Automotive polycyclic aromatic hydrocarbons (PAH)

A CONCAWE literature study reveals the need for much more work; CONCAWE will contribute.

The International Agency for Research on Cancer has classified certain PAH as carcinogenic to animals and probably carcinogenic to humans. Evidence for the carcinogenicity of some PAH is equivocal; for others there is no evidence of carcinogenic potential, and there are many others that have not even been tested. There is no common definition for the term 'polycyclic aromatic hydrocarbon'. While in some scientific disciplines PAH are understood to be individual polycyclic aromatic hydrocarbons, in other areas the same term is used to define the total of all di- and tri+ aromatic components determined in diesel fuel. Even in this area there is still some conflict, for example, the Swedish diesel fuel specification uses the term PAH to refer only to tri+ aromatics.

Due to the concern about potential health effects the European Commission will propose an Air Quality Standard for PAH under a Daughter Directive under the EU Air Quality Assessment and Management Directive. The last *CONCAWE Review* outlined the complexity of the Daughter Directive for suspended particulate matter (PM_{10}). The issue for PAH is also very complex with contributions to ambient PAH coming from a range of different emission sources. This again necessitates experts from various scientific disciplines and industries working together. In this context it is worth noting that recent studies in various locations have demonstrated that the levels of PAH in current ambient air are the lowest ever measured largely as a result of the reduced use of coal in domestic and other heating.

In order to understand the contribution from automotive vehicles emissions to ambient PAH, CONCAWE have conducted a comprehensive literature review of polycyclic aromatic hydrocarbons levels in automotive exhaust emissions and fuels. This report is soon to be published.

The following overview is based on the report of the literature study.

THE KEY TO RELIABLE DATA LIES IN REPRESENTATIVE SAMPLING AND THE ANALYTICAL APPROACH

PAH are currently unregulated pollutants in automotive exhaust emissions and there is no consensus on the major PAH to be analysed, although the 16 PAH listed by the EPA are the most commonly measured. There is also no standard analytical methodology available. The analytical situation is very complicated because a sample taken from the exhaust includes a wide range of individual compounds and complicated 'clean-up' procedures are needed to prevent interference in the analysis. The range of specific structures that the analytical techniques employed at different laboratories are capable of quantifying varies greatly. It is generally assumed by each research group that the species they identify are representative of polycyclic aromatic hydrocarbons as a whole.

PAH may be emitted to the atmosphere either in the vapour phase or associated with fine particles. Therefore, data on PAH exhaust are required on both vapour and particle phases using

appropriate sampling procedures. However, the contribution made by the vapour phase PAH has largely been neglected.

During the study it became evident 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.

PAH IN THE EXHAUST

There is a large quantity of literature available reporting on the measurement of automotive PAH emissions. The majority of the literature relates to diesel emissions and predominantly to PAH in particulate. Vapour phase PAH emissions are addressed in fewer references and there is also much less information relating to gasoline PAH emissions. The nature of gasoline emissions (i.e. predominantly vapour), and the collection systems used, mean that results given are closer to the 'total' PAH emitted.

Surprisingly, there are few authors who attempt to correlate fuel composition/PAH levels with those measured in the exhaust or, indeed, who even include the measurement of PAH in the test fuels used.

Of particular importance is the fact that total hydrocarbon (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 not well determined) fraction of the particulate borne HC, and an even smaller (and even less well determined) fraction of the vapour phase HC.

Due to the wide range of test programme configurations reported (engine/vehicle type, driving cycle, sampling and analytical procedures) it is difficult to define maximum and minimum values of PAH in exhaust.

MECHANISMS OF FORMATION OF EXHAUST PAH ARE COMPLEX; FUEL PAH IS ONE CONTRIBUTOR

Several routes of formation are involved in the generation of exhaust PAH emissions, and individual mechanisms can contribute to a greater or lesser extent (Figure 1). The fraction of the fuel PAH which survives combustion is influenced by engine design, test cycle and the compatibility of fuel and engine. Other exhaust PAH can be created from non-PAH fuel components by pyrosynthesis which can be related to the amount of soot in the exhaust and can be a substantial fraction. PAH present from either route may also undergo further modifications thus making it difficult to interpret which formation route is the dominant one. The lubricating oil may also contribute to the exhaust PAH from PAH which have built up in the oil during the combustion process. Further complications in relating PAH to its source and to obtain repeatable results may come from the exhaust sampling system which can also act as a sink or source for PAH. The major mechanisms for PAH formation in the exhaust are shown in Figure 1. Unfortunately much of the published literature does not provide information in such a form to enable interpretation of the findings.

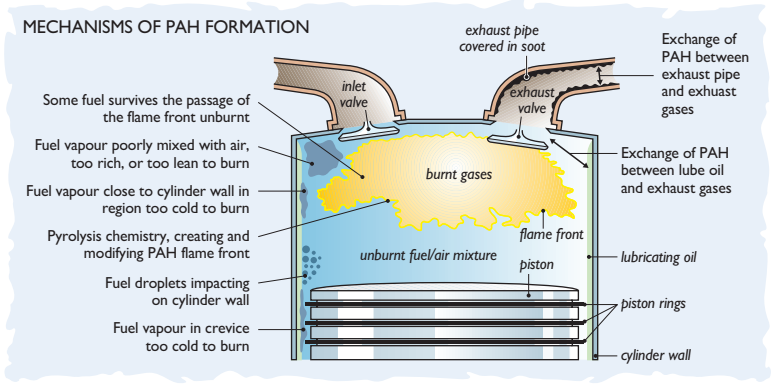
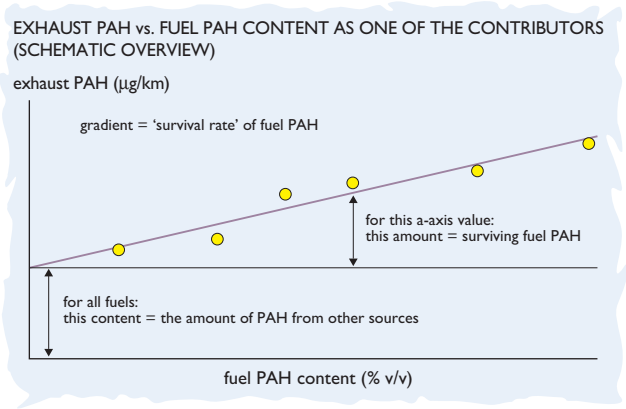


Figure 1
Several routes of formation are involved in the generation of exhaust PAH emissions.

PAH IN THE FUEL

CONCAWE attempted to summarize (from the limited data reported on commercial type fuels) the individual PAH levels most commonly determined in gasoline and diesel fuel. However, values may not strictly be comparable since different analytical methods have been used across the different references. In addition the chemical composition of a fuel depends on various factors (e.g. refinery configuration, blending streams, crude oil sources), and historical data are therefore unlikely to reflect current or future PAH content in automotive fuels. With regard to diesel fuel conflicting terms are used across the literature when describing 'PAH' in the fuel as outlined in the introduction.

Figure 2
Exhaust PAH versus fuel PAH content as one of the contributors (schematic overview)



The use of alternatives to conventional gasoline or diesel fuel is finding a growing niche market. These generally appear to 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, thus providing independent evidence for the pyrosynthetic route.

AFTER-TREATMENT IS HIGHLY EFFECTIVE IN DECREASING PAH EMISSIONS

PAH emissions from automotive sources are highly variable and are dependent on a number of factors, including fuel composition. However, published data, though limited in their scope, indicate unequivocally that after-treatment systems are a highly effective means to substantially decrease PAH emissions, with diesel after-treatment devices showing some greater variation.

CONCLUSIONS

PAH form only a small part of the fuel, particularly in the case of gasoline. Total HC emissions are very low from modern engines and the scatter in measuring exhaust PAH levels is large. Therefore, well-designed test programmes are required. To ensure comparable results, the PAH to be analysed need careful definition, and a standard analytical method is required.

The recent report by CONCAWE has allowed potential future work to be identified and defined. Whilst for gasoline, it would appear that there is sufficient literature to understand the nature of current vehicle PAH emissions, more work is needed for diesel, both light- and heavy-duty. Published results on diesel 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 PAH content.

CONCAWE IS ACTIVE

Following the literature survey, CONCAWE has become involved in practical work to address some of the reported uncertainties. In preparation of a test programme, Ricardo Consulting Engineers and CONCAWE have conducted work in a cooperative research programme to develop a technique applicable to the simultaneous collection and measurement of both vapour phase and particulate bound PAH in exhaust emissions (SAE paper 982727).

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.