded as if they are carcinogenic to man;
Category 3 = Substances which cause concern for man owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment.

2. AIMS OF THE PROGRAMME

The aims of the programme were developed in view of the following conclusions and knowledge gaps identified in the literature survey:

- There is no standard analytical methodology for measuring exhaust PAH emissions.
- There is no consensus on which PAH should be measured.
- It is difficult to compare data in the literature because of the range and variability of analytical techniques and the lack of consensus on the measured PAH species.
- There are insufficient data available on automotive exhaust emissions to determine to what extent the level of the PAH emissions is related to the poly-aromatics content of the fuel.
- There has been a lack of work on total (vapour phase and particulate-bound) PAH emissions.
- The presence of a three-way catalyst on gasoline vehicles appears to reduce PAH emissions to very low levels.
- Diesel exhaust after-treatment systems appear to be highly effective in reducing PAH emissions.

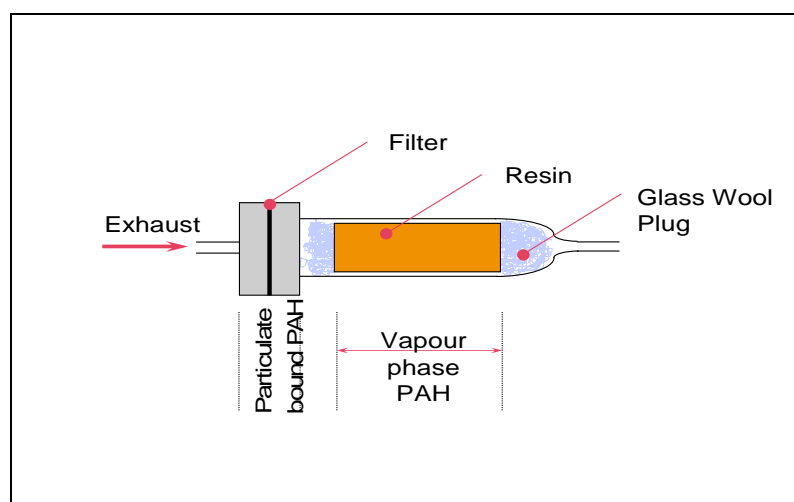
Key objectives were:

- To investigate the effect of advanced light-duty diesel vehicle technologies on PAH emissions.
- To identify possible effects of diesel fuel poly-aromatics content on PAH exhaust emissions.
- To verify that modern gasoline cars give very low PAH emissions.

3. EXPERIMENTAL DESIGN

Currently, there is no standard sampling protocol or analytical procedure for measuring PAH in automotive exhaust emissions. As this programme aimed to address both particulate-bound and vapour phase PAH, a common analytical system was required. In conjunction with Ricardo Consulting Engineers, a sampling system was developed which comprised a glass holder containing both a filter and absorbent resin (**Figure 1**). This was used to sample both particulate-bound and vapour phase PAH from a standard dilution tunnel, using a separate sampling port to that routinely used for the regulated particulate filter. Sampling was carried out by drawing dilute exhaust through the holder for the duration of the LD test cycle (NEDC) [7]. The advantages of this system are that both exposed filter (particulate-bound) and resin (vapour phase) PAH are measured from a common exhaust flow and that analysis of both the filter and the resin extracts is performed by the same technique. Toluene is used to extract the PAH from both resin and filter. Following extraction, a clean-up procedure is required to isolate the parent PAH from other compounds (e.g. alkylated PAH) in the extract that would interfere with the analysis. During this stage, the solvent is exchanged to methanol which allows separation of the PAH to be made using high performance liquid chromatography (HPLC) with subsequent quantification by fluorescence. Details of this apparatus and analytical procedure have already been published [8].

Figure 1 Schematic diagram of the Total PAH sampler (TPS)



The same sampling system was adapted for the HD engine testing, which used the legislated ECE R49 procedure [9]. As for the legislated particulate measurements, a weighted mean PAH sample was obtained by activating exhaust flow through the PAH sampler for periods in accordance with the weighting factors for each of the 13 test modes.

This technique was developed from a sampling system originally developed for gaseous hydrocarbons and carbonyls [10].

The programme was carried out in two phases. The first series of tests included Euro-1 and 2 engine and vehicle technologies. In Phase 2, more modern vehicles were tested. Although vapour phase and particulate-bound PAH were measured separately, only the sum of the measurements ("combined" PAH data) is reported. This is because there will always be some transfer of PAH between the vapour and particulate phase in such a sampling system. For some PAH species and selected speed/load conditions, exhaust vapour phase molecules could be trapped in the particulate phase, whilst at other conditions some exhaust particulate phase PAH may be "blown off" into the vapour phase. Phase partitioning of PAH in the exhaust will also change once the emissions are released to the atmosphere and may also be affected as the amount of solid particulate matter in the exhaust decreases with advancing vehicle technology. A discussion of the relative contributions of gaseous and particulate-bound PAH is contained in **Appendix 7**.

In order to obtain reliable data identifying potentially small effects, each fuel (during Phase 1) was tested a total of six times over the appropriate legislated test cycle in a statistically designed pattern. Phase 2 built on the knowledge of repeatability gained during Phase 1 and hence each fuel/vehicle combination was only tested four times. System blanks were run on a regular basis during both phases.

4. SELECTION OF VEHICLES/ENGINE

4.1. LIGHT-DUTY VEHICLES

Details of the LD vehicles tested in both phases of the programme are shown in **Table 2**. The Euro 1-2 diesel passenger cars tested in Phase 1 were chosen to cover a range of vehicles representative of the major market technologies at the time of testing. Vehicle A is typical of the simpler, smaller cars, without an oxidation catalyst. Vehicle B is a larger car with an oxidation catalyst, and representative of the older cars that employed the IDI combustion system and mechanical engine controls. Vehicle C is typical of the more modern DI diesel, and employs turbocharging and electronic controls. Limited testing was also carried out on vehicle A fitted with an oxidation catalyst, as employed on modern versions of the car.

Two additional LD diesel vehicles were tested in Phase 2, chosen to represent advances in emissions control. Vehicle D is a medium-sized car equipped with an advanced oxidation catalyst, whilst vehicle E is a larger car equipped with a diesel particulate filter (DPF).

One gasoline car (vehicle X) was tested in Phase 1. This is a typical multiple point injected (MPI) engine using conventional TWC technology. The two cars tested in Phase 2 again represent advances in gasoline vehicle technology. Vehicle Y is an advanced stoichiometric MPI vehicle and vehicle Z a lean-burn direct injection (DISI). Both were certified to Euro-4 emissions level.

Table 2 Details of Test Cars

Code	Year	Fuel	Engine (litres)	Comb. System	Aspiration	Fuel Injection / Controls	EGR	Exhaust After-treatment
A	1997	Diesel	1.9	IDI	Naturally aspirated	Distributor / mechanical	Yes	None
Acat	1997	Diesel	1.9	IDI	Naturally aspirated	Distributor / mechanical	Yes	Oxidation Cat
B	1993	Diesel	2.5	IDI	Naturally aspirated	In-line / Mechanical	Yes	Oxidation Cat
C	1997	Diesel	1.9	DI	TC/Intercooler	Distributor / Electronic	Yes	Oxidation Cat (close coupled)
D	2002	Diesel	1.9	DI	TC/Intercooler	Unit injectors	Yes	Oxidation Cat
E	2001	Diesel	2.2	DI	TC/Intercooler	Common rail	Yes	DPF
X	1998	Gasoline	1.4	MPI	Naturally aspirated	Electronic fuel injection	No	TWC
Y	2002	Gasoline	1.8	MPI	Naturally aspirated Variable valve timing	Electronic fuel injection	No	TWC
Z	2002	Gasoline	1.6	Lean DI	Naturally aspirated	Electronic fuel injection	Yes	TWC+NOx trap

4.2. HEAVY-DUTY ENGINE

Although introduced around 1994, the HD engine tested during Phase 1 produced emissions performance close to Euro-2, and may be considered as typical of the bulk of the Euro-2 European HD diesel fleet. It employs conventional mechanical engine controls. Details are given in **Table 3**.

Table 3 Details of HD Diesel Test Engine

Engine type / Emissions performance	Euro-2
Combustion system	4 stroke, direct injection
Cylinders/arrangement	6-cylinder, in-line
Swept volume/cylinder (litres)	1.1
Aspiration	Turbocharged / intercooled
Max power at speed	185kW / 2200 rpm
Fuel injection system	Bosch in-line pump, multi-hole nozzles
Engine controls	Mechanical

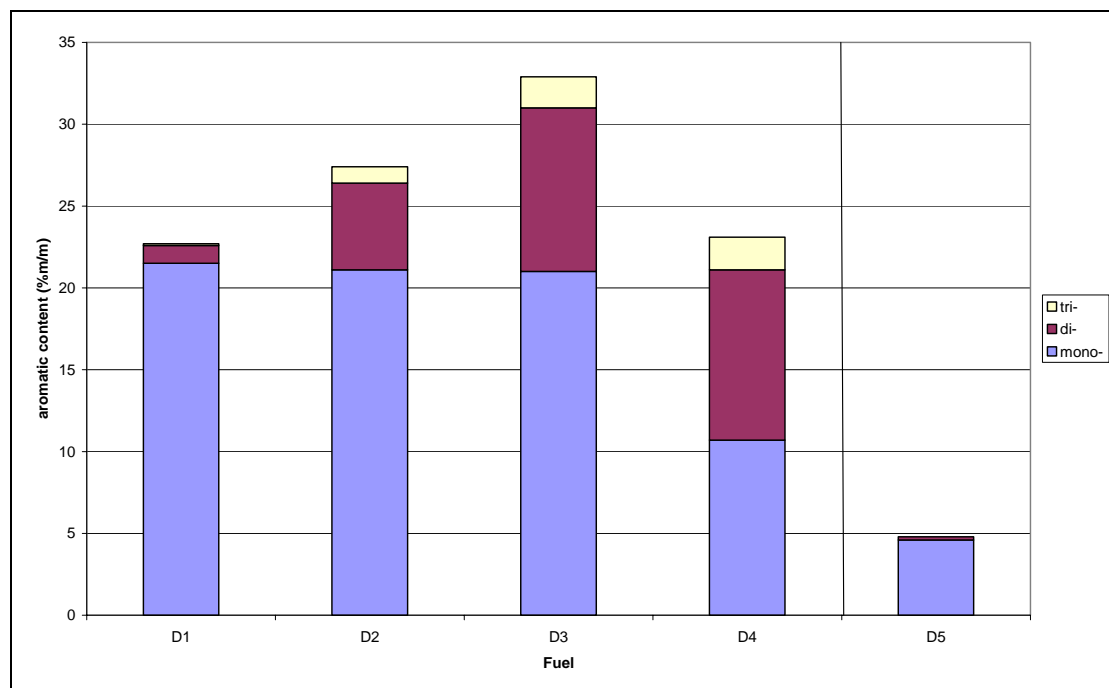
5. FUELS

5.1. DIESEL FUELS

5.1.1. PHASE 1

Five fuels (D1-D5) were tested in the three light-duty vehicles and the heavy-duty engine in Phase 1. Three fuels were blended to cover a wide range of poly-aromatics content (1, 6 and 12% m/m), with other key parameters (mono-aromatics, sulphur, density, cetane number, T95) held constant. As a consequence of this approach, these fuels had a strong correlation between poly-aromatics and total aromatics content. Therefore a fourth fuel was blended to break this correlation. These four fuels were prepared by blending a range of refinery components in different proportions. This ensured a wide range of chemical species in each fuel, as typically found in market fuels. Also, because the same high PAH blending component was used in all these fuels, the relative proportions of the various different PAH species in each fuel was very similar. All of these fuels met EN 590. Swedish Class 1 diesel was added as a more extreme test fuel. **Figure 2** shows a graphical representation of the variation in aromatic types across all test fuels. Detailed analysis of the fuels is given in **Appendix 1**.

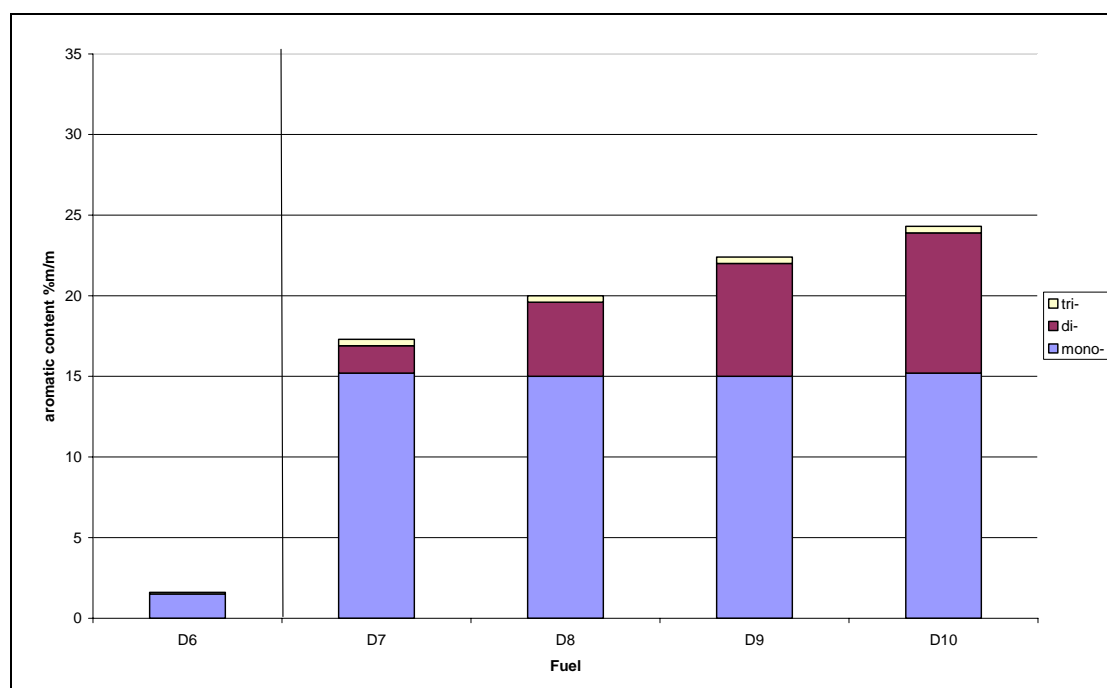
Figure 2 Aromatics content of Phase 1 Diesel test fuels (measured by IP391)



5.1.2. PHASE 2

Five fuels (D6-D10) were tested in Phase 2. In order to achieve some “read-across” between the two phases, a Swedish Class 1 fuel was also included in the matrix (D6). The other four test fuels were prepared by blending a low poly-aromatics base fuel (D7) with increasing amounts of a high poly-aromatics blending component to produce fuels D8-D10. A graphical representation of the aromatics content of the fuels is given in **Figure 3** and the analytical data in **Appendix 1**.

Figure 3 Aromatics content of Phase 2 Diesel test fuels (measured by IP391)



5.2. GASOLINES

In Phase 1, two fuels (G1 and G2) were blended to cover a wide range of aromatics and sulphur contents. Properties of both fuels were within the specification limits of EN228:1998. Detailed analysis is given in **Appendix 1**.

In Phase 2, a single gasoline (G3) was tested, which was representative of the 50 mg/kg sulphur EN228 grade required from 2005. Detailed analysis is given in **Appendix 1**.

6. RESULTS

One of the purposes of the work was to investigate the mechanisms of the formation of PAH. This aspect was discussed extensively in the CONCAWE literature survey report [6], which highlighted that by plotting exhaust PAH concentration against an appropriate fuel parameter, the following could be calculated:

- the gradient of line indicating the “survival rate” of fuel poly-aromatics,
- the intercept indicating the amount of exhaust PAH which is synthesised during combustion.

This format has been used to show the relationship between PAH emission and the poly-aromatics content of the fuel (as measured by IP391).

The system blank measurements were found to be variable and, in the case of the heavy-duty data, to show evidence of carry over. This may have been due to the manner of the blank measurement, where air, as opposed to exhaust is flushed through the hot tunnel and may strip out volatile material from the tunnel wall. They were therefore judged to overestimate the blank contribution and consequently, the data presented have not been blank corrected. To provide information on the possible influence of the background levels, average blank measurement levels are given in the figures as a line across the graph.

As a result of the careful design and preparation of the programme, it has been possible to statistically detect small fuel effects in vehicles where emissions levels were noticeably higher than background levels. In the bar charts presented in this report the error bars show the

mean value ± 1.4 x standard error of mean

The factor 1.4 was chosen for consistency with both the EPEFE [11] and recent CONCAWE reports [12-15]. Emissions from two fuels will not be significantly different from one another at $P < 5\%$ ² unless there is a clear gap between their error bars. See **Appendix 3** for further discussion.

Although data are available for all individual 16 EPA PAH species, they have been grouped for comparative purposes as follows (see also **Table 1**):

1. Sum of all EPA-16 species (referred to as “2+ ring PAH”),
2. Sum of PAHs from the EPA-16 list with 3 or more rings (referred to as “3+ ring PAH”) which are predominantly emitted to the atmosphere bound to particles,
3. Benzo(a)pyrene (BaP) selected on the basis of its proposed selection as a “marker” in air quality monitoring [3].

All the tables and graphs presented in **Sections 6** and **7** are based on the combined (i.e. vapour and particulate-bound) PAH emissions.

² $P < 5\%$ = the probability that such an event could be observed by chance when no real effect exists is less than 5%. In other words, we are 95% confident that the effect is real.

Tables 3 and 4 show the ranges (lowest & highest average emissions across the various vehicle/fuel combinations tested) of the above PAH groups, measured during Phases 1 and 2 respectively and compare these with the regulated total hydrocarbon emissions.

Table 3 Emission ranges measured during Phase 1

	"2+ ring PAH"	"3+ ring PAH"	BaP	HC*
Heavy-duty ($\mu\text{g}/\text{kWh}$)	514-2367	61-165	0.11-0.24	$0.264-0.294 \times 10^6$
Light-duty diesel ($\mu\text{g}/\text{km}$)	241-2485	46-296	0.14-1.53	$0.065-0.295 \times 10^6$
Light-duty gasoline ($\mu\text{g}/\text{km}$)	114-242	11-12	0.03-0.09	$0.116-0.128 \times 10^6$

* HC - regulated total hydrocarbon emissions

Table 4 Emission ranges measured during Phase 2

	"2+ ring PAH"	"3+ ring PAH"	BaP	HC*
Light-duty diesel ($\mu\text{g}/\text{km}$)	20-38	15-29	0.03-0.79	$0.026-0.056 \times 10^6$
Light-duty gasoline ($\mu\text{g}/\text{km}$)	55-103	15-20	0.17-0.28	$0.035-0.071 \times 10^6$

* HC - regulated total hydrocarbon emissions

Comparison of the light-duty diesel data in **Tables 3 and 4** demonstrates how effective the advances in vehicle after-treatment have been, reducing light-duty diesel HC and PAH emissions to the same order as (or below) those of gasoline.

The EU's 4th Air Quality Daughter Directive [5] has established a target level for BaP in ambient air of $1.0\text{ng}/\text{m}^3$ (annual mean). However, as this single PAH may not be representative of all sources contributing to the atmospheric burden, a further six individual PAH have been identified to be monitored alongside BaP. These are benz(a)anthracene, dibenz(ah)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, and indeno(123-cd)pyrene. All except benzo(j)fluoranthene are included in the EPA-16 list and so were measured in this programme. A brief analysis of the exhaust emissions of these particular PAHs is given in **Appendix 5**.

However, as described earlier, this report focuses on: "2+ ring PAH" emissions (the full EPA-16 list), "3+ ring PAH" emissions (representative of particulate-bound PAHs), and BaP (in view of its use as an Air Quality marker). These emissions are discussed in this order in **Sections 6.1 - 6.3**.

6.1. "2+ RING PAH"

The results for the complete EPA16 set of priority pollutants ("2+ ring PAH") are presented in **Figures 4 to 8**. As described earlier, results are shown for the combined (i.e. vapour and particulate-bound) PAH emissions.

Figure 4 Light-duty diesel: average “2+ ring PAH” ($\mu\text{g}/\text{km}$) for each vehicle/fuel combination

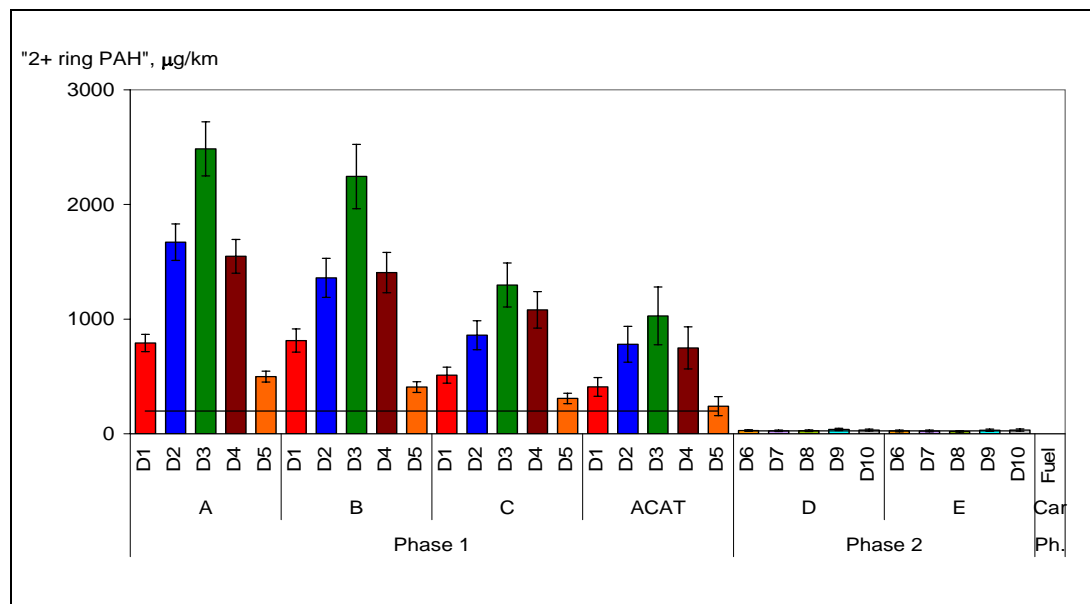


Figure 4 demonstrates the enormous progress made with diesel exhaust after-treatment. The older diesel vehicles showed higher emissions and were also sensitive to fuel quality. For older technology LD diesel vehicles the EPA-16, “2+ ring PAH” emissions were dominated by 2 ring species in the vapour phase (see also **Appendix 7**).

The two advanced diesel vehicles gave dramatic reductions in emissions. Vehicle D achieved the same low levels of “2+ ring PAH” emissions as the PM trap-equipped vehicle E. The emissions of “2+ ring PAH” from the advanced vehicles D and E are at blank level and demonstrate little or no sensitivity to fuel poly-aromatics content.

In order to further examine the fuel effects, **Figure 5** shows the average “2+ ring PAH” emission values plotted against the fuel poly-aromatics content, using fuels D1-D3 for Phase 1 and fuels D7-D10 for Phase 2.

Figure 5 Light-duty diesel: average “2+ ring PAH” emissions in $\mu\text{g}/\text{km}$ plotted against fuel poly-aromatics content (as measured by IP391)

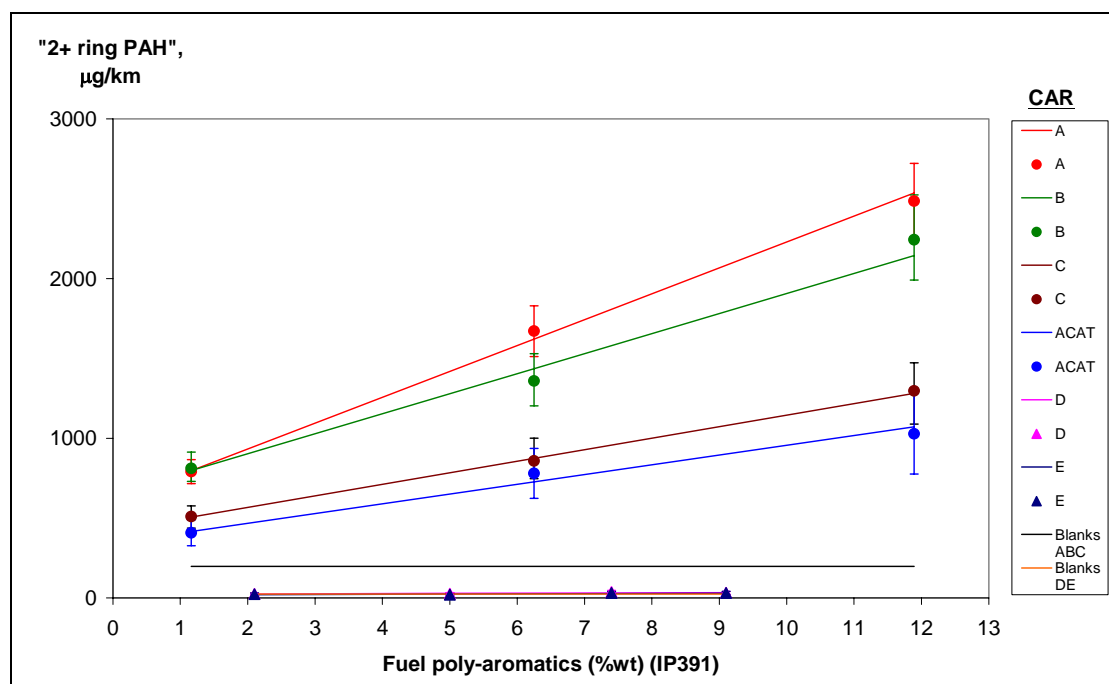


Figure 5 shows that the older technology vehicles gave an essentially linear increase in PAH emissions with higher diesel fuel poly-aromatics content. In addition, **Figure 4** shows (compare fuels D3 and D4) that increasing mono-aromatics also increases “2+ ring PAH” emissions. However, comparison of fuels D1 and D3 which have the same level of mono-aromatics and fuels D1 and D4 which have the same level of total aromatics shows that poly-aromatics has the greater influence.

Results for the heavy-duty diesel engine are shown in **Figure 6** and the relationship with diesel fuel poly-aromatics in **Figure 7**.

Figure 6 Heavy-duty diesel: "2+ ring PAH" emissions ($\mu\text{g}/\text{kWh}$)

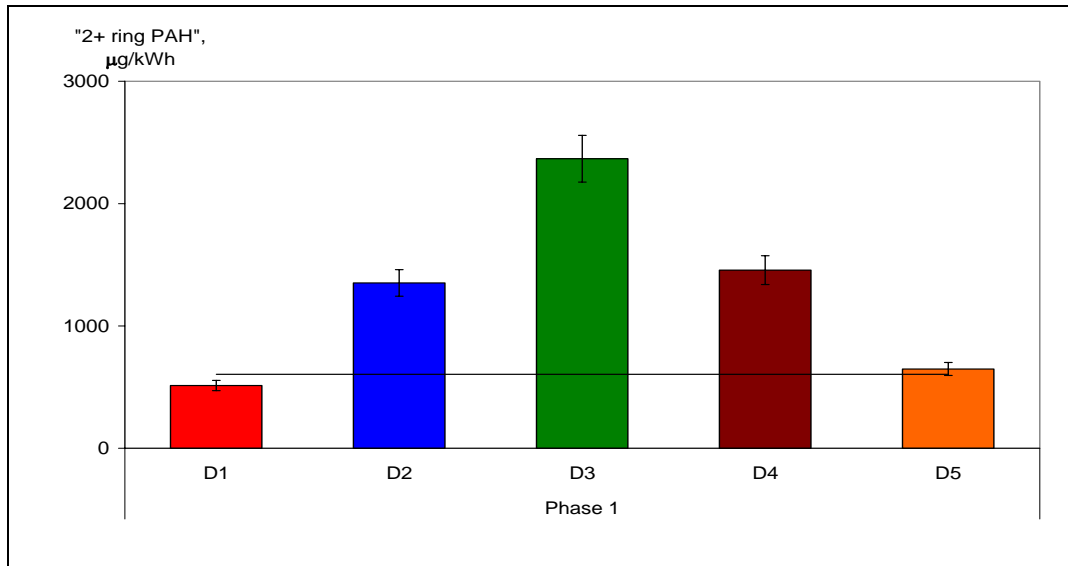
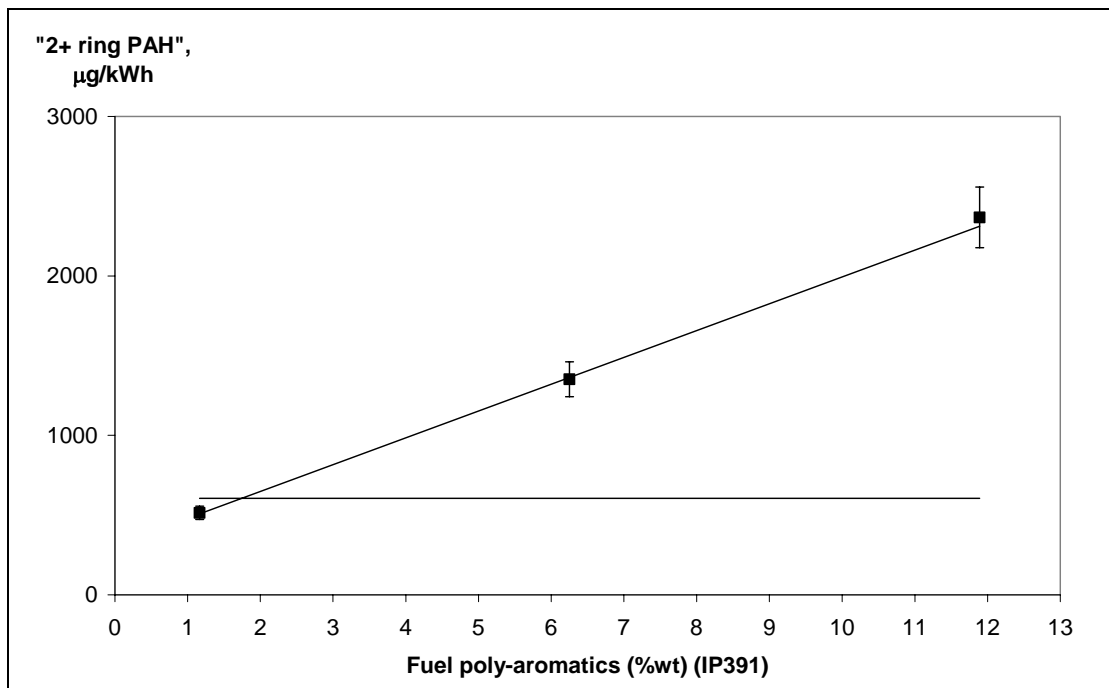


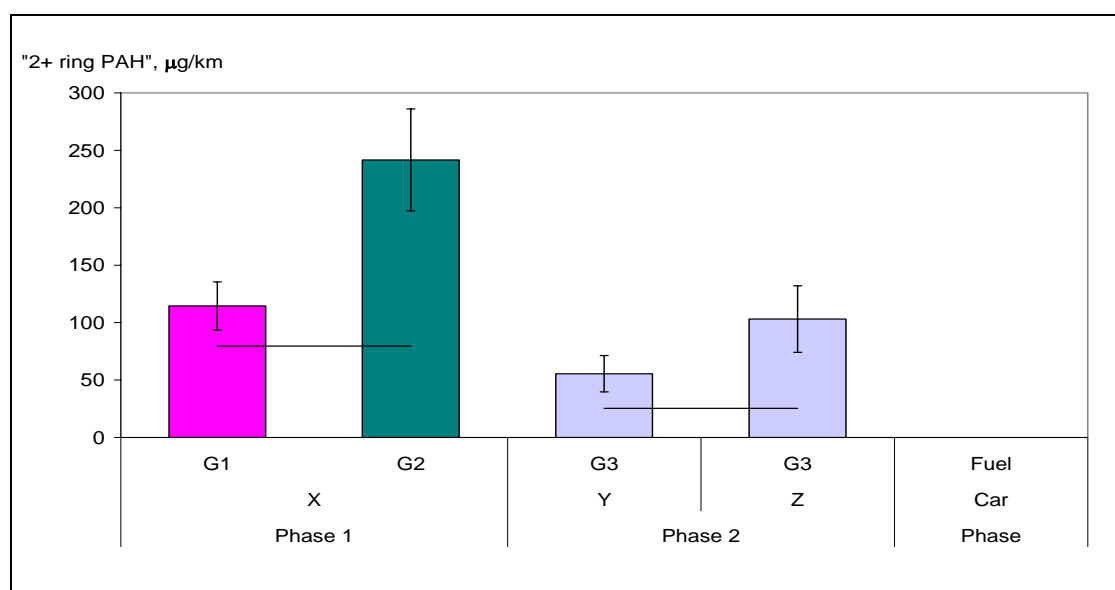
Figure 7 Heavy-duty diesel: average "2+ ring PAH" emissions ($\mu\text{g}/\text{kWh}$) for fuels D1-D3 against fuel poly-aromatics content (as measured by IP391)



Figures 6 and 7 demonstrate a clear relationship between the emissions of “2+ ring PAH” and fuel poly-aromatic content for this older HD engine. Similar trends for the relative effects of poly- and mono-aromatics were observed as in the light-duty vehicle results.

Results for the “2+ ring PAH” from the gasoline vehicles are shown in Figure 8.

Figure 8 Gasoline: average “2+ ring PAH” emissions (µg/km) for each vehicle/fuel combination



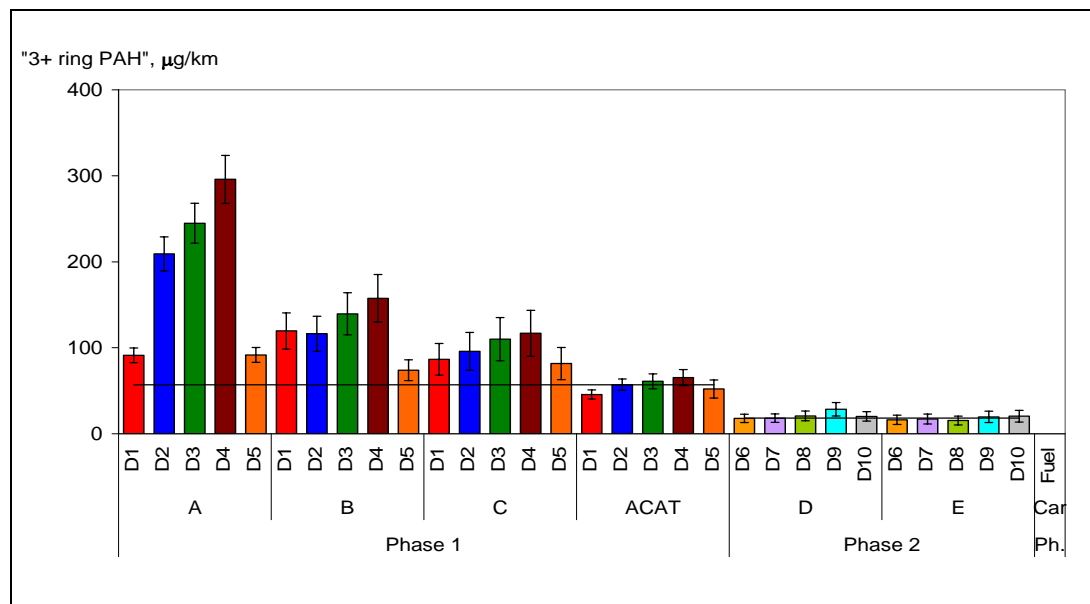
All 3 gasoline cars tested showed very low “2+ ring PAH” emissions. In Phase 1, “2+ ring PAH” emissions from the gasoline car tested were much lower than the older diesel cars. Fuel G1 gave lower “2+ ring PAH” emissions than fuel G2. In Phase 2, the advanced MPI car (Y) showed lower “2+ ring PAH” emissions, whereas the lean DI car (Z) showed “2+ ring PAH” emissions closer to those of car X, though the blank values were also lower in Phase 2.

In Phase 2, the advanced diesel cars (Figure 4) gave even lower “2+ ring PAH” emissions than the advanced gasoline cars.

6.2. "3+ RING PAH"

The results for those “3+ ring PAH” species included in the EPA-16 list are presented in Figures 9-13. All results are shown for combined (i.e. vapour and particulate-bound) PAH emissions. Figure 9 shows the “3+ ring PAH” emissions for the light-duty diesel vehicles tested during both Phases of the programme.

Figure 9 Light-duty diesel: average “3+ ring PAH” ($\mu\text{g}/\text{km}$) for each vehicle/fuel combination

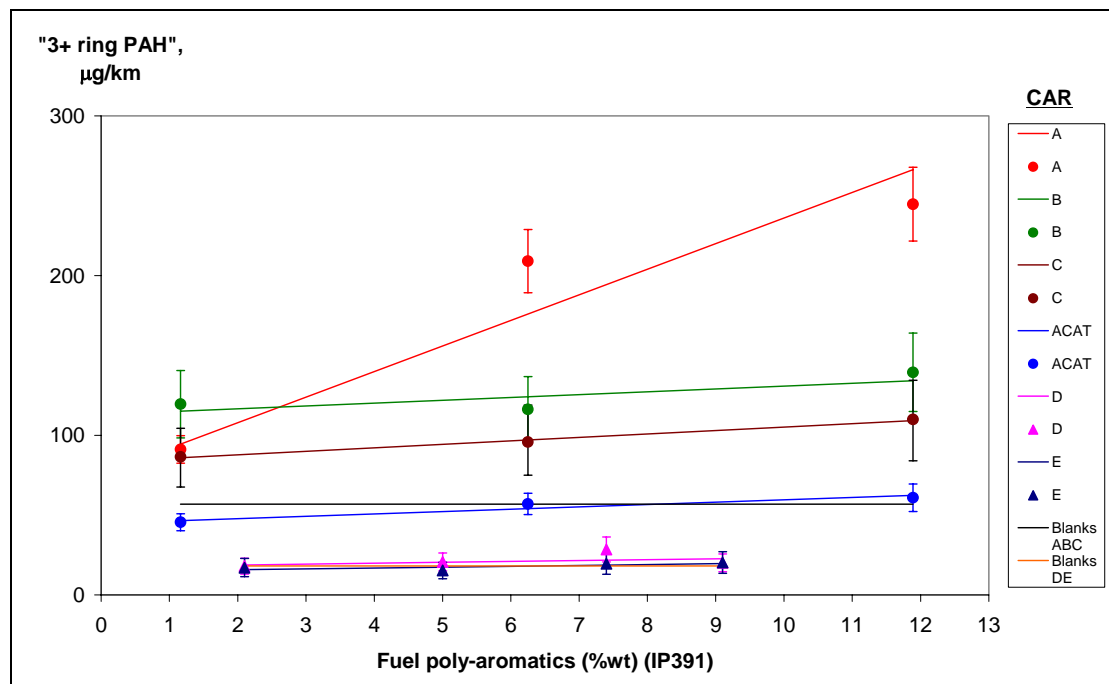


The absolute levels of “3+ ring PAH” emissions are very low compared to the “2+ ring PAH” emissions data presented earlier. In the advanced vehicles, D and E, tested in Phase 2, “3+ ring PAH” emissions are at the level of the blank measurements. Vehicle Acat also showed reduced emissions close to blank levels.

There was a significant reduction in the blank levels measured in Phase 2 compared to Phase 1, probably also reflecting the lower vehicle emissions and a reduction in the potential for carry over during PAH emissions sampling.

Figure 10 shows the average “3+ ring PAH” emission values plotted against fuel poly-aromatics content using fuels D1-D3 for Phase 1 and fuels D7-D10 for Phase 2.

Figure 10 Light-duty diesel: average “3+ ring PAH” emissions in $\mu\text{g}/\text{km}$ plotted against fuel poly-aromatics content (as measured by IP391)



Car A showed a clear increase in “3+ ring PAH” emissions with increasing diesel fuel poly-aromatics content. For the other cars, the trends were weaker than found for “2+ ring PAH” emissions. Extrapolation of fuel poly-aromatics content to zero would not result in zero “3+ ring PAH” emissions, confirming that a significant portion of the “3+ ring PAHs” is combustion derived.

In contrast to the effects on “2+ ring PAH” emissions, comparing fuels D3 and D4 (Figure 9) shows that mono-aromatics had no effect on “3+ ring PAH” emissions.

The use of advanced exhaust after-treatment reduced the absolute “3+ ring PAH” emission levels dramatically and virtually eliminated the sensitivity of “3+ ring PAH” emissions to fuel poly-aromatics content. The Euro-3 vehicle with oxidation catalyst (D) produced “3+ ring PAH” emissions as low as those from the PM trap vehicle (E).

The results for the “3+ ring PAH” emissions from the heavy-duty engine are shown in Figure 11 and emissions are plotted against the fuel poly-aromatics level (fuels D1-D3) in Figure 12.

Figure 11 Heavy-duty diesel: "3+ ring PAH" emissions ($\mu\text{g}/\text{kWh}$)

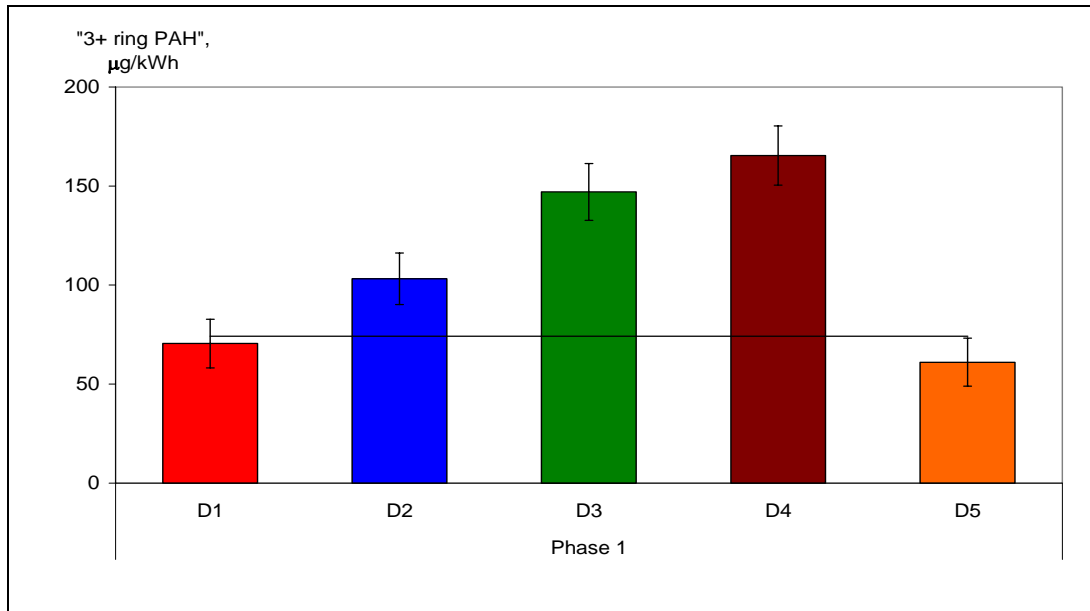


Figure 12 Heavy-duty diesel: average "3+ ring PAH" emissions ($\mu\text{g}/\text{kWh}$) for fuels D1-D3 against fuel poly-aromatics content (as measured by IP391)

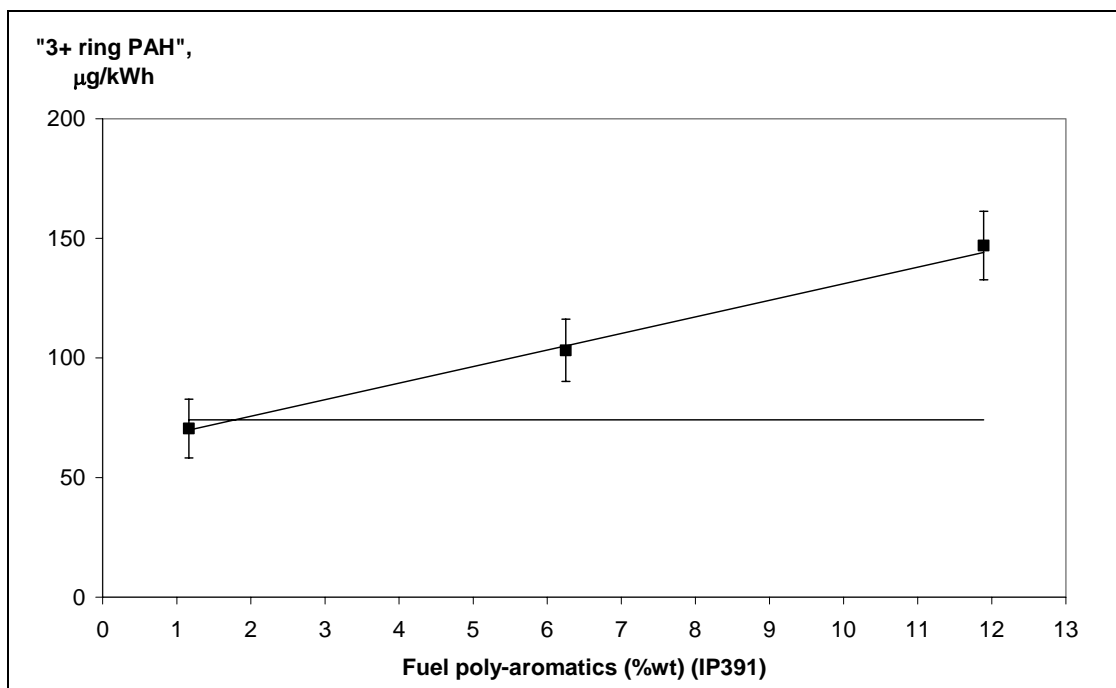


Figure 12 shows a linear relationship with diesel fuel poly-aromatics content. By comparing results from fuels D1 and D3 and fuels D1 and D4 in **Figure 11**, it can be seen that emissions are influenced by poly-aromatics but that increasing mono-aromatics at the same poly-aromatics content (fuel D3 versus D4) did not increase emissions. The trends in “3+ ring PAH” emissions for the HD engine are similar to the older light-duty diesel vehicles.

The results for the “3+ ring PAH” emissions for the gasoline vehicles are shown in **Figure 13**.

Figure 13 Gasoline: average “3+ ring PAH” emissions ($\mu\text{g}/\text{km}$) for each vehicle/fuel

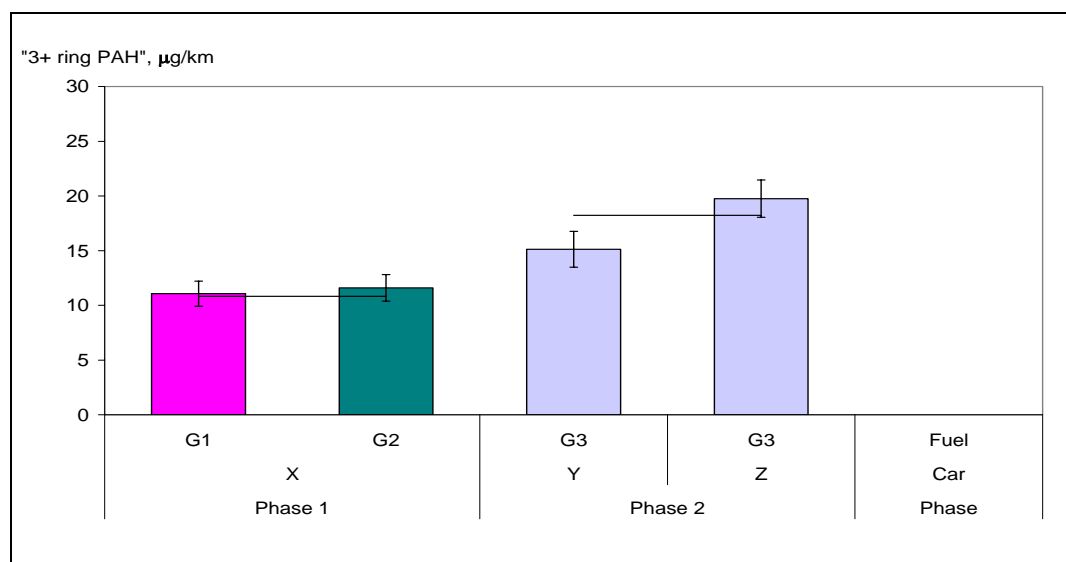


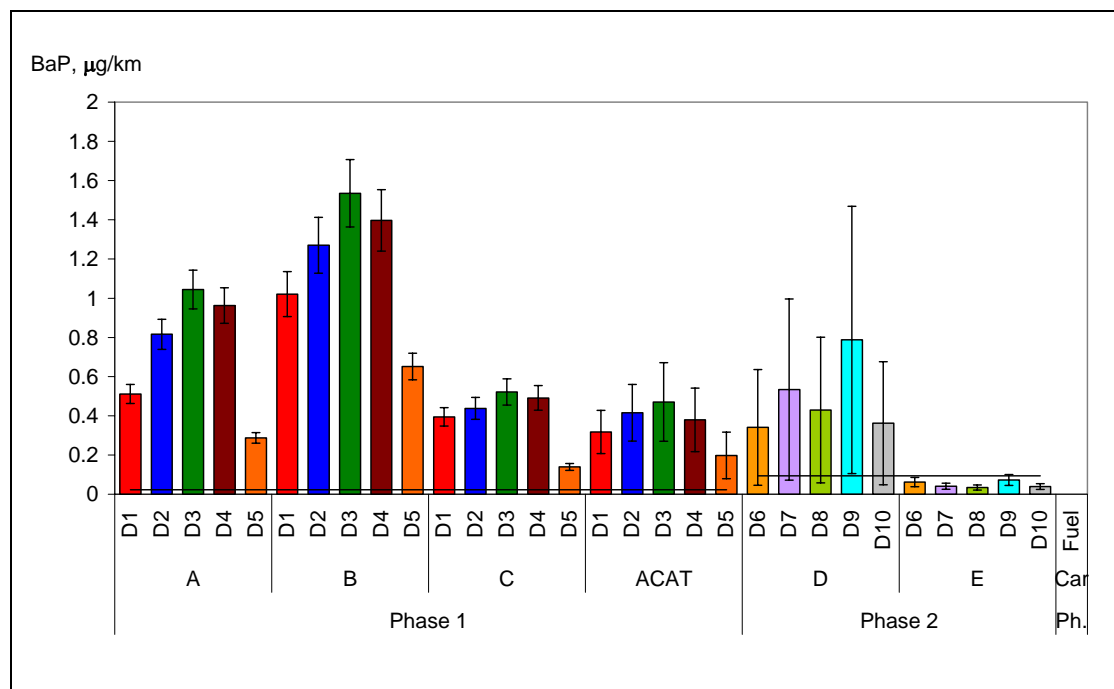
Figure 13 shows that the “3+ ring PAH” emissions from the gasoline cars, even the lean DI (car Z), were very low. A large change in fuel properties had no significant effect on “3+ ring PAH” emissions from gasoline car X tested in Phase 1. The two gasoline cars tested in Phase 2 gave slightly higher “3+ ring PAH” emissions, although the blank values were also higher. In all cases the “3+ ring PAH” emissions from the gasoline cars were close to the blank levels.

Comparing **Figures 9 and 13**, shows that “3+ ring PAH” emissions from the gasoline vehicles with TWCs were very low relative to the older diesel vehicles. However, significant improvements have been achieved with advanced exhaust after-treatment on diesel vehicles and “3+ ring PAH” emissions from the advanced diesel vehicles D and E achieved the same level as the gasoline vehicles.

6.3. BENZO(A)PYRENE (BaP)

The BaP emissions from the light-duty diesel vehicles tested during both Phases of the programme are shown in **Figure 14**.

Figure 14 Light-duty diesel: BaP emissions for each vehicle/fuel combination



The absolute BaP emission level from all cars was low, but the presence of the DPF (vehicle E) virtually eliminated the emissions of BaP, with measured values similar to those reported as blanks for all the fuels tested (**Figure 14**).

The results for BaP emissions from vehicle D were seen to be very variable for all the fuels tested. However, this variability should be compared with that for “2+ ring” and “3+ ring PAH” emissions, where vehicle D was much more repeatable. The results for “2+ ring” and “3+ ring PAHs” are considered more meaningful due to the overall higher measurement levels and lower variability (for more details on the test precision, see **Appendix 4**).

Figure 14 shows that trends in fuel effects for BaP in the older vehicles are similar to those found for “3+ ring PAH” emissions (**Figure 9**). Fuel poly-aromatics had the main effect; there was no effect of mono-aromatics.

Figure 15 shows the average BaP emission values plotted against fuel poly-aromatics content using fuels D1-D3 for Phase 1 and fuels D7-D10 for Phase 2.

Figure 15 Light-duty diesel: average BaP emissions plotted against fuel poly-aromatics content (as measured by IP391)

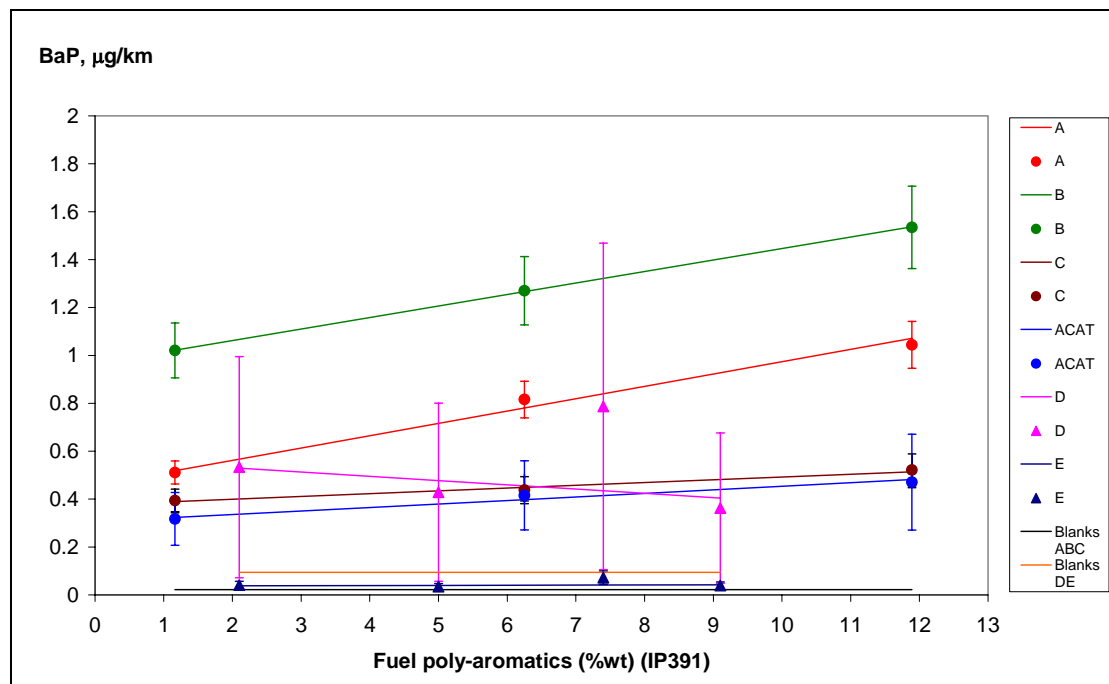


Figure 15 demonstrates that for the older vehicles (A and B), there is a linear relationship between diesel fuel poly-aromatics content and BaP emissions. However, it can be seen that extrapolation of fuel poly-aromatics content to zero would only partly reduce BaP emissions, indicating a large contribution from combustion derived BaP.

Overall emission levels from the Euro-3 vehicle with oxidation catalyst (D) were similar to those from the catalyst vehicles (Acat and C) tested in Phase 1. Vehicle E, fitted with a DPF, gave very low BaP emissions on all the fuels, at the level of the blank values.

The cars equipped with more advanced after-treatment showed reduced sensitivity to fuel poly-aromatics content, though the variability of results from vehicle D prevented clear trends being seen. The DPF-equipped car (E) showed so low emissions of BaP that no fuel sensitivity could be detected.

The BaP emissions measured from the heavy-duty engine on each fuel is shown in **Figure 16** and the relationship between the average emissions and fuel poly-aromatics content (for fuels D1-D3) is shown in **Figure 17**.

Figure 16 Heavy-duty diesel: BaP emissions ($\mu\text{g}/\text{kWh}$)

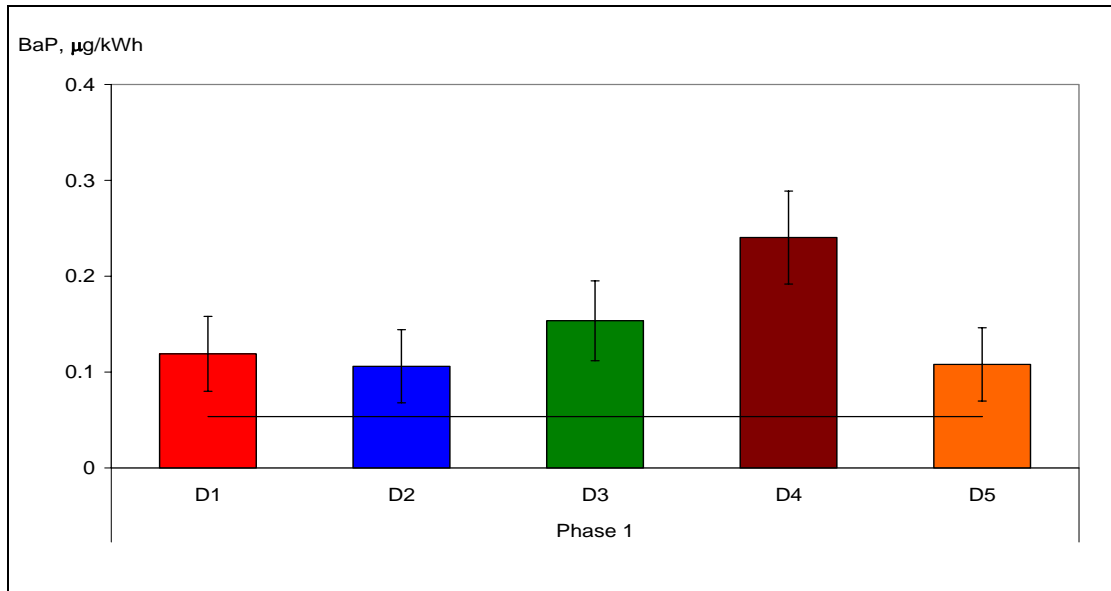


Figure 17 Heavy-duty diesel: average BaP emissions ($\mu\text{g}/\text{kWh}$) for fuels D1-D3 against fuel poly-aromatics content (as measured by IP391)

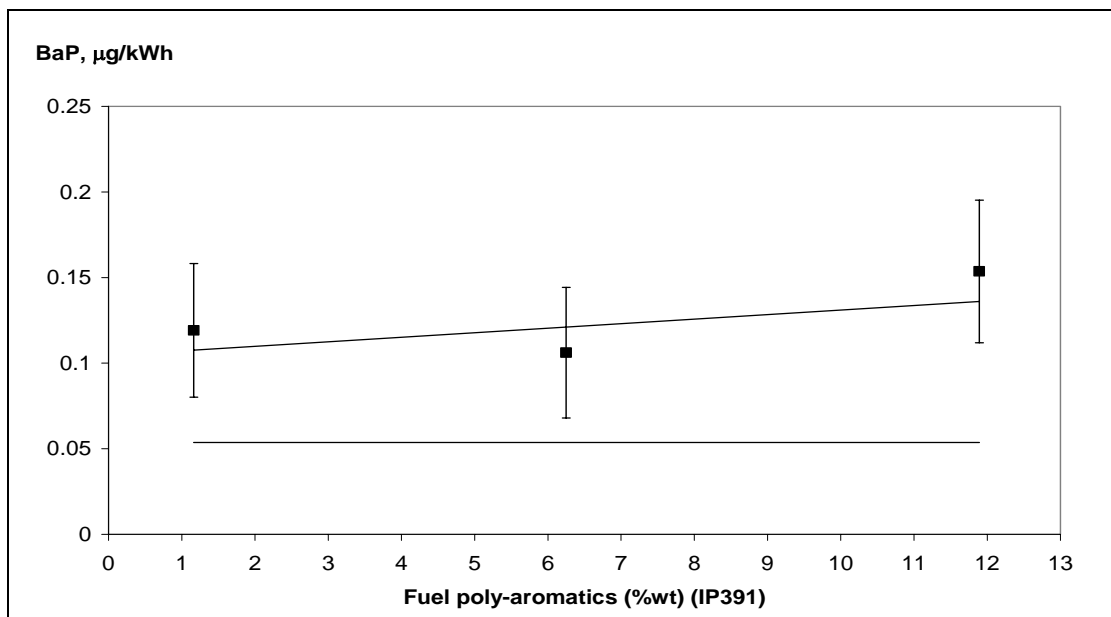


Figure 17 demonstrates that for the heavy-duty engine tested, there was only a weak trend (not statistically significant) between BaP emission and the polyaromatics content of the fuel. This result is in contrast to the findings for “3+ ring PAH” emissions described earlier. For BaP, the blank values were relatively high and the measured values of BaP were very low. There was no effect of monoaromatics.

BaP emissions for the three gasoline cars tested are shown in **Figure 18**.

Figure 18 Gasoline: average BaP emissions ($\mu\text{g}/\text{km}$) for each vehicle/fuel

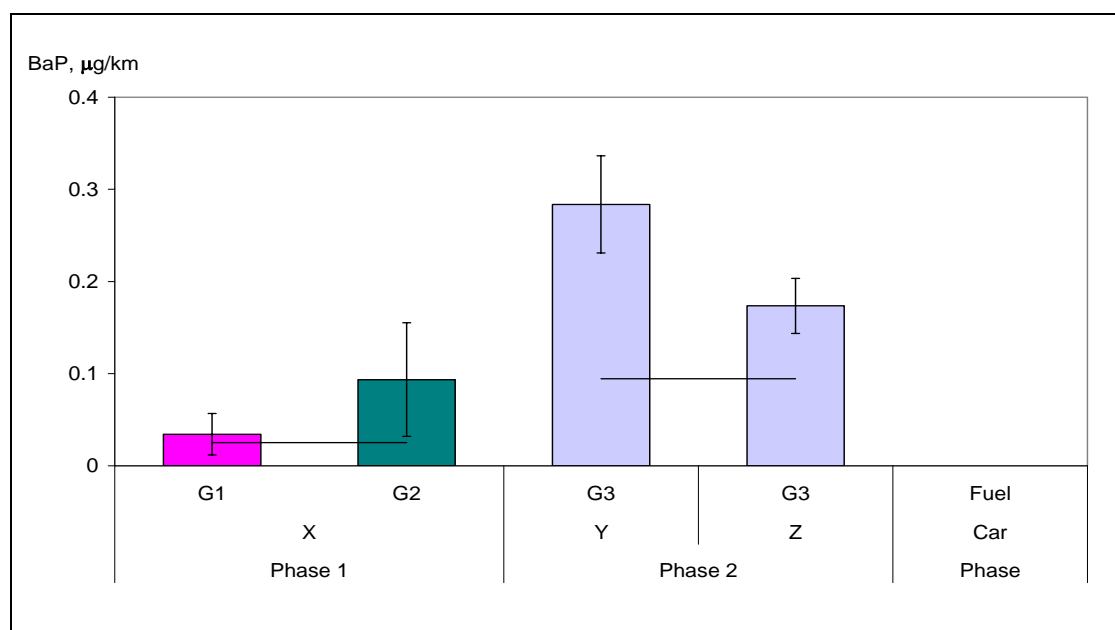


Figure 18 shows that the absolute values for BaP emissions from the gasoline vehicles are all low compared with the older light-duty diesel vehicles (**Figure 14**). However, the diesel vehicle with PM trap (E) gave even lower BaP emissions than the gasoline vehicles.

The two advanced technology gasoline vehicles emitted higher concentrations of BaP than the TWC equipped car tested in Phase 1. However, the blank values were also higher. Vehicle Z is a direct-injection vehicle and this is well known to increase the concentration of emitted particulates, therefore an increase of particulate-bound BaP is perhaps not surprising. The higher emissions from the MPI vehicle (Y) were not expected.

7. DISCUSSION

7.1. GENERAL

As shown in the previous sections, advanced vehicles have achieved very low levels of PAH emissions. These PAH emissions have been studied as 3 categories, “2+ ring”, “3+ ring PAHs” and BaP and in that order the following summary points can be extracted.

7.1.1. “2+ ring PAH” emissions

- The combined total EPA 16 PAH exhaust emissions measured (“2+ring” particulate-bound and vapour phase) was a very small percentage of the total emitted hydrocarbons. In Phase 1: LD diesel 0.6%; HD diesel 0.5%; gasoline 0.15%. In Phase 2: LD diesel 0.07%; gasoline 0.15%.³
- In Phase 1, this total was dominated by 2 ring species in the vapour phase, predominantly naphthalene. Naphthalene accounted for the following percentages of the combined total EPA-16 PAH emissions: 76% LD diesel, 64% HD diesel, 59% gasoline.
- Older diesel vehicles showed an essentially linear increase in “2+ ring PAH” emissions with higher diesel fuel poly-aromatics content. There was also a smaller contribution (presumably due to PAH precursors) from mono-aromatics in the fuel.
- All of the gasoline cars tested gave low emissions of “2+ ring PAH” emissions, an order of magnitude lower than the older technology light-duty diesel vehicles.
- Advanced diesel vehicles (with effective oxidation catalysts or diesel particulate filters) gave very low “2+ ring PAH” emissions, even lower than advanced gasoline vehicles, and no longer showed any sensitivity to fuel aromatics or poly-aromatics content.

³ It should be noted that this percentage is derived from the comparison of a subset of selected PAH (i.e. EPA16) with the total gaseous hydrocarbon emissions and does not imply that this is the value for the emissions of all PAH species.

7.1.2. “3+ ring PAH” emissions

- Absolute levels of “3+ ring PAH” emissions from diesel vehicles were low. As a percentage of total emitted hydrocarbons, “3+ ring PAH” emissions accounted for - Phase 1: LD diesel 0.07% of HC; HD diesel 0.04% of HC; Phase 2: LD diesel 0.05% of HC.
- In older diesel vehicles, there was an increase in “3+ ring PAH” emissions with higher diesel fuel poly-aromatics content. There was no effect from mono-aromatics content.
- “3+ ring PAH” emissions from the gasoline cars tested were very low, close to blank values.
- Advanced diesel vehicles with state-of-the-art exhaust after-treatment systems showed very low “3+ ring PAH” emissions, in the same range as the gasoline vehicles.
- In these advanced diesel vehicles, “3+ ring PAH” emissions were so low that there was no longer any sensitivity to diesel fuel poly-aromatics content.

7.1.3. BaP emissions

- BaP emissions are a very small percentage of the total HC emissions. In Phase 1: LD diesel 0.0004% of HC; HD diesel 0.00005% of HC. In Phase 2 LD diesel 0.0006% of HC (DPF car 0.0002%).
- In older engines/vehicles without exhaust after-treatment, reducing fuel poly-aromatics content reduced BaP emissions. However, even the extreme Swedish Class 1 diesel fuel produced significant BaP emissions in the older diesel vehicles. This indicates that the majority of BaP emissions are formed during the combustion process.
- Fuel poly-aromatics content rather than mono or total aromatics content influences BaP emissions from the older LD diesel vehicles.
- Diesel vehicles fitted with effective oxidation catalysts showed lower emissions and less fuel sensitivity than the older vehicles.
- A light-duty diesel vehicle fitted with a PM trap gave BaP emissions lower than the three-way catalyst equipped gasoline vehicles, and showed no sensitivity to fuel poly-aromatics content.
- BaP emissions from the gasoline cars were very low; close to the level of the blanks.

7.2. SUMMARY OF LIGHT-DUTY VEHICLE DATA

Figures 19-21 summarise the whole light-duty data-set by vehicle, for both gasoline and diesel. For each car, the data presented are the means of all fuels tested. The improvements in control of PAH emissions with advanced emissions control technology are immediately apparent.

Figure 19 "2+ ring PAH" emissions averages for each vehicle

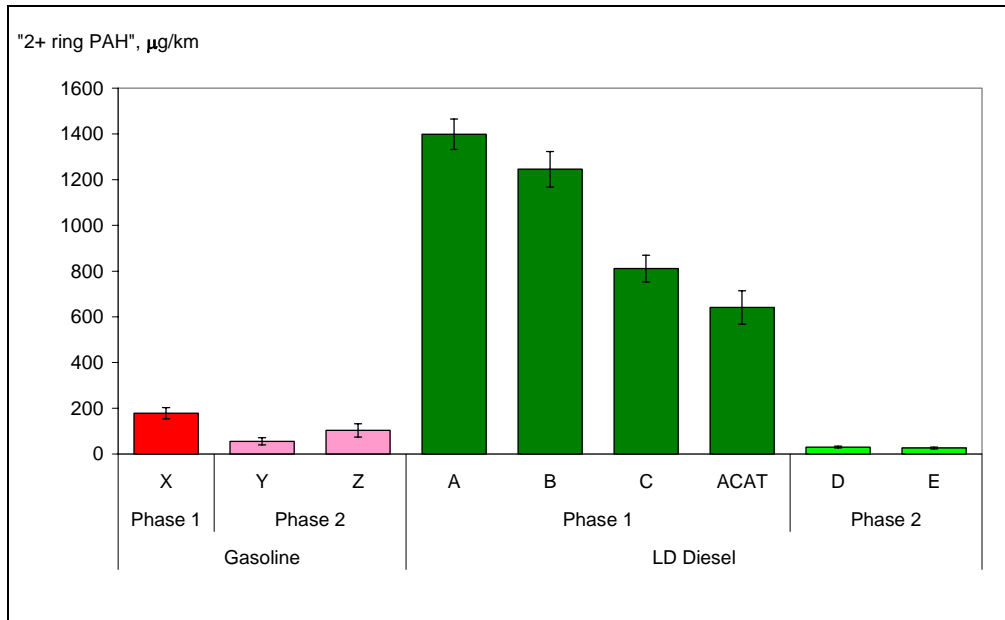


Figure 20 "3+ ring PAH" emissions averages for each vehicle

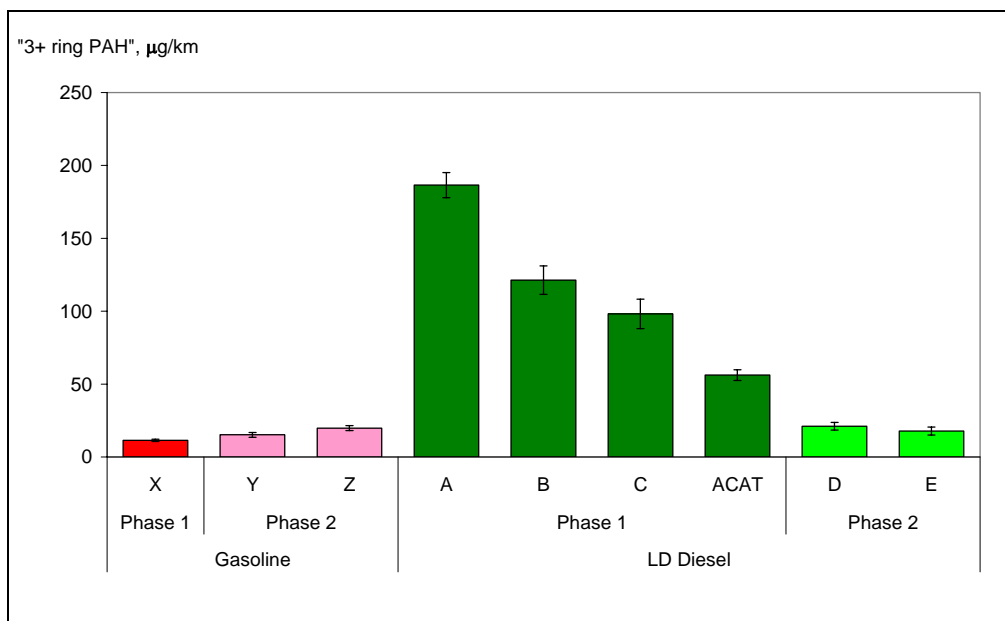
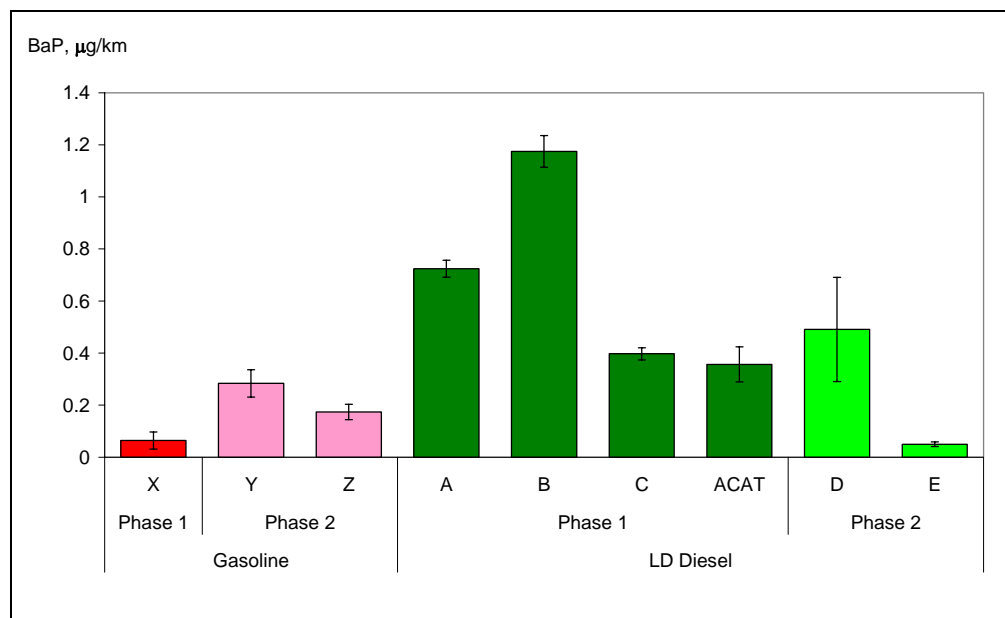


Figure 21 BaP emissions averages for each vehicle

All of the gasoline cars showed very low “2+ ring PAH” emissions (**Figure 19**). The older diesel cars showed higher emissions which reduce with the fitting of oxidation catalysts. The advanced technology diesel cars, with efficient oxidation catalysts and/or DPFs showed very low emissions, even lower than the gasoline cars.

The “3+ ring” data (**Figure 20**) showed similar trends, the only notable difference being that the advanced diesel cars achieved emissions levels equal to but not better than (as was seen for “2+ ring PAHs”) the gasoline cars.

BaP emissions were in all cases very low compared to “2+ ring” and “3+ ring” PAH emissions. The BaP data (**Figure 21**) showed slightly different trends to those seen with “2+ ring” or “3+ ring PAH” emissions. For example, car B showed higher BaP emissions than car A, whereas the reverse was true for “2+ ring” and “3+ ring” PAHs. Also the BaP data on car D were very variable. The results for “2+ ring” PAHs and “3+ ring” PAHs were at much higher levels, more repeatable and are considered more meaningful as a measure of the technology effects.

On all 3 measures of PAH emissions, the use of a particulate trap on a light-duty diesel vehicle virtually eliminated all PAH emissions.

7.3. CORRELATIONS WITH REGULATED EMISSIONS

In order to confirm that trends in PAH emissions follow the trends in regulated emissions, the “2+ ring PAHs”, “3+ ring PAHs” and BaP emissions were plotted against HC and PM emissions respectively. **Figures 22** and **23** show the scatter plots for “2+ ring” and “3+ ring PAHs” versus HC emissions. The individual points on the graphs are the averages of the data for each fuel and vehicle combination

tested. The other plots mentioned above can be found in **Appendix 6** and the average regulated emissions data can be found in **Appendix 2**.

Figure 22 "2+ ring PAH" emissions versus HC emissions

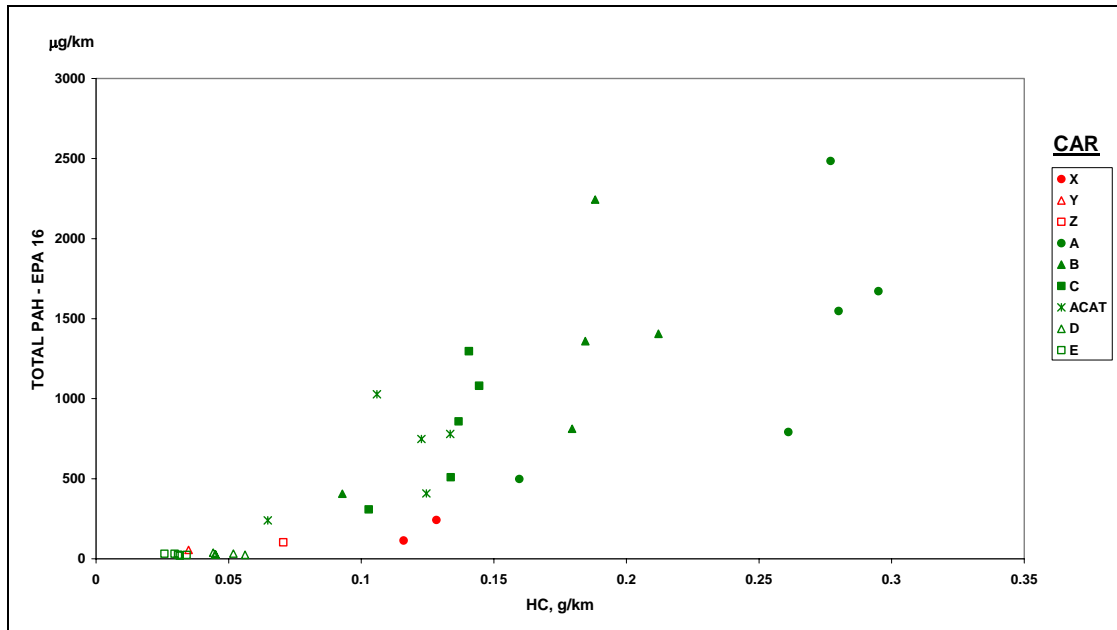
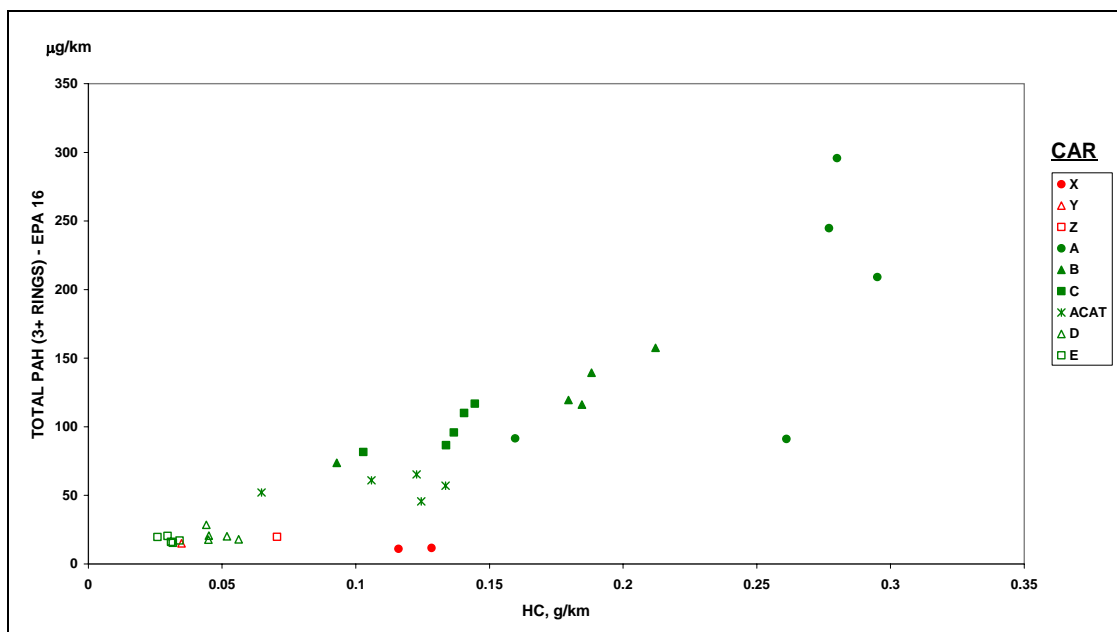


Figure 23 "3+ ring PAH" emissions vs. HC emissions

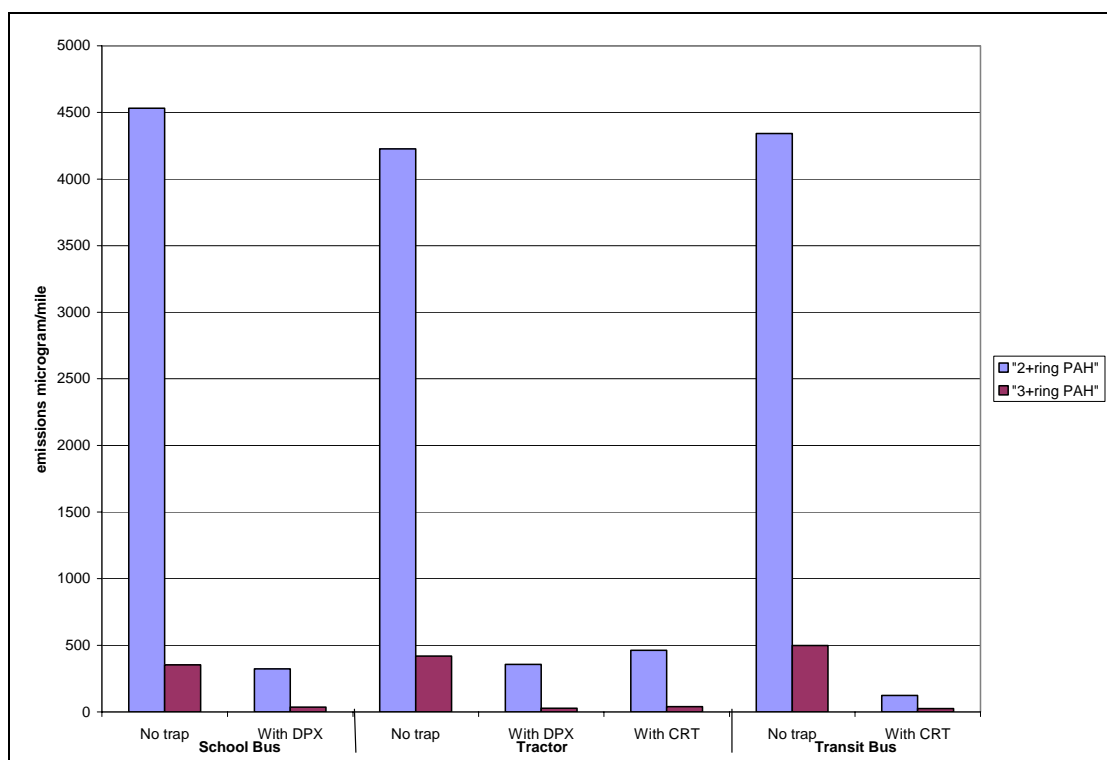


Figures 22 and 23 show clear trends for both “2+ring” and “3+ ring PAH” emissions to reduce as total HC emissions diminish. It is clear that the advanced emissions controls which are being implemented to control HC and PM emissions are also effective in controlling PAH emissions. The variability at the higher HC emissions levels is in part due to the fuel effects in older vehicles described earlier. With the advanced vehicles, low HC and PM (see also Appendix 6) emissions are accompanied by low PAH emissions and there is no longer any fuel sensitivity.

7.4. ADVANCED HEAVY-DUTY ENGINES

Advanced heavy-duty engines were not tested in this programme. However, similar trends on HD engines fitted with PM traps are evident in the literature. For example, SAE 2002-01-2873 [16] showed that fitting particulate filters (DPX, CRT) to HD vehicles in various type of service gave very large reductions in PAH emissions (Figure 24) and reduced sensitivity to fuel quality.

Figure 24 Effect of PM Traps on PAH emissions (combined vapour phase and particulate-bound) from various heavy-duty diesel vehicles (data source SAE 2002-01-2873 [16])

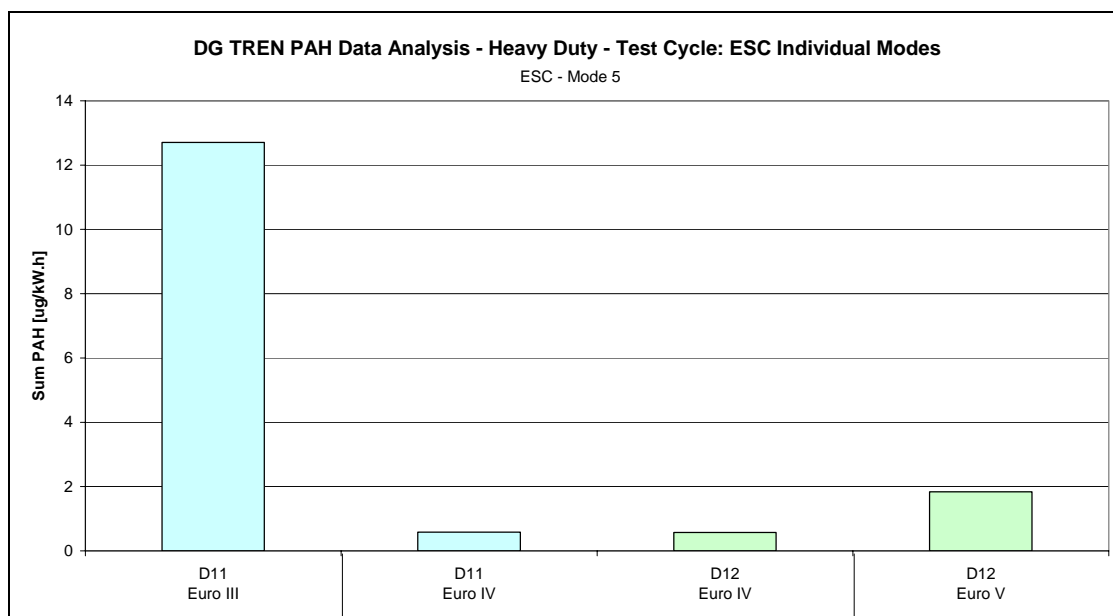


Further, CONCAWE report 2/05 describes regulated emissions results with advanced diesel engines and vehicles [15]. In this work, a prototype Euro-4 system with EGR and a CRT, and a prototype Euro-5 system with SCR/urea but without a DPF, were tested and both gave low PM emissions and very low HC emissions. In the prototype Euro-5 system, the HC emissions were so low that

they were not measurable. Assuming that the trends between PAH emissions and regulated emissions seen in the light-duty tests are also valid for heavy-duty, then very low PAH emissions would also be indicated for the heavy-duty engines.

In the tests described in CONCAWE report 2/05 [15], some limited PAH speciation was carried out, in this case only on the collected particulates, not on the vapour phase. Similar but not identical PAH species were measured in this programme and were summed as particulate-bound PAHs ("3+ ring"). **Figure 25** shows an example of data from steady state mode 5 of the ESC test.

Figure 25 Heavy-duty Engine Data - Particulate-bound PAHs



Comparisons of the three engines can be made on two different sulphur-free (<10 ppm S) fuels (D11 and D12). This confirmed very low PAH emissions for both of the advanced engines. The Euro-4 engine with CRT showed the lowest PAH emissions, but the Euro-5 prototype system also gave very low PAH emissions, probably because the SCR system also included an effective oxidation catalyst.

From all of these data, it seems clear that, for both light-duty and heavy-duty engines, the advanced after-treatment systems which are being fitted to control HC and particulate emissions are also highly effective in controlling PAH emissions.

The introduction of low sulphur fuels is assisting by enabling the widest range of after-treatment systems to be applied.

8. CONCLUSIONS

- The combined total EPA-16 (“2+ ring”) PAH exhaust emissions (particulate-bound and vapour phase) was a very small percentage of the total emitted hydrocarbons
- Older diesel vehicles showed relatively high exhaust PAH emissions and these increased linearly with higher diesel fuel poly-aromatics content.
- Reducing diesel fuel poly-aromatics, even to zero, would not eliminate exhaust PAH emissions, as a significant proportion is combustion derived.
- Gasoline vehicles with three-way catalysts or other advanced exhaust after-treatment systems showed very low PAH emissions compared to the older diesel vehicles.
- Advanced diesel vehicles with state-of-the-art exhaust after-treatment systems showed very low PAH emissions, close to or below the gasoline vehicles.
- In these advanced diesel vehicles, PAH emissions were so low that there was no longer any sensitivity to diesel fuel aromatics content.

Overall, it is clear that the advances in exhaust after-treatment, which are being implemented for the control of total hydrocarbon and particulate emissions, are also effective in controlling PAH emissions.

Lower sulphur fuels have a role in enabling the most advanced exhaust after-treatment technologies to be applied. With increasing market penetration of these advanced vehicles, PAH emissions from road transport should soon no longer be a concern.

9. ACKNOWLEDGEMENTS

CONCAWE's Fuels quality and Emissions Special Task Force, FE/STF-12, wish to place on record the contribution of staff from the following organisations to the work reported here:

- BP Research, Sunbury, UK
- BP Research, Pangbourne, UK
- Esso Research Centre, Abingdon, UK
- Ricardo Engineering Consultants, Shoreham-by-Sea, UK
- Shell Global Solutions (UK), Cheshire Innovation Park, UK.

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11. GLOSSARY

BaP	Benzo(a)pyrene
CRT	Continuously Regenerating Trap
DI	Direct Injection
DISI	Direct Injection Spark Ignition
DPF	Diesel Particulate Filter
DPX	Diesel Particulate Filter (Engelhard)
ECE	Urban driving part of the NEDC
ECE R49	Regulatory emissions test cycle for heavy-duty engines up to Euro-2
EGR	Exhaust Gas Recirculation
EN 590	European standard for diesel fuel
EN 228	European standard for unleaded gasoline
EPEFE	European Programme on Emissions, Fuels and Engine Technologies
ESC	European Steady-state Cycle
EPA	US Environmental Protection Agency
EPA-16	Sixteen PAHs designated by the EPA as Priority Pollutants
EPAQS	UK Government's Expert Panel on Air Quality Standards
EU	European Union
HC	Total emitted hydrocarbons
HD	Heavy-duty
HPLC	High Performance Liquid Chromatography
IARC	International Agency for Research on Cancer
IDI	Indirect injection
IP 391	Laboratory test for aromatics content of diesel fuels
LD	Light-duty

MPI	Multiple Point Injection
NEDC	Regulated European light-duty drive cycle
PAC	Polycyclic Aromatic Compound
PAH	Poly-aromatic Hydrocarbon
PM	Particulate Mass
SCR	Selective Catalytic Reduction
S.D.	Standard Deviation (of mean value)
TPS	Total PAH sampler
TWC	Three-way catalyst

APPENDIX 1 FUEL ANALYSIS DATA

Table A Analysis of Diesel Test Fuels from Phase 1 (averaged across all testing labs)

Mean Values						
Property	Test method	Fuel D1	Fuel D2	Fuel D3	Fuel D4	Fuel D5
		95061/98	95125/98	95039/98	95040/98	95038/98
		Low P.A.	Medium P.A.	High P.A.	Low M.A.	Sw. Cl. 1
Density (kg/m³)	various methods	0.8433	0.8430	0.8432	0.8429	0.8157
Sulphur (% m/m)	various methods	0.04	0.04	0.04	0.04	<0.01
Sulphur (mg/kg)	various methods	448	387	380	406	6
KV @ 40°C (cSt)	ASTM D445/D446	2.85	2.72	2.65	2.84	2.03
Distillation (°C)	ASTM D86					
IBP		174	185	199	208	186
5% v/v		200	208	217	223	201
10% v/v		211	217	223	230	206
20% v/v		231	232	234	241	214
30% v/v		252	249	248	252	222
40% v/v		266	263	261	262	230
50% v/v		276	274	272	270	237
60% v/v		286	283	281	278	244
70% v/v		296	293	290	286	251
80% v/v		309	306	303	298	260
90% v/v		328	325	323	319	272
95% v/v		348	344	343	339	282
FBP		361	358	357	356	295
Distillate (%)		97.8	97.8	97.8	97.9	98.1
Residue (%)		1.7	1.8	1.8	1.6	1.5
Loss (%)		0.4	0.3	0.3	0.3	0.2
Cetane Number	ASTM D613	50.2	50.5	49.7	49.5	52.9
Cetane Index	ASTM D4737	50.5	50.7	50.9	51.3	52.7
C:H Ratio (%m)	various methods					
Carbon		85.5	85.8	86.5	85.9	85.0
Hydrogen		13.4	13.3	12.9	13.0	14.0
Cal Value	various methods					
Net (MJ/kg)		42.8	42.8	42.8	42.8	43.2
Gross (MJ/kg)		45.5	45.5	45.5	45.7	46.2
Aromatics (% m/m)	IP391					
Mono		21.5	21.1	21.0	10.7	4.6
Di		1.1	5.3	10.0	10.4	0.2
Tri		0.1	1.0	1.9	2.0	0.0
Di + Tri		1.2	6.3	11.9	12.4	0.2
Total		22.7	27.3	32.9	23.1	4.7

Table B Analysis of Diesel Test Fuels from Phase 2 (single lab results)

Mean Values						
Property	Test method	Fuel D6	Fuel D7	Fuel D8	Fuel D9	Fuel D10
		SWC1				
Density (kg/m³)	IP 365	0.8093	0.8304	0.8339	0.8385	0.8415
Sulphur (mg/kg)	ASTM D2622	2	3	8	14	7
KV @ 40°C (cSt)	ASTM D445/D446	1.80	2.60	2.55	2.55	2.52
Distillation (°C)	ASTM D86					
IBP		182	178	179		177
10% v/v		196	205	208	216	210
20% v/v		203	220	221	217	223
30% v/v		209	234	234	225	236
40% v/v		216	249	248	238	249
50% v/v		225	264	261	254	261
60% v/v		234	277	275	269	273
70% v/v		244	290	288	283	286
80% v/v		255	306	303	298	300
90% v/v		269	326	323	337	321
95% v/v		279	343	339	348	338
FBP		292	351	352		353
Cetane Number	ASTM D613	55.0	54.3		51.1	
Cetane Number	IQT	49.6	50.7	49.9	47.3	48.0
Cetane Index	ASTM D4737					
C:H Ratio (%m)						
Carbon		85,7	86.1	86.4	86.9	86.9
Hydrogen		14.3	13.5	13.2	13.2	13.0
Cal Value						
Net (MJ/kg)		43.5	43.3	43.3	42.9	43.0
Aromatics (% m/m)	IP391					
Mono		1.5	15.2	15.0	15.0	15.2
Di		<0.1	1.7	4.6	7.0	8.7
Tri		0	.4	0.4	0.4	0.4
Di + Tri		<0.1	2.1	5.0	7.4	9.1
Total		1.5	17.3	20.0	22.4	24.3

Table C Analysis of Gasoline Test Fuels [single lab analysis]

Property	Units	Fuel G1	Fuel G2	Fuel G3
		Low S/Aromatics	High S/Aromatics	
Density @ 15°C	kg/m ³	0.7481	0.7672	0.7508
RVP	mbar	457	499	
RON		95.6	98.3	97.9
MON		86.5	86.7	84.8
Sulphur	mg/kg	19	154	46
Distillation				
IBP	°C	37.5	35	30
10% v/v	°C	65	57	47
20% v/v	°C	75	68.5	54
30% v/v	°C	84.5	80	61
40% v/v	°C	93	93.5	71
50% v/v	°C	98	106	84
60% v/v	°C	101.5	117.5	97
70% v/v	°C	103.5	128.5	117
80% v/v	°C	106	142.5	146
90% v/v	°C	109	159	178
95% v/v	°C	113	169.5	188
FBP	°C	132.5	201	196
Recovery	% v/v	98	96.5	99.1
E70	% v/v	15	21	39
E100	% v/v	55	45	62.5
E120	% v/v	97.5	62.5	
E150	% v/v		85	81
E180	% v/v		97.5	
Carbon	% m/m	6.64	6.87	87.0
Hydrogen	% m/m	11.69	11.57	13.0
Oxygen	% m/m	0	0	
Paraffins	% v/v	6.41	6.49	
Iso-paraffins	% v/v	45.5	31.8	
I + N paraffins	% v/v	51.9	38.3	49.9
olefins	% v/v	6.4	11.6	14.2
naphthenes	% v/v	5.59	3.61	
aromatics	% v/v	35.3	46.09	35.9
total	% v/v	99.67	99.58	100
benzene	% v/v	0.17	1.59	0.09

APPENDIX 2 REGULATED EMISSIONS

Regulated emissions are given in **Tables A.2.1 to A.2.3** below, averaged by fuel for each engine and vehicle. These data relate to the standard legislative emissions test cycles, applicable at the time, NEDC for LD and R49 for HD.

Table A.2.1 Phase 1 – LD Vehicles

Car	Fuel	HC g/km	CO g/km	NOx g/km	PM g/km
DIESEL					
A	D1	0.261	0.788	0.656	0.0699
A	D2	0.295	0.808	0.679	0.0775
A	D3	0.277	0.803	0.689	0.0770
A	D4	0.280	0.807	0.665	0.0765
A	D5	0.160	0.601	0.612	0.0318
Acat	D1	0.125	0.446	0.604	0.0387
Acat	D2	0.134	0.504	0.628	0.0420
Acat	D3	0.106	0.435	0.650	0.0404
Acat	D4	0.123	0.437	0.640	0.0409
Acat	D5	0.065	0.225	0.607	0.0283
B	D1	0.180	0.553	0.504	0.0596
B	D2	0.185	0.575	0.509	0.0649
B	D3	0.188	0.584	0.522	0.0740
B	D4	0.212	0.605	0.515	0.0673
B	D5	0.093	0.384	0.492	0.0376
C	D1	0.134	0.448	0.661	0.0734
C	D2	0.137	0.454	0.670	0.0775
C	D3	0.141	0.485	0.691	0.0786
C	D4	0.145	0.489	0.670	0.0758
C	D5	0.103	0.299	0.660	0.0538
GASOLINE					
X	G1	0.116	1.032	0.127	-
X	G2	0.128	0.914	0.124	-

Table A.2.2 Phase 1 – HD Engine

Fuel	HC g/kWh	CO g/kWh	NOx g/kWh	PM g/kWh
D1	0.264	0.511	6.488	0.0780
D2	0.266	0.501	6.798	0.0772
D3	0.281	0.494	6.852	0.0807
D4	0.287	0.512	6.539	0.0808
D5	0.294	0.516	5.976	0.0598

Table A.2.3 Phase 2 – LD Vehicles

Car	Fuel	HC	CO	NOx	PM
		g/km	g/km	g/km	g/km
DIESEL					
D	D6	0.045	0.105	0.310	0.0216
D	D7	0.056	0.130	0.319	0.0277
D	D8	0.045	0.159	0.306	0.0274
D	D9	0.044	0.165	0.329	0.0290
D	D10	0.052	0.182	0.325	0.0293
E	D6	0.031	0.074	0.426	0.0019
E	D7	0.034	0.100	0.445	0.0016
E	D8	0.032	0.109	0.454	0.0015
E	D9	0.026	0.105	0.453	0.0016
E	D10	0.030	0.108	0.455	0.0014
GASOLINE					
Y	G3	0.035	0.398	0.037	
Z	G3	0.071	0.344	0.038	

APPENDIX 3 STATISTICAL OVERVIEW

Experimental design

The selection of the test vehicles/engine and fuels is discussed in the main report.

The test procedure was comparatively new at the start of Phase 1 and was expected to be less repeatable in relative terms than (say) regulated emissions testing. Therefore a greater degree of replication would be necessary if significant effects were to be detected. It was thus decided that each fuel would be tested six times in each vehicle. The number of repeats was reduced from 6 to 4 in Phase 2 in light of the repeatability observed in Phase 1 (see **Appendix 4**).

A randomised block design was drawn up for the light-duty diesel tests in which each of the 5 fuels was tested in each car once over days 1-5, once again over days 6-10, 11-15, etc. This protected fuel comparisons against any systematic drift in emissions in any of the three cars. It also ensured that useful information would be accrued if the programme had to be cut short for any reason. The test order was balanced further to reduce the risk of bias due to carry-over effects. 15 blank measurements were made at regular intervals during the test programme. A similar randomised block design was used for the light-duty diesel tests in Phase 2.

The small Phase 1 gasoline programme tested two fuels six times each in a single car. Again a randomised block design was used in which each fuel was tested once over days 1-2, again over days 3-4, etc. Four blanks were then inserted at appropriate points to span the whole test programme. In Phase 2, four or five back-to-back tests were conducted on a single gasoline fuel in each of two vehicles.

Six tests per fuel were also conducted in the Phase 1 heavy-duty diesel programme. However, reconditioning costs meant that changing fuel after every test would be prohibitively expensive. It was thus decided that two sets of three back-to-back tests on each fuel would provide the best balance between precision and cost. A randomised block design was again drawn up in which one set of three back-to-back tests was conducted on each fuel in the first half of the programme and another set in the second half. The fuels were tested in different randomised orders in each half. A blank was conducted after each set of back-to-back tests.

Data validation

The data were validated in the first instance by the laboratories which conducted the actual tests and the subsequent exhaust PAH speciations. The resin, filter and combined data were then examined for outliers, trends and carry-over effects on both a species-by-species and a grouped basis. None of the PAH results and only one regulated particulate matter result (in Phase 1) was found to be so out of line with the rest as to warrant rejection.

Some systematic trends were seen in both the light-duty diesel (both Phases) and heavy-duty diesel results. These could have been due to (a) carry-over effects, (b) variations in ambient or other test conditions or (c) both. However, the robust structure of the experimental design meant these trends would cause minimal bias in comparisons between fuels.

Emissions from catalyst car Acat turned out to be very low in early tests and so a decision was made to remove the catalytic converter. As emissions from vehicles B and C were generally a little lower in concurrent early tests than later on, it follows that emissions from vehicle A without the catalyst may be biased upwards relative to vehicles Acat, B and C.

Blank correction

The measured blank data in both Phases exhibited noise, trends, carry-over effects and outliers in various guises. This meant that we could not “correct” individual exhaust PAH results for blanks without introducing additional sources of error. Indeed there was no universal blank correction strategy which would have been appropriate for all species and for both resin and filter results. In the interests of transparency, therefore, all the tabulated and plotted results in this report are simple averages of the uncorrected raw data (see Calculation of means below).

The PAH emissions data were recorded initially in ng, then converted to ng/l and finally to $\mu\text{g}/\text{km}$ (light-duty diesel and gasoline) or $\mu\text{g}/\text{kWh}$ (heavy-duty diesel). Blank emissions can also be converted from ng to ng/l, but the subsequent conversion to $\mu\text{g}/\text{km}$ or $\mu\text{g}/\text{kWh}$ is not meaningful. In order to make progress, we looked at the conversion factors needed to convert real test data from ng/l to $\mu\text{g}/\text{km}$. We then multiplied the average blank values in ng/l by the average conversion factor to obtain a broad estimate of the likely background PAH contribution to exhaust PAH measurements. These average background levels are superimposed on various plots in this report. Common blank levels were calculated for light-duty diesel and gasoline results in Phase 2 as these tests were conducted at the same laboratory,

Calculation of means

Some emissions programmes [17,18] have used geometric means to average emissions across repeats, fleets or fuel matrices while others have used arithmetic means [11-15]. Geometric means give excellent comparisons across a fleet/fuel matrix in percentage terms and avoid dominance by small numbers of vehicles/fuels when emissions differ by orders of magnitude. However, they underestimate total emissions to the atmosphere. Therefore we have elected to use arithmetic means in this study.

Tables and plots of arithmetic mean emissions have been calculated giving each vehicle and fuel equal weight regardless of the number of tests actually carried out. Standard errors were calculated using weighted regression techniques as described in Annex 05 of the EPEFE report [11], taking the contributions of long-repeat and back-to-back variability duly into account for heavy-duty emissions.

In several of the figures in this report, “error bars” are shown around the average emissions for the various fuels. These have been constructed so that when two fuels are significantly different from one another at $P < 5\%$, their error bars will not overlap, as in EPEFE. We can be 84% confident that the true mean lies within the limits shown. However, these error bars do not take the bias due to the background PAH etc. into account as there is too much uncertainty about the causal mechanisms to derive proper error estimates.

APPENDIX 4 MEASUREMENT PRECISION AND UNCERTAINTY

Accuracy of test results

Experimental measurements of PAH emissions are subject to two major sources of inaccuracy. The *bias* is the systematic difference between the experimental measurements and the “true” value, which in this case is the true quantity of PAH being emitted from the exhaust. Background PAH is considered to be the largest source of bias and is discussed in **Appendix 3**.

The second source of inaccuracy is *experimental error*. Repeat measurements from the same fuel in the same vehicle or engine are subject to random variations. The standard deviations of these variations increased with the level of emissions in all three test programmes. This suggests that the reported emission measurements follow the lognormal distribution which is usual in emissions studies (see EPEFE report [11], CONCAWE LD PM studies [18]).

In the two light-duty diesel programmes, the standard deviations of repeat measurements on the same fuel in the same vehicle were as follows (PAH in $\mu\text{g}/\text{km}$):

	Total “2+ ring PAH” (EPA16)	Total “3+ ring PAH” (EPA16)	BaP
S.D. (long repeats) (Phase 1)	$0.23 \times$ (“2+ ring PAH”)	$0.31 \times$ (“3+ ring PAH”)	$0.22 \times$ (BaP)
S.D. (long repeats) (Phase 2)	$0.43 \times$ (“2+ ring PAH”)	$0.42 \times$ (“3+ ring PAH”)	$1.03 \times$ (BaP)

(These figures were calculated using data from all light-duty diesel cars and fuels.)

The Phase 1 figures are influenced by the low levels of results early in the programme, and possibly also by carry-over effects. Measured levels of “2+ ring” and “3+ ring PAH” were much lower in Phase 2 than Phase 1 (see **Figures 4 and 9**) and the repeatability was in fact better in absolute terms; however the Phase 2 repeatability is worse when expressed on a relative basis. In Phase 2, car D produced BaP emissions comparable to those seen during Phase 1 (see **Figure 14**), and these were very variable.

In the heavy-duty diesel programme, the standard deviation of repeat measurements from the same fuel in the single engine was usually greater for “long repeats” (independent tests conducted some time apart, viz. in the two halves of the test programme) than for tests conducted back to back (PAH in $\mu\text{g}/\text{kWh}$):

	Total “2+ ring PAH” (EPA16)	Total “3+ ring PAH” (EPA16)	BaP
S.D. (back-to-back tests)	$0.14 \times$ (“2+ ring PAH”)	$0.10 \times$ (“3+ ring PAH”)	$0.26 \times$ (BaP)
S.D. (long repeats)	$0.14 \times$ (“2+ ring PAH”)	$0.17 \times$ (“3+ ring PAH”)	$0.37 \times$ (BaP)

Again these S.Ds may be influenced by carry-over effects and so improvements may be possible.

In the Phase 1 gasoline programme, emission levels were close to the limits of detection; no BaP at all was detected in two tests. The six total “2+ ring” (EPA16) measurements on fuel 1 ranged from 30 to 155 $\mu\text{g}/\text{km}$ and on fuel 2 from 151 to 328 $\mu\text{g}/\text{km}$. The total “3+ ring” values

were more repeatable with the S.D. (long repeats) being 0.19 × the measured value. In Phase 2, the repeatability of gasoline tests was similar to or better than that seen in the corresponding light-duty diesel tests. However the gasoline tests were conducted back-to-back with no fuel changes between repeats.

Precision of the analytical methods

Sampling and analysis methods used in this study for determination of the vapour phase and particulate-bound PAH of the exhaust are described in [8] where precision aspects are discussed especially with regard to collection efficiency, adsorbent contamination and repeatability of the sampling system.

For the determination of mono-, di- and tri+ aromatics of the fuels the IP391 method (HPLC) was used and its precision is documented in the method. It should be kept in mind that the reported study on the evaluation of the relationship between PAH emissions and fuel poly-aromatics content is therefore linked to the precision of this method.

APPENDIX 5 OTHER PAHS SELECTED FOR AIR QUALITY MONITORING

In this work, BaP was selected as the only individual PAH to be examined in detail, based on the assumption that BaP would be the PAH selected for monitoring for air quality purposes. The 4th Air Quality daughter directive [5] has indeed identified BaP as the only PAH where an air quality target level has been established (max 1ng/m³ annual mean). However, alongside BaP, the Directive also identifies a further six individual PAHs to be measured and reported. These have been chosen on the basis of their IARC classification and their “potency” as regards health effects. The following table shows these individual PAHs and their “relative” potencies, based on a potency of 1 for BaP.

INDIVIDUAL PAH	RELATIVE POTENCY
Benzo(a)pyrene	1
Benz(a)anthracene	0.1
Dibenz(a,h)anthracene	1.91
Benzo(b)fluoranthene	0.11
Benzo(k)fluoranthene	0.03
Indeno(1,2,3-cd)pyrene	0.08

(i) Benzo(j)fluoranthene is also included in the EU list of PAHs to be monitored, but is not in the EPA 16 list so was not measured in this programme.

The emissions concentrations of the above 6 PAHs are plotted (as stacked bars) in **Figure A.5.1**.

Figure A.5.1 Concentrations of individual PAH selected as markers in AQ 4th DD

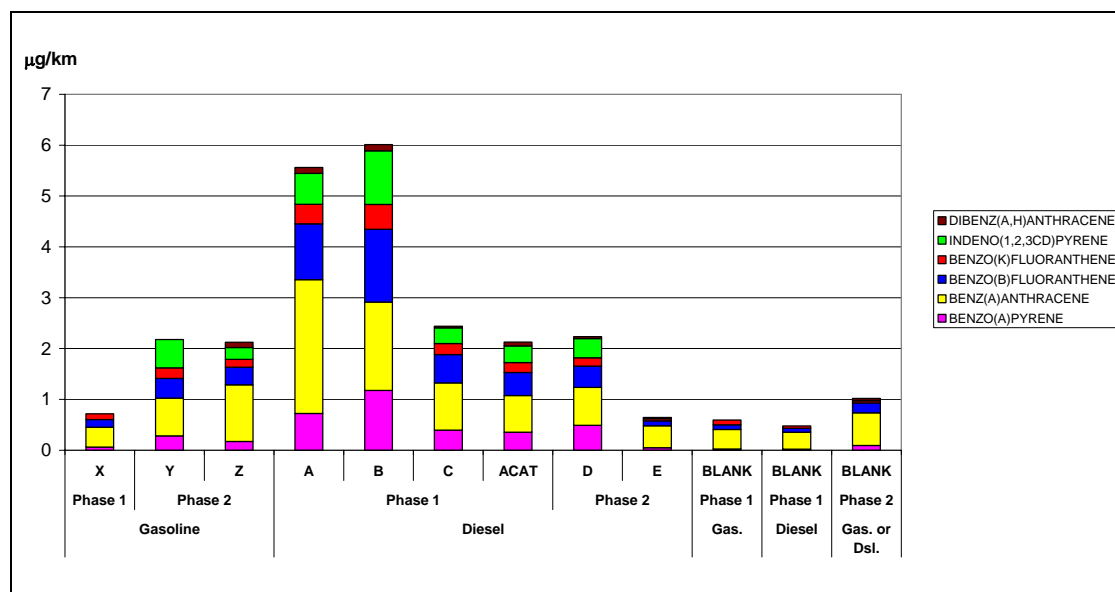


Figure A.5.1 shows that the levels of emissions of these 6 PAHs are very low compared to the total EPA-16 “2+ ring” or “3+ ring PAHs reported in **Sections 6.1** and **6.2**. The pattern of

the vehicle trends in the total of these six species follows the pattern of the BaP emissions. As mentioned earlier for BaP, this pattern differs from those for the total EPA-16, "2+ ring" and "3+ ring PAH" emissions, especially for vehicles B and D. Due to the higher emissions measured for the total EPA-16, "2+ ring" and "3+ ring PAH" emissions, it is considered that these data give a better indication of the overall impacts of technology effects than BaP or the six species reported here.

APPENDIX 6 CORRELATIONS WITH REGULATED EMISSIONS

In order to confirm that trends in PAH emissions follow the trends in regulated emissions, the “2+ ring PAHs”, “3+ ring PAHs” and BaP emissions were plotted against HC and PM emissions respectively. **Figures A.6.1 – A.6.6** show these scatter plots. The individual points on the graphs are the averages of the data for each fuel and vehicle combination tested.

The plots show clear trends of both “2+ ring” and “3+ ring PAH” emissions with total HC or PM emissions. It is clear that the advanced emissions controls which are being implemented to control HC and PM emissions are also effective in controlling PAH emissions.

Figure A.6.1 “2+ ring PAH” (EPA-16) vs. HC emissions

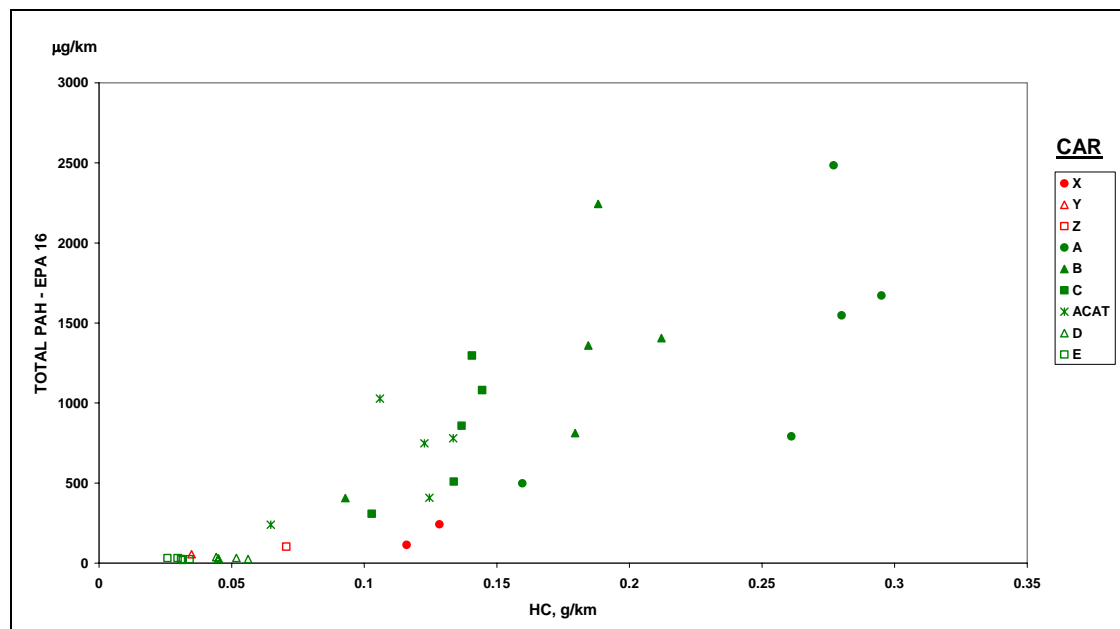


Figure A.6.2 "3+ ring PAH" vs. HC emissions

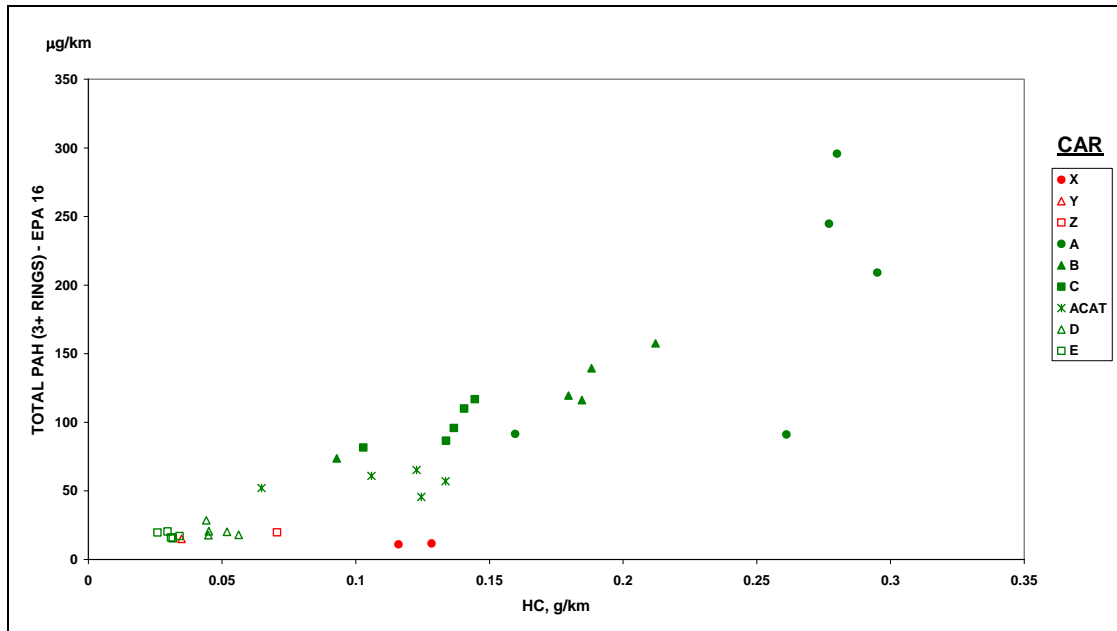


Figure A.6.3 BaP vs. HC emissions

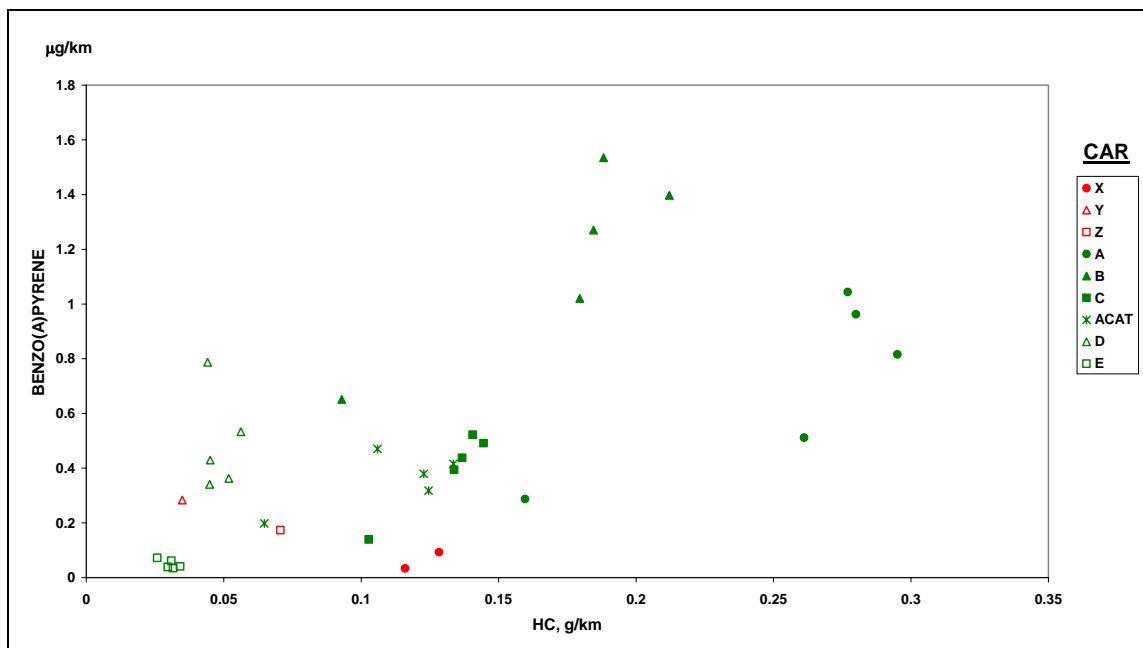


Figure A.6.4 “2+ ring PAH” (EPA-16) vs. PM emissions

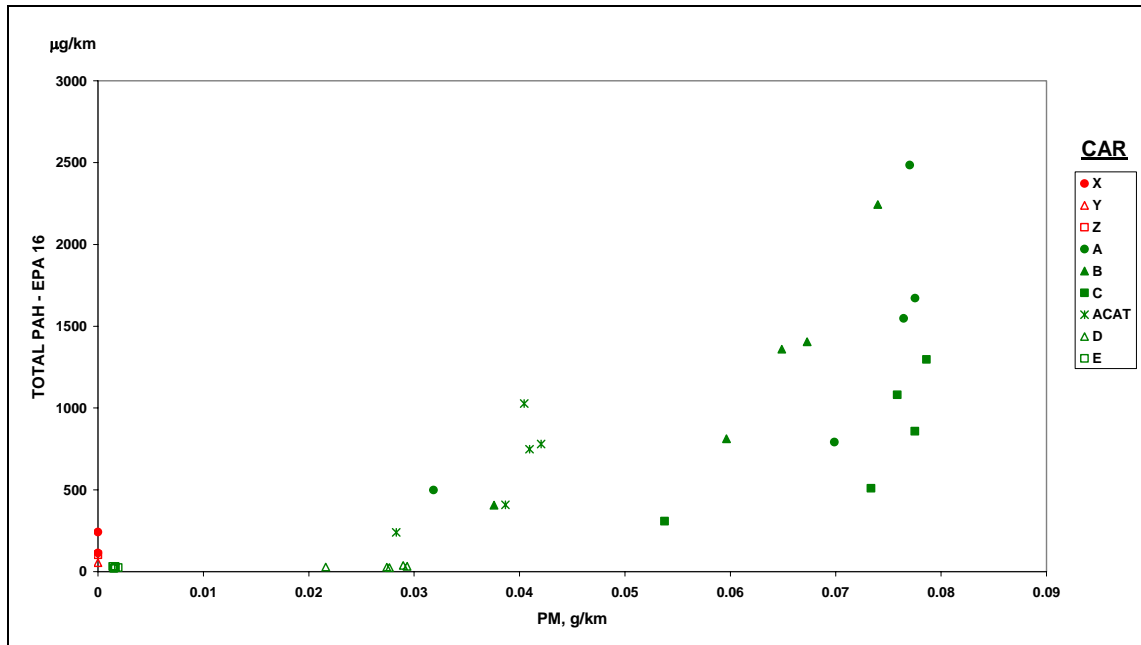


Figure A.6.5 “3+ ring PAH” vs. PM emissions

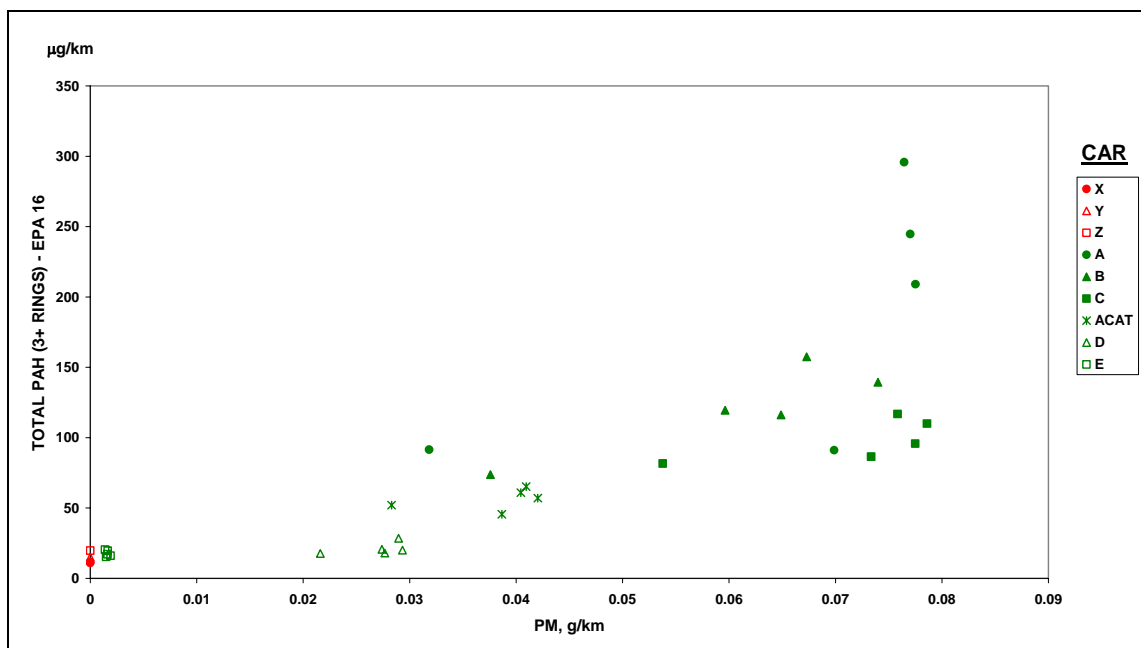
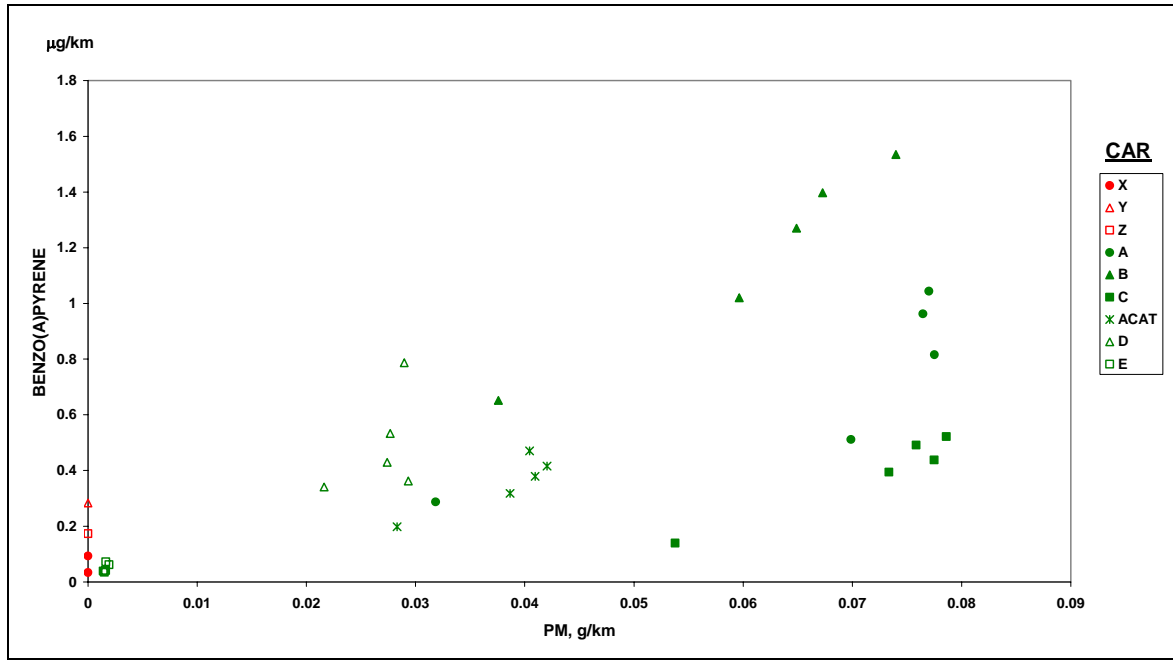


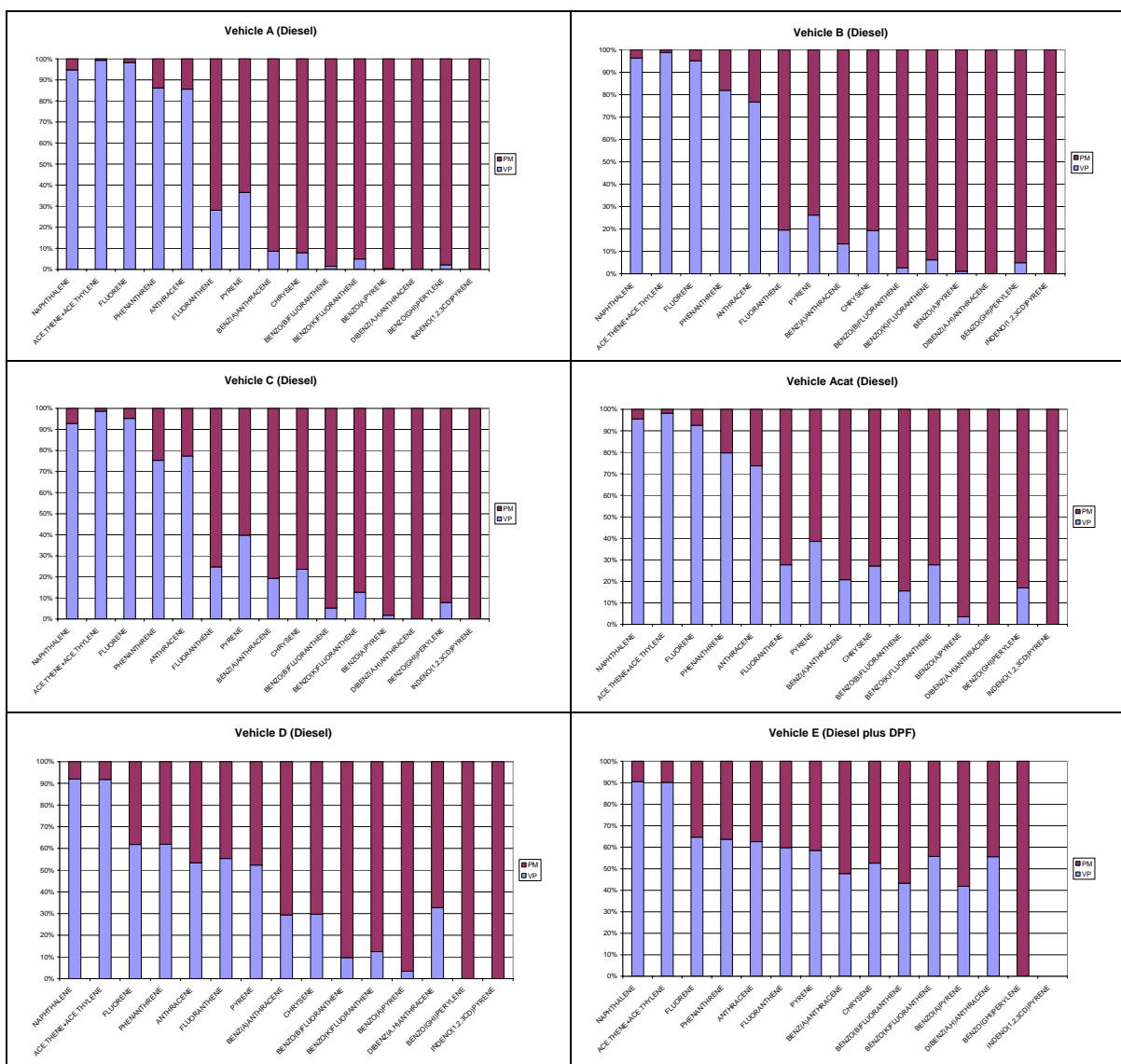
Figure A.6.6 BaP vs. PM emissions

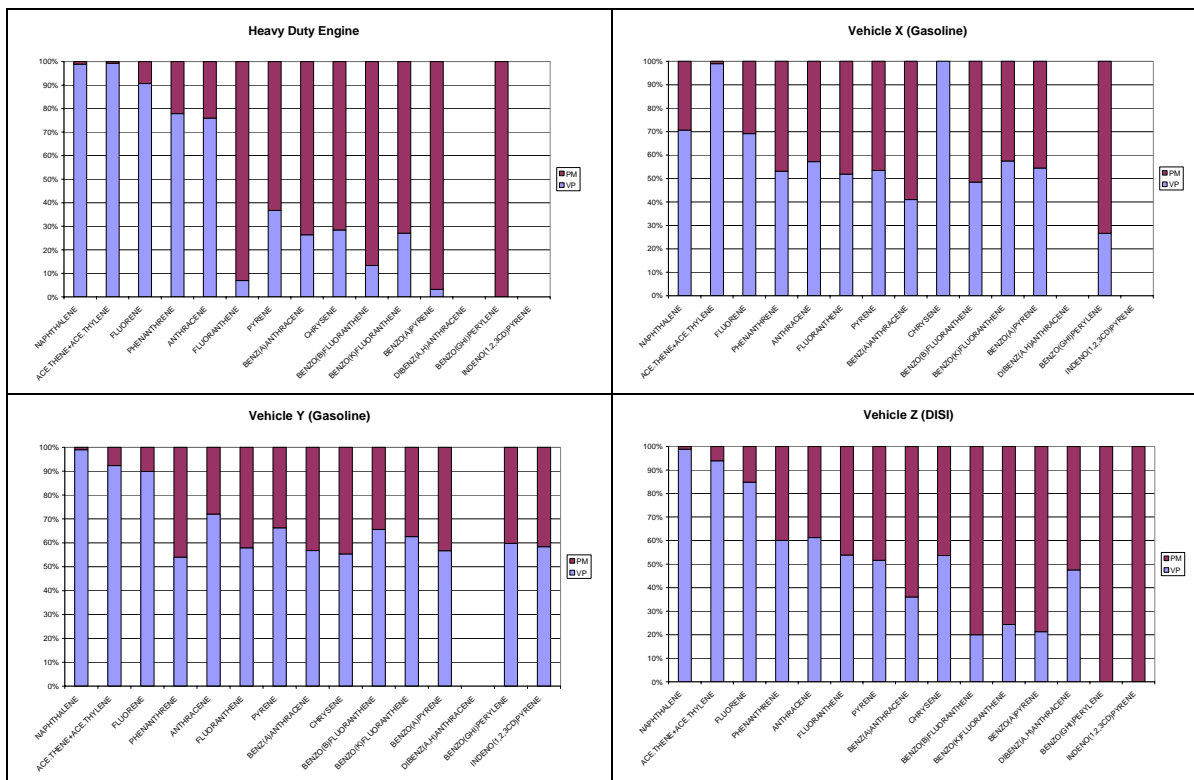


APPENDIX 7 COMPARISON OF LEVELS OF PARTICULATE-BOUND AND VAPOUR PHASE PAH EMISSIONS

Figure A.7.1 shows the split of individual PAHs between the vapour phase and particulates for the different engine and vehicle technologies tested. For each engine, the splits are based on the mean of all fuels tested.

Figure A.7.1 Split of individual PAH between vapour phase and particulates for the different engine and vehicle technologies tested





The PAH appear broadly in order of molecular weight in **Figure A.7.1** with simple 2-ring compounds such as naphthalene and acenaphthalene/acenaphthylene to the left and more complex multi-ring compounds such as indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene to the right (see [6] for chemical formulae and structural diagrams). Two-ring PAH are mostly emitted in the vapour phase while multi-ring compounds are mainly particulate-bound. Emissions of three-ring compounds such as fluoranthene may be found in both the vapour and particulate phases. As emissions of two-ring compounds, particularly naphthalene, exceed all others, it follows that by mass, most PAH emissions are in the vapour phase.

The partitioning of the individual PAH between the vapour and particulate phases differs from vehicle to vehicle. The distribution is strongly related to the total mass of particulate emitted. Thus, for older light-duty diesel vehicles and the heavy-duty engine, where there are significant particulate mass emissions (cf. Figures A.6.4-A.6.6), a greater proportion of emissions are particulate-bound, particularly for 3-ring and 4-ring compounds such as fluoranthene and pyrene. For the conventional MPI gasoline engines (X and Y), it can be seen that the majority of the 3+ ring PAH emissions are in the vapour phase, a direct result of low carbon emissions and limited available adsorption sites. For diesel vehicle E, fitted with DPF, the removal of the emitted carbon results in a phase split which resembles that of the gasoline engines. Conversely vehicle Z (DISI), which has higher particulate mass emissions than conventional gasoline vehicles, shows a phase split somewhere between those of the gasoline and the older diesel engines.

Tables A.7.1 to A.7.3 show the absolute levels of particulate-bound and vapour phase PAH emissions, for “2+ ring”, “3+ ring” and BaP, averaged across all fuels for each engine and vehicle tested.

Table A.7.1 Phase 1 – LD Vehicles

Car	Fuel	VAPOUR PHASE			PARTICULATE-BOUND			COMBINED TOTAL		
		"2+ ring" µg/km	"3+ ring" µg/km	BaP µg/km	"2+ ring" µg/km	"3+ ring" µg/km	BaP µg/km	"2+ ring" µg/km	"3+ ring" µg/km	BaP µg/km
DIESEL										
A	D1	702	65.0	0.000	89	26.1	0.511	791	91.1	0.511
A	D2	1579	151.7	0.008	92	57.4	0.808	1671	209.1	0.816
A	D3	2359	170.2	0.006	126	74.5	1.039	2485	244.7	1.044
A	D4	1420	215.0	0.000	128	80.8	0.962	1548	295.8	0.962
A	D5	397	69.1	0.000	101	22.4	0.287	498	91.5	0.287
Acat	D1	367	28.9	0.029	41	16.6	0.289	408	45.6	0.318
Acat	D2	751	38.9	0.017	29	18.1	0.399	780	57.0	0.416
Acat	D3	979	41.8	0.000	49	19.1	0.471	1028	60.9	0.471
Acat	D4	716	46.7	0.017	33	18.6	0.362	748	65.3	0.379
Acat	D5	172	31.7	0.000	68	20.3	0.198	241	52.0	0.198
B	D1	740	82.0	0.009	72	37.5	1.012	812	119.5	1.021
B	D2	1272	72.4	0.000	88	43.9	1.270	1360	116.3	1.270
B	D3	2146	91.3	0.047	98	48.1	1.488	2243	139.4	1.535
B	D4	1336	112.9	0.009	69	44.6	1.388	1406	157.5	1.397
B	D5	327	38.0	0.002	79	35.8	0.649	407	73.8	0.652
C	D1	433	55.6	0.005	77	30.9	0.390	510	86.5	0.395
C	D2	789	63.9	0.011	69	31.9	0.427	858	95.8	0.438
C	D3	1209	72.4	0.011	88	37.6	0.511	1297	109.9	0.522
C	D4	983	81.9	0.003	97	34.9	0.488	1080	116.8	0.491
C	D5	244	50.4	0.006	64	31.1	0.134	308	81.6	0.140
GASOLINE										
X	G1	76	5.7	0.015	38	5.4	0.019	114	11.1	0.034
X	G2	205	6.2	0.055	37	5.4	0.039	242	11.6	0.093

Table A.7.2 Phase 1 – HD Engine

Fuel	VAPOUR PHASE			PARTICULATE-BOUND			COMBINED TOTAL		
	"2+ ring" µg/kWh	"3+ ring" µg/kWh	BaP µg/kWh	"2+ ring" µg/kWh	"3+ ring" µg/kWh	BaP µg/kWh	"2+ ring" µg/kWh	"3+ ring" µg/kWh	BaP µg/kWh
D1	474	41.4	0.008	40	29.1	0.112	514	70.5	0.119
D2	1311	73.5	0.016	41	29.7	0.091	1352	103.2	0.106
D3	2310	113.3	0.000	57	33.7	0.154	2367	147.0	0.154
D4	1410	130.8	0.000	46	34.6	0.240	1457	165.4	0.240
D5	608	34.0	0.000	40	27.1	0.108	648	61.1	0.108

Table A.7.3 Phase 2 – LD Vehicles

Car	Fuel	VAPOUR PHASE			PARTICULATE-BOUND			COMBINED TOTAL		
		"2+ ring" µg/km	"3+ ring" µg/km	BaP µg/km	"2+ ring" µg/km	"3+ ring" µg/km	BaP µg/km	"2+ ring" µg/km	"3+ ring" µg/km	BaP µg/km
DIESEL										
D	D6	17.3	8.6	0.015	10.5	9.2	0.326	27.8	17.8	0.341
D	D7	14.7	8.2	0.018	10.8	9.9	0.516	25.5	18.0	0.533
D	D8	15.3	10.0	0.022	11.7	10.7	0.408	27.0	20.7	0.429
D	D9	24.2	16.3	0.018	13.5	12.2	0.770	37.7	28.5	0.787
D	D10	23.4	12.1	0.013	8.8	8.1	0.350	32.3	20.1	0.362
E	D6	18.1	10.9	0.014	6.5	5.3	0.048	24.5	16.1	0.062
E	D7	15.1	9.2	0.017	9.0	7.9	0.024	24.1	17.1	0.041
E	D8	11.5	8.1	0.022	8.4	7.3	0.013	20.0	15.4	0.034
E	D9	22.4	12.7	0.035	8.8	7.0	0.038	31.1	19.6	0.072
E	D10	24.7	14.1	0.017	7.2	6.2	0.022	31.8	20.4	0.039
GASOLINE										
Y	G3	47.7	8.6	0.161	7.8	6.5	0.123	55.4	15.1	0.284
Z	G3	92.1	10.7	0.037	11.0	9.0	0.137	103.1	19.8	0.174

APPENDIX 8 MEAN RESULTS FOR INDIVIDUAL PAH EMISSIONS

Table A.8.1 Phase 1 – LD Vehicles: Vapour Phase PAH Emissions, µg/km

Car	Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZO(A,H)ANTHRACENE	BENZO(GH)PERYLENE	INDENO(1,2,3CD)PYRENE
DIESEL																
A	D1	480.7	111.5	45.4	55.5	2.91	2.41	3.78	0.10	0.21	0.01	0.02	0.00	0.00	0.00	0.00
A	D2	1193.3	158.6	75.4	133.0	5.62	4.22	8.45	0.13	0.21	0.01	0.03	0.01	0.00	0.05	0.00
A	D3	1866.1	211.8	110.9	150.6	6.19	4.28	8.28	0.30	0.55	0.03	0.01	0.01	0.00	0.00	0.00
A	D4	928.3	166.5	110.4	188.2	8.15	5.17	12.11	0.46	0.82	0.01	0.01	0.00	0.00	0.00	0.00
A	D5	245.4	59.5	23.4	61.5	1.82	1.73	3.55	0.14	0.31	0.01	0.02	0.00	0.00	0.02	0.00
Acat	D1	276.3	50.1	11.9	23.9	0.64	1.67	1.75	0.16	0.37	0.14	0.09	0.03	0.00	0.19	0.00
Acat	D2	618.4	68.4	25.1	34.2	0.74	1.45	1.57	0.22	0.46	0.07	0.05	0.02	0.00	0.13	0.00
Acat	D3	862.0	59.6	15.6	36.5	0.91	1.00	2.97	0.14	0.24	0.00	0.07	0.00	0.00	0.00	0.00
Acat	D4	594.1	54.1	20.7	41.9	1.14	0.61	2.21	0.10	0.47	0.05	0.04	0.02	0.00	0.08	0.00
Acat	D5	89.1	31.0	20.5	27.2	0.45	1.38	2.00	0.12	0.29	0.09	0.02	0.00	0.00	0.17	0.00
B	D1	553.5	77.4	27.0	73.3	2.91	2.33	2.56	0.23	0.51	0.04	0.03	0.01	0.00	0.09	0.00
B	D2	1085.1	86.1	28.6	65.6	1.80	1.62	2.55	0.17	0.45	0.03	0.02	0.00	0.00	0.06	0.00
B	D3	1846.8	161.3	46.4	82.1	2.49	1.58	4.19	0.22	0.49	0.05	0.03	0.05	0.00	0.05	0.00
B	D4	1083.4	91.8	48.2	101.2	3.26	2.94	4.06	0.37	0.87	0.05	0.03	0.01	0.00	0.12	0.00
B	D5	221.3	53.5	14.5	33.4	1.41	1.24	1.45	0.17	0.33	0.01	0.03	0.00	0.00	0.02	0.00
C	D1	293.6	65.8	17.9	49.0	1.84	2.08	2.33	0.10	0.21	0.02	0.02	0.00	0.00	0.03	0.00
C	D2	621.5	78.4	25.4	57.2	1.62	1.24	3.14	0.17	0.42	0.03	0.03	0.01	0.00	0.04	0.00
C	D3	1015.9	82.4	38.6	64.7	1.28	2.51	3.22	0.19	0.44	0.03	0.03	0.01	0.00	0.02	0.00
C	D4	770.7	85.8	45.0	73.3	1.59	1.25	4.91	0.27	0.45	0.02	0.04	0.00	0.00	0.06	0.00
C	D5	111.5	58.3	24.1	45.1	1.39	1.87	1.43	0.15	0.33	0.04	0.03	0.01	0.00	0.05	0.00
GASOLINE																
X	G1	25.3	43.8	1.5	4.2	0.14	0.64	0.41	0.15	0.01	0.05	0.05	0.01	0.00	0.03	0.00
X	G2	122.3	75.0	1.7	4.2	0.16	0.87	0.47	0.17	0.01	0.09	0.07	0.05	0.00	0.07	0.00

Table A.8.2 Phase 1 – LD Vehicles: Particulate-bound PAH Emissions, µg/km

Car	Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZ(A,H)ANTHRACENE	BENZO(GHI)PERYLENE	INDENO(1,2,3CD)PYRENE
DIESEL																
A	D1	60.1	1.1	1.4	9.5	0.50	5.60	5.97	0.86	1.17	0.73	0.28	0.51	0.01	0.55	0.49
A	D2	32.7	0.8	1.2	21.8	0.97	9.91	13.46	2.55	4.61	1.21	0.43	0.81	0.15	0.78	0.76
A	D3	49.4	1.0	1.1	23.4	1.00	12.10	19.99	3.99	8.97	1.54	0.50	1.04	0.25	0.86	0.82
A	D4	44.3	1.0	1.5	29.6	1.33	12.81	19.00	4.23	9.06	1.53	0.48	0.96	0.19	0.83	0.77
A	D5	75.7	1.2	1.3	10.3	0.34	5.12	4.36	0.40	0.58	0.38	0.14	0.29	0.00	0.35	0.19
Acat	D1	22.1	0.8	1.3	8.2	0.28	2.96	2.66	0.35	0.68	0.33	0.13	0.29	0.05	0.44	0.28
Acat	D2	8.7	1.0	1.3	7.7	0.29	3.21	3.04	0.60	1.12	0.43	0.14	0.40	0.08	0.67	0.41
Acat	D3	26.9	1.0	1.8	7.2	0.30	2.81	4.13	0.85	1.35	0.50	0.19	0.47	0.16	0.74	0.40
Acat	D4	11.2	1.3	1.6	8.0	0.28	3.11	3.44	0.70	1.00	0.42	0.16	0.36	0.08	0.66	0.38
Acat	D5	45.6	0.9	1.5	10.6	0.23	3.94	3.43	0.35	0.79	0.22	0.08	0.20	0.00	0.33	0.16
B	D1	32.4	1.1	1.5	13.6	0.79	7.85	7.97	1.00	1.39	1.23	0.41	1.01	0.06	1.14	0.97
B	D2	40.8	1.2	1.6	16.6	0.67	8.33	8.37	1.60	2.21	1.56	0.50	1.27	0.16	1.43	1.18
B	D3	47.2	0.9	1.4	15.8	0.64	8.46	10.33	2.31	3.45	1.81	0.61	1.49	0.21	1.81	1.26
B	D4	21.8	1.1	1.7	14.7	0.70	8.26	9.01	2.13	3.27	1.66	0.53	1.39	0.18	1.48	1.32
B	D5	40.4	1.1	2.1	17.8	0.81	7.05	5.98	0.50	0.74	0.70	0.23	0.65	0.00	0.76	0.56
C	D1	43.5	1.1	1.5	17.6	0.58	5.51	4.06	0.49	0.83	0.49	0.19	0.39	0.01	0.39	0.29
C	D2	34.9	1.0	1.4	17.9	0.40	5.38	4.41	0.68	1.18	0.54	0.19	0.43	0.02	0.50	0.31
C	D3	47.9	1.1	1.6	20.3	0.39	5.73	5.72	1.11	1.71	0.74	0.25	0.51	0.06	0.59	0.47
C	D4	59.6	1.1	1.3	17.4	0.37	6.11	5.63	1.17	1.67	0.67	0.24	0.49	0.07	0.58	0.44
C	D5	30.2	0.8	1.6	21.7	0.51	4.46	3.03	0.29	0.57	0.21	0.07	0.13	0.00	0.18	0.03
GASOLINE																
X	G1	32.0	0.3	0.6	3.6	0.11	0.73	0.47	0.21	0.00	0.06	0.04	0.02	0.00	0.18	0.00
X	G2	29.4	0.8	0.8	3.8	0.11	0.66	0.30	0.25	0.00	0.10	0.06	0.04	0.00	0.09	0.00

Table A.8.3 Phase 1 – LD Vehicles: Combined Vapour Phase plus Particulate-bound PAH Emissions, µg/km

Car	Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZ(A,H)ANTHRACENE	BENZO(GHI)PERYLENE	INDENO(1,2,3CD)PYRENE
DIESEL																
A	D1	540.8	112.6	46.8	65.0	3.41	8.01	9.75	0.96	1.37	0.75	0.30	0.51	0.01	0.55	0.49
A	D2	1226.0	159.5	76.6	154.7	6.60	14.13	21.91	2.67	4.82	1.23	0.46	0.82	0.15	0.83	0.76
A	D3	1915.5	212.8	112.0	174.0	7.19	16.38	28.27	4.29	9.52	1.56	0.52	1.04	0.25	0.86	0.82
A	D4	972.6	167.5	111.9	217.9	9.48	17.98	31.10	4.69	9.88	1.54	0.49	0.96	0.19	0.83	0.77
A	D5	321.1	60.7	24.7	71.8	2.16	6.85	7.90	0.54	0.88	0.40	0.16	0.29	0.00	0.37	0.19
Acat	D1	298.5	50.8	13.2	32.0	0.93	4.63	4.41	0.51	1.06	0.48	0.23	0.32	0.05	0.63	0.28
Acat	D2	627.1	69.3	26.5	41.9	1.03	4.66	4.61	0.82	1.58	0.50	0.19	0.42	0.08	0.80	0.41
Acat	D3	888.9	60.6	17.4	43.7	1.21	3.80	7.10	0.99	1.60	0.50	0.25	0.47	0.16	0.74	0.40
Acat	D4	605.2	55.4	22.3	50.0	1.42	3.72	5.65	0.80	1.47	0.48	0.21	0.38	0.08	0.74	0.38
Acat	D5	134.7	31.9	21.9	37.8	0.68	5.31	5.42	0.47	1.08	0.31	0.10	0.20	0.00	0.50	0.16
B	D1	585.8	78.5	28.5	86.9	3.70	10.19	10.53	1.23	1.90	1.28	0.45	1.02	0.06	1.23	0.97
B	D2	1125.9	87.3	30.2	82.3	2.47	9.95	10.92	1.77	2.66	1.59	0.52	1.27	0.16	1.49	1.18
B	D3	1894.0	162.2	47.8	97.9	3.12	10.05	14.52	2.53	3.94	1.86	0.64	1.53	0.21	1.86	1.26
B	D4	1105.2	92.9	49.9	115.8	3.96	11.20	13.08	2.50	4.15	1.72	0.56	1.40	0.18	1.60	1.32
B	D5	261.7	54.7	16.6	51.2	2.22	8.29	7.43	0.67	1.07	0.71	0.26	0.65	0.00	0.78	0.56
C	D1	337.1	66.9	19.4	66.6	2.43	7.59	6.39	0.59	1.03	0.51	0.21	0.39	0.01	0.42	0.29
C	D2	656.4	79.5	26.8	75.1	2.02	6.61	7.55	0.86	1.60	0.57	0.22	0.44	0.02	0.54	0.31
C	D3	1063.8	83.4	40.2	84.9	1.67	8.24	8.94	1.30	2.15	0.77	0.28	0.52	0.06	0.60	0.47
C	D4	830.3	86.8	46.4	90.7	1.96	7.37	10.54	1.44	2.11	0.69	0.27	0.49	0.07	0.64	0.44
C	D5	141.8	59.1	25.6	66.8	1.90	6.33	4.45	0.44	0.90	0.25	0.10	0.14	0.00	0.23	0.03
GASOLINE																
X	G1	57.2	44.1	2.0	7.8	0.25	1.37	0.88	0.36	0.01	0.11	0.09	0.03	0.00	0.20	0.00
X	G2	151.7	75.8	2.5	8.0	0.28	1.53	0.76	0.42	0.01	0.19	0.13	0.09	0.00	0.16	0.00

Table A.8.4 Phase 2 – LD Vehicles: Vapour Phase PAH Emissions, µg/km

Car	Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZ(A,H)ANTHRACENE	BENZO(GH)PERYLENE	INDENO(1,2,3CD)PYRENE
DIESEL																
D	D6	4.5	3.8	0.4	6.1	0.07	1.12	0.89	0.19	0.18	0.04	0.02	0.02	0.01	0.00	0.00
D	D7	3.1	2.9	0.4	5.5	0.08	1.16	0.96	0.22	0.20	0.04	0.02	0.02	0.01	0.00	0.00
D	D8	2.7	1.7	0.9	7.0	0.11	1.30	1.04	0.25	0.21	0.04	0.02	0.02	0.00	0.00	0.00
D	D9	4.4	2.4	1.1	13.1	0.13	1.42	1.14	0.22	0.23	0.05	0.03	0.02	0.02	0.00	0.00
D	D10	5.8	4.8	0.8	9.0	0.07	1.37	1.11	0.22	0.20	0.04	0.02	0.01	0.01	0.00	0.00
E	D6	3.5	2.9	0.8	8.3	0.06	1.20	0.84	0.19	0.20	0.03	0.02	0.01	0.02	0.00	0.00
E	D7	2.7	2.0	1.2	6.7	0.11	1.14	0.80	0.19	0.17	0.03	0.02	0.02	0.01	0.00	0.00
E	D8	1.7	1.1	0.8	5.7	0.09	1.05	0.74	0.19	0.17	0.03	0.02	0.02	0.01	0.00	0.00
E	D9	5.1	3.3	1.3	9.9	0.09	1.24	0.85	0.25	0.20	0.07	0.03	0.03	0.03	0.00	0.00
E	D10	4.7	4.8	1.0	11.2	0.11	1.41	0.88	0.21	0.23	0.05	0.02	0.02	0.00	0.00	0.00
GASOLINE																
Y	G3	28.8	6.5	3.7	4.0	0.13	1.11	0.98	0.42	0.75	0.25	0.13	0.16	0.00	0.34	0.32
Z	G3	69.7	8.3	3.4	7.0	0.23	1.30	0.96	0.40	0.68	0.07	0.04	0.04	0.05	0.00	0.00

Table A.8.5 Phase 2 – LD Vehicles: Particulate-bound Phase PAH Emissions, µg/km

Car	Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZ(A,H)ANTHRACENE	BENZO(GHI)PERYLENE	INDENO(1,2,3CD)PYRENE
DIESEL																
D	D6	0.4	0.6	0.4	5.4	0.05	1.15	1.03	0.33	0.30	0.13	0.05	0.33	0.02	0.27	0.11
D	D7	0.3	0.2	0.4	4.6	0.19	1.00	1.01	0.64	0.45	0.36	0.13	0.52	0.02	0.59	0.36
D	D8	0.4	0.2	0.5	5.4	0.05	1.11	0.91	0.50	0.55	0.44	0.17	0.41	0.02	0.66	0.49
D	D9	0.3	0.3	0.6	6.2	0.08	1.00	0.92	0.60	0.57	0.47	0.20	0.77	0.03	0.83	0.52
D	D10	0.3	0.1	0.3	3.4	0.04	0.87	0.80	0.56	0.55	0.50	0.17	0.35	0.04	0.35	0.42
E	D6	0.3	0.3	0.7	3.4	0.04	0.74	0.55	0.25	0.18	0.06	0.02	0.05	0.02	0.00	0.00
E	D7	0.2	0.3	0.5	5.9	0.03	0.84	0.63	0.22	0.15	0.06	0.02	0.02	0.01	0.00	0.00
E	D8	0.3	0.3	0.5	5.4	0.07	0.83	0.58	0.17	0.15	0.04	0.02	0.01	0.00	0.00	0.00
E	D9	0.6	0.3	0.9	5.0	0.05	0.80	0.59	0.22	0.18	0.08	0.02	0.04	0.01	0.00	0.00
E	D10	0.4	0.3	0.1	4.2	0.08	0.84	0.55	0.26	0.21	0.04	0.01	0.02	0.01	0.00	0.00
GASOLINE																
Y	G3	0.3	0.5	0.4	3.4	0.05	0.81	0.50	0.32	0.61	0.13	0.08	0.12	0.00	0.22	0.23
Z	G3	0.8	0.5	0.6	4.6	0.15	1.12	0.90	0.71	0.59	0.28	0.12	0.14	0.06	0.09	0.23

Table A.8.6 Phase 2 – LD Vehicles: Combined Vapour Phase plus Particulate-bound PAH Emissions, µg/km

Car	Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZ(A,H)ANTHRACENE	BENZO(GH)PERYLENE	INDENO(1,2,3CD)PYRENE
DIESEL																
D	D6	4.9	4.3	0.8	11.5	0.11	2.27	1.92	0.53	0.48	0.17	0.06	0.34	0.03	0.27	0.11
D	D7	3.5	3.1	0.9	10.1	0.27	2.15	1.97	0.85	0.65	0.40	0.14	0.53	0.03	0.59	0.36
D	D8	3.1	1.9	1.4	12.4	0.16	2.41	1.95	0.74	0.76	0.48	0.19	0.43	0.03	0.66	0.49
D	D9	4.8	2.7	1.7	19.3	0.20	2.42	2.06	0.82	0.80	0.52	0.22	0.79	0.04	0.83	0.52
D	D10	6.1	4.9	1.1	12.4	0.12	2.25	1.91	0.78	0.74	0.53	0.19	0.36	0.06	0.35	0.42
E	D6	3.8	3.2	1.4	11.6	0.10	1.95	1.40	0.44	0.38	0.09	0.04	0.06	0.04	0.00	0.00
E	D7	2.9	2.4	1.7	12.7	0.14	1.98	1.43	0.41	0.32	0.09	0.03	0.04	0.02	0.00	0.00
E	D8	2.0	1.4	1.2	11.2	0.16	1.88	1.32	0.36	0.32	0.07	0.03	0.03	0.02	0.00	0.00
E	D9	5.6	3.7	2.2	14.8	0.14	2.04	1.45	0.47	0.37	0.14	0.05	0.07	0.04	0.00	0.00
E	D10	5.2	5.1	1.1	15.4	0.19	2.25	1.44	0.48	0.43	0.09	0.03	0.04	0.02	0.00	0.00
GASOLINE																
Y	G3	29.1	7.1	4.1	7.4	0.18	1.92	1.49	0.74	1.36	0.39	0.21	0.28	0.00	0.56	0.56
Z	G3	70.5	8.8	4.0	11.6	0.37	2.42	1.86	1.11	1.27	0.35	0.15	0.17	0.11	0.09	0.23

Table A.8.7 Phase 1 – HD Engine: Vapour Phase PAH Emissions, µg/kWh

Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZ(A,H)ANTHRACENE	BENZO(GH)PERYLENE	INDENO(1,2,3CD)PYRENE
D1	285.2	134.4	12.7	35.5	1.68	0.26	2.84	0.50	0.57	0.04	0.05	0.01	0.00	0.00	0.00
D2	926.6	286.2	24.9	65.8	3.07	0.08	3.49	0.36	0.54	0.11	0.05	0.02	0.00	0.00	0.00
D3	1694.4	463.0	39.1	104.6	4.12	0.00	3.99	0.30	0.25	0.00	0.05	0.00	0.00	0.00	0.00
D4	810.2	417.3	52.1	121.1	4.71	0.00	4.44	0.23	0.28	0.00	0.03	0.00	0.00	0.00	0.00
D5	266.1	290.3	17.8	29.0	1.09	0.00	2.97	0.35	0.49	0.02	0.03	0.00	0.00	0.00	0.00

Table A.8.8 Phase 1 – HD Engine: Particulate-bound PAH Emissions, µg/kWh

Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZ(A,H)ANTHRACENE	BENZO(GH)PERYLENE	INDENO(1,2,3CD)PYRENE
D1	5.6	2.0	3.4	19.5	0.87	0.81	5.65	0.82	0.89	0.22	0.10	0.11	0.00	0.11	0.00
D2	6.7	1.9	2.4	19.6	0.94	0.83	5.89	0.91	0.96	0.22	0.11	0.09	0.00	0.14	0.00
D3	17.6	2.5	3.3	21.4	0.98	1.02	7.10	1.18	1.41	0.23	0.12	0.15	0.00	0.11	0.00
D4	6.4	2.5	2.9	21.1	0.97	1.24	7.72	1.34	1.47	0.27	0.12	0.24	0.00	0.14	0.00
D5	7.7	2.4	3.1	19.6	0.89	0.60	4.18	0.62	0.64	0.20	0.09	0.11	0.00	0.14	0.00

Table A.8.9 Phase 1 – HD Engine: Particulate-bound plus Vapour Phase PAH Emissions, µg/kWh

Fuel	NAPHTHALENE	ACENAPHTHENE+ ACENAPHTHYLENE	FLUORENE	PHENANTHRENE	ANTHRACENE	FLUORANTHENE	PYRENE	BENZ(A)ANTHRACENE	CHRYSENE	BENZO(B)FLUORANTHENE	BENZO(K)FLUORANTHENE	BENZO(A)PYRENE	DIBENZ(A,H)ANTHRACENE	BENZO(GH)PERYLENE	INDENO(1,2,3CD)PYRENE
D1	290.8	136.5	16.0	55.0	2.55	1.06	8.49	1.32	1.46	0.26	0.14	0.12	0.00	0.11	0.00
D2	933.3	288.1	27.3	85.4	4.01	0.91	9.38	1.27	1.50	0.33	0.16	0.11	0.00	0.14	0.00
D3	1711.9	465.5	42.3	126.0	5.10	1.02	11.09	1.49	1.66	0.23	0.16	0.15	0.00	0.11	0.00
D4	816.6	419.7	55.0	142.2	5.68	1.24	12.17	1.57	1.76	0.27	0.15	0.24	0.00	0.14	0.00
D5	273.7	292.7	20.8	48.6	1.98	0.60	7.15	0.97	1.13	0.22	0.12	0.11	0.00	0.14	0.00