Automotive emissions of polycyclic aromatic hydrocarbons

The International Agency for Research on Cancer (IARC) has classified certain individual polycyclic aromatic hydrocarbons (PAH) as carcinogenic to animals and probably carcinogenic to humans. Current PAH concentrations in European ambient air are the lowest ever measured, largely as a result of the reduced use of coal in domestic and other heating. Nevertheless, in 1999 the European Commission created a Working Group to review the knowledge on PAH in ambient air and to consider the need for, and implications of, regulations on the concentrations of PAH under the Air Quality Framework Directive (96/62/EC).

Amongst the EU Member States, only Italy currently has legally enforceable ambient air standards for PAH but five others have issued guidance for planning and policy purposes, all based on the use of benzo(a)pyrene (B[a]P) as a marker for PAH. Road transport is a relatively small contributor to B[a]P emissions. By 2010, domestic combustion of solid fuels, in particular wood, is expected to be by far the largest contributor to total European B[a]P emissions.

In order to understand the contribution from road transport, CONCAWE carried out a literature review of PAH levels in automotive exhaust emissions and fuels. The results of this review (CONCAWE report 98/55) clarified some of the complexities in the area of automotive exhaust PAH emissions but also identified some key knowledge gaps. Although the literature on diesel PAH emissions is extensive, there is a striking lack of definitive investigations into the link between diesel fuel PAH content and PAH exhaust emissions.

CONCAWE has now studied the relationship between fuel PAH and exhaust PAH emissions from a range of vehicles and fuels in a rigorous test programme. Both particulate-bound and vapour phase PAH emissions were measured for the 16 PAH species targeted by the US EPA.

The total measured exhaust PAH represented less than 1% of the total emitted hydrocarbons, with the majority found to be in the vapour phase, dominated by naphthalene. Reducing diesel fuel polyaromatic content from 12% to near zero had a relatively small effect on B[a]P emissions, although effects on 2+ and 3+ ring species were larger. A significant portion of B[a]P emissions was shown to originate from combustion. Newer technology diesel vehicles with effective after-treatment showed reduced PAH emissions and lower sensitivity to fuel polyaromatics content. As expected, a modern three-way catalyst (TWC) gasoline car gave very low PAH exhaust emissions, even with the extreme fuel qualities investigated.

OBJECTIVES OF THE PROGRAMME

The objectives of this programme were set in view of the conclusions and knowledge gaps identified in the literature survey and were:

- to evaluate the relationship between diesel fuel polyaromatics content and exhaust PAH emissions;

- to clarify the proportion of combustion-derived versus unburned hydrocarbon PAH emissions in diesel engines; and
- to verify that a modern TWC gasoline car gives very low PAH emissions and is insensitive to extreme variations of fuel quality.

DEFINITION AND SELECTION OF PAH TO MEASURE

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

TEST PROTOCOL

There is no standardized sampling protocol for PAH from automotive exhaust emissions streams or standard analytical procedure. In order to address both particulate-bound and vapour phase PAH, a common analytical system was required. A sampling system was developed in conjunction with Ricardo Consulting Engineers, which sampled both particulate-bound and vapour phase PAH from a standard dilution system. Sampling was carried out over the relevant test cycle (MVEG cycle for light duty and ECE R49 for heavy duty). In order to identify potentially small effects, each fuel was tested a total of six times over the appropriate legislated test cycle in a statistically designed pattern. System blanks were run on a regular basis.

Although vapour phase and particulate-bound PAH were measured separately, only the sum of the PAHs are reported because there is always some transfer of PAH between the vapour and the particulate phase.

SELECTION OF VEHICLES, ENGINE AND FUELS

Four light-duty vehicles (three diesel and one gasoline) and one heavy-duty diesel engine were used in the programme. Three Euro 2 diesel passenger cars were tested in order to cover a range of light-duty vehicle technologies with and without exhaust after-treatment. One of the cars was tested both with and without an oxidation catalyst. The heavy-duty engine was a nominal Euro 2 engine typical of the bulk of the current European HD diesel fleet.

A matrix of five diesel fuels was tested. Three fuels were blended to cover a wide range of polyaromatics content (1%, 6% and 12% by IP 391), with other key parameters (sulphur, density, cetane number, T95) held constant. The other fuels were included to separate the effects of polyaromatics and total aromatics.

The gasoline car had a typical Euro 2 engine using a conventional TWC. The gasoline programme was intended only as a demonstration of the extremely low PAH emissions from conventional vehicles equipped with TWC. Hence, only two fuels were used, covering a wide range of PAH, aromatic and sulphur contents.

IMPROVING UNDERSTANDING OF PAH EMISSIONS

As a result of the careful design and preparation of the programme, it has been possible to detect small fuel effects. Although data are available for all individual 16 EPA PAH species, the report has grouped the species for comparative purposes as follows:

1. Benzo(a)pyrene (B[a]P); selected on the basis of its potential use as a 'marker' in air quality developments.
2. Sum of PAH with 3 or more rings (referred to as '3+ ring PAH'); these reflect the targeted PAH which are predominantly emitted bound to particulates.
3. Sum of all 16 species ('2+ ring PAH'); these emissions are dominated by naphthalene and this category reflects the behaviour of the targeted di-aromatics which are predominantly emitted in the vapour phase.

Table 1 shows the ranges of these identified groups and the comparison of the targeted PAH with the regulated total hydrocarbon emissions (HC). The range of results reflects the range of vehicles and fuels tested as well as the variability of the test measurements. Some effects are already clear from the table:

- The total PAH exhaust emission measured is a very small percentage of the total emitted hydrocarbons.
- The total is dominated by 2 ring PAH vapour phase emissions, principally naphthalene.
- The absolute levels of B[a]P emissions are extremely small.
- PAH emissions from the TWC gasoline vehicle are an order of magnitude lower than diesel.

Table 1
Total PAH emissions are significantly less than measured emissions of hydrocarbons.

Comparison of targeted PAH with regulated total hydrocarbon emissions

	B[a]P	*'3+ ring PAH'*	*'2+ ring PAH'*	*HC*
Heavy-duty diesel (μg/kWh)	0.11–0.24	61–165	443–2220	$264–294 \times 10^3$
Light-duty diesel (μg/km)	0.14–1.53	46–296	189–2240	$65–295 \times 10^3$
Light-duty gasoline (μg/km)	0.03–0.09	11.1–11.6	103–230	$116–128 \times 10^3$

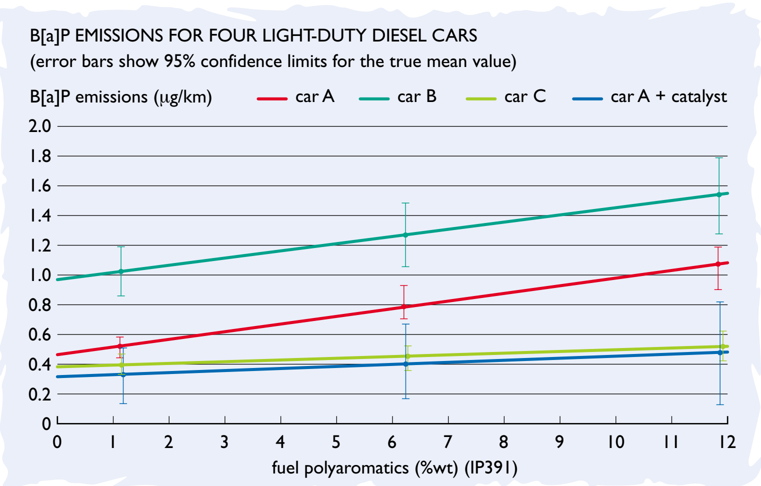
BENZO(A)PYRENE (B[A]P)

The report addresses the PAH emissions in detail based on the three groups, as described above. In view of the use of B[a]P as a marker for PAH in the current air quality debates, we focus here on the B[a]P emissions data. Figure 1 shows the data for the light-duty diesel fleet (cars A,B,C and A+ oxidation catalyst), demonstrating that:

- Reducing fuel polyaromatic content from 12% to near zero has a relatively small effect on B[a]P emissions especially for advanced technology vehicles.
- Even though B[a]P is not detectable in any of the test fuels, it is formed during the combustion process.
- Vehicle technology effects are substantial:
  - the more advanced technology vehicles produce the lowest absolute PAH emissions and have the lowest sensitivity to fuel polyaromatics content; and
  - the oxidation catalyst technology has a key influence.

Similar trends were observed in the heavy-duty engine data, though in this case, only one engine without an oxidation catalyst was tested.

Figure 1
Vehicle technology, in particular the oxidation catalyst, are key factors in influencing B[a]P emissions.



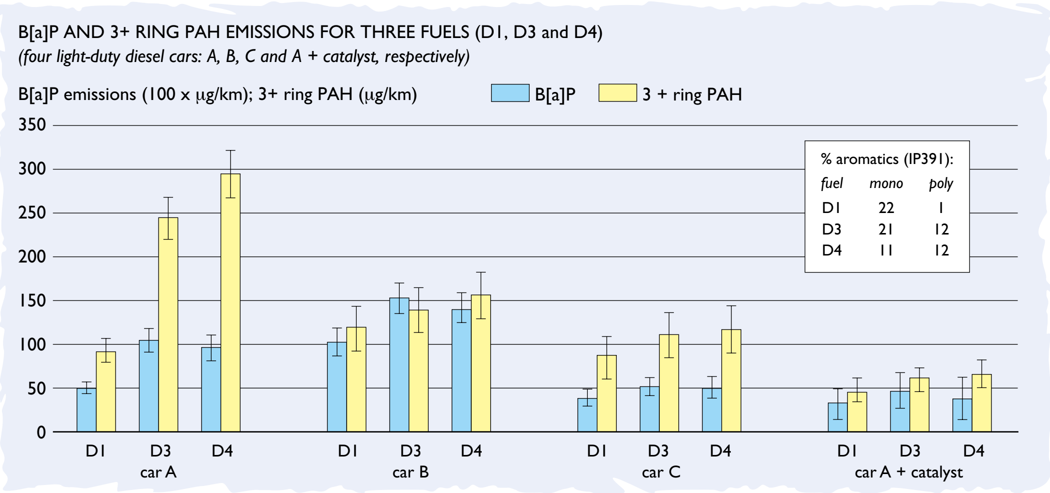


Figure 2
New vehicle technologies have a greater effect on PAH emissions than reductions in fuel PAH content.

The fuel matrix enabled the separation of the effects of poly-, mono- and total aromatics content. The data shown in Figure 2 demonstrate that:

- Fuel effects on B[a]P and 3+ ring PAH emissions correlate with polyaromatics and not with mono- or total aromatics content.
- However, PAH emissions were reduced more effectively by newer vehicle technologies, e.g., with oxidation catalyst, than by reductions in fuel PAH content

CONCLUSIONS

- The total targeted automotive PAH exhaust emissions (EPA 16; particulate-bound plus vapour phase) is a very small percentage of the total emitted hydrocarbons.
- There is no correlation between exhaust PAH and fuel total aromatics content.
- Without exhaust after-treatment, diesel fuel polyaromatics content does influence PAH emissions but a significant portion of PAH emissions is combustion-derived.
- Exhaust after-treatment is the most effective means to reduce PAH emissions and substantially reduces the sensitivity to diesel fuel polyaromatics content.
- Results from the gasoline car equipped with a TWC confirm expectations from the literature survey that PAH emissions are very low. Changes in gasoline quality over a wide range of parameters made no significant difference to B[a]P and 3+ ring PAH emissions.

Current or planned emissions abatement measures for currently legislated pollutants will contribute significantly to the reduction of exhaust PAH emissions. The key role that fuels can play in future emission control and air quality improvement is to enable the application of more efficient engine technologies, in particular exhaust after-treatment systems. In this regard, fuel sulphur content is currently the only generally recognized enabling fuel property. Reductions in fuel PAH content would have only a small and diminishing effect on ambient PAH levels.