polycyclic aromatic hydrocarbons in automotive exhaust emissions and fuels

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

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Brussels
November 1998

ABSTRACT

A comprehensive literature review of polycyclic aromatic hydrocarbons (PAH) in automotive exhaust emissions and fuels has been conducted. Sources and mechanisms of their formation in the internal combustion engine are discussed. Analytical techniques for PAH determination are described and experimental designs to elucidate the sources of PAH are proposed. PAH emissions reduction techniques employing either emissions control technology or alternative fuels are reviewed. The limitations of current understanding of polycyclic aromatic hydrocarbon formation are discussed and recommendations are made for further work. While the study reports on PAH related to automotive issues, some general information is included on environmental and health concerns.

KEYWORDS

polycyclic aromatic hydrocarbons, PAH, automotive emissions, automotive fuels, emissions control systems, alternative fuels.

ACKNOWLEDGEMENT

The contribution of Ricardo Consulting Engineers Ltd. to the sections on analytical techniques is gratefully acknowledged.

The Automotive Emissions Management Group and its Task Force also wish to thank R.C. Hutcheson, Cameron Associates, for his major editorial support.

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SUMMARY

Certain individual polycyclic aromatic hydrocarbons (PAH) have been classified by the International Agency for Research on Cancer as carcinogenic to animals and probably carcinogenic to humans. Evidence for the carcinogenicity of some other PAH is equivocal; for others there is no evidence of carcinogenic potential, whilst many others have not so far been tested. It is prudent to assume that PAH may give rise to health concerns for the general public, since they may be exposed to PAH from various sources. Although it has been shown that the levels of PAH in ambient air are lower now than at any time throughout the century, future levels of ambient PAH will be addressed by a daughter directive under the EU Air Quality Framework Directive. This will require a recommended air quality standard (limit value and associated analytical methodology) to be agreed by 1999. It is therefore important for CONCAWE and other interested parties to know and understand the factors that influence automotive PAH emissions and, in turn, their contribution to ambient PAH levels.

This report reviews a comprehensive selection of the current published literature relating to the occurrence and analysis of polycyclic aromatics hydrocarbons in automotive exhaust emissions and fuels. The subject is developing continuously and it was necessary to apply an editorial “deadline” if the report was ever to be published. Despite the enforcement of this cut-off, over three hundred and forty papers have been reviewed. The effects of vehicle technology and after treatment devices are discussed and the importance of correct sampling and choice of analytical technique is stressed. The relevance of PAH emissions to the wider issues of health and air quality is also noted.

Despite the extensive work and literature relating to the area of automotive PAH emissions, there has been a surprising lack of definitive investigations into the link between fuel PAH content and measured PAH emissions. There has also been a limited amount of work investigating total PAH emissions, i.e. particulate bound plus vapour phase emissions. Most research has, instead, concentrated on particulate bound PAH. This is especially true for diesel investigations where particulate emissions dominate and historically have been the first area to be addressed. There has been little work identified on vapour phase PAH emissions from diesel engines. The nature of gasoline emissions, i.e. predominantly vapour, and the collection systems used, means that results given are closer to “totals”, or “total targeted PM and vapour phase” PAH.

All aftertreatment devices reduce PAH emissions; however the use of aftertreatment has shown a wide range of effect. For gasoline, the presence of a 3-way catalyst effectively reduces PAH emissions to an immeasurably low level. For diesel, the presence of an oxidation catalyst shows a more variable efficiency for PAH reduction.

It is also clear that the range of PAH chosen by scientists for investigation is wide and varied and that the analytical procedures employed are not always shown to be robust. This must be taken into account when trying to compare results from different research programmes.

From the literature survey undertaken, the following conclusions can be made:

- where the data are available (e.g. UK, Japan), current PAH concentrations in ambient air are the lowest ever measured
- total HC emissions (and likewise total PAH) are very low from modern vehicles. Furthermore, targeted PAH species form only a small fraction of the particulate borne HC, and an even smaller fraction of the vapour phase HC
- a wide range of definitions as to what constitutes a “polycyclic aromatic hydrocarbon” may be found and there is no agreed definition for PAH
- there is no standard analytical methodology and a consensus on the major PAH to be measured has still to be established
- there are insufficient data available on automotive emissions to determine to what extent the level of the PAH emissions is related to the PAH content of fuel
- there has been insufficient work on total (vapour phase + PM bound) PAH emissions
- there are two main routes of PAH into the exhaust, fuel PAH survival and combustion derived PAH
- the presence of a three-way catalyst on gasoline vehicles appears to reduce PAH emissions to levels below current detection limits
- diesel exhaust after-treatment systems show greater variation but are generally highly effective in reducing PAH
- some alternative fuels may offer a limited route to some reduction in PAH exhaust emissions.

It is proposed that following this literature survey, further practical work be undertaken to address the above uncertainties. For gasoline, it would appear that there is sufficient literature to understand the nature of current vehicle PAH emissions. As the nature of gasoline emissions are more related to vapour phase than particulate, the work referenced has addressed total PAH emissions more completely than those workers looking at diesel. In the latter , for practical purposes, particulate matter and its associated PAH have dominated the collection process. However, it would be sensible to verify the conclusion relating to gasoline emissions.

For diesel, (both light and heavy duty), the results are less conclusive and a wider scoping programme needs to be carried out to gain an accurate picture of the total PAH emissions and the extent of their relationship with fuel composition.

A CONCAWE report which reviews data forming the basis for the establishment of an Air Quality Standard (focusing on inhalation carcinogenicity) is also under preparation.

1. INTRODUCTION

The occurrence of polycyclic aromatic hydrocarbons in both automotive exhaust emissions and automotive fuels is complex. Any investigation of this subject is faced with a number of difficulties:

- The range of PAH species is vast and analytical techniques are incapable of identifying every single type of compound. As a consequence, investigations "target" specific species, rather than identifying the complete range of PAH involved.
- Most PAH are present in exhaust emissions, fuels and lubricants in minute quantities, frequently at or near the limits of detection.
- The mechanisms of PAH formation are not well understood. Furthermore, inadequacies of experimental design, coupled with difficulties in sampling and measurement, make it difficult to quantify the individual contributions of potential sources to the eventual emissions.
- There are no standard techniques for measuring polycyclic aromatic hydrocarbons and different researchers have employed different techniques of varying accuracy and precision. Comparison of their findings is therefore difficult.
- Difficulties of interpretation are further complicated by the potential for artefact formation within the measurement system (e.g. dilution tunnel entrapment or release of PAH).

In view of the foregoing, it is hardly surprising that the conclusions drawn in much of the published research are often conflicting. As a result, a sound interpretation of the data is only possible after a rigorous and comprehensive review of the literature. CONCAWE have therefore studied over three hundred and forty references in the development of this authoritative understanding of the subject.

The resulting report is inevitably somewhat lengthy and, in order to aid the reader, the publication has been divided into a number of sections. An "overview" (**Section 2**) follows this introduction, which summarises the salient points of the literature review. **Section 3**, which forms the main body of the report, follows the same format as the overview, so that more in-depth information can readily be found by switching to the relevant sub-section of the main body of the publication. Section 3 is, in turn, supported by a number of **Appendices** and appropriate references.

Throughout this report the term "polycyclic aromatic hydrocarbons" (PAH) is used to define compounds with at least **two** 6-membered fused aromatic rings, comprised only of carbon and hydrogen.

CONCAWE embarked on this endeavour in the light of widespread interest in the topic and the likelihood that European legislation will be introduced. Although it is apparent that current PAH concentrations in ambient air are the lowest ever measured (e.g. UK), PAH are to be addressed by a daughter directive under the EU Air Quality Framework directive. This will require a recommended air quality standard (limit value and associated analytical methodology) to be agreed by 1999. It is important that the contribution to ambient PAH levels from automotive sources is understood and consequently CONCAWE formed a task force with the following remit:

- To conduct a literature review to establish what is known about fuel effects on automotive PAH emissions (both gaseous and particulate) and to determine which measurement techniques and procedures are suitable.
- To prepare an appropriate project proposal if it is considered that further work is required to establish the link, if any, between fuel characteristics and PAH emissions. Such a proposal would also compare fuel effects with the influence of vehicle technology.

The current review has concentrated on published literature addressing the level and identification of PAH in automotive fuels and emissions and the relationship between them (where investigated). In order to fully understand the subject substantial effort has been put into investigating the background to PAH measurement. Consequently, details are given on:

- Chemical and physical properties of selected PAH;
- Mechanisms of formation in exhaust streams;
- Control of PAH emissions;
- Sampling techniques, all of which have a substantial influence on the accurate determination and reliable interpretation of results, plus a detailed review of available analytical techniques.

While the study reports on PAH related to automotive issues, some general information is included on health and environmental concerns to bring the automotive issues into perspective. However, no attempt has been made, in this report, to review the health effects of PAH and air quality related PAH since these are complex issues and have been the subject of extensive authoritative review and studies elsewhere.

A CONCAWE report which reviews data forming the basis for the establishment of an Air Quality Standard (focusing on inhalation carcinogenicity) is also under preparation.

The **Overview**, **Section 3** and the **Appendices** all follow the same general structure.

2. OVERVIEW

2.1. INTRODUCTION

This overview presents a summary of **Section 3** and follows the same format. The reader can therefore switch between the relevant sub-sections to acquire more detailed information.

2.2. THE NATURE OF PAH

Multi-ring organic species are called “Polycyclic Aromatic Compounds” (PAC). Within this wide range are species containing heteroatoms (S, N and O) as well as those containing only carbon and hydrogen. This report concentrates on the latter i.e. “Polycyclic Aromatic Hydrocarbons” (PAH), identified in automotive emissions and automotive fuels.

A wide range of definitions as to what constitutes a "polycyclic aromatic hydrocarbon" may be found in the literature. This is largely because the range of specific structures that the analytical techniques employed at different laboratories are capable of quantifying varies greatly - some report only a handful of species, others twenty or more. It is generally assumed by each research group that the species that they can identify are representative of polycyclic aromatics as a whole. The USA's EPA "Priority Pollutants" list of 16 PAH may be taken as a typical example. It includes four species with only two 6-membered benzene rings and two species with three 6-membered rings; the remainder have between four and six. It is important to appreciate that the techniques that are capable of quantifying specific polycyclic aromatic structures do so only for a small minority of the possible structures. In particular alkylated polycyclic aromatics are generally poorly represented.

Researchers are not consistent with the PAH they select to analyse and thus comparison between workers is difficult. “Targeted” PAH indicates an individual's selection and will not be the same for other researchers. It should also be borne in mind that these “targeted” PAH will represent varying percentages of the total PAH emitted.'

PAH occur naturally in crude oils. By virtue of their size and weight they are relatively high boiling point hydrocarbons: the di-aromatic naphthalene has a boiling point of 218°C; the tri-aromatic phenanthrene one of 340°C. Consequently, they appear in gasolines at very low concentrations (generally < 1% m/m di- and < 0.1% m/m tri+ aromatics with < 10 ppm mass for any individual 4+ ring species in European gasolines, although reliable data is lacking) and in diesel fuels at low, but not insignificant, concentrations (typically 1 - 10% m/m for di-aromatics, 0.1 - 3.% m/m for tri-aromatics.

2.3. GENERAL ASPECTS ON HEALTH EFFECTS OF PAH AND ENVIRONMENTAL OCCURRENCE

The International Agency for Research on Cancer Certain has classified certain individual polycyclic aromatic hydrocarbons (PAH) as carcinogenic to animals and probably carcinogenic to humans. Evidence for the carcinogenicity of some other PAH is equivocal; for others there is no evidence of carcinogenic potential, whilst many others have not so far been tested.

Although there is sufficient evidence of carcinogenicity in animals for a handful of PAH, for most there are insufficient reliable data. Amongst the more extensively studied PAH, carcinogenicity potency estimates have been developed, and these suggest at least a thousand-fold range of potency. Most of the available data on carcinogenicity carried out in animal studies relates to studies of repeated skin exposure; very few data are available on the carcinogenicity of PAH by inhalation.

Many PAH have been evaluated in screening tests for mutagenicity, and many show activity, typically after metabolic activation. However, mutagenic potential should not be taken to indicate carcinogenic potential. Similarly, mutagenic potency should not be considered to indicate carcinogenic potency.

Exposure to PAH is seldom limited to individual compounds in the environment. More usually exposure is to complex mixtures of PAH, and these mixtures may be associated with particular industrial processes or activities. PAH have been identified in all of the environmental compartments (air, water, sediment and soil) at various locations. The concentrations of individual PAH detected, and the major sources of these compounds, will vary between compartments and from location to location. In many instances, the occurrence of PAH may be linked to fossil fuel burning (coal and petroleum fuels), but the burning of other materials and specific industrial processes are all associated with the generation and/or release of PAH into the environment (e.g. see list below).

Examples of occurrences associated with the generation and/or release of PAH into the environment.

- production and use of coal tar products
- burning of wood and biomass
- aluminium smelting, iron and steel production
- natural seeps of crude oil
- accidental spills of crude oil and some other petroleum products
- waste incineration
- contamination from used automotive engine oils
- tobacco smoke and the cooking of food

2.4. 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 the situation is very complicated because a wide range of individual compounds is being sampled, each exhibiting unique chemical and physical properties and each of which has the possibility of undergoing further reactions over time.

Historically, PAH determination has been carried out in both ambient and exhaust samples for particulate matter only. This has given information largely on the multi-ringed heavier PAH but has neglected the lighter PAH which are prevalent in the vapour phase. It has only been since the 1980's that the issue of vapour phase PAH has been addressed.

There are, at present, no standard procedures or methodologies for the sampling of PAH. There are, however, recommended procedures available for the collection of particulate (both atmospheric and exhaust) which can be used to address the particulate bound PAH. However, the procedures in question were generally not specifically developed to facilitate PAH analysis.

ISO has investigated the analysis of PAH sampled from air and have produced a draft method and a working document (covering two different analytical procedures) each with sampling protocols attached. However, the particulate collection techniques described within the methods differ from each other and also from other recommended particulate collection procedures. It has also been shown that even recommended techniques can suffer from sampling variation.

There are, in addition, no standard means of calibration for these samplers and very few references make any attempt. There are no standards for addressing collection of vapour phase PAH.

The analysis of PAH is based on chromatographic techniques, with an overall analytical approach of extraction, fractionation and end analysis. A very 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.

2.5. OCCURRENCE OF PAH IN EXHAUST

2.5.1. Introduction

There is a wide range of literature available reporting on the measurement of automotive PAH emissions. The majority of the literature relates to diesel emissions and the measurement of PAH predominantly in the particulate. There are fewer references that deal with vapour phase PAH emissions and also much less information relating to gasoline PAH emissions. Also, surprisingly, there are few authors who attempt to correlate fuel composition/PAH levels with those measured in the exhaust or indeed even include the measurement of PAH in the test fuels used. Of particular importance is the fact that total HC emissions (both vapour phase and particulate borne) are very low from modern gasoline and diesel engines. Furthermore, targeted PAH species form only a small (and ill determined) fraction of the particulate borne HC, and an even smaller (and even less well determined) fraction of the vapour phase HC.

It became increasingly clear during this study that the key to reliable data lies in representative sampling and the analytical approach employed. The majority of the references cited use different analytical systems and consequently direct comparison is not always easy. Data relating to the reproducibility of the analytical system are not often given.

Finally, the reader should be aware of the range of units employed throughout the references before attempting direct comparisons.

2.5.2. Gasoline Exhaust

Polycyclic aromatic hydrocarbons (PAH) are emitted from many combustion sources, including internal combustion engines. The published literature reported several parameters which could be correlated with PAH emissions: i.e. driving mode, air/fuel ratio, engine oil consumption, and gasoline PAH content.

Benzo(a)pyrene (BaP) and benz(a)anthracene (BaA) have often been used as indicators of the total PAH emissions. The references quoted cover work reported from 1970 to 1996 and studied PAH emissions with different vehicle technologies, driving conditions and analytical methods.

The reported levels of PAH in exhaust gas are dependent on the type of engine/vehicle, the driving cycle employed, plus the sampling and the analytical procedures used. Consequently, it is difficult to define maximum and minimum values. Analysis of diluted gas exhaust shows that there is a distribution of PAH between the gas phase and the particulate phase, related to their range of vapour pressures. The use of a dilution tunnel increases the adsorption of PAH to the particles which is especially pronounced for four, or more, ring PAH, such as pyrene. It has also been found that the amount of PAH in the gas phase increases with decreasing molecular weight and increasing vapour pressure of the compounds; a major part of 2-3 ring PAH are in the gas phase.

Examples of emissions of gas phase and particulate associated PAH are shown in **Figures 1** and **2**. These are taken from work reported in 1988 and relate to the single commercial fuel tested in the programme. The driving cycle employed was the US Federal Test Procedure (FTP-75).

Figure 1 Gas phase PAH emissions from a gasoline vehicle

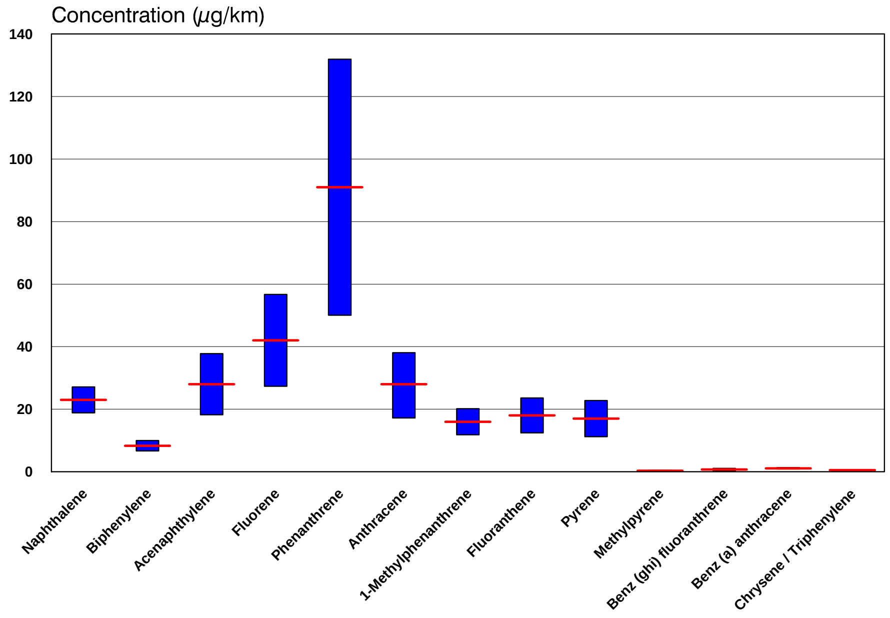
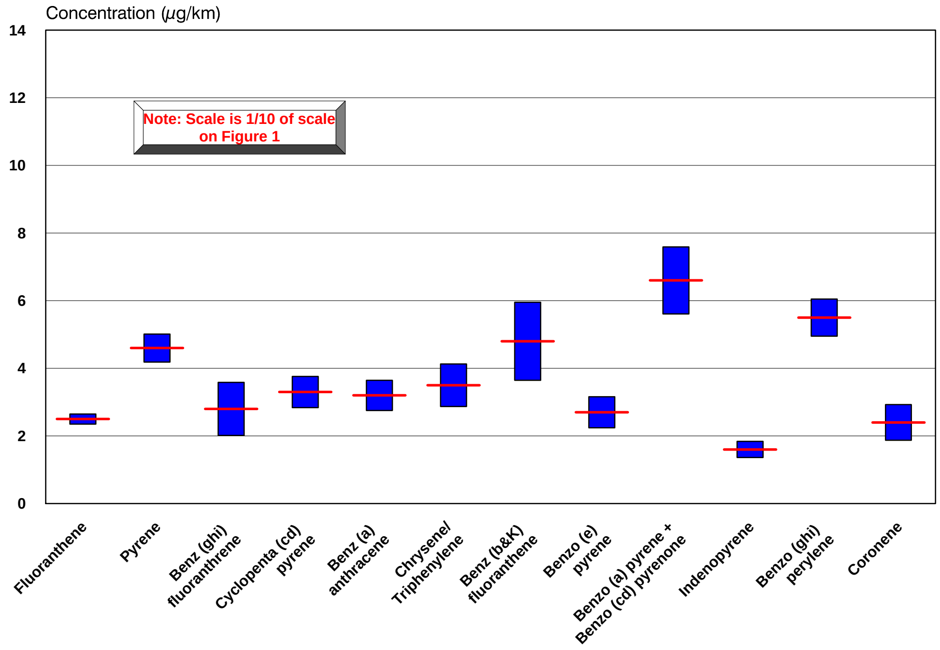


Figure 2 Particulate phase PAH emissions from a gasoline vehicle



2.5.3. Diesel Exhaust

Diesel exhaust is a complex mixture of different compounds, both volatiles and solids. Analysis of volatile organic compounds in the exhaust have concentrated on PAH, light aromatics and aldehydes.

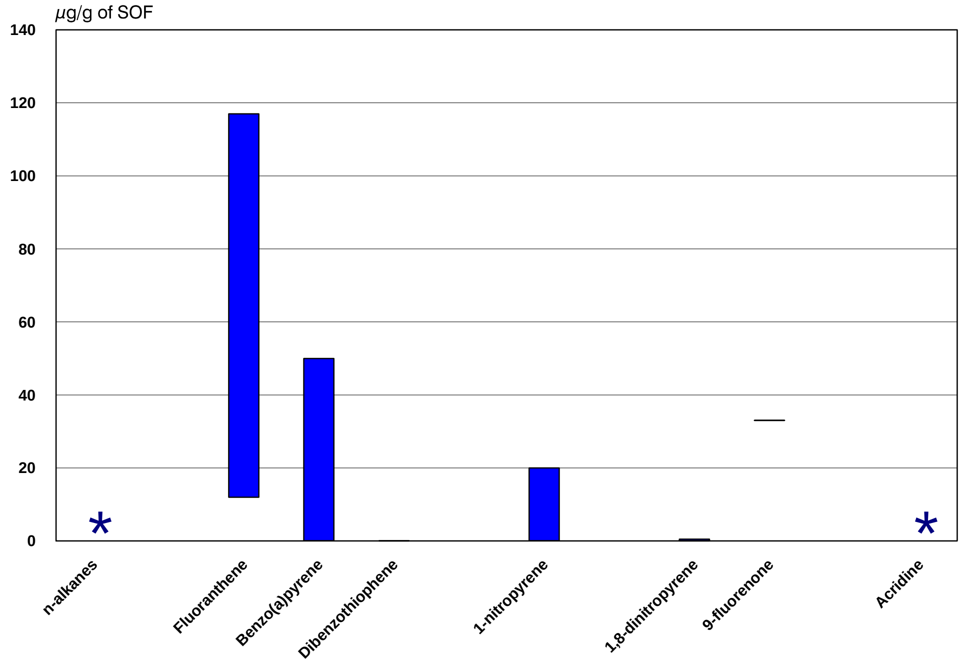
PAH compounds of four or higher ring number will generally be adsorbed to the particles, while lighter compounds are associated with the gas phase. Research indicates that 90% of phenanthrene and 15% of pyrene are found in the gas phase.

Diesel exhaust particles, or particulate matter (PM), consist of a carbon skeleton (particle core) with adsorbed organic and inorganic compounds. The particle core can vary between 40-80 wt-% of PM, whilst the organic fraction may vary between 10-60 wt-%. The remaining inorganic part includes ash, sulphates and bound water.

The soluble organic fraction (SOF) consists of unburned fuel, unburned lubricants and partial oxidation products of these materials.

Figure 3 shows some typical compounds in the SOF from a range of heavy and light duty engines tested in the 1980's and early 1990's.

Figure 3 "Typical" diesel SOF compounds



* : not quantified, only detected.

Figure 4A gives a pictorial representation of five PAH (phenanthrene, fluoranthene, Benz(a)anthracene, Benzo(b/k)fluoranthene and Benzo(e)pyrene) from emission results published in 1994 and indicates the possible spread in values across different vehicle technologies. In order to accommodate the wide range of emissions the figure has had to be plotted on a logarithmic scale. Although this scaling is a convenient way of depicting these values, it can provide a misleading impression of the actual magnitude of the emissions. **Figure 4B** presents exactly the same data plotted on a linear scale, providing a more realistic view of the differences between the emission levels.

Figure 4A Selected PAH in automotive diesel engine particulate phase exhaust (Logarithmic Scale)

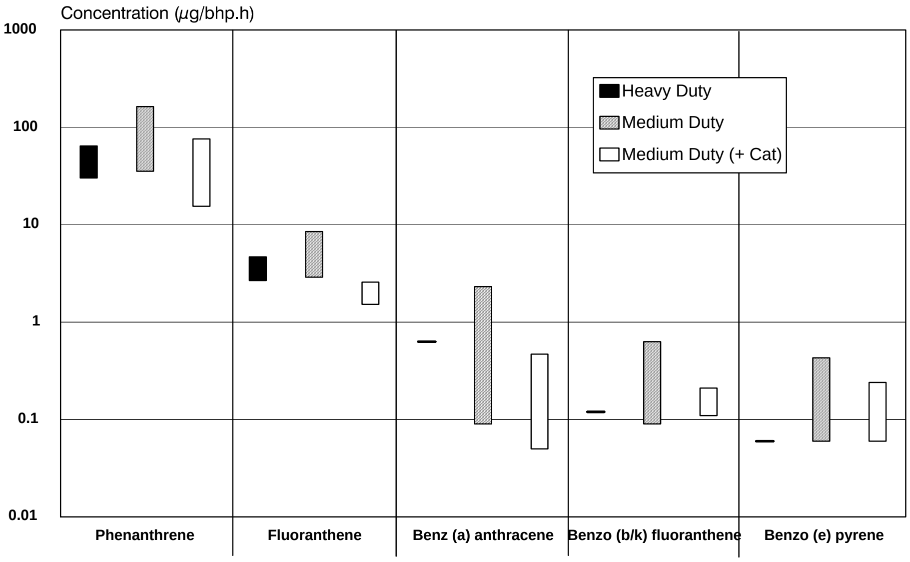
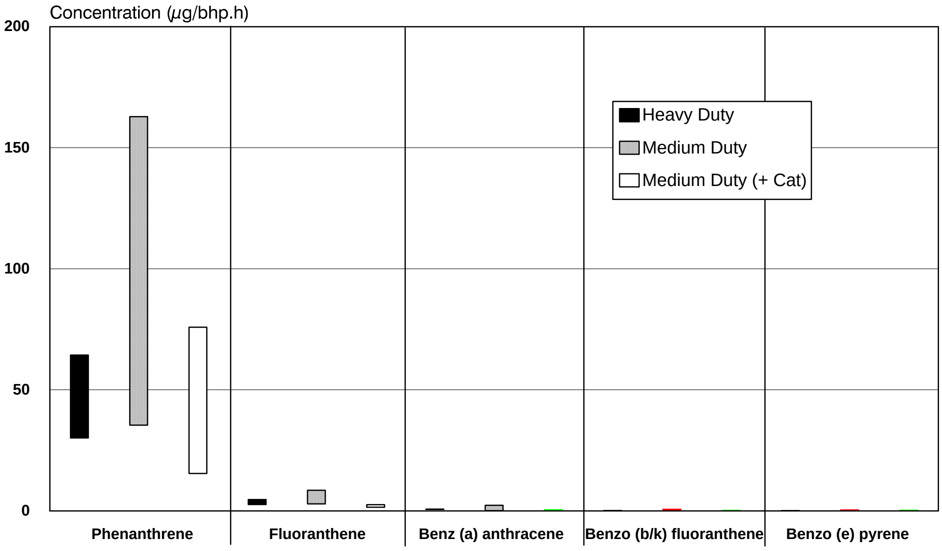


Figure 4B Selected PAH in automotive diesel engine particulate phase exhaust (Linear Scale)



2.6. MECHANISMS OF FORMATION

The mechanisms by which PAH may occur in automotive exhausts are complex and open to considerable debate between researchers. In summary, several routes can be envisaged:

- **Survival of fuel PAH during combustion:**

  This will vary for each PAH, and is also influenced by engine design, test cycle and compatibility of fuel and engine.

- **Creation of PAH by pyrosynthesis:**

  Experimental and theoretical work indicates that favourable kinetics and thermodynamics lead to PAH formation from non-PAH, including non-aromatic, fuel components. Judging by the amount of carbonaceous soot in exhausts (all formed by pyrosynthesis), a substantial fraction of the exhaust PAH could be created by this mechanism.

- **Modification of one PAH into another:**

  This represents a “grey” area between survival and creation that is very difficult to quantify experimentally, but undoubtedly occurs.

- **Contributions from the lubricating oil:**

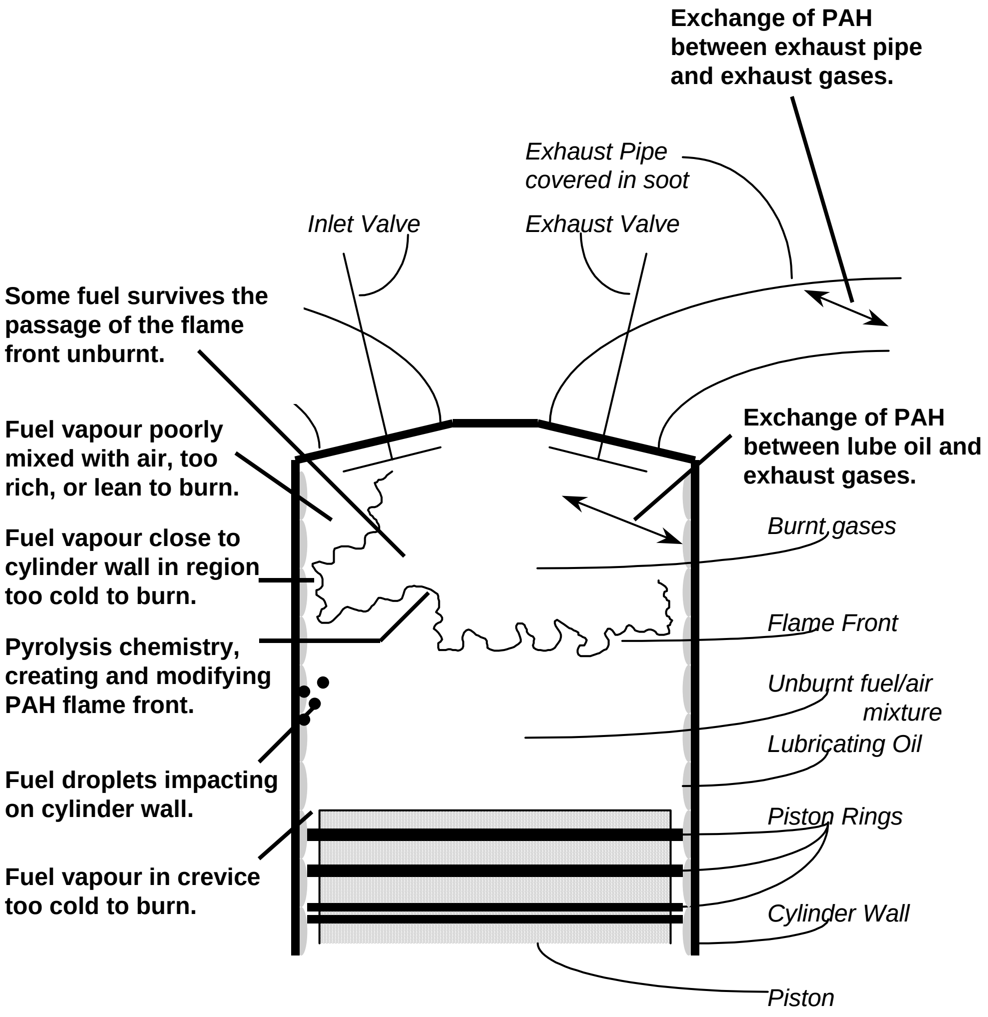
  Like PAH modification, this contribution is difficult to quantify. Lubricating oil may act either as a net source of exhaust PAH, or as a sink for them, and when acting as a source, the PAH concerned may be an original component of the lubricant (which is very low in a fully synthetic oil), or of the fuel, or have been pyrosynthesised from non-PAH fuel components.

- **Entrainment from the exhaust and sampling system:**

  Entrainment represents yet another difficult area to quantify. Exhaust and sampling systems may act either as a source or a sink for PAH, these PAH having been originally derived from any of the other sources discussed above.

A conceptual figure illustrating how these mechanisms might operate is given overleaf:

Figure 5 Mechanisms of PAH formation



2.7. OCCURRENCE OF PAH IN FUELS

2.7.1. Introduction

It is worth repeating that surprisingly few authors have attempted to correlate fuel composition/PAH levels with those measured in the exhaust or have included any measurement of PAH in the test fuels used. The sources of many of the fuels are not clear and their relevance to product quality in the market is uncertain. For example, there are clear indications that refinery processing to reduce fuel sulphur content may lead to some reduction in fuel PAH content. As a result, historical analytical data are unlikely to reflect current or future PAH contents of automotive fuels.

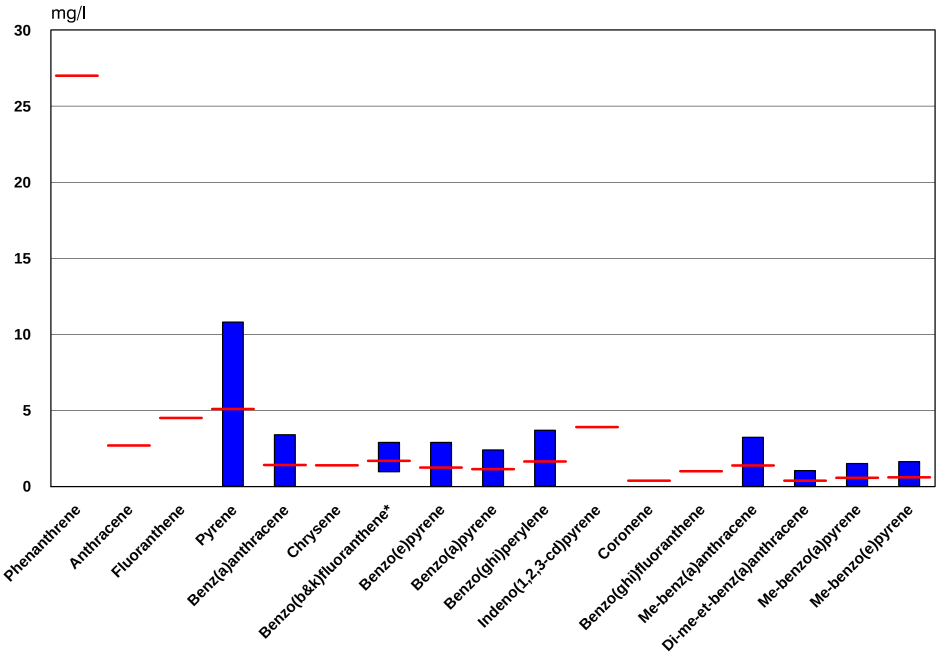
It is also appropriate to reiterate that the key to reliable data lies in representative sampling and the analytical approach employed. The majority of the references cited use different analytical systems and consequently direct comparison is not always easy. Data relating to the reproducibility of the analytical system are not often given.

2.7.2. Gasoline

There are no market surveys of commercial quality gasolines which include information on PAH content and, as a consequence, representative data is unavailable. Limited information has been found in the literature published over the last twenty five years and about twenty PAH compounds have been identified. There are probably more, lying below the levels of detection. The reported incidence of two ring PAH compounds is about twenty times higher than that for the other PAH species.

Typical values for PAH determined in a few commercial gasolines are given below. Commercial fuels are defined as being those that comply with specifications defined in the various countries in which they are sold and whose product quality is similar to that sold at the gasoline pump. It must be stressed again that different analytical methods have been used across different references and that the values may not be strictly comparable. Differences in values between mg/kg and mg/l are reported and may be due to the different analytical methods employed.

Figure 6 PAH levels in commercial gasolines



* Data only available in mg/kg

The limited data on commercial fuels found in the public domain refer to both the American and European markets from 1970 to 1996.

2.7.3. Occurrence in Diesel Fuel

Numerous PAH compounds in fuel have been identified, but there are very few quantitative data for specific PAH compounds. In a previous CONCAWE report values for the aromatic content of diesel fuel in European fuels (over the period 1993-1994) were estimated to be between 1-10% v/v for diaromatics and between 0.1 – 3% v/v for tri-aromatics.

The chemical composition of a diesel fuel varies depending on how it is blended from different refinery streams. The composition of these streams will further depend on refinery configuration, plus crude oil source, feedstock, ratio between diesel/light heating oil, product pattern, etc.

The diesel blend will therefore be a complex mixture of different aliphatic, naphthenic and aromatic hydrocarbons. Complete identification and quantification of all the individual hydrocarbons in a fuel is thought to be impossible. For example; "The number of paraffin isomers of carbon number 15 ($C_{15}H_{32}$) is estimated to be 1860. The total number of isomers in a diesel fuel is estimated to be more than ten thousand."

However, different analytical techniques can give a good characterisation of chemical groups and to a certain extent, specific chemical compounds in a diesel fuel.

There are countless references to the effect of fuel composition on exhaust emissions, especially with respect to PAH, but surprisingly few workers in the field have analysed and published the PAH content of the fuels used in their experiments. With a few exceptions, PAH emissions are investigated against fuel parameters such as density, aromatics, distillation, sulphur, viscosity and cetane number, but have not been related to the possible effects of specific PAH compounds in the fuel.

Published PAH data for diesel fuel shows that the individual PAH analysed by different centres varies enormously and depends to a certain extent on the analytical capability of that laboratory. Most results show only PAH of 3-ring or greater, ignoring 2-ring aromatics.

A range of the most commonly reported values of PAH content in commercial available diesel fuel is depicted graphically overleaf. The figure covers different qualities of diesel fuel encompassing high/low aromatic levels, high/low sulphur etc. The values are given on a logarithmic scale in **Figure 7A**. The figure indicates the wide spread of values and the variation in the levels for individual PAH and also includes the variability as a result of using different analytical techniques. Although this scaling is a convenient way of depicting these values, it can provide a misleading impression of the actual magnitude of the PAH contents. **Figure 7B** presents exactly the same data plotted on a linear scale, providing a more realistic view of the differences between the PAH present in the fuels.

Figure 7A PAH levels in commercial diesel fuels (Logarithmic Scale)

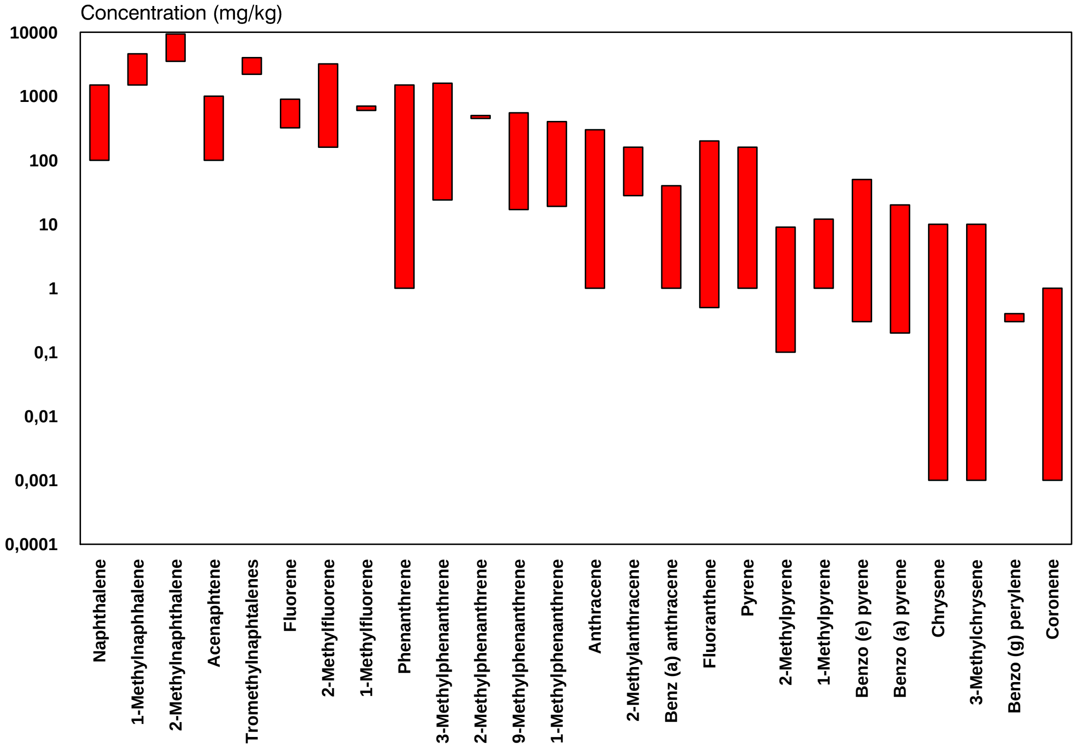
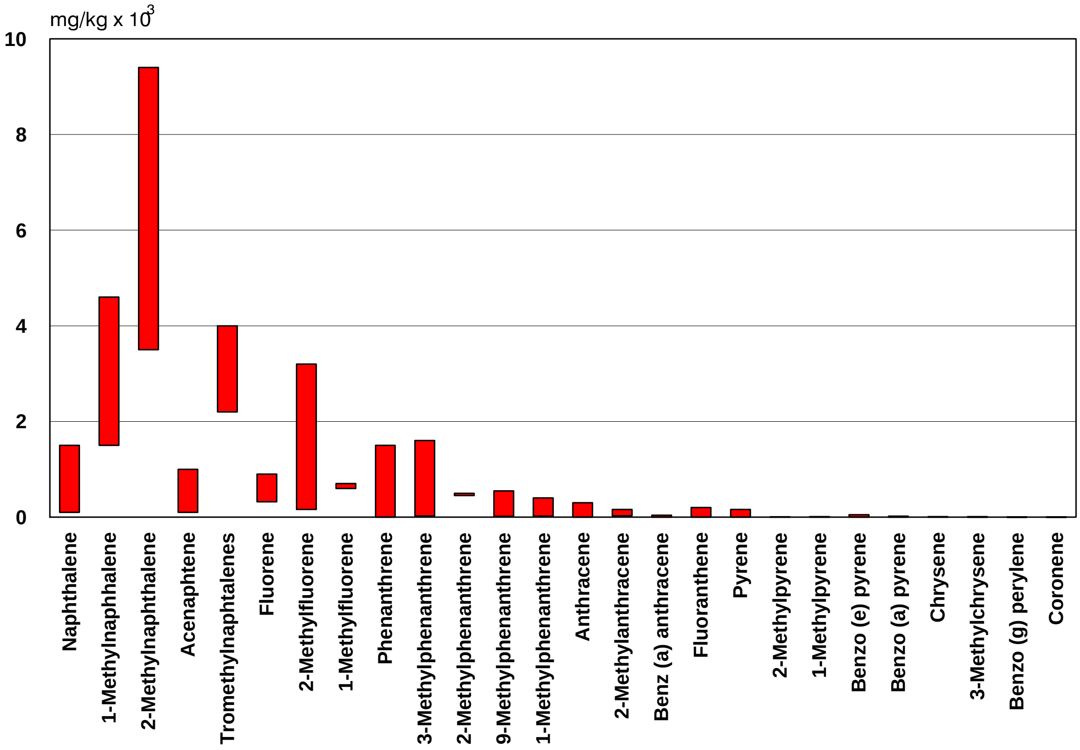


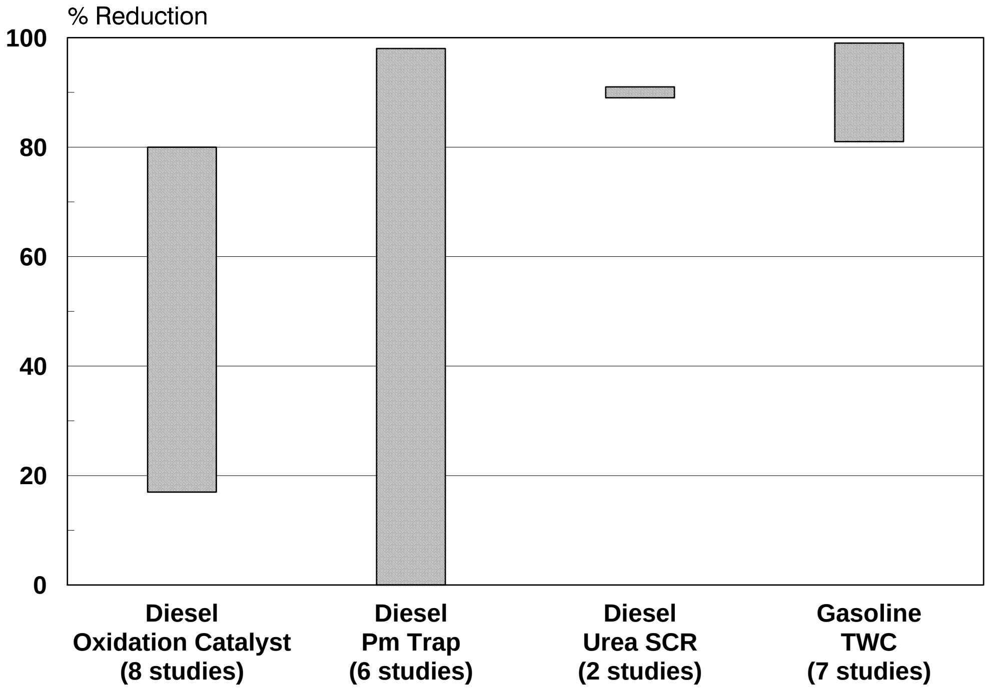
Figure 7B PAH levels in commercial diesel fuels (Linear Scale)



2.8. THE INFLUENCE OF EXHAUST AFTER-TREATMENT ON PAH EMISSIONS

The preceding sections have indicated that PAH emissions from automotive sources are highly variable and are dependent on a number of factors, including fuel composition. However, the more detailed presentation of the published data given in **Section 3** unequivocally indicates that exhaust after-treatment systems are a highly effective means of control. There are limitations in the scope of published literature, but it is clear that aftertreatment systems can substantially decrease PAH emissions. With only a few exceptions these trends hold true for all targeted individual PAH species. **Figure 8** illustrates the range of results reported for the major classes of aftertreatment system covered in the papers reviewed in this survey.

Figure 8 Summary of exhaust after-treatment effects on particulate associated PAH



The range of results for diesel oxidation catalysts and particulate traps is very broad, and it appears that many factors can be significant, including catalyst type, engine type, and the engine test procedure employed. In the case of particulate traps it is significant that those with the best PAH capability incorporated some form of catalysis. It is also notable that the urea lean de-NOx system is highly effective in decreasing PAH emissions.

It is clear that modern gasoline vehicles fitted with TWCs produce far lower levels of particle-associated PAH emissions that older vehicles without catalysts, and that the major part of this reduction is due to the catalysts.

A significant part of the overall PAH emissions are not adsorbed onto the particulate matter, and are emitted in the vapour phase. Vapour phase PAH compounds are predominantly the lighter, lower boiling point compounds, and may contain fewer of the species believed to be potentially harmful to health. However, for a complete picture, vapour phase PAH emissions must be considered as well as particulate-associated. Here most work is on diesel, and results from different studies are variable. However, the majority evidence suggests that diesel oxidation catalysts may be more effective in the vapour phase, and thus total PAH control capabilities may be higher than the particulate-associated data suggests. Conversely, particulate traps seem to deal more effectively with PAH condensed onto the particulate matter, and total PAH control capability may be lower than the particle-associated results suggest. PAH data on gasoline are very limited, but suggest that TWCs may be very effective in reducing both vapour and particulate phase PAH.

Data on the effects of aftertreatment on nitrated PAH and the associated mutagenicity of the exhaust are variable, and the results from different studies can be contradictory. This may be in part due to the higher uncertainty of the analytical methods employed.

2.9. THE INFLUENCE OF ALTERNATIVE FUELS ON PAH EMISSIONS

Alternative fuels offer another route to the control of PAH emissions. Such an approach is obviously less practical than the application of exhaust after-treatment, but the use of alternatives to conventional gasoline or diesel fuel is finding a growing niche market. Alternative fuels generally give lower PAH emissions than traditional fuels. However, PAH emissions are still detected in exhaust emissions despite the fact that most of the fuels do not contain any aromatic compounds.

There are several papers in the literature that look at PAH levels in the exhaust of vehicles powered by alternative fuels. These fuels include: liquid petroleum gas (LPG), compressed natural gas (CNG), methane, propane, methanol, alcohol-Diesel blends, alcohol-gasoline blends, rapeseed oil, rapeseed methyl ester (RME) and bioethanol.

A wide range of vehicle technology has been used to assess the impact of these fuels and the use of catalysts has varied between authors. The analytical methods used (where specified) were different and some papers examined only particle bound PAH. These factors combined make it difficult to make a direct comparison between papers, although it would appear that comparisons made within one piece of research work are valid. However, in all the literature reviewed, the use of alternative fuels generally appears to result in a reduction of the PAH measured when compared to the same engine operating on conventional fuels.

2.10. THE LIMITATIONS OF EXPERIMENTAL DESIGN, INCLUDING SAMPLING AND ANALYTICAL TECHNIQUES

A general problem when studying the effects of changes in a fuel property on exhaust emissions is that of blending a meaningful range of test fuels (a 'fuel matrix'). In a well designed matrix the property under examination must vary sufficiently to have a measurable effect on the emissions, whilst other potentially influential fuel properties are kept essentially constant and decorrelated from the characteristic under investigation. This is particularly difficult when studying the influence of fuel PAH content on exhaust PAH levels as:

1. PAH form only a small part of the fuel, particularly in the case of gasolines;

2. The experimental scatter in measuring exhaust PAH levels is large.

Most of the work reviewed in this report aims to assess the effect on levels of exhaust PAH due to changes in fuel PAH content. This therefore requires a set of test fuels where potentially critical properties such as cetane number, heavy-end distillation and density do not vary appreciably (or, if they do, where the experimental design allows one to estimate the impact of, and compensate for, changes in these parameters).

These requirements have been met in the most informative experiments reported in the public domain. However, the least informative simply ignore such possible “side effects”, although such “side effects” can, in reality, dominate those of changing the fuel PAH level. The possible options in experimental design aimed at eliminating (or at least in reducing) the influence in changes in fuel properties other than that of PAH content are discussed in more detail in **Section 3**.

Nevertheless, it would be appropriate to consider here the general approach to studying the effect of changes in fuel properties on exhaust emissions. There is an almost universal assumption in the literature that any investigation of the fuel parameters that influence *regulated* emissions should concentrate on changes in *regulated* fuel properties (i.e. “bulk” properties such as density, cetane number or RON and MON, distillation properties, etc.). However, studies focusing on fuel parameters that can influence currently *unregulated* emissions like PAH, generally concentrate on *unregulated* fuel parameters, e.g. PAH level. These assumptions are open to question:

1. Do the “bulk” fuel properties, believed to influence the preponderance of the exhaust (PM, HC, CO, NOx), play only a minor role in determining the emissions of PAH?

2. Can relatively small changes in fuel PAH concentrations (say, 0 - 3% in diesel fuel; 0 - 0.1% m/m in gasoline) dominate exhaust PAH levels?

It is also worth pointing out that there is currently no clear understanding of the relationships between the total amount of exhaust PAH, the partitioning of those PAH between the gas and particulate borne phases, the size distribution and mass of the particulates.

Sampling methods for PAH are generally divided between filters (for particulate bound PAH) and adsorbents (for vapour phase PAH) or a combination of both. Due to the variation of vapour pressures within the range of PAH usually measured, the latter is recommended, giving a “total” value. However, within this “total” it is not possible to define the fraction (due to physical reactions) originating from either phase separately. Furthermore, most studies have investigated the effect of fuel changes on PAH by investigating the PM bound PAH. If a fuel change results in a reduction of PM there is usually a concurrent reduction in absolute levels of PAH bound to the particulate. It is not known if the total PAH emissions have also been reduced or whether the vapour/PM equilibrium has been affected by the reduction in particulate material.

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 particulate measurement has provided a convenient sampling point for particulate bound PAH, although for gasoline a variety of approaches have been used.

There are, however, three problems inherent to sampling with filters:

- PAH trapped on the filter may be volatilised by the continued passage of sample over the filter surface (‘blow-off’).

- Vapour phase PAH may adsorb onto particles already trapped on the filter.

- PAH trapped on the filter medium may undergo continuing chemical reactions on the filter surface (degradation/artefact formation).

The use of a combination of filter plus a backing adsorbent can address the first two problems, but will still only give “total” values and not a precise split into particle and vapour phase PAH. Other methods of collection e.g. denuders or cryogenic samplers are also possible.

At present there are no standard procedures or methodology for PAH sampling and no accurate means of calibration.

The analysis of PAH is based on chromatographic techniques, with an overall analytical approach of extraction, fractionation, and end analysis. For the extraction of PAH from sampling media, the traditional Soxhlet method continues to dominate in both automotive and environmental applications. A variety of clean-up and fractionation techniques have been employed in automotive and environmental applications, with the degree of complexity based on the level of PAH and the selectivity of end analysis systems used.

Typically, high-performance liquid chromatography (HPLC) with fluorescence detection needs far less clean up for successful quantification of PAH than with gas chromatographic (GC) techniques. The refinement and high separation resolution of GC (suitable for volatile PAH) fitted with a variety of detectors, including mass spectrometers (MS), has led to wide spread usage of such systems in both automotive and environmental applications. For selected PAH, such as the US Environmental Protection Agency 16 priority PAH pollutants, analysis on a routine basis using HPLC with fluorescence provides the greatest sensitivity and selectivity. HPLC is also the preferred technique for the larger (up to 10 rings) and thermally unstable PAH. For trace-PAH, on-line reduction to the amino-PAH followed by chemiluminescence detection offers one of the most sensitive systems of all.

The US EPA, since 1982, have specified HPLC as the chosen analytical method for trace compounds, such as nitro-PAH.

2.11. CONCLUSIONS

- Where the data are available (e.g. UK, Japan), current PAH concentrations in ambient air are the lowest ever measured
- total HC emissions (and likewise total PAH) are very low from modern vehicles. Furthermore, targeted PAH species form only a small fraction of the particulate borne HC, and an even smaller fraction of the vapour phase HC
- a wide range of definitions as to what constitutes a "polycyclic aromatic hydrocarbon" may be found and there is no agreed definition for PAH
- there is no standard analytical methodology and a consensus on the major PAH to be measured has still to be established
- there are insufficient data available on automotive emissions to determine to what extent the level of the PAH emissions is related to the PAH content of fuel
- there has been insufficient work on total (vapour phase + PM bound) PAH emissions
- there are two main routes of PAH into the exhaust, fuel PAH survival and combustion derived PAH
- the presence of a three-way catalyst on gasoline vehicles appears to reduce PAH emissions to levels below current detection limits
- diesel exhaust after-treatment systems show greater variation but are generally highly effective in reducing PAH
- some alternative fuels may offer a limited route to some reduction in PAH exhaust emissions.

3. PAH IN AUTOMOTIVE EXHAUST EMISSIONS AND FUELS

3.1. INTRODUCTION

As described earlier, this section has the same structure as the Overview (**Section 2**). It is more detailed than the Overview and is supported by a number of **Appendices**. Every attempt has been made to minimise duplication but, as both Sections can be read as "stand alone" documents, there is inevitably some measure of repetition.

3.2. THE NATURE OF PAH

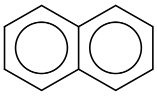
3.2.1. Introduction

This report concentrates on "Polycyclic Aromatic Hydrocarbons" (PAH), that is, compounds with two or more benzene-type rings containing only carbon and hydrogen. Brief references are made to "Polycyclic Aromatic Compounds" (PAC), containing heteroatoms (S, N and O), but there are very little data on the emissions of these compounds.

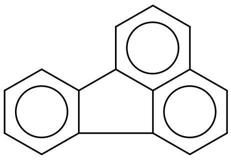
3.2.2. Nomenclature

Individual polycyclic aromatic compounds may be named according to rules laid down by IUPAC in their book "*Nomenclature Of Organic Chemistry*" which is updated from time to time as necessary. The current rules may be found in recent editions of the "Rubber Handbook" (i.e. the *CRC Handbook Of Chemistry And Physics*, published annually). The majority of small polycyclics retain their "trivial" (i.e. historical and non-systematic) names: the structures cannot be deduced from the names (e.g. pyrene). For larger species, names are increasingly likely to feature a systematic combination of trivial names or trivial names with systematic additional elements: e.g. 1-methyl-naphthalene or benzo(b)fluoranthene or benzo(a)pyrene. Applying the following rules often (but not always) allows the correct structure to be deduced:

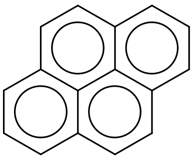
- Orientate the "parent" ring structure (naphthalene, fluoranthene and pyrene in the 3 examples, below) so that, first, the maximum number of rings (including 5-membered ones) are in a horizontal row. If a choice of orientations exists choose that which puts as many rings as possible above and towards the right hand end of those rings forming the "horizontal row". Thus the example PAH should be drawn as follows:



Naphthalene

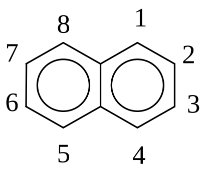


Fluoranthene

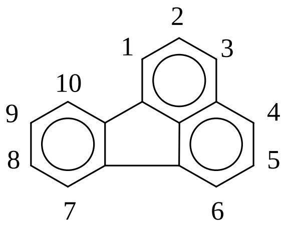


Pyrene

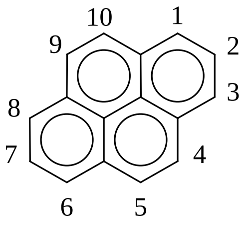
- Those carbon atoms in the parent structure that are bonded to a hydrogen atom can now be numbered 1, 2, 3, etc. starting (usually) with the first C atom above and to the right of the centre line of the "horizontal row" of rings and proceeding clockwise. Note that carbons not bonded to hydrogen atoms are not numbered and therefore the examples are numbered as follows:



Naphthalene

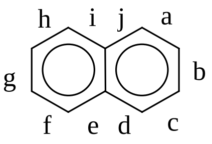


Fluoranthene

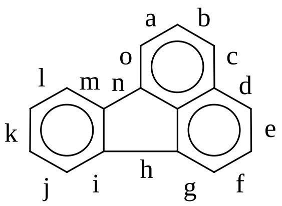


Pyrene

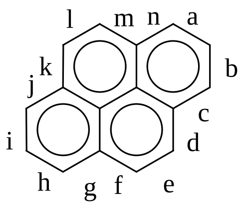
- All the external faces of the parent structure can also be lettered, starting with "a" (between C atoms "1" and "2") and proceeding clockwise:



Naphthalene

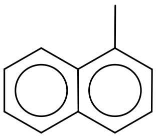


Fluoranthene

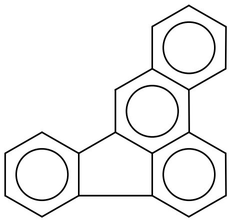


Pyrene

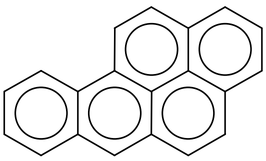
- The additional elements can now be put in their correct place. It is important to note that, the resulting structure should be re-oriented if the addition of any new ring allows a larger number of rings in a "horizontal row", as is the case with benzo(a)pyrene:



1-Methyl-Naphthalene

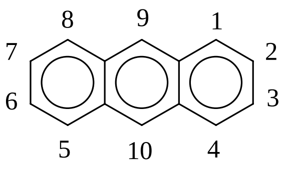


Benzo(b)Fluoranthene

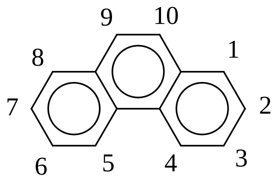


Benzo(a)Pyrene

- However, some polycyclics have non-systematic numbering systems for historical reasons, including the commonly quantified 3-ring structures anthracene and phenanthrene:



Anthracene



Phenanthrene

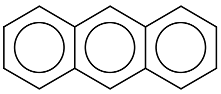
See **Appendix 1** for terms and abbreviations used in this report.

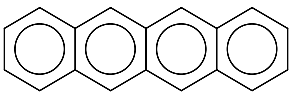
3.2.3. Chemical and physical properties of PAH

PAH occur naturally in crude oils. By virtue of their size and weight they are relatively high boiling point hydrocarbons - the di-aromatic naphthalene has a boiling point of 218°C; the tri-aromatic phenanthrene one of 340°C. Consequently, they appear in gasolines at very low concentrations (generally < 1% m/m di- and < 0.1% m/m tri+ aromatics with < 10 ppm for any individual 4+ ring species in European gasolines, although reliable data are lacking) and in diesel fuels at low, but not insignificant, concentrations (typically 1 - 10% m/m for di-aromatics, 0.1 - 3.0% m/m for tri-aromatics – see CONCAWE (1995).

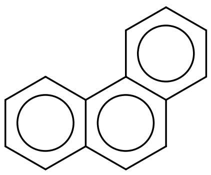
Clar (1964) has studied the physical and chemical properties of pure PAH. Those PAH with the greatest number of rings for their number of carbon atoms, called peri-condensed (e.g. pyrene), are less reactive chemically than similar sized PAH with a lesser number of rings per carbon atom (e.g. chrysene), these latter being called cata-condensed. Peri-condensed PAH tend to become increasingly stable with increasing size, whilst cata-condensed ones become increasingly reactive. Within the cata-condensed sub-class, those structures where the rings are arranged in a straight line (e.g. anthracene, tetracene , etc.; known collectively as the acenes) are more reactive than those of a similar size where the rings lie on a staggered line (e.g. phenanthrene, chrysene , etc.; known collectively as the aphenes). In general, the more staggered the arrangement of rings, the more stable a cata-condensed PAH becomes. In a staggered arrangement of rings, the double bond at the stagger point is the most reactive (e.g. the double bond between the 9 and 10 positions in phenanthrene).

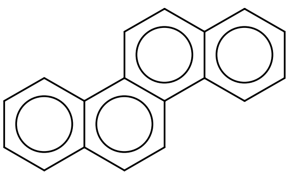
The structures of anthracene and tetracene respectively:



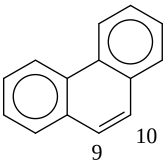


The structures of phenanthrene and chrysene respectively:





The relatively weak double bond at the stagger point of phenanthrene (i.e. between the 9 and 10 positions):



The thermodynamic stability of PAH (especially peri-condensed ones) makes them likely products of incomplete combustion (also known as pyrolysis), irrespective of the molecular structure of the fuel (i.e. the fuel need not contain PAH for there to be PAH in the flame). This is particularly true under fuel rich conditions such as those found close to the surface of an evaporating fuel droplet in a hot environment. It is also generally believed that PAH are important intermediates on the route to soot formation - see Stein (1978) and Stein and Fahr (1989) for a thermodynamic approach and Frenklach and Wang (1990) and references therein for a kinetic approach.

PAH can be found (in both exhaust and ambient aerosol) distributed between particle and vapour phases. The partitioning between these phases has been investigated by many workers and is greatly affected by the surrounding conditions - temperature, humidity etc. The variability of partitioning arises because of the range of vapour pressures that the species under investigation possess (10^{-2}kPa - <10^{-13}kPa). ISO (1997, 1998) states that PAH with a vapour pressure above 10^{8}kPa may be substantially distributed between the two phases, dependent on ambient temperature, humidity, types and concentrations of PAH and particulate matter and residence time in the air. PAH with higher vapour pressures will tend to favour the vapour phase and may well vaporise from filters during sampling. This tendency will necessitate the use of a vapour trap for measurement of PAH in both phases. Except for PAH with vapour pressures below 10^{-9} kPa, separate analyses of the filter and vapour trap will not reflect the original PAH distribution. A table of the physical properties of common PAH is shown in **Appendix 2**.

3.3. GENERAL APSPECTS OF HEALTH EFFECTS OF PAH AND ENVIRONMENTAL OCCURRENCE

3.3.1. Health effects of PAH and environmental exposure

The collective term PAH describes a large number of polycyclic aromatic hydrocarbon compounds, presenting a spectrum of biological activity. Most importantly, certain PAH have been studied and for some sufficient evidence has been found to be carcinogenic in animals. The available carcinogenicity data for PAH has been reviewed by IARC on two occasions: IARC (1973) and (1983), and the outcome of these evaluations was updated more recently, IARC (1987). The classification is given in **Appendix 3**. It also shows that no adequate data have been available to provide evidence for carcinogenicity in humans, but overall hazard assessments for humans have been established (see the classification into groups). In this context it has to be noted that evidence for the carcinogenicity of some other PAH is equivocal; for others there is no evidence of carcinogenic potential, whilst many others have not so far been tested.

Although there is sufficient evidence of carcinogenicity in animals for a handful of PAH, for most, there are insufficient reliable data. Amongst the more extensively studied PAH, carcinogenicity potency estimates have been developed, and these suggest at least a thousand-fold range of potency: UK Dept. of Health (1995). Most of the available data on carcinogenicity relates to studies of repeated skin exposure; very few data are available on the carcinogenicity of PAH by inhalation. Many PAH have been evaluated in screening tests for mutagenicity, and many show activity, typically after metabolic activation. There is also evidence for the mutagenicity of some nitrated-PAH, suggesting that in some instances, these compounds may have high activity. Nitro-PAH appear to be responsible for a substantial proportion of the direct mutagenic activity of respirable airborne particles, whilst total vapour phase mutagenicity due to nitro-PAH is approximately equal to that of the particulate phase: Finlayson-Pitts and Pitts (1997). However, mutagenic potential should not be taken to indicate carcinogenic potential, and similarly, mutagenic potency should not be taken to indicate carcinogenic potency.

The evidence for the carcinogenicity of PAH has been reviewed extensively and published elsewhere and is not reviewed further in this report. Further information can be found e.g. in WHO (1987), Boffetta et al (1997) and Baan and de Raat (1998).

Environmental exposure to PAH is seldom to individual compounds, more usually, exposure is to complex mixtures of PAH, and these mixtures may be associated with particular industrial processes or activities. Addressing automotive sources Diesel exhaust is currently classified by IARC in Group 2A (probably carcinogenic to humans), whilst gasoline exhaust emissions are classified in Group 2B (possibly carcinogenic to humans). This overall evaluation was based on an IARC review of diesel and gasoline exhaust emissions, summarised in **Table1:**

Table 1 Exhaust Emissions – IARC Evaluation (evidence of carcinogenicity)

Evaluation	Diesel Exhaust			Gasoline Exhaust	
	Whole	“Gas-phase”	“Extracts of particles”	Whole	Condensate
Carcinogenicity to animals	Sufficient	Inadequate	Sufficient	Inadequate	Sufficient
Carcinogenicity to humans	Limited	-	-	Inadequate	-

IARC (1989)

PAH have been identified in all of the environmental compartments (air, water, sediment and soil) at various locations. The concentrations of individual PAH detected, and the major sources of these compounds, will vary between compartments and from location to location. In many instances, the occurrence of PAH may be linked to fossil fuel burning (coal and petroleum fuels), but the burning of peat and wood, biomass burning, specific industrial processes (such as coke production, aluminium smelting, iron and steel production), production and use of coal tar products, natural seeps of crude oil, accidental spills of crude oil and some other petroleum products, waste incineration, contamination from used automotive engine oils, tobacco smoke and the cooking of food (especially barbecuing/broiling) are all associated with the generation and/or release of PAH into the environment.

Typical PAH profiles (fingerprints) have been defined for various types of emission, which may be useful in defining the sources for PAH determined in particular locations. For example, emission factors for specific PAHs have been measured for biomass burning (various cereal crops and tree species), coke ovens, diesel and gasoline exhaust emissions: Khalili (1995) Jenkins (1996). Such approaches have been used to develop PAH source inventories for countries or regions, for example, Wild (1995).

3.3.2. Environmental occurrence – Air

Recent studies in various locations have demonstrated that current PAH concentrations in ambient air (and fluxes to the other environmental compartments) are dramatically lower than seen in earlier years, and are lower now than at any time throughout this century: Smith (1996), Wild (1995), Coleman (1997), Matsumoto (1998). This reflects the impact of clean air legislation, especially on reducing coal burning, and the use of more efficient combustion technologies for other fuels. PAH concentrations in urban air generally show a seasonal pattern, with higher concentrations in winter, this being attributed to the contribution from coal-fired residential heating. Variations in PAH concentration are seen during individual days, reflecting, for instance, the variable amount of heating fuel burned, changing traffic flows and meteorological conditions.

Estimates of the contribution from exhaust emissions to the total PAH concentration in urban air vary. It has been suggested to be as high as 80 to 90% on weekdays in the streets of some cities: Wild (1995), Goldsmith (1977), Nielsen (1996). The apparent magnitude of the contribution from exhaust emissions will be significantly influenced by the PAH loading from other sources, by the relative abundance of gasoline and diesel fuelled vehicles, plus the influence of such factors as wind speed and direction, air temperature and humidity.

The concentrations of individual PAH will be influenced by the extent and source of the pollution, and the susceptibility of particular PAH to chemical and photochemical degradation. This will again show seasonal variation, influenced by ambient temperature and the intensity of sunlight. Much of the PAH detected in air is associated with particulate matter, though the lower molecular weight PAH are sufficiently volatile to be present in the vapour phase. The proportion of PAH in the vapour and particulate phases will be significantly influenced by the ambient temperature, and hence again show seasonal variation. In addition, this distribution may not reflect the distribution of the emissions sources. Recent work on the gas/particle partitioning of PAH in ambient aerosols has been presented by Liang (1996) and mathematical modelling approaches described by Jang (1997) and Bowman (1997).

Nitrated-PAH have been identified in exhaust emissions and in emissions from certain industrial processes. In addition, these compounds can also be produced in the atmosphere by reaction of PAH with nitrogen dioxide following hydroxyl radical attack: Kamens (1994); Smith et al (1996). The detailed profiles of nitro-PAH in direct emissions and in ambient air may differ significantly as a result of these chemical transformation reactions: Finlayson-Pitts and Pitts (1997). Similar atmospheric transformations are suggested for naphthalene and methylnaphthalenes. Overall, atmospheric formation of nitro-PAH is considered to be responsible for much of the total load: Finlayson-Pitts and Pitts (1997).

3.3.3. Environmental occurrence – Aquatic environment (water and sediment)

When present in the aquatic environment, PAH will predominantly be associated with sediments or suspended organic material, with only low concentrations in the water column (1,000 to 100,000 times higher concentrations in sediment than in water): Weldre (1977). This is a reflection of the low water solubilities and high octanol-water partition coefficients of PAH. The total PAH found in both fresh water and marine sediments are typically derived from two sources, originating from early fossilisation of plant debris as well as anthropogenic (man made) sources: IARC (1983). PAH found in sediments are often associated with other pollutants such as heavy metals, chlorinated pesticides and polychlorinated biphenyls, which complicate the assessment of specific adverse effects on aquatic organisms attributable to PAH exposure.

The principle source for anthropogenic PAH in the aquatic environment is atmospheric wash-out by rain (possibly after long-range transport), with further contributions from run-off from industrial plant, from roadway run-off and via effluent discharges. Deposition rates will vary seasonally, reflecting variation in emission rates, meteorological factors and atmospheric chemistry: Brorström-Lunden (1996).

Because of their comparatively slow rates of degradation, especially under anaerobic conditions and in the absence of light, sediments are seen to be a sink for PAH (and other persistent pollutants), and provide a historic record of pollution from all sources: Wakeham (1996), Wilcock (1995).

3.3.4. Environmental occurrence – Soil

PAH are frequently reported in soil samples, with concentration gradients usually reflecting the distance from point-sources of pollution, such as coal-gas production or coking plants. Air pollution is the principle source for soil contamination by PAH, and as previously mentioned, co-contamination with other chemicals such as heavy metals, is frequent. Soils and peat samples, like sediments, provide a historic record of pollution from all sources: Pichler (1996), Sanders (1995).

3.4. SAMPLING AND ANALYSIS OF PAH

3.4.1. Introduction

There are some extensive literature studies available relating to sampling protocols for PAH. Fox (1989) covered published literature on air pollution monitoring for 1987/88 and Clement (1995) for 1993/94 on environmental (soil, water and air) analysis. Leinster (1986) and Davis (1987) concentrated on sampling methods for PAH. All four reviews provide extensive reference lists and all acknowledge the difficulties associated with PAH measurement. Davis (1987) believed that in general, the sampling, analytical and bioassay capability have been inadequate to provide sufficient and reliable data. As recently as 1995, Clement stated that “the collection of samples may constitute, at this time of writing, the single most difficult technical issue in environmental analysis when laboratory based analytical techniques are employed. The difficulty arises from the interpretation of the findings in view of the inhomogeneity of environmental systems, the integration of sampling over time, the losses of analyte during storage or chemical changes that may occur during or after sampling, and more”. He went on to say that “the level of interest is in finding solutions to the collection of a representative sample that reflects the true composition of an environmental atmosphere”.

The first requirement of any sampling protocol is that the sample taken is representative of the sample matrix from which it has been taken and remains unchanged prior to its analysis. For PAH the situation is very complicated because a complete range of individual compounds are being sampled, each with unique chemical and physical properties which are independent of each other and each of which have the possibility of undergoing further reactions over time.

Historically, PAH determination has been carried out in both ambient and exhaust samples for particulate matter only: Coutant (1988), Halsall (1994), Westerholm (1988). This has given information largely on the multi-ringed heavier PAH but has neglected the lighter PAH which are prevalent in the vapour phase. It has only been since the 1980’s that the issue of vapour phase PAH has been addressed.

The most important property that needs consideration for the determination of PAH is the vapour pressure of the respective PAH (see **Appendix 2**). Within the matrices under investigation, PAH can exist either in vapour phase or associated with particulate matter. Generally, results show that 5-7 ring PAH are associated wholly with particulate matter, 4-ring PAH are distributed between particulate and vapour phase and <4-ring are in the vapour phase: Halsall (1994). PAH distribution between vapour phase and particulate matter will be determined by a number of factors. Temperature and humidity of the surrounding air will play a very large part. The distribution is also dependent on the available surface of particulate matter in the vicinity. Both the area and composition of the available surfaces are important and it is believed that the carbon content of the exhaust particulate may influence the extent of PAH condensation: Westerholm (1988).

There are, at present, no standard procedures or methodology for the sampling of PAH. There are, however, recommended procedures available for the collection of particulate (both atmospheric and exhaust) which can be used to address the particulate bound PAH. For exhaust particles, collection is defined by legislation EU (1994), EU (1991) whilst CEN (1996), pr EN 12341 describes the collection of the “thoracic fraction” (PM_{10}) of suspended particulate matter and compares the equivalence of high and low samplers to the Wide Range Aerosol Classifier (WRAC) which has been selected as a provisional reference instrument. Similar evaluations have been carried out by the National Institute of Public Health and the Environment (The Netherlands): RIVM (1996). Standards are in place, ISO (1995), which define the particle size fraction definitions for health related sampling.

ISO has investigated the analysis of PAH sampled from air and have produced a draft method and a working document (covering two different analytical procedures) each with sampling protocols attached. However, the particulate collection described within the methods differs from each other and also from other recommended particulate collection procedures. Rickard (1996) has shown that even recommended techniques can suffer from sampling variation.

There are, in addition, no standard means of calibration for these samplers and very few references make any attempt. Davis (1987) commented that published literature on the generation of standard atmospheres for validation is minimal, although there is a paragraph in his review addressing this area. He continued: “Development of standard PAH aerosols is not yet reported, yet such standard atmospheres are required for the validation of PAH sampling methods”.

There are no standards for addressing collection of vapour phase PAH.

3.4.2. Sampling methodology

Techniques for both atmospheric and exhaust sampling fall into the same main categories.

a. Filters

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 particulate measurement has provided a convenient sampling point for particulate bound PAH, although for gasoline a variety of approaches have been used. Legislation for diesel particulate collection specifies Teflon coated glass fibre (Pallflex) filters: EU (1994), EU (1991), and a maximum temperature of 52°C. Glass fibre filters may sometimes be used if the filter is to be analysed for carbon content.

There are, however, three problems inherent to sampling with filters: Hart (1990):

- PAH trapped on the filter may be volatilised by the continued passage of sample over the filter surface (“blow-off”).
- Vapour phase PAH may adsorb onto particles already trapped on the filter.
- PAH trapped on the filter medium may undergo continuing chemical reactions on the filter surface (degradation/artefact formation).

Thus sampling times are critical and need to be kept as short as possible to minimise the above effects: Hart (1990), but need to be long enough to enable a suitable sample to be taken for further analysis. Unfortunately, PAH concentration is low and sampling times usually need to be high to ensure that enough material has been collected for analysis.

The filter media range widely. Early work and subsequent reviews refer to the use of silver membranes, often in conjunction with glass fibre filters. This technique was used for the determination of the “benzene soluble fraction” that was originally used as a measure of PAH concentration: Leinster (1986). However, more recently, Teflon: Hart (1990), Rogge (1993), McDow (1995); glass fibre (and microfibre): Halsall (1994), Westerholm (1988), Kukreja (1976), Khalili (1995), Konig (1980); quartz: Hart (1990), Niehaus (1990), Lewis (1995); PTFE coated polystyrene membrane: Scheepers (1994); and polycarbonate membranes: Harrison (1996) have been used.

The extent of degradation of the PAH (once trapped on the filter) can be affected by light: McDow (1995) and by reactions with ozone, nitrogen and sulphur: Fox (1989). Leinster (1986) deals with all these reactions at great length.

There are several references comparing the performance of different filter media: Hart (1990, 1994), Baek (1991), although conclusions are not always in agreement. Hart (1990) concluded that where degradation occurred, these reactions were catalysed by the filter material, but in his later work he examined this artefact formation and concluded that there was no evidence that different filters behave differently. This was corroborated by de Raat (1990) who said that filter material is not a significant influence, although higher recoveries were seen from glass fibre filters. However, both Davis (1987) and Leinster (1986) contradicted this statement and claimed that Teflon gave the best recoveries. Davis suggested that this may be due to the lower absorbance of vapour phase PAH and Niehaus (1990) believes it is because Teflon has lower surface activity.

McDow (1995) has shown that there is a linear relationship between particle water uptake by Teflon filters and relative humidity and suggests that PAH decay rate may depend on particle water content.

b. Filter/adsorbent

Filters alone can only measure particulate bound PAH but may either under-estimate these as a result of PAH “blow-off”, or over-estimate them if vapour phase PAH have adsorbed onto the trapped particulate. The use of a combination of filter plus a backing adsorbent can address this problem, but will still only give “total” values and not a precise split into particle and vapour phase PAH.

Many adsorbents have been used in the literature. The most common are: Tenax: Lewis (1995); XAD-2 resin: Khalili (1995); or polyurethane foam (PUF): Halsall (1994), Lewis (1995), Harrison (1996), Thrane (1981). Many different combinations of filter material and adsorbent are possible and have been used for PAH determination. Halsall (1994) made some attempt at quality control by using filters spiked with dibenz(ah)anthracene to assess the sampling losses and final recovery. Khalili (1995) employed a “sandwich” of PUF and XAD-2 and claimed that 99% of naphthalene (the most volatile PAH) was retained.

Coutant (1988) attempted to set up a sampling procedure to distinguish between particle and vapour phase PAH, acknowledging the difficulty and the artefact formation. He concluded that, over a 24 hour sampling period, samples can change appreciably - both chemically and physically.

c. Cryogenic sampling

This techniques allows the collection of total PAH and has been used extensively for the collection of PAH from both gasoline and diesel exhausts. Davis (1987) stated that cryogenic traps and impingers are not always sufficiently rugged for field application.

d. Denuders

Denuders (e.g. Annular Denuder System, URG Corporation) function by passing air that has been drawn through a cyclone (which removes particles greater than 2.5µm) over annular denuder walls which have been etched and coated with chemicals that absorb the gaseous species of interest. They have been examined by Coutant (1992) for the collection of 3-4 ring PAH. Krieger (1994) has also used the technique to examine partitioning of PAH. Although denuders have been used regularly for VOCs, it is not so easy where the organic compounds are semi-volatile and Krieger concludes that partitioning is dependent on the vapour pressure and the amount of particles present.

Gundel (1995) has used annular denuders coated with XAD-4 resin to examine semi-volatiles and Lee (1994) addressed the use of denuders, saying that they are less prone to sampling artefacts. They may help overcome some of the problems with high volume sampling but as yet are not in common use. Multiple denuders can be used for pollutants at low concentrations.

e. Low volume, passive or diffusion sampling

The use of passive or diffusion sampling is also possible but has been used infrequently, Davis (1987), due to the long sampling times required. Personal exposure monitoring may be carried out using a low-volume sampler e.g. Grimmer (1993).

3.4.3. Atmospheric sampling

Atmospheric sampling provides a means of using characteristic ratios of PAH profiles for both quantitative and qualitative source apportionment: Harrison (1996), Allen (1996). However, according to Venkataraman (1994), limitations for this when applied to vehicle emissions are inaccuracies in sampling and measurement techniques. There is also a great deal of uncertainty relating to the chemistry of vehicle emissions as they move from the tail pipe to the ambient aerosol. It is quite likely that further reactions take place and that airborne VOCs (including PAH) may become adsorbed on emitted particles, thus confusing source apportionment.

Coutant (1988) stated that the determination of the concentration of PAH in ambient air is of considerable importance to the characterisation of air quality. The task of sampling PAH is complicated by the fact that many have equilibrium vapour concentrations that are considerably higher than their normal ambient air concentration. Venkataraman (1994) stated that under ambient atmospheric conditions, PAH with a molecular weight <202 (fluoranthene) are present mainly in the gas phase.

Most atmospheric sampling has been carried out using high-volume samplers: Clement (1995), Davis (1987), Leinster (1986), Hart (1990), Khalili (1995), Niehaus (1990), Scheepers (1994), de Raat (1990), Thrane (1981) which sample between 300-1500 l/min, usually over a 24 hour period. However, these type of samplers are known to have sampling losses due to volatilisation of the semi-volatile compounds. These samplers are fitted with filters and have been in use since the 1960's, Lee (1994), although more recently they have been used in conjunction with an adsorbent. Leinster (1986) believed that high volume sampling is only suitable for the collection of benz(a)pyrene or molecules of higher molecular weight.

Medium volume samplers (400 l/min) have also been used by Lewis (1995) with a PUF/Tenax “sandwich” to measure the vapour phase PAH.

A new analyser has been described by Agnesod (1996), which measures PAH in airborne particles by using a photoelectric aerosol sensor. The paper describes the technique and compares results with the more traditional filter paper analysis.

A recent paper by Grimmer (1997) describes work carried out in Germany to investigate both vapour phase and particle bound PAH. It was concluded that vapour phase PAH profiles were similar in the different sampling areas, whilst particle bound PAH profiles were more likely to reflect local emission sources.

3.4.4. PAH distribution across atmospheric aerosols

More recently, there have been extensive studies on size fractionated PAH measurements: Biswas (1987), Knapp (1990), Venkataraman et al (1994), Venkataraman and Friedlander (1994), Poster (1995), Allen (1996), Harrison (1996), Sheu (1996), Schnelle (1995) and Monarca (1997). Unfortunately, calibration of the various techniques is another area that has not been addressed. Biswas (1987) said that “most aerosol sizing instruments are calibrated with dry, non-volatile particles in the absence of any condensable vapours - these instruments are then routinely used to sample atmospheric or combustion exhaust aerosols at high humidity”.

Davis (1987) stated that many PAH have relatively low vapour pressures and are found adsorbed on the smaller sizes of particle because these present the greatest surface to volume ratio. This has been borne out by other workers - Harrison (1996) claimed that 95% of particulate PAH is <3.3µm with a unimodal distribution peaking between 0.4-1.1µm.

Lee (1994) agreed that most PAH are found associated with particles <2.5µm and Allen (1996) said that PAH in the atmosphere are predominantly found associated with fine aerosols (<2µm). PAH may partition to larger aerosols in warmer weather. This has been noted by Poster (1995) who believed that there is a five-fold increase of PAH associated with the smaller particles in winter and the size quoted for the most predominance of PAH is 1.4µm. The environmental fate of PAH will depend on which size particle they are associated with Allen (1996).

Several different techniques have been examined: Venkataraman (1994) used a Hering Low Pressure Impactor, Allen (1996) a micro-orifice impactor, Poster (1995) a Berner 5-stage Low Pressure Impactor and most recently Sheu (1996) a MOUDI. Harrison (1996) used a dichotomous stacked filter unit to collect fine and coarse particles. Impactor sampling is believed to minimise losses of semi-volatile PAH, although Lee believed that, as cascade impactors rely on inertial properties, there will be a pressure drop and a subsequent loss of material. Also, the use of impactors removed the need for filters and avoids artefact formation. Degradation of PAH is also minimised as the particles pile up and protect the underlying layers.

A literature review on the measurement of particulate size has recently been published by CONCAWE (1996).

3.4.5. Exhaust sampling

Legislation for particulate mass measurement from diesel vehicles or engines: EU (1994), EU (1991) imposes the use of a Teflon (Pallflex) filter. This has provided an obvious starting point for the collection of combustion material for PAH analysis. However, for gasoline sampling, there is no such legislated requirement and hence PAH collection has been carried out by different techniques. Williams (1990) presented a review of sampling and analysis of PAH from combustion systems. Most gasoline PAH are in the gas-phase and particulate collection alone does not address diesel vapour phase PAH. Westerholm (1988) believes that the distribution of PAH between particles and vapour phase is dependent on the surface (area and composition) of the emitted particles, dilution tunnel temperature and humidity of the dilution air. Other workers have investigated total PAH using a filter/adsorbent combination; Siegl (1992) using Pallflex/Tenax and Waldenmaier (1990), Dorie (1987) and Westerholm (1991) using either Pallflex/XAD-2 or Pallflex/PUF.

Collection of total exhaust PAH using cryogenic techniques was pioneered by Grimmer (1973). Condensation techniques have also been applied by Westerholm (1988), but are believed to be less effective than techniques employing a filter/adsorbent combination. Other uses of cryogenic techniques have been made by Pedersen (1980) who used a combination of cyclone battery, filter and cryogenic bath and Stenberg (1983) who applied the cryogradient technique to both gasoline and diesel exhaust. Rogge (1993) also used cyclone separators downstream of the dilution tunnel but only collected filter samples.

A novel collection technique for total PAH in diesel exhaust has been developed by Petch et al (1987), called the Total Exhaust Solvent Scrubbing Apparatus (TESSA). This technique samples from the exhaust manifold (i.e. engine out, not tail-pipe emissions) where there has been no ageing or dilution effects and any continuing chemical reactions are quenched. Consequently, all organic emissions are collected, irrespective of whether they would exist in particle or vapour phase and can be analysed to give a better understanding of the combustion process. This apparatus has been used extensively to investigate reactions involving PAH in exhaust: Collier (1995), Tancell (1995), Tancell (1996), Rhead (1996).

During regulated emissions testing, the partitioning of species and the resultant final equilibrium is related to the tunnel conditions and it might be expected that results obtained from chemical analysis could vary accordingly. There is a surprisingly good agreement between the ratio of more commonly measured particulate PAH and those measured from the TESSA, which would imply that, although absolute levels will differ, the PAH profiles measured are consistent.

3.4.6. Analytical techniques

Details of analytical techniques suitable for the measurement of PAH in fuel, exhaust emissions and air quality samples are described in **Appendix 4**. The analysis of PAH is based on chromatographic techniques, with an overall analytical approach of extraction, fractionation and end analysis.

Extraction and concentration can be achieved by the traditional Soxhlet method. Ultrasonication can be useful for rapid extractions, as can the more recent advances in supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE). The high extraction efficiencies, particularly where larger 4-6 ring PAH are involved, makes toluene the preferred extraction solvent. The Soxhlet method continues to dominate in both automotive and environmental applications, whilst the quicker ultrasonication and (in some cases) the more efficient supercritical fluid and accelerated solvent extraction methods are increasingly being employed.

A variety of clean-up and fractionation techniques have been employed in automotive and environmental applications, with the degree of complexity based on the level of PAH and the selectivity of end analysis systems used. Typically, high-performance liquid chromatography (HPLC) with fluorescence detection needs far less clean up for successful quantification of PAH than gas chromatographic (GC) techniques. Gaseous and vapour phase PAH can be directly injected into gas chromatographic systems, often with concentration on sorbent tubes such as Tenax or Carbotrap, before thermal desorption and cold trapping onto the GC.

The refinement and high separation resolution of GC (suitable for volatile PAH) fitted with a variety of detectors, including mass spectrometers (MS), has led to widespread usage of such systems in both automotive and environmental applications. Gas chromatography using universal flame ionisation detection is suitable for routine PAH profiling, provided the levels are sufficiently high for detection. The power of GC fitted with an ion trap mass detector (ITD) allows detailed characterisation at trace levels.

For selected PAH, such as the US Environmental Protection Agency 16 priority PAH pollutants, analysis on a routine basis using HPLC with fluorescence provides the greatest sensitivity and selectivity. HPLC is also the preferred technique for the larger (up to 10 rings) and thermally unstable PAH. For trace compounds, such as nitro-PAH, on-line reduction to the amino-PAH followed by chemiluminescence detection offers one of the most sensitive systems of all. The US EPA have specified HPLC as the chosen analysis method for trace PAH since 1982.

As stated earlier, fractionation and isolation techniques are dependent on the PAH of interest and the end analysis being used. For prominent PAH, classical column clean-up can be used, with solid-phase extraction (SPE) technology providing a rapid and reliable method. For detailed characterisation of PAH, especially for trace nitro-PAH or where detector selectivity is not great (such as gas chromatography with flame ionisation detection), extensive fractionation is needed using normal phase HPLC.

On a practical basis, separation using gas chromatography is suitable for volatile PAH with up to 4-5 rings. Gas chromatography with flame ionisation detection (FID) can be used as a routine tool for detailed PAH profiling. Furthermore, the GC fitted with a range of element specific detectors, such as electron capture and nitrogen-phosphorus detectors, can selectivity detect specific PAH of interest. The use of GC with mass spectrometry enables comprehensive identifications, with ion trap mass detectors (ITD) providing the most spectral detail whilst maintaining the greatest sensitivity. Conversely, GC-FID has moderate sensitivity compared with the HPLC fluorescence systems and both GC-FID and GC/MS suffer from interferences requiring extensive clean-up.

Reverse phase HPLC with fluorescence detection systems enable sensitive and selective analysis of selected PAH (2 - 10 ring range), such as the US EPA 16 PAH priority pollutants, with little clean-up. The weakly fluorescent acenaphthalene is difficult to detect at trace levels by fluorescence detection. The use of on-line reductive columns can enable routine analysis of nitro-PAH to be achieved. The use of chemiluminescence detectors enables further increases in the selectivity and sensitivity of HPLC methods.

3.5. OCCURRENCE OF PAH IN EXHAUST

3.5.1. Introduction - PAH emissions in perspective

As stated in the previous Section, it became increasingly clear during this study that the key to reliable data lies in representative sampling and the analytical approach employed. The majority of the references cited use different analytical systems and consequently direct comparison is not always easy. Data relating to the reproducibility of the analytical system are not often given. Note also that units employed throughout the references differ and this should be taken into account when attempting comparisons of the findings.

It is worth putting the emissions levels of current technology engines, running on current specification fuels, over the existing legislated cycles, in context. The best source of data in this area is the recent EPEFE report produced jointly by ACEA and EUROPIA. This provides detailed results for the emissions from a wide range of light-duty gasoline and diesel vehicles and heavy-duty diesel engines running on fuels blended only from the refinery streams currently used to make commercial automotive fuels. The focus below is on the carbon based emissions as these are of most relevance to PAH emissions; i.e. HC, PM and (where available within the speciated particulate results), “carbon+”, “lubricant VOF” and “fuel VOF”.

Heavy-Duty Diesel

The results for the five heavy-duty engines tested on five fuels (coded EPD1 - EPD5) are tabulated below. These fuels covered a wide range of densities (0.83 - 0.86 kg/l) and di+ aromatic levels (1 - 8%v/v). Typical HC and particulate emissions levels, plus speciated PM compositions, are given, whilst the “comments” column makes some effort to put these emissions in context.

Table 2 Heavy-duty diesel engine carbon based emissions (ECE-R49 Cycle)

Emission Type	Level [g/kWh]	Comment	EPEFE Reference [Chapter/Page]
Fuel Consumption	225	Assuming a typical fuel C : H ratio of ~ 1 : 1.8 implies a fuel carbon consumption rate of ~ 196 g/kWh.	5/51
Hydrocarbons	0.26	HC emissions ~ 0.1%m/m of the fuel consumed.	5/51
Particulate Matter	0.12	PM emissions ~ 0.05%m/m of the fuel consumed.	5/51
‘carbon+’	0.08	‘carbon+’ emissions ~ 0.04%m/m of the fuel carbon emitted as carbonaceous soot.	5/60
‘fuel VOF’	0.012	‘fuel VOF’ emissions ~ 0.005%m/m of the fuel consumed.	5/60
‘lube VOF’	0.017		5/60

Note that the ‘carbon+’ emissions have been described as a fraction of the mass of the fuel carbon, rather than of the entire fuel, as hydrogen does not contribute significantly to carbonaceous soot.

Light-Duty Diesel

The results for the nineteen light-duty diesel vehicles tested over the same five fuels (EPD1 - EPD5) are shown in **Table 3**. Again, typical HC and particulate emissions, and speciated HC compositions are presented.

Table 3 Light-duty diesel vehicle carbon based emissions (MVEG Cycle)

Emission Type	Level [g/km]	Comment	EPEFE Reference [Chapter/Page]
Fuel Consumption	56	Estimated from a CO_2 emissions rate of ~ 180 g/km, assuming a typical fuel C : H ratio of ~ 1 : 1.8 and implying a fuel carbon consumption rate of ~ 49 g/kWh.	5/35
Hydrocarbons	0.1	HC emissions ~ 0.18%m/m of the fuel consumed.	5/35
Particulate Matter	0.055	PM emissions ~ 0.1%m/m of the fuel consumed.	5/35
‘carbon+’	0.05	‘carbon+’ emissions ~ 0.09%m/m of the fuel carbon consumed	5/60
‘fuel VOF’	0.004	‘fuel VOF’ emissions ~ 0.007%m/m of the fuel consumed.	5/60
‘lube VOF’	0.004		5/60

Note that the ‘carbon+’ emissions have been described as a fraction of the mass of the fuel carbon, rather than of the entire fuel, as hydrogen does not contribute significantly to carbonaceous soot.

Light-Duty Gasoline

The results for the sixteen light-duty gasoline vehicles tested over four fuels (coded EPGA1 - EPGA4) are summarised in **Table 4**. These gasolines covered a wide range of aromatic levels (20 - 50%v/v.) and E100 values (35 - 50°C). As before, typical HC emissions are given in the table.

Table 4 Light duty gasoline hydrocarbon emissions (MVEG Cycle)

Emission Type	Level [g/km]	Comment (Data from Chapter 3, Page 4 of EPEFE report)
Fuel Consumption (ECE+EUDC)	93	Assuming a typical fuel C : H ratio of ~ 1 : 2.1 implies a fuel carbon consumption rate of ~ 79 g/km.
FC (ECE only)	130	Estimated fuel carbon consumption rate of ~ 111 g/km.
FC (EUDC only)	71	Estimated fuel carbon consumption rate of ~ 60 g/km.
Hydrocarbons (ECE+EUDC)	0.20	HC emissions ~ 0.22%m/m of the fuel consumed.
HC (ECE only)	0.49	HC emissions ~ 0.38%m/m of the fuel consumed.
HC (EUDC only)	0.022	HC emissions ~ 0.031%m/m of the fuel consumed.

Data are given for the ‘combined’ cycle (i.e. ECE and EUDC) and also for the 2 sections separately. The effect of fully warmed up catalysts during the EUDC part of the cycle is particularly evident.

Summary

It can be seen from these data that, for modern vehicles and engines, running over their legislated cycles, the mass of all the vapour phase hydrocarbons and of all the particulate borne hydrocarbons equates to only a small fraction of the mass of the fuel consumed. Furthermore, it is also the case that the targeted PAH species in any experimental programme forms only a small (and ill determined) fraction of the particulate borne HC, and an even smaller (and even less well determined) fraction of the vapour phase HC. Given that the emissions are small in relation to the amount of fuel consumed, it is apparent that experimental programmes in this field will not be easy. Firstly, changes in a wide range of test parameters (e.g. air/fuel ratio, density, cetane number, etc. as well as fuel PAH content) may have a significant impact on PAH emissions levels. Secondly, even assuming that the test parameters can be controlled sufficiently well for variations in individual parameters (such as fuel PAH level) to be studied, accurately measuring the levels of PAH emissions in such tests is not easy.

3.5.2. Gasoline Exhaust

Levels of PAH in exhaust gas are dependent on the type of engine/vehicle, the driving cycle employed, the sampling protocol and the analytical procedure used. Consequently, it is difficult to define maximum and minimum values. **Table 5** gives both a list of PAH typically analysed, whilst the second column indicates the number of papers that address that specific PAH.

Table 5 Literature references to gasoline PAH types in the exhaust

PAH Compound	Reference Frequency	PAH Compound	Reference Frequency
Naphthalene	5	Triphenylene	4
Acenaphthylene	2	Dibenz(aj)anthracene	1
Acenaphthene	1	Dibenzo(al)pyrene	1
Fluorene	3	3-methyl-cholanthrene	1
Phenanthrene	8	Benzo(cd)pyrenone	2
Anthracene	8	Methylbenz(a)anthracene	1
Fluoranthene	11	Dimethyl/ethylbenz(a)anthracene	1
Pyrene	13	Methylbenzo(a)pyrene	1
Benzo(a)fluorene	1	Methylbenzo(e)pyrene	1
Benzo(b)fluorene	3	1-Methylanthracene	3
Benz(a)anthracene	15	2-Methylanthracene	1
Chrysene	11	Indeno(1,2,3-cd)fluoranthene	1
Benzo(b)fluoranthene	9	1-Methyl naphthalene	3
Benzo(k)fluoranthene	8	2-Methyl naphthalene	2
Benzo(j)fluoranthene	1	Biphenyl	2
Benzo(ghi)fluoranthene	2	Biphenylene	2
Benzo(e)pyrene	9	Methylbiphenyl	1
Benzo(a)pyrene	15	Methyl/ethylnaphthalene	1
Perylene	6	Trimethylnaphthalene	1
Indeno(1,2,3-cd)pyrene	9	Methylfluorene	1
Benzo(ghi)perylene	10	Dimethyl/ethylfluorene	1
Dibenz(a,h)anthracene	3	Methylphenanthrene	3
Coronene	7	Dimethylphenanthrene	1
Benzonaphtho(2,1-d)thiophene	1	Methylfluoranthene	1
Benzo(ghi)fluoranthene	3	1-Methylpyrene	1
Benzo(c)phenanthrene	1	2-Methylpyrene	1
Cyclopenta(cd)pyrene	4	1-Methylphenanthrene	1
Anthanthrene	3	4-Methylphenanthrene	1
1-nitro-pyrene	3	9-Methylphenanthrene	1
3,6-dimethyl phenanthrene	1	3-Methylphenanthrene	1

Analysis of diluted gas exhaust show that there is a distribution of PAH between the gas phase and the particulate phase, related to their range of vapour pressures. The use of the dilution tunnel increases the adsorption of PAH to the particles which is especially pronounced for four ring PAH such as pyrene: Egebäck (1983). It was found that the amount of PAH in the gas phase increases with decreasing molecular weight and increasing vapour pressure of the compounds; a major part of 2-4 ring PAH are in the gas phase: Westerholm (1988). Essentially, all from naphthalene to trimethylnaphthalenes (including their biphenyl, biphenylene and alkyl derivatives) were in the gas phase. Less than 1% is found on the particles at a dilution temperature of 30°C, although their boiling points all exceed 200°C. Pyrene (boiling point 398°C) is gaseous to approx. 50% at 30°C; BaA, with a boiling point of 438°C is found in the gas phase to approx. 30%.

More than 90% of the mass of the heavier PAH was found on particles with a diameters below 1 µm: Pedersen (1980).

Examples of emissions of gas phase and particulate associated PAH are in **Tables 6** and **7**: Westerholm (1988). The driving cycle employed was the US Federal Test Procedure (FTP-75).

Table 6 Emissions of gas-phase associated PAH (µg/km) from gasoline vehicles for four fuels (F1 to F4)

PAH Compounds	Emissions							
	F1		F2		F3		F4	
	µg/km	± s.d. (%)	µg/km	± s.d. (%)	µg/km	± s.d. (%)	µg/km	± s.d. (%)
Naphthalene	7.2	46	18.0	21	10.0	16	23.0	18
Biphenylene	5.5	5	5.4	37	12.0	40	8.3	20
Acenaphthylene	25.0	29	13.0	35	37.0	19	28.0	35
Fluorene	11.0	29	12.0	54	29.0	31	42.0	35
Phenanthrene	21.0	35	33.0	28	51.0	35	91.0	45
Anthracene	5.3	23	12.0	27	21.0	11	28.0	36
1-Methylanthracene	6.0	16	12.0	21	19.0	5	nd	-
1-Methylphenanthrene	0.96	20	3.3	21	12.0	5	16.0	26
Fluoranthene	8.8	3	10.0	31	18.0	19	18.0	31
Pyrene	13.0	6	11.0	18	15.0	17	17.0	34
Methylpyrene	0.56	10	nd	-	0.77	15	0.32	39
Benzo(ghi)fluoranthene	0.38	14	1.2	10	0.89	21	0.69	57
Benz(a)anthracene	2.0	54	0.82	10	3.3	35	1.1	20
Chrysene/Triphenylene	2.1	27	1.3	10	6.3	10	0.51	13

- ± s.d. is ± standard deviation (%).
- nd = Not detected

Figure 9, overleaf, gives a pictorial representation on a logarithmic scale of the values (along with the reported standard deviation) for fuel F4. This fuel was chosen because, amongst the fuels tested, it was a commercial grade.

Figure 9 Emissions of gas-phase associated PAH from a gasoline vehicle (Logarithmic Scale) with fuel F4 (see **Table 7**)

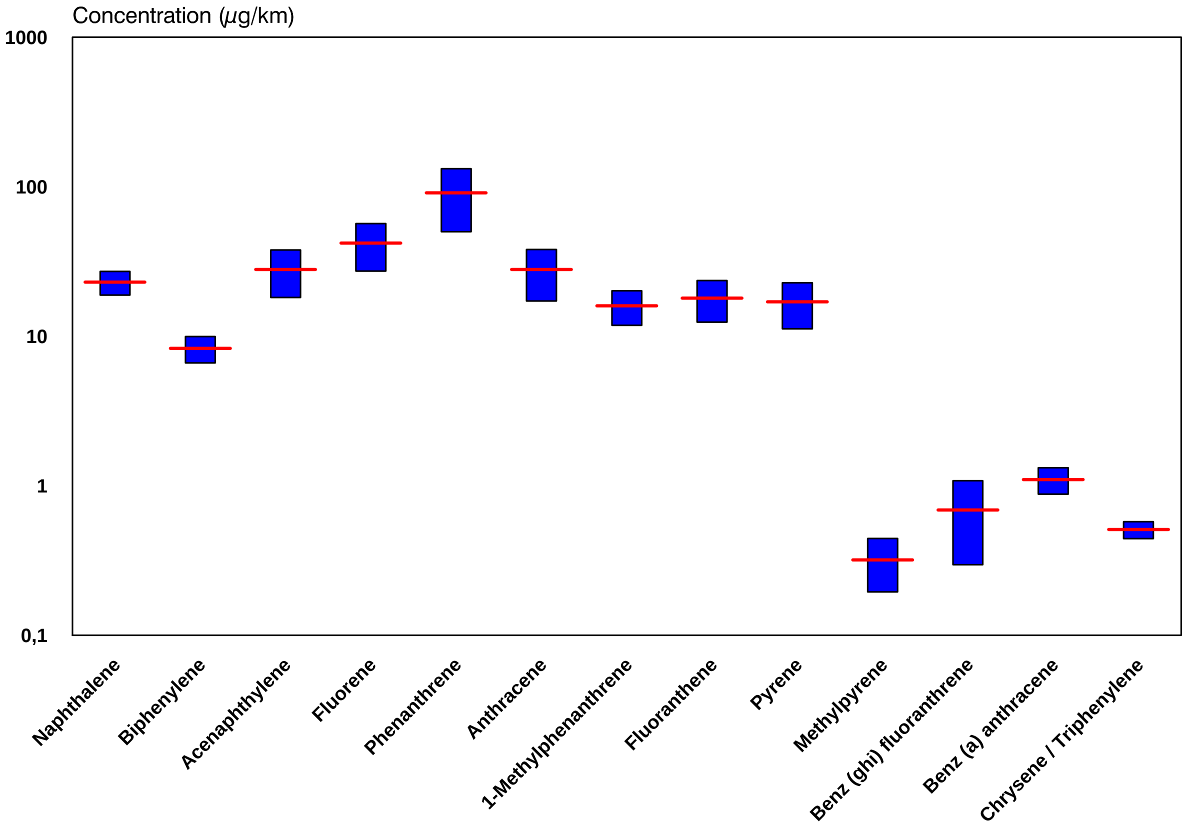


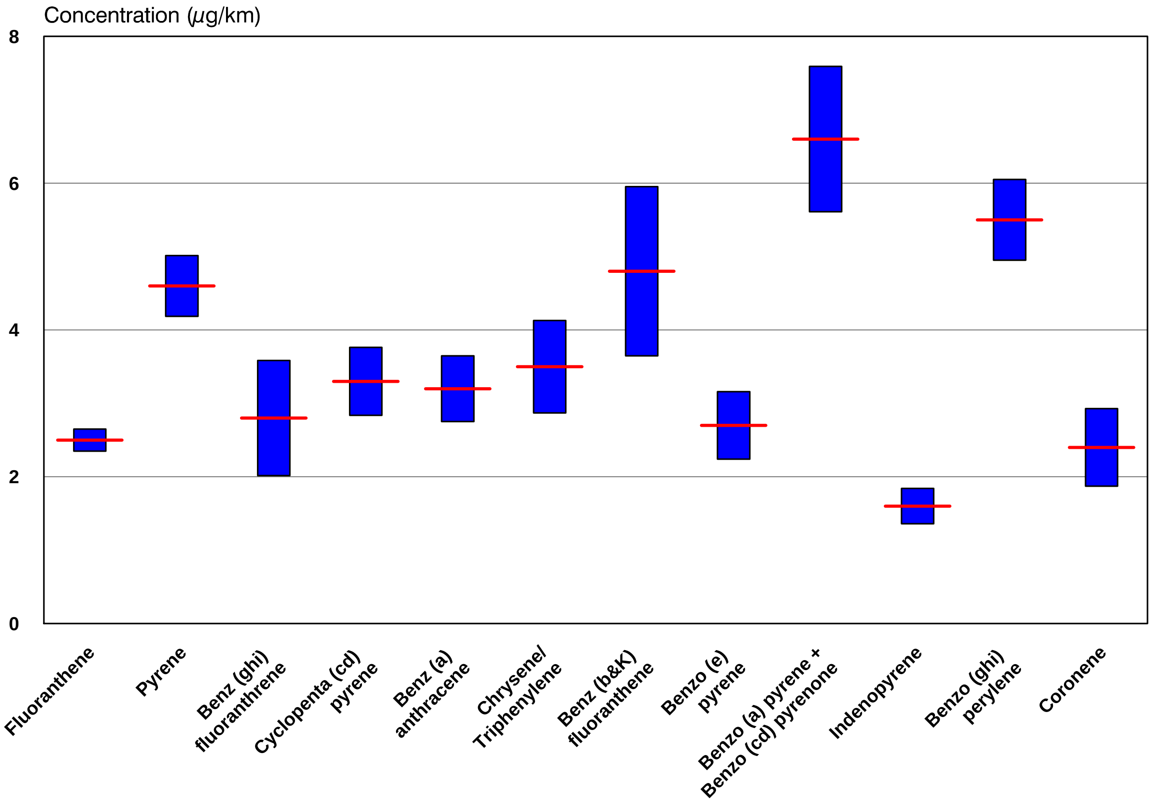
Table 7 Emissions of particulate associated PAH ((g/km) from gasoline vehicles for four fuels (F1 to F4)

PAH Compounds	**Emissions**							
	F1 (n=2)		F2 (n=3)		F3 (n=3)		F4 (n=4)	
	µg/km	± s.d. (%)	µg/km	± s.d. (%)	µg/km	± s.d. (%)	µg/km	± s.d. (%)
Phenanthrene	0.28	13	0.28	2	0.35	15	nd	-
Anthracene	0.11	34	0.08	30	0.24	15	nd	-
Fluoranthene	1.2	15	1.6	20	2.9	19	2.5	6
Pyrene	2.6	31	2.4	22	4.7	18	4.6	9
Benzo(ghi)fluoranthene	1.8	25	2.8	32	5.0	30	2.8	28
Cyclopenta(cd)pyrene	2.4	30	2.8	17	4.9	29	3.3	14
Benz(a)anthracene	nd	-	2.0	19	3.1	30	3.2	14
Chrysene/triphenylene	0.71	22	2.2	15	2.9	28	3.5	18
Benzo(b&k)fluoranthene	0.87	26	2.7	31	2.0	26	4.8	24
Benzo(e)pyrene	0.63	20	1.2	33	1.8	17	2.7	17
Benzo(a)pyrene + Benzo(cd)pyrenone	1.1	18	2.1	35	6.8	32	6.6	15
Indenopyrene	0.65	30		1.3 (35)		2.8 (29)		1.6 (15)
Benzo(ghi)perylene	2.0	27		2.1 (35)		4.5 (13)		5.5 (10)
Coronene	nd	-		1.4 (30)		3.7 (29)		2.4 (22)

- s.d. is ± standard deviation (%).
- nd = Not detected

Figure 10 gives a pictorial representation of the values (along with the reported standard deviation) for fuel F4. Again, this fuel was chosen because, amongst the fuels tested, it was a commercial grade. This time the figure is shown only with a linear scale, demonstrating that the levels of particulate bound PAH are all within the same order of magnitude.

Figure 10 Emissions of particulate phase associated PAH from a gasoline vehicle (Linear Scale) with fuel F4 (see **Table 8**)

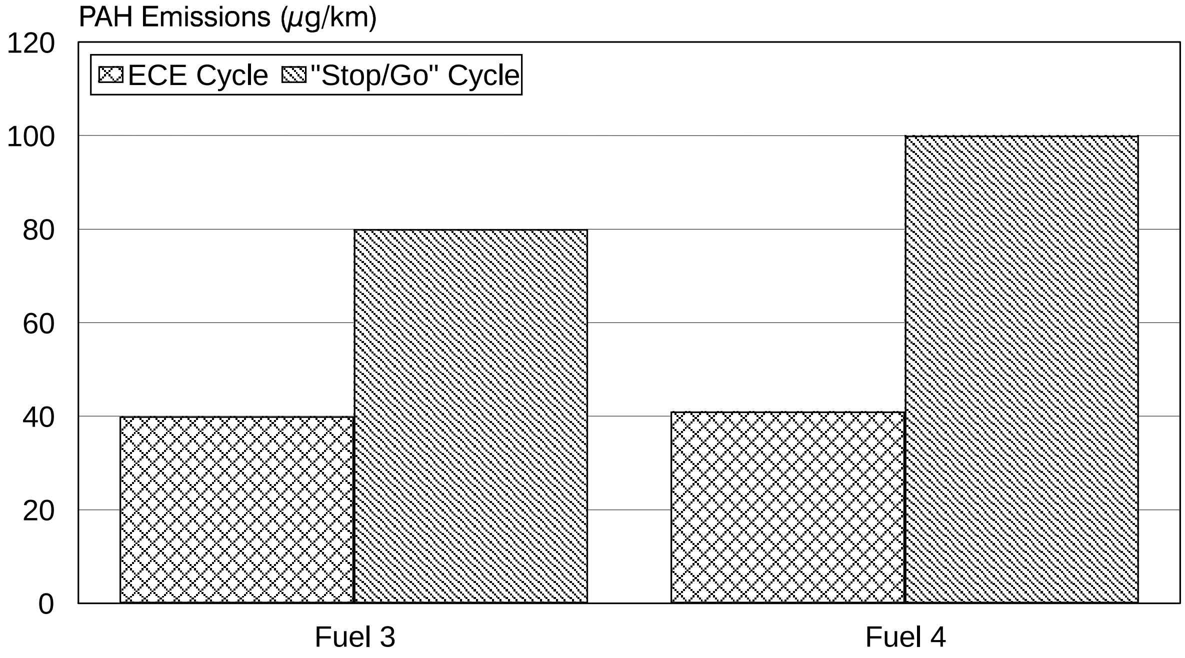


It has been reported, Egebäck (1983), Westerholm (1988) that although the exhaust emission of PAH is partially fuel dependent, a major part of PAH present in the fuel is burned during the combustion process and a significant fraction of emitted PAH are formed in the combustion process. Similar results are reported by Laity (1973), where “the type (but not the concentration) of PAH produced in the exhaust .... is substantially independent of the fuel composition”. The accumulated PAH in engine combustion chamber deposits have been stated by Gross (1974) as being a critical factor in the control of PAH emissions.

Other important influences on PAH emissions involve engine operating conditions - BaP and BaA concentrations in deceleration modes were nearly ten times greater than the average for cruise modes and about five times greater than in acceleration modes: Begeman (1970). Air fuel ratio (AFR) also influences PAH emissions - with an engine tuned AFR = 10 (i.e. fuel rich), PAH emissions of BaP and BaA were about thirty times greater than at AFR = 14 (just fuel lean of stoichiometric): Begeman (1970). Increased engine load promotes PAH formation to a larger extent than particle formation and therefore increases the proportion of PAH found adsorbed onto the particles. PAH emissions from automotive exhausts have been found to be greatest during cold engine operations: Hoffman et al (1971).

Transient driving conditions and, in particular, stop/go driving increase PAH emissions. DePetris (1993), compared PAH emissions over the ECE15 cycle with PAH emissions during stop/go operations. Their results, for two fuels, are shown in **Figure 11**, below:

Figure 11 Influence of “stop/go” driving versus ECE15 cycle conditions on PAH emissions from gasoline vehicles



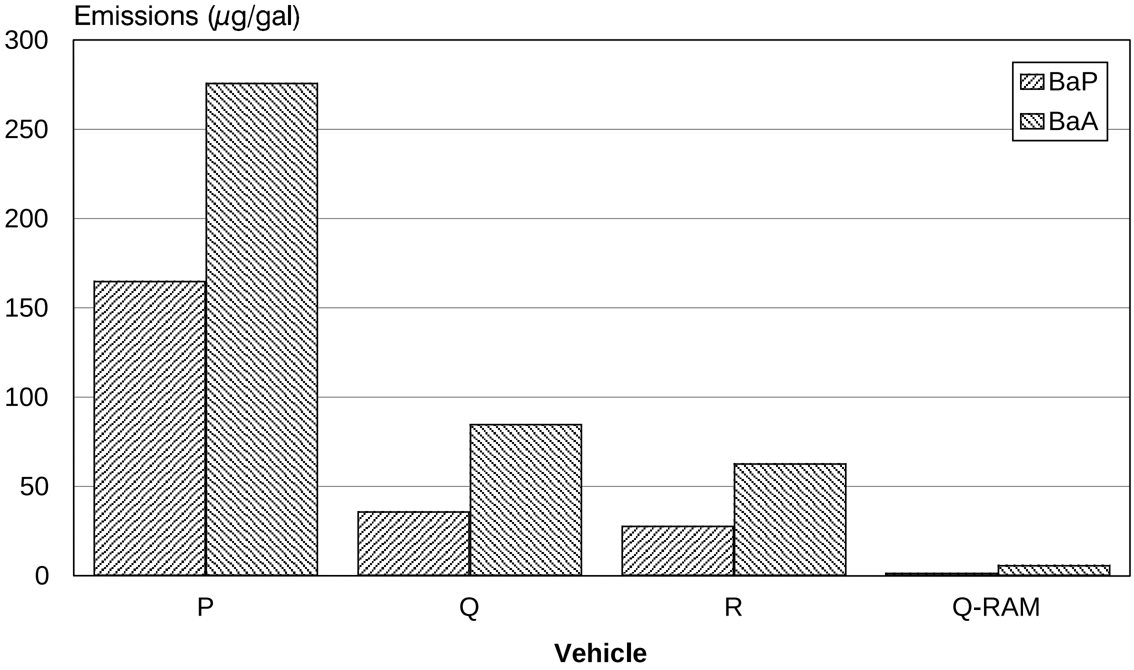
In 1972 Gross reported on the effect of engine technology on PAH exhaust emissions. Although these data are from pre-catalyst cars, it does give some indication of the variation that might be expected in engine-out emissions (**Table 8**):

Table 8 Effect of engine technology on PAH emissions: Gross (1972)

Vehicle	BaP emissions (µg/gal)	BaA emissions (µg/gal)
P	165	276
Q	36	85
R	28	63
Q-RAM	1.6	6.0

These data are reproduced as **Figure 12**, below:

Figure 12 Effect of gasoline engine technology on PAH emissions: Gross (1972)



3.5.3. Diesel Exhaust

Diesel exhaust is a complex mixture of different compounds, both volatiles and solids. Although most analysis has focused on particulates, analysis of volatile organic compounds in the exhaust has concentrated on PAH, light aromatics and aldehydes.

PAH compounds of four or higher ring number will generally be adsorbed to the particles, while lighter compounds are associated with the gas phase. Examinations by Westerholm (1991) have shown that 90% of phenathrene and 15% of pyrene are found in the gas phase.

Diesel exhaust particles, or particulates (PM), consist of a carbon skeleton (particle core) with adsorbed organic and inorganic compounds. The particle core can vary between 40-80% m/m of PM, whilst the organic fraction may vary between 10-60% m/m. The remaining inorganic part includes ash, sulphates and bound water.

The soluble organic fraction (SOF) consists of several compounds which can be divided into five main groups of increasing polarity; aliphatic, PAH, nitro-PAH, dinitro-PAH and more polar compounds.

Table 9 shows some typical compounds in the SOF fraction: Westerholm (1991) SRM 1650, Choudbury (1982), Henderson (1982), Schuetzle (1992), Barbella (1988), Farrar-Kahn (1991), CONCAWE 92/51 (1992).

Table 9 "Typical" SOF compounds in diesel particulates

Fraction	Typical Compound	Concentration µg/g
Aliphatic	n-alkanes	(1)
Aromatics	Fluoranthene	12 - 117
	Benzo(a)pyrene	0.04 - 50
	Dibenzothiophene	0.001 - 0.032
Nitro-PAH	1-nitropyrene	0.061-20
Dinitro-PAH	1,8-dinitropyrene	0.013 - 0.50
	9-fluorenone	33
Polar	Acridine	(1)

(1) not quantified, only detected.

The above data are presented graphically in **Section 2**, **Figure 3**.

Schuermann (1990) performed a test to identify and quantify unregulated components in the exhaust emissions of 18 passenger cars, both gasoline and diesel. The diesel engines were not equipped with catalysts. From their conclusions it can be read that several hundred PAH and PAH derivatives have so far been detected in motor vehicle exhaust gases, of which only a relatively small proportion has been quantified.

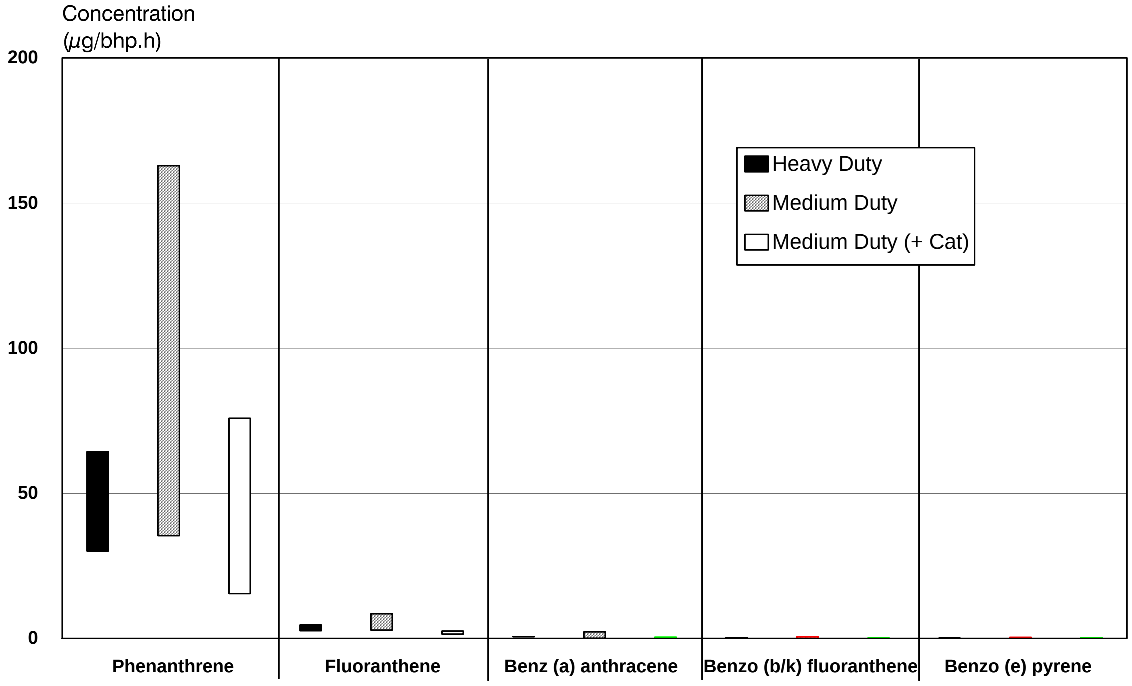
Table 10 shows the emission results published by Schuermann (1990) and Mitchell (1994).

Table 10 Examples of total PAH in diesel exhaust

Component	**Passenger Car** µg/mile	**HD Engine** µg/bhp.h	**MD Engine** µg/bhp.h	**MD + Catalyst** µg/bhp.h
2,6 Dimethylnaphthalene	1.72-40.24	3.89-233.56	0.00-38.54	
Acenaphtylene	4.62-21.55	7.79-34.09	0.28-6.22	
Acenaphtene	1.15-9.33	0.71-22.65	0.57-4.63	
Fluorene	11.66-22.19	4.53-48.55	1.87-13.37	
2-Methylfluorene	10.60-29.79	14.23-38.05	1.39-39.47	
Phenanthrene	30.12-64.38	35.41-162.89	15.48-75.85	
Anthracene	1.55-2.34			
Fluoranthene	112.0	2.67-4.68	2.90-8.50	1.52-2.57
Pyrene	107.7	4.21-31.60	3.76-66.41	1.5-10.76
Benzo(a)Fluorene	0.68-3.48	0.63-6.12	0.41-1.36	
Benzo(b)Fluorene	0.11-0.35	0.11-3.54	0.05-0.96	
1-Methylpyrene	0.34-15.51	0.25-63.95	0.17-6.37	
Benzo(g,h,i)Fluoranthene	0.17-0.52	0.00-1.79	0.11-0.47	
Benz(a)anthracene	5.4	0.00-0.63	0.09-2.32	0.05-0.47
Chrysene	20.8			
Chrysene & Tryphenylene	0.17-1.94	0.29-4.77	0.11-1.15	
Benzo(b/k)fluoranthene	17.1	0.12	0.09-0.63	0.11-0.21
Benzo(e)pyrene	24.7	0.06	0.06-0.43	0.06-0.24
Benzo(a)pyrene	7.6			
Perylene	0.9			
Indeno(123-cd)pyrene	6.3	0.11-0.23		
Benzo(ghi)perylene	16.7	0.02-0.34	0.06-0.21	

Five PAH (phenanthrene, fluoranthene, BaA, Bb/kF and BeP) from the above table are plotted as **Figures 4** and **4B** in Section **2** and demonstrate the spread in values across the different vehicle technologies. The linear scale graph is reproduced here for ease of reference:

Figure 13 Selected vapour and PM phase PAH in automotive diesel engine exhaust (Linear Scale)



From a chemical point of view it might be considered reasonable to explain the PAH in the exhaust by the fuels aromatic content. This has been done by several authors. However, some authors claim within the literature study (review article by Westerholm and Egebäck (1991)) that the engine exhaust PAH-emission is more sensitive to engine operating conditions than to fuel composition. Only for extremely high aromatic fuels, >40% aromatics, is there a significant increase in PAH in the exhaust.

3.6. MECHANISMS OF FORMATION

3.6.1. Introduction

The mechanisms by which PAH can occur in automotive exhausts are complex and several routes are possible. It is important to appreciate that the following mechanisms are not mutually exclusive and it is probable that all of them contribute to a greater or lesser extent to the PAH content of the exhaust.

3.6.2. Survival of fuel PAH

This is the most obvious mechanism by which PAH may appear in the exhaust. The *absolute* amount of PAH in the exhaust as a result of fuel PAH surviving combustion will be influenced, not only by the ease with which that PAH burns and the abundance of PAH in the fuel (both of which terms will vary considerably from one PAH to another), but also by the combustion efficiency of the engine, plus an "interaction term" according to the compatibility of the fuel and engine. Combustion efficiency is a combination of the engine's innate performance, the degree of maintenance and its response to the test cycle employed.. The "interaction" term, or "cross" term, is dependent on a fuel's cetane or octane number, density, distillation range, etc. (i.e. fuel parameters, other than PAH content, around which the engine is designed and calibrated).

3.6.3. Creation of PAH from non-PAH fuel components

There is a considerable amount of literature, both from fundamental combustion studies and from engine and vehicle tests, which shows that PAH are readily created during the partial combustion of non-PAH and even non-aromatic hydrocarbons. This can be attributed both to favourable combustion kinetics and to the thermodynamic stability of PAH. The scope of such pyrosynthesis reactions are very familiar - engines running on both gasoline (molecules typically in the C_5 – C_{10} range) and diesel fuel (molecules typically in the C_{12} – C_{24} range) produce emissions ranging from methane (C_1) to soot (upwards of a million C atoms per particle). Such reactions easily have the potential to create sufficient PAH to account for those found in exhaust emissions.

An illustrative calculation showing how much carbon can be turned into soot via pyrosynthetic chemistry can easily be accomplished using data for diesel vehicles from the recent EPEFE programme. Within that programme, one aspect of the work was to investigate the effect of di- and tri+ aromatics on emissions. Particulate analysis provides information on the "carbon +" part of the particulates (i.e. excluding the sulphate and volatile organic fraction, which accounts for most of the non-carbonaceous material). The data for these current/modern production vehicles and engines run over the European legislated cycles are given in **Table 11**:

Table 11 Typical "carbon +" PM for EPEFE vehicles and engines

Light Duty Vehicles [MVEG Cycle]		HD Engines [ECE R49 Cycle]	
"Carbon +" PM (g/km)	Fuel Consumption (l/100km)	"Carbon +" PM (g/kWh)	Fuel Consumption (g/kWh)
0.05	9.3	0.08	220

For the purposes of calculation, an average fuel density of about 0.84 kg/l and typical values for fuel C:H ratio of 1:1.8 and for the fixed carbon C:H ratio of 10:1 will be assumed. It is then apparent that, for these test cycles, about 0.10% of the carbon consumed by a light duty vehicle and about 0.04% of the carbon consumed by a heavy duty engine undergo the very extensive chemical reactions necessary to produce “soot”.

It might be asked if such conversion rates indicate that pyrosynthesis could play a significant part in determining the PAH emitted from vehicles. Fixed carbon forms the majority of the particulate matter (~ 80% m/m for LD, ~ 70% m/m for HD), whilst in contrast fuel derived hydrocarbons (of all sorts, not just PAH) form less than 5% m/m (LD and HD). The amount of fixed carbon, all of which is produced via chemical reactions, plainly exceeds by at least an order of magnitude the amount of PM borne fuel derived hydrocarbons of all types. It is thus quite plausible that sufficient pyrosynthetic chemistry occurs to create a significant fraction of the exhaust PM borne PAH.

3.6.4. Modification of fuel PAH

There are, of course, a whole range of intermediate possibilities lying between the creation of PAH from non-PAH fuel components, and the survival of fuel PAH, essentially structurally unaltered. These may be classified as "modifications" of fuel components. Attention is specifically drawn to those possibilities for the following reasons. Firstly, the definition of “PAH” is rather loose and what to some may seem like the “creation” of a PAH may, to others, seem more akin to “survival”. For example, either case could be made for fuel naphthalene molecules which undergo pyrosynthetic reactions resulting in the formation of phenanthrene, which may then pass to the exhaust. Secondly, depending on the experimental design and the analytical capabilities of any test programme, it can be difficult or impossible to determine whether exhaust PAH material has been “created”, “modified”, or has just “survived”. This latter point is dealt with more extensively below in the experimental techniques section, but obviously has a great impact on our ability to determine the source of exhaust PAH, and thus the likely impact of any potential measures designed to mitigate such emissions.

3.6.5. Contributions from the lubricating oil

Although new lubricating oils can contain very low concentrations of PAH, these are a potential source of exhaust PAH. Additionally, lubricants slowly absorb both fuel PAH and those pyrosynthesised in the engine. Therefore, depending on the format of the test programme, and the type and age of the oil, the lubricant may act either as a net sink for, or as a net source of exhaust PAH. Regular monitoring of lubricant consumption and of lubricant PAH levels is required to assess the extent of the possible contribution to exhaust PAH, but such measurements are not generally seen in the literature.

It should be noted that there is a distinct difference in the degree to which the lubricating oil is exposed to the fuel in gasoline and diesel engines. In the former, the fuel charge is sucked in to the cylinder as the piston descends, exposing a large area of oil film covered piston wall. The degree of fuel dilution of gasoline engine lubricant (which often reaches 1 - 2%, and can reach 5% over 10,000 km) is indicative of the extent to which the fuel spray contacts the lubricant. Any gasoline fuel droplet traversing the cylinder will evaporate and its PAH concentration will progressively increase due to the relative involatility of the PAH. A gasoline droplet that impacts with the cylinder wall can thus be expected to take a large proportion of its original PAH with it into the lubricant.

In contrast, the fuel enters a diesel engine when the piston is close to top dead centre. Very little of the cylinder wall is therefore exposed, and fuel dilution of the lubricant is consequently much less. Dilution levels are typically 0.1-1.0%v/v for heavy duty engines for properly maintained vehicles run over typical drive patterns. Somewhat lower figures can be expected for light duty vehicles.

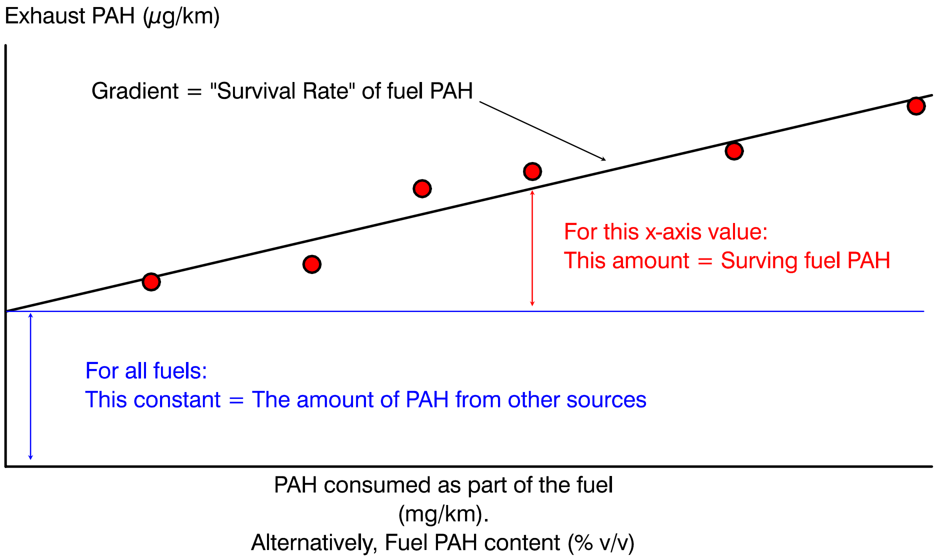
3.6.6. Entrainment from PAH deposited in the exhaust and sampling system

Finally, it must be acknowledged that in most engine exhaust sampling systems, both the exhaust pipe and the sampling/dilution tunnel may also be either a net sink for, or net source of exhaust PAH. In fact, the exhaust and sampling system could act both as a sink for exhausts with a particularly high PAH content and as a source for those with a particularly low PAH content during the same research programme. The influence of the exhaust system may be minimised by sampling close to the exhaust manifold. However, many of the programmes reviewed in this report follow the legislated procedures for regulated emissions and sample from the end of the tailpipe via an extensive dilution tunnel. These studies generally tacitly assume that the exhaust and sampling system make no net contribution to exhaust PAH (and PM) levels. It seems likely that this assumption will be more nearly true for PM, and less so for the more mobile PAH, these latter being subject to both gas phase and particulate phase exchanges between the exhaust and the exhaust/sampling system. The ^{14}C labelled work of Rhead et al, reviewed herein, is recommended to the reader as the work best able to overcome the problems of contamination from the sampling system: see also the discussions in **Section 3.3.3**.

3.6.7. Interpretation - The evaluation of the relative contribution of the different mechanisms

In terms of the mechanisms by which PAH enter the exhaust stream, the results from experiments where a range of fuels are tested are most easily appreciated graphically. If one plots exhaust PAH as a function of fuel PAH and fits a linear regression to the points, a graph of the form sketched below is obtained:

Figure 14 A plot of exhaust PAH level vs. fuel PAH content, with a best fit linear regression (y = m.x + c) added.



Such plots provide the following information. The constant (“c”) defines the amount of PAH in the exhaust arising from sources other than surviving fuel PAH. The gradient (“m”) defines the survival rate of the fuel PAH, providing both axes are in the same units (e.g. mass of PAH emitted as part of the exhaust per unit of power output vs. mass of PAH consumed as part of the fuel per unit of power output). The reader should also note that, in order to see any gradient at all on such plots, the scale of the y-axis has to be greatly exaggerated relative to that of the x-axis (e.g. y-axis marked in steps of micrograms/kWh, x-axis marked in steps of milligrams/kWh).

If the majority of exhaust PAH arise from fuel PAH that survive combustion, then the constant will be small and the best fit line will pass close to the origin. Conversely, if the constant is relatively large, then a significant amount of exhaust PAH must arise from some source other than surviving fuel PAH. The point along the x-axis where the constant accounts for half the total exhaust PAH equates to the level of fuel PAH below which surviving fuel PAH are responsible for a minority of the exhaust PAH.

The effects of changes in engine technology can also be established from changes in the gradient of such plots. An engine working under less efficient conditions will leave a greater amount of fuel unburnt, and thus produce a plot with a steeper gradient than one working at optimum efficiency.

It is worth clarifying what is meant by “survival rate”. Herein, the survival rate of a fuel component PAH is the fraction of those PAH in the fuel that survive combustion unchanged and appear in the exhaust. Only if no PAH are created, and none entrained from other sources (such as the lubricating oil), is this the same as the amount of PAH in the exhaust divided by the amount that passed in to the engine as part of the fuel. As will be seen in the review section, significant amounts of PAH do appear to be created in the engine and a separate term is thus needed to identify this second type of calculation. The phrases “recovery rate” and “apparent survival rate” have been used in the literature (see also discussions in **Sections 3.1** and **3.2** on this matter).

The above discussions notwithstanding, it is sometimes beneficial to plot figures of the type shown in **Figure 14** in which the axes do not share the same dimensions. Certain audiences find it more useful to see the x-axis plotted in terms of "% v/v of tri+ aromatics in the fuel", rather than "mg of PAH consumed per km". Whilst changes such as this are useful in getting broad messages across to specific audiences (and may be necessary if data on the concentration of specific PAH in the fuel and on fuel consumption is not available), some care is required. Firstly the gradient no longer describes an absolute survival rate. Secondly the influence of fuel composition on fuel consumption is no longer included in the plot. This factor could be significant if fuels with differing oxygenate content, and/or vehicles with significant variations in fuel consumption were being compared.

3.6.8. PAH formation – A literature evaluation of the different mechanisms

It is unfortunate that the authors of much of the published literature have not chosen to adopt the approach described in the preceding Section when interpreting their results. Indeed, the majority of authors provide insufficient data for graphs of the type shown in **Figure 14** to be plotted. However, a few papers allow some evaluation of the mechanisms of formation of PAH and these are discussed below. In each case a summary of the paper is given, conclusions are drawn and the results are presented in the graphical format described above.

Mitchell (1994)
(Authors from a range of oil, vehicle and environmental concerns)

Experimental Design

This recent programme investigated one heavy-duty (HD) engine, a DDC Series 60 (DI, TC, 11 L, 6 cylinder with electronically controlled injection) and one medium-duty (MD) engine, a Navistar DTA-466 (DI, TC, 7.6 L, 6 cylinder) which could, optionally, be fitted with either of two palladium based oxidation catalysts. Both engines were of modern design, meeting the US 1994 emissions specifications. Both engines were tested on four fuels, each specially blended from refinery streams so as to break any correlation between mono-aromatics and PAH levels. Sulphur content was held constant at 0.05%m/m, and cetane improver was used to keep the CN in the range 40.5 - 44.3 (the US specification requiring CN $\geq$ 40). Some increase in density, viscosity and final boiling point could not be avoided for the high tri+ aromatics fuel. Total aromatics covered the range 13-28%m/m whilst tri+ aromatics covered the range 0.2-5.8%m/m. The concentrations of the targeted PAH in the fuels were *not* established.

The engines were tested over the US EPA's transient heavy-duty cycle. Both PM and gas phase PAH emissions from one cold and six hot cycles were combined to form composite exhaust samples, this being done in at least duplicate for each fuel. The levels of twenty one PAH with from 2 to 6 rings and of seven nitro-PAH with from 2 to 5 rings were quantified; the levels of a further nine PAH were too low to quantify.

Results and Discussion

None of the regulated emissions, or the SOF levels, showed consistent fuel effects, despite the total aromatics ranging from 13-28%m/m. Data for the reference fuel showed the total hydrocarbon emissions (THC) to be 0.19 g/bhp.h for the HD engine (~ 0.11%m/m of fuel consumed) and 0.29 g/bhp.h for the MD unit (~ 0.15%m/m of fuel consumed), reducing to 0.19 g/bhp.h when using a catalyst (~ 0.10%m/m of fuel consumed). The SOF varied from 0.021 - 0.032 g/bhp.h in the HD engine (equivalent to 18 - 26%m/m of the PM or only 0.012 - 0.018%m/m of the fuel consumed) and from 0.044 - 0.068 g/bhp.h in the MD unit (equivalent to 43 - 51%m/m of the PM or only 0.023 - 0.036%m/m of the fuel). The catalysts reduced the PM by 22 - 32%m/m and the SOF by 22 - 56%m/m in the MD engine.

Total targeted PAH emissions (gas and PM phases combined) ranged from 131 - 160 µg/bhp.h in the HD case to 181 - 343 µg/bhp.h for the MD case. The catalysts reduced this value by 62 - 81%m/m (i.e. a greater reduction than was seen for either the SOF or the PM - a fact that was attributed to the greater ease with which the catalyst could adsorb the PAH molecules). The average exhaust PAH levels were plotted against the fuel tri+ content (using the SFC data) and regression lines were fitted, in the manner of **Figure 14**. **Figure 15** shows these data, and the best fit lines are given below. Unfortunately, in the absence of data giving the concentrations of the targeted PAH in the fuels, the gradient cannot be expressed as a “survival rate” for comparison with that of the THC given above.

Heavy-duty case: $\text{PAH}_{\text{exhaust}} = 50 + 10 \times \text{tri+}_{\text{fuel}}$

Medium-duty case: $\text{PAH}_{\text{exhaust}} = 44 + 33 \times \text{tri+}_{\text{fuel}}$

Medium-duty with catalyst: $\text{PAH}_{\text{exhaust}} = 41 + 5.4 \times \text{tri+}_{\text{fuel}}$

where:

- $\text{PAH}_{\text{exhaust}}$ is the total targeted exhaust PAH in µg/bhp.h;
- $\text{tri+}_{\text{fuel}}$ is the fuel tri+ PAH content in %m/m
- the constant is in units of µg/bhp.h and the gradient in units of µg/bhp.h/%m/m tri+

These equations show that, in the case of the HD engine, when running on fuels of less than 5%m/m tri+ aromatics, the majority of the exhaust targeted PAH are not surviving fuel components (other fuel parameters being assumed not to vary significantly). The comparable figure for the MD unit is 1.3%m/m (without oxidation catalyst) and 7.6%m/m (with catalyst). A study of the individual test results (those plotted in **Figure 15** are averages of between two and five tests) also shows that the scatter in the measurement on any one fuel is about as large as the difference between fuels.

These equations and the associated graph demonstrate that both engines emitted similar levels of PAH that cannot be attributed to surviving fuel components. As discussed previously, similar levels of PAH pyro-synthesis in different engines running on the same cycle may be expected as the factors controlling PAH pyro-synthesis (temperature, pressure and C:H ratio in the flame front) will not vary. It may also be postulated that the similarity of these numbers suggests that entrainment of significant lubricant PAH is unlikely. This is expected to be strongly engine dependent. It is also apparent that the engines have different gradients describing their emissions rates. This may be attributed to the influence of engine technology. Unsurprisingly, the larger engine, with its lower surface area to volume ratio and possibly better mixture preparation demonstrates a greater combustion efficiency.

The nitro-PAH data showed that emissions levels were two orders of magnitude less than those of the PAH, typically less than 1 µg/bhp.h in total for the seven targeted species. Mitchell et al chose not to plot a similar figure to that for the PAH, but provide sufficient data for a graph to be constructed. The result is given in **Figure 16**, with the best fit regressions being shown below.

Heavy-duty case: $\text{Nitro-PAH}_{\text{exhaust}} = 0.058 + 0.14 \times \text{tri+}_{\text{fuel}}$

Medium-duty case: $\text{Nitro-PAH}_{\text{exhaust}} = 0.39 + 0.58 \times \text{tri+}_{\text{fuel}}$

Medium-duty with catalyst: $\text{Nitro-PAH}_{\text{exhaust}} = 0.37 + 1.1 \times \text{tri+}_{\text{fuel}}$

where:

- Nitro-PAH exhaust is the total targeted exhaust nitro-PAH in µg/bhp.h
- tri+ fuel is the fuel tri+ PAH content in %m/m
- the constant is in units of µg/bhp.h and the gradient in units of µg/bhp.h/%m/m tri+

Large difference between the engines are seen in terms of both the constants and the gradients. The gradients and constants are such that the majority of exhaust nitro-PAH can be attributed to nitrated fuel component PAH for fuels with more than ~ 0.7%m/m tri+ aromatics. Note also that nitro-PAH *are formed across the catalyst*; nitro-PAH emissions rates were found to be from 31 to 206% higher with a catalyst fitted.

Summary

In this study the effects of both fuel tri+ and total aromatics levels on exhaust PAH levels in one heavy-duty and one medium-duty engine (both 1994 designs) running on the US heavy-duty transient cycle were assessed. The medium-duty engine could (optionally) be fitted with a catalyst (two designs were available). As can be seen from **Figure 15**, the interpretation of the results is heavily reliant on data for the fuel with the highest PAH levels. Bearing this in mind, the results indicated that there was "*no relationship between total fuel aromatics and the total measured PAH emissions*": however, "*fuel PAH content was found to have an influence on PAH emissions, the results also suggested that this was not the only source*" as "*a significant proportion of the PAH emissions comes from the lubricating oil or is formed in the combustion process*".

The relative effects of changes in fuel composition, engine technology and the impact of after-treatment devices can be gauged from the best fit lines for the experimental results. The HD engine, which was the more efficient at combusting fuel PAH, emitted 10 µg/bhp.h for every extra 1%m/m tri+ aromatics in the fuel; the comparable figure for the MD engine was more than 3 times larger at 33 µg/bhp.h. However, the introduction of an oxidation catalyst reduced this value to only 5.4 µg/bhp.h. Furthermore, even for the MD engine without a catalyst, the PAH emissions from fuels with no/negligible tri+ aromatics were more than half those from fuels with up to 1.5%m/m tri+ aromatics. (Note that a recent survey of European diesel fuels found average tri+ aromatics levels below 1.5%m/m in five out of six countries: CONCAWE (1995).

Nitro-PAH were emitted at levels typically two orders of magnitude less than PAH. Their rate of increase with increasing fuel PAH was roughly one tenth that of unnitrated PAH, although there was evidence of some formation of Nitro-PAH across the catalyst.

Figure 15 Particulate borne PAH levels as a function of fuel tri+ aromatics content

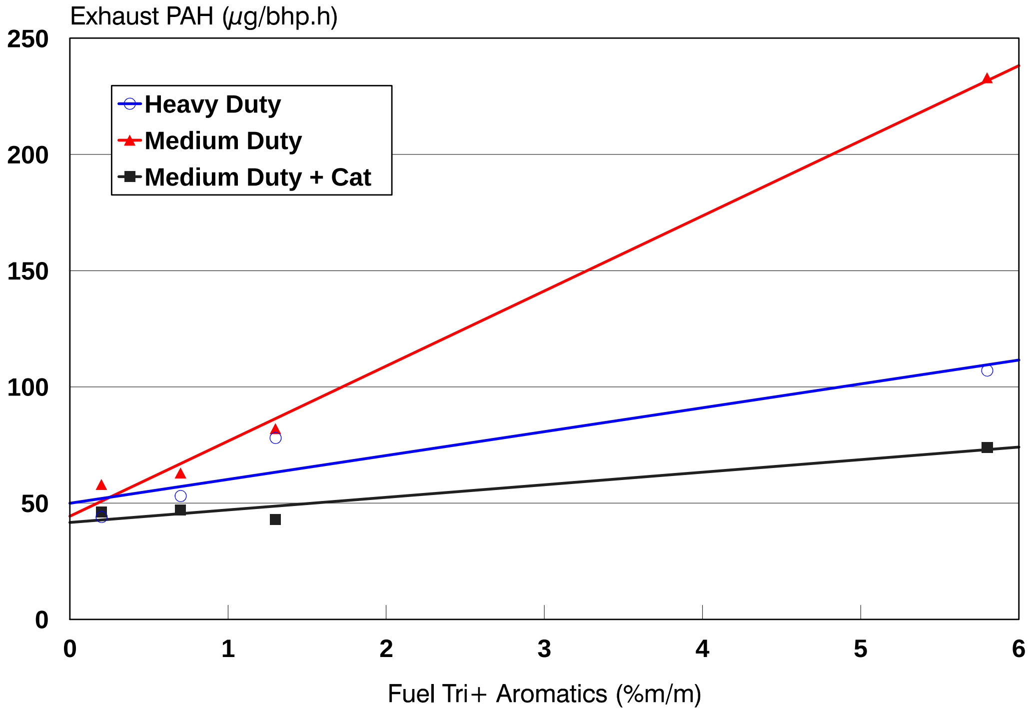
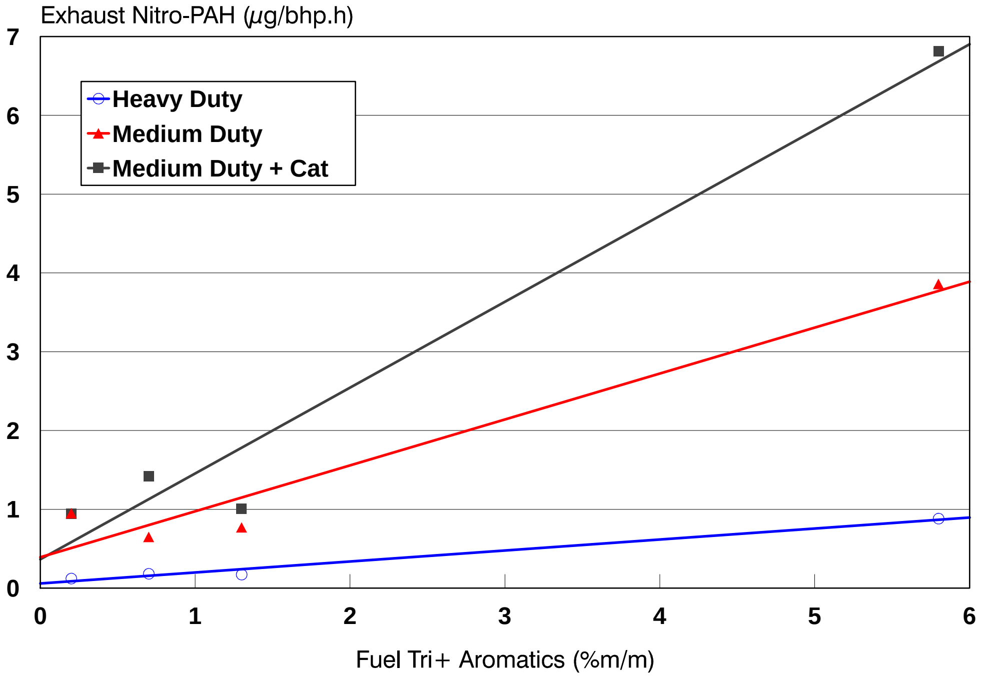


Figure 16 Particulate borne nitro-PAH as a function of fuel tri+ aromatics content (Note change in y-axis scale compared to **Figure 15**)



Grägg (1995)
(Swedish Motortestcenter, Swedish Environmental Protection Agency)

Experimental Design

A number of tests were performed using a Volvo truck (six cylinders, 12 L, DI, TC, EEM) meeting the ‘Euro2’ emissions specifications. The tests were carried out using a “bus cycle”. PAH levels (both PM borne and gas phase) were measured in quadruplet tests on both a commercial Swedish Class 1 fuel and a fuel of the type used as a reference in the EPEFE programme, and meeting the EN590 specifications. This meant that none of the fuel parameters were held constant, making it impossible to associate changes in any individual fuel properties with changes in the emissions levels. The concentrations of nine PAH were measured in both fuels, a further thirteen potentially quantifiable species being not present or below the detection limit.

Results and Discussion

It was found that a number of PAH that were not quantifiable in the fuels were detected in the exhausts, and conversely, some PAH that had been quantified in the fuels were not observed in the exhausts.

Data is available for only two fuels, so any regression analysis must be treated with some caution. However, in the context in the context of a wide ranging review, and to facilitate comparison with other work in the field, a regression fit has been calculated. **Figure 17**, below, shows the variation in targeted exhaust PAH (i.e. PM plus gas phase) as a function of targeted PAH consumed in the fuel (i.e. fuel consumption × PAH concentration[1]). The result is:

Euro2 HD lorry on “bus cycle”:

$$\mathrm{PAH}_{\mathrm{emitted}} = 160\ (\pm 40) + 1\times10^{-3}\ (\pm 1\times10^{-4})\ \mathrm{PAH}_{\mathrm{consumed}}$$

where:

- $\mathrm{PAH}_{\mathrm{emitted}}$ is the total targeted PAH emitted over this cycle in µg/km;
- $\mathrm{PAH}_{\mathrm{consumed}}$ is the total targeted PAH consumed over this cycle, again in µg/km;
- the constant is in units of µg/km and the gradient is dimensionless.

It is apparent from **Figure 17** that, when running on the fuel meeting the EN590 specification, the surviving fuel PAH account for about 80 - 85% of the exhaust PAH, although (as with other work by Grägg, Westerholm and co-workers) the simultaneous changes in so many of the influential fuel parameters prevent any one from being preferentially associated with the reduction in exhaust PAH.

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[1] “Targeted PAH” have been taken to be those which were quantifiable by the analysis method, irrespective of whether they were present at sufficient levels (in the fuel or exhaust) to be quantified: i.e. phenanthrene through to coronene in Grägg's results tables. A very similar result (within 1 standard deviation) is obtained if, instead, “targeted PAH”' are taken to be only those PAH which were actually quantified in *both* the fuels and the exhausts (i.e. phenanthrene through to pyrene in Grägg's tables).

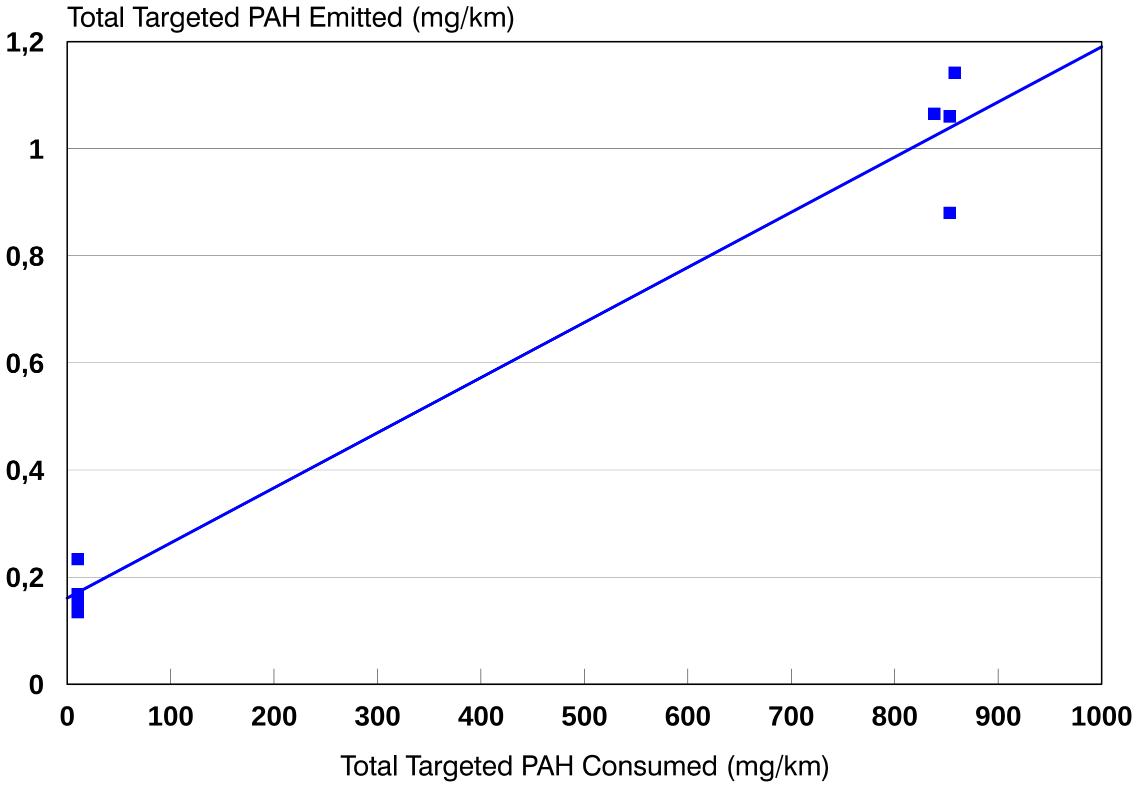
Grägg also reports data for total hydrocarbons and PM emitted over the “bus cycle” , with the PM being further divided into carbon, fuel derived HC, oil derived HC, sulphates, etc. These data can be combined with the fuel consumption figures to calculate what fraction of fuel hydrocarbons are emitted as HC or carbonaceous particulate matter.

The following values have been taken: fuel consumption ~ 340 g/km; HC ~ 0.35 g/km; PM ~ 0.32 g/km, of which ~ 80% is carbon or fuel derived HC. Thus very close to one part in a thousand (by weight) of the fuel hydrocarbons are emitted as gas phase HC and about 0.8 parts in a thousand (by weight) are emitted as PM. Following the earlier discussions, these figures should be regarded as “recovery rates”, or “apparent survival rates”, rather than “true survival rates”. However, the close similarity between these values and the value of 1×10^{-3} for the true survival rate obtained for the PAH from Grägg's work indicates that PAH are burnt as easily as other components in the fuel rather than being a “special case” of a relatively poorly combusting class of hydrocarbons.

Summary

A tentative (being based on data for only two fuels) linear regression fit to a plot of [*targeted exhaust PAH*] vs. [*targeted PAH consumed as part of the fuel*] has been drawn. This suggested a true survival rate in the region of 1×10^{-3}, similar (as far as could be determined) to that for other hydrocarbons. Surviving fuel PAH were indicated to be responsible for ~ 80% of the exhaust PAH in the case of the EN590 type fuel. However, the fuels used were such that all the potentially influential fuel properties varied, making the influence of fuel PAH content *per se* impossible to judge.

Figure 17 Exhaust tri+ PAH (PM and gas phase) as a function of PAH consumed in the fuel.



Note the expansion of the y-axis, relative to the x-axis. The gradient is 0.001 ± 0.0001, i.e. for this combination of engine and test cycle approximately one in a thousand PAH molecules in the fuel survive combustion to appear in the exhaust.

Doel (1996) (Shell)

Experimental Design

The influence of fuel PAH content on exhaust PM PAH levels was investigated for a modern heavy-duty engine (DI, TC, 6 L, six cylinders) designed to meet the 1996 ‘Euro 2’ emissions limits. Five fuels were tested, four having been specially blended from refinery streams such that cetane number, density, heavy-end distillation and mono-aromatics levels were kept almost constant whilst di- and tri+ aromatic levels were varied independently. It should be noted that this is the first time results from so many tests using fuels where the tri+ and/or di-aromatics levels were varied *independently* from other potentially influential fuel properties have been reported. A fifth fuel, included to assess the effects of an extreme low aromatics fuel, additionally had a very high cetane number (71.5) and a low density (0.80 kg/L). The concentrations of the sixteen PAH on the USA EPA priority pollutant list were measured for each fuel.

The fuels were tested over the ECE-R49 cycle between three and five times each, the engine being pre-conditioned with the test fuel before each R49 cycle. The PM was collected and analysed for sixteen targeted PAH. A fresh, low PAH, lubricating oil was used. Periodic PAH analyses of the lubricant showed that negligible changes in the lubricant PAH levels occurred over the relatively short duration of the programme.

Results And Discussion

The results showed that exhaust PM borne PAH levels varied very little as a function of fuel PAH content. In particular, the extreme low aromatics fuel (0.3%m/m mono-aromatics, < 0.1% m/m di- and tri+ aromatics combined) gave almost as much exhaust PAH as the high tri+ aromatics fuel (mono-aromatics 21%m/m, di-aromatics 6%m/m, tri+ aromatics 3%m/m).

Plots of exhaust PAH vs. PAH consumed in the fuel, and their best fit linear regressions, were given for both the total targeted tri+ and tetra+ species. These are shown below (**Figures 18** and**19** respectively).

$$\text{Tri+ PAH}_{\text{emitted}} = 0.10\ (\pm\ 0.01) + 7\text{x}10^{-5}\ (\pm\ 9\text{x}10^{-5})\ \text{Tri+ PAH}_{\text{consumed}}$$

$$\text{Tetra+ PAH}_{\text{emitted}} = 0.022\ (\pm\ 0.02) + 2\text{x}10^{-4}\ (\pm\ 2\text{x}10^{-4})\ \text{Tetra+ PAH}_{\text{consumed}}$$

where:

- PAH $_{\text{consumed}}$ is the total targeted tri+ or tetra+ PAH emitted over the R49 cycle in mg/kWh;
- PAH consumed is the total targeted tri+ or tetra+ PAH consumed via the fuel, in mg/kWh;
- the constant is in units of mg/kWh and the gradient is dimensionless.

As discussed above, direct comparison with Mitchell's or Westerholm's results is not possible as the results were acquired over very different drive cycles and each measures a different sub-set of PAH by a different technique.

However, as with Westerholm, the gradients, being dimensionless, are true survival rates and imply that in excess of 99.9% of the fuel PAH were combusted, even allowing for the relatively large uncertainty in both gradients, this being a consequence of the test-to-test scatter exceeding the fuel-to-fuel variability (see **Figures 18** and **19**). The fact that the gradients are smaller than those found by Westerholm may be attributed to the better combustion attained under the steady-state ECE-R49 cycle than under the transient “bus cycle”, and the fact that there is little or no contribution to the emissions due to variation in other fuel properties (e.g. cetane number, density, etc.).

Although no data for the regulated emissions from this engine were given, the recent EPEFE programme gives values for a number of similar engines driven over the same cycle. This indicates that about 0.05 - 0.25% of the mass of the fuel consumed is emitted as gas phase hydrocarbons (of all species) and about 0.03 - 0.1% of the mass of the fuel is emitted as PM. Thus a PAH survival rate of the order of ~ 0.02%, as indicated by the best fit regressions is not out of keeping and demonstrates that PAH combust to much the same extent as other diesel fuel components.

Summary

Data have been presented from a test programme where fuel properties other than di- and tri+ aromatic levels were held near constant. This work demonstrated that, for a modern design of heavy-duty engine, running over the legislated ECE-R49 cycle on current quality fuels, the majority of the exhaust PAH are pyro-synthesised, rather than being surviving fuel components. Monitoring of lubricant PAH levels indicated that these contributed negligibly. A comparison of the calculated PAH survival rate with data from the recent EPEFE programme indicates that the PAH survival rate of ~ 0.02% is similar to that generally seen for diesel fuel components.

Figure 18 Exhaust PM PAH as a function of fuel tri+ PAH

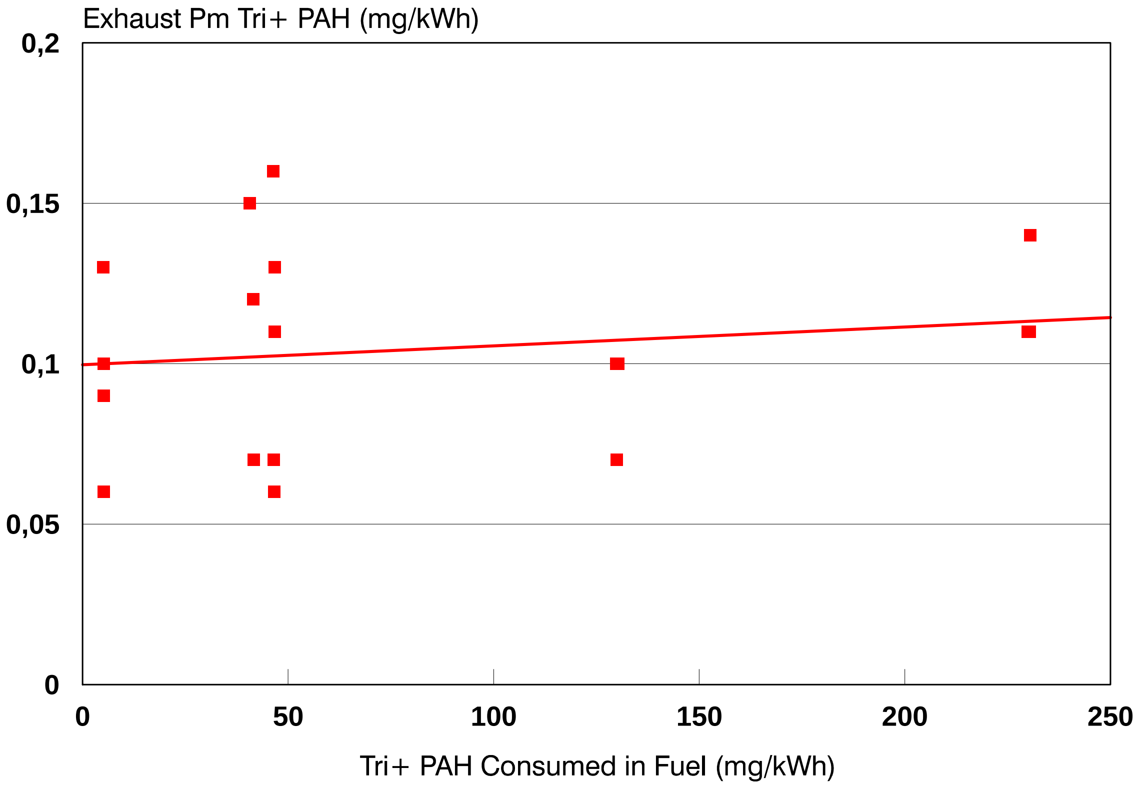
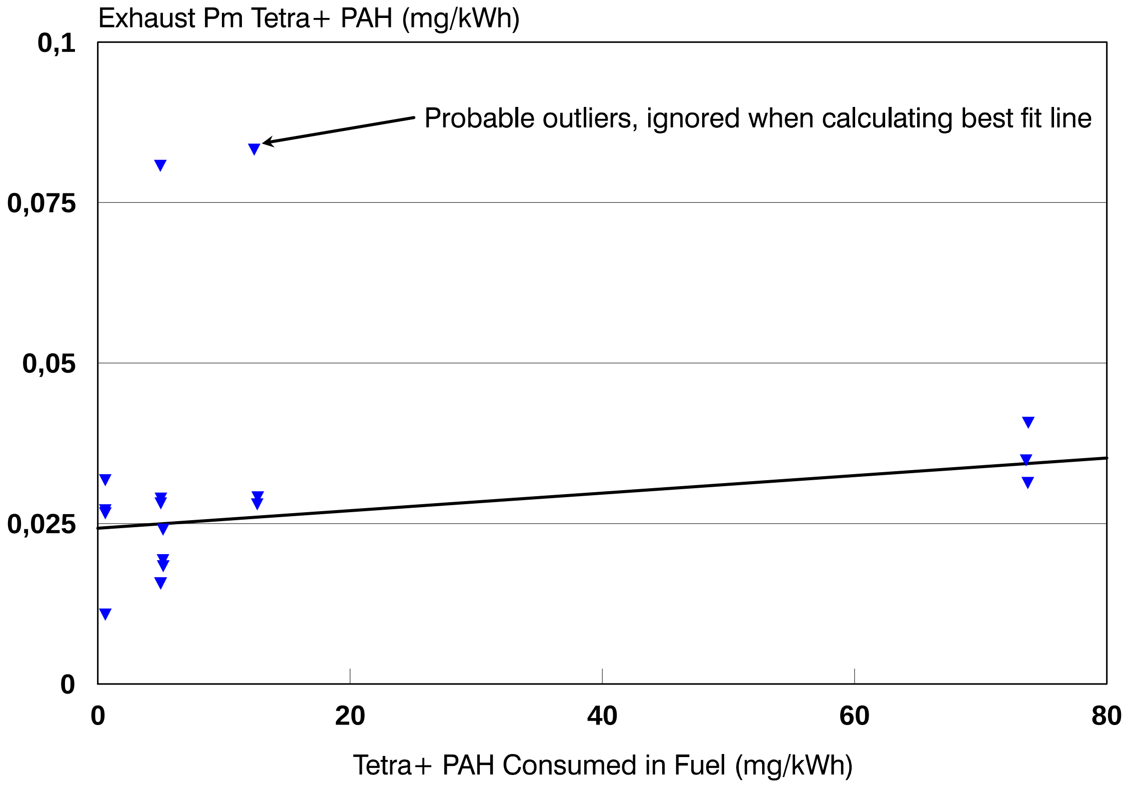


Figure 19 Exhaust PM PAH as a function of fuel tetra+ PAH



3.7. OCCURRENCE OF PAH IN FUELS

3.7.1. Introduction

Some of the published literature postulates that the principal contributor to exhaust PAH are fuel PAH species which “survive” combustion. However, as discussed in the previous section, there are many mechanisms by which exhaust PAH may be created. In addition, surprisingly few authors have attempted to correlate fuel composition/PAH levels with those measured in the exhaust, or to include any measurement of PAH in the test fuels used. Furthermore, many researchers appear to have ignored the potential for side effects when using fuels where properties other than PAH content can significantly influence emissions performance. These factors should be borne in mind when studying the following data.

3.7.2. Occurrence of PAH in gasoline

Typical values for PAH determined in gasoline fuels are given in **Tables 12** and **13**. It must be stressed here that different analytical methods have been used across different references and that values may not be strictly comparable. The references also cover a range of both commercial fuels and refinery stream blends, but not artificial additivation using pure PAH or chemical streams. More details on the fuels used are given in **Appendix 5**.

Commercial fuels are defined as being those that comply with specifications defined in the various countries in which they are sold and whose product quality is similar to that sold at the gasoline pump. Some measured values from commercial fuels are shown in **Table 12**. Differences in values between mg/kg and mg/l may be due to the different analytical methods employed. Values listed in **Appendix 5** have been converted to common units.

Table 12 PAH levels in commercial gasolines (ranges given in mg/km and mg/l as found in the literature; data not linked)

Compound	**mg/kg**			**mg/l**		
	min	**ave**	**max**	**min**	**ave**	**max**
Phenanthrene	55.0	56.7	58.0	27.0	27.0	27.0
Anthracene				2.7	2.7	2.7
Fluoranthene	2.8	4.17	6.8	4.5	4.5	4.5
Pyrene	14.0	15.67	18.0	0.03	5.1	10.8
Benz(a)anthracene	0.68	2.04	4.0	0.007	1.41	3.4
Chrysene	1.1	1.8	3.0	1.4	1.4	1.4
Benzo(b&k)fluoranthene	0.97	1.69	2.9			
Benzo(e)pyrene	1.4	2.26	4.0	0.007	1.24	2.9
Benzo(a)pyrene	0.67	1.62	3.1	0.007	1.14	2.4
Benzo(ghi)perylene	0.69	2.17	3.7	0.014	1.65	3.7
Indeno(1,2,3-cd)pyrene	0.26	0.51	1.0	3.9	3.9	3.9
Coronene	0.45	0.53	0.61	0.38	0.38	0.38
Benzo(ghi)fluoranthene	0.26	0.26	0.26	1.0	1.0	1.0
Me-benz(a)anthracene				0.009	1.38	3.23
Di-me-et-benz(a)anthracene				0.003	0.38	1.05
Me-benzo(a)pyrene				0.004	0.57	1.51
Me-benzo(e)pyrene				0.005	0.60	1.63
Group 1 (1)				420	1556	2630
Group 2 (2)				26.0	63.0	85.0

(1) Group 1 includes naphthalene to coronene (see **Appendix 5**, Laveskog (1996))

(2) Group 2 includes phenanthrene to coronene

The commercial fuels considered refer to both the American and European markets from 1970 to 1996.

During the preparation of test fuels Hoffman (1971), found that the PAH content of gasoline arises from reformate blending components. Gross (1972) added reformated still-bottoms to increase BaP in his base test fuels. Westerholm et al (1988) prepared three test fuels with three different PAH levels by using different fractions of regular reformate obtained by distillation at different temperatures. **Table 13** summarises the PAH levels of all the fuels covered in the literature search (finished fuels and components), including values from **Table 12**:

Table 13 PAH levels in commercial gasolines and gasolines blended from refinery streams (ranges given in mg/km and mg/l as found in the literature; data not linked)

Compound	**mg/kg**			**mg/l**		
	min	**ave**	**max**	**min**	**ave**	**max**
Phenanthrene	45.0	53.7	58.0	1.6	12.1	27.0
Anthracene				0.33	1.88	2.7
Fluoranthene	1.1	4.5	7.0	0.1	3.1	4.6
Pyrene	11.0	15.5	18.0	0.03	3.55	10.8
Benz(a)anthracene	0.68	1.69	4.0	0.002	1.3	3.7
Chrysene	0.26	1.26	3.0	1.1	1.6	2.3
Benzo(b&k)fluoranthene	0.32	1.22	2.9			
Benzo(e)pyrene	0.48	1.65	4.0	0.007	0.91	2.9
Benzo(a)pyrene	0.07	1.45	4.4	0.0008	0.72	3.4
Benzo(ghi)perylene	1.0	2.1	3.7	0.014	1.22	3.7
Indeno(1,2,3-cd)pyrene	0.22	0.41	1.0	3.9	3.9	3.9
Coronene	0.32	0.64	1.4	0.38	0.55	0.72
Benzo(ghi)fluoranthene	0.06	0.26	0.42	0.8	0.97	1.1
Me-benz(a)anthracene				0.009	1.24	3.23
Di-me-et-benz(a)anthracene				0.003	0.39	1.06
Me-benzo(a)pyrene				0.004	0.58	1.61
Me-benzo(e)pyrene				0.005	0.60	1.63
Group 1 (1)				18.0	942.0	2630.0
Group 2 (2)				0.47	38.0	85.0

(1) *Group 1 includes naphthalene to coronene (see **Appendix 5**, Laveskog (1996))

(2) *Group 2 includes phenanthrene to coronene

Fuel aromatic content was reported to influence particle-bound PAH emissions: Pedersen et al (1980). Some workers who have examined refinery components, claimed to have found a relationship between fuel aromatic content and PAH emissions: Hoffman et al (1971); Gross (1972). Increasing the heavy aromatics (alkylated C_{10} - C_{14} components) in a low-PAH fuel by addition of 20% heavy catalytic naphtha or 0.7% of a C_{10} - C_{14} catalytic reformate fraction increased the emissions of several PAH species by 16% to 110%: Gross (1974). Candeli et al (1974) have found a relationship between higher molecular weight aromatics and PAH emissions.

Gross (1974) identified a linear correlation between PAH in the fuel and PAH emissions. The equations found are reported overleaf in **Table 14**:

Table 14 Summary of correlations for nine PAH species in fresh-deposit emissions and in gasolines - Correlation of emissions (µg/gal) with fuel content (µg/gal)

PAH species	**Vehicle**	**Corr.Coeff.**	**Intercept (µg emitted/ gal fuel consumed)**	**Slope (equivalent to PAH survival rate)**
Pyr	P	0.827	1065	0.0774
	Q and R	0.896	317	0.0297
BaA	P	0.989	66.3	0.0568
	Q and R	0.936	24.1	0.0264
MBaA	P	0.955	24.4	0.0306
	Q and R	0.949	12.3	0.0159
DM/EBaA	P	0.841	0.4	0.0342
	Q and R	0.967	3.2	0.0101
BaP	P	0.942	49.8	0.0254
	Q and R	0.976	11.0	0.0085
BeP	P	0.914	112.2	0.1622
	Q and R	0.967	44.0	0.0528
BghiP	P	0.839	177	0.0542
	Q and R	0.671	77.4	0.0110
MBaP	P	0.775	20.3	0.0135
	Q and R	0.968	3.9	0.0038
MBeP	P	0.877	18.8	0.0977
	Q and R	0.985	12.9	0.0338

In recent work, Laveskog (1996), it was reported that a low PAH concentration in gasoline is more important than its monoaromatic content as a determinant of PAH emissions for a number of vehicles. However, PAH emissions were not directly proportional to the PAH content of the fuel.

It has been found that retention of PAH in the gasoline engine lubricant plays a role in the subsequent emissions. Some PAH enter the crankcase directly from unburned gasoline and other PAH, formed by pyrolysis of fuels and oils in combustion chamber, may be absorbed in the remaining oil film on the cylinder wall. This will then be scraped into the crankcase: Pedersen et al (1980). PAH in engine oil had no effect on PAH emission at normal oil consumption, but increasing the oil consumption fourteen to thirty five times caused high PAH emissions: Begeman (1970); Gross (1974).

3.7.3. Occurrence of PAH in diesel fuels

Numerous PAH compounds in fuel have been identified, but there are very few quantitative data for specific PAH compounds. In a previous report, CONCAWE (1995), CONCAWE estimated values for the aromatic content of diesel fuel in European fuels (over the period 1993-1994) to be between 1-10% v/v for diaromatics and between 0.1 – 3% v/v for tri-aromatics.

The chemical composition of a diesel fuel varies depending on how it is blended from different refinery streams. The composition of these streams will further depend on refinery configuration and, most importantly, crude oil source and feedstock. The diesel blend will therefore be a complex mixture of different aliphatic, naphthenic and aromatic hydrocarbons. Complete identification and quantification of all the individual hydrocarbons in a fuel is thought to be impossible. Ogawa (1995) have given an example; "The number of paraffin isomers of carbon number 15 (C_{15} H_{32}) is estimated to be 1860. The total number of isomers in a diesel fuel is estimated to be more than ten thousand."

As discussed earlier, several authors have documented a relationship between PAH emissions and fuel poly-aromatic content, but combustion reactions and lubricating oils are also known to contribute significantly to the occurrence of PAH in diesel exhaust. Research on combustion mechanisms have also shown that n-paraffins may be involved in the formation of PAH by dehydrogenation/polycondensation.

Published PAH data for diesel fuel shows that the individual PAH analysed by different centres varies enormously and depends to a certain extent on the analytical capability of that laboratory. Most results show only PAH of 3-ring or greater, although Abbass (1991) has given a detailed breakdown of the 2-ring components of diesel (**Table 15**).

Table 15 Analysis of 2-ring PAH (mg/kg) of diesel fuels: Abbass (1991)

2-ring PAH	mg/kg
Naphthalene	2056
2-Methylnaphthalene	5306
1-Methylnaphthalene	3784
Biphenyl	699
Methylbiphenyl	3167
2,6 and/or 2,7 Dimethylnaphthalene	1398
1,7 Dimethylnaphthalene	1686
2,3 and/or 1,4 Dimethylnaphthalene	2673
1,5 Dimethylnaphthalene	2756
1,2 Dimethylnaphthalene	2756
1,4 and/or 2,3 Dimethylnaphthalene	2673
C3-naphthalenes	6370
C4-naphthalenes	2706
C5-naphthalene	287

There is a wide range of PAH that can be measured and a typical list is given by Westerholm (1991) in **Table 16**:

Table 16 List of PAH found in diesel fuels (Westerholm and Egebäck)

2-methyl-9H-fluorene	Fluoranthene	Benzo(b&k)-fluoranthene
Dibenzothiophene	Pyrene	Benzo(e)pyrene
Phenanthrene	1-methyl-7-isopropylphenanthrene	Benzo(a)pyrene
Anthracene	Benzo(a)fluorene	Perylene
4-methyl-dibenzothiophene	2-methyl-pyrene	Indeno(1,2,3-cd)fluoranthene
3-methyl-dibenzothiophene	1-methyl-pyrene	Indeno(1,2,3-cd)pyrene
3-methyl-phenanthrene	Benzo(ghi)fluoranthene	Picene
2.methyl-anthracene	Cyclopenta(cd)pyrene	Benzo(ghi)perylene
4 & 9 methyl-phenanthrene	Benz(a)anthracene	Coronene
1-methyl-phenanthrene	Chrysene/Triphenylene	

Table 17 lists a range of the most commonly reported values of PAH content in commercial available diesel fuel, although there might be other PAH compounds determined and reported in the references cited: Abbass (1991); Westerholm (1991); Lee (1992); Williams (1986)

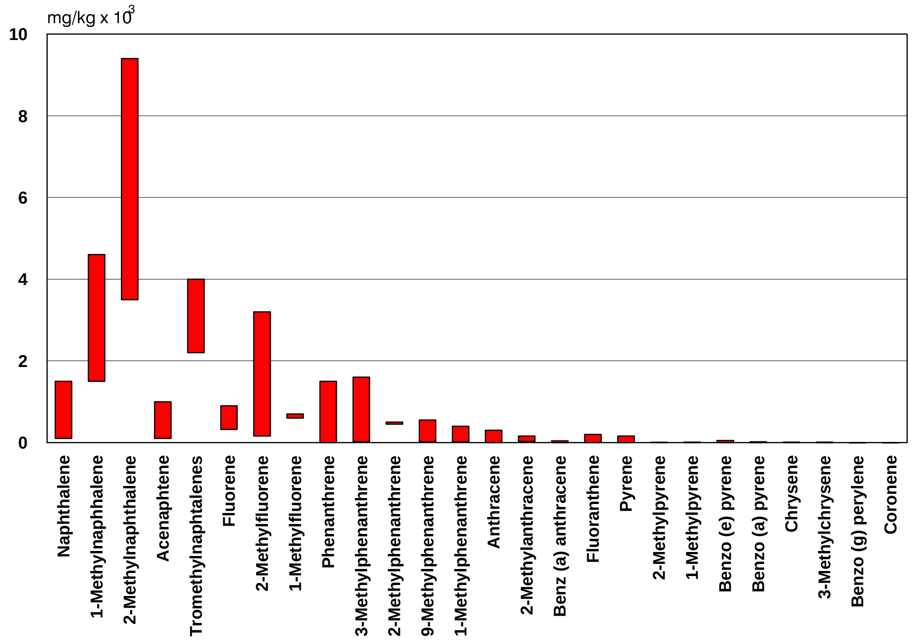
The table covers different qualities of diesel fuel encompassing high/low aromatic levels, high/low sulphur etc.

Table 17 PAH content of diesel fuels

Compound	**PAH Content (mg/kg)**	**Compound**	**PAH Content (mg/kg)**
Naphthalene	100-2056	Anthracene	1-300
1-methylnaphthalene	1500-4600	2-methylanthracene	28-160
2-methylnaphthalene	3500-9400	Benz(a)anthracene	1-40
Acenaphthene	100-1000	Fluoranthene	0.5-200
Trimethylnaphthalenes	2200-4000	Pyrene	1-160
Fluorene	320-900	2-methylpyrene	0.1-9
2-methylfluorene	160-2300	1-methylpyrene	1-12
1-methylfluorene	600-700	Benzo(e)pyrene	0.3-50
Phenanthrene	1-1500	Benzo(a)pyrene	0.2-20
3-methylphenanthrene	24-1600	Chrysene	<10
2-methylphenanthrene	450-500	3-methylchrysene	<10
9-methylphenanthrene	17-550	Benzo(g)perylene	0.3-0.4
1-methylphenanthrene	19-400	Coronene	<1

Figure 20 depicts the values given in **Table 17** on a linear scale. The figure indicates not only the wide spread of values and the variation in the levels for individual PAH but also incorporates the variability arising from the use of different analytical techniques.

Figure 20 PAH levels in commercial diesel fuels (Linear Scale)



From their own investigation, Westerholm and Egebäck (1994), concluded that an important parameter was fuel PAH content; i.e. lowering the PAH content gave a reduction in exhaust emissions of PAH. Furthermore, particulate associated nitro-pyrene emissions were emitted in the range of 0.1-0.3 µg/km and were, in their opinion, fuel dependent.

Bertoli et al (1992) examined the effect of cetane number, sulphur and aromatic structure (influenced by hydrotreating) in a DI light duty diesel engine. They found that hydrotreated diesel fuel gave the lowest amount of PAH in the exhaust. The PAH emission was significantly higher from fuels with a di-aromatic content between 7-11% m/m and a tri-aromatic content between 1-3% m/m, compared to fuels with a lower di/tri - content (virtually zero).

Opris et al (1993) also looked at the effect of different sulphur concentrations in fuel on a heavy duty engine operating under steady state conditions. They found that with a very low sulphur fuel (0.01% m/m) the smaller nuclei-mode particles virtually disappeared. Several significant differences in PAH emissions were found between the two fuel sulphur levels (high sulphur 0.29% m/m) with higher PAH levels usually associated with low sulphur levels. Mutagenic activity, measured on solvent extracts from both particulates and the semi-volatile fraction, generally decreased with increasing fuel sulphur concentration.

Rantanen et al (1993) presented work performed on four heavy duty engines (ECE R49 cycle), looking especially at the effects of distillation, sulphur, aromatics, triaromatics and cetane number. They concluded that particulate SOF emission increased with increasing fuel 95% distillation point and particulate PAH emission increased with increasing triaromatic content. The research included four diesel fuels, Rapeseed Methyl Ester (RME) and a RME blend. The four diesel fuels were: (a) typical commercial Finnish summer grade, (b) low sulphur winter grade and (c) two different distillation ranges of almost sulphur free “reformulated” fuel .

They reported that particulate mutagenicity (solvent extracted) increased both with increasing particulate PAH emissions and with increasing fuel triaromatic content, although from the matrix investigated it is possible that there was not sufficient decorrelation of the fuel properties to identify one property. For further information on fuel matrix design, see **Section 3.10**.

González (1993) also concluded that PAH emissions were influenced by fuel 2+, 3+ aromatics. Arai (1992) looked particularly on the effect of cetane number and sulphur content and showed that SOF was reduced by a catalyst, but the ratio between fuel- and lubricant derived contents in the total SOF did not change. Total PAH was effectively reduced by the catalyst. The reduction was significant for some PAH (fluoranthene, pyrene and chrysene) but other PAH emissions were not significantly changed. For a detailed explanation on aftertreatment devices see **Section 3.8**.

Fujiwara et al (1993) published a report in which they investigated the influence of n-paraffins in diesel fuels on particulate SOF as a result of combustion in an IDI diesel engine. They found that when the fuel was introduced into the combustion chamber and heated due to the compression temperature it subsequently decomposed into low boiling point hydrocarbons. Benzene was formed as a result of dehydrogenation and polycondensation. Alkyl radicals can attach to the benzene and the process progresses to form alkyl benzene and multiple ring components until the final PAH are formed. PAH are precursors for particulates and supersaturated PAH may form the nucleus of the droplets that are the precursors of the particulate. The particulate grows from this, and the part of the gases where carbonization is incomplete is emitted as SOF.

3.7.4. Lubricant Effects

Manni et al (1995) looked at the effect of physical characteristics of lubricating oils on emissions, fuel economy and oil consumption in a light duty diesel engine. Five oils with different characteristics were used - Mineral oil SAE 40, 20 and 10W-40, Synthetic SAE 20 and Part Synthetic SAE 40. They found that the "10W-40" grade was the only oil tested which gave a significant variation in total particulate emissions compared to "SAE 40". It also gave the lowest contribution to total PAH. Low viscosity oils seemed to give a lower lubricant contribution to the SOF compared to SAE 40; but resulted in a higher fuel contribution to SOF.

Schramm et al have shown that even if new lubricating oil contains an insignificant amount of PAH compounds, the lubricant may still act as a potential source of PAH emissions from diesel engines. The PAH concentration in a lubricant builds up during engine operation because PAH from both the unburnt fuel and its combustion products enter the oil. The PAH concentration is claimed to stabilize at a certain level, which is dependent on the engine type.

Experiments on a six cylinder, 5.393 L direct injection diesel engine showed that PAH is transported from the crankcase lubricant to the exhaust gas in significant concentrations. The mechanism of this transportation is not simply a matter of lubricant consumption, since the consumption measured on the engine could not account for much of the total PAH found in the exhaust. In some way the PAH (in this case pyrene) was released from the lubricant. Suggested mechanisms are a release from the cylinder wall oil film to the combustion chamber, or a release from the crankcase lubricant to the crankcase gases, followed by transportation to the combustion chamber past the piston rings.

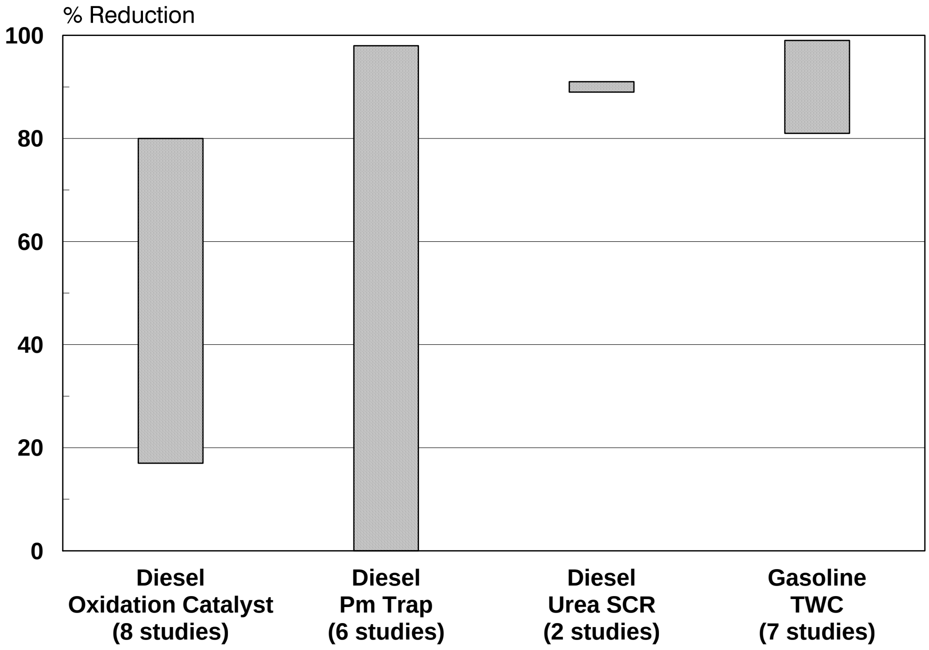
3.8. EFFECT OF AFTERTREATMENT ON PAH EMISSIONS

3.8.1. Introduction

Although there is a relatively small amount of published work which considers the effects of exhaust aftertreatment on emissions of PAH, the papers which have been reviewed cover all the major categories of aftertreatment systems. Most of this work has been published since 1990, and is concerned with diesel engines, and the performance of oxidation catalysts fitted to both HD and LD engines is well described. Several different types of diesel particulate traps have also been evaluated, and in addition the performance of a diesel lean de-NOx system (selective catalytic reduction using urea as reductant) fitted to a small diesel has been reported. Less work has been published regarding gasoline engine aftertreatment effects on PAH emissions, but there is sufficient information available to give a clear picture of the performance of three-way-catalysts (TWCs).

Whilst there are limitations to the scope of published literature, it is clear that aftertreatment systems can substantially decrease PAH emissions. These trends hold true for all targeted PAH species with only a few exceptions. **Figure 21** illustrates the range of results reported for the major classes of aftertreatment system covered in the papers reviewed in this survey.

Figure 21 Summary of exhaust after-treatment effects on particulate associated PAH



PAH exhaust emissions are collected in two ways; PAH condensed onto the particulate matter and vapour-phase PAH which are typically collected using foam plugs or adsorbent resins after the filter papers. All of the reviewed work considers particulate-associated PAH, but only about half also consider vapour phase PAH. The number of PAH compounds identified is variable. However, in most work attention is targeted on a small number (typically around five) of the most abundant compounds or those that are considered by the researchers concerned to pose the highest potential health risks. Many studies also include measurement of some nitrated PAH compounds, and mutagenicity evaluations using the Ames test techniques are also reported.

Where fuel effects are mentioned, they are usually concerned with effects on overall emissions performance and durability, with sulphur content the most studied variable. However, there are a few studies which specifically consider fuel effects on the PAH reduction performance of aftertreatment.

3.8.2. Gasoline catalysts

Three-way-catalysts (TWCs) are now universally employed in new gasoline vehicles that have to meet the strict emissions requirements of the US and Europe. Provided that the air/fuel ratio is maintained close to stoichiometric they provide very effective control of HC, CO, and NOx emissions.

It is clear from all studies that vehicles with TWCs have substantially lower particulate-associated PAH emissions than non-catalyst vehicles. Since non-catalyst vehicles are typically of generally different and older design and may have been tested using leaded fuel, this effect cannot always be attributed to the catalyst alone. Nevertheless, it is clear that the catalyst plays a major part in controlling PAH emissions. Similar conclusions have also been drawn from work in the 1980's with "lean burn" vehicles using oxidation catalysts. Since most of the studies considered only particulate-associated PAH it is difficult to draw firm conclusions regarding total PAH emissions, and opinions regarding the quantity and importance of the vapour phase PAH are divided. However, in the cases reported the catalyst efficiency is maintained at similar high levels for vapour phase PAH, although further work would be required to confirm this in the latest generation vehicles.

In an investigation of sources of "fine" organic aerosols, Rogge et al (1993) compared PAH emissions from six non-catalyst gasoline cars with seven catalyst cars. The vehicles were taken from the "in use" fleet in the Los Angeles area, and represented a wide range of vehicle ages (1970 to 1983) and accumulated mileages. The sampling technique used in this study selected only particulate matter of less than 2 micron size, and thus the findings are relevant only to that part of the PAH emissions which are associated with the smaller particulate. More than thirty individual PAH and alkyl-PAH compounds were quantified. The authors found that "a more than 25-fold higher total PAH emission rate was observed for autos without catalytic converters than for autos equipped with catalytic exhaust emission control devices". Vapour phase PAH emissions were not considered in this study.

In 1989 Volkswagen AG reported the unregulated emissions results from work carried out over the previous eight years. In this comprehensive study, the PAH emissions of four non-catalyst and seven TWC equipped cars were compared using a large amount of data obtained from multiple runs using three different drive cycles. Eleven individual PAH compounds were measured, but only particulate-associated PAH considered. The authors found that all PAH components of the gasoline engine vehicles with TWCs were at least one order of magnitude smaller than those without (**Table 18**). Furthermore, the test procedures and different engine types had no definite influence on the PAH emissions.

Table 18 PAH emissions from catalyst and non-catalyst equipped gasoline engine vehicles

Component	Gasoline engines without catalyst µg/mile	Gasoline engines with catalyst µg/mile	Decrease due to catalyst %
Fluoranthene	69.7	4.4	94
Pyrene	69.2	4.7	93
Benz(a)anthracene	8.3	0.3	96
Chrysene	13.5	0.6	96
Benzo(b/k)fluoranthene	10.4	0.8	92
Benzo(e)pyrene	8.3	0.4	95
Benzo(a)pyrene	6.3	0.4	94
Perylene	1.5	0.1	93
Indeno(1,2,3-cd)pyrene	3.8	0.4	89
Benzo(ghi)perylene	9.7	0.6	94
Total	**196.0**	**12.5**	**94**

Westerholm et al (1992) compared the emissions performance of more recent gasoline vehicles, including carburettor non-catalyst, TWC, and turbocharged/TWC. In all, five vehicles were tested, all made by Volvo and using engines from the same design family. Testing was carried out at both steady state and under accelerating/decelerating conditions, designed to be representative of the FTP-75 drive cycle. More than one commercial quality 95 RON unleaded fuel was used, but no fuel effects are reported in this study. Particulate was sampled from the dilute exhaust using standard filter paper techniques, and twenty-three individual PAH compounds were recorded. The results show that total particulate-associated PAH emissions from the catalyst equipped vehicles are much lower (in the order of ten times) than from the non-catalyst vehicle, and that all measured individual PAH compounds are substantially decreased. 1-nitropyrene was also measured, and showed similar trends. Mutagenicity of the particulate extracts was also much lower for the catalyst equipped vehicles, although these results were not always found to be statistically significant. Once again, vapour phase PAH emissions were not measured.

Work carried out by Cooper and Shore (1989) using a TWC vehicle and a lean burn vehicle using an oxidation catalyst confirmed these high reductions in particulate-associated PAH, nitrated-PAH, and mutagenicity, with catalyst efficiencies for all targeted compounds in the 80-99% range. These authors claim that "the bulk of the biologically important PAHs and their derivatives are predominantly present in the particulate phase of exhaust when tested using US EPA procedures", and thus do not carry out vapour-phase sampling.

Conversely, work carried out by Rijkeboer (1986) for TNO, finds that "most of the PAH and mutagenicity is present in the gaseous phase, (with) the particulate phase contributing typically some 5-20%". This study is one of the few which measured vapour phase as well as particulate-associated PAH, and confirmed the effectiveness of both TWC and oxidation catalyst systems for decreasing total PAH and mutagenic emissions. Indeed, the authors found that at most test conditions the total PAH emissions from catalyst equipped vehicles were so low that they hardly rose above the background level.

Work by Siegl (1992) was focussed on the development of analytical techniques for the measurement of vapour phase PAH, and included measurements on a 1987 model car both with and without a catalyst. Once again the catalyst was found to be very effective with decreases in vapour phase PAH of at least 90% for the targeted compounds. In this case particulate material was removed by a filter and not measured.

3.8.3. Diesel oxidation catalysts

Background

Oxidation catalysts have been in use in some European diesel passenger cars for over six years, and are becoming increasingly common as emissions limits are tightened. They have also found limited application for some specialised HD applications such as city buses and mining equipment. Oxidation catalysts decrease emissions of HC and CO, and can significantly decrease total particulate emissions by oxidising the adsorbed hydrocarbons. Exhaust odour may also be lessened by decreasing strong smelling species such as aldehydes. Some of the latest designs also have a limited de-NOx capability (see **Section 3.8.6**).

The parameters influencing the overall performance of oxidation catalysts are complex, and are described by Zelenka et al (1990) and Herzog (1995). An important factor is the formation of sulphates from fuel sulphur. These appear as particulate matter which is collected on the filter papers in the legislated emissions tests. Sulphate formation increases with exhaust gas temperature, and even with low sulphur fuels (e.g. 0.05%m/m) can result in a net increase in particulate emissions when engines/vehicles are operated on high load test cycles such as the European ECE-R49 HD emissions test. However, the sulphur tolerance of catalysts is improving, and it is possible that oxidation catalysts may become feasible for HD engines running under high load conditions.

Effects of Oxidation Catalysts on PAH Emissions

All the reviewed work finds that oxidation catalysts decrease particulate-bound PAH emissions, although the removal efficiency varies considerably. Although vapour phase PAH is not measured in all studies, where data are available oxidation catalysts are found to decrease PAH in this phase too, in several instances with greater efficiency than for the particulate-associated phase.

The results of recent work by Hammerle et al (1995) are representative of the performance of modern oxidation catalysts in LD applications. Two different oxidation catalysts were tested on the same IDI passenger car, using both the future European MVEG and current US FTP-75 drive cycles. A light duty truck with a DI engine was also tested with a single oxidation catalyst. Only particulate-associated PAH was measured, and results are presented for four selected PAH compounds (**Table 19**).

Table 19 Particulate associated PAH emissions from an IDI passenger car and a DI light duty truck

Catalyst	Fuel S%	Fluoranthene	Pyrene	BaP	BeP	Total	% Reduction of Total PAH with catalyst
IDI Passenger Car - MVEG Cycle Emissions (µg/km)							
None	0	3.01	3.65	0.22	0.47	7.35	**-**
Cat A	0.05	1.18	1.18	0.17	0.51	3.04	**59**
Cat B	0	1.1	1.13	0.04	0.06	2.33	**68**
IDI Passenger Car - FTP Cycle Emissions (µg/km)							
Catalyst	**Fuel S%**	**Fluoranthene**	**Pyrene**	**BaP**	**BeP**	**Total**	**% Reduction of Total PAH with catalyst**
None	0	3.46	3.75	0.28	0.45	7.94	**-**
Cat A	0.05	1.93	2.22	0.22	0.65	5.02	**37**
Cat B	0	2.29	2.46	0.27	0.27	5.29	**33**
DI Light Duty Truck - MVEG Cycle Emissions (µg/km)							
Catalyst	**Fuel S%**	**Fluoranthene**	**Pyrene**	**BaP**	**BeP**	**Total**	**% Reduction of Total PAH with catalyst**
None	0.05	6.86	4.93	0.07	0.24	12.1	**-**
Cat C	0.05	5.54	4.26	0.01	0.24	10.05	**17**
DI Light Duty Truck - FTP Cycle Emissions (µg/km)							
Catalyst	**Fuel S%**	**Fluoranthene**	**Pyrene**	**BaP**	**BeP**	**Total**	**% Reduction of Total PAH with catalyst**
None	0.05	4.83	4.17	0.23	0.48	9.71	**-**
Cat C	0.05	3.18	2.26	0.03	0.22	5.69	**41**

- BaP = Benzo(a)Pyrene, B(e)P = Benzo(e)Pyrene

Although in all cases the total particulate-associated PAH is decreased, there is a wide variation in efficiency (17% to 68%). Although it is clear that both catalyst/vehicle and drive cycle are important, no clear pattern can be identified, and one vehicle shows the biggest decreases over the MVEG cycle, whilst the other is more efficient over the FTP cycle. Consideration of the four individual compounds measured in this study shows that in most cases all are decreased by the catalysts, with those with the highest concentrations (fluoranthene, pyrene) showing the most consistent decreases. Results for BaP and BeP are more variable, and the differences seen are probably not statistically significant. Two fuels were used (a practically zero sulphur Swedish Class 1 and the same fuel doped to 0.05%m/m sulphur), but due to the experimental design fuel effects cannot be separated from hardware effects.

Two other LD vehicle studies report consistent results for particulate-associated PAH. Zelenka et al (1990) tested several LD vehicles over the US FTP-75 drive cycle including IDI and DI engine types. Ten PAH compounds were measured, and the catalysts decreased the total targeted PAH emissions by around 30-50%. When only the suspected carcinogenic compounds were considered (this eliminated some of the lighter compounds occurring at higher concentrations such as fluoranthene and pyrene) catalyst efficiency was reduced to 20-30%. Berg and Holmes (1992) reported work in a Mercedes 250D car over the FTP-75 cycle and found that fitting an oxidation catalyst decreased particulate-associated PAH emissions by about 30%. Nitrated PAHs were decreased by about 40%, and mutagenicity (Ames test) was decreased by 40 to 90%.

In part of a study by Mitchell et al (1994), two different sizes of otherwise similar oxidation catalysts were tested on a Navistar 7.6 litre DI medium-duty engine using the US HD transient test procedure. In this case particulate and vapour phase PAH samples were combined before analysis. Average overall PAH decreases across the catalysts were 76% and 62% for the larger (8.5 litre) and smaller (5 litre) catalysts respectively. However, total nitrated PAH emissions were found to be increased by the catalyst. Four low sulphur (< 0.05%m/m) fuels were used in this work, with varying total, 2-ring and 3+ring aromatics contents. Whilst fuel effects on catalyst PAH conversion were small, there appeared to be considerable differences between fuels for the increases seen in nitrated PAH. However, the authors conclude that further work would be necessary to confirm these results.

Several papers differentiate between vapour phase and particle-associated PAH, all from work with HD diesel engines. Michigan Technological University has been active in this field, and results from work published by McClure et al (1992) are representative. In this study an oxidation catalyst was tested on a Caterpillar medium duty 7 litre IDI mining equipment engine. A special light duty test cycle was chosen, reflecting the tendency for hydrocarbon emissions to be higher at low loads. The catalyst (Englehard PTX 10 DVC Ultra-10) is of a relatively low activity type, and was chosen for its resistance to sulphate conversion. Seven PAH compounds were reported. The overall PAH emissions from the combined particulate-associated and vapour phase samples were found to be decreased by about 45% by the oxidation catalyst. This decrease was composed of a 40% decrease in particulate-associated PAH, and a 60% decrease in vapour phase PAH. Although nearly all individual PAH compounds were decreased in both phases, there was evidence of some increases in two of the heavier compounds (BaP and BkF), which are found predominantly in the particulate associated phase. This work also gives some data on fuel effects on catalyst performance. Two fuels, both of approx. 0.04% m/m sulphur, but of differing total aromatics content (11% versus 20%) were used, but no significant effects on catalyst performance were observed.

In work sponsored by the Danish Ministry of Transport, Hansen et al (1994) also found that oxidation catalysts preferentially reduce vapour phase PAH. A low sulphate formation oxidation catalyst made by Svenska Emissionsteknik was tested on a six cylinder HD DI truck/bus engine of Euro 1 emissions performance. Testing was conducted over a 5 mode version of the ECE-R49 steady-state emissions test and Danish "Ultra Light" Diesel fuel was used. Very high PAH reductions were observed across the catalyst - 80% and 90% reductions for particulate-associated and vapour phase respectively. However, in this study the more abundant lighter aromatics (e.g. naphthalene, phenanthrene) were classified as PAH, and were efficiently removed by the catalyst, thus exaggerating the total PAH reductions.

Work carried out at Michigan Technological University by Gratz, Pataky, et al was first published in 1992, and subsequently reported in more detail in a 1994 SAE paper. An oxidation catalyst using a metallic substrate coated with platinum (supplied by Degussa) was tested on a prototype 1991 Cummins HD DI diesel engine at three steady-state test conditions using a 0.01% m/m sulphur fuel. Contrary to this group's findings in the Caterpillar IDI engine, McClure (1992), in this case the catalyst decreased particulate-associated PAH more than vapour phase. There are many differences between these studies, including the catalysts, engines, fuels, and test procedures. However it should be noted that the engines are markedly different, the Caterpillar being a much older design with substantially higher emissions levels. In general, nitrated PAH and mutagenicity (Ames test) were also decreased by the catalyst, although these results were variable. Mutagenicity effects were engine load dependent, and significant decreases were generally only seen at the lower load and temperature engine operating conditions.

3.8.4. Diesel particulate traps

Background

Trapping particulate matter by passing exhaust through a filtering medium (typically a porous ceramic monolith) does not present any major technical difficulties, and high trapping efficiencies are typically obtained. However, regeneration of the trap to remove the trapped particulate matter is more problematic. In a non-catalysed trap the ignition temperature of the trapped particulate is above the normal exhaust temperature, and the trap must be periodically regenerated using fuel burners or electrical heaters to raise the temperature above the ignition point. During regeneration the trap is normally taken out of service, although in some designs this can be accomplished whilst exhaust gases are still passing through the trap. An alternative approach is to lower the ignition temperature of the particulate by use of a catalyst, and thus achieve regeneration during normal operation on the vehicle. This may be achieved using catalyst coatings on the trap itself, or via the use of catalytic fuel additives.

Particulate traps have found applications in specialised situations such as fork-lift truck operations and mining machinery, where duty cycles are predictable and trap regeneration can be controlled. However, widespread application is still limited by the difficulties of achieving reliable regeneration during typical road driving patterns and acceptable long term durability.

Effect on PAH Emissions, Non-Catalysed Particulate Traps

The PAH decreases reported for non-catalysed traps are highly variable and it is difficult to draw clear conclusions. Particulate-associated PAH decreases range from around zero to 80%, but in those cases where vapour phase PAH was measured there was either little change or a substantial increase.

Gratz et al (1991) and Bagley et al (1991) tested a non catalysed ceramic trap on a 1988 Cummins HD engine at two steady-state load conditions, using a commercial US No. 2 diesel fuel with 0.3% m/m sulphur. In this case regeneration was achieved using electrical heating, during which time the trap was taken out of service and exhaust gas was passed directly to atmosphere. Although the trap decreased total HC emissions, no overall decreases in PAH or nitrated PAH emissions were observed. When examined in more detail, the effects of the trap on PAH emissions were seen to be highly variable, with both increases and decreases observed. No clear pattern was evident, and results varied with engine load, individual PAH compound, and phase (particulate-associated or vapour phase). However, use of the trap seemed to decrease mutagenicity of the vapour phase fraction, but not of the particulate-associated fraction.

Further work using the same engine and test procedures, Troy (1992) included an assessment of fuel effects on trap performance. The trap used was a similar electrically regenerated non-catalysed type, but of slightly different construction. The original 0.3% m/m sulphur commercial fuel used in the first tests was compared with a fuel intended to be representative of a low sulphur commercial fuel. These fuels came from different refineries, and it can be seen from **Table 20** that they varied in many important aspects as well as sulphur.

Table 20 Key fuel properties in work by Troy

fuel property	Commercial No.2 Diesel Fuel	"low sulphur" diesel fuel
API gravity	38.4	34.5
(approx. specific gravity at 60°/60°F)	(0.833)	(0.852)
T50 °C	254	269
sulphur (% m/m)	0.32	0.01
cetane number	52.8 (1)	42.4
total aromatics	23.5	29.9

(1) measured at end of test programme

As in the earlier work, it can be seen from **Table 21** that the trap did not produce decreases in overall PAH emissions; in fact overall PAH emissions were increased. However, in this work a clear pattern is evident, with the decreases in particulate-associated PAH more than offset by increases in vapour phase PAH. Seven individual PAH compounds were reported (fluoranthene, pyrene, chrysene, BbF, BkF, BaP), and with few exceptions the trends for individual compounds follow the overall pattern for both fuels and at both engine loads, leading the authors to conclude that the operation of the trap was not affected by fuel properties. It is however noticeable that with the low sulphur fuel the trap activity is higher (for both *decreases* in particulate-associated PAH and *increases* in vapour phase PAH) than with the higher sulphur fuel.

Table 21 Changes in PAH emissions with a non-catalysed Particulate Trap

Fuel type	Particulate-associated PAH	Vapour phase PAH	Overall PAH
commercial No.2 (0.32 % S)	- 25 %	+ 15 %	+ 2 %
“low sulphur” (0.01 % S)	- 65 %	+ 140 %	+ 18 %

The work of Hammerle et al (1995) included an electrically heated non-catalysed trap, fitted to a 2.5 litre DI light duty truck. This trap was of the sintered metallic type, and employed multiple electrical elements that allowed partial regenerations to proceed throughout normal operation, to avoid bypassing exhaust during regeneration. When tested over the FTP-75 and MVEG drive cycles using typical 0.05% m/m sulphur European fuel, particulate-associated PAH reductions across the trap were approximately 80% and 70% respectively. However, in this work vapour phase PAH was not measured, so the effect on overall PAH emissions cannot be determined.

Effect on PAH Emissions, Catalysed Particulate Traps

From the limited evidence reviewed, it appears that catalysed traps may have a higher potential for decreasing PAH emissions than non-catalysed traps, but further work would be needed to confirm this.

Bagley et al (1991) tested the performance of a catalysed trap, using the same Caterpillar 3304 HD IDI mining engine that was used for the oxidation catalyst work discussed earlier: McClure (1992). The trap, which was supplied by Englehard, was based on a Corning EX-66 ceramic substrate, to which was applied a precious metal coating. Due to the catalyst, regeneration of the trap took place automatically during the higher load parts of the test cycles, and no additional regeneration was needed. Testing was carried out over a transient cycle, and also at steady state conditions, using a single low sulphur (0.04% m/m) fuel. In contrast to the non-catalysed traps discussed earlier, this catalysed trap was very effective in decreasing both particulate-bound and vapour phase PAH, giving decreases of 98% and 90% respectively over the transient test cycle (Steady state results gave similar particulate-bound PAH decreases, but vapour phase PAH was not measured). Mutagenicity of extracts collected from both phases was also decreased by 75% to 80%.

More recent work at Michigan Technological University by Harvey et al (1994) examines the effects of a ceramic trap used in conjunction with varying treats of a copper fuel additive. A 1988 Cummins HD engine was operated on a low sulphur (0.02% m/m) fuel at two steady-state test conditions. Consistent with earlier work, when tested without the copper additive the effect of the trap was variable, with increases in some PAH compounds evident at some engine conditions, due primarily to increases in the vapour-phase component. However, when used together with the copper additive the trap efficiency was consistently high, with considerable reductions in total PAH emissions (vapour-phase + particulate-associated) observed for every targeted PAH compound at both engine operating conditions. The effects on nitrated-PAH and mutagenicity did not show straightforward trends.

The work of Hammerle et al (1995) included cordierite traps using fuel additives to catalyse regeneration. As in the oxidation catalyst work, 2.5 litre DI light duty trucks were used with a 0.05% m/m sulphur fuel, tested over the MVEG and FTP-75 drive cycles. Fuel additives were blended into the fuels; iron at 67 ppm (as ferrocene), and potassium at 50 ppm (as alkyl salicylate), and the results indicated that trap regenerations were occurring at regular intervals during testing. Both fuel additive/trap systems were effective in decreasing particulate-associated PAH emissions, with 80% to 85% decreases reported. Vapour phase PAH was not measured.

These findings are generally consistent with earlier work reported in 1989 by Smith and Paskind using two European diesel passenger cars. Two prototype catalysed traps were tested, one using an iron fuel additive, and the other a silver alloy coated monolithic "trap oxidiser". A wide range of semi-volatile organic compounds were collected from both the particulate and the vapour phase of the exhaust. Although the results were too variable to draw quantified conclusions, the authors found that particulate-associated semi-volatile material was definitely decreased by both trap systems, but in this case it was not possible to detect significant effects on the vapour phase material.

3.8.5. Lean De-NOx systems

In order to meet expected legislation beyond the year 2000, it is probable that diesel engines will require an effective de-NOx aftertreatment system. The reduction of NOx under the conditions of excess oxygen which are present in the exhaust of the diesel engine is difficult without the addition of a suitable reductant. Some current diesel oxidation catalysts achieve modest NOx reductions (e.g. 10-15%) by employing the naturally occurring unburned hydrocarbons as the reductant. Higher conversion efficiencies are possible if additional fuel is injected in front of the catalyst, but the technology is still at an early stage and there is an inevitable fuel economy penalty. Advances in lean burn direct injection spark ignition engines provide further incentives for the development of effective lean de-NOx technology, although in this case different solutions (e.g. NOx storage catalysts) may prove attractive.

At present only selective catalytic reduction "SCR" appears capable of high NOx reduction efficiencies. Although used for many years in stationary applications, the development of a practical SCR system for automotive use presents many difficulties, and is still at an early stage. However, two evaluations of a prototype automotive SCR lean de-NOx system (using urea as the reductant) have been published: Hammerle (1995); Lüders (1995). In both cases the vehicle was a light-duty truck, fitted with a 2.5 litre DI engine, and using a 0.05% m/m sulphur fuel.

One report, Lüders (1995), describes the catalyst system, which uses two stages - a lean de-NOx catalyst with urea injection upstream, followed by an oxidation catalyst to ensure that any ammonia "slippage" from the de-NOx catalyst is eliminated. Emissions results include 14 selected particulate-associated PAH compounds measured over the FTP-75 drive cycle, and show that the system decreases total particulate-associated PAH by 90%. The other report, Hammerle (1995) gives further emissions results for a similar system, and demonstrates that a comparable 90% to 95% decrease is achieved over both the MVEG and FTP-75 tests. This report includes data with just the oxidation catalyst part of the system, which shows that most of the PAH decreases are due to the de-NOx catalyst. However, total PAH removal efficiencies cannot be determined since vapour phase PAH was not measured in either of these studies.

3.9. THE INFLUENCE OF ALTERNATIVE FUELS ON PAH EMISSIONS

3.9.1. Introduction

There are several papers in the literature that look at PAH levels in the exhaust of vehicles powered by alternative fuels. These fuels include: liquid petroleum gas (LPG), compressed natural gas (CNG), methane, propane, methanol, alcohol-Diesel blends, alcohol-gasoline blends, rapeseed oil, rapeseed methyl ester (RME) and bioethanol. In all the literature reviewed, the use of alternative fuels generally appears to result in a reduction of the PAH measured.

3.9.2. Alcohols

Investigations into the effect of alcohols and alcohol blends have been carried out since the early 1980's.

Thring (1983) stated that PAH emissions are reduced when operating on methanol rather than gasoline and Ecklunk (1982) noted that in methanol-gasoline blends, the effect of PAH emission reduction tends to be small and inconsistent, often masked by vehicle-to-vehicle and test-to test variability. He also believed that there is some evidence that the leaning effect of the methanol-gasoline blend is the principle mechanism for any reduction in PAH output. Larger effects have been reported for neat methanol fuels, including reductions for up to 90 per cent in PAH emissions. Conti (1993) compared a 15% methanol blend with gasoline and reported lower PAH emissions for the blend.

Early work by Weidmann (1984) also identified a substantial reduction of PAH when using alcohol/diesel blends compared to diesel fuel. A methanol-diesel blend produced 50 per cent less, and an ethanol-diesel blend reduced PAH by almost 75 per cent. However, this conclusion was based entirely on measurements of particle bound BaP using TLC-fluorescence. Tritthart (1990), used a similar analytical technique and claimed that there was very little PAH on particles derived from a methanol fuelled engine.

Later work by Egebäck (1994) looked at bioethanol (used in bus engines) and measured a reduction of about 80% in the PAH emissions in both particulate phase and semi-volatile phase. However, despite these reductions, biological activity similar to Swedish Class I diesel was also monitored. This is in contrast to earlier work, Ecklunk (1982); Weidmann (1984), who investigated blended alcohol-diesel fuels and found that these fuels produce noticeably smaller quantities of PAH than unblended diesel fuel, with the reduction being especially obvious in the biologically active emissions.

3.9.3. Rapeseed Oil, Rapeseed Methyl Ester

Several authors have investigated the effect of both rapeseed oil and its methyl ester (RME) on exhaust PAH emissions. Both blends and the neat fuel have been examined.

Results from testing of rapeseed oil are not conclusive. Richter (1996) reported a reduction of PAH emissions with an IDI engine but an increase with a DI engine. Krahl (1996) tested rapeseed oil (against conventional diesel fuel) and saw an increase in PAH over the ECE-15 light duty test, but a reduction over the ECE-R49 heavy duty test. Krahl believed the increase in PAH to be promoted by transient operations.

A review on the effects of RME on diesel pollution has been prepared by Staat (1992) who claims that its use reduces PAH emissions. Earlier, Tritthart (1990) had reported that the differences in PAH emissions between diesel and RME were negligible but this was believed to be due to the variability of the analytical technique used (TLC-fluorescence). Alfuso (1993) monitored total PAH emissions (using a cold trap) from neat RME but restricted discussions to five individual compounds. Both light and heavy duty applications were tested and it was concluded that a PAH reduction was only observed under transient heavy duty operation.

Grägg (1994) investigated blends of RME and diesel and although he reported a reduction in total PAH (compared to diesel) he also reported that the particle bound biological activity was seen to be higher. Particle bound PAH reductions increased as the proportion of RME in the blend increased. A similar trend was seen in the volatile phase, although the differences were smaller. This work also looked at nitro-PAH but these were found to be below the limit of detection.

In later work, Konig (1995) stated that a move to RME would reduce PAH emissions by approximately 70%, although no analysis or sampling details are given and the PAH investigated are not defined. Krahl (1996) also investigated RME and claimed a significant reduction in PAH when compared to diesel. Montagne (1996) tested 5% and 20% blends of RME with diesel fuel and observed a successive reduction in PAH over regulated cycles, both with and without the use of a catalyst.

3.9.4. LPG, CNG

Many papers have looked at LPG and CNG, and have shown that they are both better than conventional fuels as far as PAH emissions are concerned, with LPG being superior to CNG. Menrad (1985) claimed that a vehicle optimised for LPG gave significantly lower PAH emissions than a comparable engine running on gasoline, although no actual data are presented.

Gambino (1993) investigated PAH emissions from a HD engine running on CNG over the ECE-R49 cycle. He concluded that total PAH emissions were about three orders of magnitude lower than for diesel. Unich (1993) reported a similar programme but based his conclusions on data presented by Gambino.

Conti (1993) also looked at gasoline engines optimised for CNG and compared PAH emissions with a 15% methanol blend and with gasoline. CNG PAH levels were reported to be at background levels. Fuels were tested both with and without a catalyst and although no absolute data are given, it appears that engine-out PAH levels from CNG are inherently lower than for gasoline, which show a marked catalyst effect.

Extensive work was carried out by TNO (1993) comparing CNG and LPG with gasoline and diesel. Twenty two PAH were measured (both particle bound and vapour phase) in a fleet of vehicles dedicated to each fuel. Nitro-PAH were found to be below the levels of detection. TNO concluded that (averaged over the respective fleets), CNG gave the lowest PAH emission, followed by LPG and gasoline, with diesel PAH emissions being an order of magnitude higher. This work was also published by Rijkeboer (1994) as an SAE paper.

Recent work by Hupperich (1996) claims a 75% reduction in PAH relative to gasoline and a 50% reduction from HD engines operating over the ECE-R49 cycle. However, no sampling or analysis details are given.

Mansurov (1985) looked at the soot flames of methane and propane. No comparison with conventional or other alternative fuels was made, but it was found that methane soot extracts comprise about 30 per cent PAH, and propane soot extracts comprise about 50 per cent PAH.

3.10. THE LIMITATIONS OF EXPERIMENTAL DESIGN, INCLUDING SAMPLING AND ANALYTICAL TECHNIQUES

3.10.1. Introduction

A general problem when studying the effects of changes in a fuel property on exhaust emissions is that of blending a meaningful range of test fuels (a 'fuel matrix'). In a well designed matrix the property under examination must vary sufficiently to have a measurable effect on the emissions, whilst other potentially influential fuel properties are kept essentially constant and decorrelated from the characteristic under investigation. This is particularly difficult when studying the influence of fuel PAH content on exhaust PAH levels as:

(a) PAH form only a small part of the fuel;

(b) The experimental scatter in measuring exhaust PAH levels is large.

Most of the work reviewed herein aims to assess the effect on levels of exhaust PAH due to changes in fuel PAH content, and thus requires a set of test fuels where properties such as cetane number, heavy-end distillation and density do not vary appreciably (or, if they do, where the experimental design allows one to estimate the impact of the changes in these parameters).

These requirements have been met in the most informative experiments reported in the public domain: the least informative simply ignore such possible “side effects”, although such “side effects” can dominate those of changing the fuel PAH level. Possible options in experimental design aimed at eliminating (or at least in reducing) the influence in changes in fuel properties other than that of PAH content are discussed below. In addition, the weaknesses of existing methodology, sampling and analytical techniques, described in **Section 3.4**, are highlighted again.

There is an almost universal assumption in the literature that any investigation of the fuel parameters that influence *regulated* emissions should concentrate on changes in *regulated* fuel properties (i.e. “bulk” properties such as density, cetane number or RON and MON, distillation properties, etc.). However, studies focusing on fuel parameters that influence currently *unregulated* emissions like PAH, generally concentrate on *unregulated* fuel parameters, e.g. PAH level. These assumptions, particularly with regard to research in the latter area, are open to question:

1. Do the “bulk” fuel properties, believed to influence the preponderance of the exhaust (PM, HC, CO, NOx), play only a minor role in determining the emissions of PAH?

2. Can relatively small changes in fuel PAH concentrations (say, 0 - 3% in diesel fuel; 0 - 0.1% m/m in gasoline) dominate exhaust PAH levels?

It is also worth pointing out that there is currently no clear understanding of the relationships between the total amount of exhaust PAH, the partitioning of those PAH between the gas and particulate borne phases, the size distribution and mass of the particulates.

3.10.2. Dedicated Fuel Matrix Blending

Access to a large range of refinery blend streams, each with its own particular properties (e.g. density, cetane number, tri+ aromatics content, etc.) may allow a dedicated matrix of tests fuels to be blended. It is then possible to combine the blend streams in such a way that only the property of interest varies significantly. Alternatively, if several properties are of interest, the potential exists for blending matrices in which each property varies independently of the other(s), or at least in a highly de-correlated fashion.

The advantages of such a strategy are that the test fuels are composed of very many different hydrocarbons. They are therefore more likely to reflect the behaviour of commercial fuels, particularly in terms of their distillation curves and flame front chemistry. The results are thus considered to be the most applicable to commercially marketed fuels.

However, there are a number of practical difficulties associated with this option:

(a) Access to a wide variety of refinery streams is required.

(b) Dedicated blending facilities are necessary.

(c) The properties of each of the refinery streams must be known, requiring extensive initial analysis.

(d) The blending behaviour of the streams must be well understood - not all properties combine linearly when two components are mixed (e.g. MON).

For many research workers this approach is just not feasible.

3.10.3. Fuel Doping

An alternative approach intended to minimise changes in fuel parameters other than the PAH level is “spiking” (or doping) of a base fuel with increasing amounts of a particular PAH. This has the advantages that:

(a) It is easy and relatively cheap;

(b) Any available PAH can be added to a fuel at a range of specially chosen concentrations.

Problems with this approach include:

- The assumption that the dopant PAH combusts in a way that is representative of all PAH.

- The assumption that the addition of a few percent of a single PAH would not alter the physical properties of the heavy-end of the fuel, in the same way that the addition of a few percent of a wide range of PAH does not.

- The requirement that the dopant is used at a concentration sufficiently low for contamination (or “carry-over”) via the lubricating oil or exhaust/sampling system not to effect other tests in the experimental programme.

Currently, programmes using fuel spiking are not common. As sampling and analytical techniques improve the level of dopant required to give a detectable change in the exhaust will decline, thus reducing the extent of the latter two problems.

3.10.4. Radio-labelling

A similar, but rarely used approach, is that of isotopic labelling of fuel component PAH (e.g. the work of Rhead et al at Plymouth University, U.K., with radio-active ^{14}C). The advantages of such a technique are significant:

(a) The survival rate of fuel PAH can be unambiguously determined by measuring the fraction of the radio-labelled molecules in the exhaust. This allows the calculation of the amount of exhaust PAH from other sources and highlights the difference between the "true survival rate" and the "apparent survival rate".

(b) The amounts of PAH that must be added to the fuel to obtain a quantifiable level of radio-labelled PAH in the exhaust are so small that the bulk properties of the fuel are unaffected. This ensures that the combustion of the test fuel was representative of commercial fuel.

(c) Potentially, it is also possible to determine the extent to which exhaust PAH are the products of modified fuel PAH and/or other non-PAH components. However, in practice the amounts of ^{14}C labelled material used are so small that the abundance of the various hydrocarbons produced by partial combustion of the labelled species cannot be quantified.

(d) It is relatively easy to establish that the engine and other test equipment has not carried over ^{14}C from one experiment to the next. Contamination from the lubricating oil, exhaust and sampling system may therefore be avoided.

Unfortunately, the disadvantages of using ^{14}C labelled species are also considerable:

(a) Health and safety considerations are extensive.

(b) The material is expensive, and only a few labelled PAH are available, and these are not necessarily representative of the PAH in fuels.

Labelling with other nuclei (e.g. ^{2}H or ^{13}C, followed by GC/MS analysis) is an option that does not seem to have been used.

3.11. CONCLUSIONS

- Where the data are available (e.g. UK, Japan), current PAH concentrations in ambient air are the lowest ever measured
- total HC emissions (and likewise total PAH) are very low from modern vehicles. Furthermore, targeted PAH species form only a small fraction of the particulate borne HC, and an even smaller fraction of the vapour phase HC
- a wide range of definitions as to what constitutes a “polycyclic aromatic hydrocarbon” may be found and there is no agreed definition for PAH
- there is no standard analytical methodology and a consensus on the major PAH to be measured has still to be established
- there are insufficient data available on automotive emissions to determine to what extent the level of the PAH emissions is related to the PAH content of fuel
- there has been insufficient work on total (vapour phase + PM bound) PAH emissions
- there are two main routes of PAH into the exhaust, fuel PAH survival and combustion derived PAH
- the presence of a three-way catalyst on gasoline vehicles appears to reduce PAH emissions to levels below current detection limits
- diesel exhaust after-treatment systems show greater variation but are generally highly effective in reducing PAH
- some alternative fuels may offer a limited route to some reduction in PAH exhaust emissions.

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APPENDIX 1 - TERMS AND ABBREVIATIONS

The literature in this field contains a large number abbreviations and specialist terms, but no universally agreed definitions. The terms and abbreviations most commonly encountered in the literature are discussed below and definitions of the terms used herein are provided.

PAC	*"Polycyclic Aromatic Compounds".* Generic term covering all multi-ring species
PAH	*"Polycyclic Aromatic Hydrocarbon(s)".* Used loosely to indicate multi-ring compounds containing only carbon and hydrogen. Most authors use the term to mean tri+ aromatics, but some (including the current tripartite EPEFE programme) include di-aromatic species.
PCA	*"Polycyclic Aromatic(s)".* Often synonymous with "PAH". Sometimes used to include species containing hetero-atoms (i.e. those other than C and H).
PNA	*"Polycyclic Nuclear Aromatic(s)".* Often synonymous with "PAH". Sometimes used to include species containing hetero-atoms (i.e. those other than C and H).
NPAH	*"Nitro-Polycyclic Aromatic Hydrocarbon(s)".* PAH with 1 or more nitro- (NO_2-) groups attached to the ring.
PANH	Sometimes used to denote polyaromatic species containing nitrogen in the ring system.
PASH	Sometimes used to denote polyaromatic species containing sulphur in the ring system (e.g. dibenzothiophene (1)). Such species are most abundant in high sulphur crudes and fuels made therefrom.
PM	*"Particulate Matter".* The particulate matter (or "soot") in automotive exhaust gases is comprised of a carbon core onto which are adsorbed an organic fraction and an inorganic fraction (sulphates, nitrates etc). PM is one of the four components of automotive exhaust emissions for which legislation specifies upper limits. The legislation defines set test and sampling procedures to ensure consistency. Different countries follow different test procedures and thus specify different limits (the major blocs being the EU, the USA and Japan).
SOF	*"Soluble Organic Fraction".* The condensate on the particulate matter (PM) that can be extracted by an organic solvent such as dichloromethane (DCM). The SOF is mainly comprised of heavy hydrocarbons including surviving fuel and lubricant and the products of partial combustion.
VOF	*"Volatile Organic Fraction".* The condensate on the particulate matter (PM) that can be driven off by heating, either by thermal desorption or thermal gravimetric techniques.

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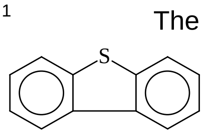
[1] The structure of dibenzothiophene:



Aromatic	The “aromatic” portion of a fuel is defined as all the molecules that contain at least one benzene ring. The most common aromatics in gasolines are toluene and the xylenes; in diesel fuel they are those mono-aromatics with side chains of between 8 and 12 carbons (in total). The aromatic content of a fuel is quoted in % m/m. or % v/v (depending on analytical technique) and includes the material in the side chains. In diesel fuel the side chain material generally accounts for about half of the aromatic fraction.
Aromaticity	The “aromaticity” of a fuel is fraction of the carbon atoms that lie in an aromatic ring. Material in side chains to aromatic rings are thus excluded when determining aromaticity (c.f. the “aromatic” portion).
Parent PAH	A term occasionally used to denote a PAH without side chains or hetero-atoms. Thus, for instance, pyrene is the parent PAH to both 2- methyl-pyrene and 1- nitro-pyrene[2].
Total PAH (or PNA,PCA)	Frequently used loosely to indicate the total of those PAH species (*commonly EPA 16, see* **Appendix 2***)* that could be individually quantified by a particular analytical method. Such a value is invariably much less (typically by a factor of 10 to 100) than the values obtained by methods that are not isomer specific (such as IP391) as there are very many PAH isomers. This is particularly important if the numerous alkyl substituted isomers are taken into account. These are more abundant than their non-alkylated parent PAH isomers, although conclusive data on this subject is lacking.
Total targeted PAH (or PNA, PCA)	A more rigorous term sometimes used in place of “total PAH”. The “targeted” PAH are those that can be quantified on an individual species by species basis and invariably form only a small fraction of the true total of PAH.
IP391	An HPLC/refractive index based Institute of Petroleum method (with statistically determined repeatability and reproducibility) used to determine the mass fraction of a diesel fuel comprised of mono-, di- and tri+ aromatics.
Tri+ aromatics	Compounds with three or more benzene rings (e.g. phenanthrene (3), fluoranthene (4)). These species may be present in the heavy-end of a diesel fuel.

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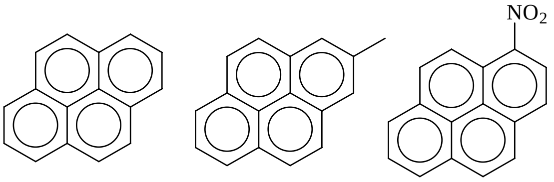
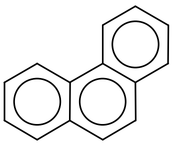
[2] The structures of pyrene, 2-methyl-pyrene and 1-nitro-pyrene respectively:



[3] The structure of phenanthrene:



Di- aromatics	Compounds with two benzene rings, almost always fused (e.g. naphthalene) but not necessarily so (e.g. fluorene (5)). Compounds with two benzene rings and a third, fused, five membered ring (e.g. acenaphthalene, acenaphthylene (6)) are classed as di-aromatics by the method IP391.
Mono- aromatics	Compounds with a single benzene ring. A fused non-aromatic ring may also be present (e.g. tetralin, indane (7)) as may any number of side chains. As a result of the distillation specifications, the mono-aromatics in diesel fuels generally contain about as many side chain carbons as ring carbon atoms (see also “aromaticity” and “aromatic”).
Peri-condensed	Those PAH with the greatest number of rings for their number of carbon atoms and consequently higher C:H ratios, e.g. pyrene (4 rings, 16 C atoms, 10 H atoms). These PAH are thermodynamically more stable than cata-condensed ones of similar size.
Cata-condensed	Those PAH with a lesser number of rings for their number of carbon atoms and consequently lower C:H ratios, e.g. chrysene (8) (4 rings, 18 C atoms, 12 H atoms).
Pyrolyis	The chemical reactions and physical processes occurring as fuel vapour is heated. A surprisingly extensive amount of chemistry can occur, particularly in oxygen deficient environments - for instance, the soot in a flame forms as a result of pyrolysis reactions in the very fuel rich zone of a fuel-air mixture (e.g. the fuel cloud surrounding an evaporating fuel droplet).

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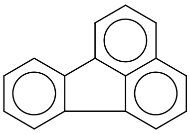
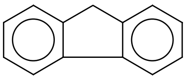
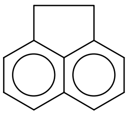
[4] The structure of fluoranthene:

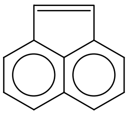


[5] The structure of fluorene:

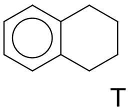


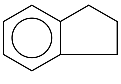
[6] The structures of acenaphthalene and acenaphthylene respectively:



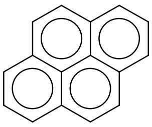


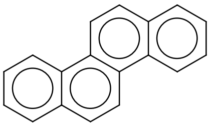
[7] The structures of tetralin and indane respectively:





[8] The “compact” structure of pyrene (a peri-condensed PAH) and the “extended” structure of chrysene (a cata-condensed PAH) respectively:





Stoichiometry (λ, ϕ)	A measure of the ratio of fuel to oxygen. Several definitions are in use, including: $\lambda = \frac{air\ required\ to\ burn\ fuel\ to\ CO_2\ and\ H_2O}{air\ available} = \frac{1}{\phi}$ $\phi = \frac{air\ available}{air\ required\ to\ burn\ fuel\ to\ CO_2\ and\ H_2O} = \frac{1}{\lambda}$
True Survival Rate	The fraction of fuel molecules of a particular type that survive combustion unaltered. This may be determined, for instance, by adding ^{14}C radio-labelled pyrene to a fuel in a known amount and measuring the ^{14}C pyrene level in the exhaust (see the work of Rhead et al in the review section).
Apparent Survival Rate, or Recovery Rate	The ratio of molecules of a particular type in the exhaust to those in the fuel consumed in producing the exhaust sample. The apparent survival rate differs from the true survival rate. This is because the former calculation includes exhaust molecules that have been created from small radicals via pyrosynthetic reactions in the flame front and those that have been produced by small modifications such as de-alkylation of a structurally related PAH molecule. The apparent survival rate is always greater than the true survival rate. See **Section 3.6** for a detailed discussion.

APPENDIX 2 – FORMULAE AND PHYSICAL PROPERTIES OF SELECTED PAH

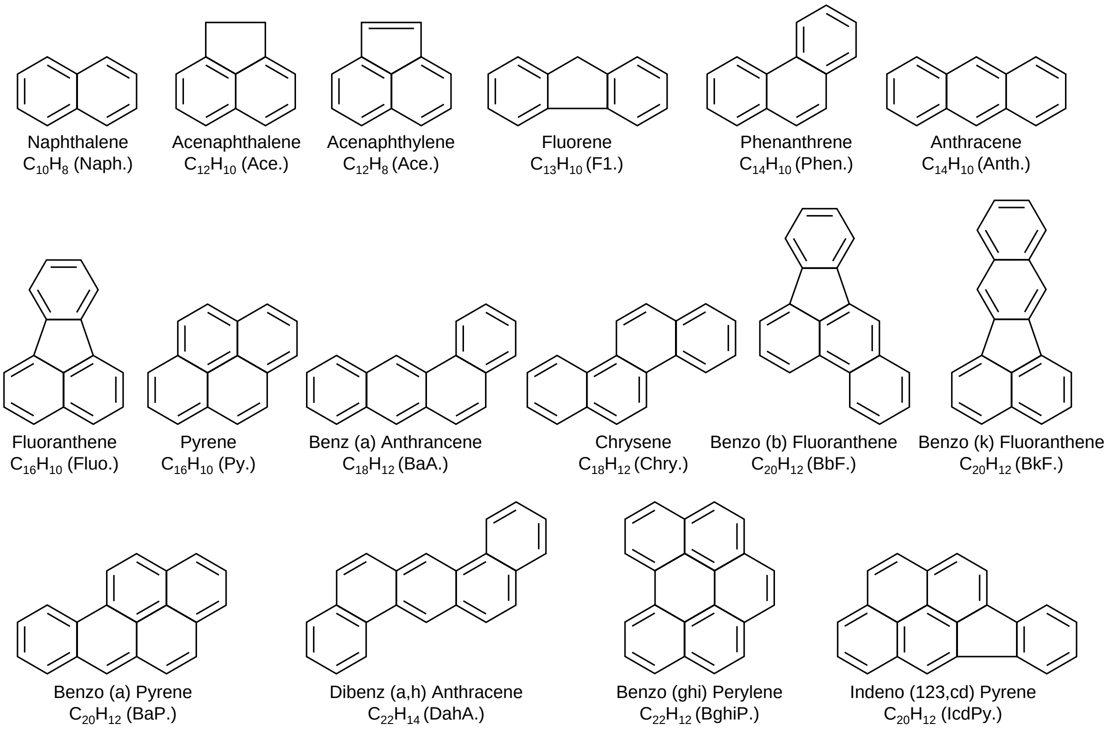
Table A.2.1 Formulae and physical properties of selected PAH

Compound (common name)	**Formula**	**Molecular Weight**	**Melting Point °C**	**Boiling Point °C** (1)	**Vapour Pressure kPa at 25°C**
Naphthalene	$C_{10}H_8$	128.18	80.2	218	$1.1x10^{-2}$
Acenaphthylene	$C_{12}H_8$	152.20	92-93	265-280	$3.9x10^{-3}$
Acenaphthene	$C_{12}H_{10}$	154.20	90-96	278-279	$2.1x10^{-3}$
Fluorene	$C_{13}H_{10}$	166.23	116-118	293-295	$8.7x10^{-5}$
Anthracene	$C_{14}H_{10}$	178.24	216-219	340	$3.6x10^{-6}$
Phenanthrene	$C_{14}H_{10}$	178.24	96-101	339-340	$2.3x10^{-5}$
Fluoranthene	$C_{16}H_{10}$	202.26	107-111	375-393	$6.5x10^{-7}$
Pyrene	$C_{16}H_{10}$	202.26	150-156	360-404	$3.1x10^{-6}$
Cyclopenta (cd) pyrene	$C_{18}H_{10}$	226.28	ca 275?	-	ca 10^{-7}
Benz (a) anthracene	$C_{18}H_{12}$	228.30	157-167	435	$1.5x10^{-8}$
Chrysene	$C_{18}H_{12}$	228.30	252-256	441-448	$5.7x10^{-10}$
Benzo (b) fluoranthene	$C_{20}H_{12}$	252.32	167-168	481	$6.7x10^{-8}$
Benzo (k) fluoranthene	$C_{20}H_{12}$	252.32	198-217	480-481	$2.1x10^{-8}$
Perylene	$C_{20}H_{12}$	252.32	273-278	500-503	$7.0x10^{-10}$
Benzo (a) pyrene	$C_{20}H_{12}$	252.32	177-179	493-496-	$7.3x10^{-10}$
Benzo (e) pyrene	$C_{20}H_{12}$	252.32	178-179	493	$7.4x10^{-10}$
Benzo (ghi) perylene	$C_{22}H_{12}$	276.34	275-278	525	$1.3x10^{-11}$
Indeno (1,2,3-cd) pyrene	$C_{22}H_{12}$	276.34	162-163	-	ca 10^{-11}
Dibenz (ah) anthracene	$C_{22}H_{14}$	278.35	266-270	524	$1.3x10^{-11}$
Coronene	$C_{24}H_{12}$	300.36	438-440	525	$2.0x10^{-13}$

(1) Many of these compound sublime.

- Source:- ISO

Figure A.2.1 Structures and formulae of the most common PAH



Naphthalene
$C_{10}H_8$ (Naph.)

Acenaphthalene
$C_{12}H_{10}$ (Ace.)

Acenaphthylene
$C_{12}H_8$ (Ace.)

Fluorene
$C_{13}H_{10}$ (F1.)

Phenanthrene
$C_{14}H_{10}$ (Phen.)

Anthracene
$C_{14}H_{10}$ (Anth.)

Fluoranthene
$C_{16}H_{10}$ (Fluo.)

Pyrene
$C_{16}H_{10}$ (Py.)

Benz (a) Anthrancene
$C_{18}H_{12}$ (BaA.)

Chrysene
$C_{18}H_{12}$ (Chry.)

Benzo (b) Fluoranthene
$C_{20}H_{12}$ (BbF.)

Benzo (k) Fluoranthene
$C_{20}H_{12}$ (BkF.)

Benzo (a) Pyrene
$C_{20}H_{12}$ (BaP.)

Dibenz (a,h) Anthracene
$C_{22}H_{14}$ (DahA.)

Benzo (ghi) Perylene
$C_{22}H_{12}$ (BghiP.)

Indeno (123,cd) Pyrene
$C_{20}H_{12}$ (IcdPy.)

APPENDIX 3 – IARC CLASSIFICATION OF REVIEWED PAH

Table A.3.1 IARC Classification

PAH	Evidence for carcinogenicity		Group	PAH	Evidence for carcinogenicity		Group
	Animals	**Humans**			**Animals**	**Humans**	
Anthanthrene	Limited	ND (1)	3(2)	Dibenzo[a,e]pyrene	Sufficient	ND	2B
Anthracene	Insufficient	ND	3	Dibenzo[a,h]pyrene	Sufficient	ND	2B
Benz[a]anthracene	Sufficient	ND	2A(3)	1,4-dimethylphenanthrene	Insufficient	ND	3
Benzo[b]fluoranthene	Sufficient	ND	2B(4)	Fluoranthene	Insufficient	ND	3
Benzo[j]fluoranthene	Sufficient	ND	2B	Fluorene	Insufficient	ND	3
Benzo[k]fluoranthene	Sufficient	ND	2B	Indeno[1,2,3-cd]pyrene	Sufficient	ND	2B
Benzo[ghi]fluoranthene	Insufficient	ND	3	2-methylchrysene	Limited	ND	3
Benzo[a]fluorene	Insufficient	ND	3	3-methylchrysene	Limited	ND	3
Benzo[b]fluorene	Insufficient	ND	3	4-methylchrysene	Limited	ND	3
Benzo[ghi]perylene	Insufficient	ND	3	5-methylchrysene	Sufficient	ND	2B
Benzo[c]phenanthrene	Insufficient	ND	3	6-methylchrysene	Limited	ND	3
Benzo[a]pyrene	Sufficient	ND	2A	1-methylphenathrene	Insufficient	ND	3
Benzo[e]pyrene	Insufficient	ND	3	Perylene	Insufficient	ND	3
Chrysene	Limited	ND	3	Phenanthrene	Insufficient	ND	3
Coronene	Insufficient	ND	3	Pyrene	Insufficient	ND	3
Cyclopenta[cd]pyrene	Limited	ND	3	Triphenylene	Insufficient	ND	3
Dibenz[a,h]anthracene	Sufficient	ND	2A				

(1) ND = No adequate data

(2) Not classified as carcinogenic to humans

(3) Probably carcinogenic to humans.

(4) Possibly carcinogenic to humans.

APPENDIX 4 – ANALYTICAL METHODOLOGY

4.1 Introduction

This appendix study reviews the different approaches to the analysis of PAH and PAH derivatives following sample collection. Appendix 3 examines the methodology used for automotive PAH analysis, covering diesel and gasoline exhausts (gas, vapour and particulate) and fuels. Environmental PAH analysis applications, such as atmospheric studies, are also documented to highlight the extent of usage of particular techniques. The practicality and consistency of the different approaches for routine analysis are assessed on a relative rather than an absolute basis. The objectives of this Appendix are:

1) To review and document the different approaches to PAH analysis.

2) To identify common features to the analytical approaches in automotive and environmental applications.
3) To highlight important considerations on the different analytical approaches.
4) To summarise with recommended approaches depending on the aim of the analysis.

4.2 Technical approach

Following sample collection, using a combination of filters and traps, the PAH require extraction before analysis can proceed. The complexity of combustion sources resulting in PAH formation is normally such that a series of steps are needed to isolate the PAH of interest before end analysis. These steps, commonly referred to as clean-up, range from a simple concentration of the extracted sample to a multi-step clean-up, where different interfering groups are removed or the sample modified in some way to enhance sensitivities.

The separation of polyaromatic hydrocarbons (PAH) and PAH derivatives, such as nitro-PAH, is based on chromatographical techniques. Chromatography uses the partition coefficient or affinity of different compounds (solutes) to distribute between stationary and mobile phases. Since different solutes have varying distribution coefficients between the two phases, separation of the mixture along a column containing the stationary phase occurs. The larger the distribution coefficient the greater the period of time that will elapse before the solute is eluted, termed retention time, compared with a compound which has a smaller distribution coefficient. Once the separation has occurred the individual components can be detected at the end of the column.

4.3 Extraction techniques for PAH

Following sampling, the organics collected on filters and sorbent traps require extraction. The extracted samples are referred to as the soluble organic fractions (SOF).

Common extraction techniques are those of Soxhlet and ultrasonic extraction. Soxhlet extractions, in which the extracting material is in continuous contact with the boiling solvent over a period of several hours (typically 6-8), have been used for many years and have high extraction efficiencies: Williams (1990); Rhead and Trier (1992). However, the long sampling times have led to the quicker (30 minutes) ultrasonic method being adopted in some cases. Ultrasonication uses agitation by high-intensity ultrasonic vibration (20 kHz) with an organic solvent for rapid extractions: Williams (1990).

Various solvents have been recommended for extractions, with dichloromethane (DCM), benzene and toluene being the most favoured: Shore (1986); Williams (1990); Montreuil et al (1992). The relative extraction efficiencies for various solvents are shown in **Table A.4.1**. Benzene and its methyl derivatives toluene and xylene all have similar extraction efficiencies, with toluene the greatest for benzo(a)pyrene from diesel particulates. In fact, many studies have found toluene as the best overall extraction solvent, especially where larger 4-6 ring PAH are involved: Tritthart (1984). Montreuil et al (1992) found that of dichloromethane (DCM), methanol, acetone, and acetonitrile solvents, the DCM solvent extracted the greater mutagenic fraction of the four solvents at 97%. Solvent choice can be used to extract specific PAH. For example, the addition of methanol to benzene enhances the extraction towards heterocyclic PAH, Williams (1990), whilst cyclohexane reduces the amount of polar interferences extracted: Bartle et al (1981). Selective solvent extraction reduces the clean-up needed before end analysis.

The large solvent volumes (up to 250ml per extraction) and incomplete recoveries of large PAH associated with Soxhlet and ultrasonication methods has led to the development of super critical fluid extraction (SFE) and accelerated solvent extraction (ASE) techniques: Peltonen and Kuljukka (1995); Chester et al (1996); Richter et al (1996).

SFE uses the supercritical state of the extractant to enhance the solubility of the sample molecules and increase the rate of transfer between the solid matrix and solvent phase. Typically, in SFE, a fluid at high pressure and moderate temperature is contacted with the sample matrix: McNally (1995). The most popular solvent in SFE has been non polar carbon dioxide, due to its low supercritical properties. The addition of a polar modifier, such as methanol, is used to increase the extraction efficiencies for PAH: Furton et al (1993). SFE has been used to extract PAH from matrices such as urban air dust and diesel exhaust particulates: Paschke et al (1992); Hawthorne et al (1992); Kanagasabapathy et al (1995); Miao et al (1995). One of the major advantages of SFE is its compatibility with other chromatographic techniques, in particular gas chromatography (GC) and supercritical fluid chromatography (SFC). Coupled SFE-GC and SFE-SFC have been applied for the determination of PAH from environmental samples: Furton et al (1993).

The recent development of accelerated solvent extractions (ASE) uses solvents at high pressures (500-3000psi) and at temperatures above the solvent boiling point (50-200°C) to enhance extraction performance in a fraction of the time associated with Soxhlet extractions. ASE has been used to efficiently extract PAH from standard reference material (SRM) urban dust (SRM 1649) using DCM/acetone (1:1) in 10 minutes: Richter et al (1996).

Gaseous and vapour phase PAH can be directly injected into gas chromatograph (GC) systems using gas sampling valves. Alternatively, the PAH can be concentrated on sorbent traps before using thermal desorption-cold traps to inject into the gas chromatographic system (section 4.6.2).

Since PAH concentrations are usually at trace levels (sub ppm), great care must be taken during extractions to avoid the introduction of contamination. This requires high grade solvents and rigorous cleaning of equipment prior to extractions. During extractions the apparatus should, where possible, be wrapped in aluminium to avoid photo-degradation of the PAH.

4.4 Clean-up/fractionation techniques

The complexity of the soluble organic fraction (SOF) necessitates some form of sample clean-up before end analysis of the PAH. The number of clean-up steps is dependent to a large extent on the level of PAH in the extracted sample or SOF. Trace PAH, such as nitro-PAH, require extensive isolation to remove large concentrations of co-eluting and hence interfering compounds. However, the development of a clean-up method has to be designed with the extraction and end detection systems borne in mind. For instance, the use of a selective detector, such as fluorescence, for the analysis of PAH within the SOF of diesel particulates is not affected by aliphatic interferences. The selective detector enables the clean-up procedures to be kept simple. By contrast, the same clean-up approach with the universal flame ionisation detection would not identify the PAH, due to the more abundant alkanes masking the presence of the lower PAH concentrations. In this case, a multi stage clean-up procedure would be used.

Classical fractionation commonly proceeds by packing simple glass columns with a suitable chromatographical adsorbent, and sequential elution with organic solvents separates the PAH fraction: Williams (1990). Suitable adsorbents are alumina, chromatography grade silica gel and lipophilic gel such as Sephadex LH-20: Bechtold et al (1985); Williams (1990); Fernandez and Bayona (1992). The simple and inexpensive gravity flow open column method has led to the technique being widely used in the clean-up of automotive fuels and exhaust samples: Ciccioli et al (1986); Williams et al (1989); Götze et al (1991); Mitchell et al (1994). However, the highly adsorptive properties of the column packing can lead to sample degradation and irreversible bonding of PAH to the packing. The reproducibility of the separation is also highly dependent on the water content of the adsorbent, necessitating careful storage of the column packing: Later et al (1985). The reproducibility problem can be avoided by deactivating the silica adsorbent with 5-10% water: Later et al (1985). Increasingly, pre-manufactured solid-phase extraction cartridges (SPE) are replacing the labour intensive column packing method: Obuchi et al (1984); Theobald (1988); Baumeister et al (1989); Bundt et al (1991); Dumont et al (1993); Wajsman et al (1996). Solid-phase extraction cartridges enable rapid and reproducible separations with a wide selection of packing materials. Other simple fractionation methods include liquid-liquid partitioning, commonly with dimethylsulphoxide, to concentrate PAH in one liquid whilst retaining interferences in the other liquid: Williams (1990).

For detailed characterisation of SOF, particularly for detection of trace PAH derivatives, a multi-step fractionation is often used. This typically involves a simple preliminary clean-up step, followed by semi-preparative normal-phase (NP) high-performance liquid chromatography (HPLC). Preparative HPLC, using an underivatised silica as the stationary phase, has been widely used for fractionation of environmental samples, including diesel extracts: Levine and Skewes (1982); Liberti et al (1984); Ciccioli et al (1986); Bayona et al (1988); Smith et al (1996). The separation is similar to that achieved with open column silica chromatography, however the separation efficiencies and reproducibility are far greater than with the classical method. The separations with the silica stationary phases are based on chemical class, with the classes eluted in order of increasing polarity. The complexity of HPLC fractionations are offset by isolating the specific elution window associated with the PAH of interest, established by prior injection of standard mixtures. The ability to fractionate precisely allows a much greater concentration step. Chemical modifications to the silica, usually with an amino group, have enabled separations by ring size: Niles and Tan (1989). Recently, direct coupling of the HPLC fractionation system to GC systems has enabled the analysis of PAH without the losses normally associated with normal remote clean-up and fractionation procedures: Kelly et al (1992).

The clean-up steps used in PAH analysis may also include sample modifications or derivatisations designed to help facilitate the detection of the PAH. One such approach is to reduce the weakly fluorescent nitro-PAH to strongly fluorescent amino-PAH in order to greatly increase the sensitivity of the fluorescence method. This can be achieved by reductive agents such as sodium borohydride, Shore (1986), or on-line during the end analysis by using reductive columns prior to the analytical column, Hayakwa et al (1992); Li and Westerholm (1994); Veigl et al (1994). Derivatisation methods add a distinctive tag to the structure of PAH to enhance detector response. For example, PAH can be chlorinated to increase the response of the derivatised PAH to electron capture detection: Peltonen and Kuljukka (1995). Derivatisation steps are commonly used when a mass spectrometer is the end detector to provide unique ions with which to identify the compounds of interest: Sellström et al (1987).

As for extraction methodology great care in terms of sample handling is needed and rigorous testing of the materials used during the clean-up is necessary. The need for caution is illustrated by the recent evaluation of solid-phase cartridge clean-up by Gundel et al (1995). The 137 % recovery of pyrene led the researchers to conclude that solvent rinsing of the cartridges leached highly fluorescent species, which severely interfered with the end fluorescence detection. To avoid the leaching problem, the authors recommended using glass barrels packed with the stationary phase.

4.5 Analysis techniques for PAH

The two most common end separation techniques used for PAH analysis are gas chromatography (GC) (**Section 4.5.1**) and high-performance liquid chromatography (HPLC) (**Section 4.5.2**). Relatively new chromatographical systems such as supercritical fluid chromatography (SFC) and capillary electrophoresis (CE) are increasingly being used for PAH analysis (**Section 4.5.3**).

4.5.1 Gas chromatographic analysis of PAH

Gas chromatography, in which the partition is between the stationary phase and a gas phase, is one of the most widely used separation techniques. GC analysis is best suited to the smaller more volatile PAH, since molecules must be volatile within the temperature ranges applied. This limits the range of PAH which can be analysed to around 7 - 8 ring PAH: Lee (1995); Peltonen and Kuljukka (1995). However, the degree of condensation is a significant factor in the volatility of PAH. Less condensed PAH such as pyranthrene ($C_{30}H_{16}$) can be easily analysed by GC, whereas the more condensed naphtho[8,1,2-abc]coronene ($C_{30}H_{14}$) requires high temperature GC: Lee (1995). The high resolving power of GC allows the analysis of complex mixtures, such as in the combustion processes involved with the formation of PAH, to be achieved. For a detailed review of general GC analysis refer to Eiceman (1996).

The origins of GC go back more than forty years to the work by James and Martin, with the first separation of PAH by high resolution capillary GC taking place in 1964: Lee (1995). Since then there has been considerable enhancements into the technique, especially with regards to increasing column thermal stability. This has led to more consistent and reproducible retention times, enabling greater confidence in identification of PAH complex mixtures. Recently, further column improvements have enabled high temperature columns to be produced and research has identified the relationships between PAH molecular shape and GC retention times: Furton et al (1993). Optimisation of parameters such as the injection technique conditions (solvents, temperature, and retention gaps) have been examined: Galceran and Moyano (1993).

The most favoured detector for PAH analysis is the flame ionisation detector (FID), due to that detector's universal response, stability and wide linear range. The power of a mass spectrometer (MS) to provide detailed characterisation and the ease of interface between GC and MS has led to GC/MS being widely used for quantification of PAH. For most PAH analysis, the GC/MS is operated in the electron impact ionisation mode. Chemical ionisation has also been used, both in positive (PCI) and negative (NCI) modes. The compatibility of GC with element specific detectors, such as electron capture (ECD) and nitrogen-phosphorous detectors (NPD), allows trace PAH derivatives not within the sensitivity of FID (nanogram range) to be selectively monitored.

In a recent evaluation of GC coupled to mass spectrometers with HPLC systems connected to diode-array UV and fluorescence detectors for analysis of PAH, Castello and Gerbino (1993) found that the ion trap mass detector (ITD) proved more sensitive than HPLC with UV or fluorescence detection. The ITD in full scan mode was also more sensitive than a quadruple analyser mass spectrometer operated in selective ion monitoring (SIM). For example, the detection limit for the EPA 16 priority pollutant PAH ranged from 20-80 picograms using GC-ITD compared with 100-500 picograms using GC/MS in SIM mode. The authors concluded that the sensitivity of the ITD in full scan mode (where all spectra data can be assessed) enabled the greatest identification and quantification with the technologies available at that time. The authors also comment that the uniform response of FID to PAH allows GC-FID to be used as a routine quantification technique provided that the levels are within the detection limits of the detector.

4.5.1.1 Automotive PAH analysis using gas chromatography

Focusing on the extent to which GC analysis with different detectors, including mass spectrometers, have been employed in automotive exhaust analysis, clearly shows not only the degree to which GC has existed as a technique, but also the progression achieved with GC over the years (**Table A.4.2**).

One of the earlier studies by Kraft and Lies (1981) used gas chromatography with flame ionisation detection to analyse the PAH in gasoline and diesel exhaust. The authors also used the liquid chromatographic technique of thin layer chromatography (TLC) with fluorescence detection. The two techniques compared favourably in terms of results. The GC method enabled greater identifications when using retention indices than the TLC method which focused on selected PAH. Bundt et al (1991) also used GC-FID with retention indices to characterise the PAH content of diesel fuels following simple silica column fractionation. The use of retention indices and additional analysis by GC/MS enabled detailed characterisation of the naphthalene, biphenyl, fluorene, phenanthrene, and their alkylated derivatives. Lai and Song (1995) found that the use of a combination of retention indices and a library of mass spectra led to much faster and accurate automatic peak identifications.

Several studies used GC analysis to characterise the PAH content of fuel and oil: Westerholm et al (1988), (1994); Barbella et al (1988), (1989); Bundt et al (1991); Lai and Song (1995). A typical procedure for the analysis of fuel is documented in the study of the effect of fuel PAH content on PAH exhaust emissions by Westerholm and Li (1994). The authors used classical clean-up with glass columns packed with silica gel and then further fractionated with NP HPLC. Some studies, such as that by Bundt et al (1991), used only silica column clean-up.

Several studies found that the identification capabilities of GC/MS enable detailed characterisation, far greater than possible with HPLC. The identification of compounds on a retention basis restricts HPLC analysis to a selected suite of PAH, such as the US EPA 16 PAH priority pollutants. An earlier study which utilised GC/MS was the characterisation study by Yu and Hites (1981) on the organic compounds associated with diesel particulates. The co-workers used a combination of GC-FID and GC/MS to provide detailed information on over eighty PAH and oxy-PAH contents of diesel exhaust extracts. The MS detector was found to be useful in confirming GC identifications. Jensen and Hites (1983) found GC/MS useful for monitoring the effect of engine settings (retard injection and engine loads) on the ratios of PAH, such as the methylphenanthrenes and methylanthracenes using the molecular mass/charge ion (m/e) of 192. Alsberg et al (1985) also found the power of GC/MS essential for assigning identification to the more polar oxygenated PAH derivatives, such as fluoren-9-one and a range of alkyl derivatives.

GC/MS with SIM was found especially useful by Paschke et al (1992) in removing a great deal of interferences and enabling detection of PAH and 1-nitropyrene by molecular ions. Levin et al (1984) used GC and GC/MS for the analysis of PAH from two stroke chain saw engines. The authors found that SIM rather than full scan acquisition was the better quantification approach, since in the full scan acquisition tailing from solvent peaks caused interference problems.

The compatibility of GC with specific element detectors proved useful for the detection of a number of trace PAH derivative, particularly for nitro-PAH: Robbat et al (1986); Niles and Tan (1989). Robbat et al (1986) showed that GC's fitted with a chemiluminescence detector could selectively analyse nitro-PAH without extensive clean-up, with detection limits of 50 -100 picograms. Similarly, Niles and Tan (1989) used GC with thermal energy analyser (TEA) to analyse nitro-PAH in diesel and air particulates. The use of the highly sensitive, selective and linear TEA detector enabled nitro-PAH to be detected.

GC analysis enables direct injection of gaseous mixtures either by gas sampling valves or by concentration onto adsorbents such as Tenax, packed into glass tubes or cartridges, followed by thermal desorption cold trapping (TCT) onto the front of the GC column. Andersson (1994) proved the effectiveness of GC directly coupled to a ion trap mass detector (ITD) with TCT injection for detailed analysis of a variety of automotive exhaust samples collected in Tedlar bags. The vapour phase PAH were drawn through glass tubes packed with Tenax adsorbents followed by thermal desorption and cryogenic-focusing onto the GC. The use of the sensitive ITD enabled full spectra collection, resulting in the identification and quantification of PAH and a number of important combustion products without any sample work-up. Zielinska and Fung (1994) demonstrated the use of stainless steel and Tenax solid adsorbents to sample the air in the road Caldecott Tunnel in San Francisco. Samples were directly injected on to the GC column using thermal desorption cold trapping (TCT). The GC was connected either to FID or infrared-mass spectrometer (IRD/MSD) to detect individual hydrocarbons. The use of an infrared spectrometer allowed infrared library searches for identifications. The research revealed the presence of light PAH, such as naphthalene. The recent study by Wajsman et al (1996) preferred the use of higher temperature sorbent material, such as Carbotrap C, rather than Tenax (upper limit of 250^{o}C). These sorbents are stable up to 400^{o}C and have low background levels of compounds, helping to reduce the risk of contamination of the sample, which, if occurring, may lead to misidentifications later on during analysis. The authors found that the use of thermal desorption gas chromatography provided a rapid screening tool for the volatile 2- 3 ring PAH.

Compared with HPLC coupled to fluorescence detection, most researchers found that before the GC and GC/MS analysis of PAH, extensive fractionation was required: Yu and Hites (1981); Mills et al (1984); Tong et al (1984); Alsberg et al

(1985); Niles and Tan (1989). The work of Paputa-Peck et al (1983) is a good example of the extent to which fractionation is necessary for GC/MS, and to a lesser extent GC-NPD, to provide detailed characterisation. The authors used NP HPLC to provide eight fractions for end analysis. Similarly, the research by Tong et al (1984) used NP HPLC to produce six fraction prior to GC/MS analysis.

The suitability of GC analysis for volatile PAH is shown in a number of studies: Barbella et al (1988), (1989), (1990). In this series of studies, Barbella et al used GC/MS for lighter 2-3 ring PAH and alkyl derivatives. However, for larger PAH the sensitivity of GC-FID and GC/MS were no match for HPLC with selective detectors such as fluorescence. Mills et al (1984) found that the sensitivity limits of the GC/MS in the electron impact (EI) made detection of larger ring PAH, such as benzo(a)pyrene, difficult. Resolution of isomers of PAH was also a problem with GC analysis. In the study of the effect of fuel PAH on exhaust PAH emissions, Westerholm et al (1988) also had difficulty to resolve the benzo(b)fluoranthene and benzo(k)fluoranthene isomers using gas chromatography, even after considerable cleanup steps.

In the investigation of gas chromatographical analysis of gasoline and diesel exhaust extracts, Mashaly et al (1985) found deposition of non volatile fractions of diesel extracts in the on-column injector interfered with subsequent analyses. No such problem was encountered with the lighter gasoline extracts, and the authors recommended removing the first coil of the capillary column (injector side). Since then the use of guard columns (retention gaps) have gone some way to removing the problem, but careful monitoring of the chromatography on GC systems is still needed, with regular changing of the guard column.

4.5.1.2 Environmental PAH analysis using gas chromatography

There have been a number of environmental studies which are of interest in terms of analysing PAH (**Table A.4.3**).

Research by Pitts et al (1985), Arey (1986), Atkinson (1987), (1990), Helmig et al (1992), Sasaki et al (1995), and Zielinska et al (1989), on various reactions, particularly atmospheric nitration, have exploited GC/MS to determine which PAH isomers are favoured. For example, 1-nitropyrene is a direct exhaust product whilst 2-nitropyrene is formed in the atmosphere. The atmospheric formation is thought to occur by OH addition at the 1-position of pyrene followed by NO_2 addition at the 2-position, with final dehydration to leave 2-nitropyrene. Similar to the automotive applications, a number of the atmospheric studies exploited Tenax cartridges, enabling concentration of samples before direct thermal desorption on to the GC column. Selective ion monitoring was used in a number of cases to remove interfering formation products, for example the molecular ion mass/charge (m/e) of 187 was used by Zielinska et al (1989) to monitor the methylnitronaphthalenes. Arey et al (1987) used GC/MS with selective ion monitoring to monitor the PAH and nitro-PAH concentrations in the atmosphere during a wintertime high-NOx episode in the Los Angeles Basin.

Detailed characterisation of urban and semi-urban air samples was achieved by Fernandez and Bayona (1992) using a combination of GC and GC/MS to analyse PAH, nitro-PAH, and oxy-PAH. The limits of detection for the urban air particulate matter (NIST 1649) were 8.8 ng/g for pyrene and 4.7 ng/g for 1-nitropyrene. Bodzek et al (1993) used the power of GC/MS to distinguish PAH, nitro- and oxy-PAH in airborne particulate matter following classical LC fractionation. In the study of airborne particulate Halsall et al (1994) noted that GC/MS operated in SIM mode was up to fifty times more sensitive than HPLC with fluorescence detection for a selection of PAH. Both Kanagasabapathy et al (1995) and Chai and Pawliszyn (1995) demonstrated the power of gas chromatography/mass spectrometry to identify trace PAH with molecular ions. For instance, the 128 molecular ion was used to identify naphthalene, while phenanthrene and fluoranthene were identified with the 178 and 202 ions respectively.

With respect to automotive applications the complexity of the environmental samples and the lack of selectivity resulted in the need for significant work-up procedures (except when specialist MS techniques, such as selective ion monitoring or chemical ionisation, were used).

4.5.2 High-performance liquid chromatographic analysis of PAH

Compared with the history of gas chromatography as a separation technique, high-performance liquid chromatography is a relatively new separation science, with the first HPLC separation of PAH being reported by Schmit et al in 1971: Peltonen and Kuljukka (1995). The use of reverse-phase HPLC, in which chemically bonded octadecylsilane (ODS) stationary phases are used, continues to be the preferred method for PAH analysis: Wise (1993). Although the separation associated with HPLC cannot rival high resolution gas chromatography, HPLC does offer a number of distinct advantages for PAH analysis. The use of a liquid mobile phase enables the larger, less volatile and thermally sensitive compounds to be analysed, with up to ten ring PAH, such as ovalene, being reported: Lee (1995). The use of gradient elution with a variety of solvent polarities results in good selectivity in separating individual PAH compounds, especially for isomers such as benzo(k)fluoranthene and benzo(b)fluoranthene: Peltonen and Kuljukka (1995). The use of selective and sensitive detectors, such as fluorescence (FL) and chemiluminescence (CL) enables the detection of trace PAH with less sample clean-up than is needed for GC analysis: Lee (1995).

HPLC is commonly used in multi-dimensional chromatographic analysis of PAH, in which normal-phase HPLC is used for the pre-fractionation and isolation of the PAH of interest, followed by end analysis using reverse-phase HPLC or GC. Preparative HPLC is widely used due to its high efficiency, ease of automation and on-line coupling potential to other techniques, including gas chromatography: Kelly et al (1992); Peltonen and Kuljukka (1995).

The greater ability to modify both the stationary phase and the mobile phases results in HPLC analysis being more flexible than GC. Method development for GC centres primarily on selection of the stationary phase coated on the capillary columns, with fine tuning of the temperature programme used to increase resolutions in some cases. For a detailed review of general HPLC analysis refer to Dorsey et al (1996); Hargis et al (1996); Rothman (1996); Warner et al (1996).

The US EPA have specified HPLC as the chosen analysis method for PAH since 1982. Wise et al (1981) established that for isomeric PAH the HPLC retention increased with increasing length-to-breadth ratio of the PAH structure i.e. cata PAH structures elute more slowly than peri PAH structures. Dong and DiCesare (1982) demonstrated the fast analysis times possible with HPLC analysis.

Hansen et al (1991) developed an improved HPLC fluorescence PAH method which used multiple changes in excitation and emission wavelengths to achieve a sensitive and reliable method. Liu and Robbat (1991) investigated the optimisation of HPLC for the detection of nitro-PAH using diode-array UV, FL, and CL detectors. The authors used a reductive column packed with zinc to reduce the nitro-PAH to the amino-PAH on-line. The use of FL and CL detectors greatly increased selectivity and sensitivity compared with diode array UV. For example, whereas the detection limits were between 2-12ng of nitro-PAH injected for UV, the limits were 10-15 picograms for FL. Escrivá et al (1994) evaluated GC, HPLC, and gas chromatography/mass spectrometry (GC/MS) for analysis of PAH in air samples. The detection limits in ng of BaP injected were as follows: GC-FID at 0.7, HPLC with UV at 6.1, HPLC with FL at 0.03 and GC/MS in SIM mode at 0.04. The authors concluded that of the four techniques, HPLC with fluorescence detection was the best system. The authors point out that, although the GC/MS analysis operated in selective ion monitoring mode was comparable to the fluorescence results, fluorescence has the advantage of being more suited to routine analysis. Williams et al (1994) modified the US EPA method 610 (established in 1990), enabling 15 of the 16 priority PAH pollutants to be satisfactorily resolved at low detection limits with elimination or reduction of chromatographic interferences. Acenaphthylene exhibited low fluorescence intensity and was not able to be quantified at the desired levels using fluorescence. Standard injections were performed with NIST 1647a and detection limits were of the order of 1 - 72 ng/l (not including acenaphthylene).

4.5.2.1 Automotive PAH analysis using high-performance liquid chromatography

LC analysis with different detectors have been employed extensively in automotive exhaust analysis (**Table A.4.4**).

One of the early studies to use HPLC for the analysis of PAH in diesel engine particulates was carried out by Zierock et al (1983). The authors used HPLC fitted with an octadecylsilane (ODS) column and fluorescence detection. The whole analytical procedure, including extraction of ultrasonication extraction of the filters with cyclohexane and clean up, was completed in one hour. The clean-up method consisted of purification on silica gel column (deactivated with 10% water), followed by solvent exchange to acetonitrile prior to injection on the HPLC. Detection limits were in the range of 1 ng, except perylene which was an order of magnitude lower.

The studies by Hering et al (1984) and Miguel (1984) demonstrated the resolution power of RP HPLC with ODS columns for a range of PAH (3-7 ring). Good resolution of benzo(b)fluoranthene and benzo(k)fluoranthene isomers was achieved for particulate samples taken from road tunnels.

The study by Gibson (1982) was one of the first to use HPLC to analyse nitro-PAH in gasoline, diesel exhaust particulates and air samples. Sensitivity was increased by off-line reduction of the weakly fluorescent nitro-PAH to yield the strongly fluorescent amino-PAH using a reducing agent containing sodium borate and copper chloride. The selectivity of this method for the trace nitro-PAH enabled a simple work-up procedure to be used. Pederson et al (1984) also demonstrated the sensitivity of fluorescence detection for the detection of nitro-PAH. In this study extensive clean up was used, including normal-phase HPLC. However, the degree of fractionation used was aimed at simplifying the mutagenicity testing rather than the chemical analysis. Research at Ricardo, Shore (1984), (1986), (1987); Cooper and Shore (1989), also utilised the selectivity and sensitivity of fluorescence detection, enabling simple silica column clean-up. Nitro-PAH were quantified using off-line reduction with sodium borohydride and Shore (1986) determined the PAH content of ten fuels using HPLC.

The recent evaluation of GC-FID and HPLC with fluorescence to detect particulate 4 - 6 ring PAH from diesel exhaust by Wajsman et al (1996) established the superior selectivity of fluorescence and the importance of appropriate clean-up steps. Following Soxhlet extraction of the particulate PAH samples, a simple solid-phase extraction cartridge (silica packing) clean-up was employed to remove aliphatic and polar interferences. However, the identification of PAH using the universal carbon flame ionisation detector was difficult, indicating insufficient isolation clean-up steps. By contrast, when the same samples were analysed by HPLC with fluorescence detection the 4- 6 ring PAH were clearly identified.

The reduction method for nitro-PAH was developed further by performing the reduction of the nitro-PAH to the amino-PAH on-line: Tejada et al (1986); MacCrehan et al (1988); Götze et al (1991); Hayakawa et al (1992); Veigl et al (1994); Li and Westerholm (1994).

The majority of researchers used fluorescence as the detector in the HPLC analysis of PAH and nitro-PAH in automotive applications. However, a number of the studies also found chemiluminescence detection to offer increased sensitivity and selectivity. For example, Li and Westerholm (1994) found that with chemiluminescence and on-line reduction of the weakly fluorescent nitro-PAH to the strongly fluorescent amino-PAH, detection limits were of the order of 1 to 10 picograms for nitro-PAH standards. The research successfully used chemiluminescence for detection of trace levels of 1-nitropyrene and dinitropyrenes in diesel samples.

4.5.2.2 Environmental PAH analysis using high-performance liquid chromatography

There have been a number of environmental studies which are of interest in terms of analysing PAH by HPLC (**Table A.4.5**).

As for the automotive applications, the environmental applications showed that HPLC in combination with fluorescence detection enables minimal work-up to be used. For example, Maher et al (1989) found that little if any sample clean up was required for detection of 12 PAH in air particulate extracts. The authors also found that greater reproducibility in terms of chromatography was obtained when the dichloromethane from the extraction process was replaced with acetonitrile before HPLC analysis. The run time was also short at 45 minutes, with detection limits between 50 - 300 pg. Dumont et al (1993) used disposable solid-phase extraction cartridges packed with amino stationary phase to provide a simple, rapid, but effective clean-up step prior to end analysis. The research by Sigvardson and Birks (1984) showed that selective chemiluminescence with an on-line zinc packed reductive column could detect a range of nitro-PAH without any major work-up. By contrast, even after NP HPLC, analysis by GC/MS in selective ion monitoring mode failed to detect the nitro-PAH. The detection limit of the chemiluminescence method was 0.25 picograms for 1-nitropyrene. Smith et al (1996) demonstrated the power of on-line reduction HPLC with fluorescence detection to selectively detect trace levels of nitro-PAH in urban air samples.

Gundel et al (1995) proved the effectiveness of HPLC with a dual-programmed fluorescence detector for the analysis of gas- and particulate-phase PAH in environmental tobacco smoke. Relative precision averaged at 8 % for NIST SRM 1649 standards. The authors found that the use of selective fluorescence enabled a reduction in clean up steps, which were necessary if GC/MS was used.

4.5.3 Miscellaneous PAH Analysis Techniques

Thin-layer chromatography (TLC) used in the early days of PAH analysis has continued to be used where separation of individual PAH is not essential. The technique is convenient for chemical class profiling and can be combined with several powerful techniques such as laser mass spectrometry (LMS) to distinguish partly overlapping PAH: Furton et al (1993).

Supercritical fluid chromatography has recently been developed and enables greater control of the separation mechanisms involved before detection by FID and MS: Furton et al (1993); Chester et al (1996).

Capillary electrophoresis (CE) is a powerful technique and is suited to complex mixtures due to its high separation capability. However, the use of CE for PAH analysis is in the preliminary stages, since the electophoretic separation of neutral and highly hydrophobic PAH is difficult. Recently CE was used with UV-laser-excited native fluorescence for ultra sensitive determination of PAH: Peltonen and Kuljukka (1995). The reported mass detection limits were in the order of 10^{-20} mol with linearity over 4 orders of magnitude.

4.6 Conclusions

The analysis of PAH is based on chromatographic techniques, with an overall analytical approach of extraction, fractionation, and end analysis.

Extraction and concentration can be achieved by the traditional Soxhlet method. Ultrasonication can be useful for rapid extractions, as can the more recent advances in supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE). The high extraction efficiencies, particularly where larger 4-6 ring PAH are involved, makes toluene the preferred extraction solvent.

Fractionation and isolation techniques are dependent on the PAH of interest and the end analysis being used. For prominent PAH, classical column cleanup can be used, with solid-phase extraction (SPE) technology providing a rapid and reliable method. For detailed characterisation of PAH, especially for trace nitro-PAH or where detector selectivity is not great, such as gas chromatography with flame ionisation detection, extensive fractionation is needed using normal phase HPLC.

On a practical basis, separation using gas chromatography is suitable for volatile PAH with up to 4-5 rings. Gas chromatography with flame ionisation detection (FID) can be used as a routine tool for detailed PAH profiling. Furthermore, the GC fitted with a range of element specific detectors, such as electron capture and nitrogen-phosphorus detectors, can selectivity detect specific PAH of interest. The use of GC with mass spectrometry enables comprehensive identifications, with ion trap mass detectors (ITD) providing the most spectral detail whilst maintaining the greatest sensitivity. Conversely, GC-FID has moderate sensitivity compared with the HPLC fluorescence systems and both GC-FID and GC/MS suffer from interferences requiring extensive clean-up.

Reverse phase HPLC with fluorescence detection systems enable sensitive and selective analysis of selected PAH (2 - 10 ring range), such as the US EPA 16 PAH priority pollutants, with little clean-up. The weakly fluorescent acenaphthylene is difficult to detect at trace levels by fluorescence detection. The use of on-line reductive columns can enable routine analysis of nitro-PAH to be achieved. The use of chemiluminescence detectors enables further increases in the selectivity and sensitivity of HPLC methods.

Table A.4.1 Relative Efficiencies of solvents for the Extraction of Benzo(a)pyrene from Diesel Particulates

Solvent	Relative efficiency %
Toluene	100
Xylene	98
Benzene	98
Dichloromethane	87
Cyclohexane	58
Acetone	36

- Williams (1990)

Table A.4.2 GC Analysis for Automotive Applications

Year	Sample type	Extraction used	Clean up	Detectors $^{(+)}$	Compounds detected	Ref.
1981	Diesel & gasoline		Minimal	GC-FID (TLC with FL)	PAH	Kraft and Lies
1981	Diesel particulates	Soxhlet (DCM)	Complex column clean-up	GC-FID & GC/MS	PAH and oxy-PAH	Yu and Hites
1982	Diesel particulates	Soxhlet (DCM)	Minimal	GC-FID, GC-TID, GC/MS (EI and CI), probe MS	PAH, nitro-PAH, oxy-PAH	Yergey et al
1983	Diesel	Soxhlet (DCM)	Classical	GC/MS (EI and NCI)	PAH and oxy-PAH	Jensen and Hites
1983	Diesel	Soxhlet	NP HPLC	GC-NPD (FL)	nitro-PAH	Schuetzle and Perez
1983	Vehicle tunnel particulate sample	Soxhlet (DCM)	NP HPLC	GC/MS EI	1-nitropyrene	Gorse et al
1983	Light duty diesel particulate	Soxhlet (DCM)	NP HPLC	GC-NPD & GC/MS	nitro-PAH	Paputa-Peck et al
1984	Diesel particulate		NP HPLC	GC/MS	PAH	Tong et al
1984	Diesel particulate	Soxhlet (DCM)	SPE (silica)	GC-FID, GC/MS EI	oxy-PAH and nitro-PAH	Schulze et al
1984	Diesel particulate	Ultrasonication	NP HPLC	GC-TEA	nitro-PAH	Tomkins et al
1984	Diesel exhaust	Soxhlet (benzene /methanol)	NP HPLC	GC-FID, GC-NPD and GC/MS	nitro-PAH	Liberti et al
1984	Two stroke chain saw engines	Ultrasonication (cyclohexane)	Classical	GC-FID and GC/MS	PAH	Levin et al
1984	Diesel vapour and particulate		TLC	GC/MS	24 PAH species	Mills et al
1985	Gasoline exhaust particles	Soxhlet (DCM)	Extensive, including NP HPLC	GC-FID and GC/MS	3-7 ring PAH and oxy-PAH	Alsberg et al
1986	Diesel particulate	Soxhlet (benzene /methanol)	Classical clean-up followed by NP HPLC	GC-FID, GC/MS EI	PAH and oxy-PAH	Ciccioli et al
1986	Diesel particulate	Ultrasonication (toluene and DCM)	Minimal	GC-FID, GC/MS EI, CL	Nitro-PAH	Robbat et al
1986	SRM 1650 and heavy duty diesel particulate	Soxhlet (DCM)	SPE (silica) & NP HPLC	GC-ECD	Nitro-PAH	Draper

(+) = HPLC end analysis techniques used
KEY:

SPE = solid phase extraction cartridges	TEA = thermal energy analyser	RP = reverse phase
TLC = thin layer chromatography	NICI = negative ion chemical ionisation	EI = electron impact mode
FID = flame ionisation detector	ITD = ion trap mass detector	
NP = normal phase	FL = fluorescence detection	

Table A.4.2 GC Analysis for Automotive Applications (cont.)

Year	**Sample type**	**Extraction used**	**Clean up**	**Detectors** (+)	**Compounds detected**	**Ref.**
1987	Diesel particulate		Off line reduction and derivatisation	GC/MS NICI	nitro-PAH	Sellström et al
1988	Gas and particulate emissions from 2 stroke emissions	Ultrasonication	-	GC/MS	3 - 5 RING PAH	Cosmacini et al
1988	Fuels, oils, gas and particulate samples	Soxhlet (DCM)	Preliminary	GC-FID	PAH	Westerholm et al
1988, 1989	Diesel	Soxhlet (DCM)	NP HPLC	GC/MS (RP HPLC with FL)	2-3 ring PAH	Barbella et al
1989	Vehicle tunnel semi-volatile & particulate sample	Soxhlet (DCM)	NP HPLC	GC-FID, GC/MS EI	PAH and alkyl derivatives	Benner et al
1989	Diesel	Soxhlet (benzene /methanol)	Silica gel	GC-ITD	2-5 ring PAH	Williams et al
1989	Semi-volatile and particulate diesel extracts	Soxhlet (DCM)	CLASSICAL COLUMN CLEAN-UP	GC/MS	1-4 ring PAH	Nelson
1989	Gasoline, pre- and post-catalyst	Soxhlet (toluene)	Silica gel	GC-ITD	2-5 ring PAH	Williams et al
1989	Diesel and air particulates	Soxhlet (DCM)	Extensive, including NP HPLC	GC-FID, GC-TEA	PAH and nitro-PAH	Niles and Tan
1990	In-cylinder sampling of diesel combustion	Condensation trap	Extensive, including NP HPLC	GC/MS	2 -3 ring PAH	Barbella et al
1990	Heavy duty diesel	Soxhlet	TLC	GC-FID (HPLC)	PAH and nitro-PAH	Hirakouchi et al
1990	Diesel extracts	Concentration step	Classical column clean-up	GC/MS EI	PAH and methyl derivatives	Trier et al
1990	Heavy-duty diesel exhaust and fuels	Soxhlet (DCM)	Silica column	GC-ITD	PAH	Shore and Dempster
1991	Diesel fuels	-	Column clean-up	GC-FID and GC/MS	2 - 3 ring PAH and their alkylated derivatives	Bundt et al

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KEY:

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TLC = thin layer chromatography	NICI = negative ion chemical ionisation	EI = electron impact mode
FID = flame ionisation detector	ITD = ion trap mass detector	
NP = normal phase	FL = fluorescence detection	

Table A.4.2 GC Analysis for Automotive Applications (cont.)

Year	Sample type	Extraction used	Clean up	Detectors [(+)]	Compounds detected	Ref.
1991	Heavy-duty diesel vapour phase and particulates	Soxhlet (DCM & acetone)	Classical silica gel & NP HPLC	GC/MS (FL with on-line reduction for 1-nitropyrene)	PAH and nitro-PAH	Westerholm and Li
1991	Diesel run on alternative fuels	Ultrasonication (toluene)	Silica packed columns	GC-FID	EPA 16 priority pollutant PAH	Ziejewski et al
1992	Diesel exhaust particulate matter	SFE	HPLC connected directly to GC	GC-FID	oxy-PAH	Kelly et al
1992	Diesel exhaust particulate matter	SFE	Classical	GC-FID and GC/MS (in full scan and SIM modes)	PAH and 1-nitropyrene	Paschke et al
1992	Diesel exhaust particles	Soxhlet (DCM)	NP HPLC	GC/MS with SIM	nitro-PAH	Ball and Young
1992	Diesel exhaust extracts	Soxhlet (DCM)	Classical clean-up	GC/MS EI	PAH and nitro-PAH	Mason et al
1993	Heavy-duty diesel semi-volatiles	-	-	TCT-GC/MS	PAH and alkyl-PAH	Newkirk et al
1993	Particulates from HD diesel trucks	Ultrasonication		GC/MS	PAH and oxy-PAH	Rogge et al
1994	Diesel, gasoline, and two-stroke semi-volatiles particulates	-	-	TCT-GC-ITD	PAH	Andersson
1994	Diesel and air particulates	Ultrasonication (acetone)	SPE & on-line reduction	GC/MS EI	nitro-PAH	Scheepers et al
1994	Heavy-duty diesel vapour phase and particulates	Soxhlet (DCM & acetone)	Classical silica gel & NP HPLC	GC/MS	PAH	Westerholm and Li
1991	Heavy-duty diesel vapour phase and particulates	Soxhlet (DCM & acetone)	Classical silica gel & NP HPLC	GC/MS (FL with on-line reduction for 1-nitropyrene)	PAH and nitro-PAH	Westerholm and Li
1991	Diesel run on alternative fuels	Ultrasonication (toluene)	Silica packed columns	GC-FID	EPA 16 priority pollutant PAH	Ziejewski et al

(+) = HPLC end analysis techniques used
KEY:

SPE = solid phase extraction cartridges	TEA = thermal energy analyser	RP = reverse phase
TLC = thin layer chromatography	NICI = negative ion chemical ionisation	EI = electron impact mode
FID = flame ionisation detector	ITD = ion trap mass detector	
NP = normal phase	FL = fluorescence detection	

Table A.4.2 GC Analysis for Automotive Applications (cont.)

Year	Sample type	Extraction used	Clean up	Detectors (+)	Compounds detected	Ref.
1992	Diesel exhaust particulate matter	SFE	HPLC connected directly to GC	GC-FID	oxy-PAH	Kelly et al
1992	Diesel exhaust particulate matter	SFE	Classical	GC-FID and GC/MS (in full scan and SIM modes)	PAH and 1-nitropyrene	Paschke et al
1992	Diesel exhaust particles	Soxhlet (DCM)	NP HPLC	GC/MS with SIM	nitro-PAH	Ball and Young
1992	Diesel exhaust extracts	Soxhlet (DCM)	Classical clean-up	GC/MS EI	PAH and nitro-PAH	Mason et al
1993	Heavy-duty diesel semi-volatiles	-	-	TCT-GC/MS	PAH and alkyl-PAH	Newkirk et al
1993	Particulates from HD diesel trucks	Ultrasonication		GC/MS	PAH and oxy-PAH	Rogge et al
1994	Diesel, gasoline, and two-stroke semi-volatiles particulates	-	-	TCT-GC-ITD	PAH	Andersson
1994	Diesel and air particulates	Ultrasonication (acetone)	SPE & on-line reduction	GC/MS EI	nitro-PAH	Scheepers et al
1994	Heavy-duty diesel vapour phase and particulates	Soxhlet (DCM & acetone)	Classical silica gel & NP HPLC	GC/MS	PAH	Westerholm and Li
1994	Vehicle tunnel samples	-	-	TCT-GC/IRD/MS and TCT-GC-FID	Light PAH	Zielinska and Fung
1994	Diesel particulate	Soxhlet (DCM)	Classical silica gel	GC/MS (in low and high resolution modes)	PAH and nitro-PAH	Mitchell et al
1995	Heavy-duty diesel semi-volatiles	-	-	TCT-GC/MS	PAH and alkyl-PAH	Hammerle et al
1995	Coal- and petroleum derived liquid fuels	-	Alumina columns	GC and GC/MS	PAH	Lai and Song
1996	Semi-volatile and particulate PAH from undiluted diesel gas	Soxhlet (DCM) for particulates	SPE (silica)	GC-FID (HPLC with FL)		

(+) = HPLC end analysis techniques used
KEY:

SPE = solid phase extraction cartridges	TEA = thermal energy analyser	RP = reverse phase
TLC = thin layer chromatography	NICI = negative ion chemical ionisation	EI = electron impact mode
FID = flame ionisation detector	ITD = ion trap mass detector	
NP = normal phase	FL = fluorescence detection	

Table A.4.3 GC Analysis for Environmental Applications

Year	Sample type	Extraction used	Clean up	Detectors (+)	Compounds detected	Reference
1982	Carbon black and air particulate	Soxhlet (toluene)	NP HPLC	GC/MS NICI	nitro-PAH	Ramdahl and Urdal
1985	Diesel particulate	Soxhlet (DCM)	Classical clean-up followed by NP HPLC	GC-FID, GC/MS EI	PAH, nitro-PAH and oxy-PAH	Wise et al
1985	Atmospheric study	Soxhlet (DCM	NP HPLC	GC/MS in SIM	Fluoranthene and pyrene and nitro-derivatives	Pitts et al
1986	Atmospheric study	Soxhlet (DCM)	NP HPLC	GC/MS in SIM	Fluoranthene and pyrene and nitro-derivatives	Arey et al
1987	Reaction chamber study	Soxhlet (DCM) for polyurethane plugs	NP HPLC	GC/MS in SIM (RP HPLC with UV)	Naphthalene and biphenyl and their nitro- and oxy-derivatives	Atkinson et al
1987	Atmospheric study of Los Angeles	Soxhlet (DCM) & elution of Tenax-GC cartridges (diethyl ether)	NP HPLC of PUF and filters	Cooled on-column GC/MS in SIM. Direct injection of Tenax extracts	PAH and nitro-PAH	Arey et al
1989	Reaction chamber study	Soxhlet (DCM) for polyurethane plugs	NP HPLC	GC/MS in SIM and direct TCT of Tenax GC cartridges	Naphthalene and nitro-derivatives	Zielinksa et al
1990	SRM 1649, air and burner particulates	Soxhlet (cyclohexane)	liquid/liquid & NP HPLC	GC/MS in SIM, GC-ECD	nitro-PAH	Schneider et al
1990	Reaction chamber study	Elution of Tenax cartridges (diethyl ether)	Direct injection of extract	GC/MS in SIM	PAH and nitro-PAH	Atkinson et al
1992	Airborne semi-volatiles and particulate	Ultrasonication (acetone)		GC/MS EI	PAH	Hawthorne et al
1992	Urban and semi-urban air samples	Ultrasonication (DCM)	Extensive, including NP HPLC	GC-FPD, GC-NPD, GC/MS EI	PAH, nitro-PAH, oxy-PAH	Fernandez and Bayona

(+) = HPLC end analysis techniques used

KEY:

NP = normal phase	RP = reverse phase	SPE = solid phase extraction cartridges
NICI = negative ion chemical ionisation	PUF = polyurethane foam plugs	ECD = electron capture detector
TCT = thermal desorption cold trapping	SIM = selective ion monitoring	RP = reverse phase
EI = electron impact mode	UV = ultra-violet detection	FPD = flame photometric detector
FID = flame ionisation detector	SIM = selective ion monitoring	ITD = ion trap mass detector

Table A.4.3 GC Analysis for Environmental Applications (cont.)

Year	Sample type	Extraction used	Clean up	Detectors (+)	Compounds detected	Reference
1992	Particulates from an indoor coal combustor	Soxhlet (DCM)	NP HPLC	GC/MS	PAH and alkyl derivatives	Chuang et al
1992	Reaction chamber study	Soxhlet (DCM) for polyurethane plugs	NP HPLC for PUF	GC/MS (with TCT for Tenax cartridges)	Fluorene and nitro-fluorenes	Helmig et al
1993	Particulates from a coal fired stove	Condensation trap	-	GC/MS in SIM	PAH and oxy-PAH	Knobloch and Engewald
1993	Petroleum refinery catalysts	Soxhlet (Toluene)		GC/MS	PAH	Beard et al
1993	Size fractions of airborne particulate	Soxhlet (DCM)	Classical column	GC-FID and GC/MS	PAH	Aceves and Grimalt
1993	Urban air particulate matter	Soxhlet (Benzene)	Classical silica glass columns & NP HPLC	GC/MS	PAH and chlorinated PAH	Nilsson and Ostman
1993	Leaf particulate matter	Ultrasonication	-	GC/MS	PAH	Rogge et al
1993	Airborne particulate matter	Ultrasonication	-	GC/MS	PAH and oxy-PAH	Rogge et al
1993	Particles from a residential natural gas heater	Ultrasonication	-	GC/MS	PAH and oxy-PAH	Rogge et al
1993	Airborne particulate matter	Soxhlet (DCM)	Classical	GC/MS	PAH, nitro-PAH, oxy-PAH	Bodzek et al
1994	Cigarette smoke	Ultrasonication	-	GC/MS	PAH	Rogge et al
1994	Airborne vapour and particulate	Soxhlet (hexane)	Simple florisil column	GC/MS (RP HPLC with FL)	PAH	Halsall et al
1995	Air samples	SFE	Minimal	GC/MS	PAH	Kanagasabapathy et al
1995	Reaction chamber study	Soxhlet (DCM) for PUF	NP HPLC for PUF	GC/MS (with TCT for Tenax cartridges)	PAH, nitro-PAH, nitro-oxy-PAH	Sasaki et al
1995	Urban air extracts	-	-	on-line HPLC-GC-ITD	PAH, nitro-PAH, and -oxy-PAH	Lewis et al
1995	Air samples	Solid-phase micro-extraction-	-	Direct injection GC/MS	PAH	Chai and Pawliszyn

(+) = HPLC end analysis techniques used

KEY:

NP = normal phase	FPD = flame photometric detector	EI = electron impact mode
SPE = solid phase extraction cartridges	TCT = thermal desorption cold trapping	RP = reverse phase
PUF = polyurethane foam plugs	ITD = ion trap mass detector	FL = fluorescence detection
FID = flame ionisation detector	SIM = selective ion monitoring	

Table A.4.4 HPLC Analysis for Automotive Applications

Year	Sample type	Extraction used	Clean up	Detectors	Compounds detected	Reference
1982	Diesel, gasoline particulates and air samples	Soxhlet (benzene /ethanol)	Minimal	FL (with off-line reduction for nitro-PAH)	PAH and nitro-PAH	Gibson
1983	Diesel particulates	Ultrasonication (cyclohexane)	Minimal	FL	PAH	Zierock et al
1984	Road tunnel sample			FL	large ring PAH	Hering et al
1984	Road tunnel sample	Ultrasonication (cyclohexane)	Minimal	FL	3 - 7 ring PAH	Miguel
1984	Diesel and air particulate	Soxhlet (DCM)	Extensive, including NP HPLC	FL (with off-line reduction for nitro-PAH)	PAH and nitro-PAH	Pederson et al
1984	Diesel	Soxhlet (DCM)	Silica column	FL	PAH	Shore
1985	Combustion of n-decane in a diesel engine	Ultrasonication (benzene /ethanol)	TLC	FL	PAH	Hayano et al
1986	Gasoline and diesel particulates	Soxhlet (DCM)	Minimal	FL (with on-line reductive column)	nitro-PAH	Tejada et al
1986	DI and IDI particulates	Soxhlet (DCM)	Silica column & off-line reduction of nitro-PAH	FL	PAH and nitro-PAH	Shore
1987	Light-duty diesel, conventional gasoline, and lean-burn gasoline extracts	Soxhlet (DCM)	Silica column & off-line reduction of nitro-PAH	FL	PAH and nitro-PAH	Shore et al
1988	Air & diesel particulate	Soxhlet (DCM)	NP HPLC	Electrochemical and FL with on-line reduction	nitro-PAH	MacCrehan et al
1989	Gasoline, pre- and post-catalyst	Soxhlet (toluene)	Silica column & off-line reduction of nitro-PAH	FL	4 - 6 ring PAH and nitro-PAH	Cooper and Shore

KEY:

TLC = thin layer chromatography
NP = normal phase HPLC
FL = fluorescence
SPE = solid phase extraction cartridges
CL = chemiluminescence

Table A.4.4 HPLC Analysis for Automotive Applications (cont.)

Year	Sample type	Extraction used	Clean up:	Detectors:	Compounds detected	Reference
1990	Car particulates	Ultrasonication (benzene /ethanol)	SPE (alumina)	CL after on-line electrochemical reduction	nitropyrenes	Imaizumi et al
1991	Diesel particulate	Modified soxhlet (DCM)	Classical	Photodiodearray and FL (with on-line reduction for nitro-PAH)	PAH and nitro-PAH	Götze et al
1992	Diesel and air samples	Ultrasonication (benzene /ethanol)	-	CL (with on-line reduction)	nitro-PAH	Hayakwa et al
1994	Diesel samples	Soxhlet (DCM)	Silica columns	CL (with on-line reduction)	nitro-PAH	Li and Westerholm
1994	Diesel extracts	Refluxed (toluene)	Liquid/liquid & Silica columns	FL (with on-line reduction)	nitro-PAH	Veigl et al

Table A.4.5 HPLC Analysis for Environmental Applications

Year	Sample type	Extraction used	Clean up:	Detectors (+)	Compounds detected	Reference
1984	Carbon black	Soxhlet (toluene)	Minimal (NP HPLC for GC/MS)	UV, FL, CL (GC/MS)	nitro-PAH	Sigvardson and Birks
1985	Water	Cyclohexane	Alumina column	UV and FL	15 PAH	Sorrell and Reding
1989	Air particulate samples	Ultrasonication (DCM)	Minimal	UV and FL	12 PAH	Maher et al
1993	Air particulates	Ultrasonication (DCM)	Classical silica gel clean-up	Electrochemical detection	nitro-PAH and oxy-PAH	Galceran and Moyano
1993	Cigarette smoke	Agitation with solvent	SPE (amino)	FL	4-5 ring PAH	Dumont et al
1994	Airborne particle size fractions			FL	PAH	Venkataraman and Friedlander
1994	Photochemical reaction study	Ultrasonication		FL	PAH	McDow et al
1995	Urban air particulates	Ultrasonication (benzene/ethanol)	Minimal (off-line reduction)	CL	nitro-PAH	Hayakawa et al
1995	Gas- and particulate phases of environmental tobacco smoke	Ultrasonication (cyclohexane)	Silica columns	FL	PAH	Gundel et al
1996	Airborne particulate	Soxhlet (DCM)	Silica column and NP HPLC	FL	PAH and nitro-PAH	Smith et al

(+) = GC end analysis techniques used

KEY:

NP = normal phase HPLC	FL= fluorescence	SPE = solid phase extraction cartridges
SPE = solid phase extraction cartridges	UV = ultra-violet	CL= chemiluminescence
TLC = thin layer chromatography		

APPENDIX 5 – PAH CONTENT OF GASOLINES

The following tabulates the fuels, PAH type and quantity quoted in the references reviewed for this report.

Fuels	PAH	Amount	References
Regular gasoline	BaP	1.0 ppm	Begeman and Colucci (1970)
	BaA	1.4 ppm-2.0 ppm	
Premium gasoline	BaP	2.0 ppm-2.2 ppm	
	BaA	3.2 ppm	
Indolene-30	BaP	3.7 ppm	
Indolene-clear gasoline	BaP	4.4 ppm	
Mix pump gasoline	BaP	0.8-1.0 ppm	
	BaA	1.3 ppm	
A (O5-A44)	BaP	3 µg/gal	Hoffman et al (1971)
	BaA	6 µg/gal	
B (O11.5-A10)	BaP	350 µg/gal	
	BaA	460 µg/gal	
C (O5-A15)	BaP	245 µg/gal	
	BaA	660 µg/gal	
D (O11-A22)	BaP	1855 µg/gal	
	BaA	4680 µg/gal	
E (O7-A28)	BaP	795 µg/gal	
	BaA	2410 µg/gal	
Indolene (O4-A28)	BaP	9080 µg/gal	
	BaA	13100 µg/gal	
G (O20-A31)	BaP	56 µg/gal	
	BaA	25 µg/gal	
H (010,5-A15,5)	BaP	545 µg/gal	
	BaA	935 µg/gal	
I (O9,5-A8,5)	BaP	-	
	BaA	-	
J (O1-A15,0)	BaP	-	
	BaA	-	
K (O5-A56)	BaP	-	
	BaA	-	
Refor. R-B(O3-A47)	BaP	2480 µg/gal	
	BaA	12800 µg/gal	
Refor. R-C(O1-A59)	BaP	13070 µg/gal	
	BaA	14200 µg/gal	
Refor. R-D(O0-A35)	BaP	4660 µg/gal	
	BaA	6020 µg/gal	
Refor. R-E(O0-A58)	BaP	1785 µg/gal	
	BaA	4130 µg/gal	
Refor. R-F(O0-A62)	BaP	6000 µg/gal	
	BaA	13900 µg/gal	
HALO (O3-A38)	BaP	1820 µg/gal	
	BaA	2240 µg/gal	
LALO (O4.5-A9.5)	BaP	304 µg/gal	
	BaA	1420 µg/gal	
LAHO (O17.5-A11.0)	BaP	129 µg/gal	
	BaA	461 µg/gal	
HAHO (O17.5-A39.0)	BaP	802 µg/gal	
	BaA	3980 µg/gal	

Fuels	**PAH**	**Amount**	**References**
Cat.refor./Straight-run	BaP	0.07 ppm	Zaghini et al (1973)
C9-C10 Arom. hydroc.	BaP	0.9 ppm	
A) Comm. Unleaded Prem.	Pyr	124-712 µg/gal	Gross (1974)
	BaA	28-134 µg/gal	
	MBaA	34-99 µg/gal	
	DM/EBaA	11-28 µg/gal	
	BaP	26-89 µg/gal	
	BeP	26-98 µg/gal	
	BghiP	55-74 µg/gal	
	MBaP	17-37 µg/gal	
	MBeP	19-37 µg/gal	
AHC) Same+20%442FEP H.Cat.Nap.	Pyr	1040 µg/gal	
	BaA	234 µg/gal	
	MBaA	238 µg/gal	
	DM/EBaA	97 µg/gal	
	BaP	201 µg/gal	
	BeP	204 µg/gal	
	BghiP	205 µg/gal	
	MBaP	102 µg/gal	
	MBeP	123 µg/gal	
B3P) Comm. Leaded Prem with Phosph.	Pyr	16880-41170 µg/gal	
	BaA	6920-12810 µg/gal	
	MBaA	6860-6920 µg/gal	
	DM/EBaA	1730 µg/gal	
	BaP	6320-8330 µg/gal	
	BeP	5020-10920 µg/gal	
	BghiP	5130-14060 µg/gal	
	MBaP	2220-2850 µg/gal	
	MBeP	2540-2740 µg/gal	
C3) Comm. Leaded Prem without P	Pyr	23670 µg/gal	
	BaA	10340 µg/gal	
	MBaA	12260 µg/gal	
	DM/EBaA	3990 µg/gal	
	BaP	8970 µg/gal	
	BeP	6940 µg/gal	
	BghiP	10260 µg/gal	
	MBaP	5730 µg/gal	
	MBeP	6190 µg/gal	
D) Semi-Comm. Unleaded Prem.	Pyr	20890 µg/gal	
	BaA	7810 µg/gal	
	MBaA	10320 µg/gal	
	DM/EBaA	4020 µg/gal	
	BaP	8060 µg/gal	
	BeP	6260 µg/gal	
	BghiP	9490 µg/gal	
	MBaP	6120 µg/gal	
	MBeP	5940 µg/gal	
H.Cat.Nap.	Pyr	2340 µg/gal	
	BaA	920 µg/gal	
	MbaA	1030 µg/gal	
	DM/EbaA	409 µg/gal	
	BaP	795 µg/gal	
	BeP	798 µg/gal	
	BghiP	804 µg/gal	
	MbaP	412 µg/gal	
	MBeP	520 µg/gal	

Fuels	PAH	Amount	References
G1 Leaded gasoline	Phen	55 ppm (µg/g)	Egebäck et al (1983)
	Flu	6.8 ppm	
	Pyr	18 ppm	
	B(ghi)F	<0.09 ppm	
	Cpp	<0.09 ppm	
	BaA	4.0 ppm	
	Chr	3.0 ppm	
	B(b&k)F	2.9 ppm	
	BeP	4.0 ppm	
	B(a)P	3.1 ppm	
	Ind P	1.0 ppm	
	B(ghi)P	3.7 ppm	
	Cor	0.61 ppm	
G2 Leaded gasoline	Phen	58 ppm	
	Flu	2.8 ppm	
	Pyr	15 ppm	
	B(ghi)F	<0.5 ppm	
	Cpp	<0.5 ppm	
	BaA	0.99 ppm	
	Chr	1.3 ppm	
	B(b&k)F	1.2 ppm	
	BeP	1.4 ppm	
	B(a)P	0.67 ppm	
	Ind P	0.26 ppm	
	B(ghi)P	1.9 ppm	
	Cor	0.45 ppm	
G3 Unleaded gasoline	Phen	57 ppm	
	Flu	2.9 ppm	
	Pyr	14 ppm	
	B(ghi)F	0.26 ppm	
	Cpp	<0.03 ppm	
	BaA	0.68 ppm	
	Chr	1.1 ppm	
	B(b&k)F	0.97 ppm	
	BeP	1.4 ppm	
	B(a)P	0.78 ppm	
	Ind P	0.28 ppm	
	B(ghi)P	2.4 ppm	
	Cor	0.69 ppm	
M15-1 Methanol leaded gasoline	Phen	45 ppm	
	Flu	1.1 ppm	
	Pyr	11 ppm	
	B(ghi)F	0.06 ppm	
	Cpp	<0.02 ppm	
	BaA	<0.25 ppm	
	Chr	0.26 ppm	
	B(b&k)F	0.32 ppm	
	BeP	0.48 ppm	
	B(a)P	0.12 ppm	
	Ind P	<0.04 ppm	
	B(ghi)P	1.0 ppm	
	Cor	1.4 ppm	

Fuels	PAH	Amount	References
M15-2 Methanol unleaded gasoline	Phen	52 ppm	
	Flu	7.0 ppm	
	Pyr	17 ppm	
	B(ghi)F	0.30 ppm	
	Cpp	<0.03 ppm	
	BaA	0.82 ppm	
	Chr	0.96 ppm	
	B(b&k)F	0.93 ppm	
	BeP	1.3 ppm	
	B(a)P	0.50 ppm	
	Ind P	0.22 ppm	
	B(ghi)P	1.7 ppm	
	Cor	0.32 ppm	
E23 Ethanol unleaded gasoline	Phen	55 ppm	
	Flu	6.6 ppm	
	Pyr	18 ppm	
	B(ghi)F	0.42 ppm	
	Cpp	<0.03 ppm	
	BaA	0.79 ppm	
	Chr	0.94 ppm	
	B(b&k)F	1.0 ppm	
	BeP	1.3 ppm	
	B(a)P	0.51 ppm	
	Ind P	0.27 ppm	
	B(ghi)P	1.8 ppm	
	Cor	0.36 ppm	
F1	Phen	<0.01 mg/l	Westerholm et al (1988)
	Anth	<0.01 mg/l	
	Flu	<0.01 mg/l	
	Pyr	<0.01 mg/l	
	B(ghi)F	<0.01 mg/l	
	CyPenta(cd)Py	<0.01 mg/l	
	B(a)A	<0.01 mg/l	
	Chr/Triphen	<0.01 mg/l	
	B(e)py	<0.01 mg/l	
	B(a)py	<0.01 mg/l	
	IndPy	<0.01 mg/l	
	B(ghi)pery	<0.01 mg/l	
	Cor	<0.01 mg/l	
F2	Phen	1.6 mg/l	
	Anth	0.33 mg/l	
	Flu	0.1 mg/l	
	Pyr	0.84 mg/l	
	B(ghi)F	1.1 mg/l	
	CyPenta(cd)Py	<0.01 mg/l	
	B(a)A	0.74 mg/l	
	Chr/Triphen	2.3 mg/l	
	B(e)py	0.29 mg/l	
	B(a)py	0.18 mg/l	
	IndPy	<0.01 mg/l	
	B(ghi)pery	0.32 mg/l	
	Cor	0.72 mg/l	

Fuels	PAH	Amount	References
F3	Phen	7.6 mg/l	
	Anth	2.6 mg/l	
	Flu	4.6 mg/l	
	Pyr	1.2 mg/l	
	B(ghi)F	0.8 mg/l	
	CyPenta(cd)Py	<0.01 mg/l	
	B(a)A	0.89 mg/l	
	Chr/Triphen	1.1 mg/l	
	B(e)py	0.31 mg/l	
	B(a)py	0.53 mg/l	
	IndPy	<0.01 mg/l	
	B(ghi)pery	0.43 mg/l	
	Cor	<0.01 mg/l	
F4	Phen	27 mg/l	
	Anth	2.7 mg/l	
	Flu	4.5 mg/l	
	Pyr	8.9 mg/l	
	B(ghi)F	1.0 mg/l	
	CyPenta(cd)Py	<0.01 mg/l	
	B(a)A	0.53 mg/l	
	Chr/Triphen	1.4 mg/l	
	B(e)py	1.4 mg/l	
	B(a)py	0.58 mg/l	
	IndPy	3.9 mg/l	
	B(ghi)pery	2.1 mg/l	
	Cor	0.38 mg/l	
Gasoline A	Group 1 Napht-Cor	18 µg/ml	Laveskog (1996)
	Group 2 Phen-Cor	0.47 µg/ml	
Gasoline T	Group 1 Napht-Cor	26 µg/ml	
	Group 2 Phen-Cor	0.76 µg/ml	
Gasoline 1	Group 1 Napht-Cor	420 µg/ml	
	Group 2 Phen-Cor	26 µg/ml	
Gasoline R	Group 1 Napht-Cor	2630 µg/ml	
	Group 2 Phen-Cor	85 µg/ml	
Gasoline 2	Group 1 Napht-Cor	1618 µg/ml	
	Group 2 Phen-Cor	78 µg/ml	

Egebäck et al (1983)

A common gasoline quality available in 1981 was used as the reference fuel.

The other fuels were chosen as representatives of the gasoline available before year 1990; the gasoline were made to meet the requirements of a Swedish medium gasoline, which normally is made by mixing 60% v/v of premium (RON=98) and 40% v/v of regular gasoline (RON=93).

G1 was a gasoline of medium quality blended from reformate, light straight run gasoline and butanes. The lead content was kept below 0.15 g/l.

G2 was made from regular gasoline blended from light catalytically cracked gasoline and reformate and a premium gasoline.

G3 was a lead-free quality with octane numbers below the present requirements for regular gasoline. It contained reformate, some heavy catalytically cracked gasoline, butane, straight run gasoline and a small portion of toluene.

Westerholm et al (1988)

The four unleaded gasoline were prepared as follow:

Fuel F1 was made up of 69% v/v of a fraction of reformate, obtained by distillation up to 160°C and 31% v/v of isopentane.

Fuel F2 was made up of 15% v/v of the residue from the distillation of the reformate with a boiling point higher than 160°C, 65% v/v of isooctane and 20% v/v of n-pentane.

Fuel F3 was made up of 69% v/v of reformate and 31% v/v of isopentane.

Fuel F4 was made up by a refinery to correspond to U.S. unleaded gasoline.

Laveskog (1996)

Gasoline A was a pure alkylate;

Gasoline T was composed of 79% alkylate, 16% ethanol and 5% xylenes; this gasoline is sold as a motor fuel for a fleet of taxi cars in Gothenburg;

Gasoline 1 was a stage two reformulated gasoline in Finland sold as unleaded 95 RON gasoline.

Gasoline 2 is an early batch of “environment class 2”-gasoline sold in Sweden since January 1994.

Gasoline R is an unleaded 95 RON standard gasoline sold on the market in Sweden and used as a test gasoline for the Swedish automobile manufacturers.

The PAH were added together in three groups of compounds:

Group 1 Napht-Cor

Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)fluorene, benzo(b)fluorene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(123-cd)pyrene, benzo(ghi)perylene, dibenzo(a,h)anthracene, coronene

Group 2 Phen-Cor

Phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)fluorene, benzo(b)fluorene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(123-cd)pyrene, benzo(ghi)perylene, dibenzo(a,h)anthracene, coronene

Group 3 Benzo(a)f-Cor

Benzo(a)fluorene, benzo(b)fluorene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(123-cd)pyrene, benzo(ghi)perylene, dibenzo(a,h)anthracene, coronene