fuel effects on emissions from modern gasoline vehicles part 1 - sulphur effects

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ABSTRACT

The influence of gasoline quality on exhaust emissions has been evaluated using four modern European gasoline cars with advanced technologies designed to reduce fuel consumption and CO_2 emissions, including stoichiometric direct injection, lean-burn direct injection and variable valve actuation. This report (part 1) describes the short-term sensitivity of the four cars to gasoline sulphur content. Part 2 of this report will describe the influence of other fuel effects (aromatics, olefins, volatility and FBP).

All four cars achieved very low emissions levels, with some clear differences between the vehicle technologies. Even at these low emissions levels, all four cars showed very little sensitivity to gasoline sulphur content. The results were also compared with other studies that had suggested higher sensitivity at low emissions levels. Overall it is concluded that low emissions can be achieved without significant short-term sensitivity to fuel sulphur and that sulphur sensitivity is principally influenced by catalyst system design rather than emissions level.

KEYWORDS

Exhaust emissions, gasoline, sulphur, vehicle technology, engine technology, euro-3, euro-4, direct injection

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SUMMARY

The influence of gasoline quality on exhaust emissions has been evaluated using four modern European gasoline cars with advanced technologies designed to reduce fuel consumption and CO_2 emissions, including stoichiometric direct injection, lean-burn direct injection and variable valve actuation. In this report, the short-term sensitivity of the four cars to fuel sulphur is described. Fuel sulphur effects were evaluated over a range from 4 to 150 mg/kg (the current European limit), as part of a wider programme to investigate fuel effects on advanced vehicles. The test results on fuel parameters other than sulphur will be reported separately.

Two of the test vehicles were certified to Euro-4 and two to Euro-3 standards. In all cases, measured exhaust emissions were found to be well within the respective certification limits. All four vehicles showed little or no sensitivity to fuel sulphur for all pollutants measured. Other aspects of vehicle design, such as air fuel ratio (AFR) strategy and catalyst performance, were shown to have a much greater influence on exhaust emissions.

The results were also compared with other studies that had suggested higher sensitivity at low emissions levels. Analysis of earlier California studies that had shown a stronger sensitivity to sulphur revealed that fleet average results were influenced by a number of particularly sensitive vehicles. Some vehicles in the California fleet showed low sensitivity to sulphur similar to the European vehicles tested here. Aged catalysts showed increased sensitivity to sulphur, especially for NOx emissions, but the lowest emitting vehicles were not necessarily the most sensitive to sulphur.

Additional tests on European vehicles carried out by CRC in cooperation with CONCAWE showed no evidence that sulphur sensitivity was increased after catalyst ageing and no evidence that sulphur sensitivity was greater on the US driving cycle than on the European cycle.

Overall, on the basis of these findings, it can be concluded that low emissions can be achieved without significant short-term sensitivity to fuel sulphur. Sulphur sensitivity is influenced by catalyst system design rather than emissions level. The advanced European vehicles tested showed very little short-term sensitivity to sulphur and there is no evidence of a non-linear response to sulphur at levels up to 150 mg/kg in either the European or US tests. The main driver for lower sulphur fuels remains to enable the introduction of advanced exhaust catalyst systems, including regenerative NOx storage systems, while maintaining best fuel consumption, CO_2 emissions and long-term durability. Reductions in sulphur level from 150 to 10 mg/kg seem unlikely to bring substantial emissions benefits for current Euro-3 & 4 vehicle technologies.

1. INTRODUCTION/OBJECTIVES

Over the last two decades, vehicle technologies have evolved rapidly, with substantial improvements in emissions control. Exhaust catalysts were first required on European gasoline cars with the introduction of Euro-1 emissions limits in 1993. Today's vehicles have to meet the year 2000, Euro-3 limits, with continuing evolution to Euro-4 in 2005 and Euro-5 (for heavy duty) from 2008. Vehicle manufacturers are also working towards the voluntary agreement for a European passenger car fleet average CO_2 emissions of 140 g/km by 2008.

A range of advanced gasoline and diesel engine technologies, and exhaust gas after-treatment technologies, is expected to be introduced to meet the more stringent emissions requirements together with lower CO_2. Regenerative devices such as NOx storage catalysts and diesel particulate filters are being considered. In order to enable the most advanced technologies to be employed with best fuel economy, sulphur-free fuels are being introduced. The EU Fuels Directive has recently been updated and mandates the introduction of 10 mg/kg max sulphur fuels by 2005, with 100% coverage of these fuels by 2009 [1]. Although sulphur reduction is mainly aimed at long-term durability and fuel efficiency with advanced after-treatment systems, short-term effects are also important in view of the potential impact on the existing vehicle fleet.

Much of the main European data used to establish the relationships between fuel effects, vehicle technologies and emissions is becoming rather dated, e.g. the EPEFE report [2] was based mainly on prototype Euro-2 vehicles. Given the evolution in vehicle and fuel technologies, there is a need to establish sound information on the influence of fuel qualities on emissions from more advanced engines so that future debates on fuel qualities can be taken on a firm foundation.

To update understanding, CONCAWE are continuing to test new vehicles as they enter the market. This study aimed to evaluate the impact of fuel quality on emissions from advanced gasoline vehicle technologies available in the market in 2002. Two of these were certified to Euro-3 emissions limits and two to Euro-4. The overall study has evaluated the influence of gasoline sulphur content, as well as other fuel properties (aromatics, olefins, volatility and FBP). In this, part 1 of the report on the work, only the sulphur study is covered. The results are compared with other existing data, EPEFE [2] and recent US studies [3,4,5], including a recent CRC programme [5] into which CONCAWE sponsored testing of 2 European vehicles, alongside 12 US cars.

The data obtained on the influence of aromatics, olefins, volatility and FBP will be reported later in **Part 2** of this report.

NOTE:
A glossary of terms is provided in **Section 10**.

2. TEST FUELS

The influence of fuel sulphur was evaluated by doping a low sulphur unleaded base gasoline with thiophene in order to achieve a range of sulphur levels. Four fuels (coded S1 to S4) with sulphur contents from 4 to 148 mg/kg sulphur were tested. The base gasoline (S1) used was targeted to be representative of typical 2005 gasoline composition, with sulphur as low as possible. However at this early stage, it was not feasible to achieve a typical olefins content or FBP with the available low sulphur components. It was judged that this would not affect the evaluation of the influence of sulphur, so the base fuel was accepted as suitable for the programme. Analysis of the fuels was carried out in two laboratories and the average data are shown in **Tables 1** and **2.**

Table 1 Sulphur Matrix - Base Gasoline Properties

Fuel Description			**Sulphur Matrix Base Fuel**	
Fuel Code			**S1**	
Characteristic	**Units**	**Test method**	**Target**	**Result**
RON		ISO 25164	95 - 96	**94.9**
MON		ISO 25163	85 - 86	**86.4**
Density	kg/m^3	EN ISO 3675	725 - 775	**734**
Vapour Pressure	kPa	EN 13016-1	58 ± 2	**59.5**
E70	% v/v	EN ISO 3405	30 - 40	**32.5**
E100	% v/v	EN ISO 3405	50 - 60	**58.8**
E150	% v/v	EN ISO 3405	75 min	**94.4**
FBP	°C	EN ISO 3405	195 - 205	**173**
Residue	% v/v	EN ISO 3405	2.0 max	**0.8**
Olefins	% v/v	ASTM D 1319	14 - 18	**3.5**
Aromatics	% v/v	ASTM D 1319	32 - 35	**29.7**
Benzene	% v/v	EN 12177	1 max	**0.2**
Sulphur	mg/kg	IP 373	feasible min	**4**
Induction time	minutes	ISO 7536	360 min	**>360**
Existent gum	mg/100ml	ISO 6246	5 max	**<1**
Cu Corrosion		ISO 2160	Class 1 max	**1a**
Carbon	% m/m		-	**86.9**
Hydrogen	% m/m		-	**13.1**
Oxygen	% m/m	EN 1601	-	**0**
LHV	MJ/kg		-	**43.45**

Table 2 Sulphur Matrix - Sulphur Contents

Fuel Code	**Units**	**S1**	**S2**	**S3**	**S4**
Sulphur content	mg/kg	**4**	**9**	**48**	**148**

3. TEST VEHICLES

Four vehicles were selected for evaluation in this programme. These were chosen to provide examples of those advanced gasoline vehicle technologies judged likely to become significant in the near term future car populations. Three examples of direct injection technologies (one stoichiometric and two lean-burn) and one advanced MPI system were chosen. Further information on the vehicles tested is given in **Table 3**.

Table 3 Characteristics of Test Vehicles

	Car A	**Car B**	**Car C**	**Car D**
Displacement (cm^3)	1998	1796	1997	1598
Max power (kW @ rpm)	103@5500	85@5500	107@6000	81@5800
Inertia class (kg)	1250	1360	1470	1360
No of cylinders	4	4	4	4
Valves per cylinder	4	4	4	4
Max torque (Nm @ rpm)	200@4250	175@3750	193@4100	155@4400
Compression ratio	10.0:1	10.5:1	11.4:1	12.0:1
Combustion / injection / control system	Stoichiometric DI	MPI Variable valve actuation	Lean DI	Lean DI
Catalyst system	TWC	TWC	TWC + NOx trap	TWC + NOx trap
Emissions Compliance	Euro-3	Euro-4	Euro-3	Euro-4

Initial emissions performance of the vehicles was screened on a reference fuel (fuel coded F8 from part 2 of the programme). These initial screening results are described in **Section 5**, and the properties of the reference fuel are given in **Appendix 1**. From this initial screening it was shown that all cars achieved emissions well within their respective homologation levels.

4. TEST PROTOCOL AND DESIGN

4.1. TEST DESIGN

The objective of the test protocol was to define a sound and repeatable way of measuring the short-term direct effect of fuels on regulated emissions. The test procedures and protocols were based on the well-established EPEFE methods, but modified where appropriate to the needs of this programme. These procedures assured sound test data and allowed statistically valid interpretation, so that the effects of fuel changes in the test vehicle could be accurately assessed.

The test programme was designed and analysed using rigorous statistical methods similar to those used in the recent CONCAWE diesel engine emission study [6]. Each fuel was tested over the standard NEDC emissions test on four separate occasions in each vehicle. Based on the variability levels seen in earlier programmes, it was anticipated that this degree of replication would render differences in fleet-average emissions of approximately 7% across the 4-148 mg/kg fuel sulphur range statistically significant at $P < 5\%$. Differences roughly twice this size would be needed for significance in individual vehicles. In this study the emphasis was on effects on individual vehicles in view of the different vehicle technologies tested. The variability levels and least significant effects actually achieved are tabulated in **Tables 4** and **5** in **Appendix 2**.

The 16 tests on each car were conducted in four blocks with one block consisting of one single test on each fuel. This minimised the risk of fuel effect estimates becoming contaminated by any drift in vehicle performance or other time-related effects. Repeat tests on a fuel were not conducted back-to-back to ensure that the results were truly independent.

The four fuels were tested in a different randomised order in each block and different randomisations were used for each vehicle. A typical test order was thus as follows:

	Fuel Order
Block 1	S1 S3 S2 S4
Block 2	S2 S4 S3 S1
Block 3	S2 S1 S3 S4
Block 4	S1 S4 S2 S3

A fifth test was conducted whenever large variations were seen between the four tests on a particular fuel in a particular vehicle. The following thresholds were used (based on the variability levels seen in the EPEFE programme [2]):

Emission	**CO**	**HC**	**NOx**
Ratio of highest to lowest emission on the same fuel	1.44	1.50	1.55

When the differences exceeded these limits, additional tests were carried out at the completion of the test block. The complete data set was then examined for outliers and trends (**see Section 7**).

For some vehicles, minor changes had to be made to the predetermined test order owing to operational problems. This had little effect on the analysis.

4.2. VEHICLE PREPARATION AND MONITORING

The test vehicles were in good mechanical condition and had completed a minimum of 8000 km to ensure that the exhaust after-treatment systems were adequately aged and the engine combustion chamber deposits had stabilised. Each vehicle completed its mileage accumulation with 500 km on a reference fuel and reference lubricant prior to the start of the main programme to ensure consistency between vehicles. The properties of the reference fuel are given in **Appendix 1**.

In order to limit the effect of any sulphur carry-over between tests, a sulphur purging procedure was performed on all vehicles immediately prior to each test. This procedure varied depending on whether the vehicle possessed a 3-way or a NOx storage catalyst. The principle was the same in both cases, i.e. to cause the vehicle to transiently run rich at a high catalyst temperature in order to remove accumulated sulphur via H_2S formation.

The sulphur purging procedure for vehicles with 3-way catalysts was as used in previous work [2] and consisted of the following steps:

1. Drive vehicle at 90 km/h for 5 minutes to bring the catalyst to full working temperature.
2. Reduce speed to 50 km/h for 1 minute.
3. Accelerate at wide open throttle (WOT) for a minimum of 5 seconds to achieve a minimum speed of 115 km/h. Hold at this speed for 15 seconds and then decelerate to 50 km/h.
4. Maintain 50 km/h for 1 minute.
5. Repeat steps 3 and 4 a further 4 times i.e. 5 cycles in all.

The sulphur purging procedure for vehicles fitted with NOx storage catalysts was tailored to each vehicle and followed manufacturers' guidelines where possible. In addition, a check was made for deterioration in NOx conversion efficiency during the programme. At the end of the NEDC cycle, NOx emissions were monitored, before and after the catalyst, at idle, 50, 90 and 120 km/h.

4.3. VEHICLE TESTING

A specific fuel change protocol was followed to ensure consistency between tests and to ensure minimal cross-over between test fuels. At fuel change, the fuel tank was drained, 10 litres of the new fuel were added, and the vehicle was idled for 5 minutes to allow the new test fuel to flush the fuel injection system thoroughly before the tank was drained again. A further 25 litres of the new test fuel was then added for the main emissions test.

Prior to each NEDC emissions test, a sulphur purge as described above was performed, followed by one ECE plus two consecutive EUDC cycles, but without emissions being measured. These test cycles were to ensure the vehicle was fully conditioned on the test fuel prior to starting the emissions test. The vehicle was then soaked according to the NEDC test procedure ensuring that the soak period was restricted to 12 - 18 hours.

Vehicles were then tested according to the current legislated NEDC test procedure. Exhaust gas was collected in one bag for the ECE part and one bag for the EUDC part of the NEDC test. The legislated emissions - CO, HC and NOx - plus CO_2 and PM were measured. In addition, continuous raw exhaust emissions were measured at engine-out and tailpipe to allow the interpretation of both engine and catalyst performance.

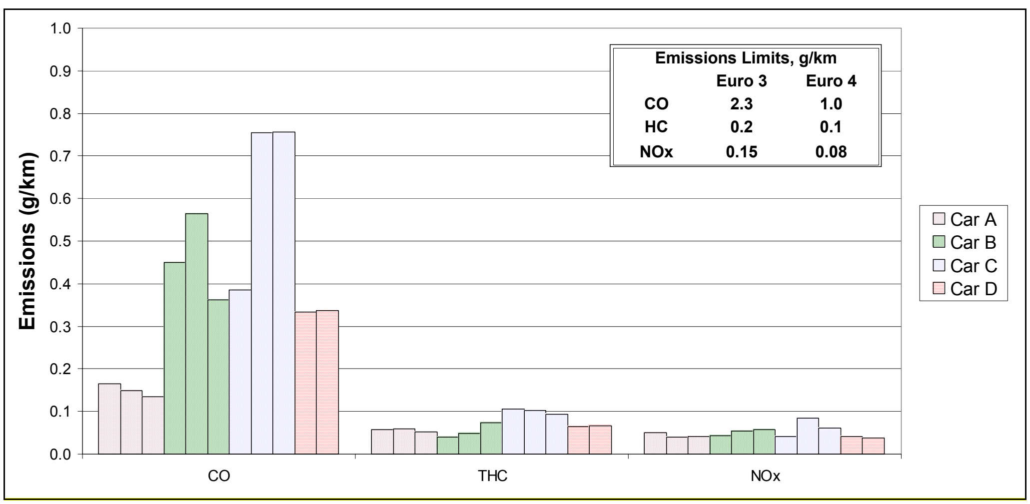
5. INITIAL SCREENING AND VEHICLE ASPECTS

In order to ensure that each test vehicle was operating in accordance with the manufacturers' requirements, a series of exhaust emissions tests was conducted to check compliance of each vehicle with the legislative requirements for carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NOx). Capture of modal (second-by-second) raw exhaust emissions both before and after the main exhaust catalyst also allowed both engine-out emissions and catalyst efficiency to be quantified. Carbon dioxide (CO_2) emissions were also measured and compared against official manufacturer's figures. Initial dynamometer road load settings were established based on coast-down data.

All initial emissions testing were carried out using test fuel F8 which was representative of EN228:2000 gasoline quality, except for the sulphur content which was blended to 50 mg/kg. For full analysis of F8, see **Appendix 1**.

The emissions results are presented in **Figure 1** together with the Euro-3 and Euro-4 emissions limits.

Figure 1 Initial Emissions Screening



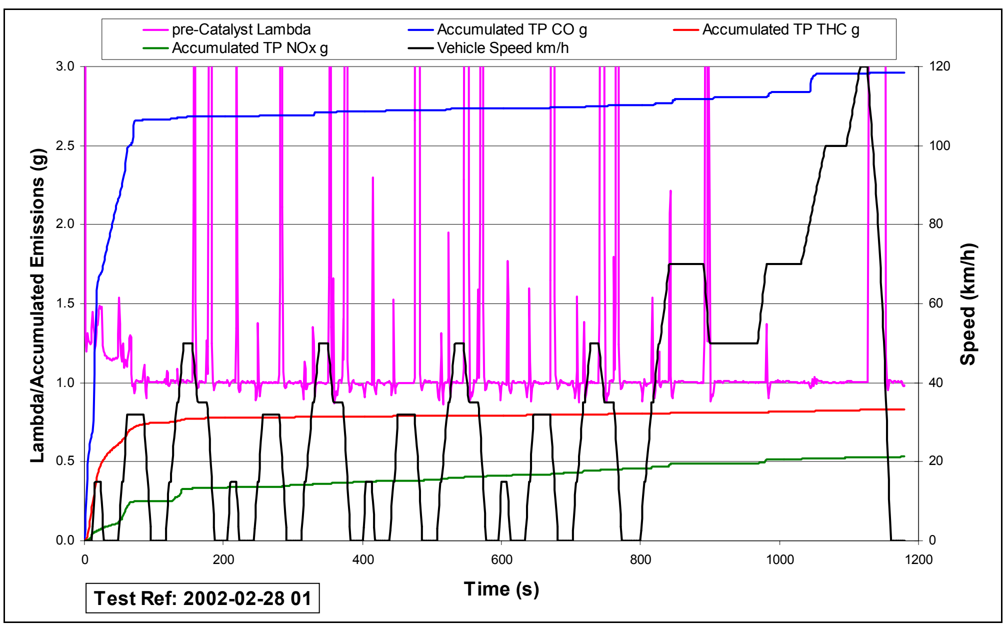
This initial testing produced useful information on the new technologies and how they operated over the NEDC cycle. This is described below for each car.

5.2. CAR B - MPI + 3-WAY CATALYST

In a similar fashion to car A, exhaust emissions on car B were measured and found to be within its emissions compliance for the Euro-4 emissions level, for all regulated pollutants. This car operated with good AFR control with lean operation during the first 100 seconds following cold start. For CO_2 emissions, a 3-run average of 194 g/km was measured which was ~16% higher than the official manufacturer's figures. This was considered to be outside of an acceptable tolerance band - continued testing at a higher CO_2 level (and corresponding higher fuel consumption) may have impacted on the results of the main test programme. It was felt that the CO_2 levels should be brought more in line with the manufacturer's figures prior to continuing to test this vehicle.

Subsequent emissions tests using the manufacturer's road load model brought the CO_2 emissions to an acceptable level and to within 7% of quoted figures. This dynamometer set-up was subsequently used for the duration of the testing programme.

Figure 3 Modal Lambda and accumulated regulated emissions for Car B

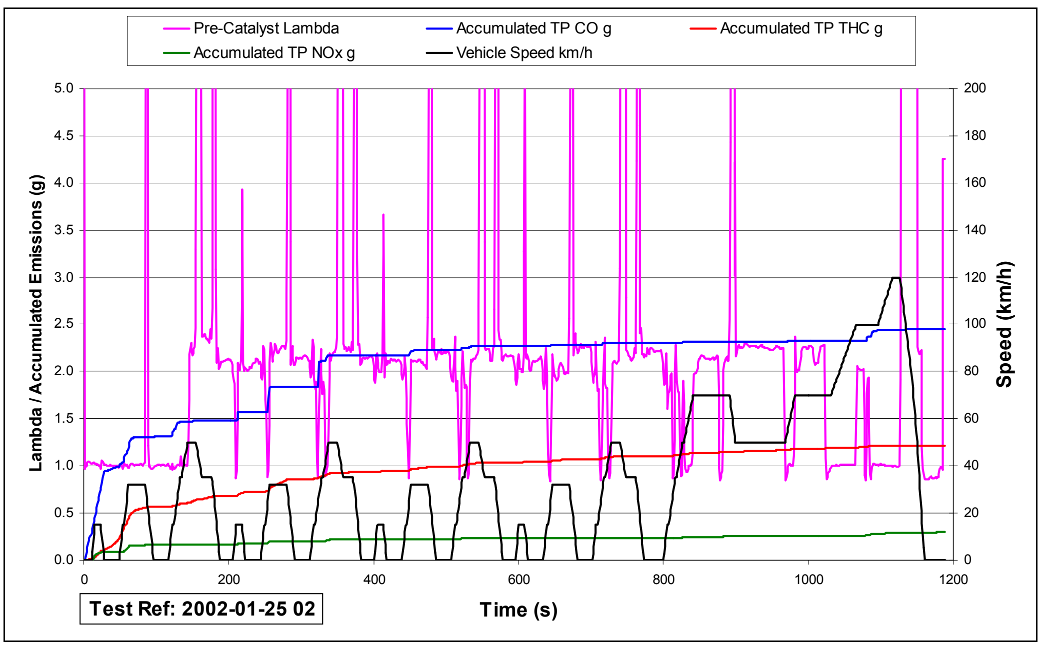


5.3. CAR C - LEAN DI + NOx STORAGE/REDUCTION CATALYST

This car comfortably met the Euro-3 emissions limits although some variations in CO and NOx emissions were encountered between the repeat tests. Analysis of the modal AFR data in **Figure 4** clearly demonstrates the various modes of operation that this lean-burn engine uses over the NEDC cycle. It can be seen that in the first 150 seconds, the engine operates at lambda = 1, suggesting no enrichment during initial cold start and subsequent operation. Thereafter, a switch to lean mode operation at approximately lambda = 2 to 2.3 is evident which is maintained (ignoring the rich AFR spikes due to transients) throughout the remainder of the ECE part of the cycle. During the first steady-state cruise of the EUDC, rich operation occurs for a few seconds, indicating the use of a HC spike in the release of NOx previously stored on the catalyst.

As previously mentioned, it was noted that there were many differences in AFR operation between the 3 repeat emissions tests and most significantly in the EUDC part of the cycle during higher speed operation. There appeared to be frequent rich AFR excursions, but these occurred sporadically and not on every test. This trend was consistent with the variability in CO emissions and also in the CO_2 emissions, which also varied by an unusually high 10% within the 3 tests.

Figure 4 Modal Lambda and accumulated regulated emissions for Car C



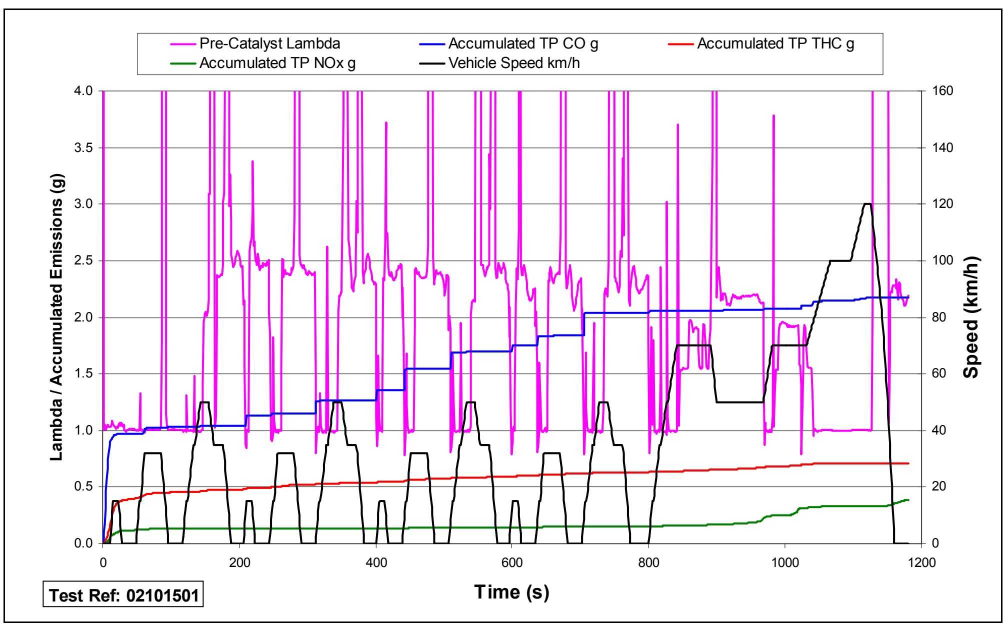
Average CO_2 emissions were measured as 217 g/km, approximately 23% higher than the official manufacturer's published figures. These were considered to be too far from the official figures to proceed with the test programme. Subsequent emissions tests using the manufacturer's road load model reduced the CO_2 emissions to an acceptable level and to within 7% of quoted figures but, in spite of this, the AFR strategy did not appear to be consistent between back-to-back tests, with periods of uncharacteristic rich operation. In case this was due to the regeneration procedure, one further sulphur purge was carried out to purge the NOx storage catalyst of any accumulated sulphur. This step appeared to solve the inconsistent fuelling strategy, and also resulted in a further drop in CO_2, matching the published figures.

5.4. CAR D - LEAN DI + NOx STORAGE/REDUCTION CATALYST

Regulated exhaust emissions were found to be well within its emissions compliance for the Euro-4 emissions level, with excellent back-to-back test repeatability for all regulated pollutants.

Analysis of the modal AFR data, as depicted in **Figure 5**, again demonstrates lambda = 1 operation on initial cold start and up to ~150 seconds - an almost identical pattern to vehicle C. Thereafter, a switch to lean mode operation of lambda = 2.3 to 2.5 is evident in the early part of the ECE cycle, reducing slightly to between 2.1 and 2.3 towards the end of the cycle, notably during periods of idle. Increasingly richer operation is evident during the first EUDC steady-state cruise although this is accompanied by an unusual lambda fluctuation between 1.5 and 2.0. At the end of the second 70 km/h cruise, a rich AFR excursion is evident, illustrating the well known HC spike used in the release of NOx in the storage part of the catalyst - an accompanying increase in the respective tailpipe NOx emissions at the same point in the cycle was also noted.

Figure 5 Modal Lambda and accumulated regulated emissions for Car D

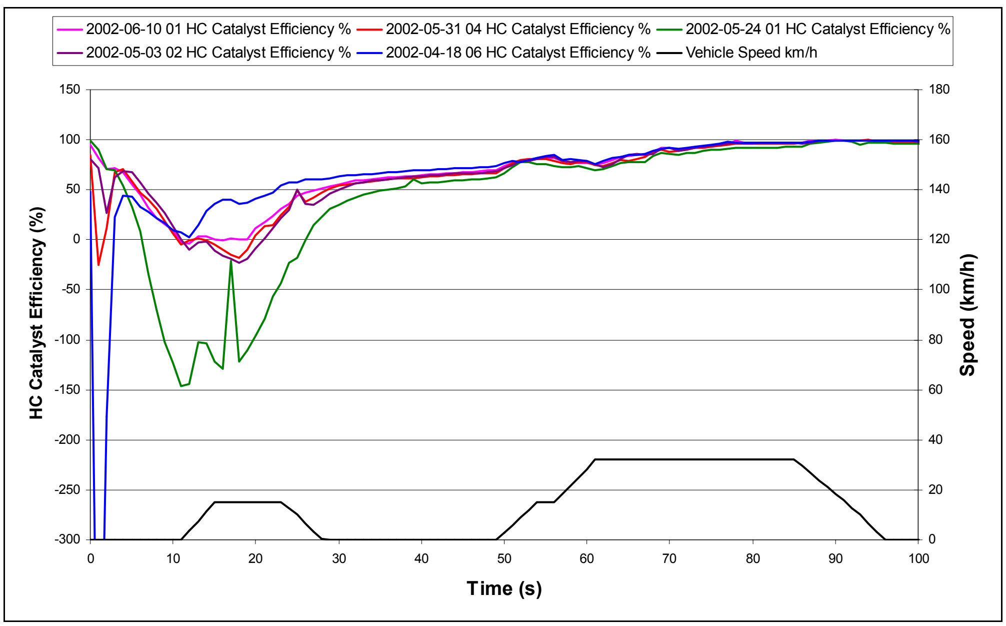


Average CO_2 emissions for this car were measured at 174 g/km, which were approximately 16% higher than official manufacturer's figures. In a similar fashion to car C, subsequent emissions tests using the manufacturer's road load model did reduce the CO_2 emissions, but only by 6%. It was difficult to see what other measures could be taken to reduce CO_2 further without compromising the set-up and hence possible calibration of the vehicle. It was therefore decided that this 10% discrepancy would be acceptable to continue with the main test programme.

Car B

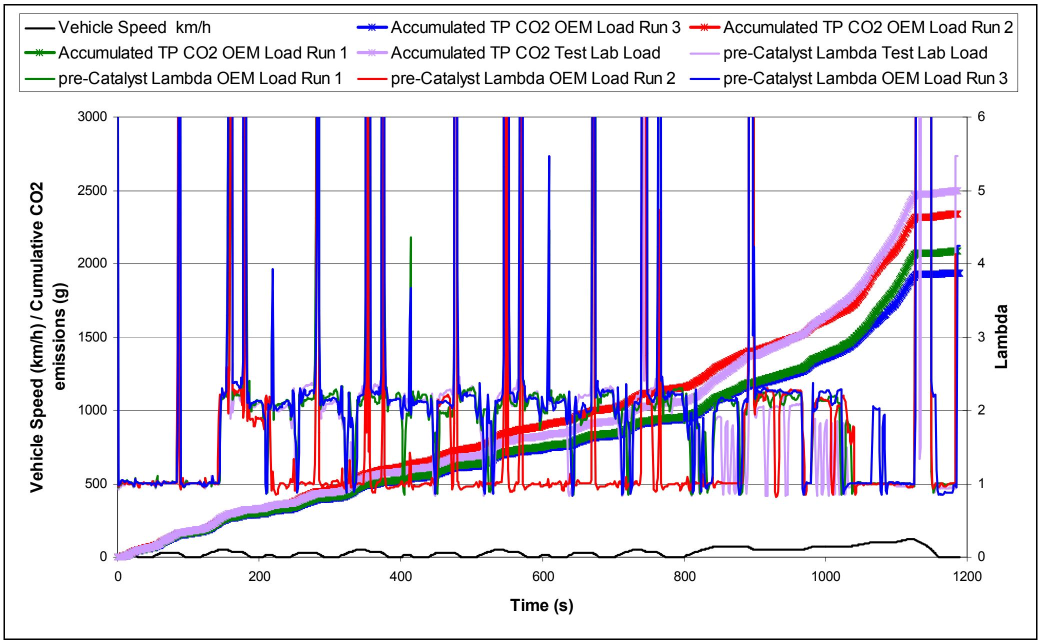
In general, this car produced a very consistent data set for the main sulphur programme although on one occasion an event occurred resulting in these tests being identified as outliers. The phenomenon was noted during the ECE part of the cycle by an unusually high level of HC emissions. Upon further investigation, this emissions increase was found to be occurring in the first 30 seconds after cold start and was attributed to a significant amount of HC storage / release from the catalyst. This resulted in almost double the overall HC test result compared to other repeat tests on the same fuel. A modal plot of tailpipe HC catalyst efficiency showing this effect is shown below in **Figure 7**. This compares a series of repeat tests on test fuel S4 and clearly shows the single test where the HC is released from the catalyst (indicated by the negative catalyst efficiency) for a period of approximately 20 seconds. After this time, the catalyst appears to perform in line with other tests on the same fuel.

Figure 7 Example of HC Storage / Release from Catalyst for Car B



No obvious explanation for this effect could be found, other than that the 3-way catalyst may have adsorbed unburned HC's during the test preconditioning. However, this also seems unlikely given the amount of transient operation and high speed cruising carried out during the preconditioning cycle.

Figure 11 Effect of engine loading on AFR control



In **Figure 11**, AFR and CO_2 emissions data were generated using a road load model developed by the test laboratory based on coast-down data, and compared with three further sets of data generated using manufacturer's load figures. All tests were carried out using the same test fuel. The differences in cumulative CO_2 emissions can be clearly seen and can be attributed to the richer lambda operation more notably in the EUDC part of the NEDC cycle.

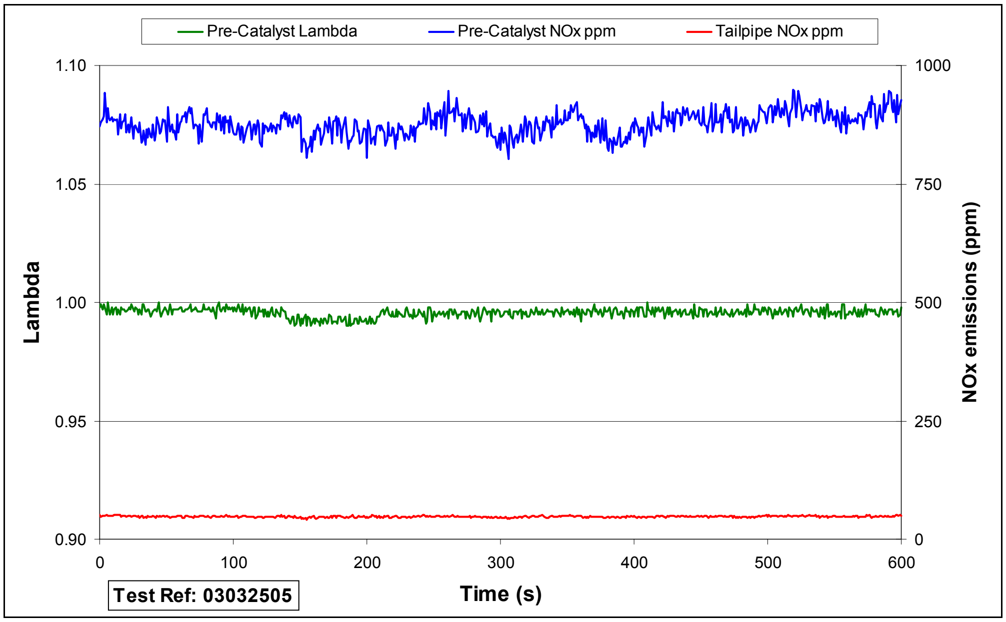
There were significant variations in AFR response within the 3 tests using manufacturer's road load. These were interpreted as an engine management strategy for the additional control of NOx emissions. This was attributed to the need for a catalyst de-sulphation due to the saturation of the NOx storage part of the catalyst - this is clearly indicated by long periods of $\lambda=1$ operation over parts of the NEDC cycle (OEM load, run 2) where the vehicle should otherwise be operating lean. A subsequent testing regime of high speed cruising (ensuring rich lambda and high catalyst temperatures) was carried out to fully purge the catalyst of accumulated sulphur - this resulted in the subsequent emissions test (OEM load, run 3) giving significantly lower CO_2 emissions and an AFR strategy consistent with previous levels.

In order to minimise the potential influence of varying AFR, a de-sulphation protocol was introduced prior to each emissions test, as a means of purging the NOx storage catalyst of any accumulated sulphur.

Car D

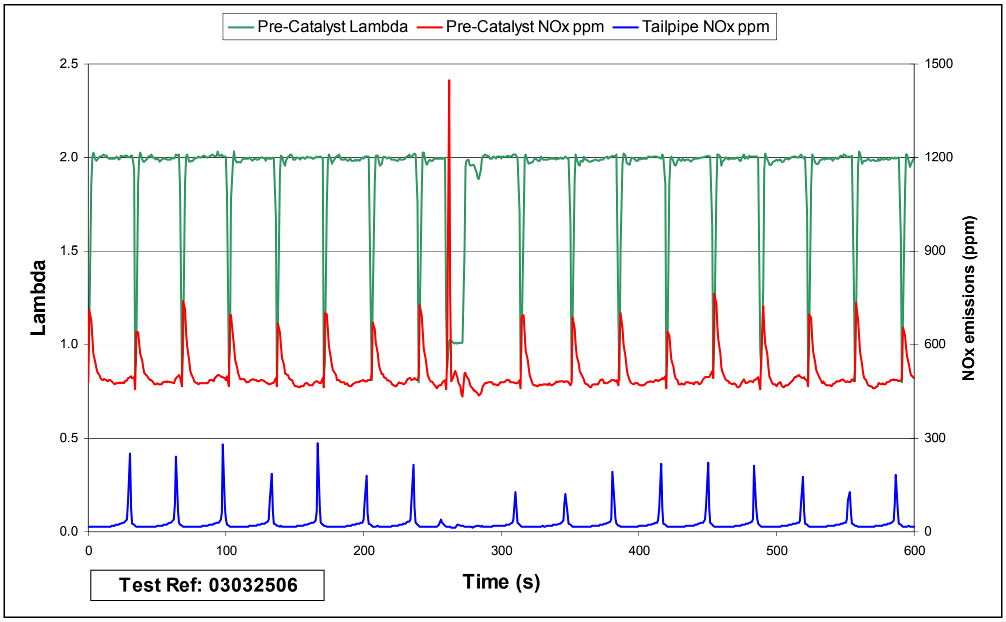
In a similar fashion to Car C, steady speed testing was conducted on Car D at 50, 70 and 90 km/h to obtain a measure of the AFR strategy and control as applied to this vehicle for NOx regeneration. Tests were conducted in both 4^{th} and 5^{th} gear as preliminary tests in 4^{th} gear showed unexpected stoichiometric, as opposed to lean, operation during the 50 km/h cruise. This was unusual given the visible lean operation at the same speed during the EUDC part of the NEDC.

Figure 12 AFR Strategy of Car D at 50 km/h



Despite undertaking steady speed tests in 5th gear, stoichiometric operation was still evident at 50 km/h as shown in **Figure 12.** It remained unclear as to why such operation was sustained at this condition given the lean AFR operation at 70 km/h, under a higher load condition, as shown in **Figure 13**. One possible explanation could be that specific engine parameters (e.g. oil / coolant) were lower on the EUDC than generated during the above steady state testing, which were conducted when the engine was fully warm. These minor differences may well be sufficient to generate different signals into the engine control unit and hence impact on AFR strategy.

Figure 13 AFR Strategy of Car D at 70 km/h



At 70 km/h, as shown in **Figure 13**, the vehicle is seen to operate at a fairly constant λ=2.0 with rich AFR spikes occurring approximately once every 30 seconds. Lean operation results in the majority of the engine-out NOx being trapped on the storage medium of the catalyst until they are subsequently released and reduced in the 3-way part of the catalyst, following the rich AFR operation. It is clear therefore that this lean / rich sequence of events is very much dependent on vehicle speed / engine load, as expected.

Figure 14 AFR Strategy of Car D at 90 km/h

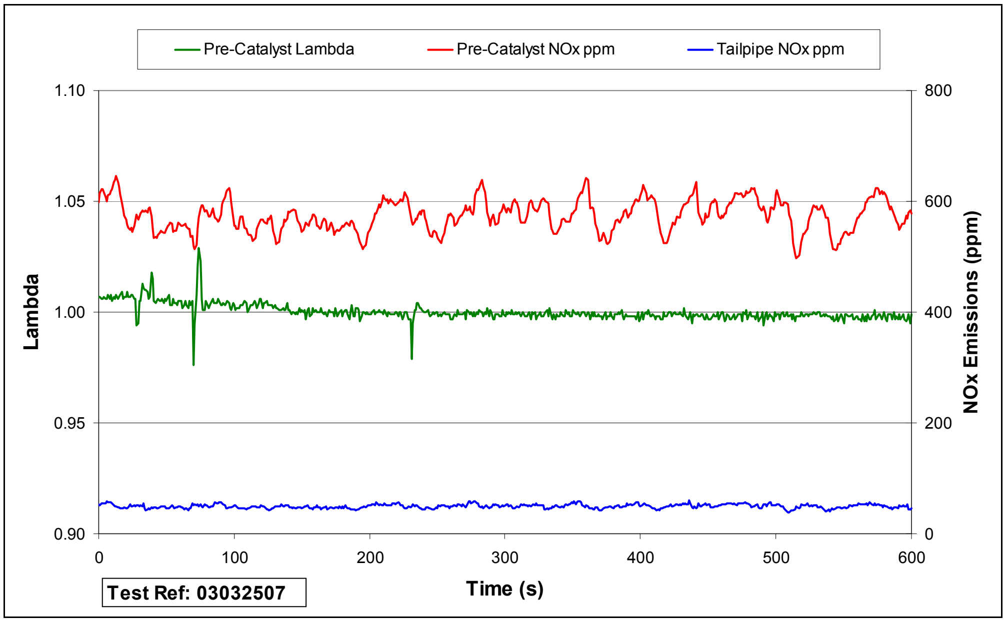


Figure 14 illustrates the constant speed operation of the vehicle at 90 km/h where consistent λ=1 operation is observed with no lean-burn strategy - this was assumed to be due only to the increase in engine load and is different to the reasons for stoichiometric operation observed at 50 km/h.

7. STATISTICAL ANALYSIS METHODOLOGY

The test programme was constructed using the principles of statistical experimental design as described in **Section 4.1.1**.

Each emission (CO, HC, NOx, PM) was examined on a vehicle-by-vehicle basis.

In the EPEFE gasoline project [2] and other previous emission studies, e.g. [6,7,8,9], the variability in emissions measurements has typically been found to follow the lognormal distribution with the degree of scatter increasing as the emission level increases. Standard deviation (S.D.) vs. mean plots suggested that the present emissions data behaved similarly although this assumption was difficult to verify rigorously as the levels of emissions differed little from fuel to fuel in any particular vehicle (see **Appendix 2**).

The data were examined for outliers by inspecting studentized residuals (residuals divided by their standard errors).

For car A, two tests were excluded from the analysis because of high outlier results. No explanation for these high results was identified. Because of test variability, a fifth block of tests was run on car A. One of these tests was rejected due to high ambient background, but was immediately repeated. For car B, one test was rejected because of abnormally high HC emissions due to a release of HC from the catalyst in the ECE as described in **Section 6**. In one test on car C, abnormally low CO_2 emissions were recorded in the EUDC and, in one test on car D, the modal exhaust sample pipe fell off. The complete test was rejected in each case.

There were some strong trends in the data with CO emissions from car C in the EUDC showing a consistent decrease as time progressed (significant at $P < 0.1\%$) and NOx emissions from car D in the EUDC and combined NEDC cycle showing a consistent increase (significant at $P < 1\%$[1]). The mean emissions from each fuel in each of these data sets were adjusted using analysis of covariance techniques to eliminate any bias which might be caused by such trends. The adjustments had relatively little effect on mean emissions owing to the robustness of the experimental design (see **Appendix 3**).

Adjustments were only made for data sets where there was an unambiguous linear trend over the full range of tests which was significant at $P < 1\%$.

In the tables and graphs in this report, simple arithmetic means are used to summarise the emissions for each vehicle × fuel combination. Linear regression analysis is used to relate emissions to fuel sulphur content on a vehicle-by-vehicle basis. Adjustments were made to the analysis to take into account the lognormality in the data using a similar methodology to that employed in the EPEFE programme [2] (see **Appendix 2**).

The error bars in **Figures 15-21** in **Section 8** show the:

$$\text{mean value} \pm 1.4 \times \text{standard error of mean}$$

[1] $P < 1\%$ = the probability that such an event could be observed by chance when no real effect exists is less than 1%. In other words, we are 99% confident that the effect is real. Likewise $P < 5\%$ = 95% confidence and $P < 0.1\%$ = 99.9% confidence.

These are constructed so that when two fuels are significantly different from one another at $P < 5\%$, their error bars will not overlap. We can be 84% confident that the true mean for each fuel lies within the limits shown.

8. SULPHUR EFFECTS ON EMISSIONS

8.1. RESULTS FROM CURRENT TEST VEHICLES

The mean emissions results for all cars over the ECE, EUDC and combined NEDC cycles are given in **Appendix 3**.

The first point of interest in the data analysis is the effect of sulphur content on the regulated emissions, NOx, HC and CO over the NEDC cycle. Plots of these emissions for all 4 cars tested are given in **Figures 15-17.** Trend lines and linear regression equations are included on the charts wherever the trends are statistically significant.

Figure 15 NEDC emissions data - NOx

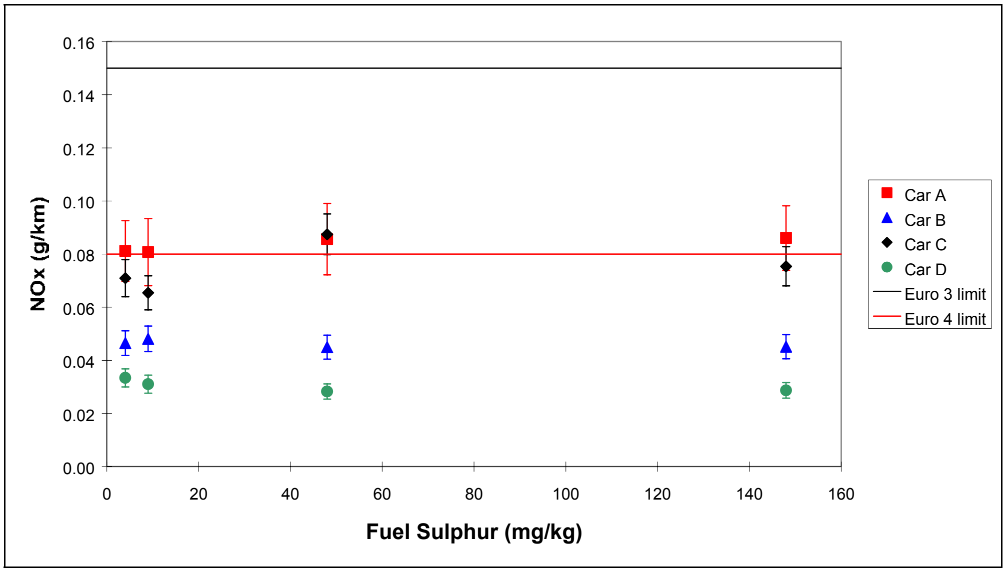


Figure 16 NEDC emissions data - HC

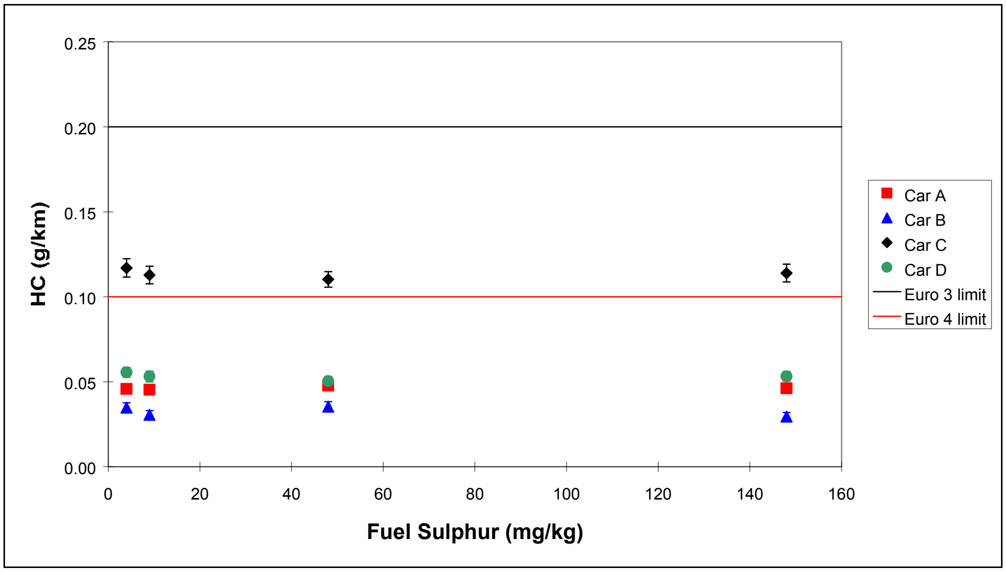
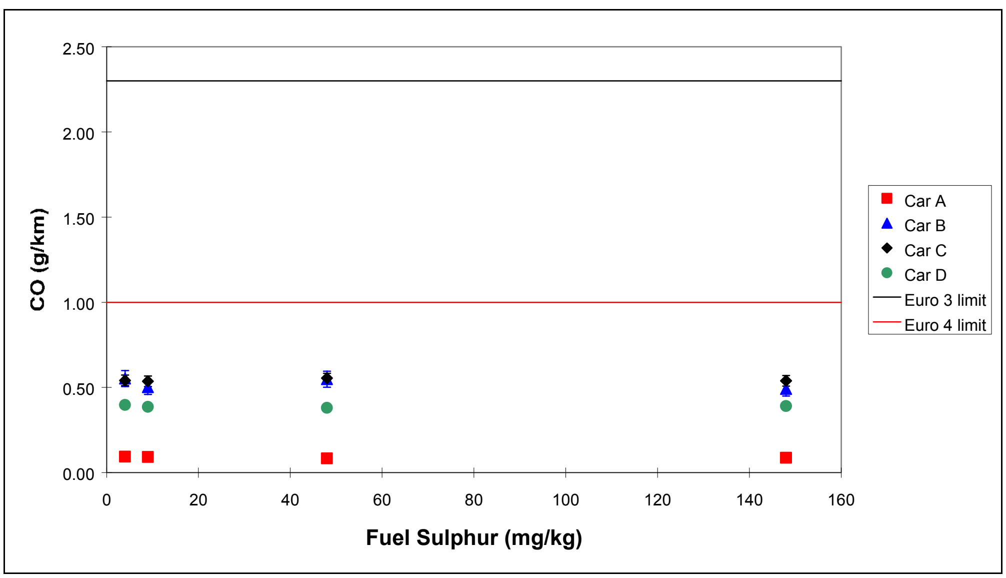


Figure 17 NEDC emissions data - CO



In all four vehicles, there was little short-term response of emissions to fuel sulphur content. There were no statistically significant sulphur effects (P < 5%) over the NEDC cycle for any pollutant in any vehicle, or indeed across the fleet. Furthermore, there is no evidence of higher sensitivity at low sulphur levels.

In all cases, the vehicles achieved very low levels of emissions, well beyond their certification levels. Car A, the Euro-3 stoichiometric DI, was just above the Euro-4 limit for NOx, but well below the Euro-4 limits for HC and CO. Car B, the advanced MPI technology vehicle, was well within the Euro-4 limits, achieving around half of the Euro-4 limit values on all 3 emissions. Car C, the Euro-3 lean burn DI, was close to the Euro-4 limits for HC and NOx, and well within the Euro-4 limit for CO. Car D, the Euro-4 lean burn DI, was well within the Euro-4 limits for all emissions.

In order to check whether larger sulphur effects on the catalysts could be observed during the hot part of the emissions cycle, when the catalyst is fully operational, the EUDC data were examined and are illustrated in **Figures 18-20** below:

Figure 18 EUDC emissions data - NOx

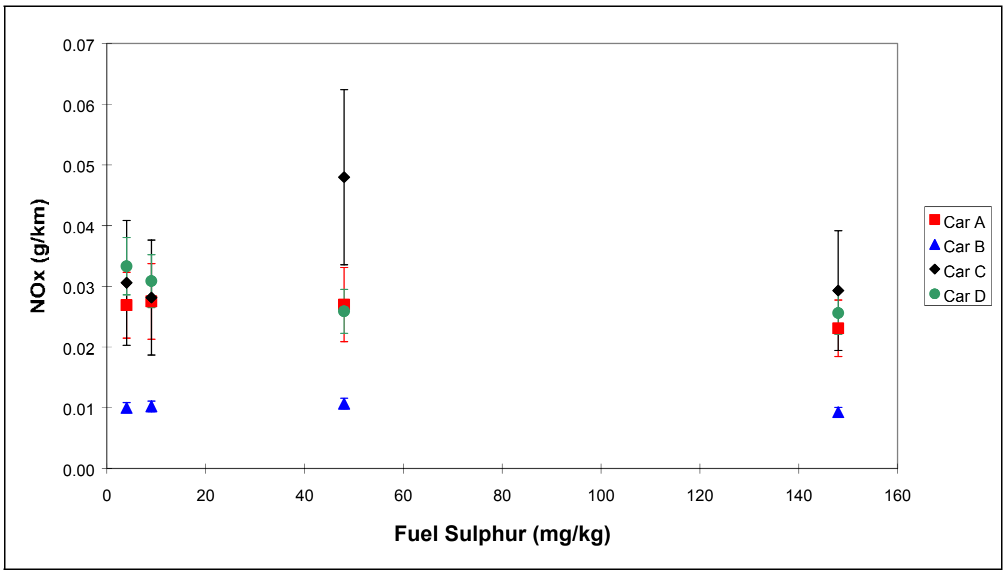


Figure 19 EUDC emissions data - HC

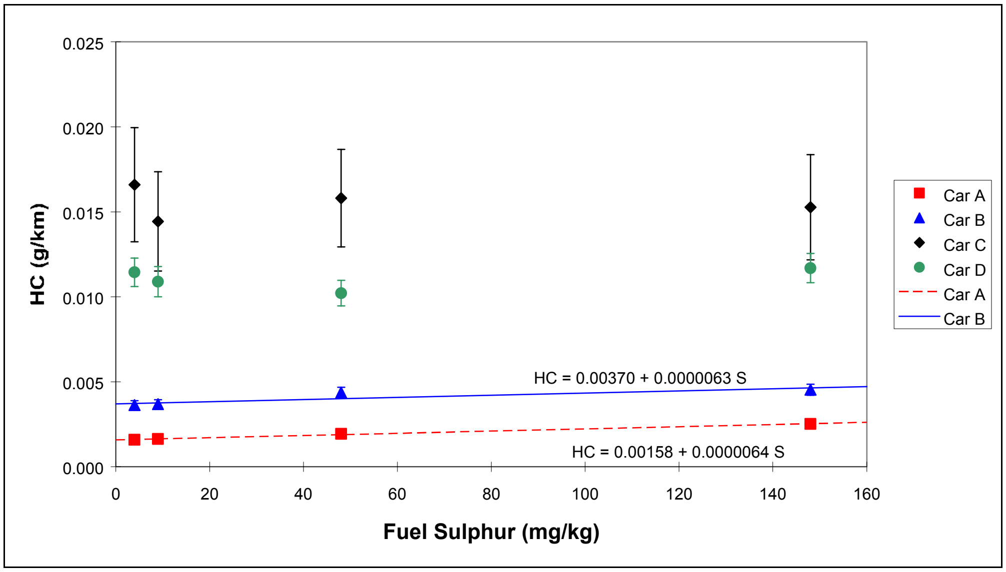
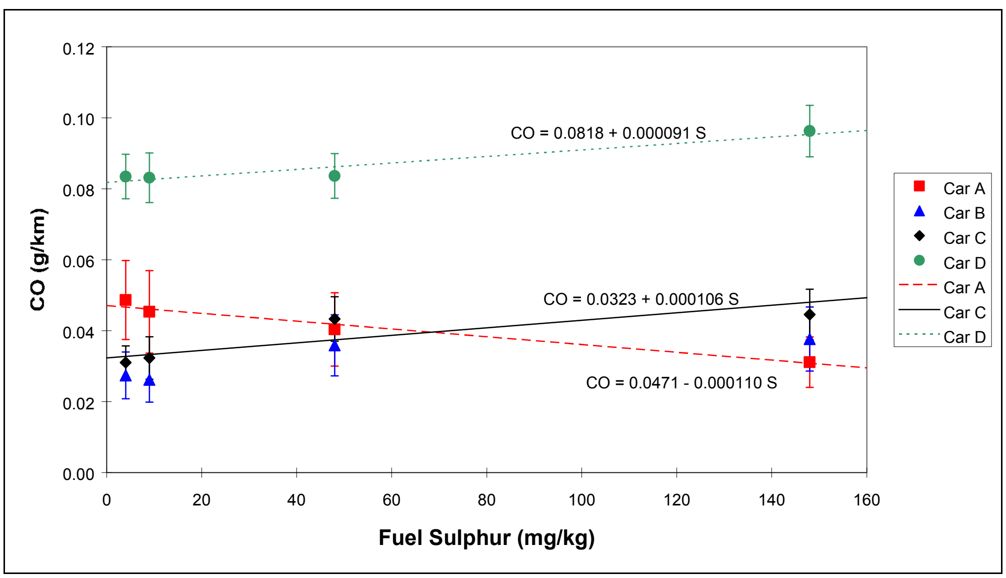


Figure 20 EUDC emissions data - CO



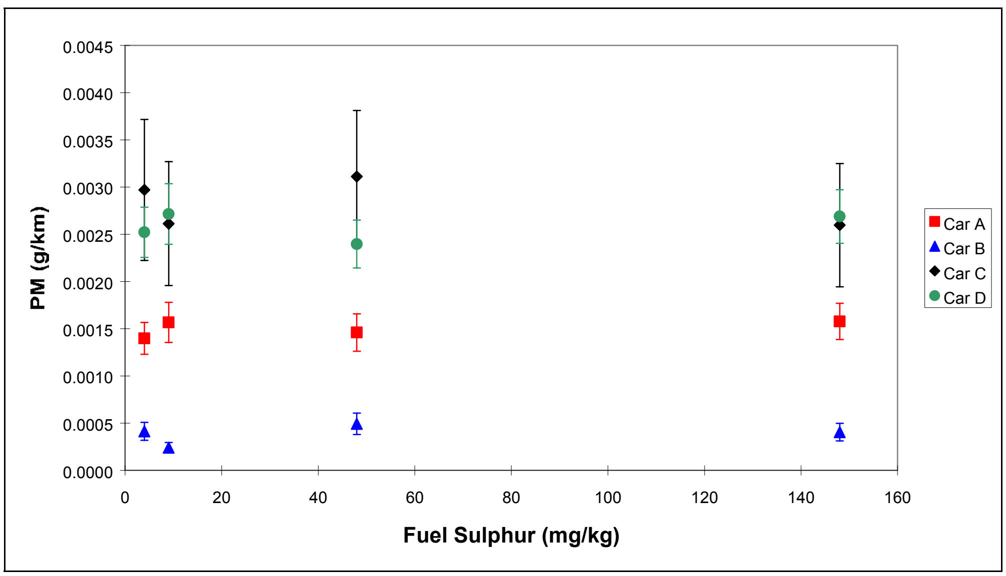
In all cases, emissions during the EUDC part of the cycle were very low. Visual inspection shows that all the sulphur effects are small relative to the prevailing emissions limits. For NOx, there was no statistically significant sulphur effect. For HC, the sulphur effect was significant in Cars A (P<0.1%) and B (P<1%). These effects appear large on a percentage basis but were small on an absolute scale and relative to the emissions limits. This can be seen from the regression equations shown on the charts. For CO, Cars C and D showed a statistically significant upward trend in emissions as sulphur increased, and Car A showed the reverse effect (P<5%).

Particulate mass (PM) emissions were also measured over the NEDC, in order to see whether there were any obvious differences between the vehicle technologies. These data are shown in **Figure 21** and show a clear ranking of PM emissions versus vehicle technology, with:

- lean-burn DI > stoichiometric DI > advanced MPI

However, even the lean-burn DI vehicles gave PM emissions an order of magnitude below the Euro-4 light duty diesel limit of 0.025 g/km. No influence of sulphur content on PM emissions was apparent on any of the vehicles.

Figure 21 NEDC emissions data - PM



8.2. COMPARISON WITH OTHER TESTS

8.2.1. EPEFE

EPEFE tested the effect of fuel sulphur content from 18 mg/kg up to 382 mg/kg. Significant effects were seen in the composite cycle for HC, CO and NOx, and linear models were fitted. These models predicted reductions in HC of 8.6%, CO of 9.0% and NOx of 10.4% when the fuel sulphur content was reduced from 382 mg/kg to 18 mg/kg. In the ECE phase of the cycle, only CO showed a significant effect. The EPEFE fleet showed largest sulphur effects, when expressed as a % change, in the EUDC phase of the cycle. The responses of the current vehicles to sulphur are therefore compared with the EPEFE response over the EUDC phase of the cycle.

Figures 22 to **24** compare the current vehicles with the EPEFE fleet average results for NOx, HC and CO respectively. Although the emissions levels are generally lower than those seen in the EPEFE fleet, the sulphur effects are small, even in the EUDC.

Figure 22 EPEFE Data - Light duty gasoline tests - NOx (EUDC)

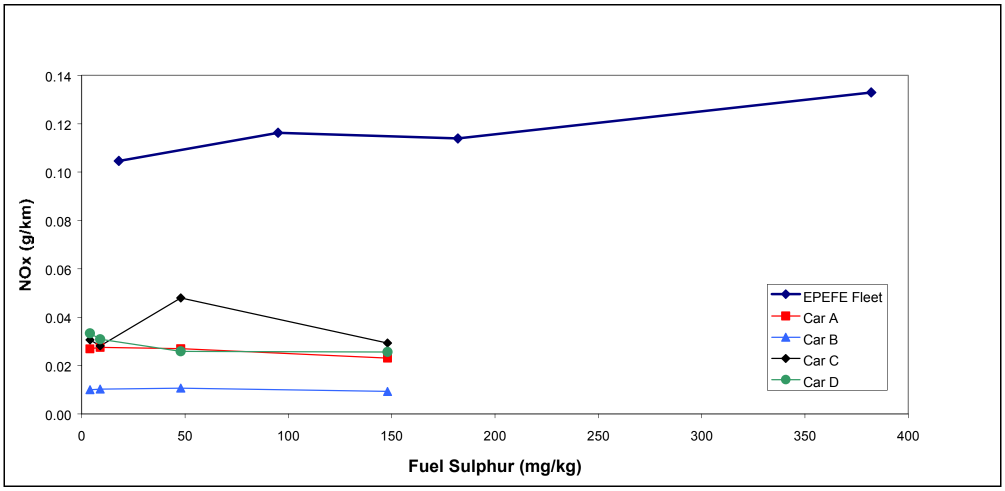


Figure 23 EPEFE Data - Light duty gasoline tests - HC (EUDC)

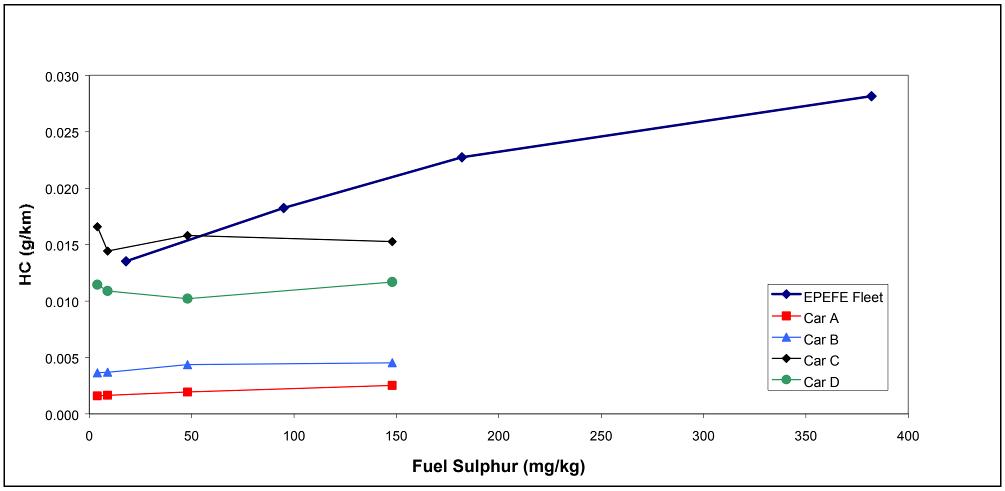
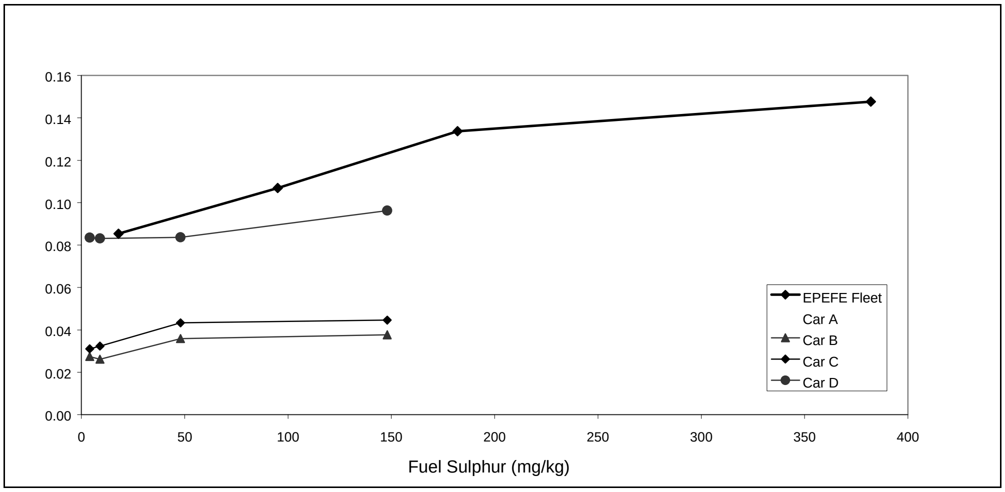


Figure 24 EPEFE Data - Light duty gasoline tests - CO (EUDC)



An analysis of the response of individual EPEFE vehicle EUDC emissions to fuel sulphur was conducted. For HC, the sulphur response was fairly consistent between vehicles (i.e. all vehicles showed a positive response, although not necessarily statistically significant). For NOx, there was much more variability between vehicles (i.e. a range of positive and negative responses to sulphur), with a positive response for the fleet. For CO there was a range of zero and positive responses. As detailed in Section 8.1 , the current vehicles showed no significant response of NOx to sulphur in the EUDC, limited response of HC and variable response of CO, despite having much lower overall emissions levels.

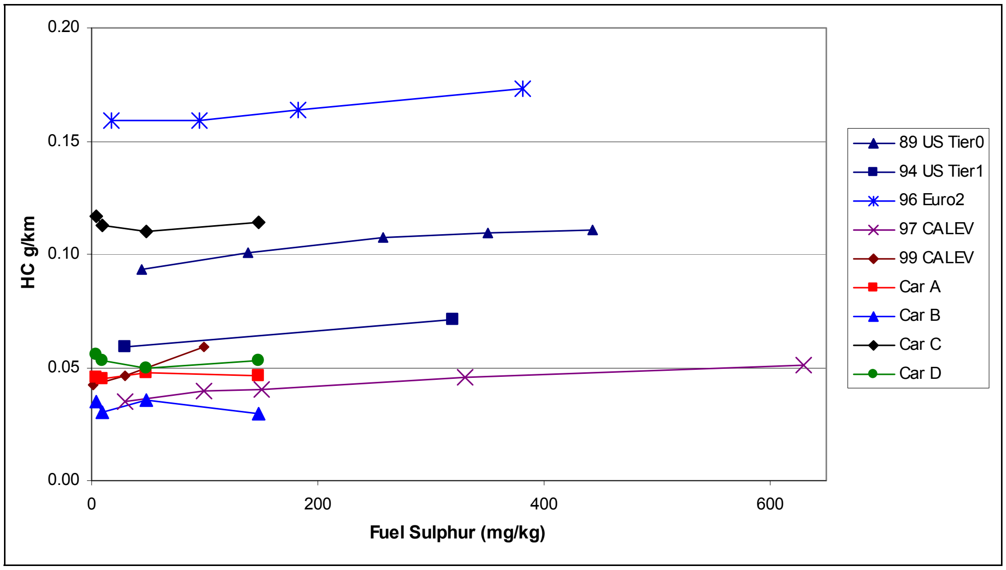
8.2.2. US studies on Low Emission Vehicles

Effects of sulphur on instantaneous emissions were studied during the 1990's in the US AQUIRP and European EPEFE programmes. More recent studies evaluated the effect of sulphur on vehicles meeting the lower emission standards in California. A CRC study [3] tested 1997 model year vehicles meeting LEV standards, and a second programme [4] by the Alliance of Automobile Manufacturers extended the work to 1999 LEV vehicles.

The fleet average results from the 1997 and 1999 California vehicles showed a stronger response to fuel sulphur than the earlier test fleets, including EPEFE, especially for NOx. This was widely interpreted as meaning that sulphur sensitivity would increase at lower emission levels. The results are shown in Figures 25-27 , converted to g/km for ease of comparison. In these figures, the EPEFE data relate to the complete test cycle rather than only the EUDC part as covered in Figures 22-24. No adjustment has been made for the test cycle differences between the US and European tests.

The results from the current study are also plotted on the same chart. Although emission levels from the four CONCAWE test vehicles are in most cases as low as the CALEV vehicles, emissions for the European vehicles do not increase with sulphur, as seen in the US studies. In addition, the European vehicles do not show

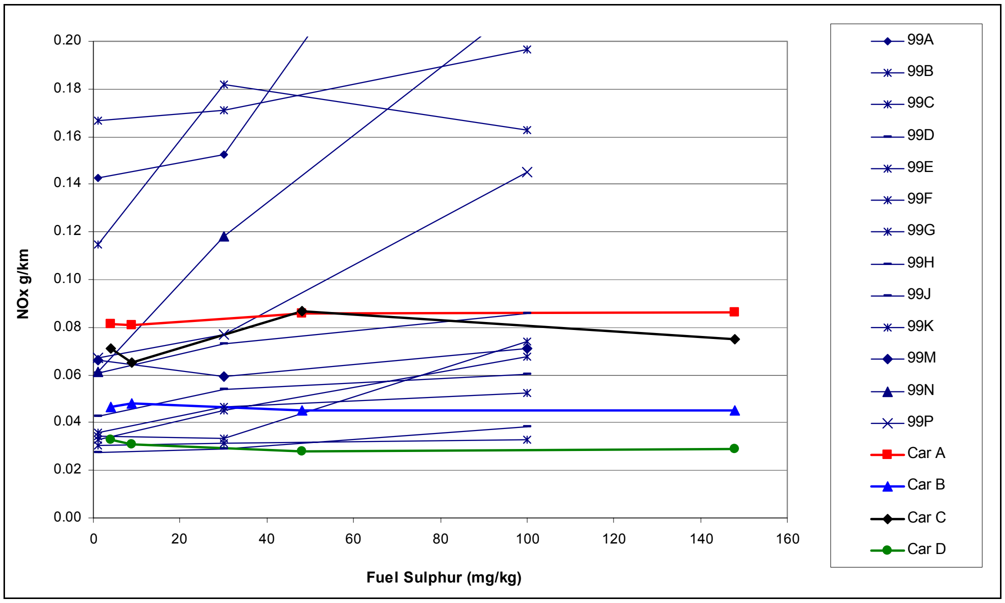
Figure 27 Comparison with earlier US and European studies, HC



In **Figure 27**, data from the European tests and the 99 CALEV test are based on total HC, whereas the 97 CALEV data are based on NMHC.

To provide insight into the possible reasons for the differences seen, the data from the US studies were investigated in more detail. For simplicity, this analysis concentrates on the NOx data. The 1999 study provides data on 13 vehicles, of which 4 were classified as light trucks. The data for individual vehicles show a wide range of sensitivity to sulphur as shown in **Figure 28**. The data from this CONCAWE study are again plotted on the same chart for comparison.

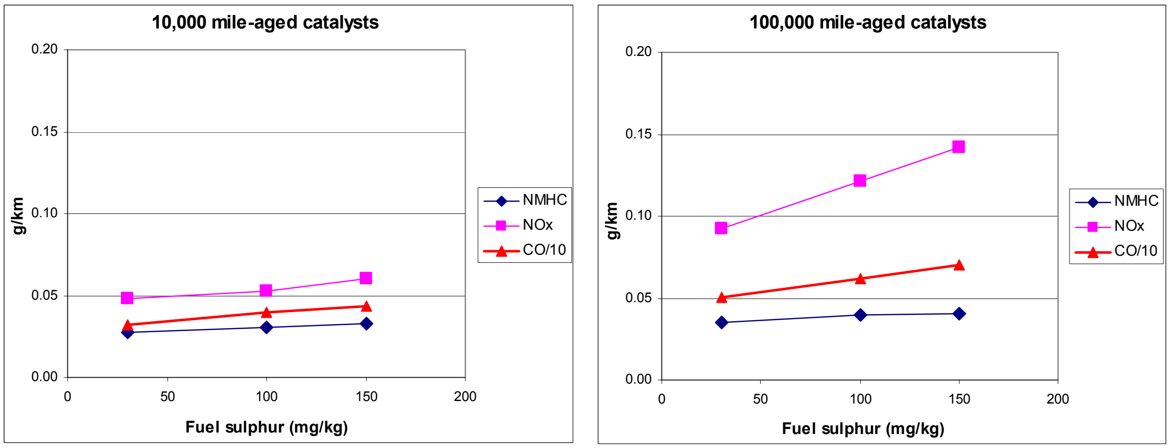
Figure 28 Comparison of this study with CALEV99 fleet, individual vehicles, NOx



Nearly all the vehicles in the California 1999 fleet showed some sensitivity to sulphur, but some responded more strongly than others. Some of the lower emitting vehicles showed a low sensitivity to sulphur, as seen in the European vehicles. Those vehicles that showed highest sulphur sensitivity did not necessarily have the lowest emissions.

In the study on 1997 CALEV vehicles [3], tests were carried out on 6 vehicles, using both catalysts aged to 10,000 miles, and in addition testing catalysts aged to 100,000 miles. The 1997 CALEV data shown in **Figures 25-27** are from these latter high mileage catalysts. In contrast, the earlier studies were carried out on catalysts with lower mileage. The impact of catalyst ageing on instantaneous sulphur sensitivity is shown in **Figure 29**, where fleet average data for the two sets of catalysts are shown.

Figure 29 Influence of catalyst ageing, from CALEV97 study
CALEV97 fleet average



With the catalysts aged to 100,000 miles, all emissions increased compared with the lower mileage catalysts. However, the sensitivity to sulphur, measured here as the percentage emission change between 30 and 150ppm S, stayed the same for HC, increased slightly for CO, but doubled for NOx. It seems, therefore, that NOx emissions are the most sensitive to catalyst condition and ageing.

It can also be seen that at these lower sulphur levels there is no evidence of a non-linear effect of sulphur on emissions - the data fit a linear profile.

8.2.3. CRC tests

Tests conducted in a joint CRC/CONCAWE programme (CRC E-60 programme) [5] provided additional data on two European test vehicles. The results allow us to investigate:

(1) the effect of catalyst ageing
(2) the impact of different test cycles

1) Catalyst Age Effects

The joint CRC/CONCAWE programme tested two European vehicles (together with 12 US vehicles), with one of the European vehicles (designated CRC-1) being the same model as Car A in the current programme. In the CRC/CONCAWE programme, three levels of fuel sulphur were tested: 3, 30 and 150 mg/kg. All vehicles were tested with the as-fitted catalysts (typically 10,000 miles) and aged catalysts[2]. The European vehicles were tested over three different drive cycles, the European NEDC and US FTP-75 and US-06 cycles. Because of the specific test objectives, long-term repeat tests were not included in this programme and detailed statistical analysis for the individual vehicles has not been attempted.

Results from the two different catalysts systems over the NEDC are compared in **Figures 30** to **32.** In the majority of cases there is an increase in the absolute emission level when running on the aged catalyst system. These increases are in

[2] Aged for 90 hours using RAT-A cycle with sulphur-free fuel – equivalent to 120,000 miles.

the range of 6 to 43%. Further analysis of the slopes of these responses showed that there was no indication of increased slope for the aged catalysts.

Figure 30 CRC E-60 Study - Response of European vehicles to Fuel Sulphur Content - NOx (NEDC)

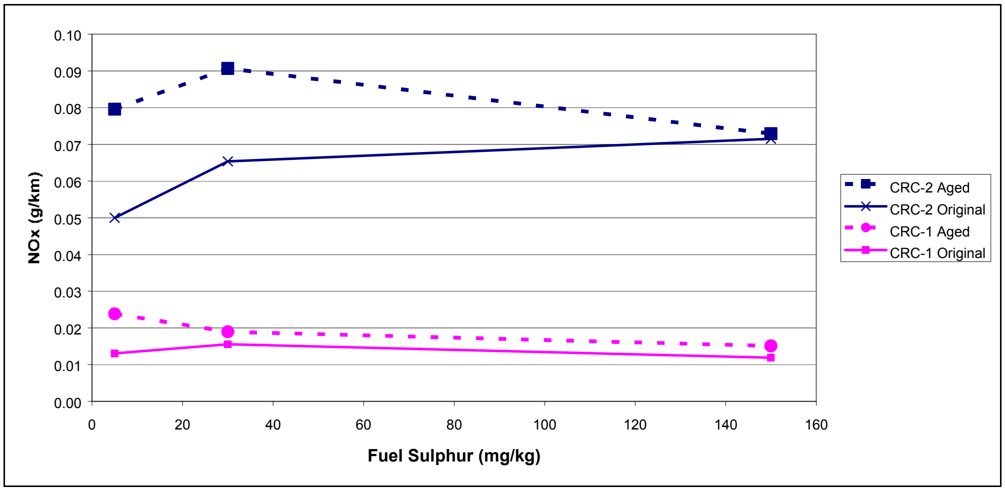


Figure 31 CRC E-60 Study - Response of European vehicles to Fuel Sulphur Content - CO (NEDC)

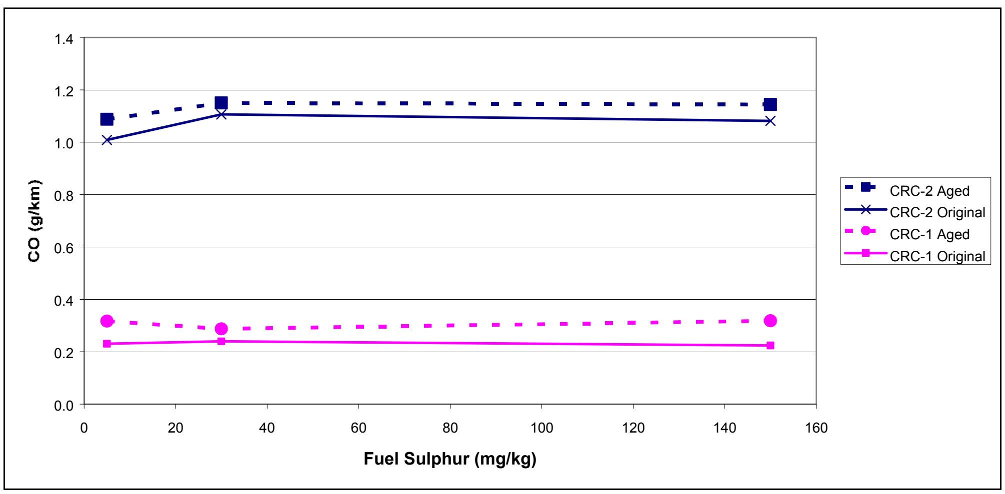
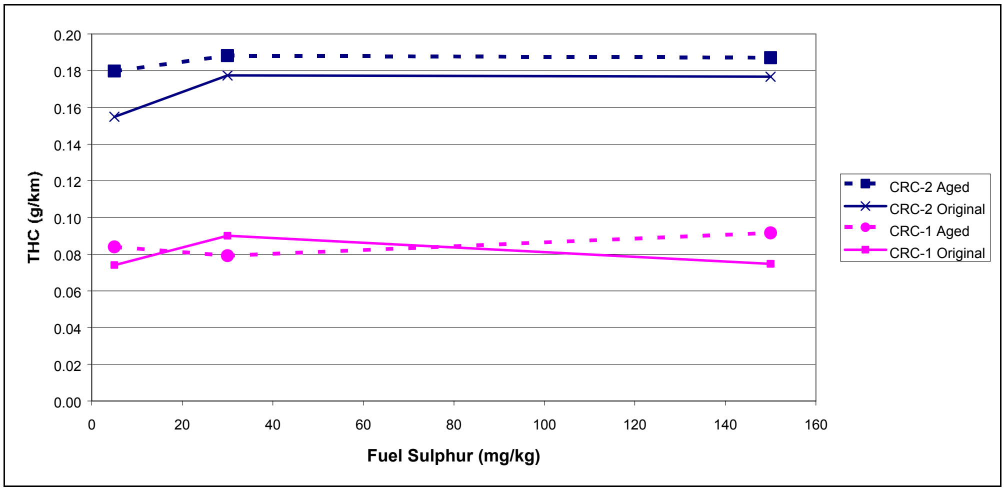


Figure 32 CRC E-60 Study - Response of European vehicles to Fuel Sulphur Content - HC (NEDC)



2) Driving Cycle Effects.

Based on the CRC E-60 programme, results from two different drive cycles (NEDC and FTP-75) with the original catalysts systems are compared in **Figures 33** to **35**. The results from the FTP-75 tests have been converted to g/km for this comparison. In the majority of cases (the exception being NOx from vehicle CRC-1) the emissions are greater from the NEDC cycle since it has effectively a greater weighting to the cold start. The analysis of the slope of the individual emission responses to fuel sulphur showed, generally, insignificant responses. There was an apparent trend for the slope to change from negative to positive in vehicle CRC-1 when going from the NEDC to the FTP cycle, and the reverse trend for vehicle CRC-2. Thus there is no systematic tendency for increased sulphur response with one particular drive cycle.

Figure 33 CRC E-60 Study - Response of European vehicles to Fuel Sulphur Content - NOx (NEDC and FTP-75)

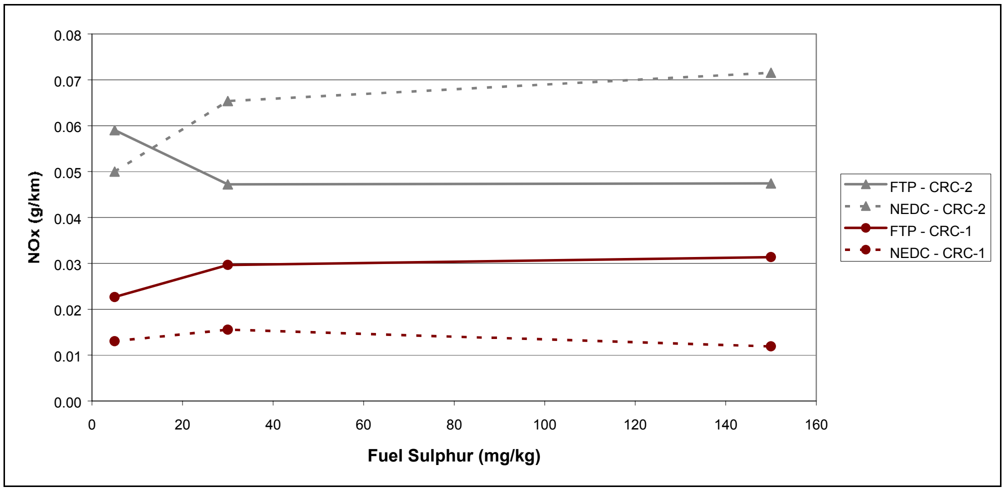


Figure 34 CRC E-60 Study - Response of European vehicles to Fuel Sulphur Content - CO (NEDC and FTP-75)

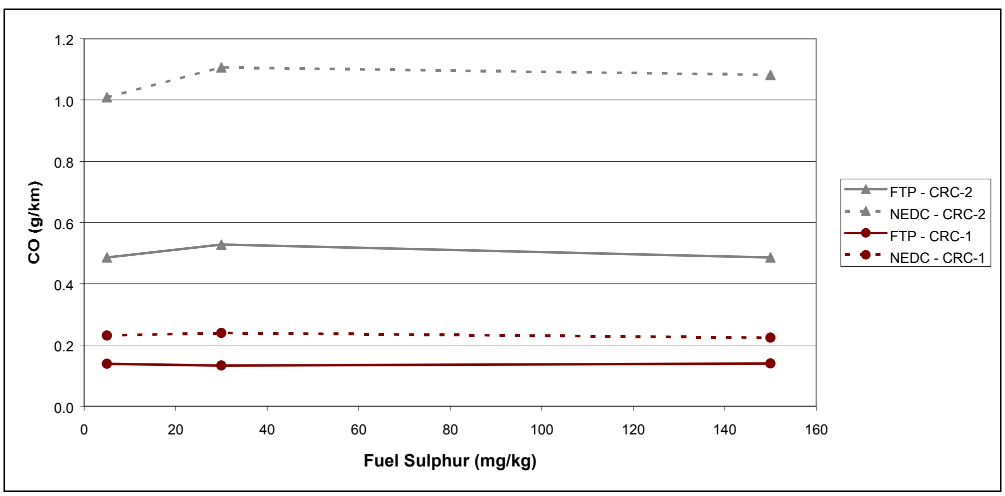
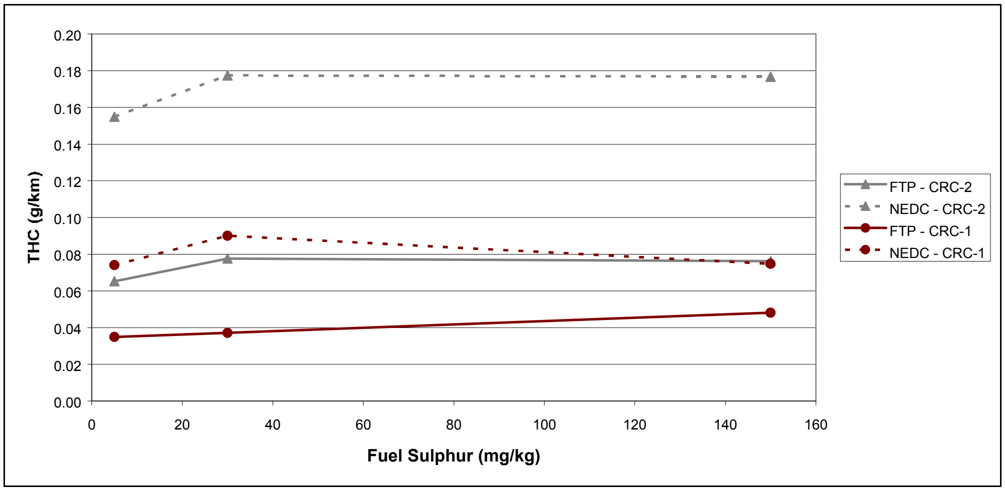


Figure 35 CRC E-60 Study - Response of European vehicles to Fuel Sulphur Content - HC (NEDC and FTP-75)



In summary, these tests on European vehicles carried out by CRC, in cooperation with CONCAWE, showed that for the European vehicles:

- Sulphur sensitivity was not increased after catalyst ageing.
- Sulphur sensitivity was not greater on the US-FTP driving cycle than on the European NEDC cycle.

9. CONCLUSIONS

- The four advanced technology, Euro 3 & 4, vehicles tested all achieved their respective emissions certification limits, and in most cases measured emissions were lower than Euro-4 limits.
- All four vehicles showed little or no short-term sensitivity to fuel sulphur content in the range from 4 to 148 mg/kg for all pollutants measured, despite having low exhaust emissions levels comparable to those from California LEV vehicles.
- Several vehicle technology design effects such as AFR strategy and catalyst performance were shown to have a much greater influence on emissions.
- Preliminary checks on the vehicles showed them to be very sensitive to dynamometer load and, in some cases, it was difficult to achieve the manufacturer's reported fuel consumption and CO_2 emission figures.

A review of earlier US studies that had shown a stronger sensitivity to sulphur demonstrated that:

1. fleet average results were influenced by a number of sensitive vehicles - some vehicles in the California fleet showed short-term sensitivity to sulphur as low as the European vehicles tested by CONCAWE,
2. catalysts that had been aged for 100,000 miles showed increased sensitivity to sulphur, especially for NOx emissions,
3. the lowest emitting vehicles were not necessarily the most sensitive to sulphur.

Additional tests on 2 European vehicles carried out by CRC in cooperation with CONCAWE showed:

- no evidence of increased sulphur sensitivity after catalyst ageing,
- no evidence that sulphur sensitivity was greater on the US driving cycle than on the European cycle.

Overall, on the basis of these findings, it can be concluded that:

- the advanced European vehicles tested showed very little short-term sensitivity to fuel sulphur,
- low emissions can be achieved without significant short-term sensitivity to fuel sulphur,
- there is no evidence of a non-linear response to sulphur at levels up to 150 mg/kg in either the European or US tests,
- fuel sulphur sensitivity is influenced by catalyst system design rather than by emissions level,
- reductions in fuel sulphur content from 150 to 10 mg/kg seem unlikely to bring substantial emissions benefits for current Euro-3 & 4 vehicle technologies.

10. GLOSSARY

AFR	Air Fuel Ratio
CALEV	California Low Emissions Vehicle
CO	Carbon Monoxide
CRC	Coordinating Research Council (USA)
DI	Direct Injection
E70	% v/v gasoline evaporated at 70°C
E100	% v/v gasoline evaporated at 100°C
E150	% v/v gasoline evaporated at 150°C
ECE	Urban driving part of the NEDC
EPEFE	European Programme on Emissions, Fuels and Engine Technologies
EUDC	Extra Urban part of the NEDC
FBP	Final Boiling Point
HC or THC	Total Hydrocarbons
LAMBDA (λ)	Actual Air Fuel Ratio / Stoichiometric Air Fuel Ratio
LEV	Low Emissions Vehicle
LHV	Lower Heating Value
MPI	Multi-Point Injection
NEDC	New European Drive Cycle
NMHC	Non-Methane Hydrocarbons
NOx	Nitrogen Oxides
OEM	Original Equipment Manufacturer
PM	Particulate Mass
SD	Standard Deviation
TP	Tailpipe
TWC	Three-way catalyst

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APPENDIX 1 ANALYSIS OF REFERENCE FUEL USED FOR INITIAL VEHICLE SCREENING

Fuel Description			**Reference Fuel used for initial vehicle screening**	
Fuel Code			**F8**	
Characteristic	**Units**	**Test method**	**Target**	**Result**
RON		ISO 25164	95 - 98	**97.9**
MON		ISO 25163	85 - 87	**84.8**
Density	kg/m^3	EN ISO 3675	725 - 775	**751**
Vapour Pressure	kPa	EN 13016-1	65 - 75	**68.5**
E70	% v/v	EN ISO 3405	38 - 40	**39.0**
E100	% v/v	EN ISO 3405	64 - 68	**62.5**
E150	% v/v	EN ISO 3405	75 min	**81.0**
FBP	°C	EN ISO 3405	200 - 210	**196**
Residue	% v/v	EN ISO 3405	2.0 max	**0.8**
Olefins	% v/v	ASTM D 1319	16 - 18	**14.2**
Aromatics	% v/v	ASTM D 1319	40 - 42	**35.9**
Benzene	% v/v	EN 12177	1 max	**0.1**
Sulphur	mg/kg	EN ISO 14596	40 - 50	**46**
Induction time	minutes	ISO 7536	360 min	**>360**
Existent gum	mg/100ml	ISO 6246	5 max	**1**
Cu Corrosion		ISO 2160	Class 1 max	**1a**
Carbon	% m/m		-	**87.0**
Hydrogen	% m/m		-	**13.0**
Oxygen	% m/m	EN 1601	-	**0**
LHV	MJ/kg		-	**43.25**

APPENDIX 2 STATISTICAL DATA ANALYSIS

This appendix provides additional information on the statistical design and data analyses discussed in Sections 4, 6 and 7.

Variability in test measurements

The variability within sets of repeat results on the same fuel in the same vehicle is quantified by the standard deviations in **Table 4**.

Table 4 Variability within sets of repeat results conducted on the same fuel in the same vehicle (combined ECE+EUDC cycle)

	CO (g/km)		HC (g/km)		NOx (g/km)	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
Car A	0.089	18.6%	0.046	7.7%	0.083	25.9%
Car B	0.523	12.1%	0.033	11.5%	0.046	14.7%
Car C	0.543	8.3%	0.113	6.6%	0.075	14.5%
Car D	0.389	7.7%	0.053	8.8%	0.030	16.3%
EPEFE[3]	1.417	10.1%	0.173	11.2%	0.172	12.0%

The variations in CO and HC results in the present programme are comparable with EPEFE in relative terms, despite the much lower levels of emissions. Variations in NOx results, however, while lower in absolute terms than EPEFE are higher in relative terms.

These variations have a large influence on the ability of the test programme to detect sulphur effects. The figures in **Table 5** show how large a fuel sulphur effect in a single vehicle, calculated as

$$\frac{\text{Fitted emissions from fuel S4 (148 mg/kg S)} - \text{Fitted emissions from S1 (4 mg/kg S)}}{\text{Fitted emissions from fuel S1 (4 mg/kg S)}} \times 100\%$$

would be needed to be statistically significant at P < 5% in a two-sided test. The size required also depends on the number of valid tests and the level of emissions, the calculation being complex due to the lognormality of the results.

3 The EPEFE S.D.s quantify the variability observed between independent (i.e. not back-to-back) single tests on the same fuel in the same vehicle in the EPEFE programme [2].

Table 5 Sizes of sulphur effects required for statistical significance at P < 5% (in a two-sided test) and the sulphur effects actually observed (effects are expressed as the difference in fitted emissions between the 148 mg/kg sulphur fuel S4 and the 4 mg/kg sulphur fuel S1 as a percentage of the fitted emissions from S1)

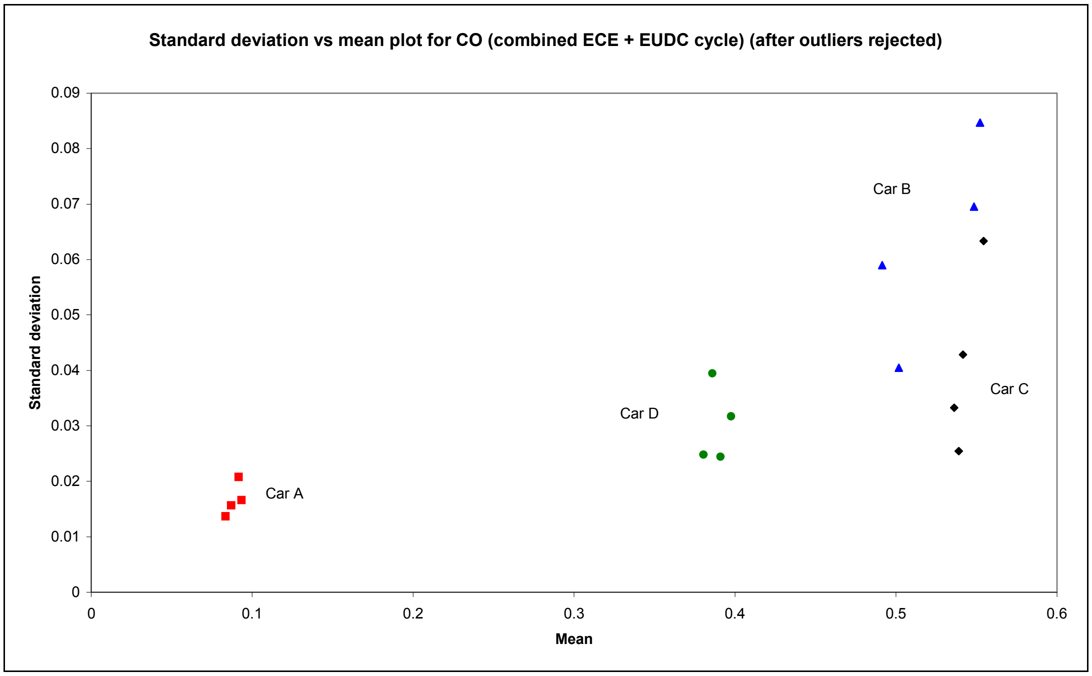
	CO (g/km)		HC (g/km)		NOx (g/km)	
	Required	Actual	Required	Actual	Required	Actual
Car A	21.1%	-5.6%	8.8%	1.2%	26.1%	6.2%
Car B	15.4%	-7.0%	15.8%	-10.0%	17.5%	-4.3%
Car C	10.3%	-0.1%	8.7%	-0.7%	22.8%	10.4%
Car D	9.0%	-0.2%	10.7%	-1.7%	26.7%	-13.8%

Standard deviation vs. mean plots

The distributions of sets of repeat measurements of automotive emissions or atmospheric concentrations are typically asymmetric or “skewed” and bear little resemblance to the standard bell-shaped normal or “Gaussian” distribution. In the EPEFE gasoline project [2] and other previous emission studies [6,7,8,9], the variability in emissions measurements has been found to follow the lognormal distribution with the degree of scatter increasing as the emission level increases.

Figure A2.1 is a typical standard deviation vs. mean graph plotting the standard deviation of the four or five CO measurements for each of the 16 vehicle × fuel combinations in the present study against the mean. Looking at each vehicle in turn, there is too little variation in mean emissions to determine whether the standard deviation increases with the mean or is constant. In the absence of evidence to the contrary, and bearing in mind the pattern across vehicles, it is assumed that the measurements in the present study do follow the lognormal distribution as mechanistically this is the most plausible model for emissions data.

Figure A2.1 Typical standard deviation vs. mean plot



Arithmetic means and regression analysis

In this report, arithmetic means are used to summarise the average emissions using each fuel in each vehicle, in line with EPEFE [2]. Geometric means are sometimes used in emissions studies as they give excellent comparisons between fuels on a percentage basis. However, they have the disadvantage of underestimating total emissions to the atmosphere.

Weighted regression analysis was used to relate emissions to fuel properties as the emissions measurements were assumed to have lognormal distribution. Each emission measurement was thus assigned a weight equal to

$$\text{weight} = 1 / (\text{mean emission for that fuel and vehicle})^2$$

(see [2], Annex 05).

In **Figures 15-21** in this report, "error bars" are shown around the average emissions for the various fuels. These have been constructed so that when two fuels are significantly different from one another at $P < 5\%$, their error bars will not overlap, as in EPEFE. We can be 84% confident that the true mean lies within the limits shown.

APPENDIX 3 EMISSIONS FOR EACH CAR X FUEL COMBINATION (ARITHMETIC MEANS)

Car	**Fuel**	**Sulphur**	**CO (g/km)**			**HC (g/km)**			**NOx (g/km)**			**CO_2 (g/km)**			**PM (g/km)**
			NEDC	**ECE**	**EUDC**	**NEDC**	**ECE**	**EUDC**	**NEDC**	**ECE**	**EUDC**	**NEDC**	**ECE**	**EUDC**	**NEDC**
A	**S1**	**4**	0.093	0.170	0.049	0.046	0.121	0.002	0.081	0.174	0.027	176.8	222.5	150.2	0.0014
A	**S2**	**9**	0.092	0.171	0.045	0.045	0.120	0.002	0.081	0.172	0.028	177.7	223.3	151.1	0.0016
A	**S3**	**48**	0.084	0.157	0.040	0.048	0.126	0.002	0.086	0.186	0.027	178.3	223.3	152.0	0.0015
A	**S4**	**148**	0.087	0.182	0.031	0.046	0.121	0.003	0.086	0.194	0.023	179.3	225.6	152.2	0.0016
B	**S1**	**4**	0.552	1.451	0.027	0.035	0.088	0.004	0.046	0.109	0.010	176.9	252.4	132.8	0.0004
B	**S2**	**9**	0.502	1.318	0.026	0.031	0.077	0.004	0.048	0.113	0.010	179.0	255.2	134.6	0.0002
B	**S3**	**48**	0.549	1.429	0.036	0.035	0.089	0.004	0.045	0.104	0.011	177.6	254.6	132.8	0.0005
B	**S4**	**148**	0.491	1.268	0.038	0.029	0.072	0.005	0.045	0.106	0.009	177.9	254.7	133.2	0.0004
C	**S1**	**4**	0.542	1.418	***0.031***	0.117	0.289	0.017	0.071	0.140	0.031	182.8	242.3	148.2	0.0030
C	**S2**	**9**	0.536	1.392	***0.032***	0.113	0.282	0.014	0.065	0.129	0.028	183.7	244.8	148.1	0.0026
C	**S3**	**48**	0.554	1.434	***0.043***	0.110	0.272	0.016	0.087	0.155	0.048	185.4	246.4	149.8	0.0031
C	**S4**	**148**	0.539	1.390	***0.045***	0.114	0.283	0.015	0.075	0.154	0.029	184.7	244.1	150.1	0.0026
D	**S1**	**4**	0.398	0.936	0.083	0.056	0.131	0.011	***0.033***	0.033	***0.033***	162.6	211.3	134.3	0.0025
D	**S2**	**9**	0.386	0.905	0.083	0.053	0.126	0.011	***0.031***	0.030	***0.031***	163.6	217.5	132.1	0.0027
D	**S3**	**48**	0.380	0.889	0.084	0.050	0.119	0.010	***0.028***	0.033	***0.026***	162.6	211.2	134.1	0.0024
D	**S4**	**148**	0.391	0.895	0.096	0.053	0.124	0.012	***0.029***	0.035	***0.026***	161.3	214.4	130.3	0.0027

Mean values before trend correction

C	S1	4			0.031										
C	S2	9			0.037										
C	S3	48			0.041										
C	S4	148			0.044										
D	S1	4							0.034		0.035				
D	S2	9							0.027		0.025				
D	S3	48							0.030		0.028				
D	S4	148							0.030		0.027				

(values in italics are corrected for systematic trends in the results)