Automotive PAH emissions

Effectively reduced with advancing emissions controls

Polycyclic aromatic hydrocarbon (PAH) emissions have been of concern for many years due to potential carcinogenic effects, with several individual PAHs having been classified by IARC as either 'probably carcinogenic to humans' or 'possibly carcinogenic to humans'. Wood burning is the largest global source of PAH emissions and is forecast to contribute by far the greatest proportion of the total EU PAH emissions by 2010. As a result of advances in technology and fuel quality, PAH emissions from automotive sources have been, and continue to be, substantially reduced. According to the EU's PAH position paper[1] they should account for only about 8% of total EU atmospheric PAH emissions by 2010.

Over the years, CONCAWE has carried out a number of studies on the relationships between fuels, vehicle technologies and emissions, including PAH emissions. In 2004, tests were completed on two advanced diesel cars using fuels with a wide range of polyaromatics content, and on two advanced gasoline cars with a fuel representative of 2005 quality with (total) aromatics content at the maximum allowed level. These data have been combined with data from tests using earlier vehicle technologies and will soon be published as a CONCAWE report.

One of the issues to contend with in a study of PAH in automotive exhaust emissions is that there is no standard sampling protocol or analytical procedure for measuring PAHs. Also there is no consensus on which PAH species should be measured, although the EU's fourth Air Quality Daughter Directive[2] has recently established a target level for benzo[a]pyrene in ambient air and requires monitoring of six other PAHs. For the CONCAWE work reported here the selection of PAHs to be measured was based on the EPA-16[3] list shown in Table 1.

Table 1 EPA-16 PAH list

This table also identifies those individual PAHs that are included in the 2+ring and 3+ring summations used in this study.

EPA 16 PAH	2+ ring	3+ ring
Naphthalene	Yes	
Acenaphthene + Acenaphthylene[1]	Yes	
Fluorene	Yes	
Phenanthrene	Yes	Yes
Anthracene	Yes	Yes
Fluoranthene	Yes	Yes
Pyrene	Yes	Yes
Benz(a)anthracene	Yes	Yes
Chrysene	Yes	Yes
Benzo(b)fluoranthene	Yes	Yes
Benzo(k)fluoranthene	Yes	Yes
Benzo(a)pyrene	Yes	Yes
Dibenz(a,h)anthracene	Yes	Yes
Benzo(g,h,i)perylene	Yes	Yes
Indeno(1,2,3-cd)pyrene	Yes	Yes

[1] *Acenaphthene/acenaphthylene cannot be separated using High Performance Liquid Chromatography (HPLC) technique.*

CONCAWE testwork

In CONCAWE's work on automotive PAH emissions, our objective was to evaluate the total PAH emissions, i.e. both particulate-bound PAH and vapour-phase PAH emissions. In order to achieve this, an analytical system was developed in conjunction with Ricardo Consulting Engineers. The sampling system used a special probe with a filter and absorbent resin, to sample both particulate-bound and vapour-phase PAH from a standard

[1] *EU Commission's position paper on PAH emissions, 2001*

[2] *EU Directive 2004/107/EC of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air*

[3] *16 PAHs designated by the US Environmental Protection Agency as Priority Pollutants*

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Table 2 A wide range of vehicle technologies were tested

Code	Phase	Year	Fuel	Engine (litres)	Combustion system	Exhaust after-treatment
A	1	1997	diesel	1.9	IDI	none
A_{cat}	1	1997	diesel	1.9	IDI	oxidation catalyst
B	1	1993	diesel	2.5	IDI	oxidation catalyst
C	1	1997	diesel	1.9	DI	oxidation catalyst (close coupled)
D	2	2002	diesel	1.9	DI	oxidation catalyst
E	2	2001	diesel	2.2	DI	particulate filter
X	1	1998	gasoline	1.4	MPI	TWC
Y	2	2002	gasoline	1.8	MPI	TWC
Z	2	2002	gasoline	1.6	lean DI	TWC+NO_x trap

IDI = indirect injection   DI = direct injection   MPI = multi point injection   TWC = 3-way catalyst

dilution tunnel[4]. Sampling was carried out using a single probe over the duration of the standard European legislative emissions test cycle (NEDC). Both exposed filter (particulate-bound) and resin (vapour-phase) PAH emissions were collected and analysed by the same technique. For evaluation of the results the particulate-bound and vapour-phase data for each PAH were added together and the total PAH emissions were then summed in two ways:

- 2+ ring PAHs—the full EPA-16 list including the volatile 2 ring species; and
- 3+ ring PAHs—those PAH species which are predominantly emitted to the atmosphere bound to particulates (see Table 1).

As mentioned earlier, PAH emissions tests were completed in 2004 on two advanced diesel cars and two advanced gasoline cars (referred to in Table 2 as Phase 2). Earlier work had been carried out on older engine/vehicle technologies (referred to in Table 2 as Phase 1)[5]. Overall, a wide range of vehicle technologies was tested, from Euro-1 through to the latest diesel vehicle technology with a particulate filter (see Table 2). A wide range of diesel fuel qualities was also tested.

Test results

Only a brief summary of the results of the studies can be given in this article. Figures 1 and 2 show the effects of advances in emissions control technologies. In these charts, all of the light-duty vehicle test data are averaged by car, across all fuels tested. Older diesel cars showed relatively high PAH emissions but the latest generation of diesel cars gave very low PAH emissions, equal to or even better than the advanced gasoline cars (depending on the specific PAHs).

In the older diesel vehicles, 3+ring PAH emissions increased linearly with diesel fuel polyaromatics content. There was a similar trend of 2+ring PAH emissions with diesel fuel polyaromatics content and to a smaller degree with mono-aromatics content. However, reducing the polyaromatics content to zero did not eliminate the PAH emissions, because a significant proportion is generated during combustion. With the advanced diesel vehicle emission control systems, the PAH emissions were very low, close to or below the limits of detection and showed no discernible sensitivity to fuel aromatics/polyaromatics content.

[4] *SAE (1998) Collier A.R., et al.* Sampling and analysis of vapour-phase and particulate bound PAH from vehicle exhaust. *SAE 982727*

[5] CONCAWE Review, *April 2001*

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Figure 1
2+ ring PAH emissions
2+ ring PAH emissions are well controlled with advanced emission control technologies. Advanced diesel vehicles achieved 2+ring PAH emissions even lower than the advanced gasoline cars tested.

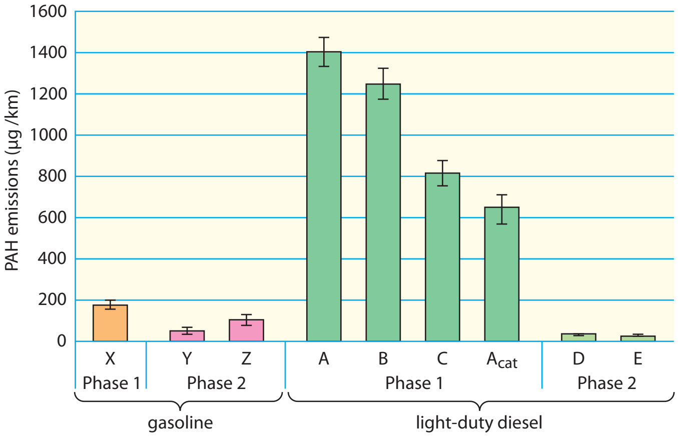
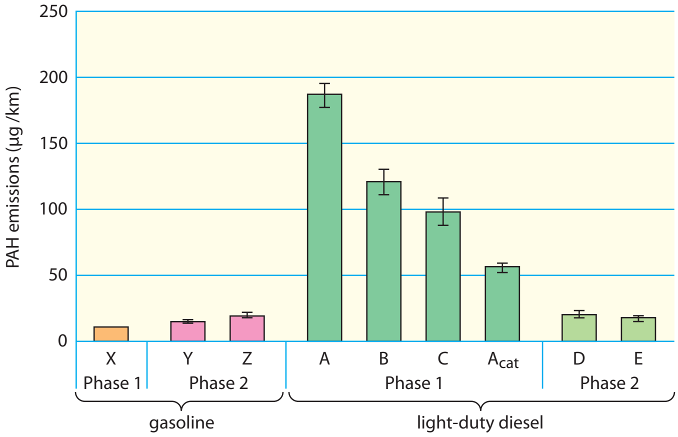
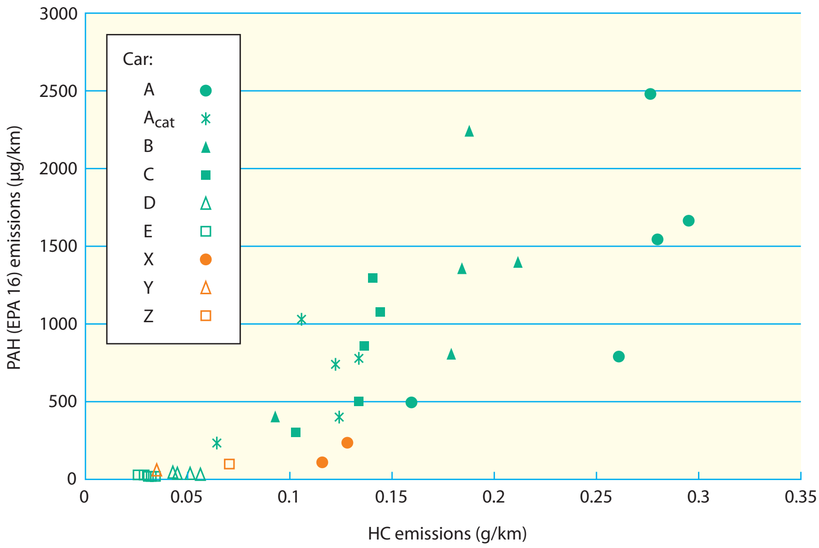


Figure 2
3+ ring PAH emissions
3+ ring PAH emissions are well controlled with advanced emission control technologies. Advanced diesel vehicles achieved 3+ ring PAH emissions as low as advanced gasoline cars.



It is clear from Figures 1 and 2 that the emission control technologies that are being employed to meet legislation on regulated emissions (HC, PM) are also controlling PAH emissions. In order to check the relationships between PAH emissions and regulated emissions, the average PAH emissions for each vehicle/fuel combination tested were plotted against HC and PM emissions. The trends were fairly consistent and confirmed that the measures taken to address regulated emissions are indeed also dealing with PAH emissions. It is also clear that the range of data, which includes fuel effects in the older technologies, becomes very small as the total HC emissions are reduced. Figure 3 shows a plot of 2+ring PAH emissions versus HC emissions for all the vehicles and fuels tested.

Figure 3
2+ ring (EPA-16) PAH emissions versus HC emissions
PAH emissions track the improvement in regulated HC emissions. Diesel fuel polyaromatics effects seen with the older vehicle technologies are no longer observed with the advanced technologies.



Overall assessment

In older diesel vehicles, there was a relationship between diesel fuel polyaromatics content and PAH emissions, although reducing diesel fuel polyaromatics content even to zero would not eliminate PAH emissions, as a significant proportion is combustion-generated. Advanced diesel vehicles, including a diesel particulate filter equipped vehicle, showed very low PAH emissions and no longer showed any sensitivity to diesel fuel polyaromatics content.

The emission control technologies that are being implemented to achieve regulated emissions limits are also controlling PAH emissions. Lower sulphur fuels have paved the way for a wide range of advanced vehicle technologies to be applied. With increasing market penetration of these advanced vehicles, PAH emissions from road transport should soon no longer be a concern.