the influence of heavy gasoline components on the exhaust emissions of catalyst equipped european vehicles

part 2 - unregulated emissions

Prepared for the CONCAWE Automotive Emissions Management Group, based on work carried out by the Special Task Force on emissions from gasoline powered vehicles (AE/STF-1) :

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ABSTRACT

This report extends the investigation published as CONCAWE Report No. 94/59, which studied the influence of gasoline back-end volatility and composition on regulated emissions. This Part 2 report describes the full hydrocarbon and aldehyde/ketone speciation measurements conducted as an integral part of the programme. The results demonstrated that cars have a much greater effect on speciated emissions than fuel parameters. No consistent trends were observed in speciated emissions with the less volatile fuels, and the minor fuel effects were more related to fuel composition than back-end volatility. Ozone forming potential was also evaluated.

KEYWORDS

Gasoline volatility, gasoline composition, unregulated emissions, speciated hydrocarbons, aldehydes, ketones, "air toxics".

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Supplementary Appendices:

The supplementary appendices, A to F, represent a very large body of data and are available on 3.5" diskettes from CONCAWE upon request. A small handling charge may be applied - please contact the Secretariat for further information.

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SUMMARY

CONCAWE has conducted a study to investigate the effects of heavy gasoline components in terms of both distillation and composition on the exhaust emissions of modern catalyst equipped cars. The US Auto/Oil AQIRP ^{2,3} reported that back-end gasoline volatility can have a major impact on vehicle exhaust emissions. However, it was not known whether these effects would be reproduced in European cars and fuels, particularly as European gasolines contain less heavy components than their US counterparts. CONCAWE Report no. 94/59 described the results obtained for regulated emissions and this publication focuses on the full hydrocarbon and aldehyde/ketone speciation measurements conducted as an integral part of the programme.

Seven experimental fuels designed with widely varying back-end distillation properties and composition were tested on ten vehicles meeting the requirements of the 'Consolidated Emissions Directive'. The investigation was conducted over the current ECE+EUDC test cycle and full speciation measurements were made over both the ECE1+2 and EUDC phases of the cycle for four cars. This data showed that emissions were very low over the extra urban driving cycle (EUDC) and many species were at or below current limits of detection. As a consequence, speciated emissions measurements for the remaining six cars were limited to the first two urban driving cycles (ECE1+2). Several repetitive speciation measurements were conducted on selected cars and fuels which demonstrated good test replication during the programme.

The results demonstrated that cars had a much greater effect on speciated emissions than fuel parameters. Most species, including the US Environmental Protection Agency "Air Toxics" were very effectively controlled once the vehicle catalysts reached their optimum operating condition. All speciated emissions were very low over the EUDC cycle and did not correlate in an obvious way with either gasoline composition or back-end volatility. Over the ECE1+2 phase some minor fuel effects were identified and, as expected, these related more to gasoline composition than back-end volatility:

- Increased fuel paraffins increased methane exhaust emissions.
- Aromatic fuels produced lower olefins but slightly higher aromatics and benzaldehyde.
- Total olefins in the exhaust were not related to total fuel olefins, but olefinic fuels tended to increase formaldehyde exhaust emissions.

All the test fuels showed slightly higher ozone forming potential than the base fuel and gasoline composition appeared to be more influential in this regard than back-end volatility.

1. INTRODUCTION

The US Auto/Oil Air Quality Improvement Research Programme (AQIRP) ²³ has reported that gasoline back-end volatility can have a major impact on vehicle exhaust emissions in modern fuel-injected catalyst cars. Phase 1 of the AQIRP programme showed significant reduction in emissions of both total hydrocarbons (HC) and the so-called 'air toxics' (defined by the US Clean Air Act Amendments as benzene, buta-1,3-diene, polycyclic organic matter (POM), formaldehyde and acetaldehyde). HC emissions from the 'current fleet' (i.e. newer US cars, all with modern 3-way catalysts) were reduced by 21% and the 'air-toxics' by 10 to 30% when T90 was reduced from 182°C to 138°C.

A more detailed study in Phase 2 of AQIRP also showed significant reductions in HC emissions with increasing mid-range to back-end volatility. Their analysis showed that these decreases in HC emissions were due to changes in distillation characteristics rather than compositional effects, although some intercorrelations between mid-range to back-end volatility and compositional parameters were present in the fuel set. HC emissions were reported to be best expressed by an equation containing non-linear terms in both E149 and E93. The 'air toxics' emissions corresponded to gasoline composition rather than distillation. Benzene emissions increased with addition of aromatic components, while buta-1,3-diene emissions increased with addition of olefinic fluid catalytically cracked (FCC) cuts or paraffinic heavy alkylate. Formaldehyde and acetaldehyde responses were more variable but generally increased with the addition of non-aromatic components.

It was not known whether these effects would be reproduced in European cars and fuels, particularly as European gasolines have lower T90 than US fuels (e.g. T90 of 155°C vs. 165-170°C). A test programme was therefore planned and carried out by CONCAWE Special Task Force (AE/STF-1) to investigate the effects of back-end volatility and composition on exhaust emissions from European catalyst-equipped vehicles.

The results of this investigation in terms of regulated emissions (HC, CO, NOx) are described in Part 1, CONCAWE report No. 94/59, which concluded that both backend volatility and composition had some effect on regulated emissions. See **Section 3** for a description of the fuels used in the programme. For HC and CO emissions, back-end volatility had a larger effect than composition, reducing backend volatility by moving from the light base fuel (B140) to the Intermediate fuel series (I160) increased total HC emissions by 9% and total CO by 14%. Further reducing back-end volatility to the heavy fuel series (H180) had no effect on HC or CO emissions. Aromatic fuels gave slightly higher emissions than paraffinic or olefinic fuels.

Fuel effects on NOx emissions were in the opposite direction to those for HC and CO. Aromatic fuels gave 7% lower NOx emissions than paraffinic fuels which in turn gave 8% lower NOx emissions than olefinic fuels, confirming the beneficial effect of aromatics on NOx control in catalyst cars. Reducing back-end volatility from the base fuel (B140) to the intermediate/heavy fuel series (I160/H180) reduced NOx emissions by 12% for aromatics and 5% for paraffins; no reduction was seen for the olefinic fuels. NOx emissions were broadly unchanged between the I160 and H180 series.

Although the test fuels were carefully designed to have constant front-end volatility (i.e. up to T50), the back-end volatility of all the test fuels varied to an increasing extent from T50 to FBP. Within this range it was not possible to ascribe the fuel

effects to any one distillation point, either T or E values. Some evidence was also found that emissions correlated equally well with fuel stoichiometry as expressed by the Fuel Volumetric Air Demand (FVAD).

This Part 2 report describes the full hydrocarbon and aldehyde/ketone speciation measurements which were carried out over both the ECE1+2 and EUDC phases of the cycle for four of the test cars and over ECE1+2 for the other six cars. Thus "air toxics", as defined by the US Clean Air Act Amendments, but excluding POM, have been measured. The study provides an insight into the way in which fuel composition can affect exhaust hydrocarbon composition.

2. OUTLINE OF PROGRAMME

The programme was designed to investigate the effects of both back-end distillation and composition on exhaust emissions from a fleet of modern fuel-injected catalyst cars.

Seven fuels were tested in a chassis dynamometer study on ten vehicles over the current ECE+EUDC test cycle. Speciated hydrocarbon, aldehyde and ketone emissions were measured over phases ECE1+2 and EUDC for 4 cars and over the ECE1+2 for the other 6 cars with some repeat testing. Speciated emissions were not measured over the ECE3+4 cycle but have been estimated using the total hydrocarbon (THC) emission data measured during the regulated emission tests. The detailed results are reported for each car over each phase in the tables and figures in the appendices.

3. FUEL DESIGN AND BLENDING

A base fuel was blended from typical refinery components, but with a low content of heavy hydrocarbons. This provided a light gasoline, containing few olefins and was not designed to be representative of typical European quality. This fuel was then blended with distillate fractions from selected heavy aromatic, paraffinic and olefinic refinery components to produce a test fuel matrix to separate physical and compositional effects. It should be emphasised that the fundamental separation of physical and compositional parameters could not be achieved with 'typical' fuels and it is therefore not possible to make comparisons between the test fuel blends and commercial products. The test fuels matrix was:

	Base (B)	Intermediate (I)	Heavy (H)
Target T90 (°C)	140	160	180
Base Fuel	B140		
	(145)		
Base Fuel + Aromatics		A160	A180
		(161)	(173)
Base Fuel + Paraffins		P160	P180
		(165)	(176)
Base Fuel + Olefins		O160	O180
		(156)	(170)

The test fuels were blended to two nominal T90 levels, 160° C and 180° C. The T90 values actually achieved are shown in parentheses. In the report the 160 fuels are collectively referred to as intermediate (I) fuels and the 180 blends as heavy (H) fuels.

Reducing back-end volatility (e.g. increasing T90) of the test fuels also reduced the mid-range volatility (e.g. increased T50) which may also have a measurable impact on vehicle emissions. Therefore to ensure a true comparison of base and test fuels, the front-end / mid-range distillation characteristics of the base fuel were carefully adjusted with light paraffinic components to provide a modified base fuel which matched the front-end / mid-range (up to T50) of the test fuels (**Figure 1**). It should be recognised that it is impossible to change only one aspect of a fuels distillation characteristic without changing other distillation points. Therefore, it will be seen from **Figure 1** that although the designed changes of T90 have been achieved, other distillation points above T50 have also been affected. However, with this fuels matrix the task force is confident that only mid-range to back-end distillation effects are being measured.

The test fuels do not exactly match the T90 target values as it was agreed that the volume of each of the heavy components (i.e. aromatic, olefinic, paraffinic) added to the common base fuel should be the same, to ensure that the base fuel compositional variation was consistent across all fuels. The addition of heavy components can affect fuel density, C/H ratio and stoichiometric AFR, particularly in the aromatic fuel series. The RVP and T50 of all the test fuels were similar and sulphur levels were kept to a minimum (9-16 ppm) to eliminate any possible exhaust catalyst deactivation effects. All test fuels were blended to a minimum 85 MON specification. Full inspection data are provided in **Table 1** and fuel composition data in **Table 2**. Full GC compositional data for all the test fuels are provided in **Supplementary Appendix 3**, available from CONCAWE.

4. TEST EQUIPMENT

All emissions test work was carried out at the BP Oil Technology Centre, Sunburyon-Thames, UK. This facility is equipped with a Froude Consine dynamometer with twin 0.5 m rollers (60 kW power capacity) linked to a Horiba VETS 9000 system, with three MEXA 9000 analyser trains for regulated emission measurements (one dilute gas and two raw gas analysers). In addition raw gas was sampled on-line to give second-by-second and modal results of engine-out and tailpipe emissions, together with catalyst efficiencies and air fuel ratio. The hydrocarbon speciated emissions, C1 to C10, (60 individual hydrocarbon compounds) were measured using a temperature programmed capillary gas chromatography technique (capillary PLOT column, temperature programmed from 32°C - 195°C at 15°C/minute for 5 minutes followed by 5°C/minute up to 195°C - see Supplementary Appendix 4, available from CONCAWE). Dilute exhaust gas samples were taken from the CVS tedlar bag into a prepared sample tedlar bag which was immediately placed into a light-proof vessel and sampled within a two hour period (max). The aldehydes and ketones were sampled through 2,4-dinitrophenylhydrazine (DNPH) impregnated silica adsorption cartridges 'on-line' from the CVS dilution tunnel. The DNPH sampling was always carried out in duplicate with back-up cartridges 'in series' to prevent any component losses. The 2,4-dinitrophenylhydrazone derivatives were subsequently analysed in the laboratory using reverse phase high performance liquid chromatography techniques (Supplementary Appendix 5, available from CONCAWE).

5. TEST PROCEDURE AND TEST VEHICLES

Prior to the start of the emissions test programme, all vehicles were subjected to a full engine service check and the crankcase lubricant was replaced using a commercial multi-grade lubricant. The carbon canisters for evaporative emission control of all the vehicles were sealed-off prior to the start of the test work, thus minimizing the need for lengthy soak/purge vehicle preconditioning prior to test commencement. Evaporative emissions were not measured in this programme. A 10 km constant speed preconditioning was carried-out, followed by an overnight soak of not less than 15 hours, at a temperature in the range of 25-30°C. One test vehicle was equipped with an 'adaptive learning' engine management system and was therefore driven a full European drive cycle prior to the test work after each fuel change, to enable the electronic adaptive learning system to adjust to the new test fuel.

Technical details of the 10 test cars which were all 3-way catalyst equipped, with closed loop lambda feed-back control, are provided in Table 3. Limited repeat tests were carried out on some cars and fuels. The speciated emissions testing was carried out over the ECE1+2 and EUDC phases of the current European emissions drive cycle representing cold start and fully warmed-up vehicle conditions for the 4 car sub-set and all 7 test fuels. The speciation data showed that emissions were very low over the EUDC and many species were at or below the current limits of detection. As a consequence, speciated emissions for the remaining 6 cars were measured over the ECE1+2 cvcle only. Speciated emissions were not measured over the ECE3+4 phase, although the gaseous 'air-toxic' emissions (benzene, buta-1.3-diene, formaldehyde, acetaldehyde) have been estimated for the ECE3+4 cycles using an approximation that is based pro-rata on the total hydrocarbon (THC) emissions data measured over the ECE1+2 and ECE3+4 phases during the Part 1 regulated emissions work ¹ (this is justified as the ECE3+4 consistently contributed only 6-7% of the total cycle HC emissions). The total cycle speciated data therefore also included this estimate for the ECE3+4 emissions.

6. RESULTS

Hydrocarbon and carbonyl speciation data (70 compounds in total) generated for all 10 cars on all 7 test fuels over the ECE1+2 cycle are provided in **Supplementary Appendix A** (**Tables 1.1** to **1.10**). **Figures A** to **J** in the same appendix show for each fuel type the trends of the 5 most predominant species from each of the 5 major emission categories (i.e. paraffins, olefins, isoparaffins, aromatics and aldehydes). These 25 species represent about 85-90% of the total HC emissions, thus simplifying and assisting data interpretation.

Hydrocarbon and carbonyl speciation data measured over the EUDC for the 4 car sub-set are given in **Supplementary Appendix B** (**Tables 2.1** to **2.4**). **Figures K-N** in the same appendix similarly show the 25 predominant species over the EUDC for these cars.

The data have also been summarized as follows:

- 10 car geometric means for each of the 25 species for all test fuels over the ECE1+2 are shown in **Table 4** and **Figure 2**.
- Geometric (i.e. logarithmic) means for the 4 car sub-set for each of the 25 species for all test fuels over the ECE1+2 are provided in **Table 5** and **Figure 3**.
- Geometric (i.e. logarithmic) means for the 4 car sub-set for each of the 25 species for all test fuels over the EUDC are shown in **Table 6** and **Figure 4**.

Geometric means provide a better comparison between fuels over a car population but tend to underestimate the absolute emissions levels. Arithmetic means have therefore been used in the ozone reactivity calculations and must be used, for example, in emission modelling studies. Arithmetic means for each species measured over the ECE1+2 cycle for the 10 cars and 7 fuels and individual hydrocarbon fuel component concentrations are given in **Table 7**.

7. DISCUSSION

The programme was conducted to test the effects of gasoline back-end volatility and composition on speciated hydrocarbon and carbonyl exhaust emissions. Results reported here refer to the speciated emissions only; the regulated emissions have been reported separately.¹ The aim of this section is to examine the extent to which fuel composition and back-end distillation influence the quantity and distribution of hydrocarbon and carbonyl compounds in tail-pipe exhaust emissions.

Several repetitive speciation measurements were carried-out on selected cars and fuels which have demonstrated good test replication during this programme of work.

7.1. ECE1+2 SPECIATED EMISSIONS - 10 TEST CARS

The bulk of the HC emissions occur in the ECE1+2 phase that represents cold start and warming-up of the engine. Visual inspection of speciated hydrocarbon data (10 car geometric means) confirms that the individual hydrocarbons do not exhibit major changes of profile as a result of changes in fuel back-end composition (**Table 4** and **Figure 2**). Nevertheless, there are some small changes in HC distribution. For example ethane, ethene and propene formation is apparently favoured slightly (relative to the aliphatic and aromatic C6, C7 species) in the order of olefins>paraffins>aromatics. Buta-1,3-diene emissions also broadly follow the same trends. Methane formation seems more favoured by the paraffinic fuels. However, these trends are not observed for the heavier (>C4+) hydrocarbons, in fact a reverse trend is observed.

Aromatic HC content of the exhaust emissions shows a slight increase with the aromatic fuels, a trend explained in part by the contribution of the unburnt fuel. Consequently, benzene, toluene, xylene and heavier aromatic emissions are slightly higher for the aromatic fuel series (A160, A180). This change in HC balance may be important for NOx control over the catalyst. The formation of both formaldehyde and acetaldehyde emissions is favoured by the fuels in the order olefins>paraffins>aromatics. Slightly higher benzaldehyde emissions are, however, observed for the aromatic fuel series as expected, although the increase is very small. Other aldehydes only make a minor contribution to the total aldehyde/ketone emissions.

An observation from all the speciation emission data is that the major fuel components which predominate in the fuels (i.e. toluene, isopentane, 2,2,4 trimethyl pentane etc.), as expected, predominate in the fuel exhaust HC composition. A comparison of the overall exhaust gas composition (i.e. paraffins, olefins, aromatics) for all 10 cars (arithmetic means) over the ECE1+2 versus fuel composition is provided in **Figure 5** for the I160 fuels and in **Figure 6** for the H180 fuels. The most striking feature of these results is the overall insensitivity of exhaust gas composition to different fuel types. In particular, the wide variation in fuel olefin content (0.2% to 15% v/v) does not obviously correlate to total exhaust gas olefin concentration, which is almost constant between 20-28%. The proportion of paraffins (32-41% w/w) in the exhaust is also very similar for all fuel types irrespective of fuel composition or distillation. Total aromatic emissions are, as expected, marginally higher for the A160 and A180 fuels, but the increase is less than the variation of aromatics in the fuels.

It is clear from a comparison of both figures that changes to mid-range to back-end distillation have little effect on overall exhaust gas composition.

7.2. 4 CAR SUB-SET - ECE1+2, 3+4 AND EUDC SPECIATED EMISSIONS

Geometric means for speciated data for the 4 car sub-set over the ECE1+2 cycle are given in **Table 5** and **Figure 3**. The 4 car geometric mean results of the ECE1+2 shows similar trends, to those discussed in **Section 7.1** for the complete 10 car data set.

Comparison of the ECE1+2 data with those for the EUDC (**Table 6** and **Figure 4**) for the 4 car sub-set confirms that the emissions yield of speciated hydrocarbons and aldehydes/ketones is much greater under warm-up conditions (i.e. ECE1+2 phase) than with the catalyst fully operational in the EUDC phase. This comment applies to all species analysed, particularly the unsaturated compounds, i.e. acetylene and buta-1,3-diene, which are almost eliminated over the EUDC when the catalyst is fully effective. Methane emissions predominate over all other species under such conditions.

The ECE1+2 contributes about 85% of the total HC produced over the total cycle; the EUDC contribution is about 7%. A comparison of the 'air-toxic' emissions over ECE1+2, 3+4, EUDC and the total cycle is shown in Figure 7 (I160 fuels) and Figure 8 (H180 fuels). These figures clearly demonstrate how effective a fully warmed-up catalyst is in substantially reducing 'air-toxic' exhaust emissions. Improvements in catalyst warm-up technology (e.g. electrically heated or closecoupled catalysts) would have a significant benefit in further reducing 'air-toxic' and other speciated exhaust emissions during the ECE1+2 part of the European drive cycle. Catalyst effects can be compared and contrasted with the minor effects that changes in fuel back-end volatility and fuel composition have on such emissions. The combined 'air-toxic' emission data for all fuels are plotted in Figure 9. This figure indicates that the less volatile (i.e. H180 blends) paraffinic and olefinic fuels show a small reduction in most 'air-toxics' compared with the I160 fuels, particularly over the ECE1+2 cycle. The reverse trend is observed for the aromatic fuels. These figures contain an estimate for the ECE3+4 and total cycle emissions for the selected species (Supplementary Appendix F).

7.3. VEHICLE INFLUENCE ON SPECIATED EMISSIONS

The 'air-toxic' exhaust emissions over the ECE1+2 cycle for each vehicle averaged across test fuels are shown in **Figure 10**. The percentage of each emission relative to the total hydrocarbon emission, is shown above each bar. It is clear that vehicle type has a major impact on the quantity of individual 'air-toxic' emissions. Vehicle 6 produced the lowest amount of all 'air-toxic' emissions which range from 5-9 times less than Vehicle 1, which proved to be the highest emitter. The proportion of each 'air-toxic' relative to the total HC was, however, similar for most vehicle types and is summarized as follows:

	% of THC	mg/km
Formaldehyde ranged from	0.5% to 1.7%	2.1 to 19.3
Acetaldehyde ranged from	0.4 to 0.9%	1.9 to 8.9
Buta-1,3-diene ranged from	0.4 to 1.1%	1.6 to 11.6
Benzene ranged from	2.9 to 4.3%	13.5 to 66.2

The THC data over the ECE1+2 cycles for each car are plotted in **Figure 11** for comparison purposes. It can be seen that Vehicles 6 and 1, were respectively, the lowest and highest THC emitters although the relative ranking of individual cars in terms of THC did not exactly mirror the 'air-toxic' observations.

The variation of 'air-toxic' emissions for each car and all fuels over the ECE1+2 cycles are shown in **Figure 12**. The bars on the graphs represent the highest and lowest emission results observed for each car. Results demonstrate that certain vehicles (i.e. Vehicle 6) are relatively insensitive to fuel quality changes whereas others are considerably more sensitive (Vehicle 2). The overall 'air-toxic' emission benefits of Vehicle 6 are clearly evident.

7.4. OZONE PHOTOCHEMICAL REACTIVITY

Ozone forming potential (OFP) of the 10 car speciated emissions (arithmetic means) over the ECE1+2 cycles have been calculated using five different models. The factors used were the 1993 CBM-1V Carter MIR (Maximum Incremental Reactivity) and MOR (Maximum Ozone Reactivity), Harwell (Photochemical Ozone Creation Potential) POCP ⁴ and IVL (normal and high NOx scenarios) POCPs ⁵. The factors employed are shown in **Table 8**.

The MIR of a compound is determined under conditions at which the maximum change in reactivity in ozone results from small additions of the particular compound, thus defining the reactivity where hydrocarbon control has its greatest benefits. Such conditions are characterised by low hydrocarbon/NOx ratios. The MOR is determined by adding small quantities of a particular compound under which ozone levels are at their peak. These conditions correspond to moderate hydrocarbon/NOx ratios in which both hydrocarbons and NOx are important for ozone formation.

A trajectory model approach was used by Harwell (UK research laboratory) to generate several sets of factors. Three trajectories were simulated; a one day episode in which the wind direction was from London towards Bristol, a five day episode from Germany towards Ireland and a five day episode from France to Sweden. The mean of the POCPs calculated over the eleven individual days were used as a basis for the development for the Harwell factors. The IVL (Swedish Environmental Research Institute, Gothenburg) factors were also generated from a trajectory modelling study, in which the emissions and chemical processes occurring in an air parcel are simulated. The meteorology and emission data were chosen to correspond to a summer high pressure condition in southern Sweden, favourable for NOx limited ozone formation. A second set of factors are reported by IVL in which an additional point source of NOx has been introduced into the model,

so that the POCP calculations are carried out in a more NOx rich environment. The reactivity of the chemical species based on this scale are consistent with the reactivities developed by Harwell.

The factors are used as multipliers of the speciated hydrocarbons mass emissions, the results for the individual species are then summed to yield the total ozone forming potential (OFP). The contribution that CO makes to the OFP is accounted for in all 5 models.

OFP results for the 5 models, based on a 10 car arithmetic mean over the ECE1+2 cycle are shown in **Figure 13**. The magnitude of the numbers generated between the different models is not of significance. The relative OFP ranking of the test fuels is in the same order for the Harwell, IVL norm and IVL high models and is as follows:

A160 > A180 = P160 > P180 > O180 > O160 > B140

The MIR and MOR models show a marginally different ranking:

A160 > P160 > P180 > O160 > A180 = O180 > B140

All the test fuels show slightly higher OFP (4-10%) than the base fuel B140, although within the I160 and H180 series a **decrease** in back-end volatility results in slightly lower OFP. Fuel composition appears more influential in OFP i.e. the A160 and A180 show marginally higher OFP than other fuel types. The OFP ranking of the intermediate and heavy fuels is in the same order, i.e.:

1160 Fuels	A160 > P160 > O160	
H180 Fuels	A180 > P180 > O180	(Harwell, IVL norm, IVL high)
	P180 > A180 > O180	(MIR, MOR)

The differences between the OFP of most of the fuels is, however, small and is not expected to make a significant impact on air quality. The contribution that evaporative emissions may have on OFP of these fuels has not been considered in this programme of work.

8. CONCLUSIONS

A 10 car exhaust emissions programme has been completed to investigate the effect of gasoline back-end volatility (e.g. increasing T90 from nominal 140°C to 160 °C and 180°C) and composition (paraffins, olefins and aromatics) on speciated emissions.

- 1. Results demonstrate that cars have a much greater effect on speciated exhaust emissions than fuel parameters.
- 2. Most speciated emissions, including the US EPA gaseous 'air-toxics', are very effectively controlled once the vehicle's catalyst has reached optimum operating condition. Improvements in catalyst warm-up technology or the application of electrically heated catalysts (EHC) would have substantial benefits in reducing 'air-toxic' and other speciated exhaust emissions during the ECE1+2 part of the European cycle.
- 3. All speciated exhaust emissions are very low over the EUDC and do not correlate in an obvious way with fuel composition or back-end volatility. Methane emissions predominate during the EUDC.
- 4. No consistent trends have been observed in speciated emissions when decreasing the back-end volatility from B140 to I160 to H180. The observed changes are, as expected, more related to fuel composition than back-end volatility effects.
- 5. The following minor fuel effects have been identified:
 - Increased fuel paraffins increase methane exhaust emissions.
 - Aromatic fuels show lower olefins but slightly higher aromatics and benzaldehyde in the exhaust emissions.
 - Total olefins in the exhaust emissions are not related to total fuel olefins.
 - Olefinic fuels tend to increase formaldehyde exhaust emissions.
- 6. All the test fuels show slightly higher ozone forming potential (4-10%) than the base fuel B140, although within the I160 and H180 fuel series a decrease in back-end volatility results in lower OFP. Fuel composition appears more influential in OFP, e.g. the A160 shows marginally higher OFP than other fuel types.

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APPENDIX 1

Table 1	Test Fuel Inspection Data
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FUEL		B140	P160	P180	A160	A180	O160	O180
Distillation	(T numbers)							
IBP	°C	21.2	33.5	32.7	33.2	34.1	34.6	33.9
5% Evapora	ated at °C	43.2	44.7	44.0	44.9	44.8	47.2	46.1
10% Evapora	ated at °C	51.7	52.7	52.0	52.8	52.4	55.9	53.5
20% Evapora	ated at °C	65.0	64.3	63.8	64.7	63.9	68.6	64.2
30% Evapora	ated at °C	78.6	76.9	75.6	77.5	76.7	82.0	75.5
40% Evapora	ated at °C	93.4	91.9	90.9	93.2	91.8	95.9	90.2
50% Evapora	ated at °C	104.2	108.2	107.0	109.1	108.2	107.1	105.3
60% Evapora	ated at °C	111.0	120.7	120.2	122.5	121.5	115.1	117.6
70% Evapora	117.2	132.5	133.1	134.5	135.4	123.5	129.4	
80% Evapora	ated at °C	126.9	147.8	152.0	149.0	154.2	136.2	146.5
90% Evapora	ated at °C	144.9	164.8	175.6	160.7	172.8	156.1	169.5
FBP	°C	179.5	189.6	200.9	182.4	199.9	193.8	203.7
Residue	%vol	1.0	1.2	1.2	0.9	1.0	0.8	1.1
Loss	%vol	2.3	2.5	2.5	2.5	2.1	2.3	2.3
Vapour Pressure	kPa	65	61	62	62	62	55	61
RON		97.9	94.4	94.2	98.1	98.1	97.5	95.8
MON		89.1	86.9	86.9	87.5	87.5	87.1	86.3
Density	kg/l	0.7475	0.7456	0.7451	0.7630	0.7650	0.7510	0.7480

Test Fuel Compositional Data Table 2

			B140	P160	P180	A160	A180	O160	O180
PIONA	(% w/w)								
Paraffins	iso normal naphthenic	Total	44.4 6.8 1.6 52.8	42.4 7.7 3.5 53.6	36.2 7.9 3.6 47.7	33.5 7.4 3.4 44.3	32.1 7.3 3.5 42.9	34.0 6.6 2.5 43.1	34.0 8.2 3.3 45.5
Olefins	iso normal naphthenic	Total	0.2 0.1 - 0.3	0.2 0.1 - 0.3	0.2 - 0.2	0.2 0.1 - 0.3	0.1 0.1 - 0.2	8.6 0.4 0.4 9.4	3.9 0.1 0.3 4.3
Aromatics			45.5	38.2	38.1	51.8	55.0	41.7	42.3
> C11			1.4	* 7.9	* 14.0	Δ 3.7	Δ1.9	# 5.8	# 7.7
GLC	(% w/w)								
Paraffins + r	naphthenes		53.9	63.0	60.8	44.9	45.5	57.8**	59.2**
Olefins			0.3	0.2	0.2	0.3	0.2	-	-
Aromatics			45.8	36.8	39.0	54.8	54.3	42.2	40.8
Sulphur	ppm		14	11	11	9	12	16	11
Benzene	% w/w		1.3	1.1	1.1	1.0	1.1	1.3	1.1
Calorific valu	ue MJ/kg		43.3	43.9	43.6	43.1	43.1	43.5	43.5
% mass Car	bon		86.9	86.8	86.5	87.5	87.5	87.0	86.9
% mass Hydrogen			13.1	13.4	13.5	12.5	12.5	13.0	13.1
Carbon:Hydrogen atomic ratio			1:1.80	1:1.84	1:1.86	1:1.70	1:1.70	1:1.78	1:1.80
Stoichiomet	ric air/fuel ratio (SAFR)	14.42	14.48	14.51	14.28	14.28	14.40	14.42
SAFR x Der	nsity		10.779	10.796	10.811	10.896	10.924	10.814	10.786

Notes:

* iso paraffins
 △ Aromatics
 # iso olefins
 ** includes olefins

VEHICLE	1	2	3	4	5	6	7	8	9	10
Capacity cm ³	1998	1392	1598	1598	1997	998	1361	1043	1597	999
Cylinders	4	4	4	4	4	4	4	4	4	4
Valves/cylinder	4	2	2	4	2	4	2	2	2	2
Compression ratio	10.5	8.5	9.2	9.1	9.1	9.5	8.8	10.1	9.0	9.0
Rated power (kW) at rpm	110	52	55	66	87	43	55	33	59	33
Rated torque (Nm) at rpm	196/ 4600	103/ 4000	125/ 3200	135/ 4000	172/ 3500	79/ 4000	109/ 4000	76/ 2800	121/ 3500	76/ 3250
Fuel system ⁽¹⁾	MPI L-JET	SPI	SPI	MPI	MPI K-JET	MPI	SPI	SPI	SPI	SPI
Catalyst type ⁽²⁾	3-way CL ADL	3-way CL	3-way CL	3-way CL	3-way CL	3-way CL	3-way CL	3-way CL	3-way CL	3-way CL
Canister	ALL CANISTERS DISCONNECTED									

Table 3	Technical Data for Test Vehicles
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Notes:

MPI = Multi-Point Injection SPI = Single-Point Injection K-JET = K-Jetronic L-JET = L-Jetronic
 CL = Closed Loop ADL = Adaptive Learning Ignition The four car "sub-set" comprised vehicles 1,2,5 and 9.

Table 410 Car Geometric Mean ECE1+225 Species Summary

FUEL PHASE	B140 ECE1+2 (mg/km)	P160 ECE1+2 (mg/km)	P180 ECE1+2 (mg/km)	A160 ECE1+2 (mg/km)	A180 ECE1+2 (mg/km)	O160 ECE1+2 (mg/km)	O180* ECE1+2 (mg/km)
PARAFFINS							
METHANE	42.2	50.3	50.1	48.3	45.4	45.0	45.3
ETHANE	13.5	14.7	15.7	12.9	12.2	16.3	16.0
PROPANE	1.5	1.6	1.3	0.8	1.3	0.7	1.8
n-BUTANE	12.4	7.5	9.0	10.3	10.3	10.0	9.8
n-PENTANE	9.7	13.9	14.6	16.4	15.3	12.2	14.3
OLEFINS							
ETHENE	44.8	51.8	53.4	51.6	48.5	53.9	53.9
PROPENE	35.5	38.9	40.7	34.6	31.5	40.0	37.6
ACETYLENE	24.8	27.1	26.6	28.9	27.2	26.4	25.6
i-BUTENE	20.1	23.5	24.1	16.8	15.1	22.6	20.9
BUTA-1,3-DIENE	5.3	6.1	6.4	5.5	5.2	6.8	6.7
ISO-PARAFFINS							
2,2,4-TRIMETHYLPENTANE	35.9	18.8	19.1	22.3	21.1	24.1	18.5
i-PENTANE	57.5	51.8	53.4	59.3	56.9	54.1	52.5
2-METHYLPENTANE	10.4	17.1	17.6	19.5	18.2	12.9	17.8
3-METHYLPENTANE	7.5	10.9	11.8	12.4	11.3	8.6	10.6
2,3-DIMETHYLPENTANE	13.4	3.8	8.1	9.5	8.7	10.0	7.5
AROMATICS							
BENZENE	34.5	31.4	33.6	38.0	36.5	32.5	31.8
TOLUENE	147.8	135.9	136.1	149.8	147.6	141.5	136.0
ETHYLBENZENE	11.7	6.7	11.3	7.0	16.0	6.4	5.5
m,p-XYLENE	61.4	57.2	55.9	64.6	67.5	56.2	58.4
o-XYLENE	19.4	19.1	18.5	18.8	21.2	17.8	18.0
ALDEHYDES							
FORMALDEHYDE	10.6	11.8	11.2	10.4	10.8	13.3	12.0
ACETALDEHYDE	5.6	5.7	5.5	5.3	5.3	6.6	6.1
ACROLEIN	0.8	0.5	0.6	0.6	0.8	0.7	1.0
CROTONALDEHYDE	0.3	0.5	0.3	0.3	0.3	0.6	0.6
BENZALDEHYDE	4.3	4.0	3.8	4.5	4.6	4.5	4.1

An offset of 0.005 has been used to calculate GM of data sets containing a zero result - see **Reference 1**, **Appendix 1**, for a description of this technique.

Table 5

4 Car Geometric Mean ECE1+2 25 Species Summary

FUEL PHASE	B140 ECE1+2 (mg/km)	P160 ECE1+2 (mg/km)	P180 ECE1+2 (mg/km)	A160 ECE1+2 (mg/km)	A180 ECE1+2 (mg/km)	O160 ECE1+2 (mg/km)	O180* ECE1+2 (mg/km)
PARAFFINS METHANE ETHANE PROPANE n-BUTANE n-PENTANE	51.7 16.4 1.5 11.4 9.3	65.4 18.6 1.3 5.1 12.9	65.9 22.0 1.0 8.0 14.4	60.8 17.3 1.1 9.7 16.2	62.4 15.9 1.2 10.0 15.5	60.1 21.7 1.0 9.9 13.1	61.1 22.9 1.8 11.2 14.5
OLEFINS ETHENE PROPENE ACETYLENE i-BUTENE BUTA-1,3-DIENE	56.3 41.9 24.8 22.2 7.1	66.0 46.7 27.1 26.5 7.5	71.0 51.1 26.6 29.3 8.1	68.5 43.4 28.9 20.1 7.6	63.9 38.7 27.2 16.5 6.5	78.3 54.0 26.4 28.5 10.4	76.6 49.5 25.6 25.6 8.3
ISO-PARAFFINS 2,2,4-TRIMETHYLPENTANE i-PENTANE 2-METHYLPENTANE 3-METHYLPENTANE 2,3-DIMETHYLPENTANE	32.3 57.1 9.5 7.5 11.9	18.1 49.0 15.9 10.6 1.2	17.8 50.5 16.5 12.0 7.1	20.4 55.7 19.3 12.6 8.7	20.5 57.6 18.3 11.7 8.2	25.0 56.6 12.9 8.2 10.2	19.7 54.1 18.2 11.4 7.5
AROMATICS BENZENE TOLUENE ETHYLBENZENE m,p-XYLENE o-XYLENE	37.0 144.2 15.2 55.5 17.6	36.7 147.4 14.9 56.8 19.3	35.4 135.3 11.8 55.7 17.4	39.5 148.6 16.9 61.7 15.4	43.2 149.5 16.1 63.8 19.8	41.4 169.0 17.2 63.9 20.2	39.6 150.1 14.4 60.3 18.2
ALDEHYDES FORMALDEHYDE ACETALDEHYDE ACROLEIN CROTONALDEHYDE BENZALDEHYDE	13.5 6.4 1.0 0.6 5.7	15.6 6.5 1.2 0.7 5.3	14.7 6.3 1.0 0.6 4.7	15.0 6.6 1.2 0.6 6.5	13.3 6.1 0.9 0.6 5.7	18.7 8.8 1.9 0.7 6.7	15.1 7.0 1.2 0.6 5.3

An offset of 0.005 has been used to calculate GM of data sets containing a zero result - see **Reference 1**, **Appendix 1**, for a description of this technique.

Table 6	4 Car Geometric Mean EUDC				
	25 Species Summary				

FUEL PHASE	B140 ECE1+2 (mg/km)	P160 ECE1+2 (mg/km)	P180 ECE1+2 (mg/km)	A160 ECE1+2 (mg/km)	A180 ECE1+2 (mg/km)	O160 ECE1+2 (mg/km)	O180* ECE1+2 (mg/km)
PARAFFINS METHANE ETHANE PROPANE n-BUTANE n-PENTANE	8.01 1.18 0.02 0.05 0.01	8.48 1.48 0.02 0.17 0.04	9.47 1.30 0.01 0.11 0.01	7.74 0.79 0.02 0.23 0.05	8.76 1.02 0.04 0.27 0.15	8.82 1.26 0.01 0.23 0.13	6.78 0.87 0.03 0.26 0.29
OLEFINS ETHENE PROPENE ACETYLENE i-BUTENE BUTA-1,3-DIENE	0.09 0.08 0.01 0.06 0.01	0.39 0.33 0.01 0.08 0.02	0.33 0.29 0.01 0.22 0.01	0.54 0.51 0.01 0.15 0.01	0.97 0.98 0.01 0.33 0.01	0.30 0.23 0.01 0.06 0.01	0.10 0.54 0.01 0.09 0.01
ISO-PARAFFINS 2,2,4-TRIMETHYLPENTANE i-PENTANE 2-METHYLPENTANE 3-METHYLPENTANE 2,3-DIMETHYLPENTANE	0.08 1.48 0.03 0.03 0.01	0.19 2.18 0.16 0.02 0.01	0.19 0.00 0.01 0.12 0.01	0.01 0.87 0.06 0.01 0.01	0.70 1.20 0.01 0.06 0.01	0.16 1.12 0.03 0.01 0.01	0.03 0.39 0.01 0.01 0.01
AROMATICS BENZENE TOLUENE ETHYLBENZENE m,p-XYLENE o-XYLENE	2.22 4.19 0.36 1.18 0.04	2.24 5.43 1.12 0.53 0.06	2.60 4.80 1.60 1.84 0.01	3.56 2.37 2.24 1.55 0.01	3.46 5.32 1.85 2.32 0.02	2.22 4.16 1.05 1.45 0.03	1.45 2.45 1.43 1.18 0.01
ALDEHYDES FORMALDEHYDE ACETALDEHYDE ACROLEIN CROTONALDEHYDE BENZALDEHYDE	0.66 0.43 0.01 0.04 0.14	0.66 0.22 0.01 0.03 0.10	0.70 0.20 0.01 0.01 0.10	0.70 0.19 0.01 0.01 0.28	0.67 0.36 0.01 0.01 0.25	0.97 0.32 0.01 0.01 0.12	0.73 0.17 0.01 0.01 0.21

An offset of 0.005 has been used to calculate GM of data sets containing a zero result - see **Reference 1**, **Appendix 1**, for a description of this technique.

Table 7

FUEL	B140 F		P16	P160		P180		A160		A180		O160		O180*	
	Emissions	Fuel													
	mg/кm	%W/W	mg/ĸm	%W/W	mg/ĸm	%W/W	mg/ĸm	%W/W	mg/кm	%W/W	mg/ĸm	%W/W	mg/кm	%W/W	
METHANE	44.20	0.00	55.33	0.00	53.24	0.00	51.98	0.00	48.57	0.00	47.94	0.00	48.15	0.00	
ETHANE	14.13	0.00	15.78	0.00	16.87	0.00	13.80	0.00	12.90	0.00	17.37	0.00	17.18	0.00	
ETHENE	50.70	0.00	59.75	0.00	61.49	0.00	58.06	0.00	54.46	0.00	60.96	0.00	61.27	0.00	
PROPANE	1.71	0.06	1.78	0.85	1.70	0.07	1.44	0.06	1.47	0.06	1.40	0.00	1.85	0.06	
PROPENE	39.55	0.00	44.36	0.00	46.06	0.00	38.25	0.00	35.15	0.00	44.08	0.03	42.17	0.00	
	7.71	1.07	0.01	0.85	5.54	0.89	0.25	0.82	5.73	0.84	5.43	0.62	5.23	0.85	
	29.31	0.00	39.95	1.00	34.24	0.00	35.02	1 70	32.82	1.00	32.14	0.00	31.03	0.00	
	14.19	2.52	2.91	0.00	10.05	0.00	2.08	0.00	2.99	0.00	3 71	0.00	3.64	0.00	
trans_BUT_2_ENE	3.89	0.00	4 11	0.00	4.00	0.00	3.56	0.00	3.45	0.00	4 29	0.00	3.87	0.00	
BUT-1-ENE	4.84	0.00	5.72	0.00	5.71	0.00	5.47	0.00	4.81	0.00	5.84	0.00	5.79	0.00	
i-BLITENE	21.97	0.02	26.36	0.01	26.93	0.02	18.36	0.01	16.32	0.01	24.41	0.02	22.88	0.01	
2 2-DIMETHYL PROPANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
cis-BUT-2-ENE	2.82	0.01	2.78	0.02	3.05	0.03	2.69	0.02	2.39	0.02	3.20	0.08	2.36	0.02	
CYCLOPENTANE	0.60	0.20	1.37	0.45	1.45	0.46	1.51	0.01	1.45	0.44	0.82	0.30	1.49	0.48	
i-PENTANE	64.74	13.85	62.06	11.69	60.49	11.86	67.29	11.26	62.35	11.57	60.20	10.88	58.73	12.09	
n-PENTANE	10.75	2.05	16.72	3.14	16.42	3.16	18.41	3.04	16.53	3.09	13.41	2.29	15.76	3.26	
BUTA-1,2,-DIENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
PROPYNE	3.68	0.00	4.01	0.00	4.36	0.00	3.50	0.00	3.14	0.00	4.24	0.00	3.96	0.00	
BUTA-1,3,-DIENE	6.05	0.00	7.10	0.00	7.35	0.00	6.16	0.00	5.78	0.00	7.74	0.00	7.32	0.00	
3-METHYLBUT-1-ENE	0.08	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.04	0.01	0.00	0.00	0.00	0.01	
trans-PENT-2-ENE	0.12	0.03	0.00	0.03	0.00	0.03	0.00	0.02	0.06	0.02	0.00	0.05	0.00	0.02	
2-METHYLBUT-2-ENE	3.48	0.05	3.43	0.04	5.01	0.04	3.16	0.03	2.43	0.03	3.72	0.08	3.46	0.04	
PENT-1-ENE	0.29	0.02	0.29	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.04	
2-METHYLBUT-1-ENE	1.37	0.03	1.13	0.02	1.34	0.02	1.21	0.03	1.01	0.02	1.26	0.04	1.53	0.02	
cis-PENT-2-ENE	0.06	0.02	0.00	0.01	0.18	0.01	0.00	0.01	0.06	0.01	0.00	0.02	0.00	0.01	
2,2 DIMETHYLBUTANE/ METHYLCYCLOPENTANE	6.19	1.44	14.45	3.49	14.55	3.47	14.80	3.41	13.88	3.43	9.29	2.29	12.56	3.63	
CYCLOHEXANE	2.22	0.40	4.98	1.11	5.44	1.07	5.30	1.08	4.86	1.08	2.77	0.74	4.53	1.15	
BUT-2-YNE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
2,3 DIMETHYLBUTANE	5.91	0.88	7.46	1.33	7.25	1.33	7.79	1.31	7.49	2.12	5.69	1.36	7.26	2.23	
2-METHYLPENTANE	11.68	2.13	19.68	3.78	19.61	3.75	21.92	3.69	19.92	3.72	14.01	2.87	19.73	3.93	
3-METHYLPENTANE	8.26	1.37	12.48	2.32	12.96	2.34	13.83	2.28	12.31	2.29	9.24	1.76	11.79	2.43	
BUT-1-YNE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	7.03	1.27	11.50	1.98	11.75	1.95	12.17	1.94	11.31	1.95	8.83	1.61	11.03	2.07	
ISOPRENE	2.49	0.00	2.50	0.00	2.89	0.00	2.26	0.00	2.08	0.00	5.13	0.00	4.43	0.02	
3-METHYLPENT-1-ENE	0.00	0.00	0.17	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	
	0.00	1.02	2.65	0.02	2.47	0.00	3.13	0.01	2.93	0.01	2.27	1.07	2.41	0.01	
	4.34	0.09	2.05	0.73	2.47	0.07	0.00	0.71	2.05	0.71	0.00	0.19	0.00	0.17	
2 3 DIMETHVI PENTANE	14.61	3.43	8.28	1.69	8.93	1.64	10.53	1.65	9.37	1.65	10.88	2.39	8.33	1 74	
3 METHVI HEYANE	3.68	0.79	3.38	0.65	3.20	0.63	3.38	0.63	3.15	0.64	3.01	0.75	3.20	0.68	
2 METHYLHEXANE	3.53	0.57	2.84	0.48	2.81	0.47	2.92	0.48	3.02	0.48	2.61	0.57	2.73	0.53	
BENZENE	37.17	1.25	34.89	1.13	36.74	1.11	41.25	1.04	39.31	1.05	35.37	1.32	34.36	1.08	
2.2.4-TRIMETHYLPENTANE	38.88	8.21	21.37	3.81	21.23	3.70	24.74	3.73	22.57	3.73	26.20	5.88	20.29	4.01	
2.4 DIMETHYLHEXANE	2.49	0.00	1.00	0.00	1.24	0.00	1.51	0.00	1.37	0.00	1.32	0.00	1.17	0.00	
2.2.3-TRIMETHYLPENTANE	2.49	0.00	1.00	0.00	1.43	0.00	0.95	0.00	1.80	0.00	1.44	0.00	1.28	0.00	
2.3 DIMETHYLHEXANE	2.81	0.00	1.36	0.00	1.42	0.00	1.79	0.00	1.70	0.00	2.48	0.00	1.66	0.00	
2,3,3-TRIMETHYLPENTANE	7.43	1.47	3.59	0.00	3.85	0.00	4.52	0.29	3.89	0.45	4.51	1.08	3.88	0.58	
3-METHYLHEPTANE	1.26	0.00	1.04	0.00	1.03	0.00	1.20	0.00	1.36	0.00	0.78	0.00	1.20	0.00	
2-METHYLHEPTANE	1.33	0.00	1.01	0.00	0.92	0.00	1.33	0.00	1.30	0.00	0.68	0.00	1.25	0.00	
TOLUENE	160.06	21.55	153.32	18.00	150.33	17.92	164.87	17.00	160.24	17.03	152.69	19.26	148.62	19.11	
ETHYLBENZENE	14.31	1.97	12.43	1.55	16.43	1.69	13.44	1.65	17.21	1.64	12.19	1.83	11.38	1.73	
m,p-XYLENE	66.20	9.80	64.46	8.00	61.09	8.59	72.02	8.27	72.64	8.19	61.06	9.13	63.64	8.81	
o-XYLENE	21.17	3.26	21.56	2.61	20.48	2.86	22.11	2.89	22.72	2.75	19.39	3.05	19.69	2.93	
1,3,5 TRIMETHYLBENZENE	3.49	1.01	2.77	0.76	3.54	0.88	3.94	2.40	4.28	1.43	2.89	0.95	2.47	0.90	
STYRENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
I-PROPYLBENZENE	5.61	0.05	6.06	0.00	7.30	0.05	14.47	0.22	8.71	0.08	4.75	0.05	5.35	0.05	
m,p ETHYLTOLUENE	8.70	0.43	11.07	0.00	9.55	0.37	24.44	1.88	12.74	0.99	8.02	0.41	7.95	0.38	
n-PROPYLBENZENE	8.25	0.34	8.36	0.25	7.42	0.29	19.27	1.23	10.63	0.52	6.51	0.34	7.24	0.33	
o-ETHYLTOLUENE	4.58	0.00	9.04	0.00	5.23	0.00	19.72	0.00	15.15	0.00	6.42	0.00	3.08	0.00	

Hydrocarbon Speciation Results - Arithmetic Means over ECE1+2 Cycles

Table 7 (cont.) Hydrocarbon Speciation Results - Arithmetic Means over ECE1+2 Cycles

FUE	B140		P160		P180		A160		Δ180		0160		O180*	
IULL								i Gual		mingiona Eucl			010	
	mg/km	%w/w	mg/km	%w/w	mg/km	%w/w	mg/km	%w/w	mg/km	%w/w	mg/km	%w/w	mg/km	%w/w
ALDEHYDES AND KETONES														
FORMALDEHYDE	12.24	0.00	13.71	0.00	13.28	0.00	12.09	0.00	12.39	0.00	15.08	0.00	13.91	0.00
ACETALDEHYDE	6.11	0.00	6.20	0.00	6.15	0.00	5.75	0.00	5.69	0.00	7.09	0.00	6.63	0.00
ACROLEIN	0.93	0.00	1.14	0.00	1.00	0.00	1.00	0.00	0.91	0.00	1.37	0.00	1.27	0.00
ACETONE	5.43	0.00	4.69	0.00	5.06	0.00	4.10	0.00	5.10	0.00	5.11	0.00	5.23	0.00
PROPIONALDEHYDE	1.09	0.00	1.05	0.00	1.11	0.00	1.00	0.00	0.91	0.00	1.12	0.00	1.24	0.00
CROTONALDEHYDE	0.50	0.00	0.59	0.00	0.51	0.00	0.42	0.00	0.45	0.00	0.59	0.00	0.62	0.00
BUTYRALDEHYDE*	0.55	0.00	0.58	0.00	0.61	0.00	0.62	0.00	0.57	0.00	0.86	0.00	0.82	0.00
BENZALDEHYDE	5.13	0.00	4.75	0.00	4.60	0.00	5.39	0.00	5.53	0.00	5.38	0.00	4.93	0.00
ACETOPHENONE	0.02	0.00	0.02	0.00	0.04	0.00	0.10	0.00	0.00	0.00	0.04	0.00	0.14	0.00
p-TOLUALDEHYDE	0.56	0.00	0.45	0.00	1.00	0.00	0.70	0.00	0.72	0.00	0.63	0.00	0.51	0.00
AIR TOXICS														
FORMALDEHYDE	12.24	0.00	13.71	0.00	13.28		12.09	1	12.39		15.08		13.81	
ACETALDEHYDE	6.11	0.00	6.20	0.00	6.15		5.75		5.69		7.09		6.61	
BUTA-1,3-DIENE	6.05	0.00	7.10	0.00	7.35		6.16		5.78		7.74		7.30	
BENZENE	37.17	1.25	34.89	1.13	36.74		41.25	1	39.31		35.37		34.51	
								1						
TOTAL AIR TOXICS	61.53		61.91		63.56		65.23	1	63.16		65.26		62.19	
								1						
TOTAL HC	786.16		816.60		811.40		880.36		812.78		774.84		771.57	
TOTAL PARAFFINS	319.89		322.11		323.17		345.46		321.64		300.25		307.83	
TOTAL OLEFINS	173.93		205.45		206.86		180.65		166.85		200.69		194.31	
TOTAL AROMATICS	292.35		289.05		281.37		354.26		324.30		273.90		269.43	
% PARAFFINS	40.69		39.45		39.83		39.24		39.57		38.75		39.90	
% OLEFINS	22.12	1	25.16		25.49	1	20.52		20.53	[25.90	ſ	25.18	
% AROMATICS	37.19		35.40		34.68		40.24		39.90	[35.35	[34.92	
TOTAL	100.00		100.00		100.00		100.00		100.00	[100.00	[100.00	

Table 8

Ozone Forming Potential Factors

	MIR	MOR	Derwent	IVL -norm	IVL-high
CO	0.051	0.034	4	4	3.2
Formaldehyde	9.5	2.58	40	26.1	37.9
2-Pronenal	0.07	2.44	55 120	82.3	01.5 82.7
Propanone	0.856	0.486	20	12.4	16
Propanal	5.34	2.01	60	17	65.2
2-Butenal	11	3.96			
Methacrolein	11	3.9			
Benzaldehyde	0	0	-35		
Acetophenone	Ū	Ŭ	00		
0-Tolualdehyde	0	0			
m+p Tolualdehyde	0	0			
Hexanal+2,5-Dimetnyibenzaidenyde					
Methane	0.01	0.006	1		
Ethane	0.22	0.125	10	12.6	12.1
Ethene	8.13	3.22	100	100	100
Propane	0.563	0.32	40	50.3	51.8
Propene	11.7	4.27	105	59.9	106
Acetylene	0.636	0.648	30	36.8	38.9 29.1
n-Butane	1.14	0.648	40	46.7	48.5
Propadiene	17.8	6.38	-	-	
trans-But-2-ene	10.5	3.82	100	43.6	102.1
But-1-ene	9.05	3.37	95	49.5	98.3
I-Butene	5.97	1.88	65 100	58	64.8 102.1
Cyclopentane	1.18	0.671	50	45.0	102.1
i-Pentane	1.15	0.653	30	31.4	34.5
n-Pentane	1.15	0.653	40	29.8	38.7
Buta-1,2-diene					
Propyne Dute 1.2 diana	1.74	2.91	105		
3-Methylbut-1-ene	7 47	2.83	90		
trans-Pent-2-ene	8.61	3.19	95	38.1	96.5
2-Methylbut-2-ene	4.89	1.93	80	45.3	78.4
Pent-1-ene	7.47	2.83	70	42.4	83.3
2-Methylbut-1-ene	5.02	1.65	80	18.1	71.7
2 2-Dimethylbutane	0.01	0.546	95	30.1	96.5
Methylcyclopentane	1.18	0.671	50		
Cyclohexane	1.18	0.671	25		
But-2-yne	6.04	2.25			
2,3-Dimethylbutane	1.15	0.656	40	50.0	50 F
2-Menthylpentane	1.15.	0.656	50 45	52.9 40.9	20.5 45.7
But-1-vne	6.04	2.25	45	40.5	43.7
n-Hexane	1.15	0.658	40	45.2	49.5
Cyclopentadiene	14.6	5.3			
Isoprene	15.8	5.1	100	58.3	76.8
3-Menthylpent-1-ene	6.42	2.47	80		
2.3 Dimethylbut-1-ene	1.51	2.11	50		
trans-Hex-3-ene	7.37	2.77	80		
2 - Methylpent-2-ene	4.28	1.67	80		
cis-3-menthylpent-2-ene	4.28	1.67	80		
4-Menthylpent-1-ene trans-2 Monthylpent-2-one	5.42	2.47	80		
trans-Hex-2-ene	7.37	2.77	80		
Cyclohexene/2-Ethylbut-1-ene/2,3- dismethylbut-2-ene	-				
2-Methylpent-1-ene	4.38	1.48			
Hex-1-ene	6.42	2.47	50		
2 4-Dimethylpentane	1 16	0.658	55		
Methylcyclohexane	1.18	0.571	35	50.2	58
2,3-Dimethylpentane	1.16	0.658	50		
3-Methylhexane	1.16	0.658	50		
2-Methylhexane	1.16	0.658	50		
n-Hentane	1 16	0.658	55	51.8	59.2
Benzene	0.212	0.126	20	40.2	31.8
2,2,4-Trimethylpentane	1.02	0.577	-	-	
2,4-Dimethylhexane	1.16	0.661			8
2,2,3 - I rimethylpentane	1 16	0.66			
2,3,4-11inethylpenane	1.10	0.66			
2,3,3-Trimethylpentane	1.02	0.577			
4-Methylheptane	1.16	0.66	45		
3-Methylheptane	1.16	0.66	4-	45 -	50.1
∠-ivieuriyineptane	1.16	0.66	45 55	45.7 47	52.4 56.5
Ethylbenzene	1.09	-0.239	60	50 4	62 1
m,p-Xylene	8.8	2.37	95	47.3	84
o-Xylene	8.8	2.37	65	16.7	59.8
i-Propylbenzene	1.72	-0.029	55	52.3	59.4
Stylene 1.3.5-Trymethylbenzene	3.95	0.606	115	33	08.0
m.p-Ethyltoluene	7.91	2.17	77.5	42.2	70.5
n-Propylbenzene	1.72	-0.029	50	45.4	53.1
o-Ethyltoluene	7.91	2.17	65	40.8	63.7
1,2,4-1 rimethylbenzene	7.91	2.17	120	33	93.8
1,2,3-111116(1))DC112C11C	1.31	<u> </u>	110	23.2	00.0

APPENDIX 2







Figure 2 10 Car Geometric Mean ECE1+2



Figure 3 4 Car Geometric Mean ECE1+2



Figure 4 4 Car Geometric Mean EUDC

Figure 5 Fuel v Exhaust HC Composition - 1160 Fuels 10 car arithmetic mean ECE1+2



% w/w HC in the Fuel

Figure 6 Fuel v Exhaust HC Composition - H180 Fuels 10 car arithmetic mean ECE1+2

% w/w HC in the Fuel

% w/w HC in the Exhaust Gas

% w/w HC in the Exhaust Gas





30



Figure 9 Air-toxics emissions - All Fuels 4 car geometric mean





 Figure 10
 Speciated emissions v car type

 Arithmetic mean emissions over ECE1+2 cycle for all test fuels

 Figure 11
 Total HC emissions v car type

 Arithmetic mean emissions over ECE1+2 cycle for all test fuels



The figures above each bar represent the contribution of the species as a percentage of THC

Figure 12 Speciated emissions v car type (the variation of speciated arithmetic mean emissions for each car and all fuels - ECE1+2)



Figure 13 Ozone reactivity ECE1+2, 10 Car Arithmetic Mean



Note: Harwell, IVL Norm and IVL High results x 10,000