the chemical composition of diesel particulate emissions

Prepared for the CONCAWE automotive Emissions management Group and based on work carried out by the Special Task Force on Diesel Fuel Emissions (AE/STF-7)

C.J.S. Bartlett (Chairman)

W.E. Betts
M. Booth
F. Giavazzi
H. Guttmann
P. Heinze
R.F. Mayers
D. Roberts

R.C. Hutcheson (Technical Coordinator)

Brussels
January 1992

ABSTRACT

In July 1990 CONCAWE published a report (1) on the influence of diesel fuel sulphur content on particulate emissions. The chemical analysis procedures employed in that programme for the identification of particulate constituents are described in this report.

Considerable problems were encountered in terms of methodology for the chemical analysis of diesel particulate. As a direct result of this CONCAWE study an Institute of Petroleum working group has been established with the objective of developing and publishing standard methods in this area.

Wide differences in particulate mass and composition were determined within engine and vehicle groups, over legislated test cycles. These differences were, however, broadly in line with published data.

When expressed on a direct mass/mass basis, polycyclic aromatic hydrocarbon (PAH) levels on particulate obtained under ECE-15+EUDC conditions were approximately an order of magnitude greater than those obtained under ECE-R49 conditions.

KEYWORDS

analytical method, diesel engine, exhaust gas, PAH, particulates, SOF, sulphate, test fuels

CONTENTS Page

SUMMARY

CONCAWE Report No. 90/54 described a programme which measured the particulate emissions from a wide range of diesel vehicles and heavy duty diesel engines on fuels of 0.31, 0.22, 0.12 and 0.055% weight sulphur content. The work also included chemical analysis of the particulates. The procedures used in that programme for the chemical analysis of particulates are described and the chemical composition data obtained are discussed.

Six light duty diesel vehicles and four heavy duty diesel engines, representative of the current European parc were tested over EC legislated cycles. Particulate samples were analysed for total carbon, sulphate, and hydrocarbons in the fuel and lubricating oil boiling ranges. In addition to the analyses given above, selected samples were analysed for total and individual polycyclic aromatic hydrocarbons (PAH).

The analysis failed to establish any trend of chemical composition with fuel sulphur content, apart from the expected decrease in particulate sulphate level with reduced fuel sulphur content. Wide differences in particulate mass and composition were determined within engine and vehicle groups, over legislated test cycles. These differences were, however, broadly in line with published data.

When expressed on a direct mass/mass basis, PAH levels on particulate obtained under ECE-15+EUDC conditions were approximately an order of magnitude greater than those obtained under ECE-R49 conditions. Wide differences in PAH emission levels were determined within vehicle and engine groups.

Considerable problems were encountered in this programme in terms of methodology for the chemical analysis of diesel particulate. These problems led directly to the formation of an Institute of Petroleum working group whose purpose is to publish standard methods in this area.

1. INTRODUCTION

In July 1990, CONCAWE published a report (1) on the influence of the sulphur content of diesel fuel and its relationship with exhaust particulate emissions from diesel engines. This gives the results of a research programme which measured the particulate emissions from a wide range of diesel vehicles (cars and light vans) and heavy duty diesel engines on fuels of 0.31, 0.22, 0.12 and 0.055% weight sulphur content. The test fuels were produced by progressively desulphurizing the base fuel, avoiding changes in other fuel quality variables.

The research programme also included chemical analysis of the particulates. It is this aspect that is covered in this present report. The procedures used for chemical analysis of particulates are described and the chemical composition data obtained are discussed.

2. TEST VEHICLES AND ENGINES

The vehicles and engines tested in this programme were as follows:

VEHICLES

VEHICLE NO. 1	1.6 LITRE	NA IDI	PASSENGER CAR
VEHICLE NO. 2	1.9 LITRE	NA IDI	PASSENGER CAR
VEHICLE NO. 3	2.4 LITRE	NA IDI	LIGHT VAN
VEHICLE NO. 4	2.4 LITRE	TC IDI	PASSENGER CAR
VEHICLE NO. 5	2.5 LITRE	TC IDI	PASSENGER CAR
VEHICLE NO. 6	2.5 LITRE	TC IDI	PASSENGER CAR
VEHICLE NO. 7	2.5 LITRE	NA DI	LIGHT VAN
VEHICLE NO. 8	1.9 LITRE	TC DI	PASSENGER CAR
VEHICLE NO. 9	2.0 LITRE	TC DI	PASSENGER CAR

(Continued overleaf)

ENGINES

ENGINE NO. 1	6.0 LITRE	NA DI
ENGINE NO. 2	6.0 LITRE	TC/IC DI
ENGINE NO. 3	9.6 LITRE	TC/IC DI
ENGINE NO. 4	12.7 LITRE	TC/IC DI

Key to engine types:

NA	Naturally Aspirated
TC	Turbo-charged
TC/IC	Turbo-charged and Inter-cooled
IDI	Indirect injection
DI	Direct injection

3. GENERATION OF DIESEL PARTICULATE SAMPLES

The particulate samples were generated from the diesel engines on test over combined EC (ECE-15+EUDC) cycles and modified ECE-R49 cycles. The analytical data on the matrix of test fuels used in the programme are given in Table 1. The same lubricating oil was used throughout all of the tests (1).

Hydrocarbon distributions for the fuels and the lubricating oil are shown in Figure 1 and Figure 2, respectively.

4. PROCEDURES FOR CHEMICAL ANALYSIS OF DIESEL PARTICULATES

Glass fibre filter papers (Whatman GF/A, 47 mm diameter) were preferred initially for particulate collection in order to facilitate determination of particulate carbon content. Particulate-loaded filter papers were stored before analysis in covered petri dishes, kept in a freezer below 0°C.

Particulate samples were analysed for total carbon, sulphate, and hydrocarbons in the fuel and lubricating oil boiling ranges. In addition to the analyses given above, selected samples were analysed for total and individual polycyclic aromatic hydrocarbons (PAH).

The recommended methods for the individual analyses were as follows.

4.1 Total Sulphate

Total sulphate contents of the particulate samples were determined using an ion chromatograph analysis procedure (2).

A weighed "pie" sector or slice of each filter paper was taken for this analysis since experiments had shown that the distribution of sulphate across the radius of the filter decreases slightly from perimeter to centre. This is considered possibly to arise from a temperature gradient across the filter. This sector of filter paper was extracted with 20:80 iso-propanol:water, and the sulphate in the extract determined by ion chromatography using a Dionex 2000i ion chromatograph. The procedure was also applied to a sector cut from an unused filter and the "blank" value subtracted from the measured value before reporting.

Values reported for total sulphate do not include bound water.

4.2 Particulate Carbon

Particulate carbon was determined by thermogravimetry (3). Small random samples (~10% of the total area) of known area were cut from the filter paper and bulked for analysis. Unlike the situation for sulphate, preliminary experiments clearly showed that particulate carbon is uniformly distributed on the filter, thus it is not necessary to take a "pie" sector for this determination. Particulate carbon was determined by thermogravimetry using a Perkin Elmer TG-S2 thermogravimetric analyser. Particulate carbon was defined as material which is involatile in nitrogen up to a temperature of 550°C, but which is completely oxidised in oxygen at the same temperature.

A blank analysis was carried out on an unused filter paper, and the "blank" value subtracted from the determined value.

4.3 Soluble Organic Fraction (SOF) - Hydrocarbons

The remaining filters from the two procedures above were bulked and extracted with re-distilled toluene using a sonic probe to obtain the soluble organic fraction (SOF). The extract was cleaned by passing through anhydrous sodium sulphate. The extract was weighed after removal of solvent by evaporation under vacuum. The SOF was analysed by high resolution capillary gas chromatography (using n-dotriacontane as internal standard) for the determination of the total concentration of hydrocarbons present and their boiling point distribution.

In order to separate fuel-derived and lubricant-derived hydrocarbons, it is necessary to obtain boiling point distributions for the fuel and lubricant used in the test under the same chromatographic conditions.

Blank unused filters are taken through the analysis as controls and "blank" values subtracted from determined values.

4.4 SOF - Total and Individual Polycyclic Aromatics (4)

SOF obtained according to the method outlined in Section 3.3 was analysed on a high performance liquid chromatograph (HPLC) and a four to six ring polycyclic aromatic hydrocarbon (PAH) fraction separated on an amino-bonded silica gel column. As the compounds eluted, they were detected by their ultra-violet (UV) absorption at 254 nm and quantified by comparing their total peak area with that of a known concentration of benzo(a)pyrene chromatographed under the same conditions. The fraction containing the four to six ring compounds was collected and applied to a Sephadex LH20 column to separate the individual parent PAHs present from the alkylated PAHs. Final separation and quantification of the individual PAHs was by high resolution capillary gas chromatography when compounds of interest were identified and quantified by direct comparison of their peak areas with that of an internal standard.

It is again essential that the SOF extracted from blank unused filters is taken through the analysis as controls.

5. PARTICULATE COMPOSITION DATA

5.1 Cars/Light Commercial Vehicles

Although duplicate combined emissions cycles (ECE-15+EUDC) were carried out for each vehicle/fuel combination, chemical analyses were only attempted from one set of filter papers per vehicle/fuel combination, in order to control costs. Thus no data on the precision of the results were obtained.

Data for soluble organic fraction (SOF), fuel derived hydrocarbon (FHC), lubricating oil derived hydrocarbon (LHC), sulphate and remainder (mainly carbon and water) are shown in Tables 2 to 6 respectively. Comparison of SOF, FHC and LHC data between vehicles shows considerable variation. Thus SOF varies in the range 10 to 65% wt, FHC from 1 to 55% wt and LHC from 3 to 55% wt. Whilst some of this variation may well be due to analytical methodology, it is apparent that different vehicles and engine types give rise to very different particulate composition.

In particular, vehicles with direct injection (DI) engines show a trend towards high SOF contents. Vehicle 7 is unusual in that it gives a high level of FHC (~50% of particulate) compared with the mean level of 10 to 20%. The mean data suggest that there is no significant difference between ECE-15 and EUDC cycles in terms of particulate composition. Similarly, for SOF, FHC and LHC there is no relationship between particulate composition and fuel sulphur content.

Similar wide variations in particulate composition have been found by other authors. Thus workers at AVL (5) found LHC varying in the range 5 to 48% on particulate, on a range of IDI vehicles operating on the US FTP test cycle.

The sulphate data shown in Table 5 are included only for the sake of completeness; the trend towards increasing % sulphate on particulate as fuel sulphur increases has been discussed in the earlier report (1). Table 6 reports "carbon" contents determined by subtracting (SOF + sulphate) from 100%. The original intention to determine carbon directly by the TGA method was not pursued owing to extreme difficulties reported with application of the proposed method. As determined by difference, carbon contents vary in the range 30 to 85%. Again, there does not seem to be any trend with fuel sulphur content. Data reported by AVL (5) in the range 42 to 86%, confirm the CONCAWE findings.

5.2 Heavy duty engines

Data for soluble organic fraction (SOF), fuel derived hydrocarbon (FHC), lubricating oil derived hydrocarbon (LHC), sulphate and remainder (mainly carbon and water) are shown in Tables 7 to 11 respectively. As for the light duty vehicles, there are considerable variations between engines in terms of particulate composition. Thus SOF varies in the range 14 to 58% wt of particulate, and FHC 10 to 35%. LHC is generally 10% or below, except for Engine No. 2 which gave ~20% LHC contribution. As previously, sulphate data are included for completeness' sake only, but now amplify the data given in the original report without affecting the conclusions.

Data on particulate "carbon", again obtained by difference, also show considerable variation, with Engine No. 2 giving the lowest values. The modern high power-output turbo-charged and inter-cooled engines (No. 3 and 4) show particularly high particulate carbon contents on a percentage basis. This reflects their excellent SOF combustion performance. It would appear that, when producing particulate matter under the steady state conditions of the ECE-R49 test, particulate carbon contents are similar to those obtained under ECE-15+EUDC conditions.

Apart from sulphate data, no trends were obtained between fuel sulphur content and particulate composition.

6. POLYCYCLIC AROMATIC HYDROCARBON (PAH) DATA: VEHICLES AND ENGINES

Data on individual and total PAH are given in Table 12 for light duty vehicles. Owing to the low level of PAH occurring in diesel particulate, the data are expressed in terms of μg/g particulate (ppm mass) and not in g/km or g/kWh. Considerable variation is apparent between duplicate runs and between different fuels and different vehicles. Two different vehicles were used in the Vehicle 3 tests and the difference in PAH emissions between them is apparent in Table 12. The total PAH levels determined on particulate generated in the ECE-R49 procedure, Table 13, on heavy duty engines are considerably lower than the levels found in particulate generated under ECE-15 and EUDC conditions. A comparison of the CONCAWE ECE-R49 benzo(a)pyrene data, in the range 1 to 3 μg/g, shows excellent agreement with published values of 1.0 to 3.8 μg/g particulate (6).

The difference between levels of PAH measured under light duty transient and heavy duty steady state conditions would appear to be genuine. No systematic study would, however, appear to have been carried out elsewhere and little relevant data have been found in the published literature.

7. PROBLEMS ARISING FROM CHEMICAL ANALYSIS PROCEDURES

During the course of this work it became apparent that few analysts agree upon a preferred procedure for analysis of SOF or particulate carbon. Since analytical methodology influences choice of filter paper, this also became a variable, together with the method used to extract/remove SOF from the filter paper.

In an attempt to minimize the number of variables, a revised procedure was suggested for filter paper analysis, as follows:

1. Generate a single primary filter paper per ECE-R49 and ECE-15+EUDC test.
2. Use Whatman or Pallflex filter papers.
3. Store and carry all filter papers in glass containers.
4. Analyse a blank filter paper for each test, taking the blank through the equilibration procedure prior to the test run, and subtract the blank value from the determined value to give the reported value.
5. Soxhlet extract equilibrated and weighed filter paper with toluene for 6 hours. Use the SOF for HC and PAH analysis using internal standards, detailing methods used.

6. Remove the toluene from the extracted paper by gentle drying (3 to 4 h at 75°C) and re-equilibrate and weigh.

7. Determine the sulphate content of the entire weighed paper using the sulphate method previously specified.

8. Calculate inorganic carbon by difference.

Preferred methods for SOF analysis were based on those of AVL (5) and of Ricardo (7).

In order to establish the reproducibility of the revised approach, a round-robin experiment was devised in which a number of filter papers were generated under Mode 3 and Mode 6 steady state conditions of the ECE R49 procedure. Sampling time was fixed at five minutes per filter to give a "constant" amount of particulate per paper within each mode. Samples of the fuel and lubricant were supplied, together with a filter paper from each mode, to each participating laboratory.

Following re-equilibration and re-weighing, each laboratory was asked to carry out an analysis according to the revised procedures. Data on SOF, FHC, LHC, sulphate and carbon (by difference) are shown in Table 14. Substantial lack of agreement is again apparent, arising from the different techniques used for SOF determination. Even the uncontroversial determination of sulphate seems to be causing analytical difficulties.

Data on individual and total PAH are shown in Table 15. Again there are considerable differences, with one laboratory in particular reporting very high values.

The data generated in the round-robin exercise serve to cast doubt on the value of the data reported on individual vehicles and engines. It should be noted, however, that data reported here are in broad agreement with published literature values. As a result of the analytical problems identified in this programme, the Institute of Petroleum (London) has now set up a Working Group to develop standard procedures for the analysis of diesel particulate. This Working Group has received strong support and shows promise of making significant progress.

8. CONCLUSIONS

Chemical analysis of diesel particulate collected from a wide range of vehicles and engines, has not established any trend of chemical composition with fuel sulphur content, apart from the expected decrease in particulate sulphate level as fuel sulphur content decreases.

Considerable differences in sulphate and HC emission levels were determined within engine and vehicle groups.

Comparison between soluble organic fraction (SOF), fuel derived hydrocarbon (FHC) and lubricating oil hydrocarbon (LHC) showed major differences between vehicles operating on ECE-15+EUDC cycles, and between engines operating under ECE-R49 conditions. These differences are, however, broadly in line with published data.

When expressed on a direct mass/mass basis, polycyclic aromatic hydrocarbon (PAH) levels on particulate obtained under ECE-15+EUDC conditions are about one order of magnitude greater than those obtained under ECE-R49 conditions. Wide differences in PAH emission levels were determined within vehicle and engine groups.

Considerable problems were encountered in this programme in terms of methodology for the chemical analysis of diesel particulate. These problems led directly to the formation of an Institute of Petroleum working group whose purpose is to publish standard methods in this area.

9. ACKNOWLEDGEMENT

CONCAWE wishes to place on record the contribution of staff from the following organizations to the work reported here.

BP Research Centre, Sunbury
Esso Research Centre, Abingdon
Euron, Milan
Mobil, Centralized European Fuels Laboratory, Wedel
Ricardo Consulting Engineers, Shoreham
Shell Research Centre, Thornton
Veba Oel, Gelsenkirchen

10. REFERENCES

1. CONCAWE (1990) The sulphur content of diesel fuels and its relationship with particulate emissions from diesel engines, Report No. 90/54. Brussels: CONCAWE

2. Small, H. Stevens, T.S. and Baumann, W.C. (1975) Novel ion exchange chromatographic method using conductimetric detection. Analytical chemistry 47, 11, 1801-1809

3. Cuthbertson, R.D. Stinton, H.C. and Wheeler, R.W. (1979) The use of a thermogravimetric analyser for the investigation of particulate and hydrocarbons in diesel engine exhaust SAE Paper 790814. Warrendale, PA: Society of Automotive Engineers

4. Pullen, D.L. and Scammells, D.V. (1988) A chromatographic procedure for the comprehensive separation and estimation of polycyclic aromatic hydrocarbons in petroleum products. Fuel 67, 251- (note that there is an error on this paper on p253 - the equation should be multiplied by 100 to give PCAs in ppm)

5. Cartellieri, W. and Tritthart, P. (1984) Particulate analysis of light duty diesel engines (IDI and DI) with particular reference to the lube oil particulate fraction. SAE Paper 840418. Warrendale, PA: Society of Automotive Engineers

6. Knuth, H.W. and Garthe, H. (1988) "Future" diesel fuel compositions - their influence on particulates. SAE Paper 881173. Warrendale, PA: Society of Automotive Engineers

7. Cuthbertson, R.D. et al (1987) Direct analysis of diesel particulate-bound hydrocarbons by gas chromatography with solid sample injection. SAE Paper 870626. Warrendale, PA: Society of Automotive Engineers

TABLE 1

ANALYTICAL DATA ON TEST FUELS USED IN THE PROGRAMME (MEAN VALUES)

Fuel No		1	2	3	4
Sulphur Content	% wt	0.055	0.12	0.22	0.31
Density @ 15°C	kg/m^3	832.7	833.0	834.2	835.1
KV @ 20°C	mm^2/s	5.41	5.44	5.57	5.58
KV @ 40°C	mm^2/s	3.44	3.44	3.46	3.47
Flash Point	°C	101	102	103	102
Cloud Point	°C	-4	-4	-4	-4
CFPP	°C	-6	-6	-6	-6
Water Content	ppm	53	58	62	76
Copper Corrosion	-	1A	1A	1A	1A
Carbon Residue	% wt	0.01	0.01	0.01	0.01
Aromatics					
FIA	% vol	25.0	25.0	24.0	25.4
HPLC (a)	% wt	24.4	24.6	24.4	24.9
HPLC (b)					
Mono-aromatics	% vol	22.0	21.3	21.7	19.8
Di-aromatics	% vol	4.6	4.1	4.5	4.9
Tri-aromatics	% vol	1.2	0.8	1.4	1.5
Total Aromatics	% vol	27.4	26.2	27.6	26.2
Cetane Number		58.2	58.1	58.4	58.9
Calculated Cetane Index (IP380)		60.2	60.0	59.6	59.3
Distillation Data					
IBP	°C	222	222	222	223
10% vol	°C	251	250	250	250
20% vol	°C	259	258	259	259
30% vol	°C	266	266	267	266
40% vol	°C	274	273	274	274
50% vol	°C	281	281	282	283
60% vol	°C	290	290	291	291
70% vol	°C	300	300	302	302
80% vol	°C	312	313	314	315
90% vol	°C	329	329	330	330
95% vol	°C	342	341	342	343
FBP	°C	354	353	354	353
Recovery	% vol	98.3	98.6	98.4	98.4
Loss	% vol	0.3	0.2	0.1	0.3
Residue	% vol	1.3	1.2	1.4	1.3

(a) IP 368/84
(b) IP 391/90

TABLE 2

LIGHT DUTY DIESEL VEHICLES - SOLUBLE ORGANIC FRACTION ON PARTICULATE (% wt)

A. ECE-15 Cycle

Fuel	Sulphur Content	Vehicle No.1	Vehicle No.2	Vehicle No.3	Vehicle No.4	Vehicle No.5	Vehicle No.6	Vehicle No.7	Vehicle No.8	Vehicle No.9	Mean Value
1	0.055	39.5	38.0	26.5	21.9	15.0	48.0	54.2	-	32.0	34.4
2	0.12	-	39.2	16.4	21.6	38.6	30.9	62.4	-	51.3	37.2
3	0.22	26.9	45.2	19.9	26.5	34.5	-	64.4	-	40.5	36.8
4	0.31	28.7	38.5	21.0	21.8	64.0	50.4	55.6	-	41.3	40.2

B. EUDC Cycle

1	0.055	18.7	31.2	35.0	50.7	26.6	35.8	49.3	-	31.3	34.8
2	0.12	10.2	38.0	27.8	28.4	64.7	59.9	53.1	-	28.5	38.8
3	0.22	11.4	36.8	24.8	30.3	54.6	-	46.8	-	32.7	33.9
4	0.31	24.8	38.7	28.0	30.8	61.5	36.9	57.7	-	31.8	38.8

TABLE 3

LIGHT DUTY DIESEL VEHICLES - FUEL DERIVED HYDROCARBON ON PARTICULATE (% wt)

A. ECE-15 Cycle

Fuel	Sulphur Content	Vehicle No.1	Vehicle No.2	Vehicle No.3	Vehicle No.4	Vehicle No.5	Vehicle No.6	Vehicle No.7	Vehicle No.8	Vehicle No.9	Mean Value
1	0.055	7.7	19.8	7.6	7.8	4.2	6.4	50.0	-	8.1	14.0
2	0.12	-	16.9	6.2	5.6	9.6	6.8	55.0	-	12.3	16.1
3	0.22	6.3	18.9	7.0	9.9	12.1	-	56.3	-	9.8	17.2
4	0.31	6.1	21.0	6.3	7.8	15.3	11.7	49.8	-	12.9	16.4

B. EUDC Cycle

1	0.055	2.3	16.6	8.1	5.3	8.2	9.2	45.9	-	10.4	13.2
2	0.12	1.2	14.8	7.1	6.3	10.3	11.4	44.4	-	6.8	12.8
3	0.22	1.1	14.3	5.9	8.5	14.2	-	37.3	-	6.4	12.5
4	0.31	4.2	15.7	5.8	9.9	12.3	9.0	51.6	-	9.4	14.7

TABLE 4

LIGHT DUTY DIESEL VEHICLES - LUBRICATING OIL DERIVED HYDROCARBON ON PARTICULATE (% wt)

A. ECE-15 Cycle

Fuel	Sulphur Content	Vehicle No.1	Vehicle No.2	Vehicle No.3	Vehicle No.4	Vehicle No.5	Vehicle No.6	Vehicle No.7	Vehicle No.8	Vehicle No.9	Mean Value
1	0.055	31.8	18.2	18.8	14.1	10.7	41.6	4.2	-	23.9	20.4
2	0.12	-	22.3	10.2	16.0	28.9	24.1	7.4	-	39.0	21.1
3	0.22	20.6	26.3	12.9	16.6	22.4	-	8.1	-	30.7	19.7
4	0.31	22.6	17.5	14.6	14.0	48.7	38.7	5.8	-	28.4	23.8

B. EUDC Cycle

1	0.055	16.4	14.6	26.8	45.4	18.3	26.6	3.4	-	20.9	21.6
2	0.12	9.0	23.2	20.7	22.1	54.4	48.5	8.7	-	21.7	26.0
3	0.22	10.3	22.5	18.9	21.8	40.4	-	9.5	-	26.3	21.4
4	0.31	20.6	23.0	22.2	20.9	49.2	27.9	6.1	-	22.4	24.0

TABLE 5

LIGHT DUTY DIESEL VEHICLES - SULPHATE* ON PARTICULATE (% wt)

A. ECE-15 Cycle

Fuel	Sulphur Content	Vehicle No.1	Vehicle No.2	Vehicle No.3	Vehicle No.4	Vehicle No.5	Vehicle No.6	Vehicle No.7	Vehicle No.8	Vehicle No.9	Mean Value
1	0.055	11.6	1.1	0.7	2.2	2.7	5.8	1.2	-	2.5	3.5
2	0.12	6.1	1.2	1.4	1.9	3.6	3.6	0.8	-	3.4	2.8
3	0.22	12.2	1.3	1.7	3.7	8.1	5.8	1.0	-	3.4	4.6
4	0.31	10.5	2.3	2.3	4.2	4.1	6.3	2.1	-	5.0	4.6

B. EUDC Cycle

1	0.055	7.8	1.7	1.8	3.7	3.8	4.6	0.9	-	3.0	3.4
2	0.12	4.7	2.7	1.4	2.7	5.7	7.5	0.6	-	2.6	3.5
3	0.22	11.8	3.0	1.3	5.9	6.2	8.1	0.9	-	3.1	5.0
4	0.31	9.4	5.8	3.4	6.2	10.1	7.0	1.7	-	3.8	5.9

* Not inclusive of bound water

TABLE 6

LIGHT DUTY DIESEL VEHICLES - CARBON* ON PARTICULATE (% wt)

A. ECE-15 Cycle

Fuel	Sulphur Content	Vehicle No.1	Vehicle No.2	Vehicle No.3	Vehicle No.4	Vehicle No.5	Vehicle No.6	Vehicle No.7	Vehicle No.8	Vehicle No.9	Mean Value
1	0.055	48.9	60.9	72.8	75.9	82.3	46.2	44.6	-	65.5	62.1
2	0.12	-	59.6	82.2	76.5	57.8	65.5	36.8	-	45.3	60.5
3	0.22	60.9	53.5	78.4	69.8	57.4	-	34.6	-	56.1	58.7
4	0.31	60.8	59.2	76.7	74.0	31.9	43.3	42.3	-	53.7	55.2

B. EUDC Cycle

1	0.055	73.5	67.1	63.1	45.6	69.6	59.6	49.8	-	65.7	61.8
2	0.12	85.1	59.3	70.8	68.9	29.6	32.6	46.3	-	68.9	57.7
3	0.22	76.8	60.2	73.9	63.8	39.2	-	52.3	-	64.2	61.5
4	0.31	65.8	55.5	68.6	63.0	28.4	56.1	40.6	-	64.4	55.3

* By difference

TABLE 7

HEAVY DUTY DIESEL ENGINES - SOLUBLE ORGANIC FRACTION ON PARTICULATE (% wt)

ECE-R49 13-Mode

Fuel	Sulphur Content	Engine No.1	Engine No.2*	Engine No.3	Engine No.4	Mean Value
1	0.055	46.2	58.4	26.7	19.8	37.8
2	0.12	30.7	48.2	22.0	20.5	30.3
3	0.22	34.4	42.8	17.5	14.0	27.2
4	0.31	34.9	40.5	24.4	13.9	28.4

* Mean of two determinations

TABLE 8

HEAVY DUTY DIESEL ENGINES - FUEL DERIVED HYDROCARBON ON PARTICULATE (% wt)

ECE-R49 13-Mode

Fuel	Sulphur Content	Engine No.1	Engine No.2	Engine No.3	Engine No.4	Mean Value
1	0.055	35.2	32.5	15.5	16.9	25.0
2	0.12	21.3	24.9	12.6	13.4	18.0
3	0.22	25.3	21.6	10.9	9.8	16.9
4	0.31	24.0	20.8	16.8	9.9	17.9

TABLE 9

HEAVY DUTY DIESEL ENGINES - LUBRICATING OIL HYDROCARBON ON PARTICULATE (% wt)

ECE-R49 13-Mode

Fuel	Sulphur Content	Engine No.1	Engine No.2	Engine No.3	Engine No.4	Mean Value
1	0.055	11.0	25.9	11.2	2.8	12.7
2	0.12	9.4	23.3	9.4	7.1	12.3
3	0.22	9.1	21.2	6.6	4.2	10.3
4	0.31	10.9	19.7	7.6	4.0	10.6

TABLE 10

HEAVY-DUTY DIESEL ENGINES - SULPHATE* ON PARTICULATE (% wt)

ECE-R49 13-Mode

Fuel	Sulphur Content	Engine No.1	Engine No.2	Engine No.3	Engine No.4	Mean Value
1	0.055	1.8	1.9	2.8	1.2	1.9
2	0.12	1.4	2.8	7.1	1.8	3.3
3	0.22	1.6	4.3	6.3	4.3	4.1
4	0.31	1.7	6.7	7.5	5.0	5.2

* Not inclusive of bound water

TABLE 11

HEAVY DUTY DIESEL ENGINES - CARBON* ON PARTICULATE (% wt)

ECE-R49 13-Mode

Fuel	Sulphur Content	Engine No.1	Engine No.2	Engine No.3	Engine No.4	Mean Value
1	0.055	52.0	39.7	70.5	79.0	60.3
2	0.12	67.9	49.0	70.9	77.7	66.4
3	0.22	64.0	52.9	76.2	81.7	68.7
4	0.31	63.4	52.8	68.1	81.1	66.3

* By difference

TABLE 12

LIGHT DUTY DIESEL VEHICLES - INDIVIDUAL AND TOTAL PAH ON PARTICULATE µg/g

Vehicle	Vehicle No.3				Vehicle No.4		Vehicle No.8			
Fuel	1	1	4	4	1	4	1	2	3	4
A. ECE-15 Cycle										
Fluoranthene	155	147	77	133	12	8	46	37	45	79
Pyrene	167	151	62	117	-	-	151	142	114	134
B(g,h,i)F/B(c)P	47	48	36	38	-	-	-	-	-	-
Benz(a)anthracene	21	22	10	14	12	-	138	160	124	138
Triphenylene/Chrysene	39	32	26	28	22	14	44	56	41	49
Benzo(b)/(j)fluoranthene	54	80	56	87	38	36	11	4	12	10
Benzo(a)fluoranthene	9	10	6	15	24	14	-	-	-	-
Benzo(e)pyrene	27	35	25	40	-	8	-	-	-	-
Benzo(a)pyrene	29	48	21	40	14	12	4	3	4	2
Perylene	3	8	7	3	24	20	-	-	-	-
Dibenz(a,j)anthracene	10	75	20	28	-	-	-	-	-	-
Indeno(1,2,3-c,d)pyrene	29	50	30	54	-	12	43	10	12	12
Dibenz(a,h)/(a,c)anthracene	3	7	-	3	14	14	3	4	8	2
Benzo(g,h,i)perylene	38	56	38	65	17	14	-	-	-	-
Anthracene	6	7	4	3	-	-	-	-	-	-
Dibenz(a,1)pyrene	8	14	17	11	-	-	-	-	-	-
Coronene/Dibenz(a,e)pyrene	20	52	21	44	-	-	-	-	-	-
Total PAH	665	842	456	723	177	152	440	416	360	426
B. EUDC "High Speed" Cycle										
Fluoranthene	117	137	140	96	16	11	81	58	238	343
Pyrene	128	144	112	73	-	11	259	181	252	287
B(g,h,i)F/B(c)P	53	61	51	40	-	-	-	-	-	-
Benz(a)anthracene	12	14	9	9	-	-	264	190	232	285
Triphenylene/Chrysene	34	33	39	28	23	14	112	65	120	138
Benzo(b)/(j)fluoranthene	57	81	65	62	88	33	28	21	36	37
Benzo(a)fluoranthene	7	15	8	10	69	14	-	-	-	-
Benzo(e)pyrene	31	33	22	24	-	-	-	-	-	-
Benzo(a)pyrene	25	33	16	16	-	-	4	3	6	-
Perylene	5	5	12	5	32	17	-	-	-	-
Dibenz(a,j)anthracene	22	78	13	25	-	-	-	-	-	-
Indeno(1,2,3-c,d)pyrene	24	43	23	37	23	-	9	5	17	6
Dibenz(a,h)/(a,c)anthracene	3	6	-	4	40	11	4	4	7	4
Benzo(g,h,i)perylene	49	43	25	40	-	-	-	-	-	-
Anthracene	-	7	-	-	-	-	-	-	-	-
Dibenz(a,1)pyrene	11	16	19	31	-	-	-	-	-	-
Coronene/Dibenz(a,e)pyrene	9	48	17	31	-	-	-	-	-	-
Total PAH	587	797	571	531	291	111	761	527	908	1100

B(g,h,i)F/B(c)P = Benzo(g,h,i)fluoranthene/Benzo(c)phenanthrene

TABLE 13

HEAVY DUTY DIESEL ENGINES - INDIVIDUAL AND TOTAL PAH ON PARTICULATE μg/g (ECE R49 CYCLE)

Engine	No.1				No.2				No.3		No.4			
Fuel	1	2	2*	4	1	1*	4	4*	1	4	1	2	3	4
Fluoranthene	11	10	10	4	16	13	17	9	16	9	32	32	52	23
Pyrene	26	22	15	13	-	-	-	-	18	7	50	64	90	24
B(g,h,i)F/B(c)P	-	-	-	-	6	3	4	3	-	-	-	-	-	-
Benz(a)anthracene	3	1	4	3	3	-	3	-	2	1	13	11	16	5
Triphenylene/Chrysene	13	8	11	10	8	8	6	6	6	4	5	7	7	5
Benzo(b)/(j)fluoranthene	4	3	3	2	7	6	10	6	5	1	1	1	1	2
Benzo(a)fluoranthene	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzo(e)pyrene	2	1	1	1	-	-	-	-	2	1	-	-	-	-
Benzo(a)pyrene	1	3	3	1	-	-	-	-	1	-	-	-	-	-
Perylene	-	-	-	-	-	-	2	2	-	-	-	-	-	-
Dibenz(a,j)anthracene	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Indeno(1,2,3-c,d)pyrene	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dibenz(a,h)/(a,c)anthracene	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzo(g,h,i)perylene	1	1	1	1	3	-	5	-	1	-	-	-	-	-
Anthracene	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dibenz(a,l)pyrene	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Coronene/Dibenz(a,e)pyrene	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total PAH	61	49	48	35	43	30	47	26	51	23	101	115	166	59

B(g,h,i)F/B(c)P = Benzo(g,h,i)fluoranthene/Benzo(c)phenanthrene

* Duplicate determination

TABLE 14

PARTICULATE ANALYSIS - DATA ON SOF, HC, SULPHATE AND CARBON FROM LABORATORY ROUND-ROBIN PRECISION EXERCISE. PARTICULATE GENERATED IN ECE-R49 MODES 3 AND 6

R49 Mode		3						6					
Filter Number		1	3	4	5	6	7	1	3	4	5	6	7
SOF (Gas Chromatography)	% wt	72.0	-	73.3	62.2	-	69.6	60.0	-	85.5	55.2	-	57.8
Fuel HC	% wt	35.8	-	25.6	44.1	-	36.1	24.8	-	31.0	34.4	-	26.6
Lubricating Oil HC	% wt	36.2	-	47.8	18.1	-	33.5	35.2	-	54.5	20.8	-	31.2
SOF (Gravimetric)	% wt	83.8	94.9	-	-	-	79.3	71.2	-	-	-	91.4	70.0
Sulphate	% wt	1.4	1.6	3.3	1.3	1.1	1.2	1.2	2.2	5.1	5.4	2.2	1.5
Carbon (By Difference)	% wt	14.8	-	-	36.1	-	19.5	27.6	-	-	39.4	6.4	28.6

Filters 1 and 7 analysed by BP
Filter 3 analysed by Esso
Filter 4 analysed by Veba
Filter 5 analysed by Ricardo
Filter 6 analysed by Euron

TABLE 15

INDIVIDUAL AND TOTAL PAH ON PARTICULATE $\mu g/g$
DATA FROM LABORATORY ROUND-ROBIN PRECISION EXERCISE.
PARTICULATE GENERATED IN ECE-R49 MODES 3 AND 6

R49 Mode	3				6			
Filter Number	1	4	6	7	1	4	6	7
Fluoranthene	2	22	31	3	7	16	28	16
Pyrene	5	26	227	16	8	13	131	24
B(g,h,i)F/B(c)P	-	-	-	-	-	-	-	-
Benz(a)anthracene	9	11	329	16	9	8	239	13
Triphenylene/Chrysene	17	13	153	28	23	9	101	36
Benzo(b)/(j)fluoranthene	<2	17	37	9	4	18	12	12
Benzo(a)fluoranthene	-	-	-	-	-	-	-	-
Benzo(e)pyrene	<2	<1	-	5	10	3	-	17
Benzo(a)pyrene	<2	2	10	4	<3	10	3	7
Perylene	<2	-	-	4	<3	-	-	7
Dibenz(a,j)anthracene	<2	-	-	5	<3	-	-	<5
Indeno(1,2,3-c,d)pyrene	<2	1	17	7	<3	-	8	<5
Dibenz(a,h)/(a,c)anthracene	<2	<1	10	6	<3	2	<1	<5
Benzo(g,h,i)perylene	<2	1	-	4	<3	3	-	<5
Anthracene	-	-	-	-	-	3	-	-
Dibenz(a,l)pyrene	-	-	-	-	-	-	-	-
Coronene/Dibenz(a,e)pyrene	-	-	-	-	-	-	-	-
Total PAH	33	93	814	107	61	85	522	132

Filters 1 and 7 analysed by BP
Filter 4 analysed by Veba
Filter 6 analysed by Euron