a study of the number, size & mass of exhaust particles emitted from european diesel and gasoline vehicles under steady-state and european driving cycle conditions

Prepared for the CONCAWE Automotive Emissions Management Group by its Special Task Force AE/STF-10:

D.E. Hall (Chairman)

C.L. Goodfellow
H.J. Guttmann
J. Hevesi
J.S. McArragher
R. Mercogliano
M.P. Merino
T.D.B. Morgan
G. Nancekievill
L. Rantanen
D.J. Rickeard
D. Terna
P.J. Zemroch

P. Heinze (Technical Coordinator)

Brussels
February 1998

ABSTRACT

This study investigates the measurement of the mass and the number of light duty automotive (diesel and gasoline) exhaust particles and their related size distributions. Different analytical techniques for particle size determination are assessed and compared and recommendations made for future work. Selected aspects of particle emissions are also investigated across a limited number of vehicles and fuels, but covering a wide range of vehicle technology and marketed fuel quality.

KEYWORDS

aerodynamic diameter, automotive exhaust emissions, diesel, electrical mobility analysers, gasoline, particle size, particulate emissions

CONTENTS

Page

SUMMARY

Under the EC Air Quality Framework Directive, Daughter Directives proposing European Air Quality Standards (AQS) are being prepared for several pollutants, including particulate matter. The limit under discussion will apply to PM_{10} (particulate with an aerodynamic diameter less or equal to 10 µm), but in alignment with proposals in the US, and responding to continued pressure from some health professionals, it is probable that future particulate standards will focus on a smaller size fraction (probably $PM_{2.5}$).

This debate has prompted consideration of whether it is the total number or the mass of the particulates in the ambient atmosphere that should be of greater concern. Clearly, the appropriate answer to this question should be determined on the basis of an assessment of health effects. At present there is limited information available relating either to the number or to the size distribution of automotive particle emissions and detailed evidence has still to be obtained. It should, however, be recognised that tailpipe emissions are only one source contributing to the ambient aerosol and that agglomeration processes will modify the dimensions of tailpipe-out particulate, once it has reached the ambient atmosphere. This is a significant further complication in the extrapolation from vehicle tailpipe particulate emissions to ambient air quality and beyond. To develop an understanding in this area of automotive particulate emissions, a programme was carried out as a scoping exercise. This has concentrated on tailpipe emissions as measured at the regulated particulate sampling point in a dilution tunnel.

The programme investigated light duty automotive particle emissions not only with respect to their total mass but also to their size distribution. A previous literature study by CONCAWE (report no. 96/56) had identified analytical techniques considered to be suitable for this application and which are capable of measuring both mass and number size distributions. Several variations of these techniques are available in the research field and the programme aimed to assess and compare their operation and performance.

Four diesel vehicles and three gasoline vehicles were tested, covering as wide a range of technology as is possible with such a limited fleet. Three diesel and two gasoline fuels with a spread of properties typical of the market place were included. The testing protocol covered steady state driving conditions as well as testing over the future European legislative drive cycle. Testing was carried out with the assistance of two contracted laboratories with particle sizing expertise and the complete programme carried out in duplicate with each contractor.

The following conclusions have been drawn:

- Particulate emissions measured from LD diesel vehicles were much higher than from LD gasoline vehicles. In mass terms, the factor was 40-85 based on results from both steady-speed and MVEG driving cycle tests. In number terms, this factor was around 200 for MVEG cycles, more than 2000 at 50 km/h, but down to around 3 at 120 km/h (see third conclusion).
- In terms of mass, more than 85% of diesel particulate emissions were <1 µm. This corresponds to over 99% by number. SMPS [1)] number data indicate that gasoline vehicles emit a higher proportion of smaller particles than diesel

1) Acronyms are explained in **Section 12**, “Glossary”.

vehicles. It follows that more than 99% of gasoline particulate number emissions are also <1 µm.

- Although diesel particulate emissions were substantially higher than gasoline emissions at 50 km/h, the number differences between gasoline and diesel decreased at high speed (120 km/h) as the consequence of a disproportionate increase in gasoline particles emitted. The reasons for this anomaly are not understood.
- The largest vehicle technology effect on particulate emissions was the gasoline/diesel effect. However, technology effects were evident within the gasoline car set, the advanced three-way catalyst (TWC) vehicle tending to give the lowest emissions. Vehicle differences within the diesel set were less pronounced.
- No clear differences were seen between the two gasoline fuels tested. Fuel effects were more demonstrable in the diesel study; for example the Swedish Class I diesel fuel emitted substantially less particulate mass than the other two diesel fuels, though in terms of the emitted particulate number, no significant differences were seen.
- Particulate emissions were lower under fully warmed-up conditions than for cold engines. In the case of diesel engines, there is some evidence that this is because more large particles are produced during a cold test.
- The comparisons conducted to cross-check on techniques showed good correlations in certain cases. Some techniques were seen to be substantially more repeatable than others, and hence appeared to be more reliable for comparative purposes than others. SMPS/DMPS, regulated mass by gravimetric methods and the impactor technique all seem to have performed satisfactorily in this study.
- There is evidence that, whether particulate emissions are judged by mass or number, the highly emitting vehicles will always be detectable. This is of great potential significance in the debate as to how number and mass should be accommodated in possible future legislative procedures.
- Experiments conducted in a high volume stainless steel container confirmed that the further dilution processes taking place after emission of particles from the tailpipe do change significantly the original distribution of particulate size and illustrate the need for more knowledge in this area.

1. BACKGROUND

For some time, the possible harmful effects of tailpipe particulate emissions from diesel-engined vehicles have been the subject of debate. The concern is reflected in legislation requiring the measurement of particulate mass emissions from diesel vehicles. [1,2] Views of the relative importance to health of either the physical nature of the particulate itself or its chemical composition (e.g. particle size; sulphate, which is a potential irritant; adsorbed polycyclic aromatic hydrocarbons, which may be potential carcinogens) have varied over time. At present, it is the likelihood of particulate matter of a given size range being retained in the lung that is being highlighted. However, there is no proven mechanism whereby low-level ambient PM could cause either early death or morbidity [3] and in terms of plausibility for increased mortality, there are no toxicology data to allow any conclusion. [4]

Under the EC Air Quality Framework Directive, Daughter Directives proposing European Air Quality Standards (AQS) are being prepared for several pollutants, including particulate matter. The limit under discussion will apply to PM_{10} (particulate with an aerodynamic diameter less or equal to 10 microns (10 000 nm)), but in alignment with proposals in the US, and responding to continued pressure from some health professionals, it is probable that future particulate standards will focus on a smaller size fraction (probably $PM_{2.5}$).

This debate has prompted consideration of whether it is the total number or the mass of the particulates in the ambient atmosphere that should be of greater concern. Clearly, the appropriate answer to this question should be determined on the basis of an assessment of health effects. It should, however, be recognised that tailpipe emissions are only one source contributing to the ambient aerosol and that agglomeration processes will modify the dimensions of tailpipe-out particulate, once it has reached the ambient atmosphere. This is a significant further complication in the extrapolation from vehicle tailpipe particulate emissions to ambient air quality and beyond.

Recently, it has been proposed that particulate matter from gasoline engines as well as that from diesel engines may make a significant contribution to total particulate emissions. Although gasoline particulate mass is low, data have been published [5,6] showing that whilst particulate number emissions from modern gasoline vehicles are much lower than those from diesel vehicles under most operating conditions, higher emission rates are seen at higher vehicle speeds. Although diesel vehicles are believed to be the main source of particulates in urban areas, the contribution of gasoline vehicles needs to be clarified, especially in view of the larger population of gasoline vehicles.

There are analytical techniques available that will characterise particulate matter, either in terms of the chemical composition or related to the physical characteristics of particle mass/volume or particle number as a function of size. As a step towards establishing some important basic information in the second area, and so provide a more informed background against which legislators and other interested parties can operate, CONCAWE has established a programme in which tests have been performed to characterise the number, size and mass of particles emitted from light duty gasoline and diesel vehicles in tests representative of European driving conditions. This work has been carried out using size measurement techniques identified in an earlier CONCAWE literature study.[7]

2. OBJECTIVES

Having decided it was necessary to develop further our understanding in this field (light duty automotive), the next step was to devise a list of key areas which this scouting study could realistically be expected to address, despite the immature state of some of the subject area. Eight key areas were ultimately identified;

- What range of particle sizes is observed?
- How is particle number distributed amongst the sizes?
- How do particulate emissions from diesel/gasoline vehicles compare?
- What diesel fuel effects are observed in the different diesel vehicles?
- What gasoline fuel effects are in evidence in the different gasoline vehicles?
- What are the differences between individual gasoline/diesel vehicles?
- How are particle number emissions related to mass emissions?
- How well do the results from different labs/by different techniques compare?

These issues are addressed in greater detail in the results section.

3. METHODOLOGY AND APPROACH

Particulate emissions are currently measured in terms of their mass collected on filter paper and established procedures[1,2] are in place for such measurements. Evaluation of particle number and size is a relatively recent development and no established procedures exist with respect to choice/performance of measuring equipment or the conduct of testing. Testing is complicated by the fact that the most effective particle size analysers require up to a few minutes to scan the full size range of interest and so cannot easily be applied to driving cycle testing. However, despite this difficulty, it was decided that the present experimental studies would be chassis dynamometer based and that particulate information should be obtained for both steady-state and legislated European cycle conditions. The final experimental schedule allowed for both cold and hot European driving cycles as well as a number of preselected steady state conditions.

Because of the absence of established methods it was felt that the comparison of results from external laboratories expert in characterising particulates should form an integral part of the study's objectives and hence become an important factor within the experiment. The comparison was made using the same vehicle/fuels sets and testing protocols in each case. The two contractors selected (AEA Technology and FEV Motorentechnik) were each experienced in their own preferred combination of particulate characterisation techniques. The range of techniques realistically available at the outset of this study has been described in an earlier report [7] and is summarised in **Table 1**.

Table 1 Scope of some of the particulate characterisation techniques available

Analytical Method	***Measurement Principle***	***Typical Coverage***	***Other Comments***
Collection on Filter Paper	Direct Mass Measurement	Min. total weight > 0.1 mg	Legislated procedure
Quartz Crystal Microbalance (QCM)	Aerodynamic Separation	25-25.000 nm	Problems encountered with particle charging during exhaust emission testing
Cascade Impactor Method	Aerodynamic Separation	25 – 11.000 nm Weighted by Mass per Size Class	Most commonly used technique for mass distribution
Electrical Low Pressure Impactor (ELPI)	Aerodynamic Separation With Number Determined by Charge		Relatively new technique not available to this study
Electrical Aerosol Analyser (EAA)	Deflection of Charged Particles in Electric Field	8 Size Classes Mean Diameter 12 - 750 nm	EAA/DMA differ in charging/counting of particles
Differential Mobility Analyser (DMA)	Deflection of Charged Particles in Electric Field	11 Size Classes Mean Diameter 12 – 200 nm	Original machine employing electrical mobility technique
Differential Mobility Particle Sizer (DMPS)	Deflection of Charged Particles in Electric Field	Up to 1000 nm	Older version of SMPS
Scanning Mobility Particle Sizer (SMPS)	Deflection of Charged Particles in Electric Field	105 Size Classes 15-700 nm	Most widely used technique for number distribution
Condensation Particle Counter (CPC)	Optical after Particle Growth by Condensation	Gives total Particle Count	Normal add-on for mobility analysers

Contractor B used a combination of EAA/DMA techniques with impactor measurements; Contractor A a combination of SMPS/DMPS and QCM (**Table 2**). Although there is a degree of similarity between the mobility techniques, the terminology DMA is retained throughout the report to differentiate between Contractor A and Contractor B.

Table 2 Techniques used by contractors

	Technique for size distribution by number	**Technique for size distribution by mass**	**Principle of operation**
Contractor A	SMPS		electrical mobility
	DMPS		electrical mobility
		QCM	sedimentation
Contractor B	EAA		electrical mobility
	DMA		electrical mobility
		Berner low pressure impactor	sedimentation

For much of the work, gravimetric filter paper measurements of particulate, (as defined in diesel legislation) were also determined. Particulate size measurements as determined by Contractor A were performed within the test laboratories of CONCAWE member companies. Gasoline and diesel test work was separated and carried out in two independent laboratories. Contractor B carried out the complete programme within their own testing facility.

Descriptions of the detailed operation of the analysers used during the programme are given in **Appendix A**.

This selected range of techniques carries within it some important internal conflicts. Many of these techniques are from the same family of methods, relying on the same measuring principles though different in the fine detail of measurement. Similar techniques can be optimised for slightly different size ranges and this may vary between laboratories using the same analyser. However, some techniques are based on completely different operating principles and the diameter measured will be determined by this principle. Thus, particle diameter may be described as 'aerodynamic diameter' or 'electrical mobility diameter', but these are not the same thing and it is important to be aware of the differences when interpreting data. Because of the lack of a standardised measurement method, data produced using different instruments, even from the same operating principle, may be expected to differ.[7]

Finally, in treating data established by the various techniques, a number/mass interconversion is often sought. This is problematical and discussed in detail in the results section.

While particulate characterisation was by far the highest priority in this study, the programme was designed also to measure the regulated emissions CO, HC, NOx and particulate weight (some gravimetric particulate measurements were also made in the gasoline study). The values obtained for these emissions would be used as a first-line indicator of test stability and comparability, as well as being of interest in their own right. Where possible, time-resolved tailpipe regulated emissions data were also targeted, partly as a check against the bagged results. The MVEG (11 sec. idle period) modification of the European legislated driving cycle was chosen for this work.

4. SELECTION OF VEHICLES AND FUELS

Vehicles and fuels were chosen broadly to cover the range of technology available in the European market, so that the extent to which vehicle and fuel effects influence particulate emissions might both be gauged.

Vehicles

Vehicles for this programme were selected to reflect advances notably in terms of emissions control performance as summarised in **Table 3**.

Table 3 Summarised information on test vehicles

VEHICLE	INJECTION SYSTEM & CATALYST	ENGINE DISP'MT	MAXIMUM POWER	MAXIMUM TORQUE
V1 (D)	IDI /OX	1.896 litre	55 kW @ 4200 rpm	150 nm @ 2400-3400 rpm
V2 (D)	DI / OX TC	1.896 litre	66 kW @ 4000 rpm	202 nm @ 1900 rpm
V3 (D)	DI	2.496 litre	52 kW @ 4000 rpm	145 nm @ 2500 rpm
V4 (D)	DI / OX TC	1.896 litre	66 kW @ 4000 rpm	202 nm @ 1900 rpm
V5 (G)	MPI	1.781 litre 2 vpc	82 kW @ 5400 rpm	159 nm @ 4000 rpm
V6 (G)	SPI / TWC	0.999 litre 2 vpc	34 kW @ 5250 rpm	75 nm @ 3250 rpm
V7 (G)	MPI / TWC	1.985 litre 4 vpc	136 kW @ 5500 rpm	263 nm @ 2100 rpm

(D) Diesel
(G) Gasoline
OX Oxidation catalyst
TWC Three-way catalyst
VPC valves per cylinder
Other abbreviations: see **Section 12**, “Glossary”.

The diesel vehicles V1 and V2 were the IDI and DI catalyst equipped variants of the same model vehicle, whereas V3 represented a DI light commercial vehicle with no catalyst. This choice of vehicles provides non-catalyst vs. catalyst comparisons for DI vehicles, and a DI/IDI comparison across nominally the same catalyst vehicle. At a later stage in the programme, a further vehicle (V4 - DI/catalyst equipped) was included to complement data from the diesel testing.

The gasoline vehicles (V5, V6, V7) represented the broad advance of gasoline vehicle and emissions control technology, i.e. non-catalyst, early catalyst and later, more advanced catalyst. V5 represented the older technology (2 valve MPI non-catalyst), V6 represented current technology (1.0 l, SPI, TWC) and V7 was an advanced vehicle meeting TLEV . (Note that the injection system on the non-cat V5 is more sophisticated than that fitted on the catalyst-equipped V6).

Fuels

Inspection data on the gasoline and diesel fuels used in this programme are given in **Table 4** (parts a & b).

The gasolines used in this programme differed principally in having either higher aromatics and higher sulphur (G2) or lower aromatics and lower sulphur content (G1). Other fuel parameters were kept as constant as possible (e.g. max 10% v/v olefins, 2-3% v/v benzene, with similar distillation curves). The diesel fuels selected for this study were commercial European fuels representing extremes of Summer/ Winter specification (EN 590) together with Swedish Class I diesel fuel (D3).

Table 4 (a) Key properties of test gasolines

	FUEL G1	FUEL G2	Test Methods
Density @ 15°C kg/m^3	**735.5**	**767.8**	**D 4052-95**
RON/MON	**97.5 / 87.0**	**97.6 / 86.2**	**D 2699/2700-86**
RVP kPa	**62.0**	**60.1**	**BS EN 12:94**
Distillation			**ISO 3405:88**
E 70 % evap. at 70°C	**24**	**27**	
E 100 % evap. at 100°C	**51**	**48**	
E 120 % evap. at 120°C	**75**	**79**	
E 150 % evap. at 150°C	**90**	**91**	
E 180 % evap. at 180°C	**97**	**96**	
H/C (molar)	**1.860**	**1.630**	**Calculated from full GC**
Carbon Wt Fraction (CWF)	**0.8658**	**0.8804**	
Sulphur mg/kg	**90**	**373**	**IP 373**
Aromatics % v/v	**29.2**	**48.4**	**D 5543-94**
Olefins % v/v	**8.9**	**9.0**	**"**
Benzene % v/v	**2.6**	**2.2**	**"**
AFRst	**14.56**	**14.23**	**calculated from CWF**

Table 4 (b) Key properties of test diesel fuels

		FUEL D1	FUEL D2	FUEL D3	Test Methods
Density @ 15°C	**kg/m^3**	**851.7**	**835.2**	**809.9**	**D 4052-95**
KV @ 40°C	**mm^2/s**	**3.68**	**2.34**	**2.07**	**IP 71**
Cetane number		**53.7**	**50.3**	**56.8**	**D 613**
Cetane index		**52.1**	**48.8**	**56.7**	**IP 380**
Distillation:					**D 86**
IBP	**°C**	**178**	**180**	**195**	
10%	**recov. at °C**	**231**	**206**	**216**	
30%	**recov. at °C**	**272**	**227**	**229**	
50%	**recov. at °C**	**296**	**250**	**240**	
70%	**recov. at °C**	**320**	**284**	**253**	
95%	**recov. at °C**	**365**	**353**	**280**	
FBP	**°C**	**373**	**367**	**290**	
H/C	**molar**	**1.827**	**1.873**	**1.991**	**D 5291**
Carbon wt fraction		**0.867**	**0.865**	**0.856**	
Sulphur	**mg/kg**	**367**	**394**	**<1**	**IP 373**
Aromatics	**% m/m**				**IP 391:95**
Mono-		**27.2**	**20.6**	**5.2**	
Di-		**5.8**	**6.1**	**0.2**	
Tri+		**0.8**	**0.9**	**<0.1**	
TOTAL		**33.8**	**27.5**	**5.4**	
Calorific Value	**calc**				**D 4868-90**
Nett / Gross	**MJ/kg**	**42.73 / 45.52**	**42.92 / 45.76**	**43.21 / 46.13**	

5. EXPERIMENTAL DESIGN AND PROCEDURES

Emissions experiments were set up according to normal engineering practice, vehicles being matched to the dynamometer in the usual way via rundown times etc. Thereafter, emissions testing was carried out under steady state or MVEG cycle conditions according to the agreed procedure (see later in this section). Gaseous emissions measurements were obtained from 3 bags for gasoline (as ECE1/2, ECE3/4 and EUDC) and from 2 bags for diesel (ECE and EUDC). Measurements of the regulated emissions CO (CO_2), NOx and HC were made on diluted exhaust gas via a dilution tunnel/CVS system, using the customary methods based on IR, chemiluminescence and FID respectively. All laboratories measured regulated particulate emissions (diesel and gasoline) over the MVEG cycle and in addition some laboratories also measured the gravimetric particulate emission at steady state.

Particulate sampling from the dilution tunnel was performed at a suitable rate under isokinetic sampling conditions via a sampling tube having no sudden changes of angle, and set at a distance at least 10 tunnel diameters away from the mixing/dilution point. The conduit from the vehicle tailpipe to the mixing tee was of smooth curvature and no more than 2.5 metres in length (if uninsulated). The study aimed to keep this distance/configuration to the mixing tee comparable in all experiments so as to minimise the scope for differential agglomeration of the particulate prior to tunnel dilution. Existing guidelines for dilution tunnel operation, including sampling for gravimetric measurements of particulate, were always followed. Between tests, the dilution tunnel and ancillary equipment were returned to base condition using the applicable EPEFE protocol. [8]

The test design was organised to provide consistency within the engineering requirements of the programme. For example, the fuels order in each of the experimental sets was organised so that there was a regular check-back on regulated emissions levels for one fixed fuel to monitor whether any vehicle/dyno drift had occurred. The overall programme was designed so that a full controllable repeat of the first day's testing was always carried out before moving on to the next fuel. **Table 5** summarises this daily schedule.

Scanning the complete size distribution of particles produced under steady-state conditions is practicable if the steady state condition is properly maintained for sufficient time. This feature was readily incorporated into the programme. However, it was not possible to obtain simultaneous data on a range of particulate sizes during transient testing (ECE/EUDC driving cycles). It was therefore decided that some repetition of driving cycle runs would be carried out where each separate run would monitor a given size range. Two analysers were used in parallel for each run, thus allowing 2 separate size fractions to be monitored over the cycle. For one run each day, both analysers measured the same size fraction, thus allowing a comparison of the two analysers. Using the regulated emissions data it could be shown that acceptable test replication was being achieved, thus a means of obtaining a range of particulates data for different size ranges under transient conditions has been established.

The testing schedule allowed for a number of comparisons including the following:

(i) A comparison of five steady-state speed conditions, idle, 30 km/h, 50 km/h, 70 km/h, 120 km/h, corresponding to the load points of the European test cycle.

(ii) A comparison of hot cycles and cold cycles (where the term "cold" refers to the legislated test procedure; 'hot' cycles were controlled by using a common oil or water temperature as a starting point.)

(iii) A number of repeat hot cycles (total 3) every day to allow a range of particulate size measurement to be achieved, thereby providing a fuller set of data on particulate number vs. particle size over the chosen driving cycle.

Table 5 The Daily Schedule

Testing Element	Testing Details
I	Formal Cold-Start ECE+EUDC Cycle
II	First Hot-Start ECE+EUDC Cycle
III	Second Hot-Start ECE+EUDC Cycle
IV	Third Hot-Start ECE+EUDC Cycle
V	First Steady-State Measurement
VI	Second-Steady-State Measurement
VII	Third Steady-State Measurement
VIII	Fourth Steady-State Measurement
IX	Fifth Steady-State Measurement
X	Fuel Change if necessary. Precon with ECE+EUDC Cycle ready for Item I next day

* regulated emissions were measured over all elements (predominantly as a quality control for the steady state conditions).

Testing in cooperation with Contractor A adhered strictly to this protocol, but the protocol for Contractor B was modified by the inclusion of a further particulate measurement. This consisted of a high volume stainless steel container (approx. 500 litres) into which continuous samples of exhaust were passed over the duration of the test. Continuous collection of this type cannot be used to obtain an integrated test cycle emission figure, as is done for gaseous emissions, because the particulate matter changes with time due to agglomeration processes. However, at the completion of the test (either steady state or cycle) the particle size distribution from this container could be measured as a function of time and so provide an estimate of how particulate agglomeration occurring in the minutes/hours after initial sampling of the tailpipe emissions affected the observed distribution.

Note*: Although such an experiment provides a qualitative indication of the effect of a dilution process on the dynamics of particle agglomeration, data from this specific experiment should not be overinterpreted, since container conditions cannot be expected to reflect accurately the development of particle agglomeration mixing/ chemical reaction in the atmosphere.*

Thus, the introduction of this aspect within Contractor B's laboratories meant a necessary lengthening of the protocol to 2 days. Drive cycle work was performed on one day and the steady state testing on the second. All other protocol specifications were respected. Contractor B also provided mass distribution data on all elements of the schedule using the Berner low pressure impactor.

Scheme of Testing and Daily Schedule.

The test schedule required one (two for Contractor B) full days testing for a single evaluation of a vehicle/fuel combination. To provide repeatability data, each vehicle/fuel combination was tested twice to the agreed schedule. To determine any drift, fuels G1 and D1 were tested several times in each vehicle.

(i) Gasoline testing

Each car was tested on both fuels before moving on to the next vehicle. For each vehicle, the testing order for the 2 test fuels was set at G1/G1/G2/G2/G1. These decisions minimised the opportunity for the base state of the vehicle to change. Fuel G1 was reintroduced at the end of the fuel sequence to allow a check-back on whether any drift in the emissions data had occurred.

(ii) Diesel testing

The same overall strategy was applied as for the gasoline cars. Each vehicle was dealt with in total in turn. However, since there were 3 fuels, the fuels testing order applied was D1/D1/D2/D2/D1/D3/D3/D1. It was admissible to interchange the block of 2 tests on fuel D2 for the block of 2 tests on fuel D3. Fuel D1 was used as the check-back fuel.

The transient emissions testing was conducted according to the MVEG modified European drive cycle. The steady state and hot drive cycle testing was carried out so as to be repeatable; hence the repeated hot-start tests were initiated from a common oil- or water-temperature and the same principles were applied in ensuring the comparability of steady-state tests conducted under equivalent conditions on different days.

6. VALIDATION OF RESULTS

The output of the various experiments needed a formal engineering validation, to reinforce the rigorous protocol developed to control the testing.

The first stage in the validation was an examination of regulated emissions results via the EPEFE repeatability criteria, i.e. the test of whether repeat runs are different by as much as 40% (CO), 30% (HC) or 30% (NOx). Such a variation would give cause for concern that one or other of the two tests had not been properly executed, or that the base state of the vehicle had changed, and therefore that the particulates data might be suspect. The next step was to view the actual particulates data and determine to what extent any anomalies in the regulated emissions data had been further transmitted to the particulates data. With the benefit of this "double validation" it was then possible to take a first view of the particulates data knowing where likely difficulties might occur in the data analysis, and thence to make decisions about whether certain trends observed for particulates were valid or not on the basis of the original data quality in that area. In this work, rejection of particulate data points was carried out only when the equivalent regulated emissions data could clearly be classified as dubious. However, in the main, particulates data tended to be retained unless gross differences in repeat experiments were observed; this outcome is a reflection of the fact that particulates data had an intrinsically greater variability than that of the regulated emissions, so as a direct result the internal criteria for acceptance or rejection of particulate data points became less demanding than for the regulated emissions.

The only values which were actually rejected as a result of the CONCAWE validation process were (a) the SMPS results from one set of three hot-cycle tests for fuel G1 in gasoline vehicle V7 and (b) the filter paper results obtained by Contractor A for five ECE+EUDC tests on gasoline vehicles where negative values were recorded.

A number of values were recorded as ‘below detection limit’, ‘zero’, ‘error’ or ‘missing’. ‘Below detection limit and ‘zero’ values were replaced by the detection limit, whilst erroneous and missing values were excluded from the analysis.

It was discovered that the data gathered by the QCM was not repeatable (due to a low and erratic mass recovery) and consequently not reliable. The believed reason was that the exhaust aerosol was acquiring a small electrostatic charge within the dilution tunnel and the subsequent inertial separation was causing these charged particles to impact on the incorrect collection surface, thus distorting the observed distribution. Consequently data from the QCM was not further analysed.

7. HANDLING OF PARTICULATES DATA

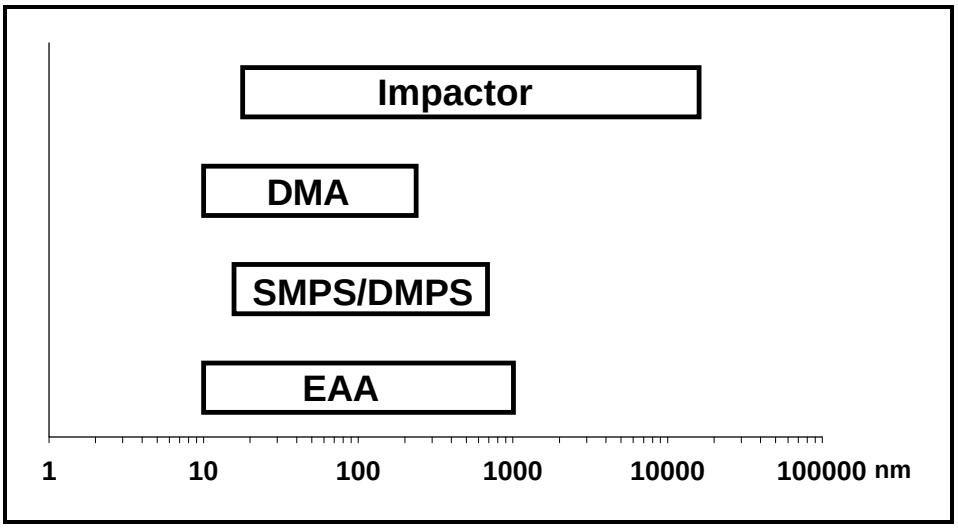
Steady-state particulate size distributions were measured by four different techniques, three measuring particle numbers and one particle mass. Each technique measured particulate distributions over a different size range, these being summarised in **Table 6** and explained in the next paragraph.

The measurement range was divided in each case into a number of contiguous size intervals of equal width (on a log scale). For example, the measurement intervals for the EAA in steady-state tests were 10.0-17.8, 17.8-31.6, 31.6-56.2, 56.2-100.0, 100.0-177.8, 177.8-316.2, 316.2-562.3 and 562.3-1000.0 nm in the original units, the upper limit being 1.78 times the lower limit in each case. The number or mass of particulates emitted per sec or per km was measured for each interval. Actual and not nominal speeds were used to convert particles per sec to particles per km. Typical particulate size distributions are highly skewed and so a log scale is invariably used for the (horizontal) particulate diameter axis when these are plotted. Thus the mid-points of the 8 measurement intervals for the EAA are at 13, 24, 42, 75, 133, 237, 422 and 750 nm in the original units.

Table 6 Particle size ranges covered by each measurement technique.

Technique	Number or mass	Particle diameter range (nm)	No of size intervals	Interval width (log_{10} scale)	Ratio of Upper limit / lower limit
SMPS/DMPS	Number	15.7 - 685.4*	105	0.015625	1.0367
DMA	Number	10 - 237.2	11	0.125	1.33
EAA	Number	10 - 1000	8	0.25	1.78
Impactor	Mass	17.9 - 16000	10	0.295	1.97

* The total SMPS emission figures in this report are derived over the ranges 16 - 750 nm (steady state) and 25 - 400 nm (ECE + EUDC cycles)



The numbers of particles measured by the various analysers cannot be compared directly as the measurement intervals are of very different widths (see **Table 6**). To allow such comparisons, the emission measurements were normalised to what they

would have been had the measurement interval been 1 unit in width on a $\log_{10}$ scale in each case. By convention, the notation $dN / d\log_{10} d_p$[1] (or $d\ mass / d\log_{10} d_p$) is used to describe the units of such measurements. In this particular study, the numbers of particulates of different sizes often differed by several orders of magnitude and so the values of $dN / d\log_{10} d_p$ were usually plotted on a log scale (vertical axis). Mass varied less dramatically with size and so the values of $d\ mass / d\log_{10} d_p$ were plotted on a natural scale.

Direct measurements of the total numbers of particles between 16 and 750 nm in size were obtained for each steady-state test using the SMPS. For the EAA, DMA and impactor, the total number (or mass) of particles emitted over the full measurement ranges in **Table 6** were computed by adding the normalised values $dN / d\log_{10} d_p$ (or $d\ mass / d\log_{10} d_p$) and multiplying the total by $\log_{10}$ scale interval width; this is equivalent to adding the actual numbers (or masses) of particulates measured in each size interval.

The SMPS/DMPS, was only able to measure particles within a single size interval during any ECE+EUDC cycle test. Each set of three hot-start ECE+EUDC cycle tests (see **Table 5**) yielded SMPS measurements in size intervals centred at 25, 60 and 100 nm and DMPS measurements centred at 100, 200 and 400 nm. These intervals, however, were very narrow (mid-point $\pm$ 1.8%) and particulates of intermediate sizes were not recorded. Approximate particulate size distributions for ECE+EUDC cycle tests thus had to be obtained by normalising the SMPS/DMPS measurements to the usual $dN / d\log_{10} d_p$ units and joining the values at 25, 60, 100, 200 and 400 nm with a series of straight lines (cf. **Figure 4)**. Estimates of the total number of particles emitted per km between 25 and 400 nm in diameter were obtained by calculating the areas under each such line (but with the $dN / d\log_{10} d_p$ values plotted on a linear and not a log scale) The mathematical formula used is given in **Appendix B**.

The DMA was likewise only able to measure particles within a single size interval during any ECE+EUDC cycle test. These intervals (mid-point $\pm$ 15.4%) were centred at 21, 37 or 115 nm for gasoline vehicles and 21, 37, 65, 115 or 154 nm for diesel vehicles. The EAA was constrained in a slightly different way in ECE+EUDC tests, the measurement in any one test being of the number of particles larger than some chosen lower limit, this being 10, 56, 100, 178, 240 or 316 nm.

The impactor yielded a full particulate-size distribution for ECE+EUDC cycle tests and the data were handled in the same way as the steady-state results.

The variability in most emission measurement processes increases as the actual level of emissions increases. It is natural therefore to use geometric (logarithmic) means instead of simple arithmetic means when averaging particulate emission measurements, be this across repeats, across fuels or across vehicles. Geometric means were used in averaging both distributions (units $dN / d\log_{10} d_p$ or $d\ mass / d\log_{10} d_p$) and total emissions (units *N*/km or mg/km). Each fuel was given equal weight when calculating the average (geometric mean) emissions for each vehicle irrespective of the actual number of tests conducted with each. Likewise, each vehicle was given equal weight when calculating the fleet average emissions

[1]The notation is mathematically correct only if *N* is regarded as the number of particles *smaller than or equal to* d_p in diameter emitted per km .

for each fuel (excluding those vehicles for which no data at all was available using the analyser in question) (cf. **Appendix C, Tables C.1, C.2**).

In the gasoline tests, emissions were often very low and measurements in some size intervals fell below the corresponding detection limits. These values were taken as zero when summing across size intervals to calculate total emissions. In some situations, the total emissions from a test (measured directly or by summation) fell below the detection limit. In such circumstances, the detection limit was used as the value from that test in any subsequent geometric mean calculations.

8. RESULTS AND DISCUSSION

General

Some general points should be recognised at the outset in this section. The work programme generated large quantities of data which it is not practical to try to describe in every detail. Therefore, the approach taken is to use information averaged over the vehicles and/or fuels where this is justified and to provide typical examples. In this way, it is possible to construct a true picture of the project output at the required level of detail while maintaining some degree of conciseness and readability. It will be noticed (for example) that SMPS/DMPS data are regularly used in preference to data obtained by the other comparable techniques to summarise observations at lower sizes; this is because greater confidence could be attached to observations using the former techniques (further justification will be presented later). Also, fuels D1 and G1 tend to be used as the principal examples for gasoline/diesel comparisons; this is because the use of D1 and G1 respectively as check-back fuels led to more data on these fuels and hence better precision.

The summary tables (**Appendix C, Table C.1, C.2**) provide an overview of the results that have been obtained in the overall study. The results presented are averaged totals (geometric means – see **Section 7**) per kilometre. Information for tests using the European driving cycle (MVEG 11 sec. idle variant) is for the composite cycle. The summary table allows immediate appreciation of where the larger effects are observed, for example:

- in the impactor results for diesel vs. gasoline, showing particulate mass from the diesel vehicles to be 40-85 times higher than from the gasoline cars
- in the SMPS/DMPS data comparison for gasoline vehicles at 50 km/h and 120 km/h, showing the large increase in the number of particles emitted at 120 km/h.

These effects are treated in more detail later.

It is important to appreciate that the large numbers associated with ambient and tailpipe particulate distributions carry with them an error of different scale from that normally seen in emissions work. Thus, differences of around half an order of magnitude (i.e. factor of 3) can often be thought of as reasonable when discussing particulate numbers at a given size, whereas for HC measurements, for example, differences of 10% might be thought of in an equivalent way (as indeed is also the case for gravimetric estimates of total particulate mass as determined in regulated diesel emissions testing). The low particulate emissions measured from the gasoline vehicles often meant that recorded values were on, or close to, the limit of detection for some analysers.

Across a range of given particle size, particulates may be described either with respect to total mass, total number, mass distribution or number distribution. One or more of these descriptions may be of interest at any one time. Unless otherwise stated, any effects reported as significant are so at the 95% confidence level or higher.

8.1. MASS MEASUREMENT

This section discusses total mass measurements and considers the feasibility of conversion of particle number to mass.

The gravimetric results obtained as part of the regulated emissions diesel testing, together with results for gasoline, are given in the more wide-ranging summary of **Figures C.1** and **C.2** (**Appendix C**) and are based on tests performed by Contractor B. The key comparison for present purposes is that much higher particulate weights were obtained for the case of diesel vehicles (**Appendix C, Tables C.1, C.2**).

During the diesel steady state testing, significant vehicle and fuel effects were seen for particulate mass at both 50 km/h and at 120 km/h (**Figure C.1**).

In the case of the gasoline study, at 50 km/h filter paper yields were very low and below the detection limit in one test. However, significant vehicle differences were observed with V5 giving higher emissions than V7 and V6 (**Figure C.2**). Fuel differences were not significant. Although vehicle and fuel differences at 120 km/h were not significant at 95% confidence levels, they were significant at 90% confidence levels.

Gravimetric emissions measured differed significantly from diesel vehicle to vehicle over hot cycles with V4 giving the greatest emissions, followed by V3, V2 and V1 (see **Figure 5**). Averaged across vehicles, fuel D3 gave slightly fewer emissions than D1 and D2 (significant at P<10%, but not at P<5%). The vehicles responded to the different fuels in different ways.

The tests performed by Contractor B included mass measurement using the impactor. **Table 7** shows the comparison between regulated filter mass (cold cycles) and impactor totals for each vehicle (averaged over fuels).

Table 7 Comparison of regulated particulate filter weights and impactor mass (Contractor B)

		Regulated filter (mg/km)	**Impactor total (mg/km)**
Diesel	Vehicle V1	55.3	39.9
	Vehicle V2	168.4	119.8
	Vehicle V3	294.9	288.1
Gasoline	Vehicle V5	1.51	2.00
	Vehicle V6	1.04	2.72
	Vehicle V7	0.41	4.00

In the case of the diesel tests, the measurements show reasonable agreement, with both techniques ranking in the same order. The impactor results show more variability than the regulated filter measurement partially as a result of the multiple weighings required (see **Sections 8.6** and **8.7**). It should also be noted that the absolute gasoline masses are very low.

Table 7 shows that the non-catalyst diesel vehicle V3 emitted about twice the mass of particles emitted by vehicle V2 and about 5 to 7 times more by mass than V1.

Table 8 shows the average numbers of particles above and below 1 µm size emitted by each vehicle for each fuel and across hot and cold cycles.

Table 8 ECE+EUDC tests on diesel vehicles
Total mass (mg/km) of particulates measured by the impactor (1)

Vehicle	All particles	Small (2) particles	Large(3) particles	Small (%)	Large (%)	Data used
V1	36.9	31.6	4.3	88.0	12.0	all fuels; hot/cold cycles
V2	112.6	97.8	13.0	88.3	11.7	"
V3	261.7	211.3	46.3	82.0	18.0	"
Fuel						
D1	108.2	91.1	15.0	85.8	14.2	all vehicles; hot/cold cycles
D2	130.4	111.1	16.6	87.0	13.0	"
D3	77.1	64.6	10.4	86.1	13.9	"
Cycle						
Cold	111.2	89.6	19.4	82.2	17.8	all vehicles/all fuels
Hot	95.1	84.1	9.7	89.6	10.4	"
Overall	102.9	86.8	13.7	86.3	13.7	all vehicles; all fuels; hot/cold cycles

(1) geometric mean emissions giving each vehicle, fuel and cycle equal weight

(2) "small" particles are those between 17.9-1000 nm

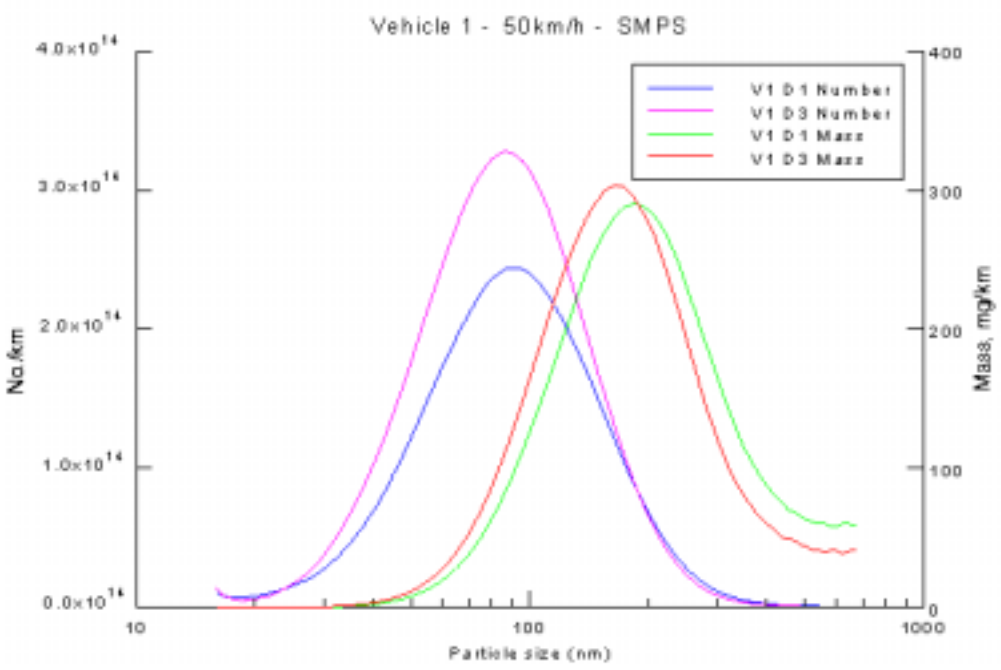
(3) "large" particles are those between 1000 and 16000 nm in size

Proportionally, V3 emitted a higher mass of large particles (18.0%) than V1 (12.0%) and V2 (11.7%). The yield of emitted small particles was significantly affected by fuel with emissions on D2 being 21.9% higher than those for D1 which, in turn, were 40.9% higher than emissions on D3. Fuel D3 gave similar reductions of large particles, but this was not significant at the 95% confidence level.

Particulates have been characterised in this study by a variety of methods. As already indicated, each of these has a given measuring principle and an optimum measuring range. Number and mass of particles are both of interest and attempts are often made to convert number to mass. **Figure 1a** illustrates a typical theoretical

conversion. This conversion makes the assumption that particles are spherical and that the density across different size particles (and potentially variable chemical composition) is constant (ρ=1.0 kg/l) across the sizes. It is clear that number distribution lies more towards lower sizes than the corresponding mass distribution, and that (i) very small absolute differences in number at the larger size values can make a major impact on mass, and (ii) the small particles contribute relatively little to the overall mass.

Figure 1a Typical diesel particle number distributions measured using the SMPS and theoretical calculated mass distributions.



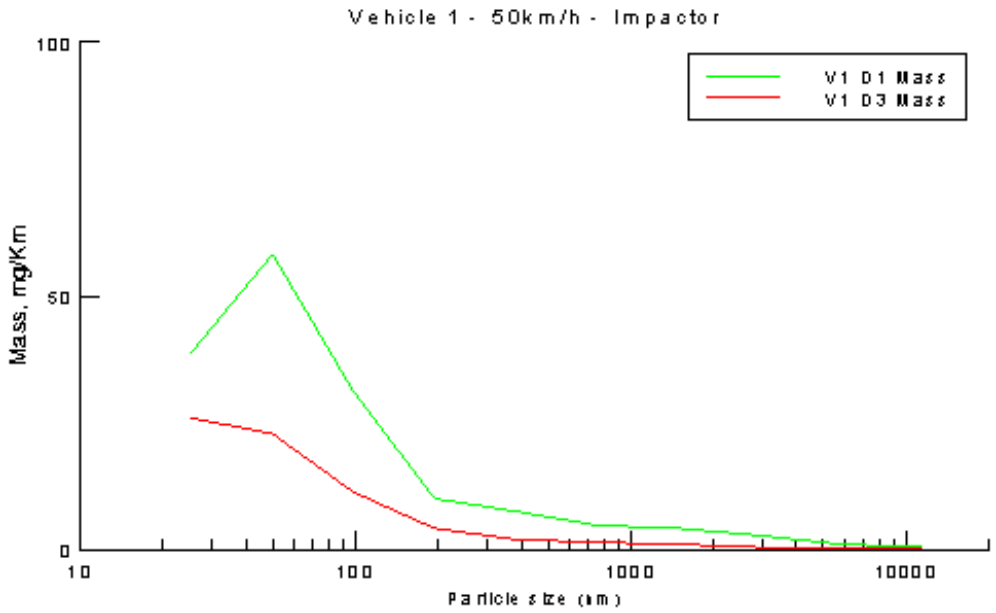
(geometric means normalised to $dN / d\log_{10} d_p$ and $d\,\text{mass} / d\log_{10} d_p$)

Figure 1b shows the size distribution (by mass) measured by the impactor for the same diesel vehicle/fuel combinations as in **Figure 1a**; the total mass is the area under each curve, i.e. 47.2 mg/km (V1 D1) and 20.7 mg/km (V1 D3). The masses obtained from the SMPS data by integrating the theoretical calculated mass distributions in **Figure 1a** were much larger at 157.0 mg/km (V1 D1) and 156.5 mg/km (V1 D3), despite the shorter size range covered. The SMPS calculated masses were also much larger than the corresponding filter paper results, viz. 70.0 mg/km (V1 D1) and 29.9 mg/km (V1 D3). The difficulty in assigning a representative density to the particle has already been mentioned. Exhaust particulates are believed to consist of loose agglomerations of very small units (ca 10 nm) which are rarely spherical and more typically long chains (see **page 8** of **ref. 9**). Because the aerodynamic diameter of such particles will be larger than a spherical particle of the same mass, converting number to mass on the basis of spherical particles will result in an overestimation of the mass.

The mass produced by a gasoline vehicle is very low and a figure showing the distribution of this mass will not be meaningful.

For the reasons given above, conversion from number to mass has been avoided in this report.

Figure 1b Measured diesel particle mass distributions using the impactor.



(geometric means normalised to $d\,\mathrm{mass} / d\log_{10} d_p$)

8.2. RANGE OF PARTICULATE SIZE OBSERVED

The range of particulate sizes observed is ideally assessed on the basis of one common technique. However, this is not possible because individual measurement methods address distribution either with respect to mass or number and as such operate on different physical principles. In estimating the proportion of particles above and below a given size, there are inevitable limitations in the information because of the size range constraints on the individual measurement methods. Data for gasoline are additionally more difficult to quantify because of the low masses and numbers involved at many size values. However, finite quantities of particulate were seen for diesel vehicles/fuels across the full range of sizes accessible by the various techniques (here from 18 to 16000 nm).

Figures 1a and **1b** also demonstrate the typical size range of particles measured (both with respect to mass and number) from diesel vehicles.

The technique with the widest range is the impactor. Such data from the diesel vehicles indicate (see **Table 8**) that, on average, 86% (by mass) of particulates are smaller than 1 µm with 14% larger than 1 µm. While conversion from mass to number is not reliable (as discussed above), it can be estimated that the equivalent

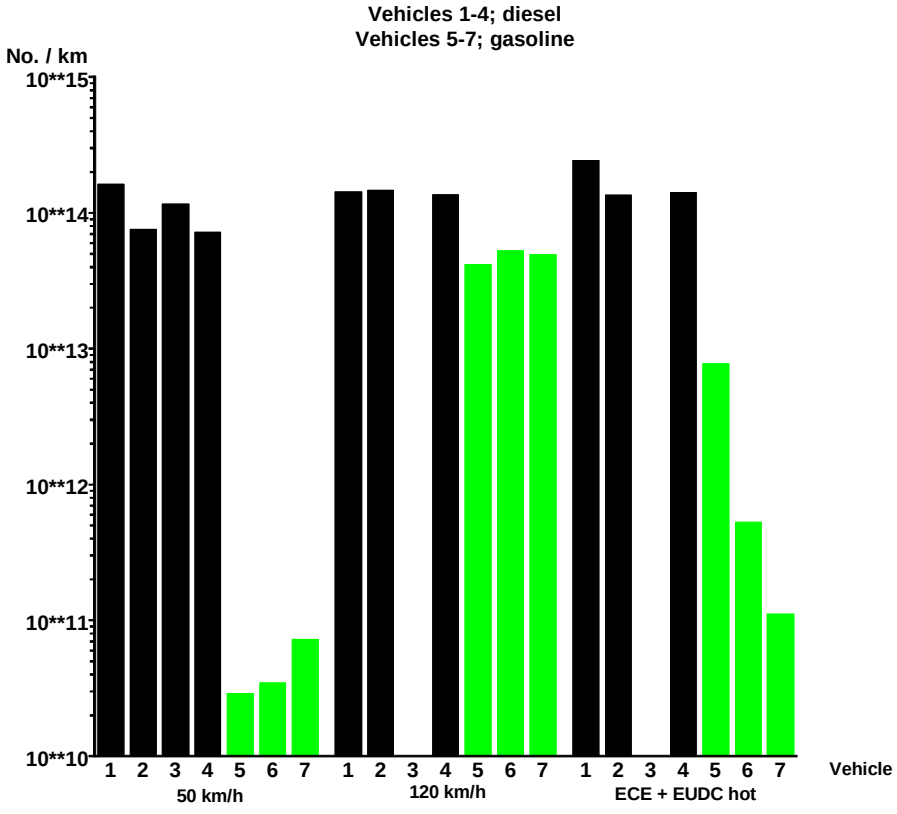
percentage of particles (by number) is 99+%, thus justifying the use of particulate number analysers with an upper bound of around 1 µm (**Table C.2**).

Impactor measurements of mass distribution from gasoline vehicles show a low level of mass (generally below 3 mg/km) across the full range. However, such low mass data are not meaningful as outlined earlier in **Section 8** (**Table C.1**).

8.3. TOTAL NUMBER EMISSIONS

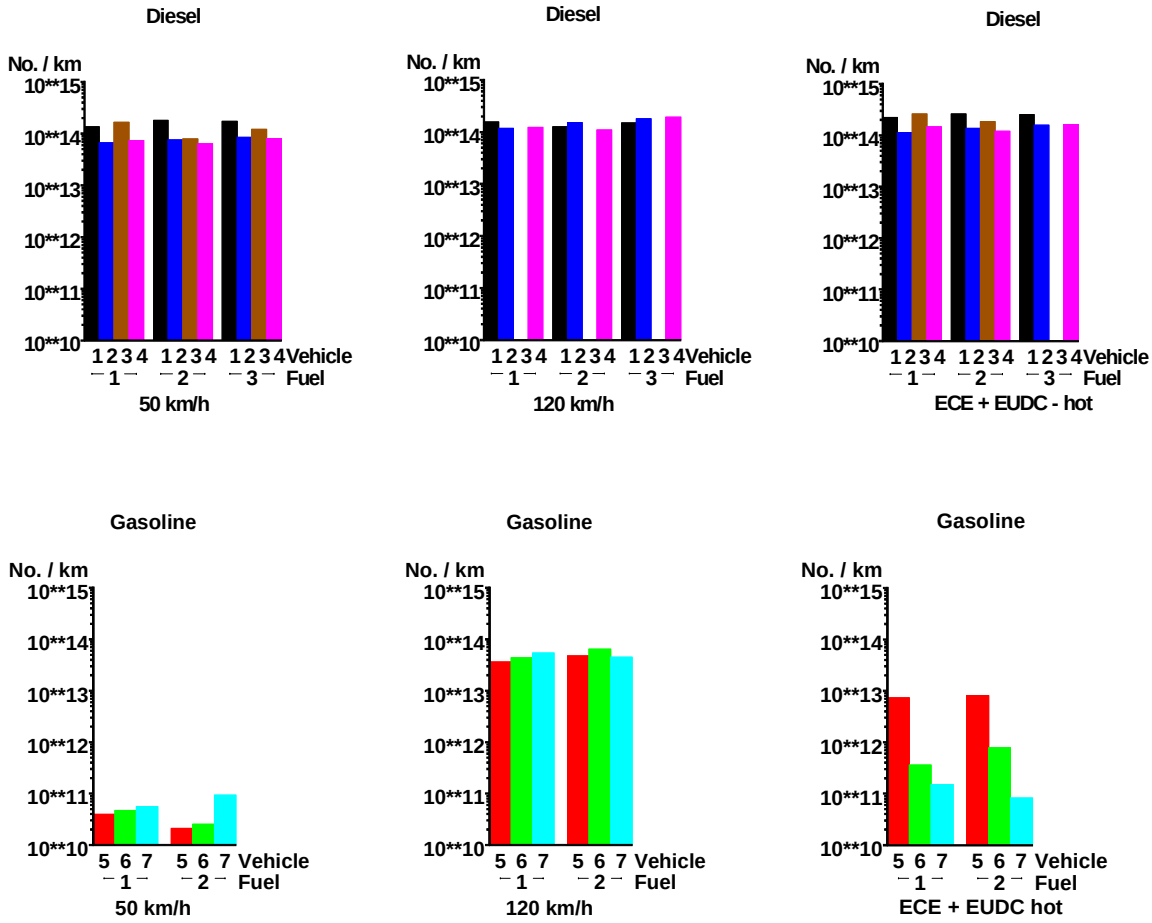
The data on the total number of particles emitted per kilometre are presented in **Figures 2 and 3**, using SMPS data. Note that the scale is logarithmic and the zero is suppressed. For vehicle V3, the data set is incomplete due to power/speed limitations.

Figure 2 Total number of particles emitted per km for each vehicle, averaged over fuels (SMPS)



(geometric means normalised to $dN / d\log_{10} d_p$)

Figure 3 Total number of particles emitted per km for each vehicle/fuel combination (SMPS)



(geometric means normalised to $dN / d\log_{10} d_p$)

The diesel vehicles emitted higher numbers of particulates than the gasoline vehicles at all conditions although at 120 km/h this difference reduced considerably as the gasoline particulate emissions increased sharply while the diesel emissions remained effectively the same. Diesel emissions by number were higher than gasoline by a factor of around 200 for MVEG cycles, more than 2000 at 50 km/h, but around 3 at 120 km/h (**Appendix C, Tables C.1, C.2**).

The hot combined cycle results seem to reflect the features of both sets of steady speed results; diesel emissions are at the same level while gasoline results lie much lower, generally between the previous values for 50 km/h and 120 km/h conditions. Differences in the emissions response of the diesel vehicles were observed. Although differences were small it appeared that the performance of vehicles V2/V4 (DI equipped with catalyst) was generally better than the IDI equivalent. The absence of a V3/D3 result makes it difficult to give precise statistical statements about fuel effects. However, it is clear from **Figure 3** that these are small in practical terms.

The gasoline fleet showed some interesting car-to-car differences; over the transient cycle there was a progressive reduction in particulate number emissions (in

line with increasingly more advanced emissions control) whereas at 50 km/h the reduction in particulate number production was in the reverse order i.e. V5 < V6 < V7, which was unexpected. The disproportionate increase in particulate number emissions from 50 to 120 km/h is also in line with recently reported data (5,6) and it is noteworthy that the three gasoline vehicles behave very similarly in this regime.

Fuel and vehicle effects on particulate number emissions are summarised in **Table 9**, showing that significant effects of fuels were only observed for diesel and only at drive cycle conditions.

Table 9 Fuel and vehicle effects on particulate number emissions

	Fuel effects		Vehicle effects	
Test condition	gasoline	diesel	gasoline	diesel
50 km/h	-	-*	✔	✔
120 km/h	-	-	-	-
ECE/EUDC	-	✔*	✔	✔

✔ implies a significant effect was observed at (at least) the 95% significance level

* indicates a significant vehicle/fuel interaction

From **Figures 2** and **3** and **Table 9**, the following conclusions may be drawn regarding the effects of vehicles and fuels on particulate emissions:

- higher particulate numbers were emitted for diesel than for gasoline under all test conditions
- there was a marked difference between diesel and gasoline particulate number emissions at 50 km/h
- this difference was much smaller at 120 km/h
- there was no difference between diesel fuels at steady state
- there was an indication of a small but significant effect of diesel fuel over the cycle
- there was no significant effect of gasoline fuel at any condition
- vehicles did not always rank fuels in the same order
- vehicle effects were more pronounced than fuel effects

Taking all the steady state tests in the diesel study as one single data set and those in the gasoline study as another, it is possible to calculate the geometric mean emissions giving each vehicle, fuel and speed equal weight (**Table 10**). It can be seen that the variation in total number/km was greatest with speed.

Table 10 Particulate Emissions (Geometric means (SMPS data))

	Vehicle	*N*/km	Fuel	*N*/km	Speed	*N*/km
Diesel	**V1**	1.86E14	**D1**	1.42E14	**30**	2.45E14
	V2	1.09E14	**D2**	1.37E14	**50**	1.03E14
	V3	2.01E14	**D3**	1.59E14	**70**	1.13E14
	V4	1.11E14			**120**	1.57E14
Gasoline	**V5**	2.77E11	**G1**	3.38E11	**30**	0.83E11
	V6	2.99E11	**G2**	3.16E11	**50**	0.42E11
	V7	4.21E11			**70**	0.69E11
					120	4.76E13

(Note: statistically estimated emission values were used for V3 emissions at 120 km/h)

Thus, the following conclusion can be made:

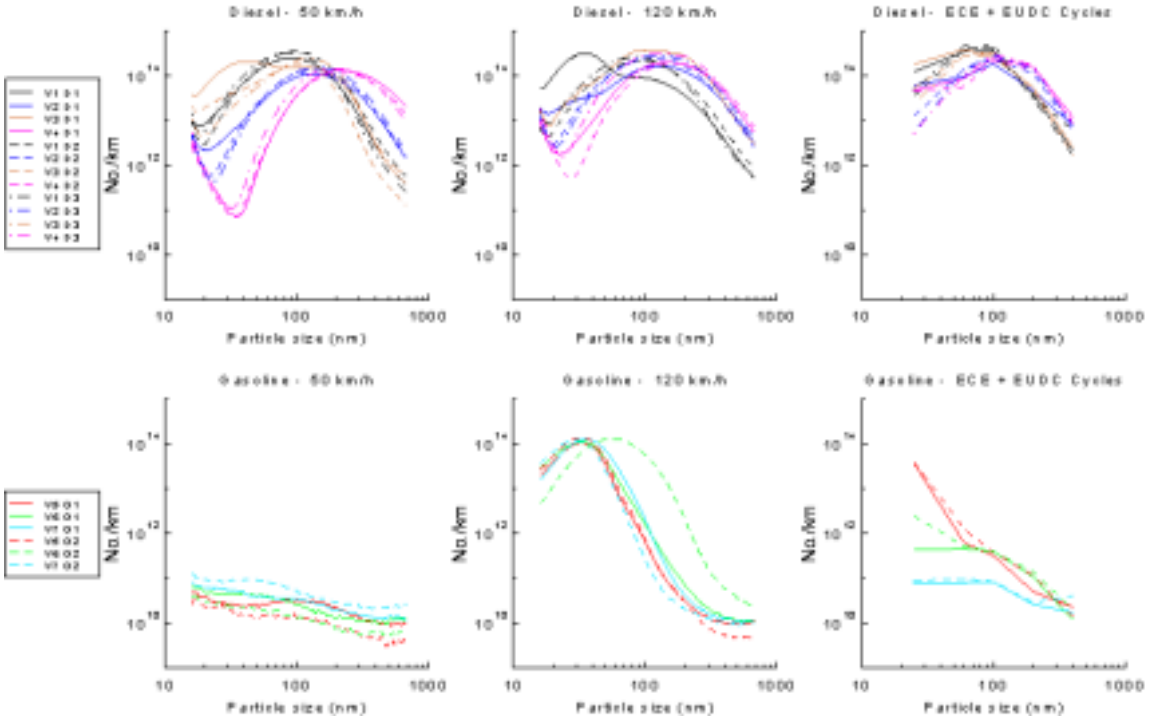
- throughout the programme, speed had the largest effect on the number of particles emitted

8.4. NUMBER DISTRIBUTION OF PARTICLES EMITTED

Section 8.3 dealt with the total number of particles emitted. However, within each total there is a related distribution. The effects of vehicles and fuels on size distribution (as measured by the SMPS) are shown in **Figure 4**. The gasoline vehicles showed very similar distributions to each other at the given steady speeds, but the large increase in particle number/km between the 50 km/h and 120 km/h conditions was accompanied by the emergence of a well-defined peak at around 30-40 nm. Substantial numbers of particles were also measured below this size. The gasoline cars (over the cyclic runs) did not give a clear peak in number distribution, but rather more of a steady increase as particle size decreased.

The data from cycles and 120 km/h suggest that gasoline vehicles emit a greater proportion of smaller particles than diesel vehicles. The diesel vehicle set shows bigger internal differences in particle size distribution profile, particularly around the 30-40 nm size and below. Around the 100 nm size, the diesel vehicles emit similar particulate numbers. Many of these features are difficult to rationalise, although the non-cat diesel vehicle, V3, is always amongst the highest emitters if not the highest.

Figure 4 Particle number distributions for each vehicle/fuel combination (SMPS)



(geometric means normalised to $dN / d\log_{10} d_p$)

In some cases, number distributions showed signs of a developing second peak or large distribution tail at the lower end of the size range. This effect was not always consistently observed. Due to problems with the design of the SMPS a 'kick-up' is often seen at the lowest sizes of SMPS scans. This is caused by carry over of particles from the previous scan combined with the high correction factor the SMPS uses on the lowest size particles. (The correction factor accounts for the reduced efficiency of passing smaller particles through the electrostatic classifier compared to larger particles.)

From the above the following conclusions can be drawn:

- the largest effect on distribution is the variation between diesel and gasoline vehicles
- at all test conditions, diesel emissions showed a bell-shaped distribution peaking between 80-200 nm
- gasoline vehicles show a difference both in the number and in the shape of the distribution between 50 km/h and 120 km/h
- differences due to diesel vehicle technology were most apparent at 50 km/h
- differences due to gasoline vehicle technology were most apparent over the cycle
- there were no consistent differences in distribution attributable to fuel.

8.5. EXPERIMENTAL RELATIONSHIP BETWEEN PARTICULATE NUMBER AND REGULATED MASS EMISSIONS

8.5.1. ECE/EUDC

An important element throughout this work is the relationship between number and mass, and between their distributions. The experimental data provide an opportunity for further examination of the number vs. mass correlation by comparing, in this instance, total number derived from the SMPS (or equivalent) data with particle weights from the gravimetric (filter paper) measurements made in studies over the driving cycle. These data, described as averaged emissions, are available as a comparison between SMPS/DMPS and the gravimetric data only over hot cycles (see **Figure 5**). **Figures 5** and **6** compare averaged number with mass emissions. **Figure 6** shows how the broad picture of particulate emissions effects is still dominated by the diesel/gasoline engine difference and that vehicle technology and fuel quality effects play a progressively smaller role in turn. Whilst there is no direct correlation between mass and number within fuel sets, **Figure 6** illustrates the point that for the tested vehicle set a broad trend can be seen, distinguishing between gasoline and diesel vehicles. However, within the diesel set, vehicles and fuels are ranked in different order depending on mass or number measurement e.g. the combination V1/D3 shows emissions of the lowest mass but highest number.

Figure 5 Particle number (SMPS) and mass (filter paper) emissions measured by contractor A for the hot ECE+EUDC cycle (geometric means)

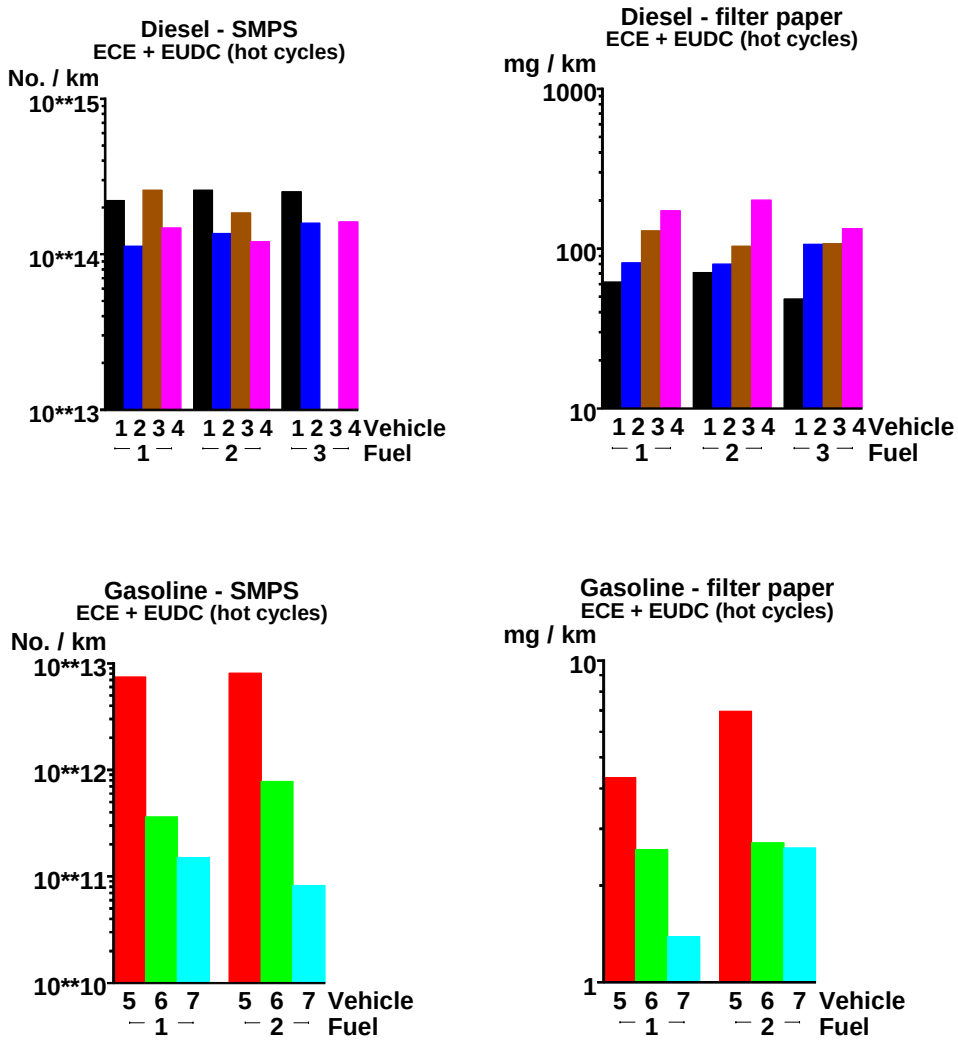
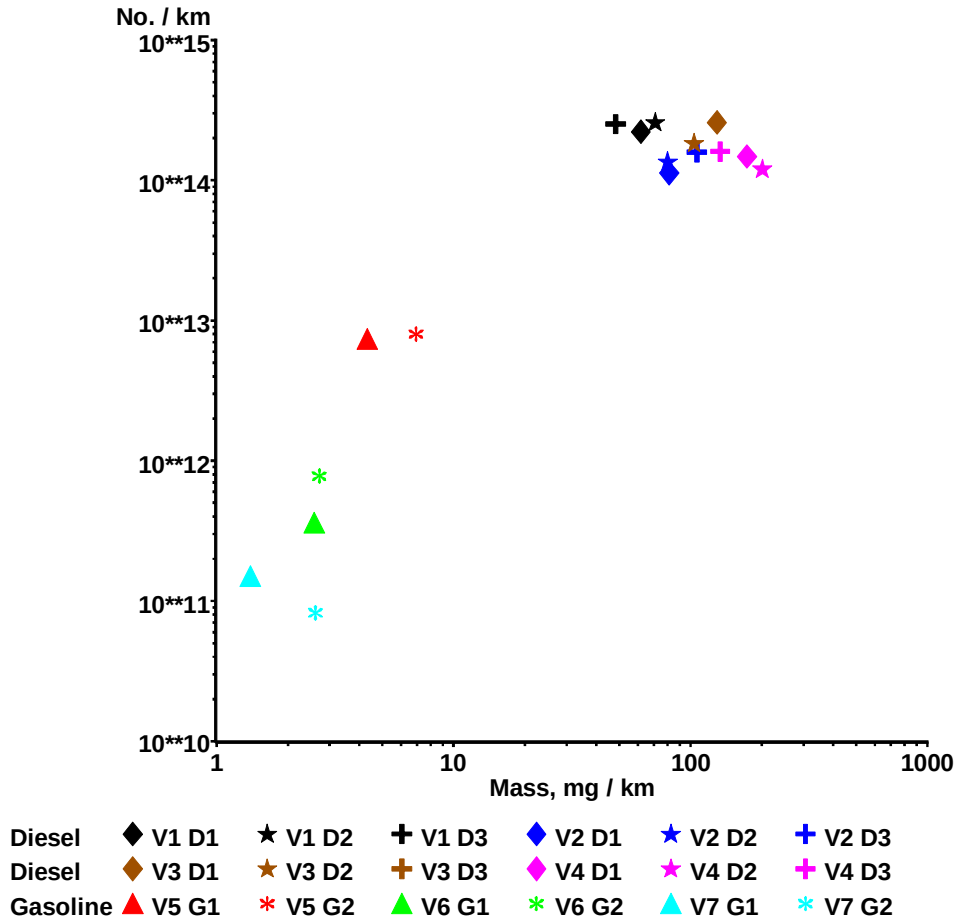


Figure 6 Particle number (SMPS) and mass (filter paper) emissions for the hot ECE+EUDC cycle (measured by contractor A) (geometric means)



8.5.2. Steady State

Measurements performed by Contractor B allowing a comparison of number and mass data are shown in **Appendix C, Figures C.1** and **C.2**. These figures show the total number emissions (measured by each analyser across their respective size ranges; see **Section 7** for mode of estimation) and filter paper mass for each vehicle/fuel combination averaged across repeats (geometric means). This comparison has been carried out at 50 and 120 km/h.

For the diesel testing performed at 120 km/h the analysers ranked the vehicle effects in the same order (although not the fuels), whereas for gasoline testing at both 50 and120 km/h it was the fuel order that the analysers recorded consistently.

Again, it is worth repeating that the errors on size measurement are greater than gravimetric filter mass measurement (see **Sections 8.6** and **8.7**) and that the absolute values for gasoline emissions were very low.

8.6. PARTICLE ANALYSER REPEATABILITY

An attempt to quantify the repeatability of measurements from the different laboratories/analysers has been made using the steady state test data obtained by SMPS/DMPS, EAA, DMA, and impactor. The values for standard deviation (SD) in **Appendix C, Table C.3** represent the standard deviations of repeat measurements of the total number of particles emitted using the same fuel in the same vehicle at the same speed. These SD values all increase as the number (or mass) of particles, N, measured increases and are thus expressed as a constant times N (or mass) . The same constants can be used for measurements in N/sec and measurements in N/km. The data indicate that SMPS/DMPS and the impactor were the most repeatable combination of techniques in this series of tests. It is on this basis that SMPS/DMPS data has been used as the primary reference for particulate number throughout this report.

The fact that gasoline particulate emissions are much lower than diesel emissions under all test methods may well explain why the repeatability is poorer in relative terms for gasoline. Also, in the gasoline tests, many DMA and some impactor results were below the detection limit. These values have been ignored in the repeatability calculations.

8.7. REPEATABILITY OF FILTER PAPER MEASUREMENTS

A similar process to estimate repeatability has been undertaken on the gravimetric data from the transient (driving cycle) tests. The standard deviations (SDs) shown in **Appendix C, Table C.4** are those of repeat measurements of total particle mass using the same fuel in the same vehicle. The SDs all increase as the mass increases and are thus expressed as a constant times mass. The same constants can be used whatever units filter paper mass is measured in (e.g. mg, mg/km, g or g/km).

"Short" SDs (**Table C.4**) measure the closeness of agreement within sets of consecutive hot-cycle measurements on the same vehicle and fuel forming part of the same composite run (i.e. stages II-IV in **Table 5**). "Long" SDs (**Table C.4**) measure the closeness of agreement between individual non-consecutive measurements on the same vehicle and fuel, these forming (parts of) different runs. Not surprisingly, the long SDs are in general much larger than the short SDs. It should also be noted that five gasoline tests carried out with Contractor A (1 cold, 4 hot) gave negative weight gains and these data were rejected as outliers. The SDs shown may therefore be underestimates.

By comparing **Tables C.3** and **C.4** it can be seen that measurement of mass using the legislated filter paper technique is the most repeatable measurement of total particulate emissions.

8.8. COMPARISON OF TECHNIQUES

The main features and scope of the different analysers have been described in earlier chapters. Within the range of particle number analysers used, similar principles of operation, and different (but often overlapping) coverage of particulate size range were seen. Thus, the comparison of techniques/laboratories has been extended to compare the relative numbers of emitted particulates observed using different analysers. **Figures C.3** and **C.4** (**Appendix C**) indicate the total number

emissions (Contractor A - SMPS/DMPS, Contractor B - EAA and DMA) for selected vehicle/fuel combinations averaged across repeats (geometric means). Also plotted are the corresponding particle size distributions, again averaged across repeats (geometric means). Where the observed particulate numbers are relatively high, the agreement between techniques seems usually to be quite reasonable. At lower particle number values, the comparisons are less favourable, with some large differences evident between the methods on occasions. These concerns are reflected in the distribution comparisons, which are a much sterner test of the technique comparison. Even at the higher particle numbers, there are some features that give concern; at lower numbers, the comparative results begin to lack coherence. It is clear that a given analytical method may be very useful for comparative purposes, but that derived absolute numbers must be treated with caution. In such a situation, it may be prudent to base a selection of preferred technique on criteria such as repeatability.

Considering the diesel study first, using the DMA, significant diesel vehicle effects were observed at 50 km/h with V2 giving lower emissions than V1 and V3 which were similar. Significant vehicle effects were also observed at 120 km/h where V3 gave higher emissions than V2 which in turn gave higher emissions than V1 (**Figure C.1, Appendix C**). No significant fuel effects were seen at either speed. Using the EAA, significant vehicle and fuel effects were seen at 50 km/h along with a significant vehicle/fuel interaction, the patterns being as shown in **Figure C.1**. At 120 km/h, vehicle differences were significant but fuel effects were not.

In the gasoline study, the repeatability of the DMA was poor (see **Table C.3, Appendix C**). At 50 km/h, low emissions were recorded and the observed vehicle and fuel differences, although seemingly substantial (**Figure C.2**, **Appendix C**), were not statistically significant (note that fuel effects came very close). At 120 km/h, DMA emission measurements were higher and vehicle differences were significant but again fuel effects just failed to be so. Data obtained by the EAA method showed significant vehicle differences at 50 km/h and 120 km/h and also significant fuel differences. A significant vehicle/fuel interaction was seen at both speeds.

8.9. COMPARISON OF HOT AND COLD CYCLE EMISSIONS

Differences in particulates response seemed to be evident between the hot and cold cycles according to data from the impactor referred to earlier (**Table 8**). Proportionally more (by mass) of the larger particles were produced in cold cycle tests (17.8% by mass) than in hot cycle tests (10.4%). The increase reflects the production of twice the mass of larger (bigger than 1000 nm) particles in cold cycle tests than in hot cycle tests (99.6% increase) whilst the mass of small particles (less than 1000 nm) remained essentially constant (6.5% increase, not significant). Considerable further information is available on this issue because of the way the study was designed. Therefore, the SMPS/DMPS results have been examined, as also have the gravimetric data, in an attempt to obtain a better appreciation of hot vs. cold cycle behaviour in both number and mass terms.

In the ECE+EUDC experiments, each run consisted of one cold cycle test followed by three hot cycle tests for a particular vehicle/fuel combination. In each of these four tests, as previously explained in **Section 5**, it was only possible to measure emissions in one small size range using the SMPS and another small size range using the DMPS. The three SMPS tests measured particles 21, 60 and 100 nm in size and the three DMPS tests particles 100, 200 and 400 nm in size. One of these three SMPS sizes and one of the three DMPS sizes was chosen arbitrarily for each

cold cycle test. Within each set of four tests, therefore, the SMPS cold cycle result could be compared with the single subsequent hot cycle result for the same size range. A similar comparison could be made using the DMPS results. A regression analysis was conducted on the differences between pairs of log results defined as above. It has been calculated that cold cycle particulate number emissions were (on average) 21% higher than hot cycle emissions for diesel tests and 11% higher for gasoline tests, but these differences were not statistically significant. No significant vehicle or fuel differences were observed, nor did the size of the difference vary with the size of particle being measured. (The sizes of the observed differences in log results were very variable and there were a number of potential outliers. To avoid such results having undue influence, the non-parametric Wilcoxon signed rank test (9) was conducted but again no statistically significant pattern emerged. For diesel, the cold result was higher on 33 occasions and the hot result was higher 26 times. For gasoline, the higher result was cold 19 times and hot 9 times).

Filter paper measurements were more amenable to cold v hot cycle comparisons as a measurement of total mass emissions was available for each individual test. For each run, the mean of the three hot-cycle log results was calculated and this was subtracted from the log result for the one cold-cycle test. A regression analysis was then conducted on these differences. In the diesel tests conducted by Contractor B, cold cycle emissions were significantly higher (16%) on average. The size of the difference did not vary with vehicle or fuel in any significant way. In the diesel tests conducted by Contractor A, cold cycle emissions were also higher on average but the difference varied from vehicle to vehicle with a 29% difference for V3 but less than 5% for V1, V2 and V4.

In the gasoline tests conducted by Contractor B, cold cycle mass emissions were significantly higher (30%) on average. The size of the difference did not vary with vehicle or fuel in any significant way. In the gasoline tests conducted by Contractor A, cold cycle emissions were actually 47% higher on average but the high variability in these low results meant that the difference was not statistically significant.

It seems clear that more particulate mass is emitted in cold start tests than in hot tests. The impactor data suggest that this reflects the production of more large (and hence more massive) particles under cold start conditions. If this is the case, then the lack of any difference in the particulate number measurements is not surprising since these are made in the size range <1 micron where the impactor data (**Table 8**) suggest there is little difference in the emissions from hot-start and cold-start tests.

8.10. COMPARISON OF ECE AND EUDC CYCLE PARTICULATE EMISSIONS

Attempts have also been made to assess the relative contributions of the ECE and EUDC phases to overall particulates production. The SMPS/DMPS data on the diesel fleet (for hot cycles only) showed the fleet-averaged particulate number emissions to be 40% higher during the ECE than the EUDC. However, this was the case only because of a large effect in V1 (163%higher in ECE), the other vehicles V2-V4 all giving only 11-14% more in ECE. SMPS/DMPS data on the gasoline fleet, again for hot cycles only, gave ECE particulate emissions 33% lower by number, but this difference was not significant; no significant vehicle or fuel effects were found.

Using the gravimetric (filter paper) data to address the same question gave better information. For the gasoline study, assessing cold and hot cycles together, fleet-averaged ECE emissions were found to be 30% lower than EUDC emissions, with 99.9% confidence. Further analysis showed no significant vehicle, fuel or hot/cold effect on the ECE/EUDC split. For the diesel case, the gravimetric data gave a

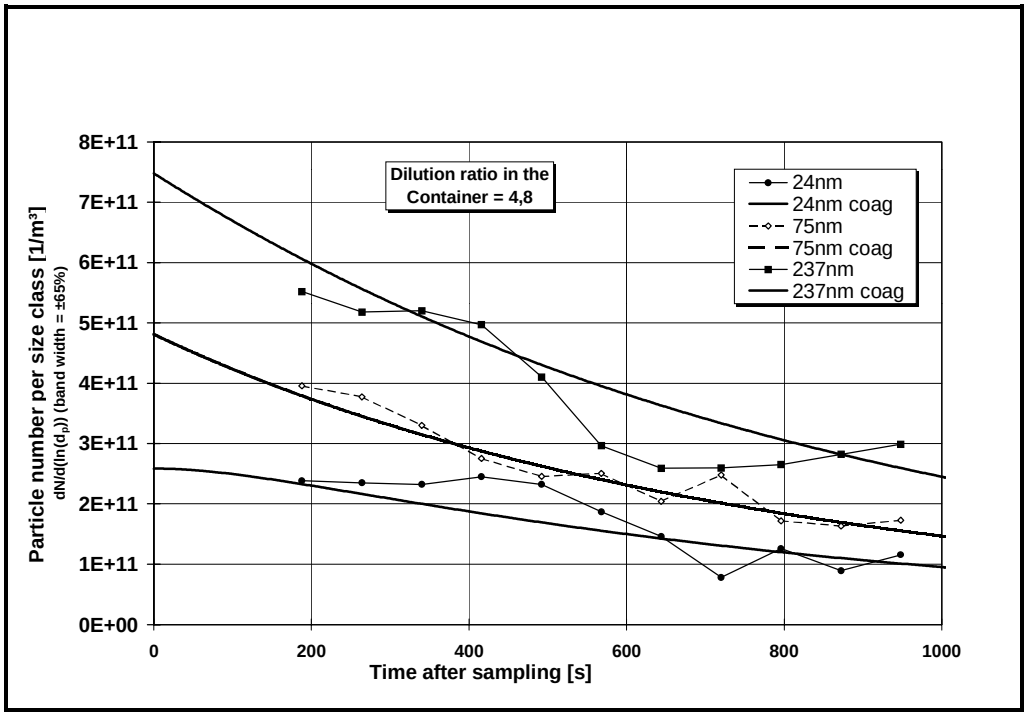
complex answer; vehicles V1-V3 gave averaged ECE emissions only 3% higher than EUDC emissions. However, there were large car-to-car differences whereby V1 gave 106% higher emissions in ECE, V2 gave 8% higher emissions in ECE, but V3 gave 51% lower emissions in ECE than EUDC. V3 is the only non-catalyst diesel vehicle. A big hot/cold cycle effect on the ECE/EUDC split was seen only for V3 (ECE gave 36% lower emissions than EUDC for cold cycles, compared with 62% lower for hot cycles).

8.11. EFFECT OF TIME ON PARTICULATE DISTRIBUTION

As indicated in an earlier chapter, some container measurements were carried out so as to ascertain the rate of particle number decrease in diluted exhaust. To achieve this, diluted exhaust gas produced in the standard emissions experiment was further diluted to a known extent, and collected in a 500 litre stainless steel container. At the end of the test, the contents of the container were analysed using the EAA (over time) to provide an indication of the agglomeration kinetics.

The results of such an experiment are shown in **Figure 7** for V2 at 70 km/h. It is clear that very substantial loss of particle number has occurred within 10 minutes of the original dilution; however, the scatter in the data does not allow further detailed assessments to be made, for example, of how the agglomeration rate varies with particle size (although there are established agglomeration theories available from which to calculate this e.g. as shown in the graph).

Figure 7 Particle size distribution in a sealed container as a function of time (measured by the EAA)



An important message to be drawn from this experiment is that tailpipe particle size distributions, of themselves, are only one aspect of a far more complex series of

processes ultimately determining ambient air quality in respect of particulate burden and size distribution.

8.12. REGULATED EMISSIONS RESULTS

Regulated emissions measurements were conducted throughout this work, largely as a means of testing the robustness of the integrated experimental set. To this extent it was most successful, repeats usually lying well within the EPEFE criteria; and where repeat measurements gave more dubious results, this could be used to register a more cautious approach to results.

Some measurements were made of modal regulated emissions during the MVEG cycle. These provided an indication of where particulate of chosen sizes tended to form as a function of driving mode. An example is given in **Figure C.5, Appendix C**. Some time was spent trying to correlate the particulate number behaviour with the various regulated emissions. No one parameter correlated that well under all conditions, but the modal particulate plots were usually in line with either the CO_2 or HC modal behaviour.

9. CONCLUSIONS

- Particulate emissions measured from LD diesel vehicles were much higher than from LD gasoline vehicles. In mass terms, the factor was 40-85 based on information from both steady-speed and MVEG driving cycle tests, while, in number terms, it was around 200 for MVEG cycles, more than 2000 at 50 km/h, but down to around 3 at 120 km/h (see third conclusion).
- In terms of mass, more than 85% of diesel particulate emissions were <1 µm. This corresponds to over 99% by number. SMPS number data indicate that gasoline vehicles emit a higher proportion of smaller particles than diesel vehicles. It follows that >99% of gasoline particulate number emissions are also <1 µm.
- Although diesel particulate emissions were substantially higher than gasoline emissions at 50 km/h, the number differences between gasoline and diesel disappeared at high speed (120 km/h) as the consequence of a disproportionate increase in gasoline particulate emissions. The reasons for this anomaly are not understood.
- The largest vehicle technology effect on particulate emissions was the gasoline/diesel effect. However, technology effects were evident within the gasoline car set, the advanced 3WC vehicle tending to give the lowest emissions. Vehicle differences within the diesel set were less pronounced.
- No clear differences were seen between the two gasoline fuels tested. Fuel effects were more demonstrable in the diesel study; for example the Swedish Class I diesel fuel emitted substantially less particulate mass than the other two diesel fuels, though in terms of the emitted particulate number, no significant differences were seen.
- Particulate emissions were lower under fully warmed-up conditions than for cold engines. In the case of diesel engines, there is some evidence that this is because more large particles are produced during a cold test.
- The comparisons conducted to cross-check on techniques showed good correlations in certain cases. Some techniques were seen to be substantially more repeatable than others, and hence appeared to be more reliable for comparative purposes than others. SMPS/DMPS, regulated mass by gravimetric methods and the impactor technique all seem to have performed well in this study.
- There is evidence that, whether particulate emissions are judged by mass or number, the highly emitting vehicles will always be detectable. This is of great potential significance in the debate as to how number and mass should be accommodated in future legislative procedures.
- Experiments conducted in a high volume stainless steel container confirmed that the further dilution processes taking place after emission of particles from the tailpipe do change significantly the original distribution of particulate size and illustrate the need for more knowledge in this area.

One of the questions that is raised concerns the nature of the particulate at the different sizes. This study cannot elucidate what different particle compositions and characteristics may be represented by the full spectrum of materials measured in this study as "particulates".

10. ACKNOWLEDGEMENT

CONCAWE's Automotive Emissions Special Task Force AE/STF-10 wish to place on record the contribution of staff from the following organisations to the work reported here:

AEA Technology, Harwell, UK

BP Oil International Ltd. Sunbury, UK

FEV Motorentechnik, Aachen, Germany

Shell Research Ltd, Thornton, UK.

The Automotive Emissions Management Group and the Task Force wish to acknowledge the contribution of R.C. Hutcheson in coordinating the starting phase of the programme.

11. REFERENCES

1. EU (1994) Directive 94/12/EC of the European Parliament and the Council relating to measures to be taken against air pollution by emissions from motor vehicles and amending Directive 70/220/EEC. Official Journal of the European Communities No. L100, 19.04.1994

2. EU (1991) Council Directive of 1 October 1991 amending Directive 88/77/EEC on the approximation of the laws of the Member States relating to the measures to be taken against the emission of gaseous pollutants from diesel engines for use in vehicles (91/542/EEC). Official Journal of the European Communities No. L295, 25.10.1991

3. CONCAWE (1995) Air quality standard for particulate matter. Report No. 95/62. Brussels: CONCAWE

4. Schlesinger, R.B. (1995) Toxicological evidence for health effects from inhaled particulate pollution: does it support the human experience? *Inhalation Toxicol 1, 99-105*

5. Greenwood, S.J. and Coxon, J.E. (1996) An investigation of the particulate size distributions from petrol, diesel and natural gas fuelled vehicles. SAE Paper No. 961085. Warrendale PA: Society of Automotive Engineers

6. Rickeard, D.J. et al (1996) Exhaust particulate size distribution: vehicle and fuel influences in light duty vehicles. SAE Paper No. 961980. Warrendale PA: Society of Automotive Engineers

7. CONCAWE (1996) The measurement of the size range and number distribution of airborne particles related to automotive sources - a literature study. Report No. 96/56. Brussels: CONCAWE

8. EPEFE (1995) European programme on emissions, fuels and engine technologies

9. Kittelson, D. (1997) Characterizing particulate matter in motor vehicle exhaust - diesel and gasoline engines. *HEI Communication No. 5, 8-13*

10. Snedecor, G.W. and Cochran, W.G. (1967) Statistical Methods, 6th ed. Ames IA: Iowa State University

12. GLOSSARY

AFRst	Air Fuel Ratio (Stoichiometric)
AQS	Air Quality Standard
CONCAWE	Conservation of Clean Air and Water in Europe (the oil companies' European organisation for environment, health and safety)
CP(N)C	Condensation Particle (Nucleus) Counter
CVS	Constant Volume Sampling System (FTP)
DI	Direct Injection
DMA	Differential Mobility Analyser
DMPS	Differential Mobility Particle Sizer
EAA	Electrical Aerosol Analyser
ECE	Urban Driving Cycle
ELPI	Electrical Low Pressure Impactor
EPEFE	European Programme on Emissions, Fuels and Engine Technologies
EUDC	Extra Urban Driving Cycle
FID	Flame Ionization Detector
IDI	Indirect Injection (diesel engine)
IR	Infra-Red
LD	Light Duty
MPI	Multi Point Injection
MVEG	Motor Vehicle Emission Group - 11 second variation to European Driving Cycle
$PM_{[x]}$	particles with an aerodynamic diameter less or equal to [x] micron
QCM	Quartz Crystal Microbablance
SMPS	Scanning Mobility Particle Sizer
SPI	Single Point Injection
TLEV	Transitional Low Emission Vehicle

Appendix A PRINCIPLE OF OPERATION OF ANALYSERS USED IN THE PROGRAMME

ELECTRICAL MOBILITY TECHNIQUES

Electrical mobility aerosol analysers are based on the movement of gas-borne particles carrying a known electric charge towards an electrode of opposite charge. These techniques have the potential for good size resolution in the range 0.004-1.0 µm volume equivalent diameter. Particles smaller than this lower limit are difficult to charge, whilst larger particles are prone to multiple charging. Electrical mobility analysers are the only high resolution techniques for particles smaller than 0.1 µm volume equivalent diameter. The Electrical Aerosol Analyser (EAA), and Differential Mobility Analyser (DMA) are commercially available instruments operating on these principles.

Electrical Aerosol Analyser (EAA)

The EAA consists of three main components: a unipolar diffusion charger, the mobility analyser and a Faraday-cup electrometer detector. Gas-borne particles pass through the diffusion charger at a flow rate of 4 l/min, where they acquire a well defined electrostatic charge. This charge depends on the number of ions encountered during the time spent within the charger as well as on particle size. The charged particles pass to the tubular mobility section, which consists of a central electrode surrounded by a core of clean (sheath) gas. The aerosol flow is introduced so as to surround the sheath gas in laminar flow; any aerosol leaving the mobility analyser is collected on the filter of the electrometer and the electrostatic charge measured as the current drains to earth potential. Initially, the analyser is operated with the central electrode at low voltage, so that all the aerosol collects on the electrometer filter. As this voltage is increased in a series of well defined steps, progressively fewer particles penetrate through the mobility section and the electrometer current falls to zero. The measured decrease in electrometer current between two successive settings of electrode voltage can be related to the particle number concentration associated with a particular size band.

The EAA has the capability to discriminate size bands in the range 0.013-0.75 µm; this range can be extended to 0.004 µm but the performance of the instrument below 0.013 µm is uncertain. Over the normal operating range, a size distribution may be obtained within 2 minutes if the source is stable. It should be noted that the density and viscosity of the sheath and aerosol gases should be the same for the size separation process to work correctly.

Differential Mobility Analyser (DMA)

DMAs have been developed to capture the narrow range of particle that have a common trajectory within an electrical mobility analyser. The Differential Mobility Particle Sizer (DMPS) is the most commonly encountered instrument of this type, consisting of an electrostatic classifier as the mobility analyser, which is coupled to either a condensation nucleus counter (CNC) or a Faraday-cup electrometer.

The aerosol flow rate entering the DMPS ranges from 0.1 to 1.0 l/min, although the instrument is normally operated at the flow rate of the CNC (0.3 l/min). Particles

larger than 1 µm aerodynamic diameter are initially removed in a single-stage impactor, since they may carry more electrostatic charge and result in large errors in the measured size distribution. The aerosol is then passed through a bipolar charge equilibrator consisting of a Kr-85 radioactive source contained within the electrostatic classifier section. Emerging particles carry a Boltzmann distribution of charges (the overall charge is zero, but the aerosol contains well-defined proportions of particles carrying ± 1, ± 2, ± 3 charges etc). The design of the mobility section is superficially similar to that of the EAA. However, the central electrode does not occupy the full length of the analyser; a small gap exists near to the exit pipe. The electrode voltage is initially set to a low positive potential; particles that have a narrow range of high electrical mobilities (smallest particles) enter the gap and are collected by the detector as a 'monodisperse' aerosol. As the electrode voltage is increased, the size of particles exiting the electrostatic classifier also increases, since the electrical mobility of the particles that enter the gap at the base of the electrode decreases. As the particle size increases above 0.05 µm volume equivalent diameter, the aerosol begins to consist of several monodisperse sub-fractions corresponding to the different negative charge levels allowed by the Boltzmann charge equilibrium. Thus, the signal recorded by the detector during the measurement sequence corresponds to the actual number-size distribution, modified by the presence of a known proportion of multiply-charged particles. The analyser software corrects for these particles up to 6 charges/particle. The DMPS is capable of measuring as many as 32 size channels in the range 0.01-0.9 µm electrical mobility diameter.

A recent development, allowing complete size scans to be performed in 60 seconds at a very high resolution (64 channels per decade of scan) has been the Scanning Mobility particle Sizer (SMPS). Here, the electric field strength in the electrical classifier section of the DMPS is varied monotonically, at the same time making particle number concentration measurements in rapid succession (up to 10 times/sec) using a CNC. The measurement cycle consists of repeated ramps of the central electrode voltage on an exponential scale, increasing from a defined minimum value to maximum field strength, then decreasing the field strength back to the minimum value. The particles entering the sample extraction slot of the classifier will have a monotonic variation in electrical mobility if the electric field strength is varied monotonically. Hence, after making allowances for the finite transit times of the particles within the classifier and from the extraction slot to the CNC, the entire size distribution of the incoming aerosol can be scanned both accurately and rapidly.

SEDIMENTATION/INERTIAL TECHNIQUES

These techniques determine particle aerodynamic diameter directly. General purpose inertial aerosol classifiers are by far the widest used type of particle size analyser. Cascade impactors are the most commonly encountered aerosol sampling instruments. The simplest impactor consists of a series of stages, each comprising a jet-plate which is located at a fixed distance from a horizontal collection surface. Aerosol passes through the jet-plate (containing one or many orifices); the streamlines of the flow converge on approach to the collection surface, whereas the inertia of the particles causes them to cross the streamlines. Particles of sufficient size (and inertia) describe trajectories that intersect the collection surface; smaller particles are able to remain gas-borne, passing to the next stage. The jet diameters of the second plate are smaller, increasing the gas velocity so that smaller particles are collected. The process is repeated, collecting progressively smaller particles until the bottom of the impactor is reached.

Low pressure impactors operate by passing the flow through a critical orifice, usually located towards the bottom of the stack of collection stages. The upper part of the analyser therefore operates as a conventional impactor, whereas efficient sub-micron separation can also take place in the low pressure section because the slip correction factor is greatly increased, reducing the aerodynamic drag on the particles.

This is the operating principle behind the QCM impactor, which uses vibrating quartz crystal sensors to measure mass-size distributions in the range from 0.05-25 µm aerodynamic diameter in real-time.

Appendix B MATHEMATICAL FORMULAE

Estimation of total particulate emissions in ECE+EUDC cycle tests from SMPS/DMPS measurements

Total particulate emissions between 25 and 400 nm in *N*/km were estimated from SMPS/DMPS measurements centred at 25, 60, 100, 200 and 400 nm by the trapezoidal quadrature rule

$$Total\ N/km = \frac{y_{25}(\log_{10}60 - \log_{10}25)}{2} + \frac{y_{60}(\log_{10}100 - \log_{10}25)}{2} + \frac{y_{100}(\log_{10}200 - \log_{10}60)}{2} + \frac{y_{200}(\log_{10}400 - \log_{10}100)}{2} + \frac{y_{400}(\log_{10}400 - \log_{10}200)}{2}$$
$$= 0.1901y_{25+} + 0.3010y_{60} + 0.2614y_{100} + 0.3010y_{200} + 0.1505y_{400}$$

where y_n is the value of $d(N/km)/d\log_{10}d_p$ at *n* nm. The SMPS 100 nm value was used rather than the DMPS value or the mean of the two.

Number to mass conversion

Particulate size distributions were converted from number / km ($d(N/km)/d\log_{10}d_p$) to mass / km ($d(mass, mg/km)/d\log_{10}d_p$) using the formula

$$\frac{d(mass, mg/km)}{d\log_{10}d_p} = \frac{d(N/km)}{d\log_{10}d_p} \times \frac{\pi}{6\times10^{18}} \times \frac{1}{3\log_e 10} \times \frac{{d_{p,\max}}^3 - {d_{p,\min}}^3}{\log_{10}d_{p,\max} - \log_{10}d_{p,\min}}.$$

This assumes that the particles are spherical with density 1 kg/l and that the particle diameters d_p in each size interval are uniformly distributed on a $\log_{10}$ scale between $d_{p,\min}$ and $d_{p,\max}$.

Appendix C TABLES AND FIGURES

Table C.1 **Gasoline Vehicles**

(a) Total number of particles emitted per km for each vehicle/fuel combination as measured by each analyser (geometric means)

(measurement ranges vary)

		SMPS/DMPS			EAA			DMA		
	FUEL VEH	**G1**	**G2**	**Geo. mean**	**G1**	**G2**	**Geo. mean**	**G1**	**G2**	**Geo. mean**
50 KM/H	**V5**	3.95E+10	2.11E+10	**2.88E+10**	1.08E+12	2.23E+11	**4.91E+11**	3.16E+11	7.30E+10	**1.52E+11**
	V6	4.68E+10	2.53E+10	**3.44E+10**	4.44E+12	9.92E+10	**6.63E+11**	1.43E+12	5.72E+10	**2.86E+11**
	V7	5.61E+10	9.31E+10	**7.23E+10**	3.14E+10	4.10E+10	**3.59E+10**	7.78E+10	1.06E+11	**9.10E+10**
	Geo. mean	**4.70E+10**	**3.68E+10**	**4.16E+10**	**5.33E+11**	**9.68E+10**	**2.27E+11**	**3.28E+11**	**7.63E+10**	**1.58E+11**
120 KM/H	**V5**	3.63E+13	4.78E+13	**4.16E+13**	9.32E+13	1.18E+14	**1.05E+14**	1.18E+14	1.34E+14	**1.26E+14**
	V6	4.34E+13	6.38E+13	**5.26E+13**	3.95E+13	2.14E+12	**9.20E+12**	5.57E+13	2.78E+12	**1.24E+13**
	V7	5.37E+13	4.52E+13	**4.93E+13**	9.60E+12	5.97E+12	**7.57E+12**	3.51E+13	2.62E+13	**3.03E+13**
	Geo. mean	**4.39E+13**	**5.17E+13**	**4.76E+13**	**3.28E+13**	**1.15E+13**	**1.94E+13**	**6.14E+13**	**2.14E+13**	**3.62E+13**
COLD CYCLES	**V5**									
	V6									
	V7									
	Geo. mean									
HOT CYCLES	**V5**	7.40E+12	8.03E+12	**7.71E+12**						
	V6	3.62E+11	7.78E+11	**5.30E+11**						
	V7	1.51E+11	8.24E+10	**1.11E+11**						
	Geo. mean	**7.39E+11**	**8.01E+11**	**7.69E+11**						

Note: Geometric means are also given across vehicles and across fuels, giving each vehicle and fuel equal weight.

Table C.1 **Gasoline Vehicles**

(b) Total mass of particles (mg) emitted per km for each vehicle/fuel combination as measured by each analyser (geometric means).

(measurement ranges vary)

		IMPACTOR			FILTER PAPER (Contractor B)			FILTER PAPER (Contractor A)		
	FUEL VEH	**G1**	**G2**	**Geo. mean**	**G1**	**G2**	**Geo. mean**	**G1**	**G2**	**Geo. mean**
50 KM/H	**V5**	0.84	0.67	**0.75**	0.47	0.58	**0.52**			
	V6	0.22	1.38	**0.55**	0.21	0.08	**0.13**			
	V7	1.53	0.65	**1.00**	0.18	0.10	**0.13**			
	Geo. mean	**0.65**	**0.85**	**0.74**	**0.26**	**0.16**	**0.21**			
120 KM/H	**V5**	3.27	1.57	**2.27**	4.27	2.53	**3.29**			
	V6	3.17	0.93	**1.72**	2.55	1.65	**2.05**			
	V7	1.73	0.85	**1.21**	2.01	0.76	**1.24**			
	Geo. mean	**2.62**	**1.08**	**1.68**	**2.80**	**1.47**	**2.03**			
COLD CYCLES	**V5**	3.13	1.28	**2.00**	2.23	1.02	**1.51**	6.29	6.32	**6.31**
	V6	1.52	4.85	**2.72**	1.23	0.88	**1.04**	3.44	4.71	**4.02**
	V7	2.79	5.73	**4.00**	0.40	0.42	**0.41**	2.53	4.02	**3.19**
	Geo. mean	**2.37**	**3.29**	**2.79**	**1.03**	**0.72**	**0.86**	**3.80**	**4.92**	**4.32**
HOT CYCLES	**V5**	1.58	1.37	**1.47**	1.62	1.34	**1.47**	4.32	6.94	**5.48**
	V6	1.01	0.58	**0.76**	0.86	0.66	**0.75**	2.58	2.71	**2.65**
	V7	1.38	1.10	**1.23**	0.21	0.34	**0.27**	1.39	2.61	**1.90**
	Geo. mean	**1.30**	**0.96**	**1.12**	**0.66**	**0.67**	**0.67**	**2.49**	**3.67**	**3.02**

Note: Geometric means are also given across vehicles and across fuels, giving each vehicle and fuel equal weight.

Table C.2 **Diesel Vehicles**

(a) Total number of particles emitted per km for each vehicle/fuel combination as measured by each analyser (geometric means)

(Measurement Ranges Vary)

		SMPS/DMPS				EAA				DMA			
	FUEL	**D1**	**D2**	**D3**	**Geo.**	**D1**	**D2**	**D3**	**Geo.**	**D1**	**D2**	**D3**	**Geo.**
	VEH				**mean**				**mean**				**mean**
50 KM/H	**V1**	1.35E+14	1.82E+14	1.73E+14	**1.62E+14**	1.25E+14	6.75E+13	1.52E+14	**1.09E+14**	1.29E+14	2.77E+14	8.89E+13	**1.47E+14**
	V2	6.62E+13	7.62E+13	8.50E+13	**7.54E+13**	6.55E+13	1.69E+14	1.89E+14	**1.28E+14**	7.34E+13	7.23E+13	8.84E+13	**7.77E+13**
	V3	1.66E+14	7.85E+13	1.21E+14	**1.17E+14**	1.92E+14	3.21E+14	3.89E+14	**2.88E+14**	1.27E+14	2.13E+14	1.79E+14	**1.69E+14**
	V4	7.42E+13	6.43E+13	7.99E+13	**7.25E+13**								
	Geo. mean	**1.02E+14**	**9.14E+13**	**1.09E+14**	**1.01E+14**	**1.16E+14**	**1.54E+14**	**2.23E+14**	**1.59E+14**	**1.06E+14**	**1.62E+14**	**1.12E+14**	**1.25E+14**
120 KM/H	**V1**	1.55E+14	1.26E+14	1.51E+14	**1.43E+14**	6.82E+13	2.86E+13	9.29E+13	**5.66E+13**	5.78E+13	1.14E+14	9.01E+13	**8.39E+13**
	V2	1.18E+14	1.52E+14	1.78E+14	**1.47E+14**	3.97E+13	1.13E+14	1.34E+14	**8.43E+13**	9.82E+13	9.97E+13	1.71E+14	**1.19E+14**
	V3					3.87E+14	4.76E+14	3.56E+14	**4.03E+14**	4.20E+14	3.95E+14	3.58E+14	**3.90E+14**
	V4	1.22E+14	1.09E+14	1.93E+14	**1.37E+14**								
	Geo. mean	**1.31E+14**	**1.28E+14**	**1.73E+14**	**1.42E+14**	**1.02E+14**	**1.15E+14**	**1.64E+14**	**1.24E+14**	**1.34E+14**	**1.65E+14**	**1.77E+14**	**1.57E+14**
COLD	**V1**												
CYCLES	**V2**												
	V3												
	V4												
	Geo. mean												
HOT	**V1**	2.22E+14	2.58E+14	2.52E+14	**2.44E+14**								
CYCLES	**V2**	1.13E+14	1.36E+14	1.59E+14	**1.34E+14**								
	V3	2.59E+14	1.84E+14										
	V4	1.48E+14	1.20E+14	1.61E+14	**1.42E+14**								
	Geo. mean	**1.76E+14**	**1.67E+14**										

Note: Geometric means are also given across vehicles and across fuels, giving each vehicle and fuel equal weight.

Table C.2 **Diesel Vehicles**

(b) Total mass of particles (mg) emitted per km for each vehicle/fuel combination as measured by each analyser (geometric means)

(Measurement Ranges Vary)

		IMPACTOR				FILTER PAPER (Contractor B)				FILTER PAPER (Contractor A)			
	FUEL VEH	**D1**	**D2**	**D3**	**Geo. mean**	**D1**	**D2**	**D3**	**Geo. mean**	**D1**	**D2**	**D3**	**Geo. mean**
50 KM/H	**V1**	47.2	57.0	20.7	**38.2**	70.0	84.2	29.9	**56.0**				
	V2	49.6	71.3	26.6	**45.5**	132.3	136.9	49.8	**96.6**				
	V3	88.2	116.9	35.4	**71.5**	129.8	171.7	53.7	**106.2**				
	V4												
	Geo. mean	**59.1**	**78.0**	**26.9**	**49.9**	**106.3**	**125.5**	**43.1**	**83.1**				
120 KM/H	**V1**	16.5	40.1	24.7	**25.4**	23.7	51.5	35.1	**35.0**				
	V2	92.1	104.1	97.3	**97.7**	162.5	203.9	150.1	**170.7**				
	V3	477.1	745.9	532.4	**574.3**	649.5	1656.9	618.9	**873.3**				
	V4												
	Geo. mean	**89.9**	**146.0**	**108.6**	**112.5**	**135.8**	**259.2**	**148.2**	**173.4**				
COLD CYCLES	**V1**	45.4	47.8	29.2	**39.9**	55.5	68.7	44.3	**55.3**	64.5	67.5	46.5	**58.7**
	V2	127.2	160.8	84.2	**119.8**	177.5	216.4	124.3	**168.4**	87.4	82.4	112.5	**93.2**
	V3	279.8	387.7	220.6	**288.1**	287.8	530.4	168.0	**294.9**	167.1	135.8	135.0	**145.2**
	V4									180.5	215.9	128.3	**171.0**
	Geo. mean	**117.3**	**143.9**	**81.5**	**111.2**	**141.6**	**199.0**	**97.4**	**140.0**	**114.2**	**113.0**	**97.6**	**108.0**
HOT CYCLES	**V1**	34.6	44.4	26.7	**34.5**	49.1	60.2	33.7	**46.4**	61.7	70.9	48.3	**59.6**
	V2	111.8	125.7	85.3	**106.3**	156.5	196.4	118.8	**154.0**	81.3	80.2	106.6	**88.6**
	V3	263.2	295.3	172.9	**237.7**	256.4	383.0	148.0	**244.0**	129.2	103.5	107.6	**112.9**
	V4									173.1	201.2	133.5	**166.9**
	Geo. mean	**100.6**	**118.1**	**73.3**	**95.5**	**125.4**	**165.5**	**84.0**	**120.3**	**102.9**	**104.3**	**92.7**	**99.9**

Note: Geometric means are also given across vehicles and across fuels, giving each vehicle and fuel equal weight.

Table C.3 Steady state tests – total number or mass of particles N/sec (or N/km) – test-to-test standard deviation for each method

	Gasoline					Diesel				
Method	**Overall S.D.**	Speed	S.D.	Veh	S.D.	**Overall S.D.**	Speed	S.D.	Veh	S.D.
SMPS	**0.498×N**	Idle	0.458×N	V5	0.547×N	**0.191×N**	Idle	0.134×N	V1	0.120×N
		30	0.569×N	V6	0.584×N		30	0.107×N	V2	0.127×N
		50	0.508×N	V7	0.325×N		50	0.176×N	V3	0.220×N
		70	0.641×N				70	0.190×N	V4	0.260×N
		120	0.197×N				90	0.228×N		
							120	0.314×N		
EAA	**0.689×N**					**0.527×N**	Idle	0.572×N		
							30	0.508×N		
							50	0.309×N		
							70	0.450×N		
							120	0.497×N		
DMA	**0.981×N**					**0.340×N**	Idle	0.276×N	V1	0.502×N
							30	0.401×N	V2	0.208×N
							50	0.447×N	V3	0.226×N
							70	0.200×N		
							120	0.317×N		
Impactor	**0.834×mass**	Idle	0.370×mass			**0.320×mass**				
		30	1.142×mass							
		50	0.426×mass							
		70	1.273×mass							
		120	0.584×mass							

Note: Geometric means are also given across vehicles and across fuels, giving each vehicle and fuel equal weight.

Using Bartlett's test (ref. 10), standard deviations differed from speed to speed for SMPS – gasoline ($P < 5\%$) & diesel ($P < 0.1\%$), EAA – diesel ($P < 5\%$), DMA – diesel ($P < 5\%$) and the impactor – gasoline ($P < 1\%$). Standard deviations also differed from vehicle to vehicle for SMPS – gasoline ($P < 10\%$) & diesel ($P < 0.1\%$) and DMA – diesel ($P < 0.1\%$).

Table C.4 Cyclic tests – filter paper measurements (mg/km) – test-to-test standard deviations

		Gasoline		Diesel	
		Short	**Long**	**Short**	**Long**
Contractor A	**Cold**	-	0.394 × mass	-	0.158 × mass
	Hot	0.565 × mass	0.677 × mass	0.056 × mass	0.206 × mass
Contractor B	**Cold**	-	0.618 × mass	-	0.267 × mass
	Hot	0.279 × mass	0.480 × mass	0.064 × mass	0.253 × mass

Note:

"Short" SDs are the SDs of consecutive hot-cycle measurements on the same vehicle and fuel forming part of the same composite run (stages II-IV in **Table 5**). "Long" SDs are the SDs of non-consecutive measurements on the same vehicle and fuel, these forming parts of different runs.

Figure C.1 **Diesel**

(a) DMA, EAA and filter paper results obtained by contractor B
at 50 km/h
(geometric means giving each vehicle and fuel equal weight)

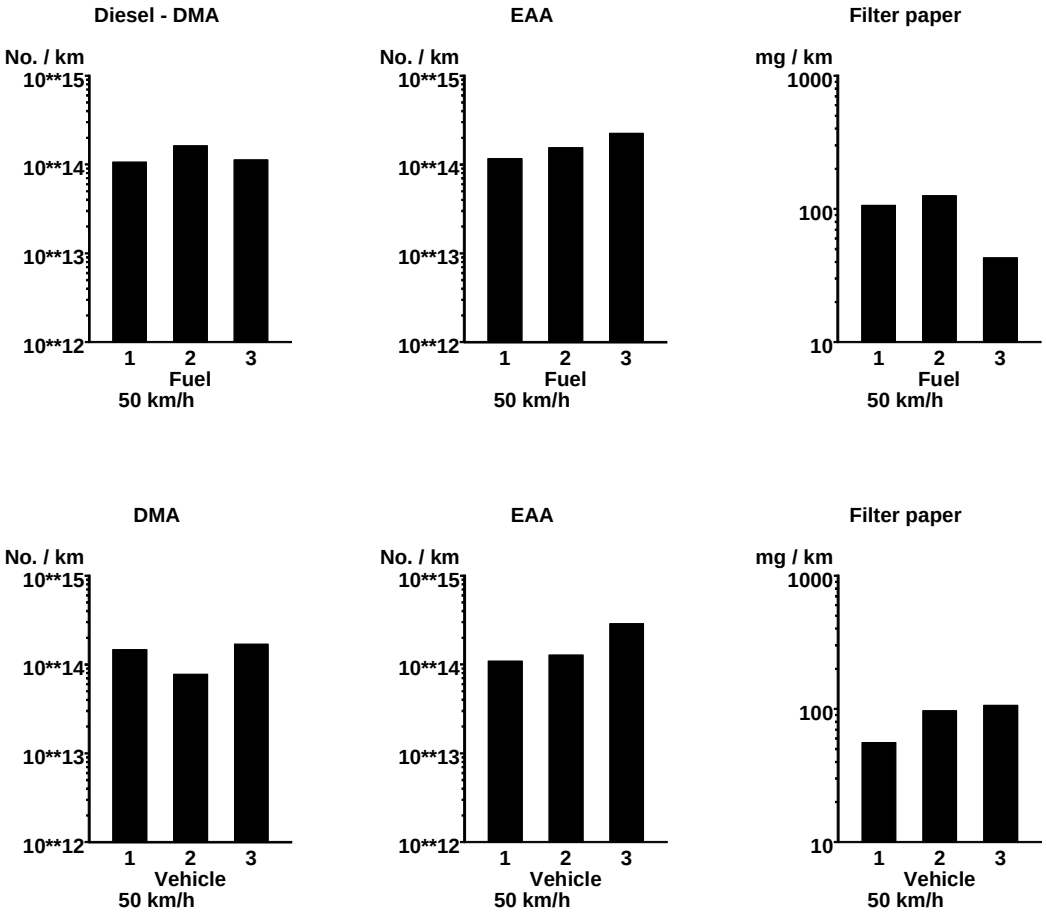


Figure C.1 **Diesel**

(b) DMA, EAA and filter paper results obtained by contractor B
at 120 km/h
(geometric means giving each vehicle and fuel equal weight)

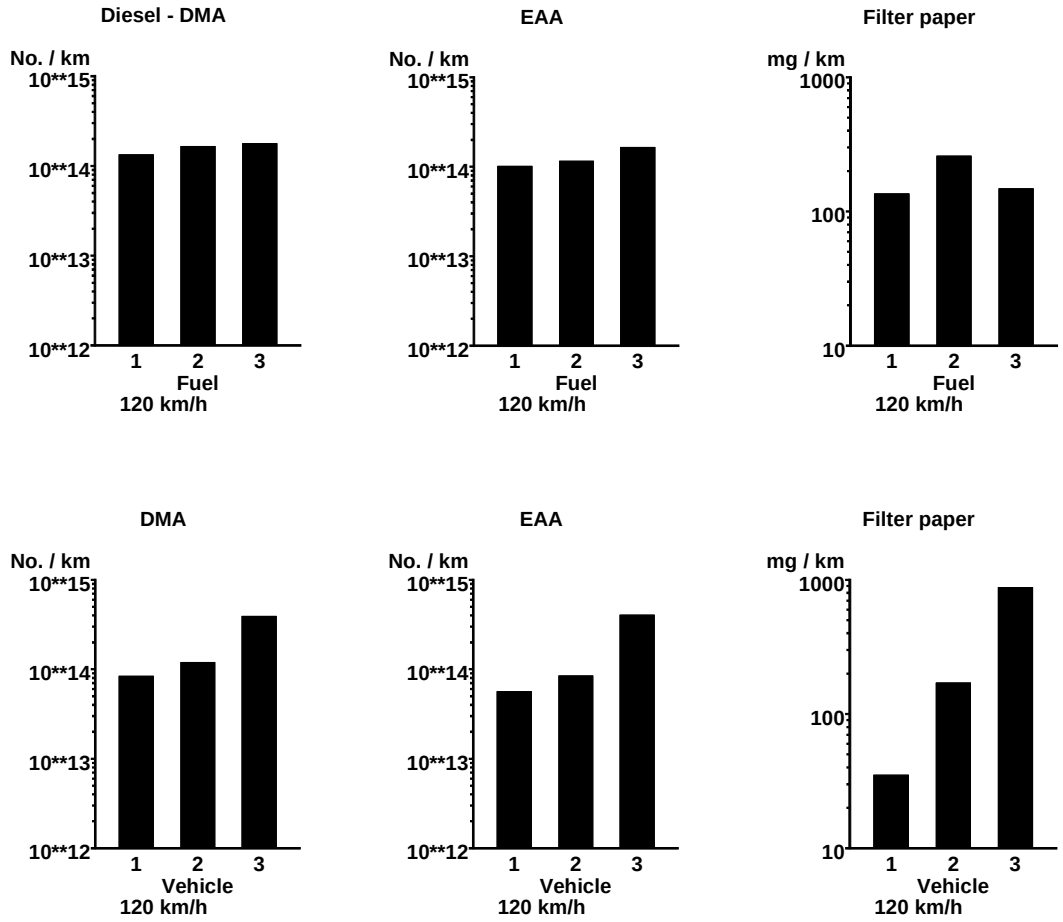


Figure C.2 **Gasoline**

(a) DMA, EAA and filter paper results obtained by contractor B
at 50 km/h
(geometric means giving each vehicle and fuel equal weight)

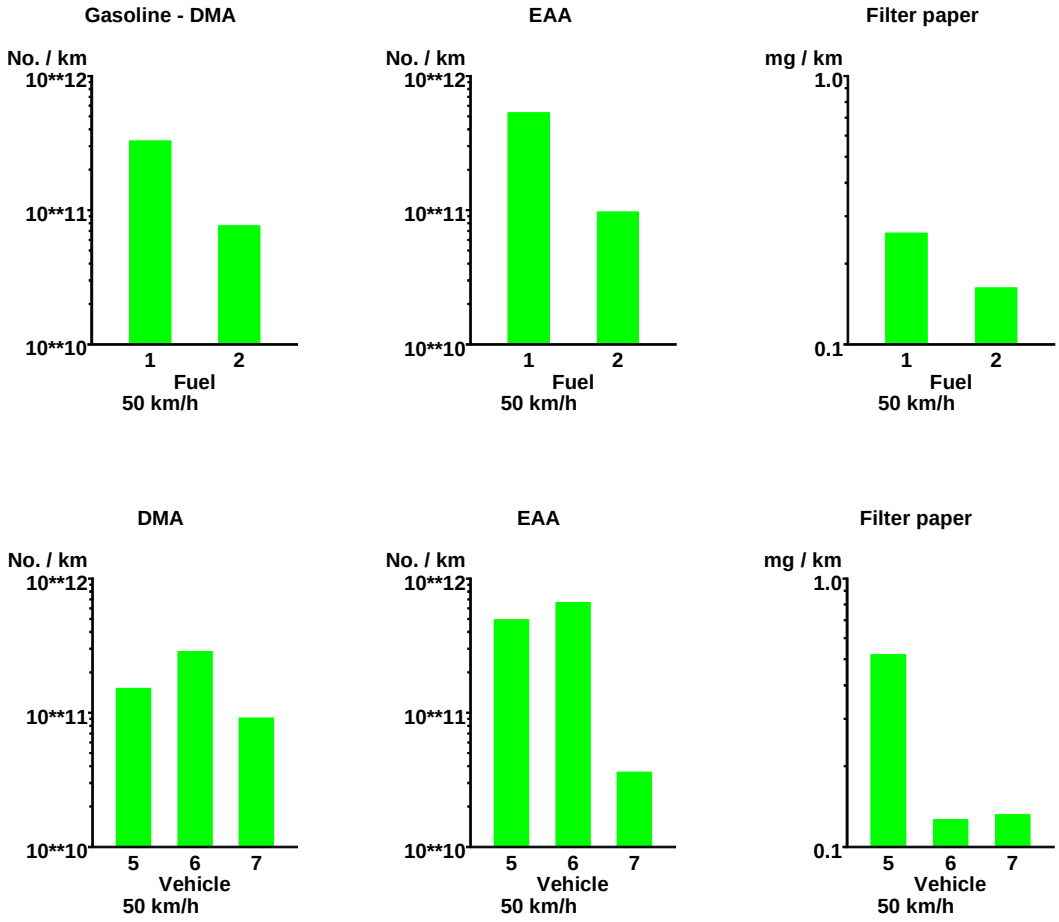


Figure C.2 **Gasoline**

(b) DMA, EAA and filter paper results obtained by contractor B
at 120 km/h
(geometric means giving each vehicle and fuel equal weight)

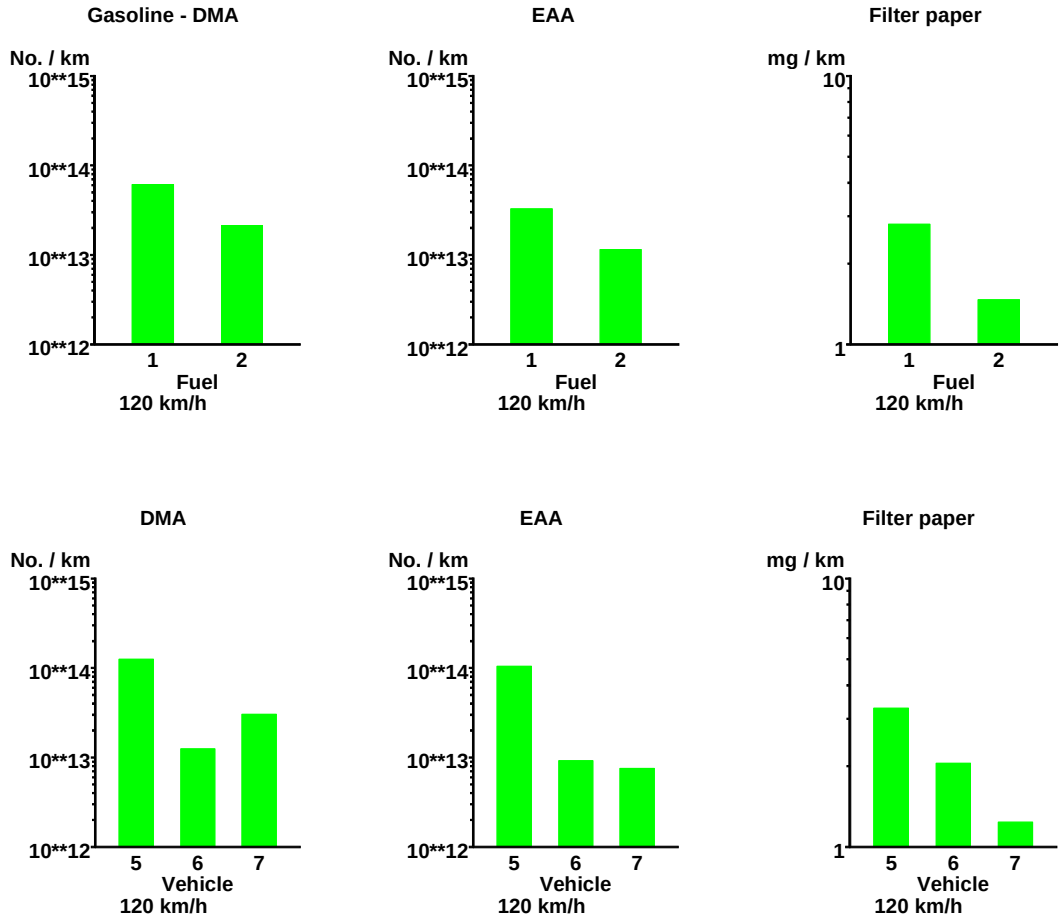


Figure C.3 Vehicle speed effects as measured by SMPS, EAA and DMA

(a) **Diesel**
(Vehicles 1 and 2, Fuel D1)
(geometric means)

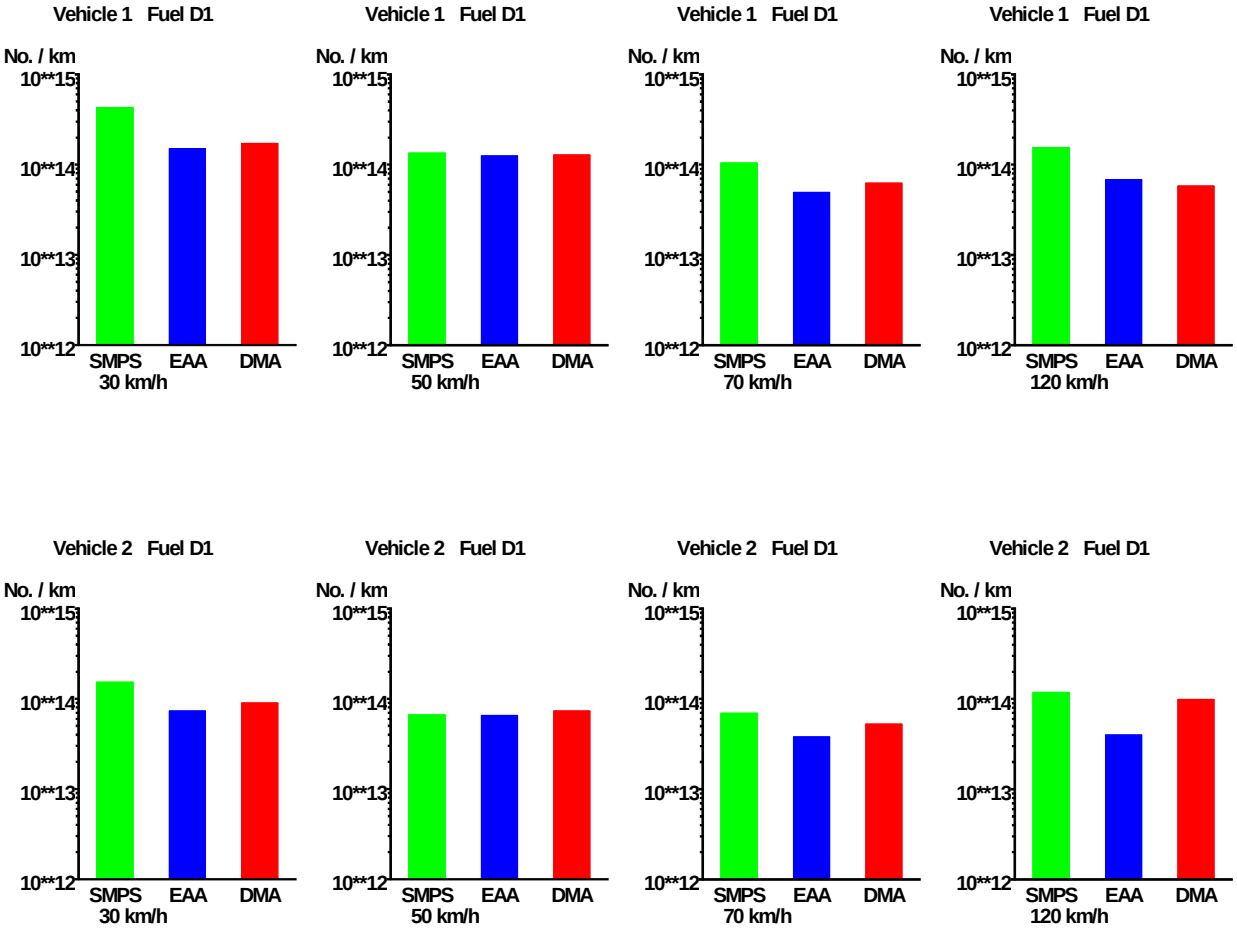


Figure C.3 Vehicle speed effects as measured by SMPS, EAA and DMA

(b) **Gasoline**
(Vehicles 5 and 7, Fuel G1)
(geometric means)

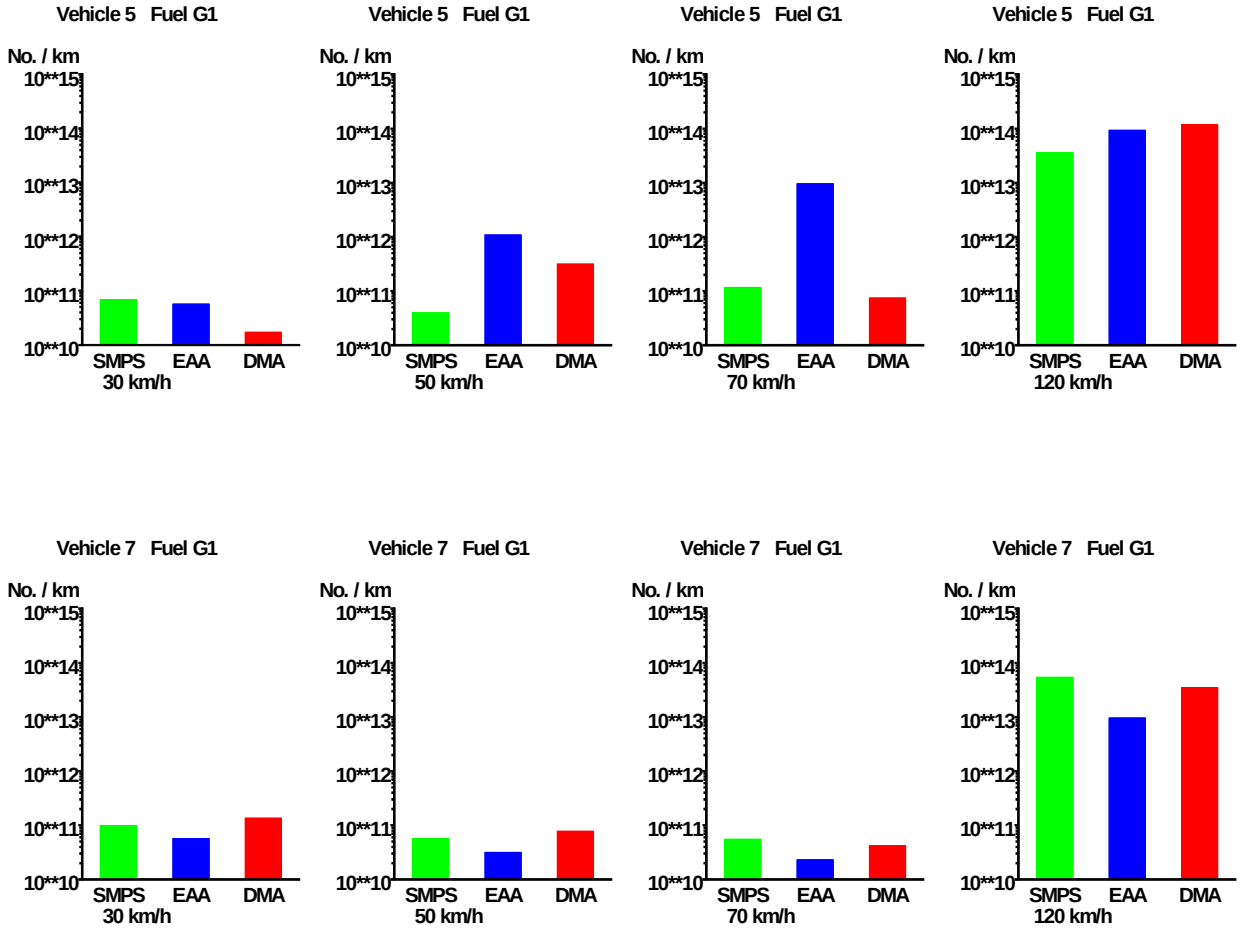
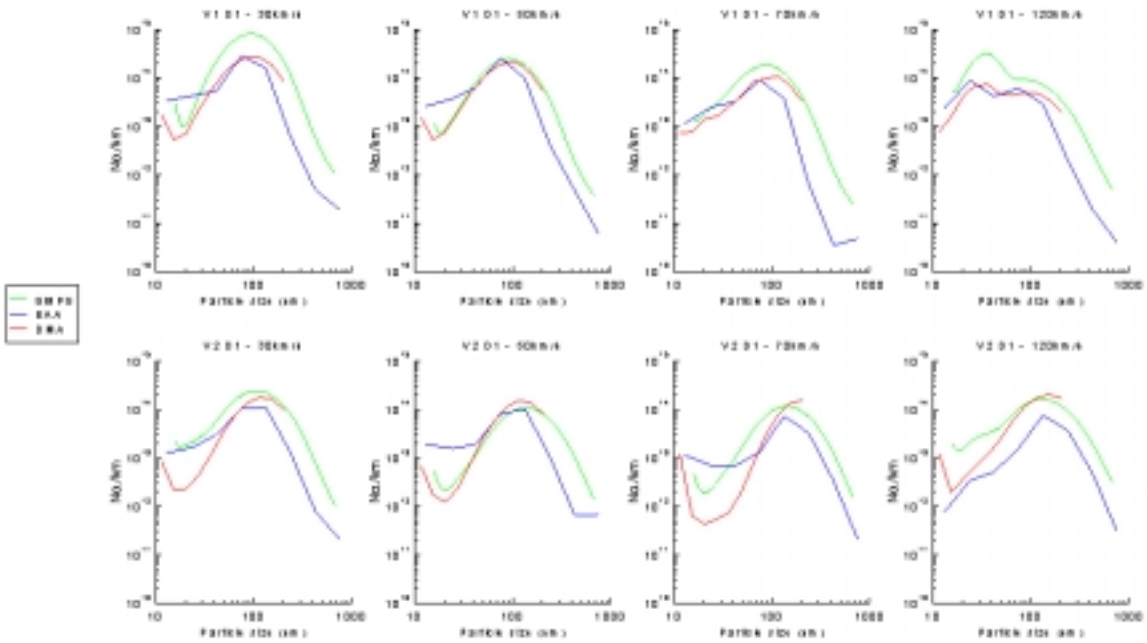


Figure C.4 Comparison of particle number distributions measured by SMPS, EAA and DMA;

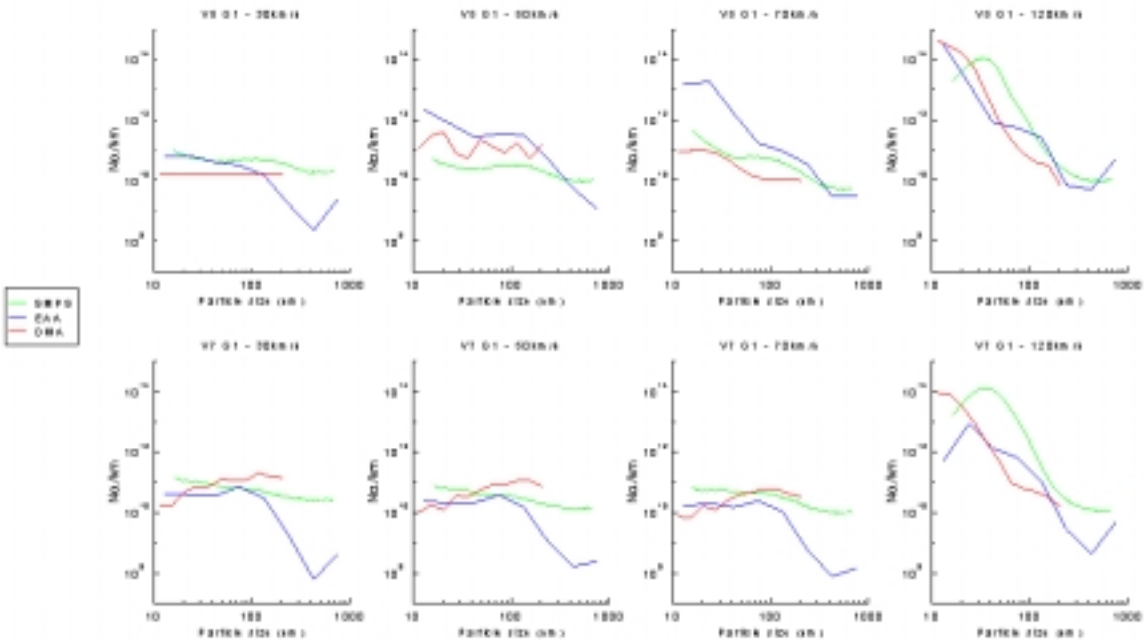
(a) **Diesel**
(Vehicles 1 and 2, Fuel D1)



(geometric means normalised to $dN / d\log_{10} d_p$)

Figure C.4 Comparison of particle number distributions measured by SMPS, EAA and DMA;

(b) **Gasoline**
(Vehicles 5 and 7, Fuel G1)



(geometric means normalised to $dN / d\log_{10} d_p$)

Figure C.5 Modal particulate emissions data for the hot ECE+EUDC cycle (SMPS); example for a gasoline vehicle – V5