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# **Size and Compositional Analysis of Particulate Emissions from Alternative-fuelled Vehicles**

Final Report

Philip Whiteman

August 1998

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<b>Title</b>	Size and Compositional Analysis of Particulate Emissions from Alternative-fuelled Vehicles
<b>Customer</b>	IEA Implementing Agreement on Alternative Motor Fuels (Annex XII)
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# Executive Summary

This is the final report of Annex XII of the IEA Implementing Agreement on Alternative Motor Fuels. The main objective of the project was to characterise the particulate matter emitted from alternative-fuelled vehicles in terms of particulate size distribution and composition.

This report covers the experimental work carried out to complete the project. It should be read in conjunction with the interim report, published in March 1997 (ref.no. RYCA 18841001/Interim/1) which concerned itself with:

1. A world-wide survey of the data available on particulate emissions from alternative fuelled vehicles.
2. A review of the current understanding of the health impacts caused by particulate emissions from vehicle tail-pipes.
3. The methods that are currently recommended for carrying out experimental work on the characterisation of particulate matter from alternative fuelled vehicles.

Historically, the particulate emissions of diesel vehicles have been studied in great depth. However, the information on particulates from other fuels is more limited. A comparison of suitable data has already shown that considerable reductions in the total particulate mass emitted by heavy duty vehicles can be achieved by the use of alternative fuels such as liquefied petroleum gas (LPG) and compressed natural gas (CNG) rather than conventional diesel. For light-duty vehicles, the benefits of switching to alternative fuels have been less clear because gasoline, which is the predominant fuel for such vehicles, produces approximately an order of magnitude less particulate matter than diesel. The literature suggests that alternative spark ignition fuels produce a similar mass of particulate to gasoline.

Reliable particle sizing and compositional analysis techniques have only been developed recently. Most of the past data on particulate emissions in vehicle exhausts have been mass-based and make no reference to the size or composition of the particulate matter collected. Significantly, major differences in fuel or engine characteristics - affecting whether the total mass is dominated by a relatively small number of large particles, or by a very large number of ultra-fine particles - would not have been apparent in such studies.

Epidemiological studies have identified a threat to health from airborne particulate matter; especially from fine particles such as those which would be classed as PM<sub>2.5</sub> (smaller than approximately 2.5 µm). Within this size range, attention has increasingly focused on ultrafine particles, smaller than 100 nm, as these behave more like a gas and diffuse efficiently onto the surface of the lung. Research into ultrafine particles has found that even biologically inert chemicals like titanium dioxide can irritate lung tissues when inhaled as an aerosol of this size.

There are a number of theories which attempt to explain these health effects, but the underlying principle behind them all is that the harmful effects of any material are made worse when it is inhaled in the form of ultrafine particles. This leads to the conclusion that the number of particles in the size range below 2.5 $\mu\text{m}$  might be more important as an indicator of adverse health effects than the simple measurements of total particulate mass currently used (such as  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ ).

Recent measurements (for instance in the UK Government's Particulates Research Programme) have shown that the majority of the particulates emitted by gasoline vehicles are in, or close to, the ultrafine region, defined by a particulate diameter of less than 100 nm. The particulates produced from diesel vehicles tend to be slightly larger than for gasoline vehicles, although they are still generally in or close to the ultrafine cut-off.

The experimental work for this programme was carried out on a bi-fuel LPG van and a dedicated CNG van. They both produced remarkably low particulate emissions, in terms of overall mass. For the greater part, the mean size of the particles emitted was found to be similar to those from gasoline vehicles. However, large numbers of very small particles (10-20nm mobility diameter) were found when operating under steady-speed conditions on LPG, and both LPG and CNG consistently produced large numbers of small particles at a high, steady road speed.

CNG produced similarly-sized exhaust particles to gasoline under operating conditions from engine idle to moderate vehicle speed at road-load, the peak particle size being approximately 80 nm. However, at higher speed and load (over 90 km/h) a second peak appeared in the size distribution at approximately 20-30 nm. At the highest speed investigated, 120 km/h, the peak particle size was only 40 nm. There is an overall trend in peak particle size falling with increasing road speed/load. (In general, mean particle size *increases* with engine speed and load for diesel engines).

Repeated testing of the LPG vehicle gave inconsistent particle size data, although there was no apparent shift in gaseous emissions. Possibly, the dilution tunnel and vehicle exhaust required a longer conditioning period than had been allowed for, and particle losses had not reached equilibrium during the initial phase of measurements. The original set of LPG data suggested a very small peak particle size, 10 nm or less, although the number count from the sizing instrument (SMPS) is not very reliable at this level. The size distributions found in the second set of LPG runs appeared to be more credible, in that the peak size (typically 60-80 nm) was similar to that found in the past for gasoline engines and it was much more like the CNG peak size. However, at the highest speed and load (120 km/h), the peak size was distinctly lower (approximately 20 nm).

Over the combined drive cycle, virtually all LPG particles were found in the 40 and 70 nm bands. There was no difference in particle size between the low-speed ECE and high-speed EU drive cycles. A significantly higher particle flux (total number of particles flowing) was found for CNG, particles being spread across all three size-bands investigated (15, 40 and 70 nm). For CNG, a greater proportion of smaller particles was emitted during the EU drive cycle, which is consistent with the steady-speed results.

One other possible factor which would influence particle emissions is fluctuation in the level of lubricating oil ingress to the combustion chamber. Indeed, lubricating oil combustion may account for a significant proportion of the total amount of particulate produced when operating on gaseous fuels. Unfortunately, it proved impossible to quantify the particulate solvent organic fraction (SOF) and no attempt was made to quantify the fuel/lubricating oil split. Alternatively, CNG may contain a trace of compressor oil introduced at the refuelling stage.

Very small quantities of metals and anions at similar levels were found in the particulate emissions from LPG and CNG. None of the 16 EPA priority polynuclear aromatic hydrocarbon compounds (PAH's) were found in significant quantity.

A brief comparison of the LPG van results with data for a catalyst-equipped diesel van obtained during the UK Government's Particulates Research Programme indicates:

- much greater emissions of larger particles (50-200nm) from the diesel vehicle;
- a five to seven fold increase in the rate of emission of particles at the peak of the particle size distribution, for diesel relative to LPG.

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# 1. OBJECTIVE

The objective of the test programme was to apply recently-developed exhaust particle sizing/compositional analysis techniques to liquefied petroleum gas (LPG) and compressed natural gas (CNG).

In completing the work, the specific aims were:

1. To determine the size distribution of particulate matter emitted in the exhaust stream from LPG and CNG engines, when operated under steady-state conditions and over the combined ECE+EUDC European regulation drive cycle.
2. To carry out compositional analysis of the particulate matter collected.

## **2. METHODS**

### **2.1 Regulated Emissions: Methods And Equipment**

#### **2.1.1 Test Vehicles**

For the purposes of this demonstration programme, two test vehicles were obtained on loan. These were a 2.0 litre gasoline-engined Ford Transit 2000 converted to run on LPG and a 3.3 litre dedicated CNG litre Chrysler Caravan of similar body size and overall weight. The basic vehicle specification data were as follows:

##### **Ford Transit 2000 (LPG, bi-fuel)**

Engine Type:	Gasoline, 2.0 litre, 8-valve DOHC, distributor-less electronic ignition system.
Fuel Injection Type:	Standard gasoline multi-point, electronic injection system plus Necam multipoint gas injection system (gas injectors mounted in manifold, downstream of gasoline injectors).
Designated Emissions Control:	Heated lambda sensor, 3-way catalyst.
Transmission:	5-speed manual
Odometer Reading at Start of Test:	13,230 km.

##### **Chrysler Caravan (CNG, dedicated)**

Engine Type:	Gasoline, 3.3 litre V-6.
Fuel Injection Type:	Dedicated multi-point, electronic gas injection system of US manufacture.
Designated Emissions Control:	Heated lambda sensor, 3-way catalyst
Transmission:	4-speed automatic
Odometer Reading at Start of Test:	18,643 km.

#### **2.1.2 Test Fuel**

A controlled supply of LPG was made available by the company who owned the Transit and this was used in all tests. Cylinders from this batch were made available to TNO when they completed further, independent tests with the vehicle (selected results from TNO's tests are reproduced in Appendix B).

The natural gas vehicle was fuelled at a single filling centre, which was supplied with UK mains gas.

No independent analysis was made of either fuel by AEA Technology.

### **2.1.3 Test Vehicle Preconditioning**

The detailed operating history of the LPG Transit was not known. The vehicle had been loaned to various operators prior to test, and it was possible that it had been run on gasoline for extended periods (rather than just being started and operated on gasoline for a few seconds, as the vehicle's electronic control unit (ECU) requires automatically). In an attempt to ensure that the exhaust system was in representative condition prior to dynamometer testing, and to minimise any possible gasoline carry-over effect, the Transit was run for an extended period (200 km +) on LPG by its owner.

The Caravan was not felt to need any special preconditioning, as it could only run on gas and it was, in any event, confined to a narrow selection of operational duties by its short range.

### **2.1.4 Test Equipment**

The test vehicles were mounted on a standard MRW chassis dynamometer and their exhaust tailpipes connected to a Cussons PDP-type Constant Volume Sampling (CVS) system, fitted with a 8" (200 mm) diameter dilution tunnel designated for gas vehicle testing. (Of course, the analytical equipment was the same as used in conventional fuels test work.) To minimise the danger of deposits flaking off from the duct walls, rigid tubing was used to the fullest extent possible. Gaseous exhaust samples were collected in 60 litre Tedlar bags and passed through a Signal model 4000 chemiluminescent analyser to determine oxides of nitrogen (NO<sub>x</sub>), Signal model 2000 non-dispersive infra-red (NDIR) analysers to determine carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), and a Signal model 3000 flame ionisation detector (FID) to determine total hydrocarbons (THC). Particulate samples were collected on 47 mm filter papers (either Teflon-coated Pallflex TX40 H120 or high-density polythene-backed Teflon membrane Millipore 'Fluoropore' FHLP 047 00, depending on the subsequent analysis required).

### **2.1.5 Test Protocol**

The test work was carried out in accordance with EC emission testing regulations, and a modified form of the published EPEFE test protocol was followed for dilution tunnel conditioning. In its normal form, the protocol calls for the tunnel to be operated prior to testing, with the vehicle exhaust uncoupled and 90% of the dilution-air intake blocked off, for 15 minute periods, until a subsequent 10 minutes of particulate sampling gives less than 0.25 mg PM. For the purposes of this programme, where far lower sample weights were anticipated, the target figure was reduced to 0.025 mg. Tunnel conditioning was carried out each morning and prior to any change in test type (e.g. upon completing the steady-state sizing tests and moving on to drive cycle measurements).

To minimise any operator effects, all cycles were driven by one individual.

## 2.2 Particle Sizing

### 2.2.1 Instrumentation

A Scanning Mobility Particle Sizer (SMPS, TSI, USA) was used to measure particle size from the dilute engine exhaust stream in the CVS tunnel.

It should be noted that the sample probe for the SMPS was not fitted with a shielding cone of the type specified for the standard particulate sample probe. This item was omitted in an effort to minimise any probe effect on the particle size distribution measurements. (It has been shown in the UK Government's Particulates Research Programme that non-isokinetic sampling, e.g. due to a cone, will distort the collection efficiency of the probe non-uniformly across the particle size range).

#### SMPS - Scanning Mobility Particle Sizer

**Operating range:** 0.004 - 1.0  $\mu\text{m}$   
**Advantages:** range suitable for measurement of primary particles and small aggregates; good particle number concentration discrimination  
**Disadvantages:** scanning time across particle size range, unable to determine large aggregates

### 2.2.2 Sampling

#### Sampling Regime

Steady-state running was carried out on the chassis dynamometer at selected speeds and under road-load conditions (the nominal operating conditions are set out in Table 2.1). Predetermined gear ratios were used with the (manual) Transit. Other than at idle, when neutral was selected, the automatic Caravan transmission was operated in 'Drive' throughout.

**Table 2.1 Nominal road speeds for steady-state tests**

Mode	Speed	Gear (Man.)	Gear (Auto.)
1	idle	Neutral	Neutral
2	15 km/h	2	D
3	30 km/h	3	D
4	50 km/h	4	D
5	70 km/h	5	D
6	90 km/h	5	D
7	100 km/h	5	D
8	120 km/h	5	D

At each target speed, the oil temperature was allowed to stabilise before any size measurements were made. The SMPS was operated repeatedly until two consecutive scans gave consistent results and only then were the data recorded.

An analysis of the steady-state SMPS size-distribution plots provided base-line information on the particle size and concentration characteristics of each engine/vehicle combination. Three size bands were selected to cover the emissions anticipated from the combined ECE+EU drive cycle.

The steady-state work was followed by transient tests over dynamometer drive-cycles. Combined ECE+EUDCs were completed in sets of three, the SMPS being set to scan continuously at fixed particle size. Three sets of three cycles were run, the nominal SMPS particle size being changed for each set.

### **Sampling Details**

The sample probe for the particulate sizing instruments was located in the dilution tunnel, at the same distance downstream of the dilution air inlet as the 'regulation' sample probe for the mass collection filters. At this point in the tunnel the flow is assumed to be fully mixed. The sizing probe was formed from a 350 mm long, 4 mm i.d., 20 SWG tube. This was bent through 90° on a 50 mm radius, to form an unshielded, pitot-type probe facing the flow. It was located on a radial line from the centre of the tunnel, mid-way between the mass sample probe and the tunnel wall, in order to minimise any potential wall effects. Sampling was not isokinetic. (The ideal probe location is on the tunnel centre line, but this would have prevented simultaneous sizing and mass measurement.)

## **2.3 Composition**

### **2.3.1 Particulate Sampling**

Diluted exhaust gas was drawn from the regulation (shielded) sample probe through two pairs of pre-conditioned, pre-weighed filters. Each pair consisted of a main sample paper and a back-up. The pumps for the two sample trains were run at the same nominal flowrate. To ensure that sufficient sample was collected, filters were retained for a number of combined ECE+EU drive cycles (the rolls distance covered being 11.01 km per ECE+EUDC, and the duration of each combined cycle being 19 min 40 sec). The amount of sample collected was expected to be very small and repeat measurements were made with the tunnel operating at a reduced total flow (giving a higher exhaust gas concentration). For the same reason, both the primary and backup filter were weighed and submitted for analysis. [Refer to Appendix A for further details of the test conditions.]

### **2.3.2 Sampling Media**

Following the recommendations made in the Task 1 Discussion Report (Appendix A), Millipore 'Fluoropore' (high-density polythene backed Teflon membrane) filter papers, type FHLP 047 00 were used as a sample collection medium where anion and

metals compositional analysis was to be carried out. To minimise the existing, 'as-found', level of these components, these papers (blank and sample papers alike) were pre-extracted with the appropriate solvents (see Appendix A). Fluoropore papers tend to hold a static charge, requiring charge neutralisation before weighing. 'Pallflex' sample papers, which are more robust and less prone to static effects, were used in particulate collection for straightforward mass determination and for PAH analysis.

**Table 2.2 Sampling media**

<b>Analytes</b>	<b>Sampling media (47 mm diameter)</b>	<b>No of samples</b>
Regulation mass	'Pallflex' 0.3µm retention, type TX40H120WW	2 pairs
Anions - sulphate, sulphite, nitrate, nitrite, chloride, bromide and phosphate	Millipore 'Fluoropore', 0.5µm FHL P 047 00	2 pairs
Metals - Cd, Cr, Cu, Fe, Ni, Pt, Pd, Rh, V, Zn	Millipore 'Fluoropore' 0.5µm, FHL P 047 00	2 pairs
Organics - SOF, EPA's 16 priority PAHs	'Pallflex' 0.3µm retention, type TX40H120WW	2 pairs

### **2.3.3 Analytical Procedures**

The results of the various analyses were reported as nanograms (ng) or micrograms (µg) found on the filters. Blank filters were also analysed, these being pre-extracted in the same way as the sample papers. In this report, results are quoted both as total µg of analyte found and g analyte per km. In either case, for the purposes of reporting, the blank level has been subtracted from the amount found in each sample, and quantities of less than an order of magnitude more than the limit of detection have been taken to be not significant.

#### **Anions**

The 'anion' filters were extracted with 10 ml of 10% propan-2-ol in water containing 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate. The resulting extract was then measured using Ion Chromatography.

#### **Metals**

The 'metals' sample papers were ashed in silica crucibles at 500° C, and the residue dissolved by refluxing with a mixture of 5 ml concentrated HCl and 10 ml concentrated HNO<sub>3</sub> for approximately 2 hours. Any remaining filter residue was washed off the container wall and the sample reduced to 1 ml in the crucible. The sample was then diluted to 10 ml with deionised water.

Two different analytical techniques were used for the analyses: Inductively Coupled Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

**Polynuclear Aromatic Hydrocarbons (PAHs)/Soluble Organic Fraction (SOF)**

The 'PAH' filters were extracted with dichloromethane. The extracts were then analysed using Gas Chromatography - Mass Spectrometry (GC-MS) with deuterated internal standards (d8 naphthalene, d8 acenaphthylene, d10 acenaphthene, d10 fluorene, d10 anthracene, d10 pyrene, d10 chrysene, d12 benzo(b)fluoranthene, d14 dibenzo(ah)anthracene, d12 benzo(ghi)perylene, d10 fluoranthene).

To determine SOF, filters were extracted with DCM, dried, conditioned and reweighed.

### 3. RESULTS

Two sets of results are shown for the LPG Transit, which was re-tested when the original dynamometer setting was found to be in error (the road-load was too low at speeds above 90 km/h). The repeat test results are shown with an -R suffix and are set out in italics in the tables.

For comparison, Appendix C provides a few results from gasoline and diesel vehicles obtained using a similar experimental approach in the UK Government's Particulates Research Programme.

#### 3.1 Steady State

##### 3.1.1 'Regulated' Emissions

Regulated emissions and fuel consumption were measured during the steady-state particle size testing and the results are given in Tables 3.1 and 3.2

**Table 3.1 LPG Transit: steady-state emissions**

Speed km/h	Run code	CO <sub>2</sub> g/km	CO g/km	THC g/km	NO <sub>x</sub> g/km
15	102	184	0.080	0.089	0.020
30	103	136	0.071	0.012	0.002
50	104	113	0.068	0.031	0.000**
<i>50 R</i>	<i>200</i>	<i>108</i>	<i>0.070</i>	<i>0.022</i>	<i>0.003</i>
70	105	121	0.043	0.031	0.173
90	106	140	0.033	0.032	0.219
<i>90 R</i>	<i>201</i>	<i>150</i>	<i>0.048</i>	<i>0.028</i>	<i>0.216</i>
100	107	149	0.035	0.027	0.408
<i>100 R</i>	<i>202</i>	<i>170</i>	<i>0.033</i>	<i>0.027</i>	<i>0.462</i>
110*	108	155	0.039	0.023	0.449
<i>120</i>	<i>203</i>	<i>192</i>	<i>0.031</i>	<i>0.013</i>	<i>0.993</i>
Idle figures in g/minute					
Idle	1	31.6	0.039	0.020	0.001

Notes: \*Incorrect operating speed; should have been 120 km/h. \*\*Suspect instrument failure. Figures in italics refer to the repeat tests, which were made at a later date.



**Table 3.2 CNG Caravan: steady-state emissions**

Speed km/h	Run No	CO <sub>2</sub> g/km	CO g/km	THC g/km	NO <sub>x</sub> g/km
15	2	187	0.043	0.196	0.070
30	3	129	0.047	0.164	0.062
50	4	111	0.037	0.096	0.275
70	5	122	0.028	0.051	0.232
90	6	149	0.029	0.061	0.685
100	7	163	0.036	0.042	0.984
120	8	191	0.452	0.088	0.112
Idle figures in g/minute					
Idle	1	40.0	0.016	0.125	0.010

The measurement of regulated emissions was not a prime objective of this programme. However, it is interesting to note that the CNG vehicle produces very similar CO<sub>2</sub> figures to the Transit, less CO at low road-load but approximately 100% more total hydrocarbons (THC). These observations are consistent with CNG having a lower proportion of carbon than LPG and the fact that methane, its principal constituent, is relatively unreactive and is not oxidised as efficiently as other hydrocarbons in vehicle exhaust catalysts.

The tests repeated with the Transit gave figures very similar to the first set of results, suggesting that the error in setting vehicle road-load had little impact on gaseous emissions, at least.

### 3.1.2 Particle Size

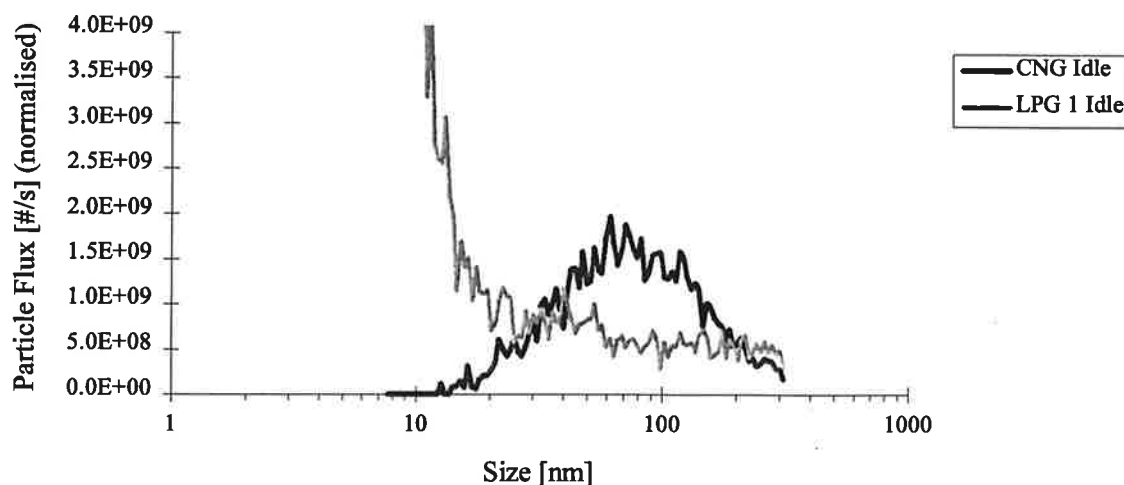
The Scanning Mobility Particle Sizer (SMPS) was used to measure particle size distributions at all 8 steady-speed test points. The individual size distribution and particle concentration for each road-load speed are plotted in Figures 3.1 - 3.8 and the total particle flux is summarised in Figure 3.9. In these figures, the legend 'LPG1' refers to the original set of tests made on the Transit and 'LPG2' refers to repeat tests made on the same vehicle several weeks later, with the correct (higher) road-load at speeds above 90 km/h. Throughout the plots:

$$\text{Normalised Flux} = dN/d\log(D_p),$$

where N = number of particles/sec and D<sub>p</sub> = particle diameter.

*[Although the LPG1 results relate to non-standard test conditions, the differences between the LPG1 and LPG2 particle size distributions were so large that it is worth reporting them in some detail.]*

**Figure 3.1 Particle size and concentration distribution at idle (point 1)**



**Figure 3.2 Particle size and concentration distribution at 15 km/h (point 2)**

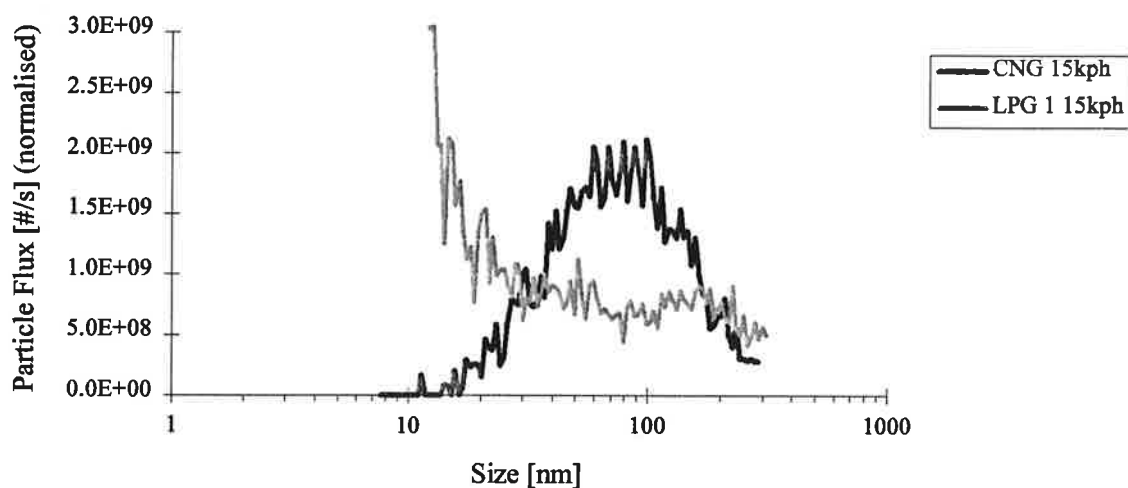


Figure 3.3 Particle size and concentration distribution at 30 km/h (point 3)

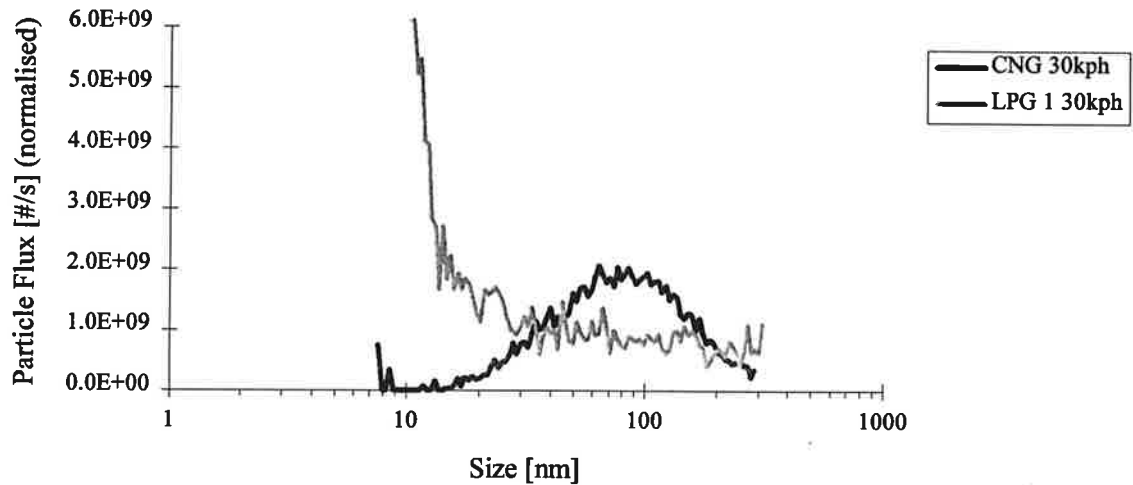


Figure 3.4 Particle size and concentration distribution at 50 km/h (point 4)

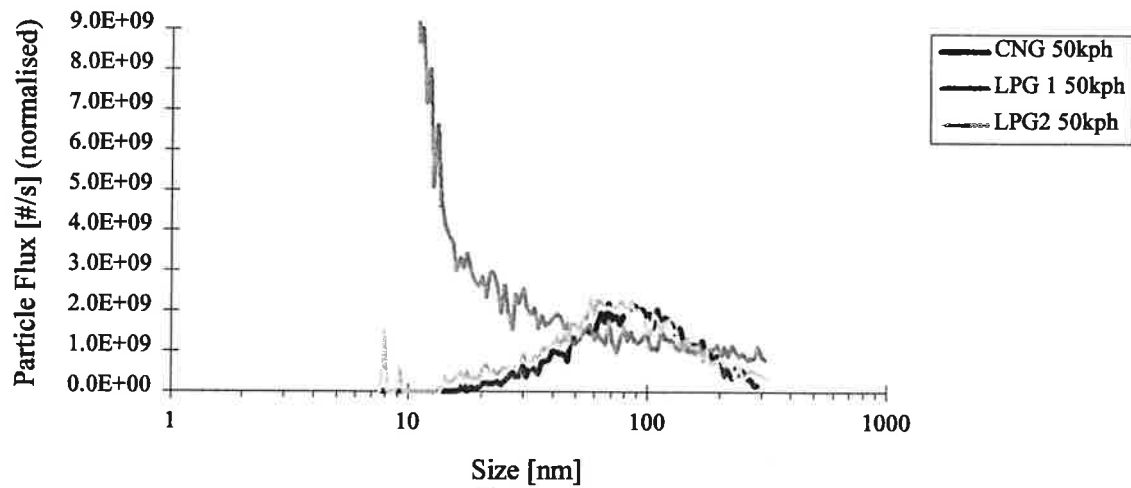


Figure 3.5 Particle size and concentration distribution at 70 km/h (point 5)

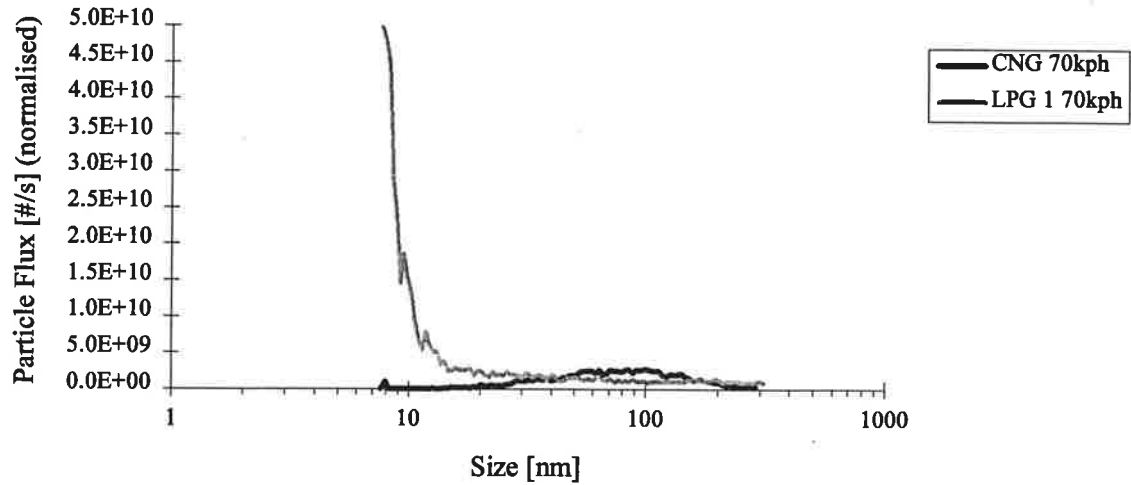


Figure 3.6 Particle size and concentration distribution at 90 km/h (point 6)

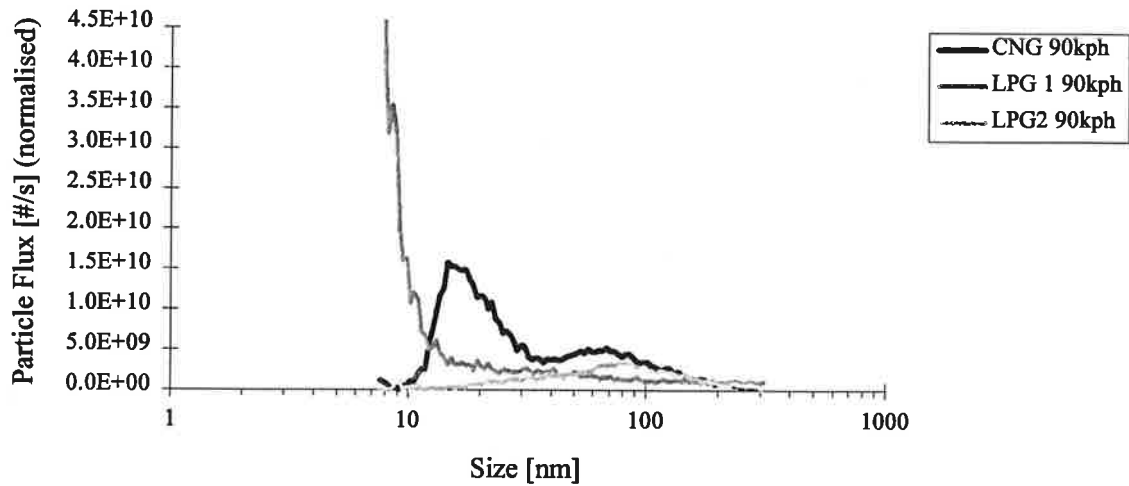


Figure 3.7 Particle size and concentration distribution at 100 km/h (point 7)

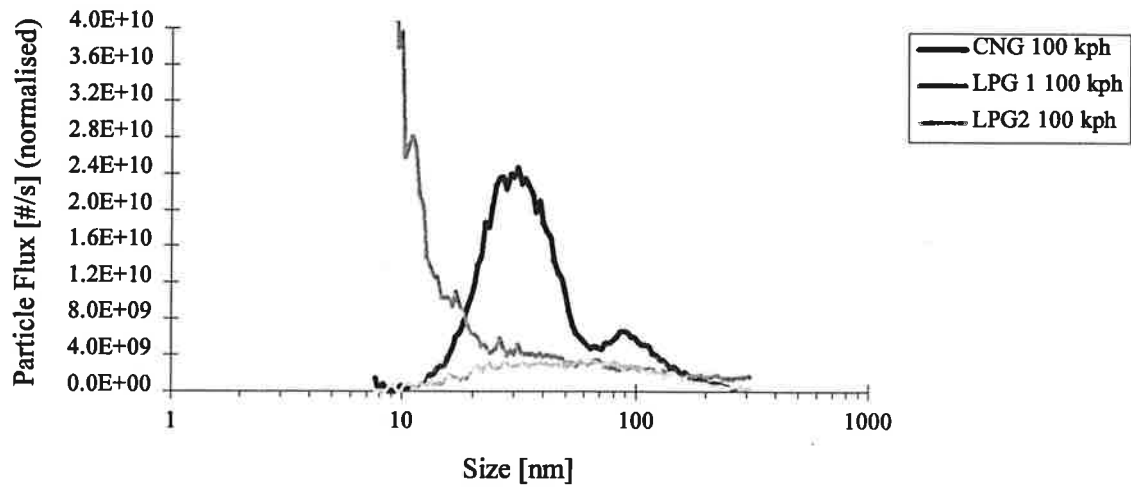
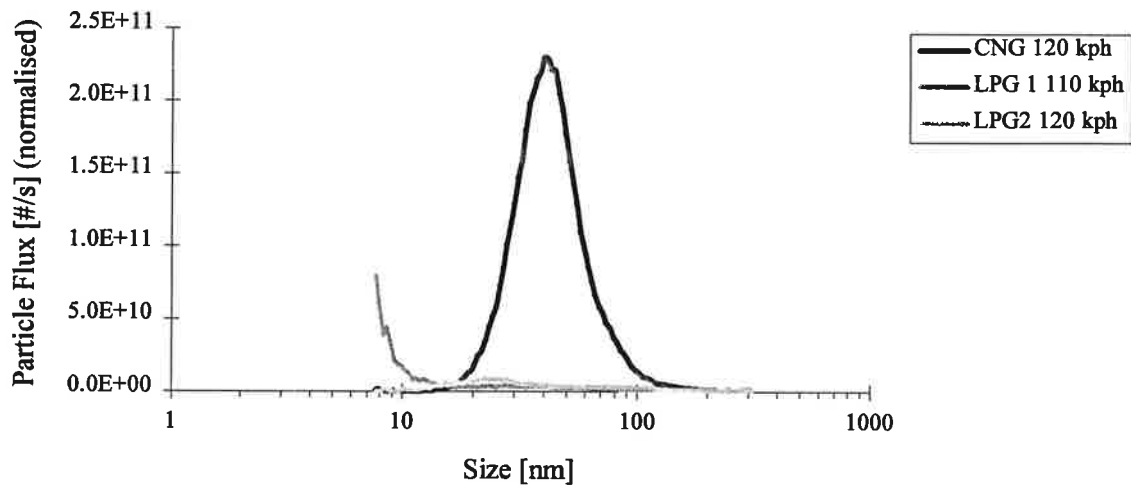
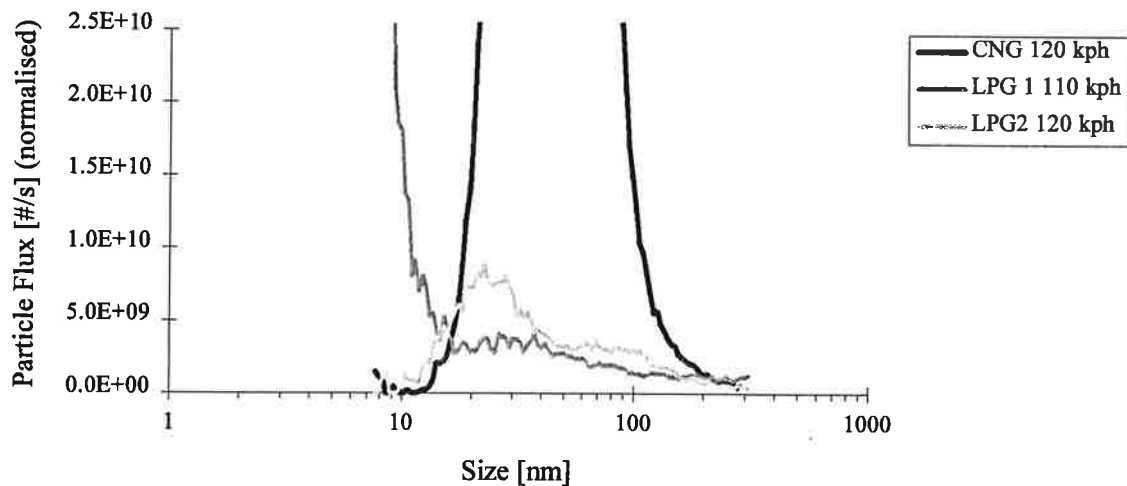


Figure 3.8(a) Particle size and concentration distribution at 110/120 km/h (point 8)



**Figure 3.8(b) Particle size and concentration distribution at 110/120 km/h (point 8), enlarged scale**



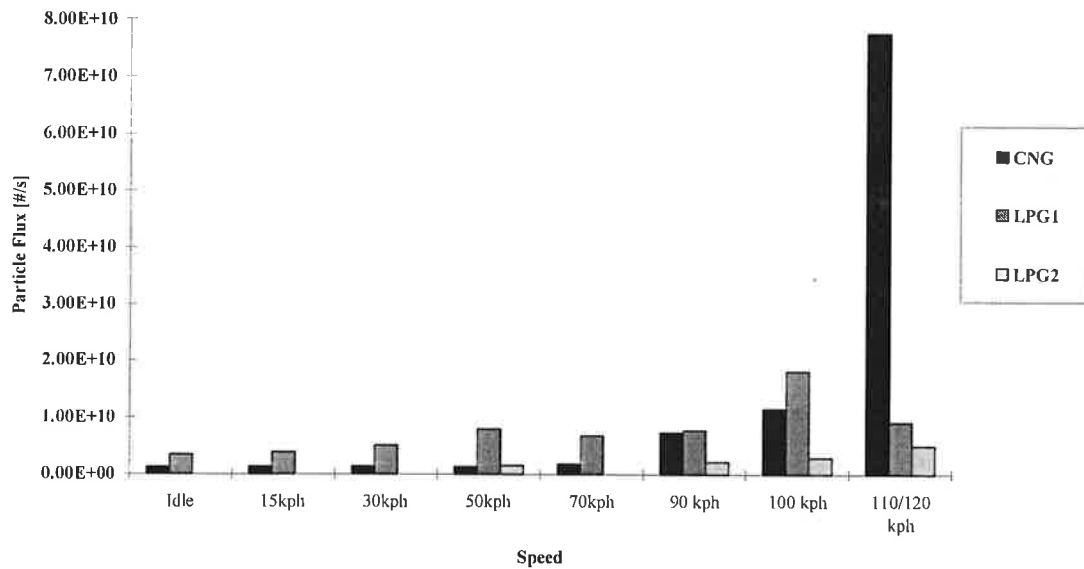
It must be said that the original set of LPG data ('LPG1') look very odd in comparison with the CNG data, the repeat LPG data ('LPG2') and, indeed, any of the past size-distributions seen from diesel and gasoline vehicles. On face value, they suggest a peak particle size (on a number distribution basis) of 10 nm or less. At this very small particle size, data from the SMPS are not very reliable because the proportion of very small particles following the correct flow path through the instrument is low and a correction factor is applied to the count.

The size distributions found in the repeat LPG runs ('LPG2') appear more credible, in that the peak size (typically 60-80 nm) is similar to that found in the past for gasoline engines and it is much more like the CNG peak size. However, at the highest speed and load (120 km/h), the peak size was distinctly lower (approximately 20 nm).

At idle and at road-load for speeds below 70 km/h, the peak size of CNG particles appears to be steady at approximately 80 nm. At 90 km/h there is evidence of a double peak (70/20 nm) or bi-modal distribution. The double peak is still seen at 100 km/h (90/30 nm), but seemingly disappears at 120 km/h - where there is a single peak at 40 nm. As with LPG, there is an overall trend in peak particle size falling with increasing road speed/load.

An idea of the total number of particles present in the exhaust stream at each operating condition is given by the average particle flux (number of particles/second), which is summarised in Figure 3.9 below:

**Figure 3.9 Average particle flux, steady-state runs**



At speeds below 70 km/h, the CNG vehicle seems to produce a lower average particle flux than the LPG one. However, at 90 to 100 km/h - where reliable LPG data are available (i.e. at the correct road-load) - the average particle flux for CNG appears to be higher.

Table 3.3 shows the particle size at the main peak in the number distribution together with any secondary peaks seen in the steady-state data. These data were used in determining the three sizes to use for the SMPS measurements over the combined ECE+EUDC runs.

**Table 3.3 Main peaks at steady-state points - SMPS**

Steady-state point	Main peak (nm) LPG	Main peak (nm) CNG	Secondary pk. (nm) LPG.	Secondary pk. (nm) CNG
1 (idle)	<10	70	none	none
2 (15km/h)	<10	80	none	none
3 (30km/h)	<10	80	none	none
4 (50km/h)	<10(1), 70(2)	80	none	none
5 (70km/h)	<10	90	none	none
6 (90km/h)	<10(1), 80(2)	20	none	70
7 (100km/h)	<10(1), 70(2)	30	none	90
8 (120km/h)	<10(1), 20(2)	40	none	none

Note: Figures in italics refer to the repeat runs

On the basis of these number-distribution measurements, it was decided that drive cycle measurements should be conducted at nominal diameters of 15 nm, 40 nm and 70 nm.

## 3.2 Measurements - Driving Cycles

### 3.2.1 'Regulated' Emissions

Tables 3.4 and 3.5 show the gaseous emissions data for the two vehicles operating over the combined ECE and EU drive cycle. Three sets of ECE+EUDC cycles were run: one set of 9 runs with the CVS running at 65% of full capacity (i.e. its normal operating point, dilution ratio 25:1) for particle sizing and for the collection of particulate samples for metals and particulate-phase hydrocarbons, a second set of 4 x ECE+EUDC at 30% (reduced CVS flow) for anions and hydrocarbons (repeat), and a third set of 4 x ECE+EUDC at 30% for metals (repeat) and anions (repeat). 'Regulation' gaseous emissions were recorded for the first and last run in each set and for the middle run of the 9-run set.



**Table 3.4 LPG Transit - gaseous emissions measured by standard methods during particle sizing experiments (combined ECE and EU drive cycles)**

Run no.	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>
	<b>g/km</b>			
9	176	1.09	0.069	0.220
13	177	1.10	0.063	0.207
17	177	1.65	0.119	0.200
18	180	1.69	0.102	0.175
21	178	1.29	0.065	0.172
22	179	1.46	0.057	0.100
25	179	1.26	0.072	0.182
<i>204(R)</i>	<i>169</i>	<i>1.34</i>	<i>0.095</i>	<i>0.183</i>
<i>208(R)</i>	<i>175</i>	<i>1.20</i>	<i>0.073</i>	<i>0.174</i>
<b>Average</b>	<b>178</b>	<b>1.36</b>	<b>0.078</b>	<b>0.179</b>

NB Figures in italics refer to the repeat testing made at a later date. They are not included in the average.

**Table 3.5 CNG Caravan - gaseous emissions measured by standard methods during particle sizing experiments (combined ECE and EU drive cycles)**

Run no.	CO <sub>2</sub>	CO	THC	NO <sub>x</sub>
	<b>g/km</b>			
10	194	0.091	0.102	0.088
11	206	0.082	0.088	0.129
18	203	0.075	0.075	0.148
19	211	0.184	0.083	0.060
22	196	0.132	0.094	0.074
23	200	0.124	0.041	0.071
26	201	0.155	0.058	0.081
<b>Average</b>	<b>202</b>	<b>0.120</b>	<b>0.077</b>	<b>0.093</b>

The similarity between the two sets of Transit data suggest that the suspected error in dynamometer loading had no significant effect on gaseous emissions over the combined ECE+EUDC drive cycle.

Interestingly, and in contrast to the steady-speed results, the CNG vehicle gave similar hydrocarbon emissions to the LPG vehicle over the combined drive cycle. It also produced 50% less NO<sub>x</sub>. These apparent inconsistencies probably arise as a result of the differences in the engine operation strategies of a manual 2.0 litre four-cylinder engine and an automatic 3.3 litre V-6, and perhaps highlight the hazard in comparing European and Federal specification types over the European drive cycle alone.

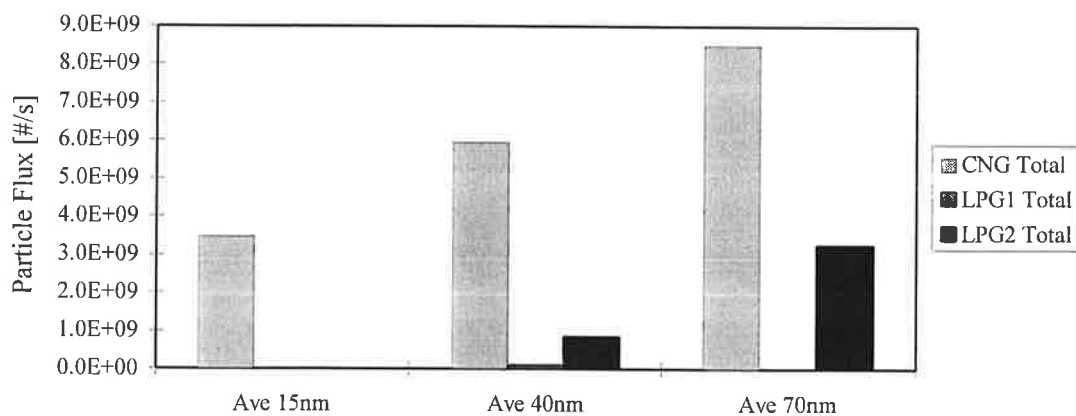
As it is, with no independent laboratory's or manufacturer's emissions data available for these specific vehicles, it is difficult to verify the figures. However, the results are similar to those from LPG and CNG vehicles of the same technology level tested for the purposes of the UK Alternative Fuels Trial (public domain report prepared by ETSU to be published shortly).

### 3.2.2 Sizing

#### Combined ECE+EU Drive Cycle

The SMPS was used to monitor particle concentrations at fixed, nominal particle sizes over the course of triplicate runs of the combined ECE and EU drive cycle. Diameters of 15, 40 and 70 nm were selected as they spanned the median sizes determined in the steady-state measurements for each vehicle

**Figure 3.10 Average particle flux at three sizes over combined ECE+EU drive cycle**



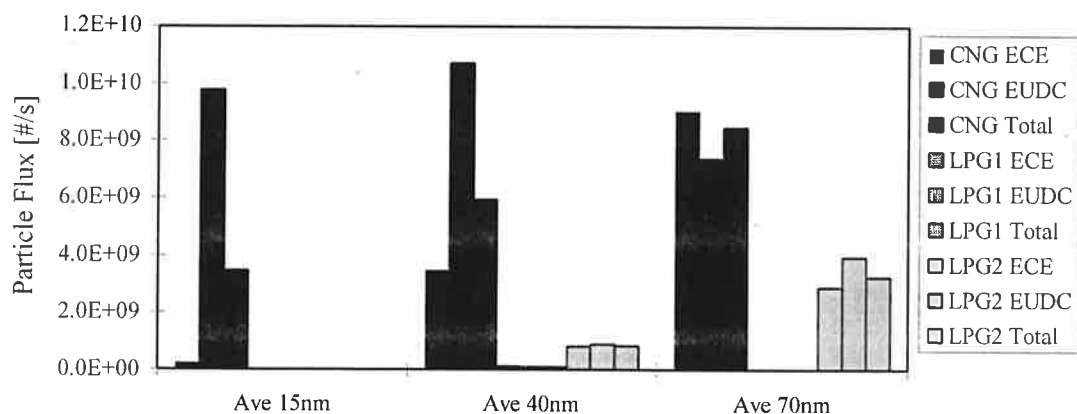
It is curious that the LPG vehicle produced such a low particle flux over the combined drive cycles during the original tests ('LPG1'). This could be consistent with the peak particle size genuinely being less than 10 nm, as the initial steady-speed tests suggested it was, but there is also a possibility that the dilution tunnel and vehicle exhaust system had not reached equilibrium in the time anticipated: it may simply be that there was excessive particle loss to the walls during the initial measurement phase.

The repeat LPG tests ('LPG2') showed a significant number of particles in the 40 and 70 nm bands, which is also consistent with the repeat steady-speed data (showing a shift toward larger particles).

In all cases, the particle flux appeared to be significantly higher with CNG.

In Figure 3.11 the average particle flux at each of the measured sizes has been split between the ECE and EU sections of the cycle. (The bars at each size are plotted in the same order as shown in the legend.)

**Figure 3.11 Average particle flux at three sizes over ECE and EU drive cycles**



This Figure shows that similarly-sized particles are emitted under low- (ECE) and high-speed (EU) drive cycles alike when operating on LPG, despite the trend in peak particle size falling with increasing speed seen in the (repeat) steady-speed data.

By contrast, a greater proportion of smaller particles is emitted at higher speeds on CNG. This is consistent with the steady-speed CNG results, where additional peaks at a smaller particle size were seen to appear at higher speeds.

### 3.2.3 Composition

Samples for mass and compositional analysis were collected using filter papers mounted in the standard paper-holders used for regulation emissions measurement. Prior experimentation (Appendix A) had shown that the low particulate mass-emission characteristics of the test vehicles would require multiple drive-cycle runs and that a reduced total CVS flow would help to ensure sufficient sample was collected, either for simple sample weighing or compositional analysis. The original scheme called for a set of 9 ECE and EU drive cycles with the CVS running at 65% of full capacity (normal setting, dilution ratio 25:1) for particle sizing and the simultaneous collection of metals and particulate-phase hydrocarbon samples, 4 x ECE+EUDC at 30% (reduced CVS flow) for anions and hydrocarbons (repeat) and 4 x ECE+EUDC at 30% for metals (repeat) and anions (repeat). It proved possible to do this for the LPG Transit, but excessive condensation occurred in the sample train with the CNG Caravan when the CVS was run at 30%. For this reason, the CVS flow had to be restricted to a minimum of 40% of maximum flow, rather than 30%, when the CNG vehicle was on test.

Great difficulty was experienced in weighing the filter papers, which had captured extremely low sample masses despite the number of runs made and the reduction in CVS flow. The papers were reconditioned in a temperature- and humidity-controlled room and static build-up was neutralised using an ion gun of the type used for gramophone records. Nevertheless, reweighings still produced variations in the apparent mass collected, or even indicated a net weight *loss* from certain papers.

#### Anions

As extremely small quantities of analyte were found, it is important to consider the findings on a rational basis: where the quantity of anion detected was equivalent to or less than the level found in the blank filter paper, or was within an order of magnitude of the limit of detection, the result was deemed not significant.

**Table 3.6 LPG Transit - particulate anion weights**

Run No.	Total PM	Cl <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>
	mg	µg of analyte				
18	0.267	1.50	0.70	0.80	2.00	0.60
22	0.152	0.10	n.s.	0.20	n.s.	n.s.
	g/km	g analyte/km				
18	0.0015	8.43x10 <sup>-6</sup>	3.94x10 <sup>-6</sup>	4.50x10 <sup>-6</sup>	1.12x10 <sup>-5</sup>	3.37x10 <sup>-6</sup>
22	0.0009	5.92x10 <sup>-7</sup>	n.s.	1.18x10 <sup>-6</sup>	n.s.	n.s.

n.s. = no significant quantity found

**Table 3.7 CNG Caravan - particulate anion weights**

Run No.	Total PM	Cl <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>
	mg	µg of analyte				
19	0.183	2.9	n.s.	2.4	n.s.	17.5
23	0.082	0.6	n.s.	1.3	n.s.	5.3
	g/km	g analyte/km				
19	0.0010	1.59x10 <sup>-5</sup>	n.s.	1.31x10 <sup>-5</sup>	n.s.	3.37x10 <sup>-6</sup>
23	0.0007	5.11x10 <sup>-6</sup>	n.s.	1.11x10 <sup>-5</sup>	n.s.	n.s.

**Metals**

Results are shown in Tables 3.8 and 3.9.

Where the quantity of a metal detected was equivalent to or less than the level found in the blank filter paper, or was within an order of magnitude of the limit of detection, the result was set aside as not being significant.

**Table 3.8 LPG Transit - particulate metal weights**

Run No.	Total PM	Cd	Cu	Ni	Fe
	mg	µg of analyte			
9	0.383	0.010	n.s.	0.12	1.70
22	0.490	n.s.	n.s.	0.07	0.93
	g/km	g analyte/km			
9	0.0020	5.23x10 <sup>-8</sup>	n.s.	6.27x10 <sup>-7</sup>	8.88x10 <sup>-6</sup>
22	0.0025	n.s.	n.s.	3.57x10 <sup>-7</sup>	4.74x10 <sup>-6</sup>

**Table 3.9 CNG Caravan - particulate metal weights**

Run No.	Total PM	Cd	Cu	Ni	Fe
	mg	µg of analyte			
10	0.183	n.s	0.12	0.29	1.60
23	0.082	n.s.	0.10	0.13	3.00
	g/km	g analyte/km			
10	0.0010	n.s	$6.57 \times 10^{-7}$	$1.59 \times 10^{-6}$	$8.76 \times 10^{-6}$
23	0.0007	n.s.	$8.52 \times 10^{-7}$	$1.11 \times 10^{-6}$	$2.55 \times 10^{-5}$

The predominant metal found, iron, is of course the material from which the engine blocks and exhaust systems are made.

### **Polynuclear Aromatic Hydrocarbons ( PAHs)**

Analysis of the samples from the LPG Transit, extracted with DCM, indicated that the levels of the 16 EPA priority PAH's present were below or at the limit of detection of the method used. Samples from the same vehicle extracted with toluene showed apparently significant levels of mid-range PAH's. However, the samples from repeat runs with the same vehicle, extracted with DCM and toluene respectively, had no detectable levels of PAH's present. This was also the case for samples taken from the CNG Dodge Caravan.

### **Soluble Organic Fraction**

Attempts were made to determine the soluble organic fraction (SOF) in the deposits found on several of the Pallflex filters. These attempts were not successful due to a combination of a) the very low weight of the particulate matter collected, and b) the loss of fibres from the filters during the DCM extraction processes. These factors resulted in the extracted filters apparently weighing less than they did in their clean state, before exposure to the exhaust gas: this is clearly irrational.

## **4. DISCUSSION**

### **4.1 Regulated emissions**

The measurement of regulated emissions was not a prime objective of this programme. Indeed, it would be wrong to give too much weight to a comparison between a dual-fuel European vehicle (LPG) and a dedicated alternative fuel, Federal specification vehicle (CNG).

However, it was interesting to note that under steady-speed conditions the CNG vehicle produced less CO at low road-load than the LPG one, but approximately 100% more total hydrocarbons (THC). These observations are consistent with CNG having a lower proportion of carbon than LPG and the fact that methane, its principal constituent, is relatively unreactive and is not oxidised as efficiently as other hydrocarbons in vehicle exhaust catalysts.

In contrast, the CNG vehicle emitted no more THC than the LPG vehicle over the combined ECE+EUDC drive-cycle and it also gave a marked (50%) reduction in NO<sub>x</sub>. However, this may well be a result of the two vehicles having very different drivetrains and being designated for different legislation and markets, which is likely to entail very different engine operation strategies.

### **4.2 Particle Sizing**

Repeated testing of the LPG vehicle gave inconsistent particle size data, although the gaseous emissions, at least, were consistent from one test series to another. This may be a reflection of some real effect: one possibility is that the dilution tunnel (and perhaps even the vehicle exhaust system) required a longer conditioning period than had been allowed, and thus particles were being lost to the duct walls during the original set of tests. However, TNO conducted sizing tests on the same vehicle using the same fuel immediately after AEA Technology's first set of tests, and they too found a large concentration of smaller particles (TNO's data are presented in Appendix B). AEAT's original series of tests suggested a peak particle size of 10 nm or less (although the number count from the sizing instrument (SMPS) is not very reliable at this level). TNO's suggested one of 20-30 nm.

The size distributions found in the repeat set of AEAT LPG runs appeared to be more like the typical gasoline, diesel or even CNG pattern, in that the peak size was 60-80 nm. However, at the highest speed and load (120 km/h), the peak size was distinctly lower (approximately 20 nm). Neither set of results gave the distinct, secondary peaks at 150 and 400 nm found by TNO in their steady-state testing (Appendix B).

At idle and at road-load and speeds below 70 km/h, the peak size of CNG particles appeared to be steady at approximately 80 nm. At 90 km/h there was evidence of a double peak (70/20 nm) or bi-modal distribution. The double peak was still seen at 100 km/h (90/30 nm), but seemingly disappeared at 120 km/h - where there is a single

peak at 40 nm. As with LPG, there was an overall trend in peak particle size falling with increasing road speed/load. In general, mean particle size *increases* with engine speed and load for diesel engines.

At speeds below 70 km/h, the CNG vehicle seemed to produce a lower average particle flux than the LPG one. However, at 90 to 100 km/h the average particle flux for CNG appeared to be higher. In contrast, TNO found what they have described as an “explosion in particle numbers” at high road speed with the LPG Transit (Appendix B), giving higher flux values than AEAT found for either test vehicle at 90 km/h and above. (To some extent, this must be a reflection of the dynamometer loading they used, which was approximately 20% higher than even AEAT’s revised setting at 90 km/h and above).

Over the combined drive cycle, particles were found in the 40 and 70 nm bands for LPG. A significantly higher particle flux was found for CNG, particles being spread through all three size-bands investigated (15, 40 and 70 nm). For LPG, TNO found particles extending up to a far greater size, in 23, 35, 153 and 356 nm nominal size bands (Appendix B). Curiously, as much as four orders of magnitude more of the largest particles were found than small ones, directly contradicting their steady-state results, which suggested there should be more of the small particles. TNO report that the small-particle count steadily rose and took at least ten minutes to stabilise during the steady-speed tests. They postulate that this “time effect” kept down the number of small particles during the rapidly-changing speed profile of the drive cycles

AEAT and TNO’s work alike show that there is no great difference in particle size distribution between low-speed (ECE) and high-speed (EUDC) parts of the combined drive-cycle when operating on LPG. By contrast, a greater proportion of smaller particles is emitted at higher speeds on CNG. This is consistent with the steady-speed CNG results, where additional peaks at a smaller particle size were seen to appear at higher speeds.

### **4.3 Composition - standard filter paper analysis**

It proved possible to make measurements for most of the analytes requested, although many were found to be present at very low levels as reported in Section 3.2.3. Despite the collection being made over a large number of runs, only a small amount of sample was obtained.

The Soluble Organic Fraction (SOF) determination was unsatisfactory.



## 5. CONCLUSIONS

Methods developed for determining exhaust particle size distribution and composition on diesel and gasoline vehicles can be used on the LPG and CNG alternatives.

However, for compositional analysis, the weight of sample collected per drive cycle is so small that multiple drive cycle runs, optimised analytical procedures and utmost care in sample handling are essential to ensure the reliability of results.

The LPG and CNG vehicles tested produced remarkably low particulate emissions, in terms of both mass and the number of particles present. Under most conditions, the mean size of the particles emitted was similar to those from gasoline vehicles, tested in the UK Government's Particulates Research Programme. However, very small particles were found under certain conditions, especially at higher engine speed and load.

In several instances LPG and CNG particle size distributions were similar. However, inconsistent particle size data were found when measurements were repeated on the LPG vehicle, possibly due to dilution tunnel conditioning effects, which must impose a measure of doubt over certain of the results. However, the possibility of some real effect causing a variation in LPG particle size distribution with time cannot be ruled out.

Another possible factor which would influence particle emissions is fluctuation in the level of lubricating oil ingress to the combustion chamber. Indeed, lubricating oil combustion may account for a significant proportion of the total amount of particulate produced. No attempt has been made in this programme to quantify the fuel/lubricating oil split. Alternatively, it is possible that CNG picks up a trace of compressor oil at the fuelling station.

Annex D provides a brief comparison of the LPG van results with data for a catalyst-equipped diesel van obtained during the UK Government's Particulates Research Programme. Key features are:

- much greater emissions of larger particles (50-200nm) from the diesel vehicle;
- a five to seven fold increase in the rate of emission of particles at the peak of the particle size distribution, for diesel relative to LPG.

Inter-fuel comparison remains a problem. Owing to the inherent vehicle-to-vehicle variability in emissions, inter-fuel differences may be masked or exaggerated in test data. Either a significant number of vehicles and models of each fuel type has to be tested to provide statistically reliable benchmark emissions factors, or bi-fuel vehicles need to be tested on both fuels to provide a back-to-back comparison. In addition, tests need to be carried out over drive cycles representative of real-life operating conditions, since the relative performance of two fuels (especially diesel versus spark ignition fuels) can vary with duty cycle and ambient temperature.

## 6. RECOMMENDATIONS

The gaseous alternative fuels are generally seen as having their greatest potential in substituting for diesel fuel in vans, buses and trucks. This reflects:

- the strong interest in reducing particulate emissions from heavy-duty diesel engines for health reasons - whereas light-duty gasoline engines produce substantially less particulate already;
- the higher potential for market entry by CNG and LPG into fleet operations, especially in urban applications where centralised refuelling minimises the fuel infrastructure requirement.

This IEA programme has provided initial indications of the potential of CNG and LPG to produce low numbers of particles (as well as low total mass). However, to confirm the advantages of these alternative fuels relative to diesel, it is recommended that the following work is undertaken:

1. More vehicles should be tested, focusing on urban applications where CNG and LPG have the greatest potential to substitute for diesel. In particular, vans and medium-duty truck engines (e.g. 6 cylinder, 6-9 litre) would be of interest. (Heavy-duty engines for buses and inter-urban heavy trucks might also be studied, but capital cost and other limitations suggest that gaseous fuels may have less potential in these applications).
2. Back-to-back testing between the gaseous and gasoline operation of individual bi-fuelled vehicles should be used to give a more reliable comparison. Similarly, dedicated gaseous vehicles should be tested in parallel with equivalent diesel comparators (including catalysts and traps as appropriate) built to the same emissions test specification.
3. Tests should be run over drive cycles typical of real-life operating conditions, as well as the regulatory drive cycles. A number of candidate cycles exist (for instance, developed by TNO and the former Warren Spring Laboratory in the UK).
4. The test work should involve extended vehicle and dilution tunnel conditioning, to ensure that emissions results are stable and reproducible.
5. Research should be developed to determine the contribution to overall particulate emissions from combustion of lubricating oil (and possibly CNG compressor oil).
6. In addition to tests on current technology vehicles, work on a standard test engine might be considered. In particular, this could be used to compare LPG and CNG. Such test work would confine changes to the fuel alone, although it would fail to evaluate the benefits of optimising the engine technology for each fuel type.

# APPENDIX A: DEVELOPMENT OF TEST METHODOLOGY

## 1. INTRODUCTION

The overall aim of this IEA study has been to characterise the particulate emissions from LPG and CNG fuelled light commercial vehicles.

Task 1, Development of Test Methodology, was aimed at increasing the amount of particulate matter (PM) collected, over and above that obtained from a single ECE + EUDC drive cycle, on a filter medium having lower blank levels than those previously employed. To this end, the work was split into two main areas:

1. Methods of increasing the amount of PM, and,
2. Methods of reducing the filter medium blank levels.

The vehicle studied during this Task was loaned by Shell UK Ltd. It was a Ford Transit Van powered by a 2 litre DOHC 8 valve gasoline engine, motor code NSF, converted with a Necam LPG vapour injection system and optimised for lowest emissions. The vehicle's exhaust system included a three-way catalyst. For all the runs described in this report, the vehicle was fuelled on LPG from suppliers located at Newbury and at Witney.

### 1.1 Methods of increasing the amount of PM

There are several ways in which this can be achieved:

- by increasing the number of drive cycles sampled on to the same filter;
- by increasing the flowrate of diluted exhaust gas through the filter;
- by decreasing the exhaust dilution ratio;
- by changing the design of the sampler for increased efficiency;
- by choosing alternative filter media offering higher flow rates.

Increasing the diameter of the filter used and simultaneously increasing the flowrate would also increase the amount of PM. However, this would also increase the blank levels due to the filter medium, e.g. changing from 47 to 70mm diameter filters would increase the blank levels by a factor of approximately 2.2.

### 1.2 Methods of reducing the filter medium blank levels

These methods fall into three categories:

- choosing a filter medium having inherently low blank values;
- pre-extracting the filter medium with the solvent to be used to extract the analytes of interest;
- using an extraction process that does not involve dissolution of the filter itself.

## **2. EXPERIMENTAL**

### **2.1 Increasing the amount of PM**

The aim of this part of the study was to investigate the options for increasing the weight of PM collected on the filter medium. This involved only gravimetric measurements and since no analyses were carried out at this stage, untreated standard Pallflex filters were used.

#### **2.1.1 Increasing the number of drive cycles**

This option is limited by two main factors, cost and driver fatigue. It was decided that a maximum of three, or possibly four, ECE+EUDC cycles driven back to back would be within the above limitations.

#### **2.1.2 Increasing the flowrate through the filter**

The AEA Technology Cussons filter sampling station is normally operated at a flow rate of approximately 33 l/min (550 cc/sec). Without radically altering the flow metering and pumping systems, the maximum flowrate which could be achieved, using standard 'Pallflex' filters, was approximately 35 l/min. Additionally, it was later observed that the type of filter medium used affected the flowrate e.g. using Millipore 'Fluoropore' filters reduced the flowrate to 25 l/min.

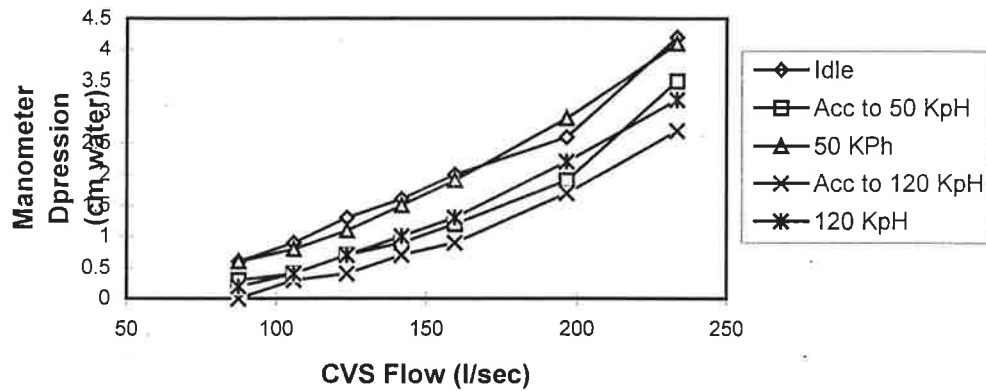
It was thought that attempting to increase the flowrate by a significant amount could be prejudicial to the filter's integrity and its ability to retain the PM without breakthrough. Hence the experiments were carried out using the 'normal' filter flow rate.

#### **2.1.3 Decreasing the exhaust dilution ratio**

The AEA Technology CVS system is normally run at a pump setting such that, for a standard ECE+EUDC drive cycle, the overall dilution ratio achieved for a 2 litre vehicle is approximately 25:1. Experiments were carried out using the Transit van, to determine the minimum pump setting necessary to ensure a reduced pressure in the CVS dilution tunnel, i.e. to confirm that the CVS was capable of coping with the highest exhaust flow from the van encountered during an ECE+EUDC drive cycle.

Figure 1 shows a plot of tunnel pressures at idle, acceleration to 50 kph, steady state 50 kph, acceleration to 120 kph and steady state 120 kph versus CVS flowrate, obtained from the van. From this it can be seen that a CVS flowrate of 105 l/sec is capable of handling the worst case exhaust output which is found on acceleration to 120 kph. This flowrate corresponds to 30% of the maximum attainable, compared to the 65% setting normally used.

**Figure 1. Effect of Reducing CVS Flow on Dilution Tunnel Pressure**



The calculated Reynolds number ( $Re$ ) for a flowrate of 105 l/sec through the 21 cm diameter dilution tunnel is 424,740. This is two orders of magnitude greater than the lower limit for turbulent flow of  $Re$  4,000.

## 2.2. Reducing the filter medium blank levels

The aim of this part of the study was to compare the reproducibility of the analytical results for anions and metals obtained from two filter media, to determine which had the lowest inherent blank values, and select the one most suitable for use.

### 2.2.1 Filter media having inherently low blank values

Manufacturers' figures for the blank levels of a selection of candidate filter media are shown in Table 1, below.

The two filters used in this study were standard 'Pallflex' Teflon bonded glassfibre, Type TX40H120WW, and Millipore 'Fluoropore' high density polythene backed Teflon membrane Type FHLP 047 00. The latter is a hydrophobic fluorocarbon polymer filter which has inherently low blank levels.

The filtration rating of the Pallflex filters is quoted as 99% for 0.3 micron particles and the Fluoropore filters chosen had a pore size of 0.5 microns.

**Table 1 Blank levels in filter media ( $\mu\text{g}$  per 47mm disc)**

Element or Anion	Regulation Pallflex (GFA for Anions)	Pallflex 'Tissuquartz'	Whatman EPM2000
Fe	44.000	<0.30	1.10
V	1.400		<0.10
Pb	0.380	<0.06	0.26
Cu		<0.30	0.07
Mo		<0.40	<0.20
As		<3.10	
Sn		<0.30	
Cd	0.013	<0.15	<0.06
Cr		<0.15	0.22
Co		<0.25	<0.06
Mn		<0.30	0.15
Ni	0.200	<.15	0.15
Zn		<0.30	0.54
Pd	0.053		
Pt			
Rh	0.034		
S			3.30
F <sup>-</sup>			51.60
SO <sub>4</sub> <sup>2-</sup>	3.20	4.7	
NO <sub>3</sub> <sup>-</sup>	3.00	0.63	
Cl <sup>-</sup>	10.00	1.25	37.00

Blanks in the Table generally indicate that the element / anion was not measured in 'Tissuquartz' or EPM200.

### 2.2.2 Pre-extracting the filter media

Pre-extraction of the filter media with the solvent to be used to dissolve the analytes of interest is the preferred method of blank level reduction. For these tests, the solvents used were ultra-pure anion-free water for the anion analyses and 10% ultra-pure nitric acid in ultra-pure water for the metals analyses.

### 2.2.3 Extraction not involving dissolution of the filter

If it is possible to remove deposits from the filter medium without digesting the whole filter this will result in further reduction in blank levels. It was considered that this could be achieved by ultrasonic treatment, therefore the pre-extraction treatment used involved immersing the filter media in the appropriate solvent and subjecting them to ultrasonic vibration. It was anticipated that after exposure, the filters would be subjected to the same treatment and that the deposit would be shaken off the filters thus eliminating the need to digest them.

### 3. TRIAL RUNS

A series of trial runs aimed at increasing the weight of PM collected was carried out using the same Pallflex filter for 3 consecutive hot start ECE+EUDC drive cycles at an ambient air temperature of 25° C. Steady state runs at 50 and 120 kph were also carried out - the run times were selected such that the vehicle covered the same distance as in the 3 x ECE+EUDC runs.

#### 3.1 Results

The weights of PM collected during the above runs are given in Table 1.

**Table 2 Mass of PM collected at a variety of CVS flow speeds and run types**

Run no.	Run type	CVS % speed	PM mass (mg)
MM01	3 x ECE+EUDC	65	0.4802
MM02	3 x ECE+EUDC	30	0.1870
MM03	3 x ECE+EUDC	30	0.1805
MM04	3 x ECE+EUDC	65	0.1126
MM05	Steady state 50 kph	30	0.0962
MM06	Steady state 120 kph	30	3.1485
MM07	Steady state 120 kph	30	2.7751

##### 3.1.1 Discussion

See Table 2 above. The filters from all the 3 x ECE+EUDC runs were dry when removed from the filter holders, showing that condensation was not a problem during these runs. The mass of PM collected from run MM01 suggested that, if the CVS speed was reduced to 30% of maximum then approximately 1 mg of PM would be collected. This is because the dilution of the exhaust would be reduced, so it would be expected that more particulate would be collected from the same volume of gas through the filter paper. This was clearly not the case, as runs MM02 and MM03 amply demonstrate - instead of a greater mass being collected a much smaller mass was collected with a reduced dilution ratio. However, a repeat run, MM04, at normal CVS speed gave approximately half the PM collected during runs MM02 and MM03; this was in agreement with the expectation of a lower mass being collected at a higher CVS speed.

The anomalous result from run MM01 may have been due to the vehicle having been driven for a considerable distance on gasoline prior to its arrival at Harwell. Despite the fact that it had been driven some 200 km at high speed on LPG prior to the first test, the exhaust system may not have been fully purged of gasoline residues. This suggests that any dual fuel vehicles tested in future should be driven solely on the test fuel for at least 1000 km prior to testing (apart from transient start-up on gasoline).

The filters from the steady state runs at 50 and 120 kph were wet when removed from the filter holder at the end of the runs and after conditioning they were stained brown. Because of this, the apparent PM weights obtained are considered to be extremely unreliable.

Drawing on the results obtained from these trial runs it was concluded that four consecutive ECE+EUDC runs would be the optimum number of runs providing sufficient PM for metals and anions analysis (estimated as between 0.1-0.2 mg as a minimum for composition analysis) while not being excessively time-consuming or expensive to perform.

#### **4. TEST RUNS**

Eight sets of four consecutive ECE + EUDC runs, MM09 - MM16, were carried out to provide PM samples for the determination of anions and metals. Duplicate samples for both sets of analytes on two different filter media, standard Pallflex and Millipore Fluoropore, were collected. All the filters used had been pre-extracted as described in Section 2.2.2.

##### **4.1 Filter Weighing**

Problems were encountered when weighing the filters both pre and post exposure. The acid-extracted Pallflex papers, marked \* in Table 3 below, did not achieve stable weights even after prolonged conditioning in a controlled environment held at 20° C and relative humidity of 45%. This was probably due to incomplete removal of nitric acid residues during the filter drying process. The Fluoropore papers were found to be so electrostatically charged that they attracted the balance pan to themselves when weighing was attempted. They could only be weighed after the static charge was neutralised using a commercial gramophone record static removal device.

The weights of PM obtained, and the total volume of diluted exhaust gas sampled, are given in Table 3.



**Table 3 Weight of PM obtained and volume of diluted exhaust gas sampled for a series of test runs**

Run number	Filter		Analytes	PM weight (mg)	Volume sampled (l)
	Number	Medium			
MM09	TXA1+2	Pallflex	Anions	0.2465	2617.0
MM10	TXA3+4	Pallflex	Anions	0.1721	2576.3
MM11	MPK1+2	Fluoropore	Metals	0.2658	1949.0
MM12	MPK3+4	Fluoropore	Metals	~0.22	1847.4
MM13	MPA1+2	Fluoropore	Anions	~0.22	2207.4
MM14	MPA3+4	Fluoropore	Anions	0.2179	1897.9
MM15 *	TXK1+2	Pallflex	Metals		2611.0
MM16 *	TXK3+4	Pallflex	Metals		2594.3

## 5. Analytical Results

### 5.1 Metals

The quantities of a suite of analytes (Ce, Cd, Fe, Ni, Pb, Pd, Pt, Rh, V, Zn) were determined after acid extraction of the filters. The analytes were those metals that are considered most plausibly to be implicated in the health effects of particulate inhalation. The measurement techniques used were ICP-AES and ICP-MS; independent quality control (QC) standards of  $10\mu\text{g}\cdot\text{ml}^{-1}$  for ICP-AES and  $50\text{ng}\cdot\text{ml}^{-1}$  for ICP-MS were analysed at the same time as the samples.

Table 4 gives the limit of detection (LOD), the mean blank levels, the levels found on the Pallflex filters and the result found for the QC standards for the analytes chosen. Table 5 gives the same data for the Fluoropore filters.

**Table 4 Mass of analyte ( $\mu\text{g}$ ) found on Pallflex filters**

Analyte	LOD $\mu\text{g}$	Mean blank	Run MM15	Run MM16	QC std $\text{ng.ml}^{-1}$	QC std $\mu\text{g.ml}^{-1}$
Ce	0.0002	2.0	2.3	2.2	50	n/a
Cd	0.002	0.02	0.31	0.2	49	n/a
Fe	0.03	115	160	160	n/a	9.8
Ni	0.07	(0.06)	12	5.5	n/a	10
Pb	0.002	0.75	1.2	0.96	49	n/a
Pd	0.0009	0.097	0.12	0.11	53	n/a
Pt	0.03	-	-	-	49	n/a
Rh	0.0002	0.047	0.057	0.055	50	n/a
V	0.03	5.2	6.4	6.5	n/a	10
Zn	0.03	210	160	79	n/a	9.7

- indicates that the result was found to be less than the LOD.

( ) indicates that the result was within an order of magnitude of the LOD and has a high uncertainty.

The measurement uncertainty for results significantly above LOD is estimated to be +/- 20%.

**Table 5 Mass of analyte ( $\mu\text{g}$ ) found on Fluoropore filters**

Analyte	LOD $\mu\text{g}$	Mean blank	Run MM11	Run MM12	QC std $\text{ng.ml}^{-1}$	QC std $\mu\text{g.ml}^{-1}$
Ce	0.0002	0.002	0.0063	0.0069	50	n/a
Cd	0.002	-	0.12	0.02	49	n/a
Fe	0.03	-	11	2	n/a	9.8
Ni	0.07	-	1	-	n/a	10
Pb	0.002	0.01	0.11	0.052	49	n/a
Pd	0.0009	-	-	-	53	n/a
Pt	0.03	-	-	-	49	n/a
Rh	0.0002	-	-	-	50	n/a
V	0.03	-	-	-	n/a	10
Zn	0.03	4.4	10	4.8	n/a	9.7

- indicates that the result was found to be less than the LOD.

( ) indicates that the result was within an order of magnitude of the LOD and has a high uncertainty.

The measurement uncertainty for results significantly above LOD is estimated to be +/- 20%.

Table 6 gives a comparison between the results obtained using the different filter media. The analyte levels quoted have been corrected for the blank contribution from the appropriate medium.

**Table 6 Mass of analyte ( $\mu\text{g}$ ) found, corrected for blank levels**

Analyte	Pallflex filter		Fluoropore filter	
	MM15	MM16	MM11	MM12
Ce	0.3	0.2	0.0043	0.0049
Cd	0.29	0.18	0.12	0.02
Fe	45	45	11	2
Ni	12	5.5	1	
Pb	0.45	0.21	0.10	0.042
Pd	0.023	0.013	-	-
Pt	-	-	-	-
Rh	0.010	0.008	-	-
V	1.2	1.3	-	-
Zn			5.6	.4

### 5.1.1 Discussion

From Table 3 it can be seen that the results for many of the analytes determined on the Pallflex filters are close to the blank levels found on the unexposed filters. The high blank levels found, together with the specified uncertainties given for the analyses, cast doubt on the validity of the results obtained for these test runs, MM15 and MM16 in Table 5 above.

This contrasts with the results reported for the Fluoropore filters (Table 4) where, although low in themselves, the levels found on the exposed filters are significantly higher than those on the unexposed filters. It is therefore considered that results obtained from these test runs, MM11 and MM12 in Table 5, are more reliable. For this reason Fluoropore filters were selected for the main part of this project.

### 5.2 Anions

The quantities of a suite of analytes ( $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{BR}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ) were determined after extracting the filters with 20 milli Molar aqueous NaOH solution. The analytes were those ions that are considered most plausibly to be implicated in the health effects of particulate inhalation. The measurement technique used was Ion Chromatography.

Table 7 gives the limits of detection (LOD), the blank levels and the levels found on the Pallflex filters for the analytes chosen. Table 8 gives the same data for the Fluoropore filters. It should be noted that the blank levels for both media were measured using a higher sensitivity than for the samples, hence the LOD values quoted are lower.

**Table 7 Mass of analyte ( $\mu\text{g}$ ) found on Pallflex filters**

Analyte	Blank		Sample	MM09	MM10
	LOD $\mu\text{g}$	Found $\mu\text{g}$	LOD $\mu\text{g}$		
$\text{Cl}^-$	0.1	<0.1	0.1	12	24
$\text{NO}_2^-$	0.1	<0.1	0.3	<0.3	<0.3
$\text{Br}^-$	0.1	<0.1	0.4	<0.4	<0.4
$\text{NO}_3^-$	0.1	0.7	0.4	48	57
$\text{PO}_4^{---}$	0.3	<0.3	1.4	<1.4	<1.4
$\text{SO}_4^{--}$	0.2	0.4	0.5	45	26

The measurement uncertainty for results significantly above LOD is estimated to be +/- 10%

**Table 8 Mass of analyte ( $\mu\text{g}$ ) found on Fluoropore filters**

Analyte	Blank		Sample	MM13	MM14
	LOD $\mu\text{g}$	Found $\mu\text{g}$	LOD $\mu\text{g}$		
$\text{Cl}^-$	0.1	<0.1	0.1	1.7	0.3
$\text{NO}_2^-$	0.1	<0.1	0.3	<0.3	<0.3
$\text{Br}^-$	0.1	<0.1	0.4	<0.4	<0.4
$\text{NO}_3^-$	0.1	0.7	0.4	4.3	3.6
$\text{PO}_4^{---}$	0.3	<0.3	1.4	<1.4	<1.4
$\text{SO}_4^{--}$	0.2	0.4	0.5	15	8

The measurement uncertainty for results significantly above LOD is estimated to be +/- 10%

Table 9 gives a comparison between the results obtained using the different filter media. The analyte levels quoted have been corrected for the blank contribution from the appropriate medium.

**Table 9 Mass of analyte ( $\mu\text{g}$ ) found, corrected for blank**

Analyte	Pallflex filter		Fluoropore filter	
	MM09	MM10	MM13	MM14
$\text{Cl}^-$	12	24	1.6	0.2
$\text{NO}_2^-$				
$\text{Br}^-$				
$\text{NO}_3^-$	47	56	4.1	3.4
$\text{PO}_4^{---}$				
$\text{SO}_4^{--}$	45	26	14.6	7.6

### **5.2.1 Discussion**

The results given in Table 9 for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , the only anions detected, are very different for the two filter media. Those obtained from the Pallflex filters are very much higher than those from Fluoropore. However, this is not reflected in the blank levels reported for the two filter media. The analysts reported that the exposed Pallflex filters were extracted for a considerably longer period than the blank filters and that this could have caused anions to be leached from the glass fibre substrate of the filters.

This fact, together with the much lower blank levels found on the Fluoropore filters, also suggests that Fluoropore filters should be used for this type of determination.

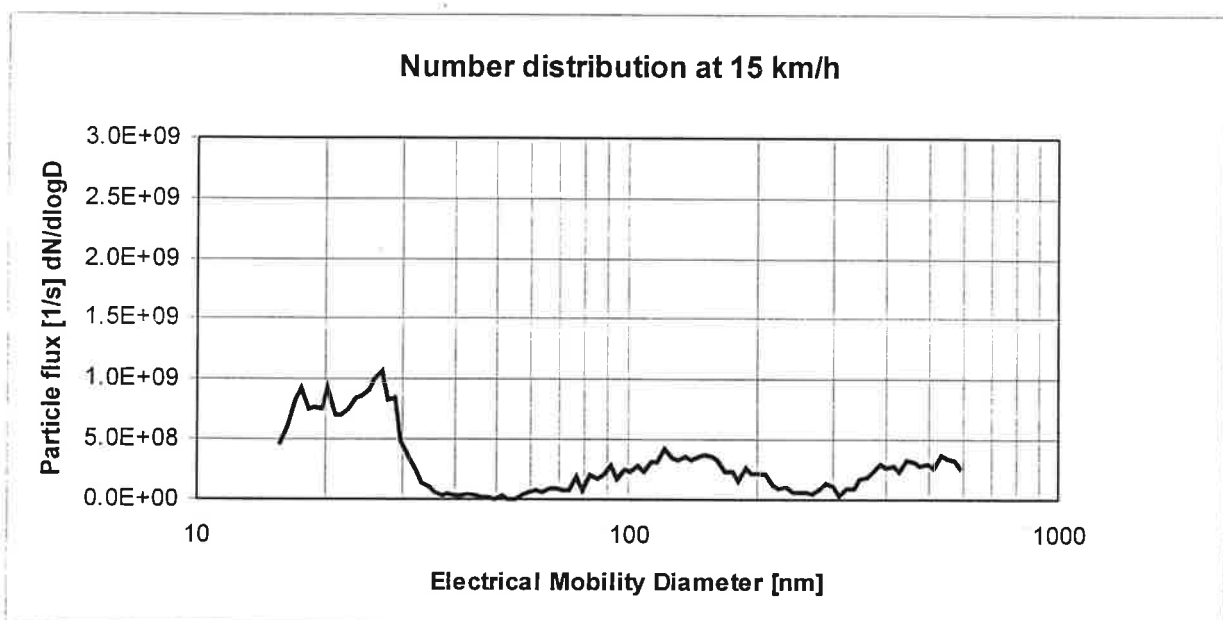
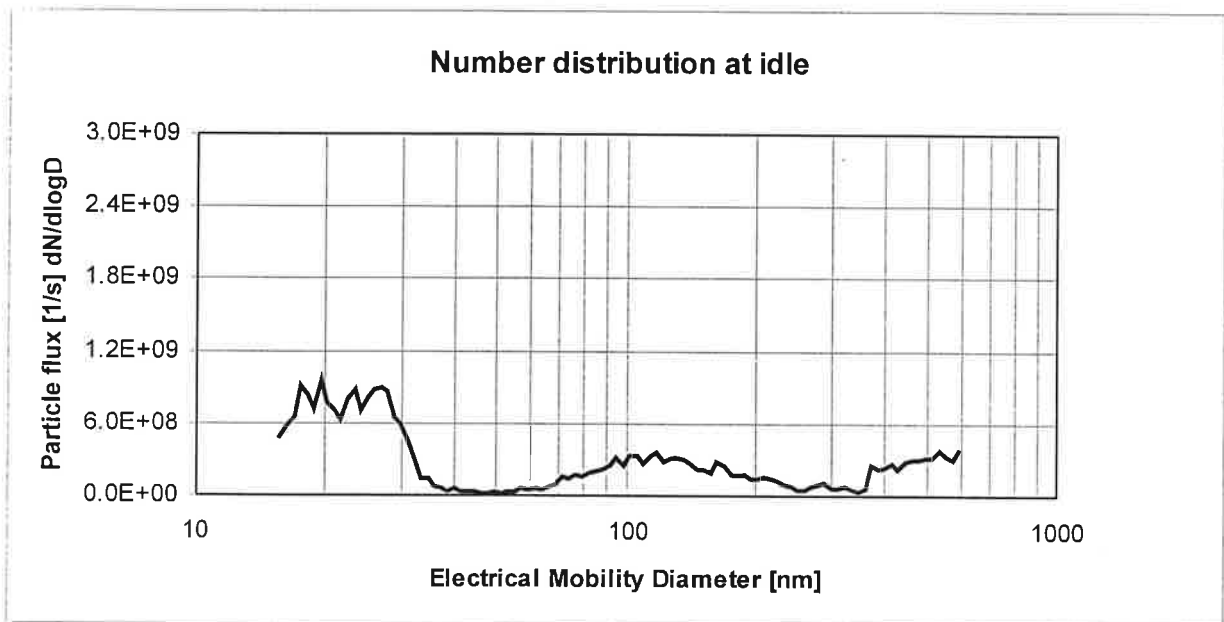
## **6. Conclusions**

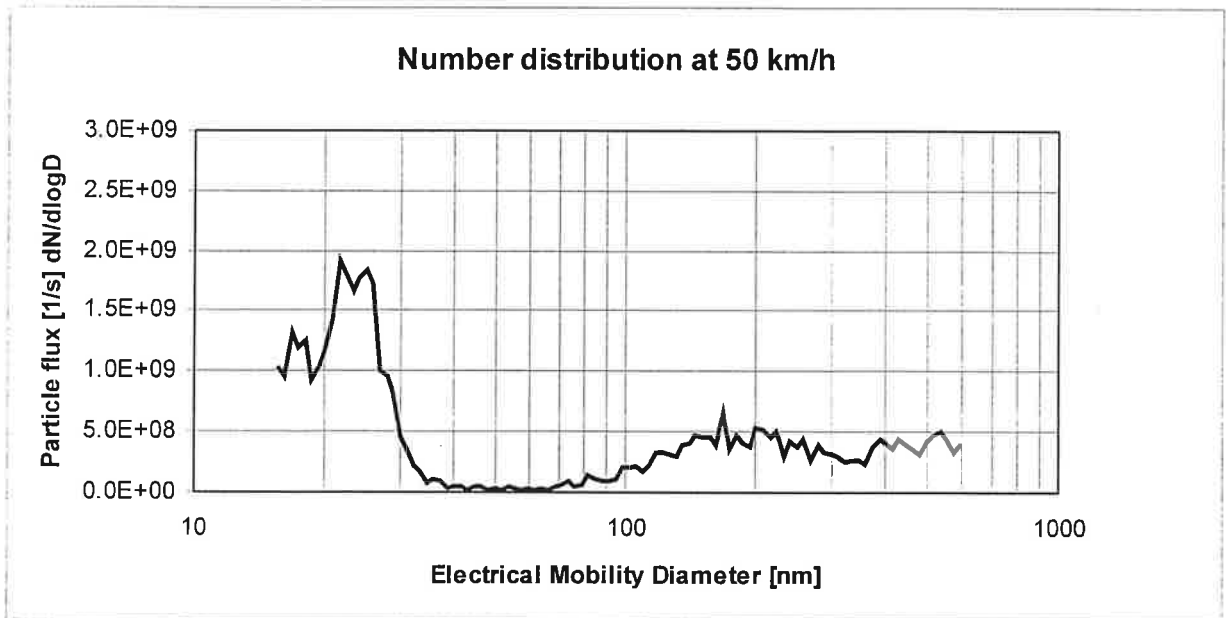
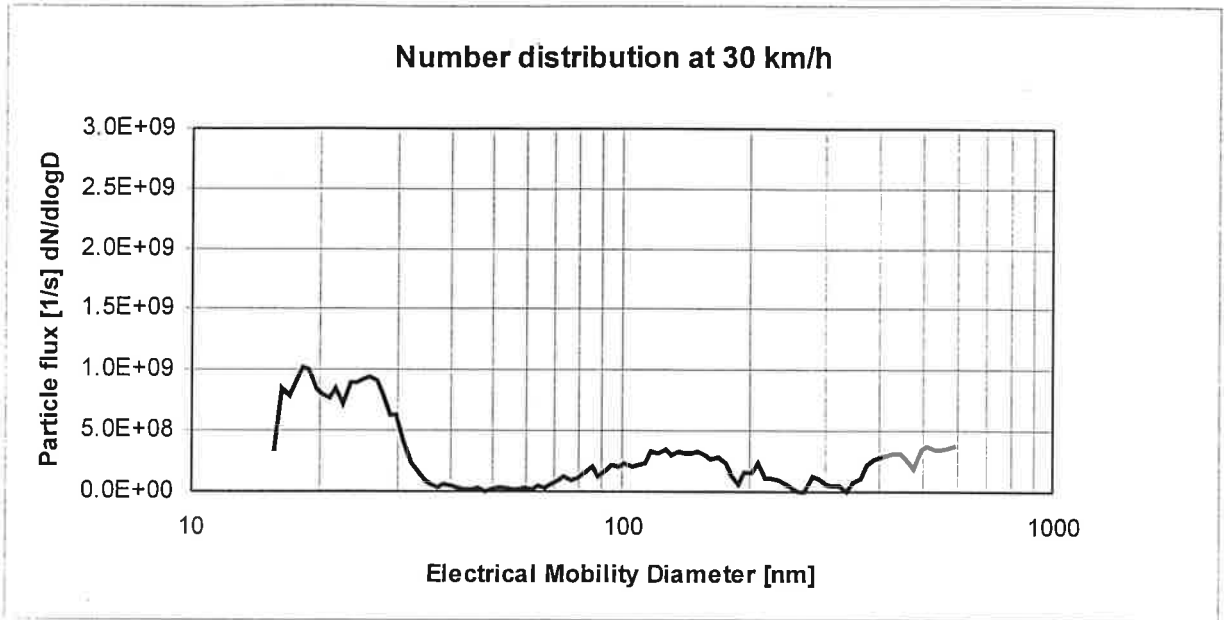
Methods of increasing the amount of PM available for analysis and decreasing the filter medium blank levels have been investigated. This work has shown that multiple drive cycles and a reduced exhaust dilution factor produce an increase in PM and that Fluoropore filters have significantly lower blank levels than the normal standard Pallflex filters. Pre-cleaning the filters also has a beneficial effect. The use of ultrasonics to remove the collected PM from the filters was not entirely successful due to the 'sticky' nature of the deposit.

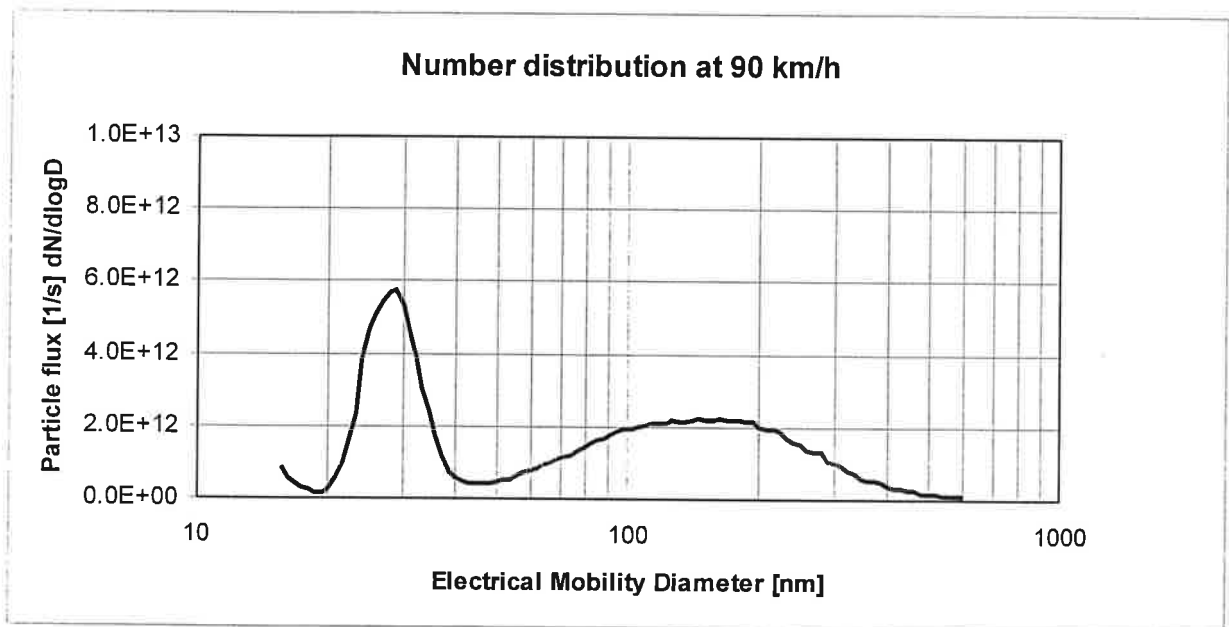
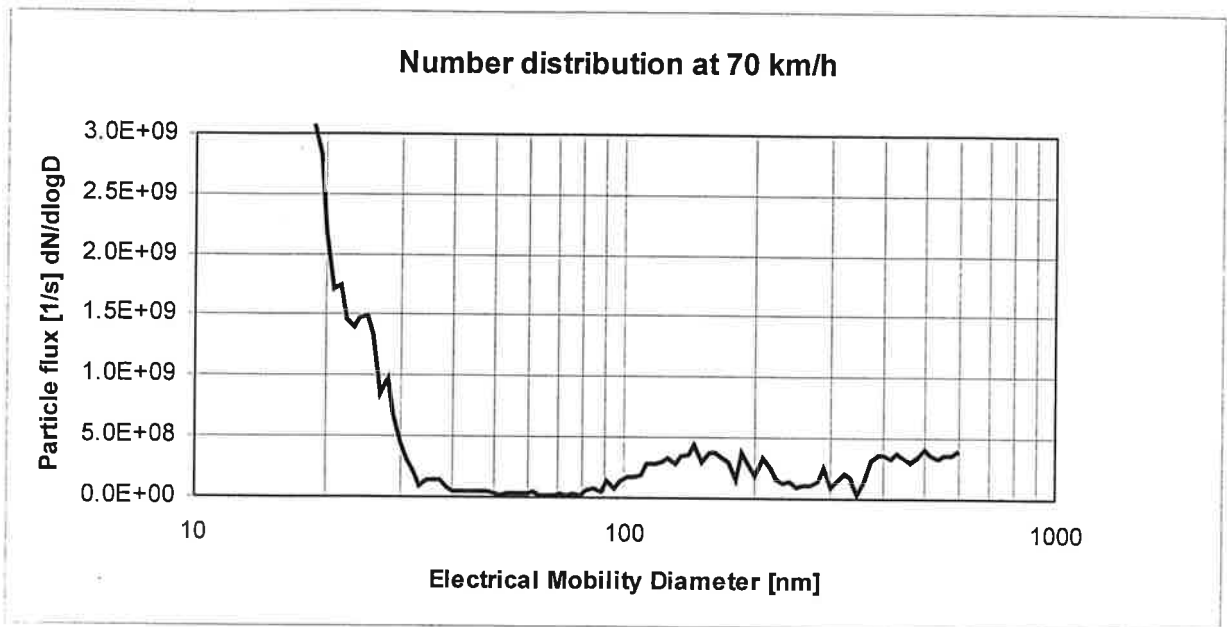
It was recommended that Fluoropore filters should be used for the main vehicle test work in this project.

## APPENDIX B: TNO RESULTS FOR LPG VAN

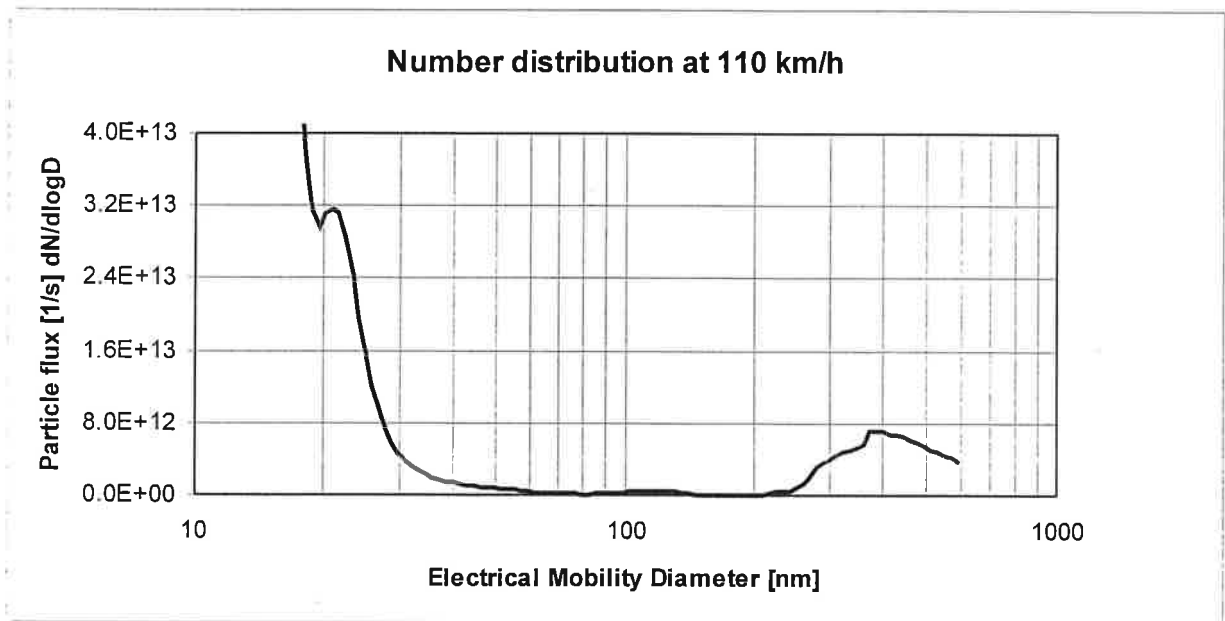
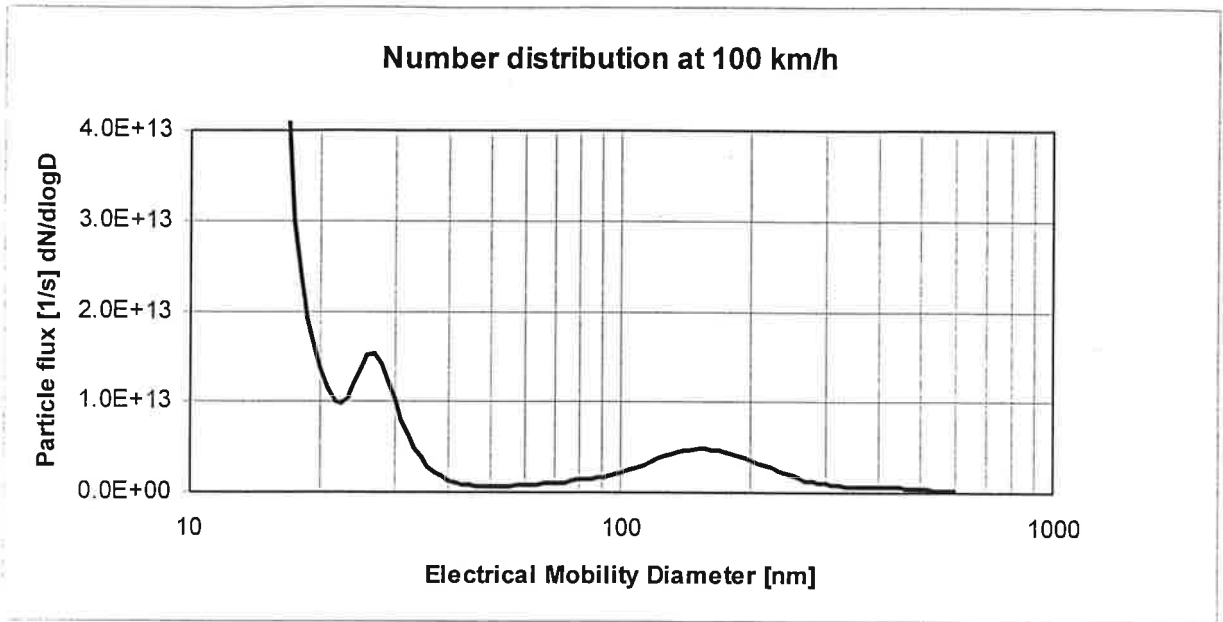
The following data were supplied by Rinie van Helden from TNO. The LPG vehicle was lent to TNO for a series of comparable tests in their laboratory. The fuel was supplied by the company that owned the Transit, and was the same fuel as that used in the work reported by ETSU. The details of the TNO work are to be reported separately - these Figures are included here for completeness. For further information, please contact Rinie van Helden, TNO Road-vehicles Research Institute P.O. Box 6033, NL-2600 JA Delft, The Netherlands (Tel: +31 15 269 73 66, Fax: +31 15 261 23 41).

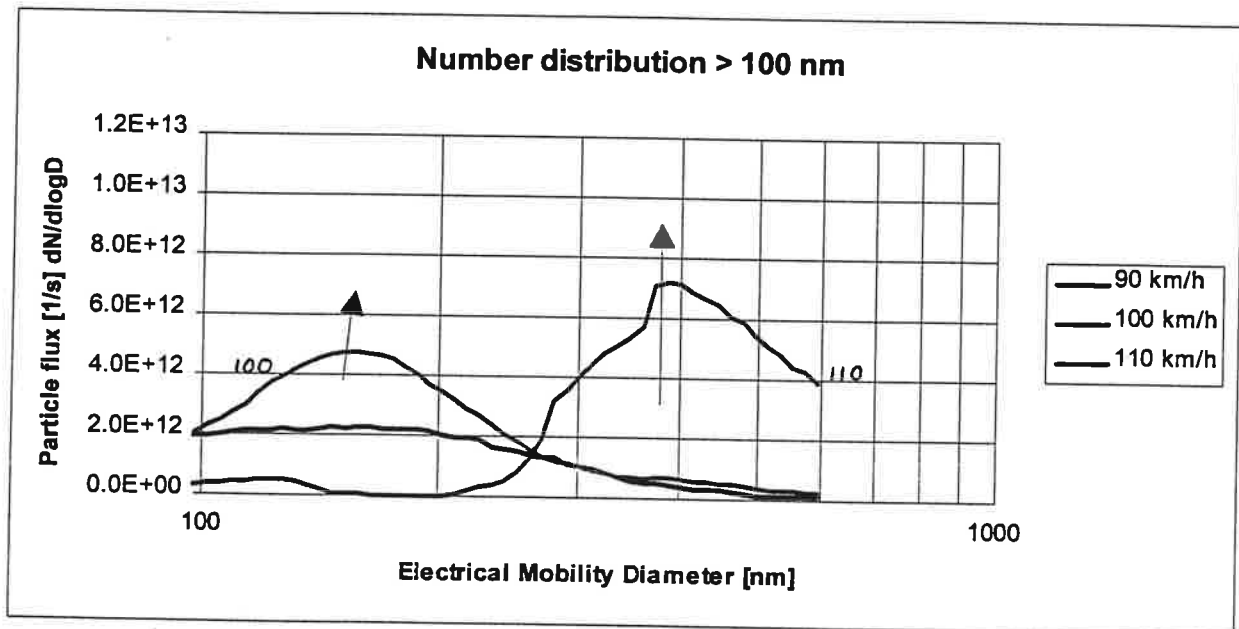
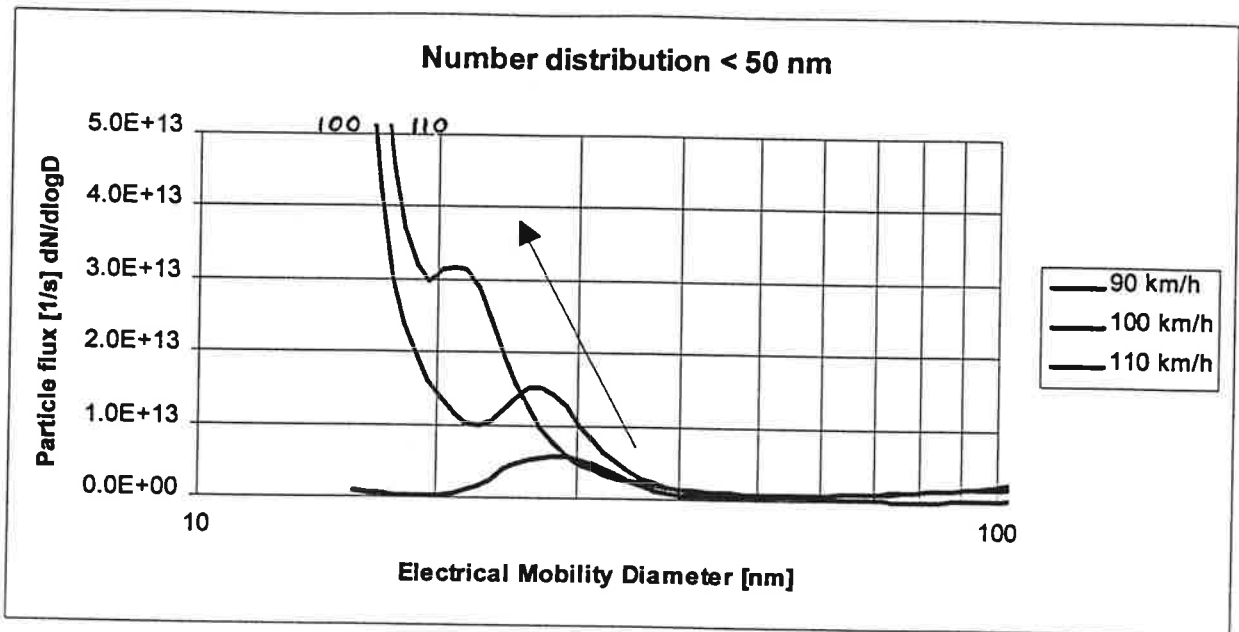


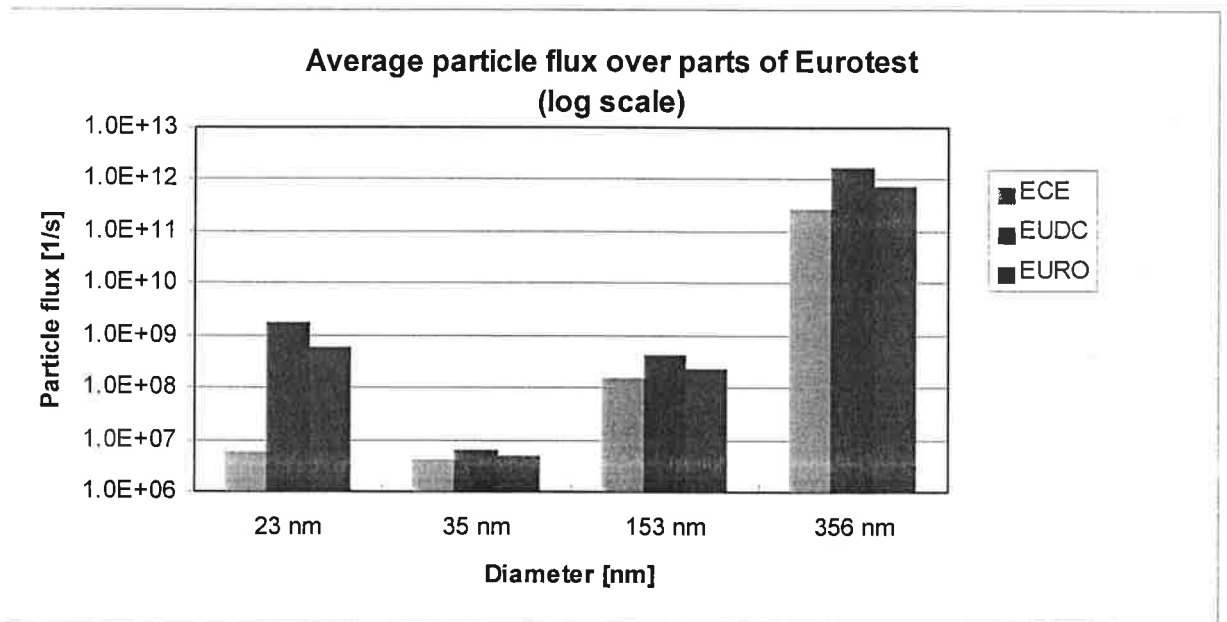
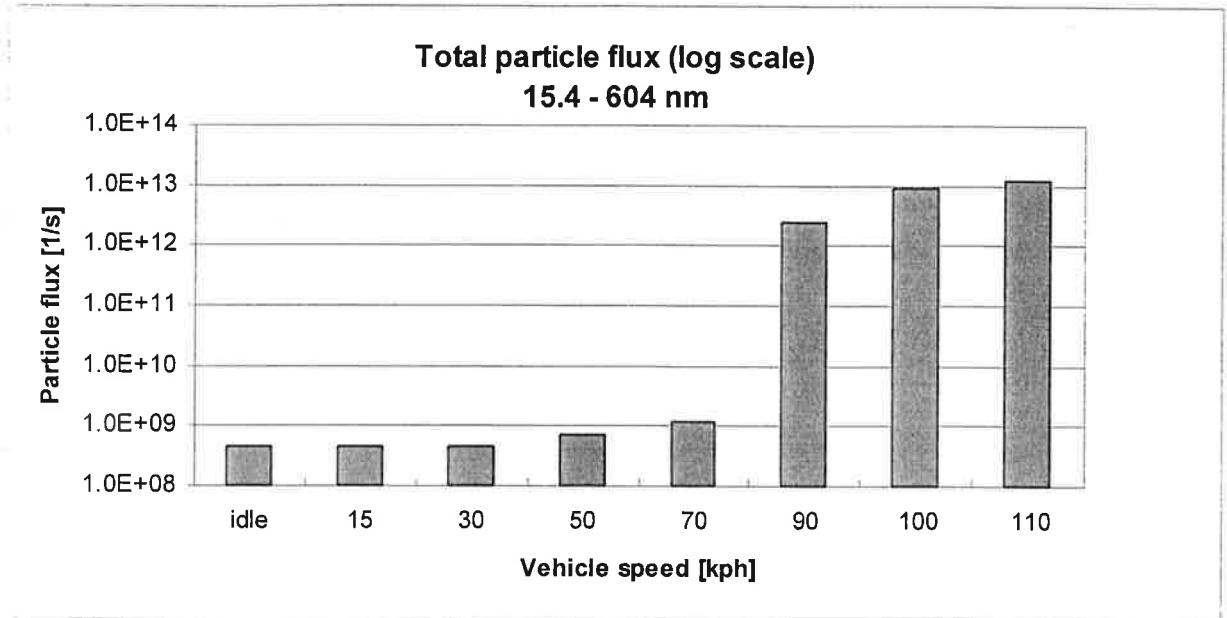












## APPENDIX C: COMPARATIVE RESULTS FROM CONVENTIONAL-FUELLED VEHICLES

To put the results of the IEA work in context, a few extracts from the ETSU Report R98 on the “UK Research Programme on the Characterisation of Vehicle Particulate Emissions” are included here. For example, Figures 2 and 3 below may be compared with Figure 3.11 in the main text of this report.

The results from Vehicle 3, a catalyst-equipped diesel van are particularly relevant. The most direct comparison is with the LPG2 results. Key features are:

- the much greater emissions of larger particles (50-200nm) from the diesel vehicle;
- the five to seven fold increase in the rate of emission of particles at the peak of the particle size distribution, for diesel relative to LPG.

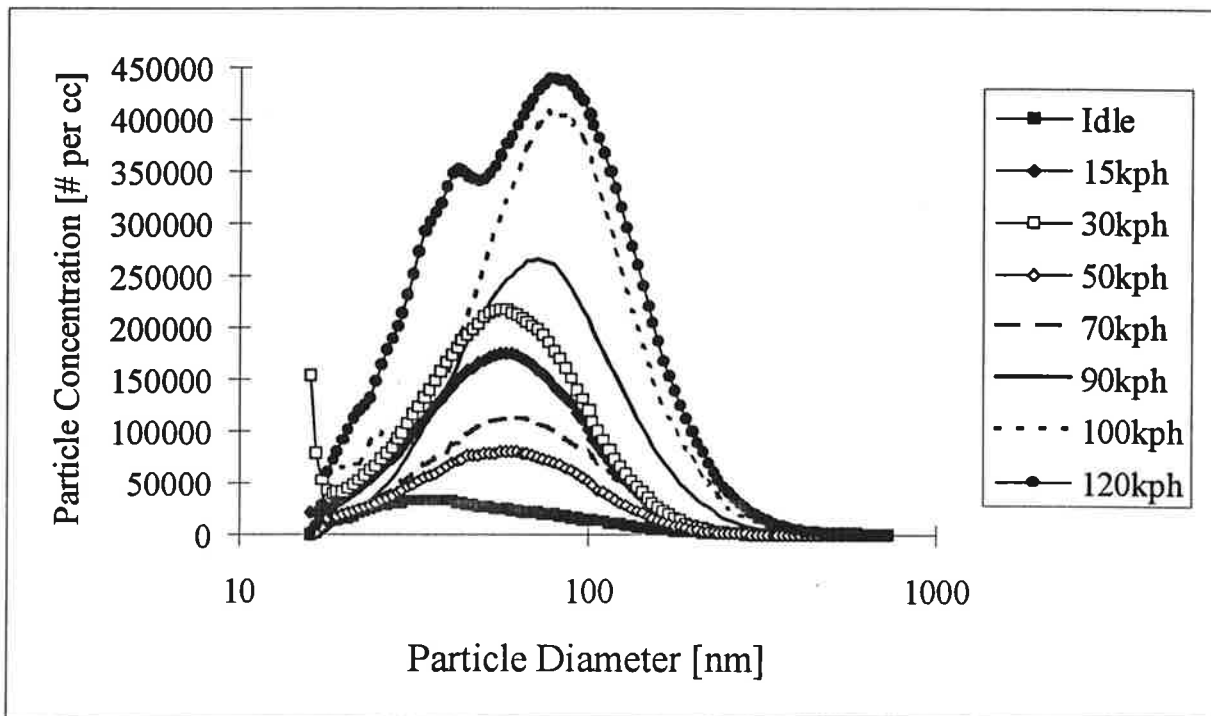
**Table 1 Test vehicles and engines**

Vehicle/ Engine Category	Vehicle/ engine identification number		Size analysis	Composition Analysis
Light-duty vehicles	1	IDI diesel, turbo-charged, non-catalyst, current technology (pilot study)	✓	✓
	2	IDI diesel, naturally aspirated, non-catalyst, old technology	✓	
	3	DI diesel, turbo-charged, oxidation catalyst, exhaust gas recirculation, current technology (van)	✓	
	4	Petrol, leaded fuel, naturally aspirated, non- catalyst, old technology	✓	
	5	Petrol, unleaded fuel, naturally aspirated, three-way catalyst, current technology	✓	✓
	6	IDI diesel, naturally aspirated, non-catalyst, old technology (vehicle 2 plus trap)	✓	
Heavy-duty engines	7	Diesel, Euro I specification	✓	✓
	8	Diesel, Euro II technology	✓	
	9	Diesel, Euro I specification (engine 7 plus trap)	✓	

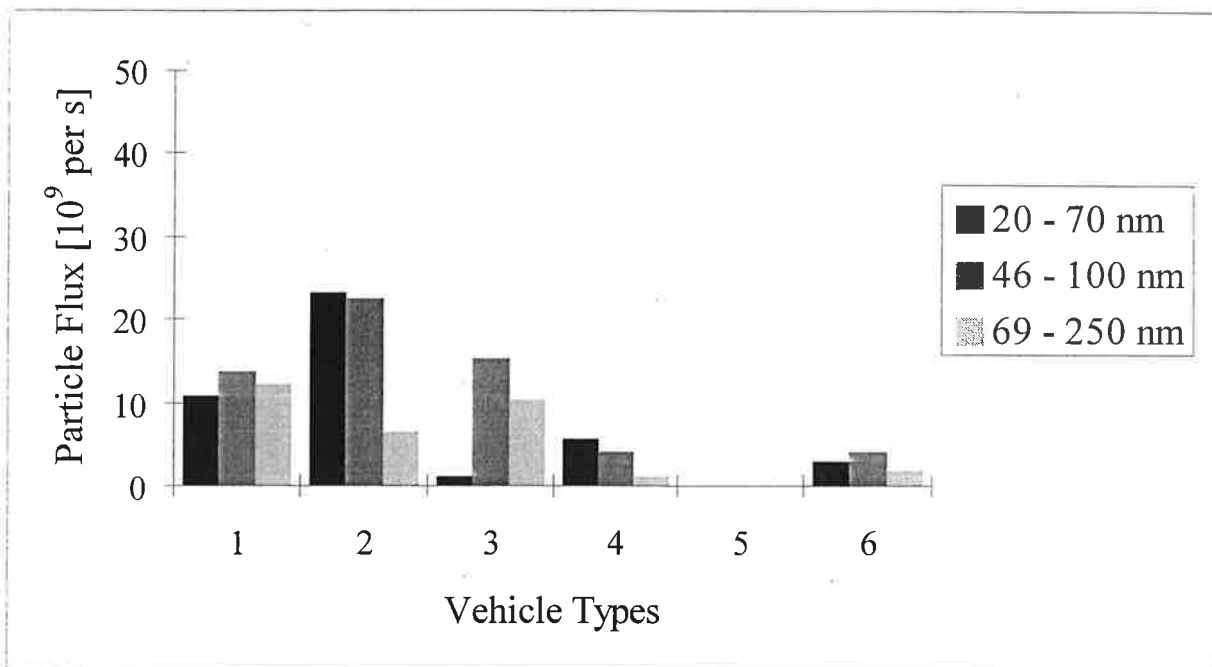
Key: DI - direct injection  
IDI - indirect injection

Note: engine 8 was designed to meet US standards which are close to the Euro II requirements.

Figure 1 Steady-state SMPS, IDI turbo-charged diesel, variation with road speed



**Figure 2** SMPS average particle flux over ECE cycle, light duty vehicles, at 3 selected particle sizes for each vehicle



**Figure 3** SMPS average particle flux over EUDC cycle, light duty vehicles, at 3 selected particle sizes for each vehicle

