Assessment of primary NO$_2$ emissions, hydrocarbon speciation and particulate sizing on a range of road vehicles

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ASSESSMENT OF PRIMARY NO₂ EMISSIONS, HYDROCARBON SPECIATION AND PARTICULATE SIZING ON A RANGE OF ROAD VEHICLES

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EXECUTIVE SUMMARY

Road transport emissions are the source of significant proportions of the air pollutants regulated by UK and European standards, though in most cases there is no direct correspondence between the compounds controlled by exhaust emission legislation and those controlled by air quality standards. Emission limits are set for carbon monoxide (CO), total hydrocarbons (THC), total oxides of nitrogen (NO_X) and, for diesel vehicles, total particulates (PM). The corresponding air quality standards concern CO, nitrogen dioxide (NO_2, one of the two gases, with nitric oxide (NO), which make up the NO_X emissions), benzene and 1,3-butadiene (two compounds found in THC) and PM_{10} (the fraction of PM with an aerodynamic diameter below 10 μm). Except for CO, direct measurement of these specific compounds is rare during vehicle emission studies.

The main objective of this research was to determine the proportion of NO_X emitted as NO_2 from a range of typical vehicles of different types and with different levels of emission control technology. The main issue to be addressed was the extent to which primary NO_2 emissions might influence the airborne concentrations of NO_2 near to roads. It is generally considered that most NO_X is emitted as NO and that this is converted to NO_2 by oxidation in the atmosphere; when this phenomenon is considered on a small scale, close to roads, the principal oxidation reaction is with ozone (O_3). Other reactions proceed at rates too slow for them to be important on this scale - the emissions are dispersed and diluted before any appreciable conversion is possible. The reaction with O_3, however, is rapid and proceeds until either the ozone is depleted or all NO is converted to NO_2. Near to traffic, there is usually an excess of NO in the air, so the limit to its oxidation is most often the depletion of available O_3. Under this assumption, controls aimed to reduce NO_X emissions might have only a small impact on NO_2 concentrations as it is not the availability of NO_X that is the limiting factor. If, though, a significant proportion of the NO_X emissions is NO_2, it will continue to add to the roadside concentration irrespective of the presence of O_3. Then, reducing NO_X emissions, provided that the reduction applies to both the NO and NO_2 constituents, will contribute to the control of NO_2 concentrations near to roads.

A second issue that was studied was the effect of the sampling and analytical technique on the observed emission rates of NO_2. In conventional tests, measurements may be made on the raw exhaust (usual for heavy duty diesel engines), or on a diluted sample (usual for light duty vehicles); the sample may be taken via a heated line to a heated analyser or via a condenser to remove water vapour to an unheated analyser. Some aspects of these procedures have the potential to promote or retard the oxidation of NO to NO_2 during sampling. Diluting the sample is likely to introduce some ozone into the exhaust, as a trace at least is present in most air. This is likely to oxidise some NO. On the other hand, the dilution process will cool the sample and reduce the concentration of NO, and both will have the effect of slowing down its reaction with both O_3 and oxygen (O_2). The gas temperature will also be influenced by the choice between a heated or unheated sampling system: in the former case it is likely that the oxidation of NO will proceed more rapidly. As well as these sampling questions, the instrument normally used to measure NO_X emissions may also cause problems. The conventional chemiluminescence analyser measures the NO by recording the intensity of the luminescence produced when it reacts with ozone. It can also measure NO_X by the same means, after the NO_2 in the NO_X has been reduced to NO over a heated catalyst. NO_2 is then determined by subtracting the NO from the NO_X. Wherever a small value is determined as the difference between two large values, there is potential for error. For that reason, the NO and NO2 emissions were also measured using the Fourier transfer infra red technique. This method, which is based on the absorption of infra red radiation by different molecules at characteristic wavelengths, is able directly to measure the concentrations of the two compounds.

Emission testing is expensive, and it was cost-effective to supplement the NO_X measurement programme with measurements of some other significant, but unregulated (in exhaust emission standards), compounds. Those that were chosen were a range of hydrocarbon species and the size distributions of the particulate emissions.

As for NO_2, the sampling and analysis of exhaust particles can also influence the results obtained. Most of the emissions are sub-micron particles existing in two modes: the "nuclei" mode consists of individual particles generally smaller than 50 nm, and the "accumulation" mode of agglomerations of 15 to 20 particles, mainly in the 50 to 100 nm range. During sampling, particles may be generated by or deposited on the lines used to convey the gas. Dilution of the sample may lead to the formation of nuclei mode particles from semi-volatile exhaust constituents, and if the dilution is substantially different from that occurring in the atmosphere, large discrepancies can occur. Three methods of particle measurement were included: average total mass emissions were determined by collection on filters and weighing (the standard method prescribed in emission legislation), PM_{10} mass emissions were measured continuously using a tapered element oscillating microbalance (TEOM), and average size distributions (by number of particles) were measured using an electrical low pressure impactor (ELPI). The filter and TEOM measurements were made on raw and diluted exhaust while the ELPI was used only on the diluted sample (concentrations in the raw exhaust were too high for the instrument).

Hydrocarbon (and other organic) species were analysed by gas chromatography. Two systems were used, one configured for low molecular weight compounds (C_1 to C_4) and one for higher molecular weight compounds (C_4 to C_{12}). Both were equipped with flame ionisation detectors. The C_4 overlap of the two instruments allowed for a check on the consistency between them. In all, 170 organic compounds were measured, though the data analysis has concentrated only on 17 of the most important.

All of the tests were carried out on a sample of 18 vehicles chosen to cover most of the types currently in use. Vehicles were classified as cars. light goods vehicles (LGV), heavy goods vehicles (HGV) and buses. The cars were further subdivided according to their engine capacity into 3 size groups. For each vehicle type, one example was tested at each of three levels of emission control standard, which were first introduced in 1983 (pre Euro 1, or Euro 0), 1993 (Euro 1) and 1996 (Euro 2). All of the cars had petrol engines and the Euro 1 and Euro 2 examples were fitted with three-way catalysts. All other vehicles had diesel engines.

Tests were carried out on each vehicle type using the appropriate legislative test and a number of more realistic cycles. Light duty vehicles were tested over cycles simulating congested urban, urban, suburban, rural and motorway driving. Heavy duty vehicles were tested over cycles simulating bus operation and more general HGV operation. Each heavy duty cycle could be further subdivided: the bus cycle into inner and outer London phases, and the HGV cycle into urban, suburban and motorway phases. For medium size petrol cars, additional tests were carried out with cold starts at three ambient temperatures (-7, 10 and 25$^\mathrm{o}$C), using the legislative test cycle, and hot starts at the same three temperatures using the congested urban cycle. Single batches of diesel and petrol were used for all tests to avoid the complication of possible effects of fuel composition. Basic physical and compositional properties of the fuels were measured.

The measured emission data, for NO_2, the NO_2/NO_X ratio, PM mass and size distribution and selected organic compounds were examined in relation to each of the vehicle-related variables - the vehicle type, size, fuel, emission standard and operation type, and for NO_X and PM, also in relation to the sampling and analytical method used. The analysis revealed a number of systematic and statistically significant variations, and many more relationships that were unclear and statistically insignificant. For example, there was no significant difference between emissions of NO_2 from HGVs in the three different legislative classes, while NO_2 emissions from Euro 0 cars were significantly different from those in the Euro 1 and Euro 2 classes; total PM mass emissions from HGVs reduced significantly from Euro 0 to Euro 1 and again from Euro 1 to Euro 2; particle numbers from cars across the whole

size range increased as the average speed of the test cycle reduced; emissions of almost all hydrocarbon species were very much higher from Euro 0 cars than Euro 1 and 2, etc.

The effect of primary NO_2 emissions on ambient roadside concentrations was evaluated using two case studies, one used modelled traffic data for an area of central Leicester, and the second traffic data recorded on part of the M25 motorway. The procedure followed for each example was very similar. Initially, emission functions were derived for each of the vehicle categories represented in the measurement programme. These gave the rate of emission (in g/km) for both NO_X and NO_2 as a function of the average vehicle speed (in km/h). Statistically significant and systematic functions were derived using a quadratic curve fitting routine. Next, the functions for individual vehicle types were combined to produce traffic weighted average functions for each main vehicle class (car, LGV, HGV, bus). This was necessary because traffic data, either from models of observations are not able to categorize the traffic acoording to some of the important variables influencing emissions, such as the Euro standard or engine type (petrol or diesel, for light duty vehicles). The weighting was carried out making use of national statistics from a number of sources. These weighted emission functions were used to estimate rates of emission (in g/m.s) for each road link in the networks under consideration.

The estimated emission rates were input to a pollution dispersion model together with appropriate meteorological data and locational data for the road links, and the dispersion and transformation of the emissions was simulated in two ways: first it was assumed that all of the NO_X emissions were NO, in which case the formation of NO_2 was limited by the atmospheric chemical processes; and secondly the NO_X was assumed to be a mixture of NO and NO_2, in the proportions indicated by the emission estimates, in which case the airborne NO_2 concentration resulted from the dispersion and oxidation of NO together with the dispersion of the NO_2 fraction of the NO_X. The effect, then, of the primary NO_2 emissions was indicated by the difference in the results obtained by the two methods. For the urban example, differences up to approximately 30% were calculated (i.e. NO_2 concentrations nearest to the road network were up to 30% higher if an allowance was made for primary NO_2 emissions). Differences for the motorway example were lower, but still appreciable, at around 15%.

ASSESSMENT OF PRIMARY NO₂ EMISSIONS, HYDROCARBON SPECIATION AND PARTICULATE SIZING ON A RANGE OF ROAD VEHICLES

ABSTRACT

As well as the pollutants regulated by emission standards (carbon monoxide, total hydrocarbons, total oxides of nitrogen and total particulates), road vehicle exhaust contains many other compounds that may be of environmental significance. Subsets of the regulated pollutants, i.e nitrogen dioxide, benzene, 1,3-butadiene and PM_{10} are controlled under national and European air quality standards, but their concentrations are rarely measured in emission test programmes. This work was carried out primarily to determine the amount of nitrogen dioxide present in the total oxides of nitrogen emissions from a range of vehicle types, and to evaluate the importance of primary nitrogen dioxide emissions in influencing atmospheric concentrations near to roads. A modelling exercise showed that nitrogen dioxide concentrations might be underestimated by as much as 30% if the primary emissions were ignored. In addition, the opportunity was taken to measure a variety of other unregulated emissions including many of the organic compounds comprising the total hydrocarbon emissions and the size distributions of the particulate emissions. Rates of emission of a selection of these pollutants were examined in relation to vehicle type, fuel, technology and operating conditions. The influence of the method of sampling and analysis for nitrogen dioxide and particulates by size was also studied.

1 INTRODUCTION

Motor vehicles emit a wide range of pollutants to the atmosphere, mainly as by-products of fuel combustion. The amounts of pollution emitted depend on a variety of factors, including the type of vehicle and its mechanical condition, the mode of operation of the vehicle, the local weather conditions, and the type and condition of any pollution control measures fitted to the vehicle. Several of the primary pollutants (i.e. those emitted directly from the exhaust) are controlled by legislation, and significant reductions in pollutant levels have been achieved over the past 20 years as a result of progressive tightening of the emission limits allowed for new vehicle models.

In relation to air quality in the UK, the pollutants that are currently causing most concern are particles (currently regulated in air quality standards as PM_{10}, i.e. particles with an aerodynamic diameter below 10 μm) and nitrogen dioxide (NO_2). There is evidence that, in some areas, concentrations of these pollutants regularly exceed air quality standards. In addition, while large numbers of hydrocarbon species are present in vehicle exhaust, vehicle emission regulations only consider total hydrocarbons, and air quality standards exist for only two species: benzene and 1,3-butadiene.

Road vehicles emit both nitric oxide (NO) and NO_2. Collectively, these two gases are known as NO_x. Total NO_x emissions are regulated in vehicle type approval. Most of the NO_x in vehicle exhaust is present as NO. Airborne NO_2 is usually formed by the reaction of NO with ozone (O_3) in the atmosphere, and roadside NO_2 levels are generally limited by the local concentration of O_3 rather than the emission of NO from vehicles. Therefore, it is generally believed that any changes in emissions of NO_x from vehicles, would have little effect on the concentrations of atmospheric NO_2. However, it is also known that a proportion of NO_2 is emitted directly by vehicles. If these emissions were significant then controlling primary emissions of NO_2 would help to reduce NO_2 concentrations. The problem remains, however, to determine whether these emissions are significant for a broad range of vehicle types and operating conditions, and whether suitable methods of detecting these emissions can be found. A greater understanding of the relative contribution of primary NO_2 to roadside

concentrations would also allow improvements to the accuracy of both emission and dispersion models.

The mass of particles emitted by road vehicles has reduced steadily over the past 20 years, following the development and application of new technologies. Current and future legislation is reducing particulate mass emissions. However, it is generally recognised that mass-based standards alone are not ideal in terms of minimising the risks to health. The *size* of particles determines how deep they penetrate into the human respiratory system and where they are deposited. Ultrafine particles (those with a diameter of less than 0.1 μm) can penetrate into the alveolar region, whereas coarser particles are likely to be deposited in the nose and throat. Also, smaller, lighter particles remain in the air for longer and are more likely to be inhaled. More information is needed on the distribution of particle size in order to inform possible future legislative action.

Total emissions of hydrocarbons are controlled in vehicle type approval by legislative standards, although, as indicated above, the individual compounds that comprise the broad range of species emitted are not determined at present. Some of these individual compounds are potentially harmful to health, and clearly more information about the range and concentrations of hydrocarbon species is required to better inform the direction of future regulation.

As a response to these issues, TRL was commissioned by the Highways Agency, the Department of Transport, Local Government and the Regions, and the Department of Trade and Industry, to carry out a programme of study of vehicle emissions. In particular, the study was commissioned to establish the quantity and relative contribution of primary nitrogen dioxide emissions from urban traffic to those measured at the roadside. The study included an assessment of cold start and transient vehicle driving cycles as well as an evaluation of sampling and analysis test procedures. In addition, the opportunity was taken to include the measurement and analysis of particulate emissions to determine size distributions and hydrocarbon emissions to determine the different species present.

In summary, the objectives of the study are to:

- Establish the quantity of primary NO_2 emissions emitted by road vehicles, and estimate the contribution of primary NO_2 to the total measured at urban roadside locations.

- Determine whether any discrepancies exist between the NO_2 levels emitted directly from the exhaust system and that measured using sampling methods based on diluting the exhaust.

- Determine the sensitivity of NO_2 emissions to cold start and transient vehicle driving cycles.

- Determine the distribution of particulate size and the relative contribution of different hydrocarbon species to total hydrocarbon emissions for a specified range of vehicle types and operating conditions.

This report describes the results of this study. It provides some further details regarding the background to the issues raised and the pollutants being examined. It describes the experimental design used, the measurements taken and the results obtained.

2 BACKGROUND

Oxides of nitrogen (NO_x) are produced as a result of fuel combustion processes that occur in the engine in the presence of air. The two NO_x gases are nitric oxide (NO) and nitrogen dioxide (NO_2). Nitric oxide is a gas that is produced naturally in the human respiratory system and is not harmful to health at the concentrations typically found in the atmosphere. In contrast, nitrogen dioxide is associated with a range of environmental and health problems. Nitrogen dioxide in the atmosphere is converted to nitric acid over a period of approximately 24 hours. It is removed from the atmosphere by two processes: direct deposition to the ground or in the form of acid rain. In either case, the nitric acid contributes to the acid contamination of the ground.

The combustion of fossil fuels is by far the biggest source of NO_x gases and road traffic is responsible for almost half of all NO_x emissions in Europe (European Commission, 2000).

2.1.1 Effects of NO₂ on health

In very high concentrations, such as those associated with industrial accidents, NO_2 can be extremely hazardous to health, and in some cases has been known to be responsible for fatalities. However, at the much lower concentrations associated with pollution episodes in urban areas, the effects of this pollutant are much less severe. Studies have indicated that NO_2 may be responsible for both acute and chronic effects on human health, with asthma sufferers being particularly susceptible (Orehek et al, 1976). Exposure to NO_2 in the range 5 ppm – 10 ppm has been shown to have detrimental effects on lung resistance to infection (Henry et al, 1969, Henry et al 1970, Goldstein et al 1973), but the effects of long term exposure to relatively low levels of NO_2 are less clear.

The importance of NO_2 as a pollutant is further augmented by the fact that it is involved in the formation of low-level ozone. Low-level ozone is associated with smog episodes which can lead to eye irritation and respiratory problems.

One of the mechanisms responsible for the formation of ground level ozone relies on NO_2 being present in the atmosphere. NO_2 absorbs energy from sunlight and breaks down to form NO and an oxygen free-radical, as shown in Equation 1.

$$NO_2 + h\nu \rightarrow NO + O\text{X} \qquad (1)$$

The free radical oxygen atom can then react with an oxygen molecule to form molecular ozone.

$$O\text{X} + O_2 \rightarrow O_3 \qquad (2)$$

2.1.2 Primary and secondary NO₂

Chemical reactions that occur between atmospheric nitrogen (N_2) and oxygen (O_2) in the internal combustion engines of road vehicles lead to the formation of NO_x gases. These reactions tend to result in high concentrations of NO being formed, but NO_2 and other gases are also directly formed during these processes. Reaction mechanisms for the formation of NO in the engine combustion chamber are given by the extended Zeldovich mechanism depicted below in Equations 3, 4, and 5.

$$N_2 + O \rightarrow NO + N \qquad (3)$$

$$N + O_2 \rightarrow NO + O \qquad (4)$$

$$N + OH \rightarrow NO + H \qquad (5)$$

NO_2 exists as a primary pollutant and a secondary pollutant due to the different mechanisms by which it is formed. Primary NO_2 emissions occur as a result of direct chemical reactions between nitrogen and oxygen in the combustion chamber of internal combustion engines. Secondary NO_2 emissions are the result of chemical reactions between nitric oxide produced in the fuel combustion process, and atmospheric ozone.

It should be noted that there are a number of other reaction mechanisms that are responsible for the generation of secondary NO_2, including reactions between partially oxidised organic (e.g. alkyl per-oxy) radicals and NO. An example of such a reaction is given by Equations 6 and 7.

$$RX + O_2 + M \rightarrow RO_2X + M \qquad (6)$$

$$RO_2X + NO \rightarrow NO_2 + ROX \qquad (7)$$
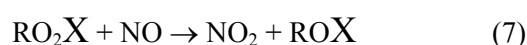
where R = alkyl group (e.g. CH_3 or CH_3CH_2) and M = another molecule

Roadside concentrations of NO_2 consist of both primary and secondary NO_2, but the majority is thought to consist of secondary NO_2. Roadside levels of NO_2 (i.e. NO_2 derived from NO) are generally limited by the local concentration of O_3 present rather than the emission of NO, therefore, it is generally believed that changes in NO_x emissions from traffic, which consists mainly of NO, would have a limited effect on NO_2 concentrations. However, the relative contribution of primary NO_2 emissions to the overall roadside NO_2 concentrations is not well understood since NO_2 cannot be measured directly during standard sampling and analysis procedures.

It has been suggested that the amount of primary NO_2 emitted may depend upon the mode of operation of vehicles (i.e. stop-start driving producing higher levels) and the proportion of vehicles operating with 'cold' engines. If the amount of primary NO_2 is appreciable it could contribute a significant proportion of the local atmospheric concentrations measured.

One of the reasons for the uncertainty surrounding the amount of NO_2 that vehicles emit is that there is potential for NO to be converted to NO_2 during the normal processes used to sample exhaust for analysis.

2.1.3 Limit values for NO_x and NO_2

Over the last ten years, the limits on emissions of NO_x gases have been substantially reduced. For light duty vehicles NO_x emissions are currently regulated by Euro 3 emissions standards, as laid down in EU Directive 98/69. From 2005, these limit values will be superseded by Euro 4 standards, also from the same Directive. These regulations (along with previous limit values) are presented below in Table 1 for all classes of vehicle.

Table 1: EU limit values for gaseous and particulate vehicle emissions

Limit Value (g/km)

Vehicle Type	Fuel type	Euro 0 (Pre 1991) 83/551		Euro 1 (1991) 91/441 93/59		Euro 2 (1994)		Euro 3 (2001)			Euro 4 (2005)		
		HC+ NO$_x$	Particulates	HC+NO$_x$	Particulates	HC+NO$_x$	Particulates	NO$_x$	HC+ NO$_x$	Particulates	NO$_x$	HC+ NO$_x$	Particulates
Cars	Petrol	4.8N/A6.5	N/A	0.97	N/A	0.50	N/A	0.15	0.2 (HC only)	N/A	0.08	0.1 (HC only)	N/A
	Diesel (all types)	4.8N/A6.5	1.1	N/A	0.14	N/A	N/A	0.5	0.56	0.05	0.25	0.3	0.025
	Diesel (IDI)[1]	N/A	N/A	N/A	N/A	0.70	0.08	N/A	N/A	N/A	N/A	N/A	N/A
	Diesel (DI)[2]	N/A	N/A	N/A	N/A	0.90	0.1	N/A	N/A	N/A	N/A	N/A	N/A
Vans* <1305 kg	Petrol	N/A	N/A	N/A	N/A	0.5	N/A	0.15	N/A	N/A	0.08	N/A	N/A
	Diesel	N/A	N/A	0.97	0.14	0.6	N/A	0.5	0.56	N/A	0.25	0.3	N/A
Vans* 1305 to 1760 kg	Petrol	N/A	N/A	N/A	N/A	0.65	N/A	0.18		N/A	0.10		N/A
	Diesel	N/A	N/A	1.4	0.19	1.1	N/A	0.65	0.72	N/A	0.33	0.39	N/A
Vans* >1760 kg	Petrol	N/A	N/A	N/A	N/A	0.8	N/A	0.21	N/A	N/A	0.11	N/A	N/A
	Diesel	N/A	N/A	1.7	0.25	1.3	N/A	0.78	0.86	N/A	0.39	0.46	N/A

Limit Value (g/kWh)

Heavy duty vehicles	Euro 0 (pre-1991) 88/77/EEC			Euro 1 (1991) 91/542/EEC Stage 1			Euro 2 (1994) 91/542/EEC Stage 2			Euro 3 (2001) 98/C173/01 ESC/ELR			Euro 4 (2005) Proposed ETC test		
	NO$_x$	THC	Particulates	NO$_x$	THC	Particulates	NO$_x$	THC	Particulates	NO$_x$	THC	Particulates	NO$_x$	THC	Particulates
Diesel	14.4	2.45	N/A	8	1.1	0.36	7	1.1	0.15	5	0.66	0.1	2	0.25	0.05

[1] IDI = Indirect fuel injection
[2] DI = Direct fuel injection

In addition to vehicle type approval regulations, the National Air Quality Strategy (NAQS) (Department of the Environment et al., 2000) describes various standards and objectives regarding acceptable concentrations of a range of airborne pollutants. With regard to Nitrogen dioxide (NO_2), the strategy proposes that by December 2005 hourly values should not exceed 105 ppb (200 $\mu g/m3$) more than eighteen times per year and provide an annual mean objective of 21 ppb (40$\mu g/m3$). Currently, annual mean concentrations of NO_2 typically fall in the range 10-45 ppb (19-86 $\mu g/m3$) in urban areas, but are lower in rural areas

2.1.4   Methods for determining NO_2 emissions

The standard method of sampling NO_x for analysis differs depending on the type of vehicle/engine tested. With light duty vehicles a dilution sampling system is used for all the emissions, whilst in the case of heavy duty diesels a raw exhaust sampling system is used for the gaseous emissions, although particulates are measured after dilution with ambient air.

The process of dilution could influence NO and NO_2 concentrations, thereby rendering comparisons between light and heavy-duty vehicle emissions unreliable. Another potential source of error is one of the approved procedures for measuring NO_x for heavy duty vehicles in which NO_x can be fed to a chiller unit via a heated line to condense the water from the sample gas before being passed to an unheated NO_x analyser. The presence of liquid water in the condenser could affect the NO and NO_2 emissions in the sample gas. An alternative system is to send the raw sample directly to a heated NO_x analyser via a heated line.

(i) Chemiluminescence

NO_x or NO emissions are usually measured using a chemiluminescence analyser. Chemiluminscence analysers rely on the reaction between O_3 and NO that gives NO_2 and O_2. During this reaction, a proportion (between 10 and 20%) of the NO_2 produced is in an unstable, electronically excited state. To return to a stable form, the NO_2 molecules emit electromagnetic radiation in the form of light, which is detected by a photomultiplier tube in the analyser. By ensuring that O_3 is present in excess, the signal detected by the photomultiplier is proportional to the concentration of NO present in the sample.

In order to determine the concentration of NO_2 emissions, the NO_2 in an exhaust sample must first be converted to NO. This is achieved by using a heated analyser and a reducing agent. Once the NO_2 in the sample has been reduced to NO, the sample can be analysed in the same way as before, using the reaction between NO and O_3 to form electronically excited NO_2. In this case, the chemiluminescence reading from the analyser will give a measurement that is proportional to the amount of NO_x gases (NO and NO_2) in the sample.

NO_2 emissions are calculated by subtracting the reading for NO from that for all NO_x gases. To achieve this continuously requires either two analysers with equivalent sampling lines and response characteristics, or a two-gas chemiluminescence analyser which can measure NO and NO_x simultaneously. In either case there is a large potential for error since NO_2 concentrations are being inferred from the difference between two larger concentrations of similar magnitude.[3]

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[3] Assuming that NO_2 is 10% of NO_x in total, then a 1% error in a NO or NO_x measurement will result in a 10% error in the inferred measurement for NO_2.

(ii) Fourier Transform Infra-Red (FT-IR) spectroscopy

An alternative method of measuring NO and NO_2, in addition to a large range of other components of the exhaust gas, is to use Fourier Transform Infra-Red spectroscopy (FT-IR). Although this is not a technique defined in legislation, it has the capability of high speed continuous monitoring of a large range of component gases.

Infra-red spectroscopy relies on the principle that different chemical functional groups absorb infra-red radiation at different frequencies. In FT-IR spectroscopy, a peak at the functional group's characteristic frequency in the IR absorption spectra indicates the presence of a particular group in the sample. Using this method, NO and NO_2 appear in the absorption spectra at different frequencies, thereby allowing their relative concentrations to be easily determined. Since with FT-IR, NO_2 is being measured directly (rather than by inference with the potential large errors as in the case of chemiluminescence) this technique is particularly appropriate for this study. However it is still important to relate the data back to legislative standards since the two types of measurement may not yield equivalent results. Consequently, measurements using both Chemiluminescence and FT-IR instruments are necessary.

It should be noted that FT-IR spectroscopy can also be used to measure and speciate hydrocarbon emissions.

2.2 PARTICULATES

2.2.1 Particle size and health

Current vehicle type-approval legislation requires the measurement of total mass of particulate matter (i.e. g/kWh for heavy-duty engines and g/km for light-duty vehicles) and applies only to vehicles powered by diesel engines. However, there are a number of reasons why alternatives to a standard based on total mass alone are desired, and why the emphasis may change from particle mass to particle size and number.

For example, the mass concentration of particles in the exhaust of diesel engines has reduced steadily over the last 20 years following the development and application of new technologies. Current and future legislation is reducing particulate mass emissions, and diesel targets, towards the threshold of reliable measurement.

Standards based solely on total particulate mass are not ideal in terms of minimising the risks to health. The *size* of particles determines how deeply they penetrate into the human respiratory system and where they are deposited. Epidemiological studies have suggested a weak link between elevated ambient PM_{10} concentrations and increases in hospital admissions and death rates (Dockery and Pope, 1994; Pope et al., 1995; Vedal, 1997). Studies have also indicated that high concentrations of ultra-fine particles could present a risk to human health, but a causal relationship between particulate matter and health effects has not been identified. Even so, the concerns about the health impacts of the finer particle fractions have led to the introduction of a size-based National Ambient Air Quality Standard in the United States ($PM_{2.5}$) and in Europe (PM_{10}).

Conventional gravimetric (*i.e.* filter) methods for assessing total exhaust particulate matter do not provide meaningful information on ultra-fine particles. Whilst ultra-fine particles form a substantial proportion of the particle number, they contribute little to the total mass; a single 10 μm-diameter particle probably weighs the same as around one million 0.1 μm diameter particles. Furthermore, as they give only an average value over the test cycle from gravimetric measurements no information can be obtained on the effects of vehicle operation on fine and ultra-fine particle emissions.

The study of ultra-fine particles in exhaust emissions is rather complex, and there are a number of issues relating to both their nature and measurement that still need to be resolved. An understanding of these issues is crucial to the interpretation of data on ultra-fine particles, and the understanding of its limitations. The existing literature has been summarised below.

2.2.2   Sampling and measurement of ultra-fine particles in vehicle exhaust

Particle emissions from engines are mainly sub-micron, and usually exist in two distinct size modes (by number): a 'nuclei' or 'nanoparticle' mode consisting of primary particles smaller than around 50 nm, and an 'accumulation' mode, consisting of particles mainly in the 50-100 nm range. Most of the exhaust particle number is found in the nuclei mode, and most of the particle mass is in the accumulation mode.

Several experiments have revealed that the chemical composition and size distribution of particles can change dramatically after the exhaust gas has left the combustion chamber, and that particle characteristics are sensitive to the sampling conditions employed. For example, between the combustion chamber and the exhaust pipe the primary particles can agglomerate to form the larger particles, with the accumulation mode particles consisting of 15-20 primary particles.

Particles may be generated from within the sample lines used to convey the gas from the exhaust pipe to the dilution tunnel. The pyrolysis of the silicone rubber material sometimes used to join the exhaust pipe to the transfer tube has been cited as one potential source in this respect.   Larger particles may be lost through deposition, and smaller ones lost through thermophoresis[4]. Almost all of the particulate matter found in the exhaust pipe before dilution is present as solid carbonaceous agglomerates, with a small amount of metallic ash.

There are concerns that modern diesel engines, which emit a low mass of particles, have high emissions of particles in the nanometre size range. For example, in a study of the steady-state emissions of a new-technology diesel engine, Baumgard and Johnson (1996) observed a particle concentration of 10^9 cm^{-3}, around three orders of magnitude greater than expected. Bagley *et al* (1996) found that there was a 15 to 35-fold increase in total particle number from a 1991 diesel engine compared with a 1988 engine, both running on very low-sulphur fuel. This was due to a 30 to 60-fold increase in the number of primary particles, and occurred despite a substantial reduction in the mass of particulate matter.

Most of the volatile nanoparticles (up to 90%), and a significant fraction of the particle mass, are formed during exhaust dilution. However, nucleation is a very non-linear process, whether in the atmosphere or in the laboratory, and the number formed is very sensitive to the nature of the sampling conditions. It has been established that the total number concentration can change by a factor of 100 by changing sampling and dilution conditions (Kittleson and Abdul-Khalek, 1998). For example, large increases were noted in particles smaller than 50 nm as the residence time is increased while the concentrations of larger particles remained almost unchanged. Similar effects were noted with decreases in dilution temperature. Clearly, the influence of sampling conditions on particle numbers makes it difficult to compare different data sources.

In addition to sampling and dilution conditions, the deposition and subsequent desorption of particles (in the dilution air as well as in the exhaust pipe) may contaminate subsequent particle samples. Volatile compounds - the particle precursors - may collect in the exhaust and sampling system during low exhaust temperature operating modes. Thermal desorption of condensed hydrocarbons can then occur from the transfer tube walls as the temperature rises during a test. Kittleson and Abdul-Khalek (1998) also found that particle number concentrations immediately following an increase to full power were ten times higher than during the stabilised idle condition. The size distributions measured during

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[4] Thermophoresis is the induced movement of particulate matter by thermal gradient effects. Transparent particles tend to move towards heat sources whilst opaque particles move away from heat sources.

the transient operation showed that virtually all of the increase in particle number was taking place in the nanometre diameter range.

Because the nanometre-size particles are especially susceptible to differences in operating conditions, future test procedures may have to simulate widely differing conditions ranging from stationary traffic in still air to motorway driving (Brear, 1999). Additionally, while nanoparticle formation may be favoured by certain laboratory dilution procedures, the well-documented existence of a large nuclei mode in the air above and near roadways shows that their formation is not a laboratory artefact. The accurate simulation of the atmospheric dilution process will be necessary to make laboratory measurements representative of actual human exposure to nanoparticles on and near roadways.

With respect to vehicle type it should be noted that although diesel engines emit higher concentrations of particles than gasoline engines, the total number of vehicle kilometres travelled by gasoline-powered vehicles is greater than that of diesels. Additionally, vehicles powered by spark ignition (SI) engines typically emit smaller particles than vehicles powered by diesel engines, and are an important source of fine particles and nanoparticles. It has been estimated that two thirds of the total fine particle mass occurs from SI engines. New gasoline direct injection (GDI) engines emit much higher particle concentrations than conventional engines and may approach diesel levels under some conditions.

2.3 HYDROCARBONS

Hydrocarbon (HC) emissions from road vehicles occur mainly as a result of the incomplete combustion of fuel in the vehicle's engine although some emissions also occur from the evaporation of fuel from the fuel tank, fuel lines, carburettor etc. HC emissions consist of a mixture of aliphatic and aromatic hydrocarbons, and include compounds such as methane, ethene (ethylene), ethyne (acetylene), 1,3-butadiene, benzene, methyl benzene (toluene) and dimethyl benzenes (xylenes). HC emissions tend to be far greater from petrol-engined vehicles than from diesel vehicles, and increase rapidly when the air/fuel mixture is significantly richer than stoichiometric.

Measurements of total hydrocarbon (THC) emissions at the vehicles' exhaust will give some information on the combustion efficiency of the engine and the overall amount produced, but will not give information on the relative concentration of the different species. This can be misleading as some components are more important pollutants than others. For example, some HC species, such as benzene, have been associated with serious health effects whilst others, such as methane, are relatively inert and have no obvious effect on human health.

The following section gives details of some of the major pollutants and their effects on health.

2.3.1   HC emissions and health effects

(i) Benzene

Benzene is a known carcinogen and it has been suggested that a lifetime of exposure to a concentration of 500 ppb induces an increased risk of leukaemia. The first extensive epidemiological study to demonstrate a correlation between leukaemia and benzene exposure was carried out in 1974 (Aksoy et al, 1974). The study of 28,500 shoe workers shows an annual incidence of leukaemia of 13 per 100,000 compared to 6 per 100,000 in the general population. Workers exposed to high concentrations (100ppm) over a long period of time have been found to have an increased risk of contracting leukaemia. For these reasons, human exposure to benzene should be kept as low as possible.

(ii) 1,3-butadiene

Like benzene, 1,3-butadiene is a known carcinogen. The compound is not present in petrol or diesel but is formed during the combustion process from the cracking of other alkenes present in vehicle

fuel. Studies have shown that people exposed to 1,3-butadiene have an increased risk of leukaemia and bone marrow cancer. Laboratory studies have shown that 1,3-butadiene causes a variety of cancers in rodents and damages the genetic structures of cells, making it a genotoxic carcinogen. However, the ambient levels of this pollutant are currently very low and consequently the risk to the general population is considered to be extremely small.

(iii) Methyl tertiary butyl ether (MTBE)

MTBE is an additive that is added to unleaded petrol as an anti-knock agent to improve combustion efficiency, as well as to reduce emissions of carbon monoxide. The main concern surrounding the use of MTBE is pollution of drinking water (Environment Agency, 2000). In the USA, MTBE from petrol has been linked to contamination of drinking water supplies. Even very small quantities (5-10 μg per litre) of this compound can significantly affect the odour and taste of water. It is not until much higher concentrations are reached that toxicity effects become important. The problem of water contamination has been significant in the USA because of the prevalence of shallow wells for drinking water supplies. In the UK, MTBE contamination is much less likely to occur because underground drinking water supplies are mainly obtained from deep aquifers.
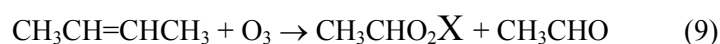
(iv) Photochemical smog

Photochemical smog is a mixture of secondary pollutants that includes ozone, peroxyacetyl nitrate (PAN), NO_2, and aldehydes. These secondary pollutants are produced as a result of complex interactions between HC and NO_x emissions in the presence of sunlight. O_3, NO_2 and PAN are very strong oxidising compounds and they can have quite significant effects on health, inducing headaches, respiratory problems and eye irritation.

Smog formation relies on the presence of low-level ozone, which is formed from NO_2 in the presence of sunlight (as shown by Equations 1 and 2, Section 2.1.1). Alkyl radical molecules are formed when alkane HC emissions react with hydroxyl radicals (OHX) as shown in Equation 8.

$$OHX + CH_4 \rightarrow H_2O + CH_3X \qquad\qquad (8)$$

Alkyl radicals of this type can then react with oxygen to form alkyl peroxy radicals as shown in Equation 6 in Section 2.1.2. As described in that section, alkyl peroxy radicals are involved in the conversion of NO to NO_2, and hence indirectly in the formation of low-level ozone.

Whilst alkane emissions will only react with OHX radicals, alkene (olefin) emissions will react with OHX, O_3 and nitrate (NO_3) radicals (Atkinson, 1994). An example of such a reaction is given in Equation 9:

$$CH_3CH{=}CHCH_3 + O_3 \rightarrow CH_3CHO_2X + CH_3CHO \qquad (9)$$

In this case, it can be seen that one of the products is ethanal (acetaldehyde), a known component of photochemical smog[5].

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[5] These are only as small selection of the reactions involved in smog formation. They are given as examples of the more important mechanisms in a very complex system.

2.3.2 Mechanisms for HC emission from internal combustion engines

Hydrocarbon emissions from petrol engines are thought to be caused by four different physical reaction mechanisms that occur in the combustion chamber. These are:

- Flame quenching at the combustion chamber walls

- crevices in the combustion chamber becoming filled with unburnt fuel mixture

- absorption of fuel vapour into oil layers on the cylinder wall during the intake and compression strokes

- poor combustion quality leading to incomplete burning of the fuel mixture

Of these mechanisms, flame quenching, combustion chamber crevices, and fuel vapour absorption are considered to be the most important, whilst poor combustion quality is more dependent on engine design and operating parameters (German, 1995, Harpster *et al*, 1995, Thompson and Wallace, 1994)

(i) Flame quenching at the combustion chamber walls

As long ago as 1957 it was shown that very close to the walls of an engine combustion chamber, a quench layer exists (Daniel, 1957). In essence, the presence of a quench layer means that fuel mixture that is adjacent to the chamber walls remains unburnt. These unburnt hydrocarbons rapidly (within milliseconds) diffuse into the burnt gases in the chamber.

Studies have shown that the majority of hydrocarbon emissions occur in the first two minutes of engine operation, when the engine and catalytic converter are still cold. It is believed that flame quenching is responsible for the majority of these emissions

(ii) Crevice mechanism

Engine combustion chambers have a number of crevices or regions of small volume where the spark flame cannot enter. Crevice regions have been found to be a significant source of unburned hydrocarbons. The most important crevice regions are those formed between the piston, piston rings and the cylinder wall.

During the compression stroke of the combustion process, unburned fuel mixture is forced into the various crevice regions. When the combustion flame arrives at the entrance to each crevice, one of two things can occur: the flame enters the crevice and either fully or partially burns the fuel/air mixture. Alternatively, the flame is quenched at the entrance to the crevice, and the mixture in the crevice remains unburned. After this stage, burned gases start to flow into each crevice, reducing the cylinder pressure but increasing the crevice pressure. When the crevice pressure exceeds the cylinder pressure, burned and unburned gas flows out from the crevices and into the cylinder.

(iii) Fuel absorption in engine oil

It has been shown that the presence of lubricating oil in fuel or on the combustion chamber walls has a marked effect on hydrocarbon emissions. Fuel containing 5% engine oil has been found to lead to between two and three times the levels of hydrocarbon emissions compared to fuel free from engine oil. During the intake and compression strokes, fuel vapour can be absorbed by oil films present on the cylinder walls. Towards the end of the compression stroke, the vapour pressure in the cylinder is increasing, thereby allowing any oil that was initially saturated during the intake stroke to continue to absorb fuel vapour. During combustion, the fuel vapour concentration drops to close to zero. Because of this, fuel vapour desorbs from the oil films and into the combustion products.

(iv) Poor combustion quality

Poor combustion quality tends to occur if the air/fuel mixture is overly lean. In such conditions, the flame quenches before fully reaching the cylinder wall. A proportion of the fuel mixture therefore

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remains unburned and is emitted with the combustion products of the burned fuel. Alternatively when the mixture is over-rich, there may not be enough oxygen present to burn all the hydrocarbons.

2.3.3   Methods for measuring HC emissions

(i) Flame ionisation detection

Flame ionisation detection is the standard method for measuring hydrocarbon emissions. The process works by burning the sample gas in a polarised hydrogen flame. Compounds in the sample that have carbon-hydrogen bonds are ionised with the level of ionisation occurring in proportion to the number of carbon atoms in the sampled gas. An electrostatic field is set up around the burner using a polarising battery. This field causes the ions to flow to the collector, and electrons to flow to the burner jet. The movement of ions and electrons results in a DC current proportional to the level of ionisation.

Flame ionisation detectors can be equipped with two measurement channels, one for total hydrocarbons and the other for methane. Such a set-up allows levels of reactive, non-methane HC emissions to be calculated by subtracting the measurement for methane from that for total HC.

Flame ionisation detection is limited by the fact that it is effectively a carbon atom counter. It can only detect the total amount of HC emissions and cannot be used to identify the HC composition of the sample gas, or the relative proportions in which each of the different compounds is present.

(ii) Gas Chromatography

The technique of gas chromatography can be used for separating mixtures of compounds based on their different volatilities. The GC method uses a column that is filled with a solid or liquid stationary phase. The compounds to be separated are mixed with an inert gas such as helium, and injected into the column. The stationary phase has absorbent properties that mean that the different constituent components of the sample mixture will pass through it at different rates. Each compound in the mixture has a characteristic retention time, which is a measure of how long it takes for the compound to pass through the column. Individual compounds can then be measured using suitable instrumentation such as a flame ionisation detector or mass spectrometer.

2.3.4   Fourier Transform Infra-Red (FT-IR) spectroscopy

Hydrocarbon emission compounds absorb infra-red radiation and therefore FT-IR spectroscopy can also be used to measure and speciate hydrocarbon emissions. The FT-IR technique was described earlier in Section 2.1.4.

3 EXPERIMENTAL METHOD

3.1 EQUIPMENT AND EXPERIMENTAL SETUP

All measurements were taken at the Millbrook test centre in their climatic chamber. Measurements were taken using standard procedures where possible. Customised procedures were developed for measurements taken of pollutants where no current standards exist.

3.1.1 Conventional exhaust gas analysis equipment

For vehicles with a gross weight of less than 3.5 tonnes (light-duty vehicles), the emissions were sampled in accordance with the current EC legislation applicable to these vehicles (*i.e.* using dilute exhaust gas sampling). For vehicles with a gross weight of more than 3.5 tonnes (heavy-duty vehicles), sampling procedures were used which were equivalent to those defined for heavy-duty engines in the current EU legislation. This method is based on the raw sampling of gaseous emissions and the dilute sampling of particulate emissions.

The following emissions were recorded continuously in terms of grams/second and converted to grams/km, grams/test, grams/kWhr and grams/mode when applicable[6].

- THC using a flame ionisation detector (FID).

- NO_x and NO using a chemiluminescence analyser.

Bag samples of NO_x were also taken over each test. Particulates were measured over each mode and test using standard filter measurement methods.

In order to give simultaneous dilute and raw gas NO and NO_x measurements a dual channel chemiluminescence analyser was used in addition to the standard cold analysers. This was used to sample the dilute CVS gas stream giving NO and NO_x at a sample rate of 1 Hz in addition to the standard tailpipe NO and NO_x samples.

Heated and unheated NO and NO_x measurements for heavy duty vehicles were compared by using a dual channel heated analyser that was run in parallel with the standard cold analysers. The dual channel analyser was used on the dilute stream for one set of heavy-duty tests and on the raw stream for the other.

3.1.2 Fourier Transform Infra-red spectroscopy (FT-IR)

A FT-IR analyser was used in addition to the standard analysers to measure NO_2 and NO directly. The advantages of using this method over chemiluminescence were described earlier in Section 2.1.4. The FT-IR also provided measurements of a wide range of additional compounds simultaneously, but since the main purpose of this aspect of the study was to investigate NO_2 and NO emissions the instrument configuration was optimised to measure these compounds. To obtain comparative measurements between different sampling methods, the FT-IR was used to measure emissions from the raw exhaust during one of the repeat tests and from the dilute exhaust in the other repeat test.

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[6] In addition carbon dioxide (CO_2) and carbon monoxide (CO) where measured continuously using non-dispersive infra red analysers and bag samples were also taken. It should be noted that although the measurements of CO_2 and CO were not used in this study the data might be of value in future work.

3.1.3 Particulate mass and size distribution measurements

When undertaking particle size distribution measurements, the sampling conditions must be clearly defined. Generally, the sampling conditions were generally held constant during the measurement programme.

(i) Sampling equipment and conditions

During each test, particulate mass samples were collected on 47 mm Teflon-coated glass-fibre filters using a regulation sample train. On-line measurements of particle mass were also recorded using a tapered element oscillating microbalance (TEOM). This equipment determines the total mass of particles emitted per second.

Particle size distributions were measured using the electrical low-pressure impactor (ELPI). A full description of this equipment and measurement method is given by Keskinen *et al* (1992). The ELPI separates particles in real time according to their aerodynamic size. It enables the on-line measurement of particles in the size range from 30 to 10000 nm. Cut points occur at 30 nm, 60 nm, 108 nm, 170 nm, 260 nm, 400 nm, 650 nm, 1 μm, 1.6 μm, 2.5 μm, 4.4 μm, 6.8 μm, and 9.97 μm. At each of these cut points, the sampling efficiency is 50%. All the particle number concentrations are reported as mean values (particles/cm^3) over a given driving cycle. However, the particle number concentration in raw (diesel) exhaust is much higher than the ELPI can accommodate and hence dilution is required.

The ELPI is intended for applications where a wide range of particle sizes are anticipated and where fast response times are required. During driving cycles with varying speed and torque, such as those performed on a chassis dynamometer, the particle size distribution can change rapidly. Consequently the ELPI is especially suitable for real-time measurement of rapidly varying or evolving size distributions of particulate exhaust emissions.

The ELPI was placed in the same position as the normal filter. Flow rates were at approximately 10 litres/min. The dilution ratio of the CVS system ranged between 5:1 and 10:1 at high load and high speed. Dilution ratios at idle were approximately 30:1.

3.1.4 Hydrocarbon emission measurements and speciation

During the emissions test a sample of the diluted exhaust gas was extracted at a constant flow rate from the CVS into a five litre tedlar bag. Separate bags were filled for each phase of the test cycle, and a single bag was filled with a sample of the tunnel dilution air, throughout the test.

The gaseous HC sample was analysed by Gas Chromatography (GC), which required two instruments, both Hewlett Packard 5890s, modified for heated gas phase sample introduction, and equipped with FID detectors. One GC had a 50 m x 0.53 mm diameter Chrompack Alumina PLOT column that separated the C_1 to C_4 HC components using temperatures in the range 20°C to 200°C. The second had a J&W 60 m x 0.32 mm diameter DB1 column that separated the C_4 to C_{12} components with temperatures ranging from –80°C to 290°C.

Calibration of the retention times for each column was performed using a Scott Gases 23 component gas mixture (ERC1 - as in standard US practice). With each pair of samples a check was made for the agreement between butane values on both columns, and between the total hydrocarbons measured using flame ionisation detection (FID) and the sum of all the GC species. Calibration for FID response was performed daily daily using a NIST traceable propane standard.

3.2 VEHICLES AND DRIVING CYCLES

3.2.1 Vehicles

In common with other studies of this type, only a relatively small number of vehicles could be accommodated within the budgetary constraints of the project. Nevertheless in determining the sample of vehicles for test, consideration was given to obtaining a sample that included most of the vehicle types used in the UK. The main objectives were to enable the investigation of trends between emissions, vehicles, technology levels, and operating conditions rather than attempt to draw global conclusions.

Eighteen vehicles were selected for the tests. These comprised nine passenger cars, three vans, three HGVs and three buses. All the vehicle types were separated into three levels of emission legislation; pre-Euro 1 (designated Euro 0), Euro 1, and Euro 2. Cars were further separated into small, medium and large sizes defined by engine capacity. The test sample therefore included most basic vehicle types currently used in the UK. All the test vehicles were tested in the 'as-received' or 'in-service' condition i.e. without any special repairs or tuning which would influence exhaust emissions. Table 2 gives some further details of the vehicles selected for the tests.

Table 2: Specification of test vehicle

Vehicle number	Vehicle group	Vehicle type	Vehicle size	Technology level	Vehicle make	Vehicle model	Engine Capacity (cc) or type	Engine Maximum power (kW)	Engine Maxiumum torque (Nm)	Transmission	Fuel type
1	Light-duty vehicles	Passenger cars	Small (<1400cc)	Euro 0	Vauxhall	Nova	1300			Manual	ULP [2]
2				Euro 1	Fiat	Cinqecento	900			Manual	ULP
3				Euro 2	Skoda	Felicia	1300			Manual	ULP
4			Medium (1400-2000cc)	Euro 0	Vauxhall	Astra LXi estate	1800			Manual	ULP
5				Euro 1	Ford	Mondeo 16v	2000	N/A		Manual	ULP
6				Euro 2	Vauxhall	Vectra	2000			Manual	ULP
7			Large (>2000cc)	Euro 0	Volvo	740GLE estate	2300			Manual	ULP
8				Euro 1	Jaguar	Sovereign	4000			Auto	ULP
9				Euro 2	BMW	328i coupe	2800			Auto	ULP
10		Vans	N/A [1]	Euro 0	Ford	Transit	2500 D			Manual	ULSD [3]
11				Euro 1	Ford	Transit	2500 DI			Manual	ULSD
12				Euro 2	Ford	Transit	2500 DI			Manual	ULSD
13	Heavy-duty vehicles	HGVs	N/A	Euro 0	Dodge-Renault	Tipper	Perkins	88 (2800)	367 (1500)	Manual	ULSD
14				Euro 1	Scania	320 113M	DSC1201	235 (1900)	1600 (1200)	Manual	ULSD
15				Euro 2	Scania	P94 360	DSC1202	265 (1900)	1665 (1300)	Manual	ULSD
16		Buses	N/A	Euro 0	Dennis	Dart	Cummins B5	96 (2500)	456 (1500)	Auto	ULSD
17				Euro 1	Dennis	Dart	Cummins B5	96 (2500)	456 (1500)	Auto	ULSD
18				Euro 2	Dennis	Dart	Cummins B5	96 (2500)	456 (1500)	Auto	ULSD

[1] N/A = Not distinguished in this test programme
[2] ULP = unleaded petrol
[3] ULSD = ultra-low-sulphur diesel

3.2.2 TEST CYCLES

Vehicle emissions were measured at the Millbrook test centre with the test vehicles undergoing different test cycles on a chassis dynamometer. Three test procedures labelled A, B and C, were used for this study. These test procedures are defined in more detail below.

All the light duty vehicles were driven over test procedure A. This includes a wide range of driving cycles encompassing both urban and motorway driving cycles. The medium sized cars were additionally driven over a type B test that included emission measurements when the vehicle was driven over a cycle from cold. All the buses and trucks were driven over type C tests which consisted of emission measurements over cycles which are specifically applicable to heavy vehicles. The vehicle types and test matrix adopted for the study is summarised in Table 3.

Type A Test

- Vehicles were first checked for exhaust integrity, then the fuel tank was drained and refilled with the test fuel (see description of test fuels below).

- Petrol fuelled vehicles were preconditioned using an ECE 15 cycle followed by two repeats of the extra urban driving cycle (EUDC). Diesel vehicles were subjected to an identical procedure except three repeats of the EUDC were performed.

- Vehicles were soaked at 25 °C. They were driven over a 96/69/EC test whilst emissions were continuously measured and recorded.

- Vehicles were conditioned to a stable temperature. They were then driven over a Warren Spring Laboratory (WSL) urban test cycle followed by the WSL suburban and WSL rural, constant 90 km/h, constant 113 km/h tests and WSL congested urban cycle in succession whilst emissions were measured and recorded.

- The test sequence was repeated for each vehicle to examine consistency.

Type B Test

- Vehicle fuel tanks were topped up with the test fuel.

- Petrol fuelled vehicles were preconditioned using an ECE 15 cycle followed by two repeats of the extra urban driving cycle (EUDC).

- Cars were soaked at –7 °C then tested from cold over the 96/69/EC test whilst emissions were continuously measured and recorded

- Cars were preconditioned as described above then driven over a hot WSL congested urban cycle whilst the ambient temperature was controlled to –7 °C.

- Cars were preconditioned as described above then Items 3 and 4 were repeated at +10 °C instead of –7 °C.

- The test sequence was repeated for each vehicle to examine consistency.

Type C Test

- Vehicles were first checked for exhaust integrity, then the fuel tank was drained and refilled with the diesel test fuel.

- Vehicles were preconditioned using a simulated 13 mode test.

- Vehicles were tested over a simulated 13 mode test hot FIGE test and Millbrook bus cycle test.

- The test sequence was repeated for each vehicle to examine consistency.

Table 3: Vehicles and test cycle matrix

Vehicle type	Euro 0	Euro 1	Euro 2
Small Cars: Petrol <1400cc	2 Type-A tests	2 Type-A tests	2 Type-A tests
Medium Cars: Petrol 1400-2000cc	2 Type-A tests 2 Type-B tests	2 Type-A tests 2 Type-B tests	2 Type-A tests 2 Type-B tests
Large Cars: Petrol >2000cc	2 Type-A tests	2 Type-A tests	2 Type-A tests
Vans: Diesel <3.5tonnes	2 Type-A tests	2 Type-A tests	2 Type-A tests
HGVs: Diesel	2 Type-C tests	2 Type-C tests	2 Type-C tests
Buses: Diesel	2 Type-C tests	2 Type-C tests	2 Type-C tests

3.2.3   Test fuels

The fuels used in the test programme were pump unleaded petrol, and pump ultra-low-sulphur diesel. The properties of the two fuels are listed in Table 4 and Table 5.

Table 4: Properties of the unleaded petrol fuel

Property	Result	Units	Method
RON [1]	96.1	-	ASTMD2699 96.
MON [2]	85.5	-	ASTMD2700 85.
Density at 15°C	0.7277	kg/litre	ASTMD4052
Vapour Pressure at 37.8°C	92.2	kPa	EN/ISO13016-1pr ASVP
Aromatics	27.7	%(v/v)	ASTM D1319
Olefins	1	%(v/v)	ASTM D1319
Benzene	1	%(v/v)	EN228
Carbon	85.94	%(m/m)	ASTM D5291
Hydrogen	13.63	%(m/m)	ASTM D5291
Total Oxygenates	2.3	%(v/v)	ASTM D4815
Sulphur	120	ppm	ISO8754
Phosphorus	<0.01	mg/litre	ASTM D3231
Lead	<1	mg /litre	ASTM D3237

[1] Research Octane Number
[2] Motor Octane Number

Table 5: Properties of the diesel test fuel

Property	Result	Units	Method
Cetane No.	53.2	-	ASTM D613
Density at 15°C	0.8366	kg/litre	ASTM D4052
Total Aromatics	28.7	%(m/m)	IP391
Monocyclic Aromatics	23.2	%(m/m)	IP391
Bicyclic Aromatics	5.2	%(m/m)	IP391
Tricyclic and Higher Aromatics,	0.3	%(m/m)	IP391
Sulphur	190	ppm	ISO 8754

4   RESULTS AND DISCUSSION

4.1 OXIDES OF NITROGEN

The results of measurements of the emissions of NO_x and NO_2 are presented in this section of the report. The results for light duty vehicles are presented separately (section 4.1.1) from trucks and buses (section 4.1.2). Also for each vehicle group, data is presented in terms of primary NO_2/NO_x ratios as well as in terms of absolute values of primary NO_2. The data presented examines the effects of different sampling and measuring systems on the results and demonstrates the influence of different drive cycles and vehicle type on emissions. A further, more detailed, statistical analysis of the results is given in Appendix A. The contribution of primary NO_2 to roadside NO_2 is considered in section 4.1.3. A discussion of the results is given in section 4.1.4.

4.1.1   Light duty vehicles

The measured NO_2/NO_x ratios for all the light duty vehicles using the five different sampling and measuring techniques are summarised in Figure 1. The values posted are averages for the sample of vehicles tested. The 95% confidence limits associated with the means are indicated in each case. The techniques examined are:

- Raw sample gas with unheated chemiluminescent (CHEM) analyser

- Raw sample gas with heated CHEM analyser, and

- Dilute sample gas with heated CHEM analyser

- Dilute heated FT-IR

- Raw heated FT-IR.

Also shown are the results for the average of the first and second repeat tests of the raw unheated CHEM analyser.

It can be seen that the results from the measurements taken using the raw heated CHEM analyser gave the highest average NO_2/NO_x ratios followed by the dilute FT-IR, the raw FT-IR, the dilute heated CHEM, and finally the raw unheated CHEM method. The 95% confidence limits for the dilute heated CHEM are relatively wide and overlap the upper FT-IR and the lower raw heated CHEM 95% confidence limits suggesting this result has a low statistical significance. There is also relatively little difference between the NO_2/NO_x measurements using dilute and heated FT-IR and the repeated raw unheated CHEM tests in relation to their confidence limits. However, the raw heated CHEM, NO_2/NO_x measurements are significantly higher than measured by the FT-IR which in turn are significantly higher than measured by the raw unheated CHEM.
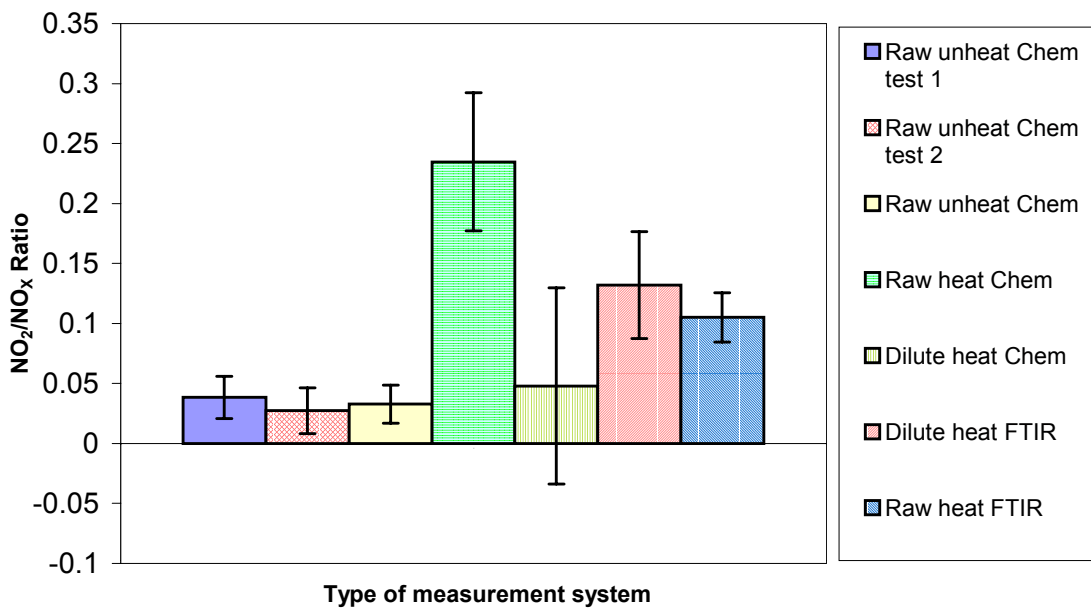

Figure 1: Comparison of NO_2/NO_x ratios for light duty vehicles using different measuring and sampling systems

Figure 2 below shows the average NO_2/NO_x ratios for each cycle using the different sampling and measuring methods used. It can be seen that the CHEM analyser sampling raw heated gas gave the highest average NO_2/NO_x with values ranging between 0.15 and 0.46 depending upon the cycle used. The unheated CHEM analyser sampling raw gas measured the lowest NO_2/NO_x ratios with values ranging between -0.02 and 0.07. In general, the congested cycle and the cycles started from a low temperature produced the greatest variation in NO_2/NO_x ratios across the different measuring techniques.
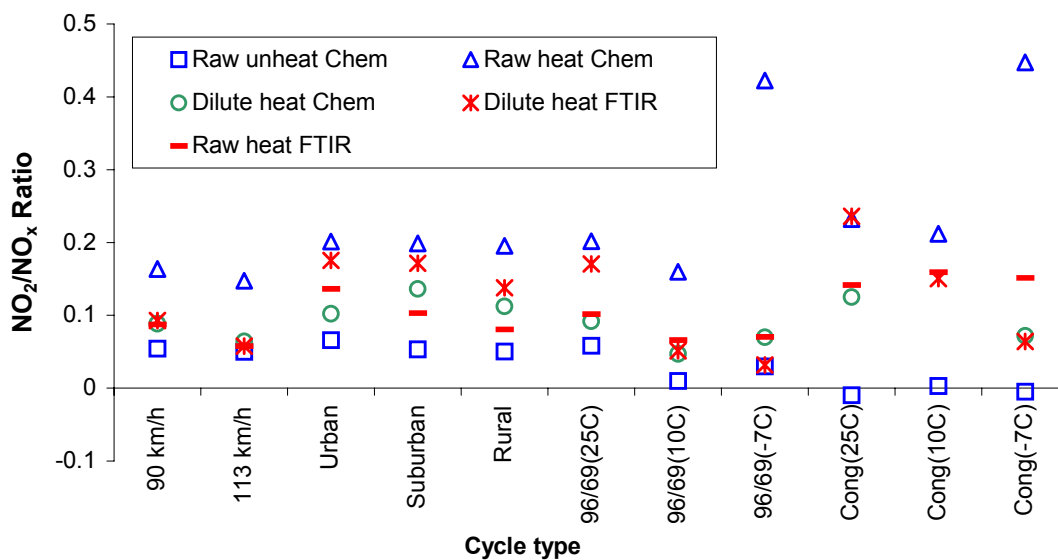
Figure 2: NO_2/NO_x ratios using different cycles and measuring methods

Figure 3 and Figure 4 show the NO_2/NO_x ratios from raw and dilute exhaust gas respectively measured using the FT-IR measurement technique. In these figures, the NO_2/NO_x ratios are averaged for all the light duty petrol vehicles, classified by legislation, and presented as a function of the driving cycle. It can be seen that again, there are large differences in these ratios depending upon the EU classification and the drive cycle used. The ratios range between 0.02 and 0.37. The greatest values of NO_2/NO_x were found using the raw sample from the Euro 0 vehicles started from 10°C and –7°C when driven over both the congested and 96/69 EEC cycles. The diluted NO_2/NO_x ratios from the Euro 2 vehicles are generally larger than for Euro 1 and Euro 0 vehicles. The remaining data do not show any clear pattern. This could be partly due to the relatively small vehicle sample size in each case.

To give an overview of the effectiveness of legislation on the values of NO_2/NO_x emissions the data for both raw and dilute measurements and all drive cycles have been averaged for each of the three vehicle legislative categories. The results of this form of analysis are presented in Figure 5.

It can be seen that the Euro 2 vehicles gave marginally the highest averages with an NO_2/NO_x ratio of 0.16 followed by Euro 0 vehicles at 0.14 and Euro 1 vehicles at 0.09. However, it can be seen that the 95% confidence limits, indicated as error bars on the figure, are of a similar order as the measured differences. Therefore it can be stated that there is no significant difference between the results indicating that legislation, for the vehicles sampled in this study, does not have a noticeable effect on the NO_2/NO_x ratio. This was confirmed by the results of the statistical analysis reported in Appendix A.
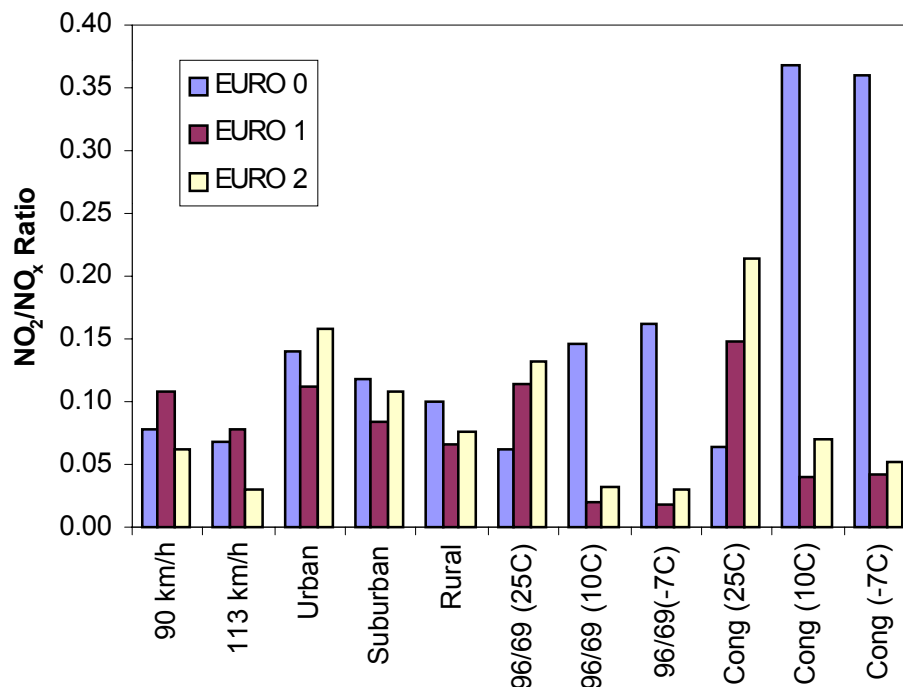

Figure 3: NO_2/NO_x ratios using different cycles and vehicles conforming to different legislation (raw sample & FT-IR)
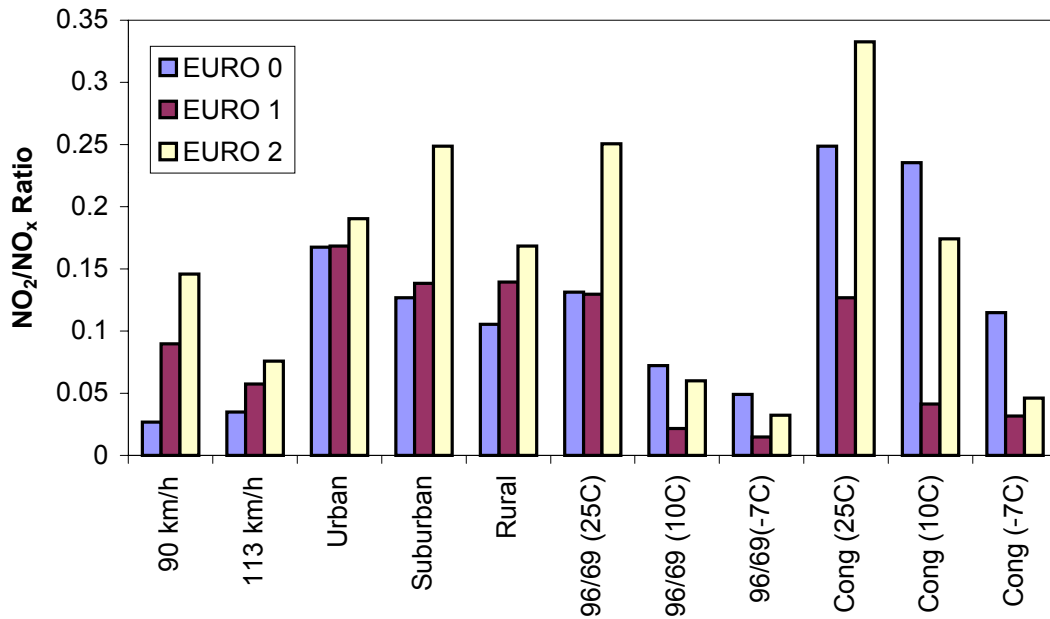
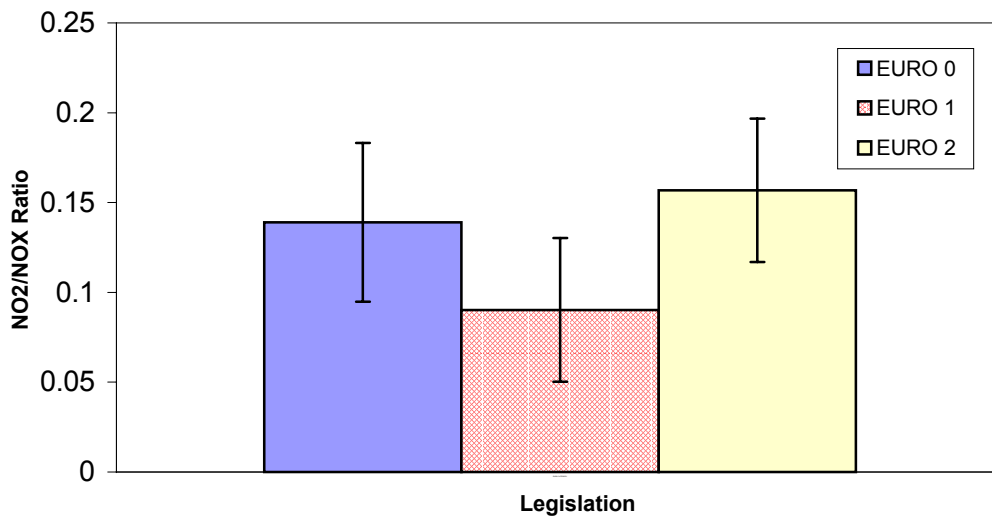**Figure 4: NO$_2$/NO$_x$ ratios using different cycles and vehicles conforming to different legislation (dilute sample & FT-IR)**

Figure 5: NO$_2$/NO$_x$ ratios using vehicles conforming to different legislation

Figure 6 shows the effect of vehicle size on the NO$_2$/NO$_x$ ratio. The smaller vehicles show an average NO$_2$/NO$_x$ ratio of 0.025 which is considerably less than the than the average NO$_2$/NO$_x$ ratios for the medium and larger vehicles at 0.08 and 0.095 respectively. There is a limited amount of overlap between the small and large car categories, which implies some uncertainty in this ranking. Since the confidence limits for the NO$_2$/NO$_x$ ratios from large and medium cars almost entirely overlap there is no significant difference between these categories. Again, this finding was confirmed by the more detailed statistical analysis reported in Appendix A.
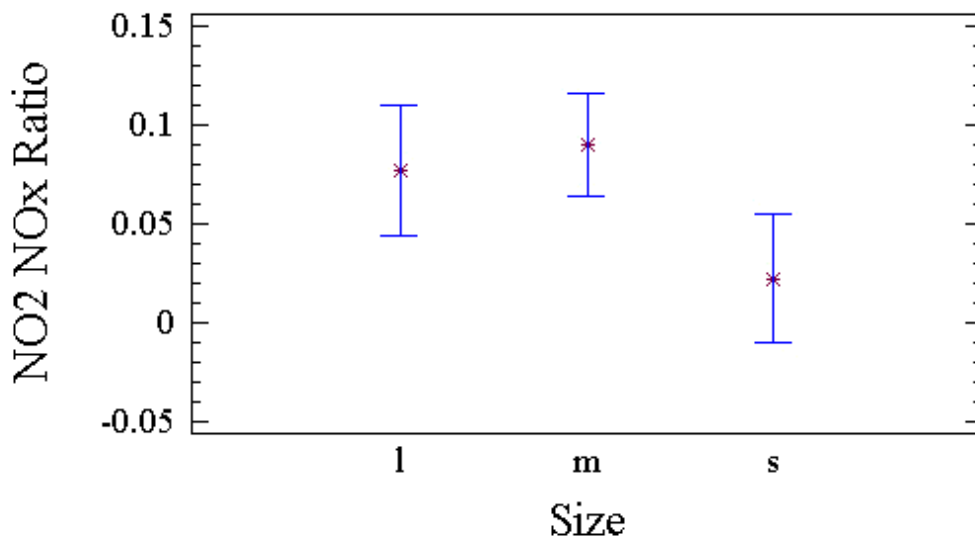
Figure 6: NO_2/NO_x ratios for different petrol vehicle sizes

Primary NO_2 emissions from the light duty vehicles, measured when using different sampling and measurement techniques, are shown in Figure 7. As before, when presenting the results in terms of NO_2/NO_x ratios, the values have been averaged for all drive cycles examined.

The results can be divided into two groups. One group consists of the heated CHEM and the dilute and raw FT-IR measurements (the fourth, sixth and seventh bars in Figure 7). These show average readings of approximately 0.0014, 0.00125 and 0.0012 g/s respectively. (NB. Due to the comparatively large confidence limits, the differences between these measurements are not statistically significant). The second group consists of the average raw unheated and dilute heated CHEM measurements, which show average readings of approximately 0.005 and 0.006 g/s. The average value of the first and second repeat tests using the raw unheated CHEM are also very similar. Again, due to the significant overlap between the confidence limits for each type of measurement, no statistically significant differences can be seen within this second group of readings either. However, the two groups show average readings which are significantly different from one another.
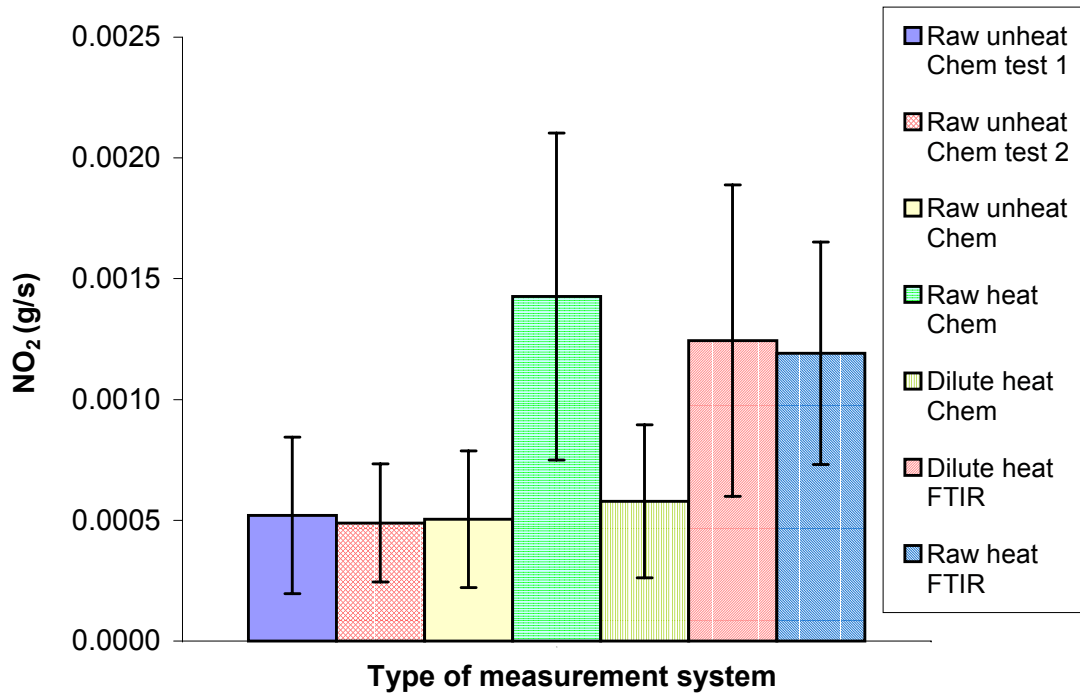
Figure 7: NO$_2$ emissions using different measuring and sampling systems
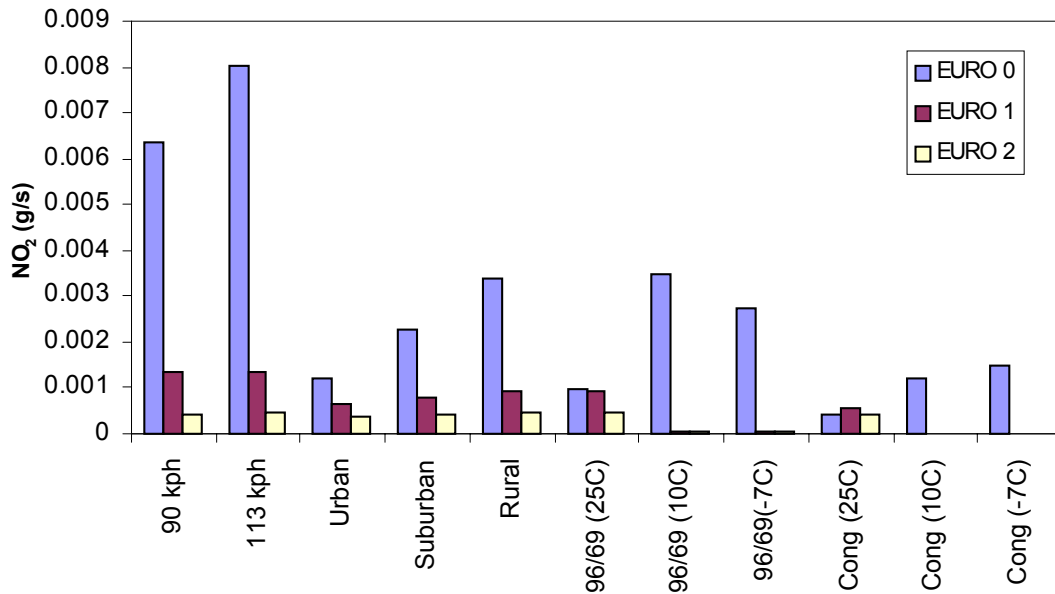

Figure 8 and Figure 9 show the NO$_2$ emissions from raw and dilute exhaust gas respectively measured using FT-IR spectroscopy. The emissions are averaged for all the vehicles classified by legislation as a function of the driving cycle.

It can be seen that greater NO$_2$ emissions are usually found using the raw sample relative to the dilute sample. This is more pronounced for the Euro 0 vehicles. Euro 0 vehicles usually show the greatest emissions of primary NO$_2$ and Euro 2 vehicles the lowest NO$_2$ of the three legislative categories. The motorway Euro 0 vehicles using the raw sample show particularly high NO$_2$ levels of 0.0063 and 0.008 g/sec at speeds of 90 and 113 km/h respectively. In contrast the NO$_2$ emissions measured from

the Euro 1 and Euro 2 vehicles over all the lower temperature tests for the 96/69 and congested cycles show very low emissions; these are near the limit of detection of the FT-IR analyser.
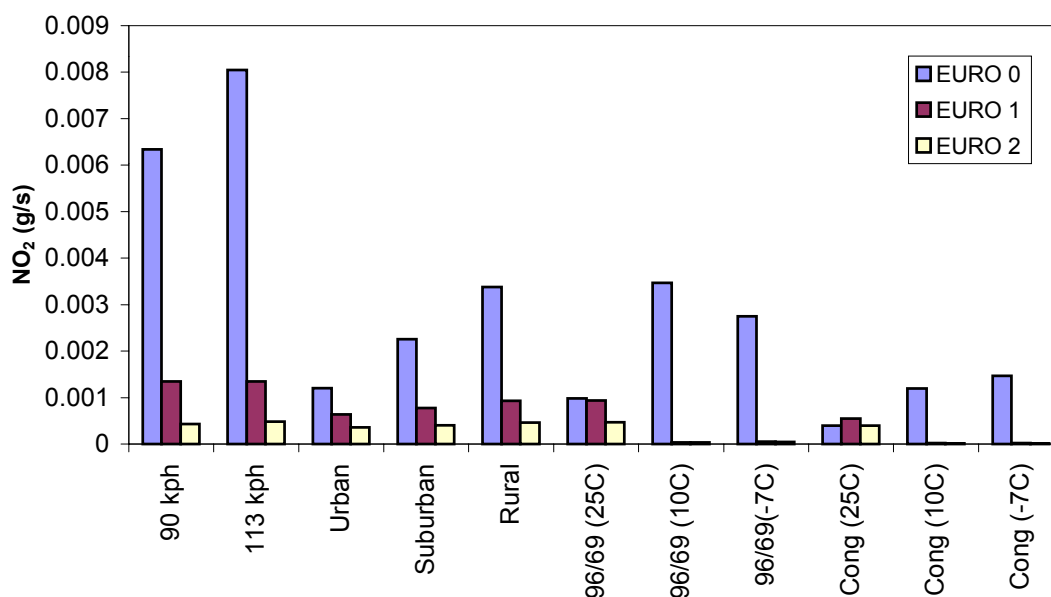

Figure 8: NO$_2$ emissions using different cycles and vehicles conforming to different legislation (raw sample & FT-IR)
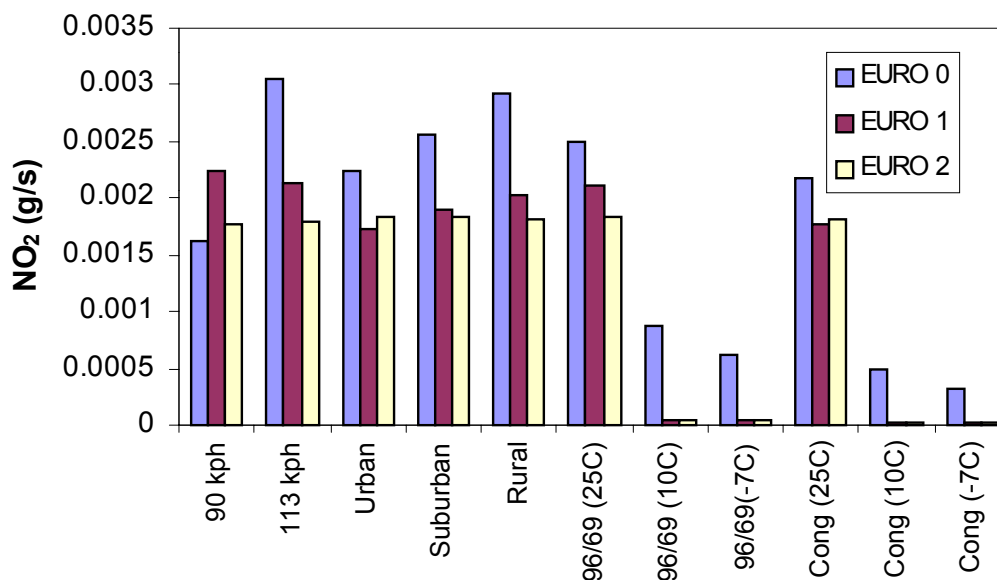

Figure 9: NO$_2$ emissions using different cycles and vehicles conforming to different legislation (dilute sample & FT-IR)

Figure 10 shows the average NO$_2$ emissions for each cycle using the different sampling and measuring methods used. The highest NO$_2$ values are usually measured over the 90 km/h and 113 km/h constant speed tests, the highest reading being an average of 0.0043 g/s when using the raw heated CHEM analyser at 113 km/h. However, very low NO$_2$ emissions were measured over the low

temperature 96/69 and congested urban cycles using the CHEM analyser with raw unheated sample gas; in fact, the measurement of NO_2 over the 10 °C congested urban cycle showed a negative NO_2 figure. This is probably the result of attempting to measure very low NO_2 concentrations combined with the error associated with inferring NO_2 from the difference between direct NO_x and NO concentration measurements.
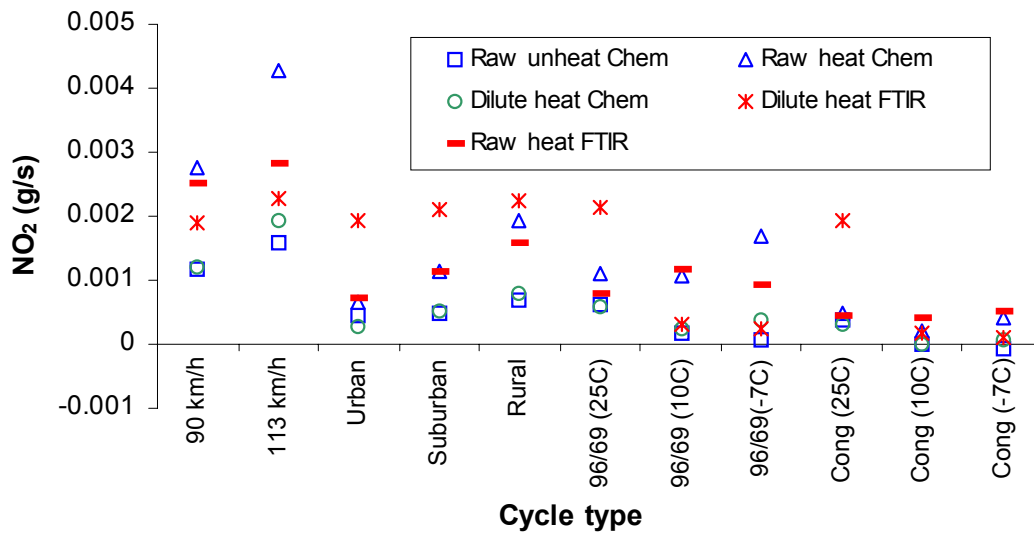

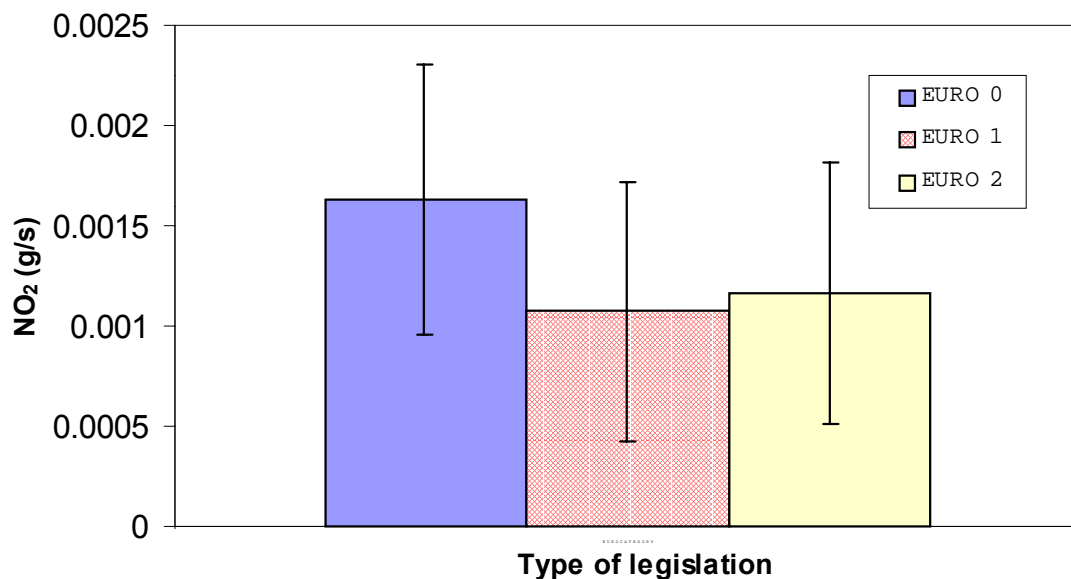**Figure 10: Average NO_2 emissions for all vehicles using different cycles and measuring methods**

Figure 11: NO_2 emissions for vehicles conforming to different legislation

Figure 11 shows NO_2 emissions averaged over all the cycles and sampling methods as measured by the FT-IR analyser. It can be seen that measurements using the Euro 0 vehicles gave the highest average NO_2 levels (i.e. 0.0015 g/s) followed by Euro 2 and Euro 1 vehicles (i.e. 0.0012 and 0.0011 g/s) respectively. However, again the 95% confidence limits associated with the data show that the measured differences between the vehicle categories are not statistically significant. It follows that although it seems possible that Euro 0 vehicles emit the greatest primary emissions of NO_2, of the three legislative categories examined, further measurements involving a larger sample of vehicles, would be needed to confirm this.
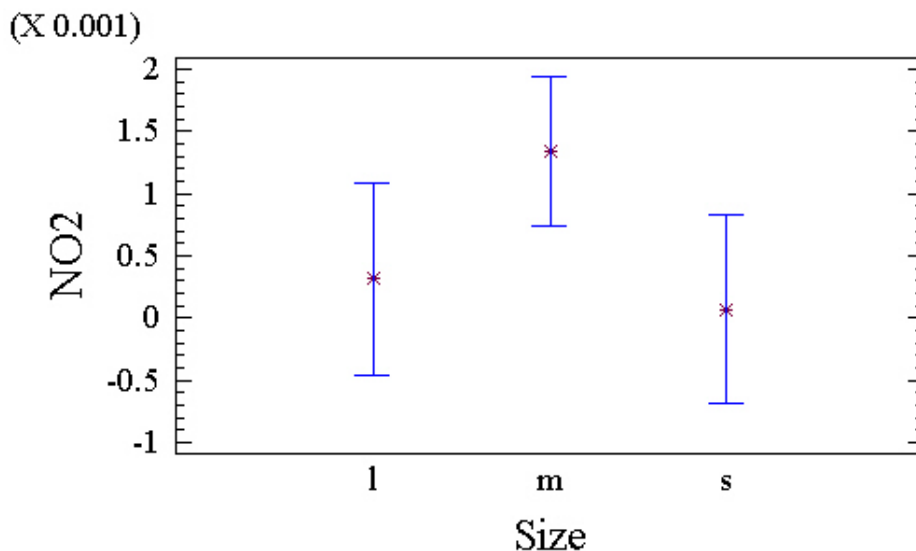
Figure 12: NO$_2$ emissions for different vehicle sizes

Figure 12 shows the effect of vehicle size on NO$_2$ emissions. Of the petrol vehicles tested the medium-sized cars showed the highest emissions followed by the large cars, and finally the small cars. However since the 95% confidence limits between the three categories overlap, no statistical significance can be associated with these measured differences.

4.1.2 Heavy duty vehicles

Figure 13 and Figure 14 show the average NO$_2$ emissions measured using the FT-IR analyser from trucks and buses conforming to different emission standards driven over various types of cycle. Figure 13 gives the results obtained by sampling raw exhaust gas and Figure 14 gives the corresponding results using diluted exhaust gas.

Using the raw sample, higher NO$_2$ emissions were generally measured from vehicles which were type approved to more modern standards, the exception being the buses when driven over the FIGE suburban and motorway routes where the highest NO$_2$ levels were measured from the Euro 0 vehicle. The Euro 0 bus, when driven over the FIGE suburban cycle, gave the highest emission of any category averaging 0.012 g/s.

The results for the dilute sample did not show any clear relationship between NO2 emissions and the emission standard or the test cycle, although the Euro 0 bus once again showed the highest emission over the FIGE suburban test averaging 0.015 g/s.
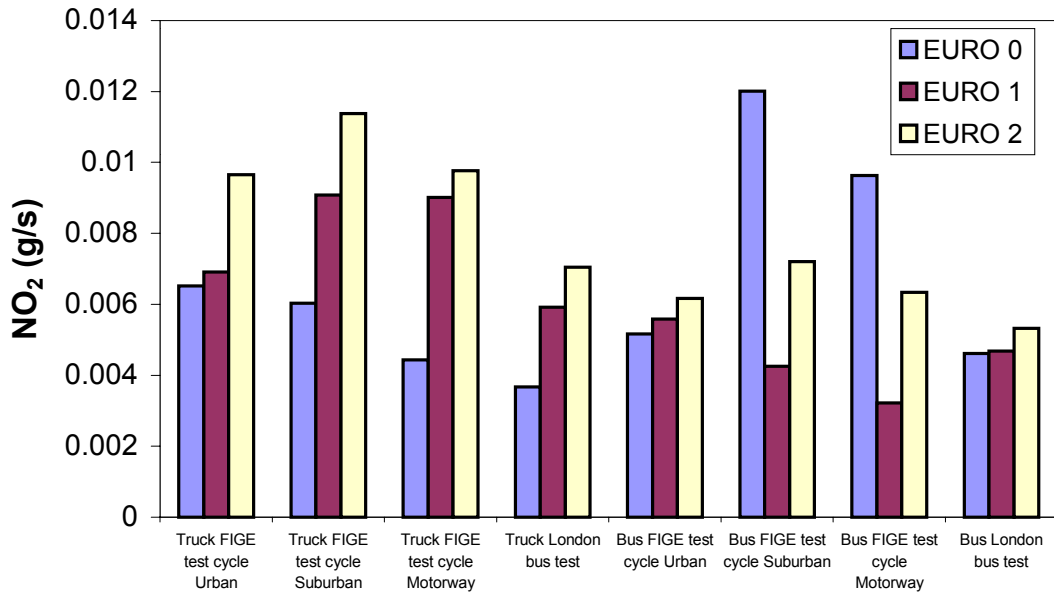
Figure 13: Heavy duty vehicle NO$_2$ emissions using raw sample gas
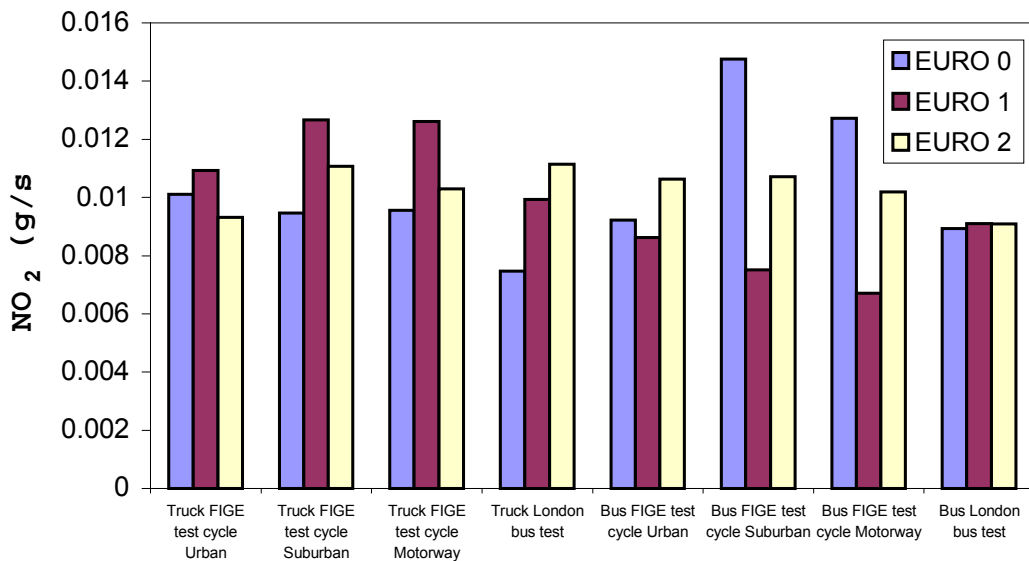
Figure 14: Heavy duty vehicle NO$_2$ emissions using dilute sample gas

A comparison of the average NO$_2$ emissions measured over all the heavy vehicles as a function of legislative category and cycle is shown in Figure 15. To limit the variability in NO$_2$ due to other factors such as the sampling and measurement method, all these figures relate to the FT-IR measurements using the dilute sample. This is probably more representative of the NO$_2$ levels in the exhaust after some dilution with the atmosphere. The NO$_2$ emissions measured from the Euro 0, Euro 1 and Euro 2 vehicles are typically of the order of 0.01 g/s. No significant difference in NO$_2$ emissions can be identified between these categories since the average levels are very similar to one another and the 95% confidence limits overlap.

Figure 15: Heavy goods duty NO$_2$ emissions by legislative category (dilute sample using FT-IR)

4.1.3   Contribution of primary NO$_2$ to roadside NO$_2$

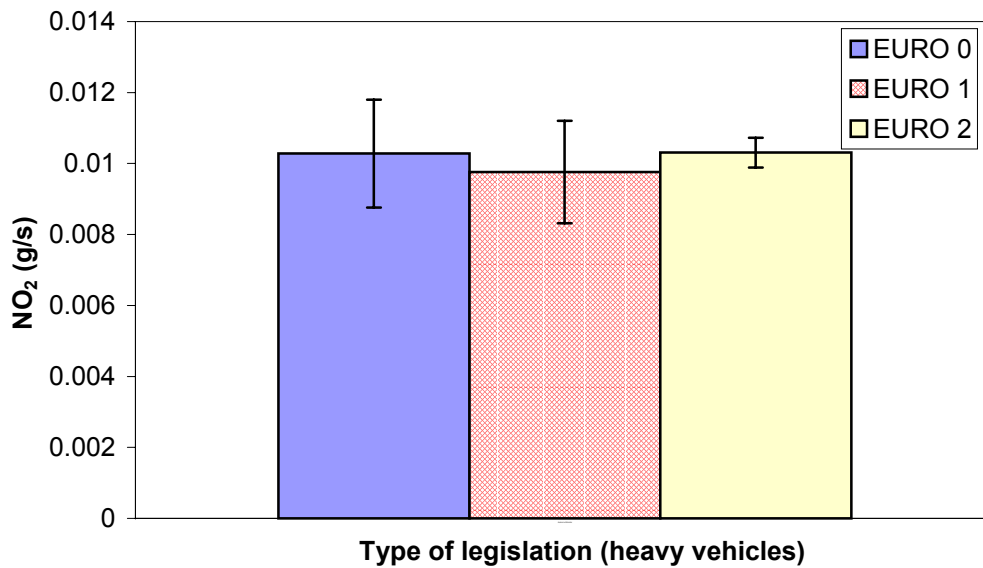This section considers the contribution that primary nitrogen dioxide could have on typical roadside concentrations of nitrogen dioxide. A modelling approach is used to simulate roadside concentrations taking the emissions data generated as part of this study. Emissions factors related to vehicle type and mode of operation are used as input to the model. These are adjusted for traffic composition and applied to a pollution dispersion model to determine roadside concentrations. Different traffic situations are evaluated and discussed.

(i) The effect of primary nitrogen dioxide emissions on atmospheric concentrations

It was stated previously in this report that conventionally, most traffic pollution models assume that emissions of oxides of nitrogen consist entirely of nitric oxide. Nitrogen dioxide is assumed to be produced subsequently by the atmospheric oxidation of nitric oxide, principally by its reaction with ozone. Some models attempt to simulate the chemical reactions, but most rely on empirical observations of the relative concentrations of total oxides of nitrogen and nitrogen dioxide. Such observations reveal a relatively simple relationship consisting of three phases:

1. Where the oxides of nitrogen concentrations are low (i.e. below the concentration of ozone), the rapid reaction with ozone will convert nitric oxide to nitrogen dioxide, so most of the oxides of nitrogen will comprise nitrogen dioxide.

2. As the oxides of nitrogen concentration increases, the formation of nitrogen dioxide will be limited by the availability of ozone; the nitrogen dioxide concentration will remain relatively stable while the nitric oxide concentration increases.

3. The third phase depends on the prevailing meteorological conditions rather than on the amounts and chemical reactions of the relevant pollutants. In this phase, nitric oxide also reacts with oxygen to produce nitrogen dioxide. Because the reaction is slow at the concentrations of nitric oxide found in air, it is usually unimportant when considering pollutant emissions and dispersion on a small scale: the emissions are diluted and transported to other areas before any significant oxidation by oxygen can take place. However, when the nitric oxide remains in the locality of its emission for a long enough period, some will be converted to nitrogen dioxide by this mechanism. Because the rate of the

reaction increases with the concentration of nitric oxide, and because the stagnant meteorological conditions needed to allow time for the reaction also restrict the dispersion of the nitric oxide and nitrogen dioxide, this phase generally occurs at high concentrations of oxides of nitrogen.

In the context of this study, it is the second phase that is of most importance. Concentrations of nitrogen dioxide are unlikely to be of concern during the first, ozone limited, phase, and the composition of the emissions is of little relevance since it can be assumed that all will be rapidly converted to nitrogen dioxide. Similarly, during the third phase, which occurs only rarely, although nitrogen dioxide concentrations are likely to be high, they do not depend primarily on the composition of nitrogen oxide emissions, but on the atmospheric conditions and reaction kinetics. In the second phase, however, the amount of secondary nitrogen dioxide depends on the availability of ozone to react with the nitric oxide and is limited by that availability. If some of the oxides of nitrogen emitted is in the form of nitrogen dioxide, however, the total nitrogen dioxide concentration will depend on the rate of emission as well as the availability of ozone.

A schematic representation of this $NO - NO_2 - O_3$ equilibrium is shown in Figure 16. The concentrations depicted are arbitrary, but reasonably typical of the ranges found near to roads. The ozone concentration (i.e. the concentration in background air transported into the area; the local concentration will be depleted by the reaction with nitric oxide) is assumed to be 40 ppb. Consequently, for oxides of nitrogen concentrations up to that level, there will be almost complete conversion to nitrogen dioxide. On the assumption that all emissions are of nitric oxide, the ozone derived nitrogen dioxide concentration will be restricted to 40 ppb because all of the available ozone has been consumed. At some higher concentration, assuming unfavourable meteorological conditions, the nitric oxide reaction with oxygen may become important and the concentration of nitrogen dioxide will again begin to increase. This has been shown in the graph at a concentration of total oxides of nitrogen of 500 ppb.

If some of the oxides of nitrogen emission is nitrogen dioxide, though, a different pattern emerges. In the graph, the second line shows the situation where 10% of the emissions are primary nitrogen dioxide. In the region before the ozone limit is reached, there is little difference from the first case: nitric oxide is rapidly converted to nitrogen dioxide. The ozone limit is reached at a slightly higher oxides of nitrogen concentration (44 ppb), because it is not consumed by the nitrogen dioxide constituent of the emissions. Once this value is reached, there will again be no further nitrogen dioxide production from atmospheric conversion of nitric oxide, but primary nitrogen dioxide emissions will continue to add to the total nitrogen dioxide. Thus, as the oxides of nitrogen concentration approaches 500 ppb, the nitrogen dioxide component continues to increase, and reaches a value of 90 ppb. Subsequently, it is again assumed that the reaction of nitric oxide and oxygen becomes important and the two lines converge as this effect dominates.
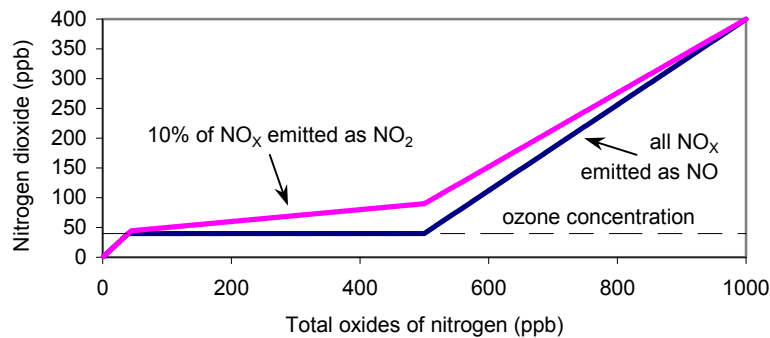
Figure 16: Schematic representation of the generation of NO$_2$ with and without primary emissions

While this example is a considerably simplified version of the mechanisms involved (there are, for example many other reactions involving the species considered here and other constituents of the atmosphere that both create and consume nitrogen dioxide), it illustrates the main principles involved. In the following paragraphs, the effect of primary nitrogen dioxide emissions is quantified using the emission data given in this report.

(ii) Oxides of nitrogen and nitrogen dioxide emission factors

In order to estimate traffic pollution concentrations in a realistic context, it is necessary to establish generalised functions to represent the emissions from the whole, mixed traffic flow rather than those for the individual vehicles used in the measurement programme. Emission functions are most often expressed in terms of two main variables: the type of vehicle and the average speed at which it is driven. The vehicle classification is designed to take into account the features of the vehicle that influence its emissions (such as its size or weight, the fuel it uses and the emission control standard to which it was designed). The average speed is a simplified analogue for the operation of the vehicle. It is well correlated with the operational aspects that have a more direct effect on emissions such as the gear selection, engine speed, rate and frequency of acceleration and deceleration, etc. This conventional approach has also been adopted in this work. It must be noted, however, that the derived functions are based in most cases on measurements from a single vehicle and cannot be considered to be representative of a particular vehicle class. In consequence, the absolute values given below (for rates of emission and, subsequently, their effects on airborne nitrogen dioxide concentrations) should not be considered to be precise, but only to indicate the general magnitude of the contribution made by primary emissions of nitrogen dioxide.

An alternative approach is to calculate the proportion of oxides of nitrogen that is emitted as nitrogen dioxide (i.e. the NO$_2$/NO$_X$ ratio in the exhaust) and to apply that proportion to the more general and representative total oxides of nitrogen emission functions that are available. This may give additional accuracy, but it must be remembered that, in this case, the NO$_2$/NO$_X$ ratio functions are based on very limited data.

(iii)   Vehicle classification

A number of considerations determine the way in which the vehicle classification has been determined:

- The types of vehicle for which emission data are available

- The features of the vehicles that influence their rates of emission

- The availability of traffic composition data (it is of no use to define a vehicle class if it is not possible to quantify its presence within the traffic)

As noted earlier, emission tests were carried out on petrol engined cars and diesel engined LGVs, HGVs and buses. In each case, an example was tested from vehicles approved to the pre-Euro 1, Euro 1 and Euro 2 emission classes, and in the case of the cars, vehicles with small (< 1.4 litre), medium and large (> 2 litre) engines were tested. These characteristics were used to define the basic classification. The main deficiencies in the data were results from diesel engined cars and from petrol engined LGVs. It was assumed that the data for cars and LGVs are interchangeable: i.e. diesel cars were assumed to emit the same as diesel LGVs, and petrol LGVs the same as petrol cars. This, of course, will introduce an additional source of error into the procedure, but, as the technologies used in the two vehicle classes are broadly similar, it is considered better than neglecting these particular vehicle types. Table 6 lists the basic classification system used.

Table 6: Vehicle classification system used for the emission functions

Vehicle type	Fuel	Size	Emission standard
Car	Petrol	Small	Euro 0
	Diesel	Medium	Euro 1
		Large	Euro 2
LGV	Petrol	Not distinguished	Euro 0
	Diesel	Not distinguished	Euro 1
			Euro 2
HGV	Diesel	Not distinguished	Euro 0
			Euro 1
			Euro 2
Bus	Diesel	Not distinguished	Euro 0
			Euro 1
			Euro 2

(iv) Derivation of the emission functions

As a preliminary stage in deriving the functions, the emission data for each of the vehicle categories were plotted against the average speeds of the test cycles used. Figure 2 shows some examples. This provided a rapid means of assessing the appropriateness of the intention to generate average speed related functions. Had the data not shown a reasonably consistent and systematic relationship with the average cycle speed, an alternative approach would have been necessary.
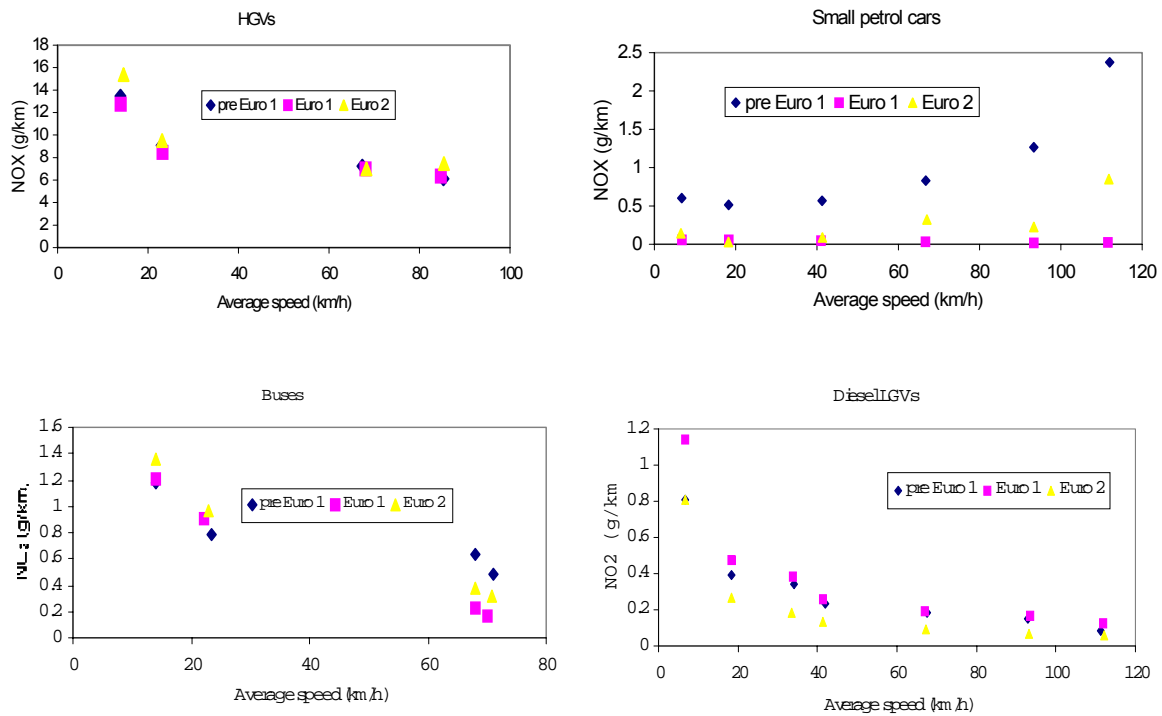
Figure 17: Some examples of the measured emission rates shown as a function of average speed

The data plotted, and subsequently used for the derivation of the emission functions, exclude those measured over the legislative test cycle (96/69/EC for light duty and simulated 13 mode for heavy duty vehicles). The data also excludes the measurements at reduced ambient temperatures as these were only carried out on medium size petrol cars. It is widely recognised that the legislative test cycles do not fully represent in-use driving conditions: they are very simplified, containing sequences of steady speeds and, for light duty vehicles, constant rates acceleration and deceleration. The exclusion of measurements at reduced ambient temperatures, by removing a source of variability, decreased the variability of the data, providing functions with a greater statistical significance.

In the graphs in Figure 2, it is notable that there is a much greater reduction in the emissions from petrol cars over the transition from the pre Euro 1 to the Euro 1 standard than for diesel vehicles (LGVs, HGVs and buses). This is perhaps to be expected since the Euro 1 standard necessitated the use of three-way catalysts on petrol vehicles, and thus introduced a large, step change in their emissions performance, while for diesels the standards were met by more general improvements to the engine. Nevertheless, these data do confirm other observations that the changes in emission standards have had relatively little influence on oxides of nitrogen emissions from diesel vehicles. One reason may be that the vehicles are designed to meet the standards using the prescribed legal test procedure, and that they are less well controlled when operated differently. Some indication of this is suggested in the data for oxides of nitrogen emissions from buses. At low average speeds, there is little difference between the rates of emission from pre Euro 1, Euro 1 or Euro 2 vehicles, while at higher speeds the difference increases, with pre Euro 1 vehicles emitting around twice the oxides of nitrogen of their successors. Operation at high speed is much more similar to the standard test conditions (constant speed and load) than lower speed operation that contains sequences of acceleration, deceleration and idling, with only a limited amount of constant speed operation under load.

Having determined that the emission rate and average speed data were related in a sufficiently systematic way for this approach to be used, best fit curves were determined for all of the vehicle types. In almost all cases, it was found that the relationship could be well represented by a quadratic equation in average speed. While more complex functions may have slightly improved the statistical

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fit of the curves to the data, their use was not justified given the limited amount of data and the relatively high statistical significance of the quadratic curves in most cases as indicated by the high R^2 values. A number of examples of the derived curves are shown in Figure 18, and they are tabulated for all of the vehicle types in Table 7.
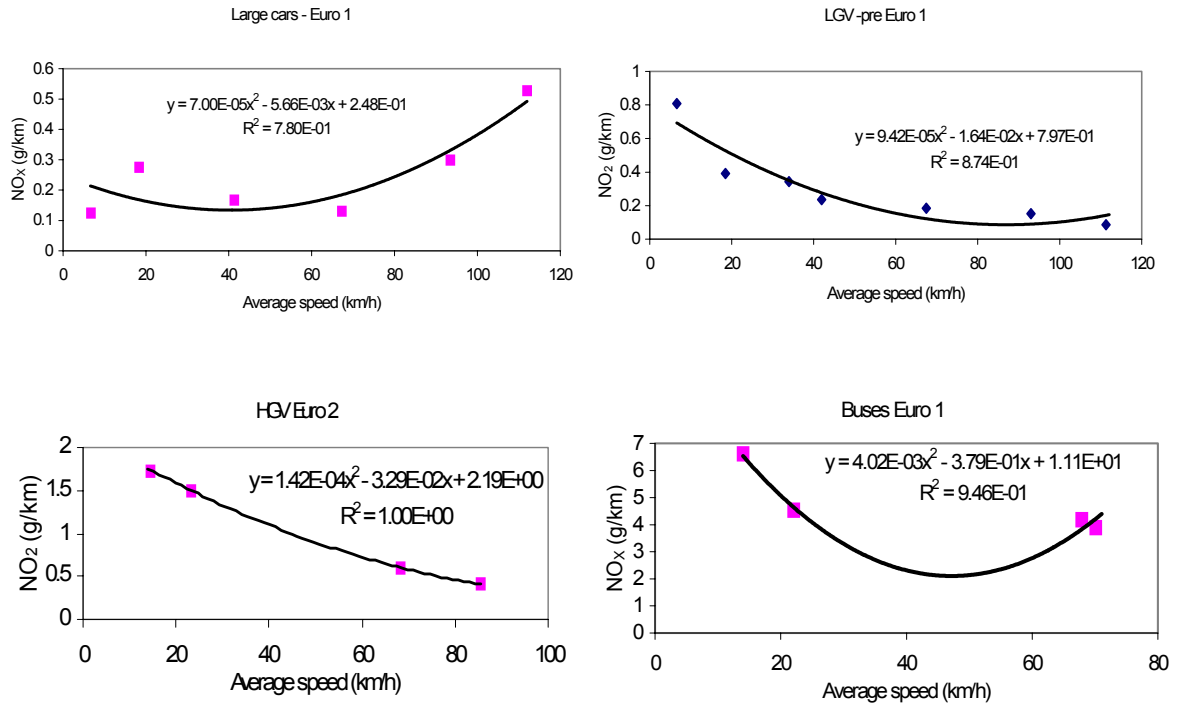

Figure 18: Emission rates plotted against average speed with fitted curves

Table 7: Coefficients of the emission functions for all vehicle types

Vehicle type	Nitrogen dioxide			Total oxides of nitrogen		
	a	b	c	a	B	c
Small car Euro 0	0.0134	-0.000392	0.00000377	0.762	-0.0189	0.000287
Small car Euro 1	0.00759	-0.000214	0.00000151	0.0643	-0.000592	0.00000165
Small car Euro 2	0.00624	-0.000137	0.000000958	0.172	-0.00707	0.000109
Medium car Euro 0	0.0221	-0.000596	0.00000878	1.39	-0.00113	0.000205
Medium car Euro 1	0.0264	-0.000800	0.00000895	0.585	-0.0138	0.000118
Medium car Euro 2	0.0113	-0.000248	0.00000170	0.178	-0.00315	0.0000224
Large car Euro 0	0.0160	-0.000402	0.00000794	1.52	0.00263	0.000246
Large car Euro 1	0.00712	-0.0000965	0.000000586	0.248	-0.00566	0.0000700
Large car Euro 2	0.0302	-0.000777	0.00000501	0.105	0.00173	0
LGV Euro 0	0.797	-0.0164	0.0000942	4.47	-0.0965	0.000639
LGV Euro 1	0.999	-0.0222	0.000134	7.40	-0.178	0.00120
LGV Euro 2	0.600	-0.0145	0.0000895	2.84	-0.0782	0.000575
HGV Euro 0	1.69	-0.0319	0.000168	15.6	-0.258	0.00178
HGV Euro 1	1.98	-0.0412	0.000269	15.2	-0.277	0.00211
HGV Euro 2	2.19	-0.0329	0.000142	20.1	-0.468	0.00383
Bus Euro 0	1.81	-0.0538	0.000514	16.2	-0.594	0.00665
Bus Euro 1	1.78	-0.0463	0.000339	11.1	-0.379	0.00402
Bus E2	2.09	-0.0595	0.000496	14.1	-0.463	0.00443

Note: Equations are of the form $x = a + bv + cv^2$, where x is NO_X or NO_2 in g/km, v is the average vehicle speed in km/h and a, b and c are the coefficients given in the table

(v) Traffic weighted emission functions

As noted previously, one of the criteria determining the appropriateness of a vehicle classification system for emission estimation is the availability of information on the traffic composition for which the estimates are to be made. Traffic data often give a simple count of all vehicles, sometimes supplemented by a fairly basic classification into vehicle types, e.g. cars, light goods vehicles, heavy goods vehicles, buses and motorcycles. Some of the vehicle characteristics that are important influences on emission rates are rarely, if ever, specified because they are very difficult to observe, manually or automatically, during a traffic survey. These features include, for example, the fuel type (petrol or diesel) of cars and LGVs, the engine capacity or weight of the vehicles and their emission standard. As these types of data are usually unobtainable, it is necessary to aggregate the emission functions for the individual vehicle types, grouping them according to the traffic data that are available. The aggregation procedure weights the emission functions in proportion to the likely prevalence of the individual vehicle types within a typical traffic flow, making use of national statistics on vehicle registration and use.

For this study, traffic composition data compiled as input to the National Atmospheric Emission Inventory (NAEI) (Murrells, 1999) have been used as the basis for the aggregation of the emission functions. These data give, for each year between 1970 and 2025, an estimate of the fraction of each type of vehicle that belongs to a particular class according to its emission standard and the percentage

of diesel vehicles in the car and LGV classes. In addition it includes, for each year, the number of vehicle kilometres driven by each vehicle class on urban, rural and motorway road types. By combining these data it is possible to calculate the traffic composition according to the variables represented in the data set. The NAEI forecasts traffic do not correspond precisely with the emission data available from this work. They do not classify cars by engine size, they distinguish LGVs into three classes according to weight, they differentiate HGVs into 'rigid' and 'articulated' types, they include motorcycles and, in some cases, they include emission standards earlier than those included in this emission measurement programme. These differences have been treated as follows:

- Cars have been classified as small (engine capacity below 1.4 litres), medium (1.4 - 2 litres) and large (above 2 litres) using data from SMMT (Society of Motor Manufacturers and Traders, 2000). SMMT provide an annual breakdown of the registered car fleet by engine capacity and year of registration, so it is possible to make this classification individually for each legislation class.

- LGVs have been treated as a single size group by combining the NAEI data.

- HGVs have been treated as a single group by combining the NAEI data.

- Motorcycles have been ignored (they account for only a very small fraction of the traffic - less than 1% on a national basis)

- Early emission standards have all been grouped into the Euro 0 (pre-Euro 1) class.

The result of this aggregation procedure is a simplified set of emission functions, giving traffic-average emission rates for cars, LGVs, HGVs and buses as a function of average vehicle speed. These functions are illustrated in Figure 19.
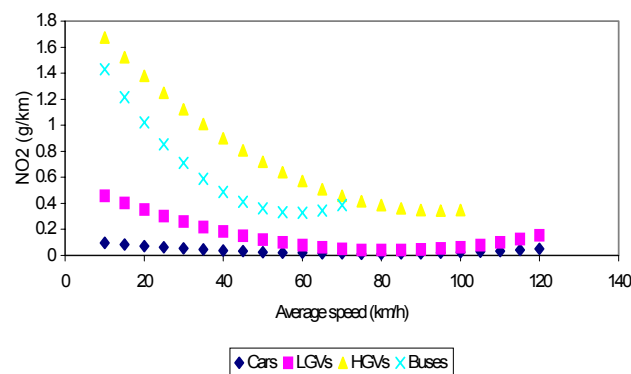
Figure 19: Traffic-average emission functions

(vi) Nitrogen dioxide concentrations

To assess the contribution of primary nitrogen dioxide emissions to atmospheric concentrations, a pollution dispersion model has been used to estimate nitrogen dioxide concentrations for two typical traffic situations. In both cases, the estimates have been made in two ways:

- Assuming that all of the nitrogen oxides emissions are in the form of nitric oxide. In this case, the nitric oxide is assumed to disperse normally away from the traffic source, and the formation of nitrogen dioxide is evaluated using a relationship between NO_X and NO_2 derived empirically from observations near to traffic.

- Assuming the emissions to contain both nitric oxide and nitrogen dioxide in proportion to the emission measurements in this project, using the functions described above. The dispersion of both nitric oxide and nitrogen dioxide is treated in the same way, and the partial conversion of the nitric oxide fraction of the emissions to nitrogen dioxide is calculated using the same empirical relationship. However, in this case, the primary nitrogen dioxide is superimposed onto that produced from the nitric oxide.

The differences between the concentrations estimated by the two methods gives an indication of the contribution of the primary nitrogen dioxide emissions.

In order that the situations represented in the examples might reflect realistic traffic and pollution conditions, traffic data have been taken from actual road networks. The first example considers part of the road system in the centre of Leicester and uses traffic data generated by Leicester City Council's Greater Leicester Traffic Model. The second example concerns part of the M25 motorway, using traffic data collected by TRL on behalf of the Highways Agency by the Motorway Incident Detection and Signing System (MIDAS).

The calculation of the pollution concentrations followed a two-stage procedure. Firstly, estimates of traffic emissions were made for each link in the road network under consideration. The second stage used these emission estimates with a pollution dispersion model to simulate the spread of the pollution from the roads. The emission calculations were performed in a simple spreadsheet based on the emission functions for total oxides of nitrogen and nitrogen dioxide described above. The dispersion was simulated using a FORTRAN computer programme formulating a model based on the Gaussian dispersion principle. This model was originally developed by TRL to estimate carbon monoxide pollution levels near to traffic, but has subsequently been adapted to calculate levels of other pollutants, including nitrogen dioxide. For this work, it was further modified to enable the separate treatment of nitric oxide and nitrogen dioxide emissions and to make it compatible with the output from the emission calculation spreadsheet. While this model is relatively simple, it has been shown to provide an accuracy comparable with those of commercially available dispersion models.

(vii)   Example 1: Urban Traffic in Leicester

The Greater Leicester Traffic Model was used to generate classified traffic flows and speeds on a network of more than 3000 road links representing the whole of Greater Leicester. A subset of these data, from part of the network in the centre of the city, was used to provide input for the calculation of nitrogen dioxide in a typical urban context. As shown in Table 8, each link is identified by the co-ordinates of its end points (nodes a and b), using the National Grid Reference (x_a, y_a, x_b and y_b), and the link length is given in metres. The traffic flow (in vehicles per hour) is given separately for cars, light goods vehicles (LGV), medium goods vehicles (MGV), heavy goods vehicles (HGV), motorcycles (M/C) and buses (PT); speeds are given separately for buses (speed PT) and other traffic (speed HW).

Table 8: An example of traffic data from the Greater Leicester Traffic Model

Node a	Node b	Xa	Ya	Xb	Yb	Length	Speed HW	Speed PT	Car	LGV	MGV	HGV	M/C	PT
331	333	458365	304358	458416	304374	60	8.0	7.2	1006	147	50	74	16	1
331	334	458365	304358	458323	304342	40	34.3	30.0	183	27	9	13	3	58
332	1498	459176	305521	459160	305635	110	24.4	17.6	352	52	18	26	5	44
333	1711	458416	304374	458410	304332	40	10.9	8.1	1006	147	50	74	16	1
334	335	458323	304342	458196	304343	130	23.6	17.0	1383	203	69	101	21	78
335	336	458196	304343	458264	304461	150	13.0	9.6	2956	433	148	217	46	80
335	457	458196	304343	458044	304338	180	45.0	30.0	917	134	46	67	14	58
336	337	458264	304461	458314	304479	50	30.0	30.0	969	142	49	71	15	80
336	338	458264	304461	458254	304577	120	25.7	18.5	1552	227	78	114	24	0
336	390	458264	304461	458285	304417	50	13.0	9.6	436	64	22	32	7	0
337	331	458314	304479	458365	304358	140	27.1	19.5	1188	174	60	87	18	59
337	392	458314	304479	458391	304513	80	8.0	30.0	524	77	26	38	8	93
338	339	458254	304577	458283	304629	60	32.7	23.6	1199	176	60	88	18	0
338	864	458254	304577	458206	304828	260	30.6	22.0	355	52	18	26	5	0

Because the vehicle classification produced by the Leicester model is not exactly the same as that of the emission functions, the data were adapted slightly for compatibility: the MGV and HGV classes were combined to give a single class of heavy goods vehicles and the motorcycles were ignored. The calculation of traffic emission rates from these data is illustrated for some of the road links in Table 9 which also contains notes describing the calculation procedure.

Table 9: Emission rates calculated from the Leicester traffic data

Length (m)	Speed (km/h) HW	Speed (km/h) PT	Number of vehicles Car	LGV	HGV	Bus	NO_x (g) Car	LGV	HGV	Bus	NO_2 (g) Car	LGV	HGV	Bus	NO_x (g/m.s)	NO_2 (g/m.s)
40	13.9	11.1	1006	147	124	1	32.0	14.9	65.1	0.4	3.5	2.5	7.7	0.1	7.80E-04	9.55E-05
460	22.7	17.6	1899	278	234	0	583.9	252.0	1168.9	0.0	59.3	41.7	141.5	0.0	1.21E-03	1.46E-04
120	27.8	20.9	2284	335	282	49	167.0	67.9	328.9	36.1	15.9	11.2	40.0	5.8	1.39E-03	1.69E-04
190	24.1	18.2	2623	384	324	57	324.6	138.0	647.2	74.8	32.5	22.8	78.5	11.8	1.73E-03	2.13E-04
50	15.0	11.9	471	69	58	0	18.3	8.5	37.3	0.0	2.0	1.4	4.4	0.0	3.56E-04	4.35E-05
30	25.5	19.2	2581	378	318	69	49.1	20.6	97.6	13.7	4.8	3.4	11.8	2.2	1.68E-03	2.06E-04
190	11.8	11.0	282	41	35	0	44.4	20.9	90.5	0.0	4.9	3.4	10.7	0.0	2.28E-04	2.79E-05
90	24.6	18.6	2581	378	318	69	149.9	63.4	298.4	42.3	14.9	10.5	36.2	6.7	1.71E-03	2.11E-04
110	15.9	12.6	2581	378	318	20	216.6	99.3	439.6	19.3	23.4	16.4	52.6	2.9	1.96E-03	2.40E-04
60	48.0	35.4	0	0	0	50	0.0	0.0	0.0	9.6	0.0	0.0	0.0	1.7	4.43E-05	7.99E-06
180	16.2	12.7	1031	151	127	20	140.9	64.5	285.9	31.4	15.2	10.6	34.2	4.7	8.07E-04	9.99E-05
460	28.3	21.2	1550	227	191	0	430.7	173.9	846.8	0.0	40.8	28.7	102.8	0.0	8.76E-04	1.04E-04
30	25.5	19.2	2199	322	271	1	41.9	17.5	83.2	0.2	4.1	2.9	10.1	0.0	1.32E-03	1.59E-04
30	25.5	19.2	2224	326	274	20	42.3	17.7	84.1	4.0	4.2	2.9	10.2	0.6	1.37E-03	1.66E-04
60	16.3	12.8	2557	375	315	1	116.1	53.1	235.6	0.5	12.5	8.8	28.2	0.1	1.88E-03	2.29E-04
130	25.3	19.1	2557	375	315	51	211.8	88.8	420.8	44.1	20.9	14.7	51.1	7.0	1.64E-03	2.00E-04
100	15.0	11.9	471	69	58	0	36.7	16.9	74.5	0.0	4.0	2.8	8.9	0.0	3.56E-04	4.35E-05
130	30.9	23.1	2087	306	258	51	157.2	61.2	305.8	36.8	14.3	10.1	37.1	6.1	1.20E-03	1.44E-04

Traffic emission rates for each link are calculated as follows:

1. The emission rate per vehicle.kilometre is calculated for each type of vehicle using the average speed related emission function and the appropriate speed for the vehicle type and link.

2. Total emissions per hour for each vehicle type and link are calculated using the emission rate from step 1, the number of vehicles per hour and the link length.

3. Total emissions per hour for each link are calculated by adding together the contributions from each type of vehicle.

4. The emission rate for each link, in grams per metre per second, is calculated from the total emissions, the link length and the number of seconds in an hour.

These emission rates were input to the dispersion model, together with the location of each link (given by the end point co-ordinates as shown in Table 9), and meteorological data, which determine the rate and direction of the dispersion of the emissions. In order to represent average dispersion conditions, the meteorological data were specified as a wind rose giving the average wind speed in each of 12 evenly spaced wind directions and the frequency of occurrence of winds in each direction. Pollutant concentrations were calculated for each speed and direction pair, and a weighted average calculated using the frequency values. Concentrations of nitrogen dioxide were estimated at all points in a 20 metre x 20 metre grid covering the area of the road network. No allowance was made for the background pollution concentration, and so the estimated values are lower than if this had been taken into account. However, as the background level would affect concentrations equally for both of the calculation methods, it would not affect the difference between them. Graphical representations of the results are given in Figure 20.
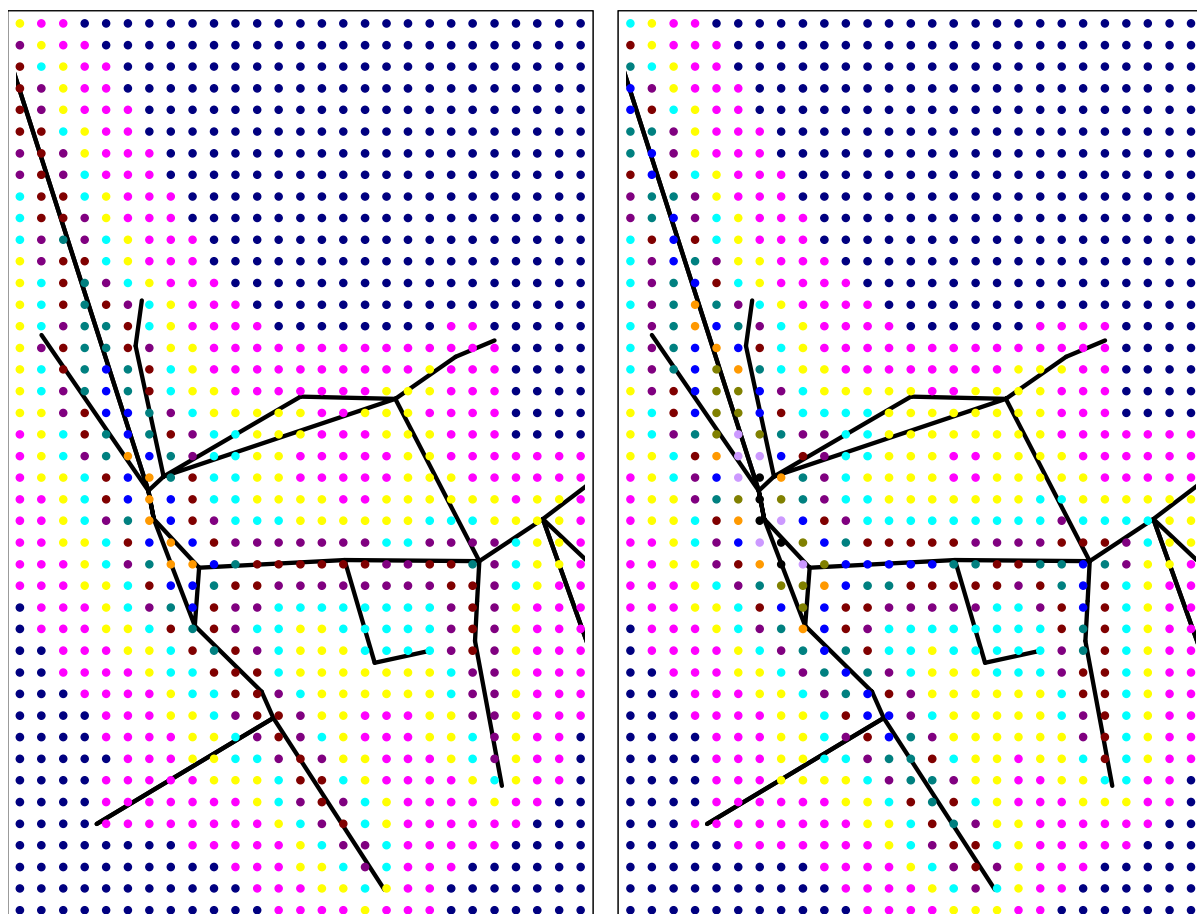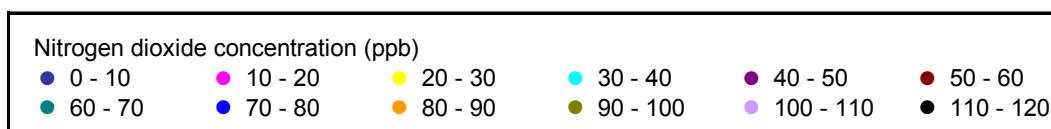

Figure 20: Concentrations of nitrogen dioxide near to a selection of roads in the centre of Leicester calculated assuming that all NO$_X$ emissions are NO (left) and with the proportion of NO$_2$ indicated by the emission measurements (right)

While the two plots in the figure show a very similar pattern of pollution concentrations, it is clear that higher concentrations occur, as expected, in the case where an allowance has been made for primary emissions of nitrogen dioxide. Where no such allowance is made, the highest predicted concentrations fall in the range of 80 - 90 ppb, while the highest concentrations are in the range of 110 - 120 ppb when primary nitrogen dioxide emissions are taken into account. In order to show the differences between the two methods of calculation more clearly, Figure 21 shows a similar plot, but with bands of percentage difference rather than concentration.
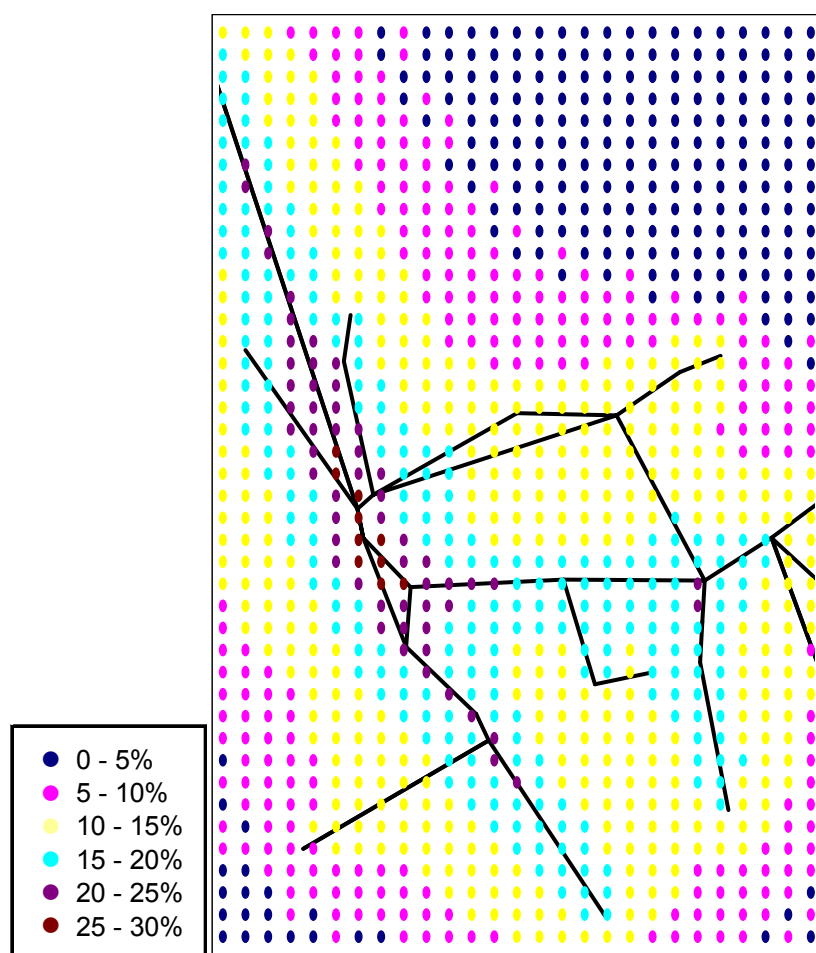

Figure 21: Percentage differences between nitrogen dioxide concentrations estimated with and without primary nitrogen dioxide emissions

The variation between the two methods of calculation approaches a value of 30% in the most polluted areas near to the centre of the network, with a difference only a little above zero in the more peripheral areas. (It should be noted, though, that these areas near the border of the region would be influenced by emissions from road links outside of the area for which the calculations were carried out, and that it is likely that nitrogen dioxide concentrations would be higher in absolute terms and the difference between the two methods of calculation would be greater if this influence had been included).

The variation in the percentage difference results mainly from the proportion of nitric oxide emissions estimated to be converted to nitrogen dioxide. As the total oxides of nitrogen concentration reduces with increasing dispersion from the road network, so the proportion that is oxidised increases, and approaches 100% at low levels. When that condition is reached, it is irrelevant whether the original

emission was of nitric oxide or nitrogen dioxide, and therefore the same result will be obtained under the two assumptions considered.

viii)   Example 2: motorway traffic on the M25

On behalf of the Highways Agency, TRL Limited analyses traffic data collected from selected sections of the English Motorway network. These data are taken from inductive loop detectors which form the basis of the Motorway Incident Detection And Signing (MIDAS) system. The paired loop detectors are used to determine the flow, speed and length (categorised) of vehicles passing over them. Data are collected from each lane separately and loop detector sites are usually located at 500 metre intervals. Basic data are reported at one-minute intervals, i.e. the number of vehicles passing over an individual loop pair and the average speed of vehicles in that minute. Categorised lengths are reported each minute but are the aggregate of all lanes for a given site, rather than individual lanes.

One of these MIDAS sites, on the M25 between Junctions 10 and 11 (to the south-west of London) was chosen as the source of data for this second example. The data recorded minute by minute were aggregated to give hourly flows, speed and traffic classification by length. Table 10 shows an example of the available data in the form reported by the MIDAS system for the early hours of the morning on 1 September 2000.

Table 10: Data on traffic flows, speeds and lengths from the M25 MIDAS system

1 September 2000

Traffic flows	A				B			
	Lane 1	Lane 2	Lane 3	Lane 4	Lane 1	Lane 2	Lane 3	Lane 4
00:00	306	317	166	15	255	295	189	24
01:00	270	206	78	3	203	179	90	3
02:00	240	179	78	2	213	214	81	4
03:00	244	195	62	1	231	251	125	8
04:00	347	304	117	6	280	245	160	17

Traffic speeds (km/h)	A				B			
	Lane 1	Lane 2	Lane 3	Lane 4	Lane 1	Lane 2	Lane 3	Lane 4
00:00	95.9	111.7	126.8	128.0	96.7	108.3	119.6	128.9
01:00	98.4	112.7	126.5	136.0	96.8	110.9	122.3	149.5
02:00	96.5	113.7	127.6	128.5	96.8	110.9	121.7	123.3
03:00	96.7	115.3	128.7	132.0	97.6	108.3	122.3	137.4
04:00	95.3	112.9	124.2	130.6	93.8	108.9	120.1	131.3

Vehicle lengths (m)	A				B			
	<5.6	5.6>6.6	6.6>11.6	>11.6	<5.6	5.6>6.6	6.6>11.6	>11.6
00:00	598	34	46	126	600	29	43	91
01:00	383	22	34	118	327	19	51	78
02:00	330	18	24	127	340	25	40	107
03:00	299	33	42	128	426	28	61	100
04:00	495	41	58	180	429	35	78	160

Certain assumptions were again necessary to ensure compatibility between the MIDAS traffic data and the data available for the calculation of emissions. MIDAS classifies vehicles by length: it was therefore necessary to define the vehicle types according to these length classes. It was assumed that all of the shortest vehicles (< 5.6 m) were cars, that all of the vehicles in the second class (5.6 - 6.6 m) were light goods vehicles and that all remaining vehicles were heavy goods vehicles. The last assumption ignores the fact that some of the longer vehicles would be buses and/or coaches. However, the number of these is likely to have been small, and their engine technology and emissions behaviour are similar to those of HGVs, so it was assumed the approximations made would have a negligible effect on the results.

Because the data on vehicle length were not available on a lane by lane basis, it was necessary separately to assign the flows of the different types of vehicles to each of the lanes. As the main objective of this example was to show the relative effect of primary NO_2 emissions rather than to produce precise absolute estimates of emissions and pollution levels, this assignment was made somewhat arbitrarily, as follows:

- Lane 1: Two thirds of the total HGV flow, one quarter of the total LGV flow, the balance between this and the total lane flow being cars

- Lane 2: One third of the total HGV flow, one quarter of the total LGV flow, with the balance again being cars

- Lane 3: One half of the total LGV flow, with the balance made up by cars

- Lane 4: All of the remaining cars

Emissions and pollution concentrations were calculated separately for six hours, selected to cover a range of different conditions of traffic flow, speed and composition. The times chosen were:

- 05:00 - 06:00 - Although at this time the total flow of traffic is rather low, the proportion of goods vehicles is high compared with other times of the day (LGV 5%, HGV 28%). Average speeds are at or above the national speed limit (90 - 135 km/h, varying by lane).

- 06:00 - 07:00 - The total flow begins to increase rapidly, the proportion of goods vehicles reduces. Speeds are slightly lower, but still indicate free flow conditions (90 - 120 km/h).

- 07:00 - 08:00 - The total flow is the highest of the day and there is still an appreciable proportion of goods vehicles (LGV 4%, HGV 10%). Speeds again fall, but remain relatively high (80 - 105 km/h).

- 17:00 - 18:00 - The flow is relatively high, but the proportion of goods vehicles is approaching its daily minimum. Average speeds on some lanes are low, indicating congestion (45 - 90 km/h).

- 18:00 - 19:00 - The total flow remains high, with slightly fewer goods vehicles. Speeds increase somewhat (55 - 95 km/h).

- 19:00 - 20:00 - The flow remains high and the proportion of goods vehicles reaches its minimum (LGV 2%, HGV 6%). Speeds are almost restored to their free-flow values (85 - 120 km/h).

Emissions and pollution concentrations were again calculated using the procedures described above, and for the assumptions that all oxides of nitrogen emissions were nitric oxide or that they were a mixture of nitric oxide and nitrogen dioxide as indicated by the emission measurements. Figure 22 shows a graphical presentation of the predicted concentrations, and Figure 23 the difference between the two calculation methods, in the same way as the results are given in the previous example. The data shown are those calculated for the period 07:00 to 08:00.
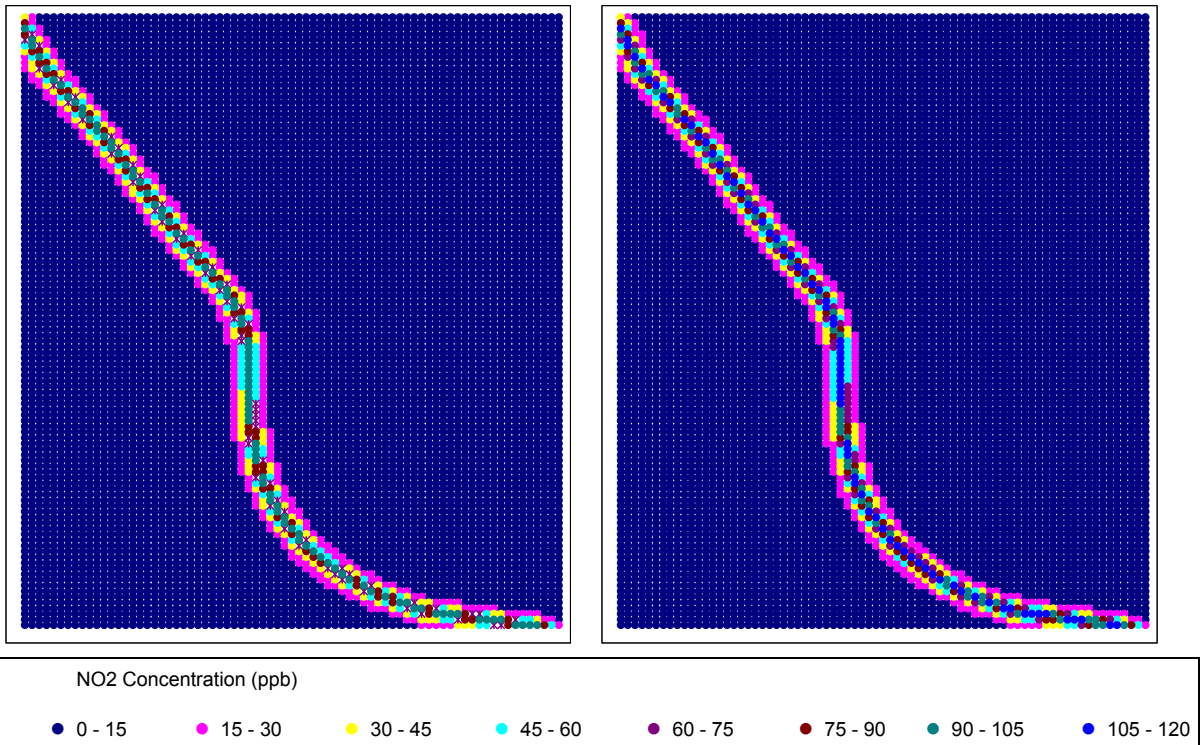
NO2 Concentration (ppb)

● 0 - 15 ● 15 - 30 ● 30 - 45 ● 45 - 60 ● 60 - 75 ● 75 - 90 ● 90 - 105 ● 105 - 120

Figure 22: NO$_2$ concentrations estimated for the period 07:00 – 08:00 between junctions 10 and 11 of the M25. Estimates on the left assume no primary NO$_2$ emissions; those on the right assume primary NO$_2$ emissions as measured in this study
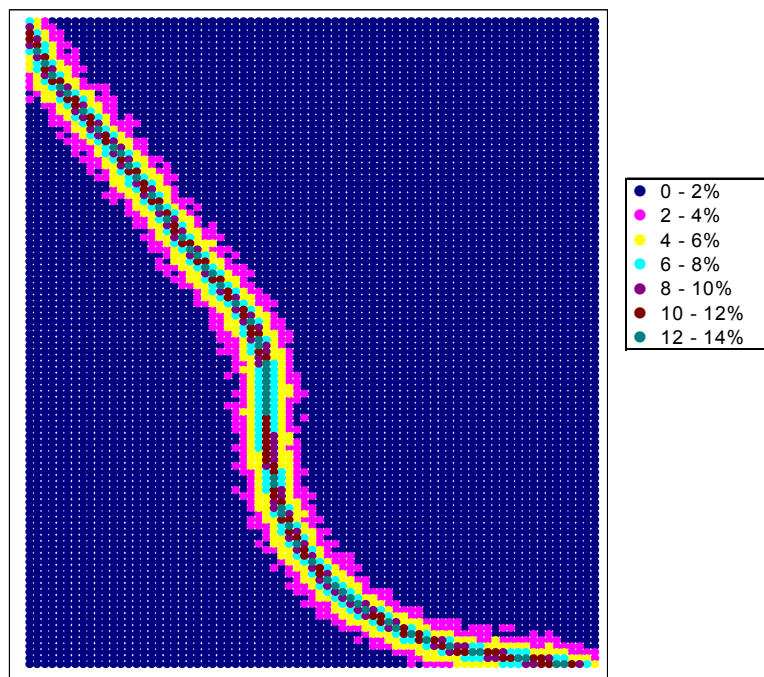

● 0 - 2%
● 2 - 4%
● 4 - 6%
● 6 - 8%
● 8 - 10%
● 10 - 12%
● 12 - 14%

Figure 23: Percentage differences between the NO$_2$ concentrations estimated with and without the inclusion of primary NO$_2$ emissions

It should be noted that the data calculated and illustrated in Figure 22 and Figure 23 do not take into account any sources other than the traffic on the M25 and, therefore, the concentrations in rather large areas of little impact do not represent real conditions. In fact, around this motorway section, there are towns and villages such as Byfleet, New Haw and Addlestone, a main railway line, an airfield and

many other possible sources of pollution that would add to the concentrations shown in the graphs. However, as regards the contribution from the motorway alone, it is again the case that higher concentrations are calculated when the effect of primary nitrogen dioxide emissions is included. The differences between the two sets of estimates are rather lower than for the urban traffic example based in Leicester, with a maximum difference of about 14% at the locations nearest to the motorway.

It is noted above that similar calculations were carried out for different times of the day when the traffic conditions on the motorway varied, either in terms of total flow, traffic composition, speeds or combinations of these three. The results have been used to examine the effect of such variations in traffic on the relative impact of the primary nitrogen dioxide emissions. The parameters that have been examined in relation to these traffic variables are the average and maximum concentrations of nitrogen dioxide, and the average and maximum values of the ratio between the NO_2 concentrations calculated with and without taking into account the primary emissions. Because a large part of the area covered by the calculations is largely unaffected by the motorway emissions (see Figure 22 and Figure 23), the analysis has been restricted to those parts of the grid where the estimated nitrogen dioxide concentration exceeded 10 ppb, i.e. where there was a noticable influence from the motorway traffic.

Initially, the pollution parameters were examined with respect to each of the traffic variables independently. As shown in Figure 24, the relationships were rather weak. For example, the highest values for the average and maximum nitrogen dioxide concentrations are not associated with the highest traffic flow of about 13000 veh/h, but with a lower flow around 8000 veh/h, and there is considerable scatter in all of the plots involving the ratio of NO_2 concentrations calculated by the two methods. These apparent inconsistencies are because the traffic related variables are, to some extent themselves intercorrelated (for example, as the flow increases speeds and the percentage of goods vehicles tend to reduce) and their effects on emissions are sometimes in opposition. At a low rate of traffic flow, with a high percentage of goods vehicles, the total emissions may be equal to those from a much higher flow with fewer goods vehicles, and so on.

Thus, when the effects of the traffic variables are considered in combination, the variability of the pollution is more readily explained. Figure 25 again shows the plots presented in Figure 24, and in addition, shows values calculated from the traffic variables using equations generated by a multiple regression procedure. The results of the regression analysis follow to a large extent the variations in the pollution data.
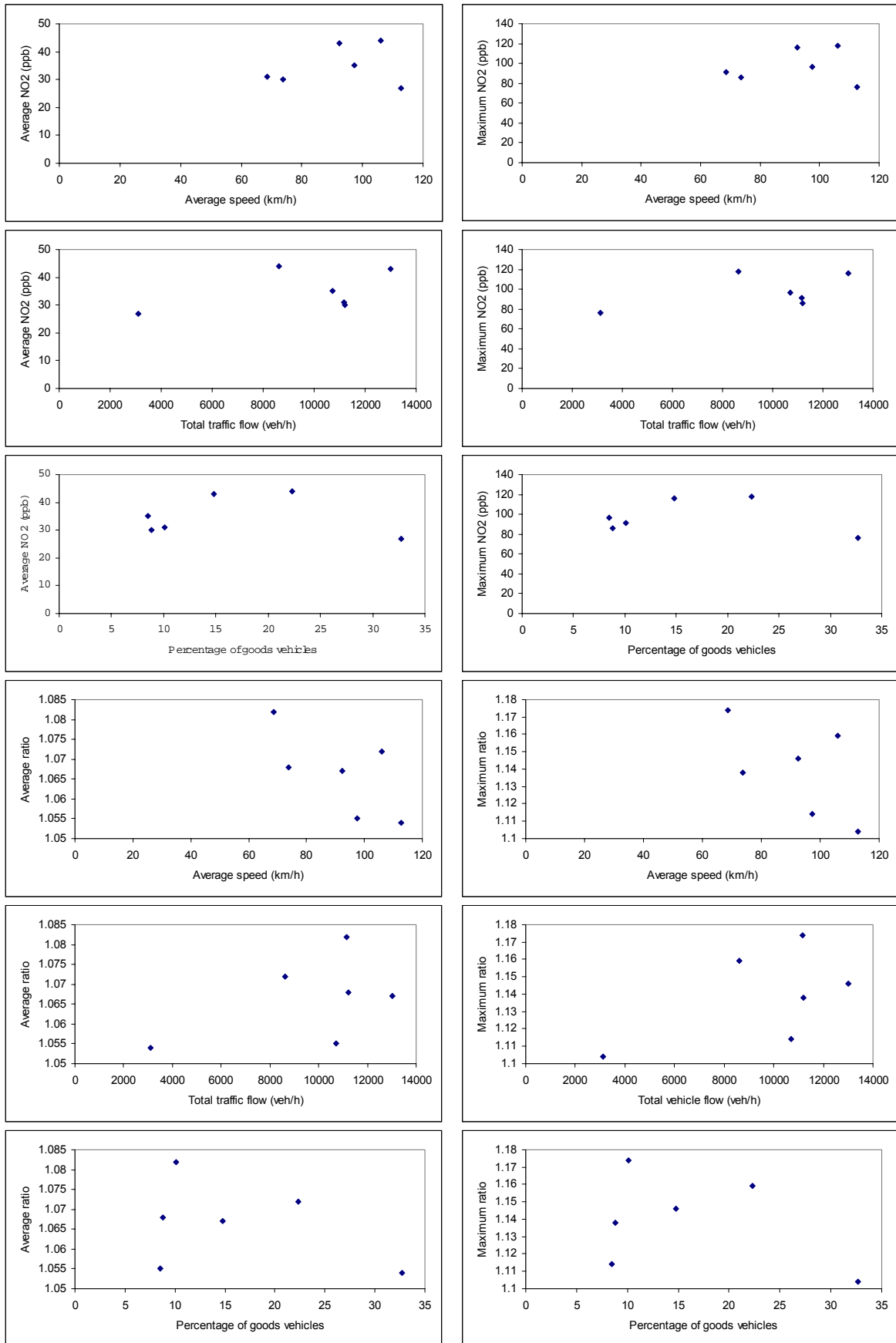
Figure 24: The variation of NO2 concentration estimates and the ratio of estimates with and without taking into account primary emissions with a number of traffic variables
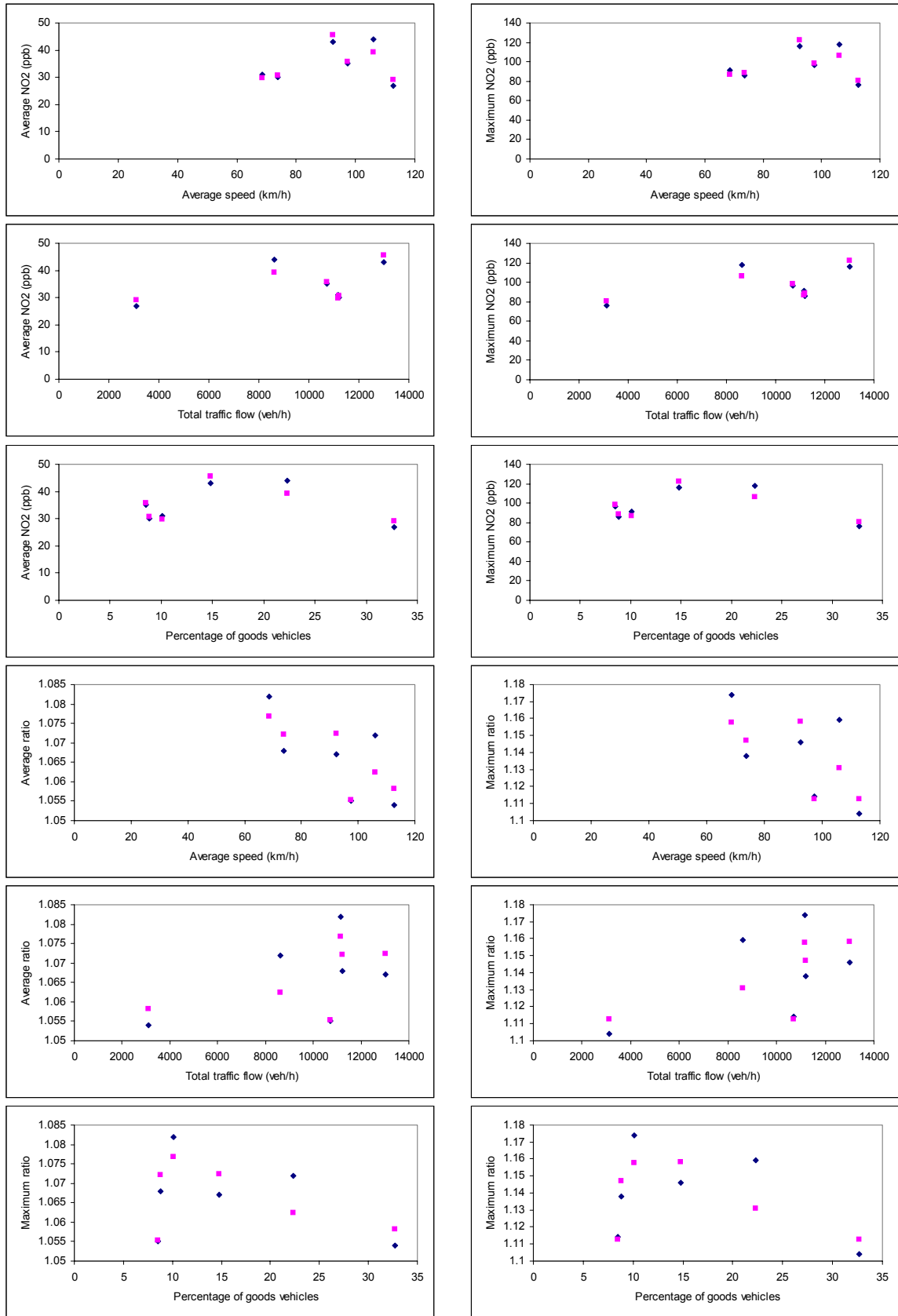
Figure 25: The variation of nitrogen dioxide concentration estimates and the ratio of estimates with and without taking into account primary emissions with a number of traffic variables

Note: Figure 25 also shows estimates of the pollution variables derived from a multiple regression model involving three traffic variables.

4.1.4   Discussion of NO_2 and NO_x results

One reason for the lack of data regarding NO_2 emissions in the literature is that standard methods of analysing NO_x using CHEM analysers measure NO or NO_x but not NO_2 directly. NO_2 can be inferred from the difference between the NO_x and NO readings, but since the amount of NO_2 emitted from vehicles is usually far less than the NO, any discrepancy in the NO_x and NO measurements can lead to very large errors in estimating NO_2. For this reason a direct method of measuring NO_2 was chosen using a FT-IR analyser which could be compared with the more standard method of inferring NO_2 from CHEM measurements of NO and NO_x.

As the FT-IR was considered to be the more reliable method of measuring NO_2 many the dependencies of this emission with the independent variables were analysed using FT-IR rather than CHEM analysis, although CHEM methods were compared with the FT-IR. Some of the NO_2 levels measured using the CHEM gave negative figures. Again this confirms the unreliability of this method.

(i) Effect of sampling and measurement method

The temperature and the concentration of reactants can influence NO_2 formation. Therefore, it was considered that the sampling method should be also examined in some detail. The sample gas was fed to the analysers in a raw state or by diluting it with ambient air, and also by using heated or unheated lines, so a variety of measurement and sampling methods could be compared.

The examination of the influence of using different sampling techniques on the measured emissions of NO_2 and the determination of NO_2/NOx ratios confirmed the importance of establishing standardised methods for both sampling and measuring these parameters. It should be noted that the results obtained using the CHEM analyser could be affected by reactions between NO and oxygen and any trace ozone present in the dilution air which could produce additional NO_2. Higher concentrations and temperatures of oxygen or ozone in the dilution air would increase the rate of reaction and therefore potentially increase NO_2 concentrations.

The results using the raw unheated gas gave the lowest average NO_2 levels. This is consistent with the expected effect of the lower oxygen content and lower temperature of the sample gas. However, this result is not significantly different from the slightly increased average NO_2 level using a dilute heated sample. The NO_2 measurements from the raw heated sample showed significantly higher average values than NO_2 levels measured using the other two techniques. So although these results are consistent with the hypothesis that higher temperature increases NO_2 formation they do not support the theory that higher oxygen concentrations due to dilution increases NO_2. The poor level of accuracy, which can be obtained by inferring NO_2 levels indirectly using CHEM analysers, could explain this apparent anomaly. It should also be noted that the rate of oxidation of NO also depends on the NO concentration, which would be reduced by dilution. Any reaction would therefore reflect a balance between lower NO and higher oxidant levels, and it is difficult to predict without further information on concentrations, temperatures, and the time available for the reaction.

Using the FT-IR, a direct comparison between the levels of NO_2 using raw and dilute sampling showed that the values obtained by the two methods were not statistically significantly different. This was confirmed after further statistical analysis was used to remove the influence of the other variables (See Appendix A). However, when the same techniques were applied to examine the NO_2/NO_x ratio, a significantly higher level of NO_2/NO_x was found in the dilute sample relative to the raw sample. Since the NO_x should be relatively constant this provides some evidence that diluting the sample will tend to give a small increase in NO_2.

(ii) Effect of legislation (light duty vehicles)

A direct comparison of the average NO_2 emissions measured from Euro 0, Euro 1 and Euro 2 vehicles show that the average levels of NO_2 from Euro 0 vehicles are higher than the Euro 1 and Euro 2 vehicles included in the study. There is, however, considerable overlap in the 95% confidence limits between all these categories suggesting that the measured average differences between the vehicle groups is probably not significant. However, after the effect of the other independent variables have been eliminated (see Appendix A), it has been shown that the NO_2 emissions from Euro 0 vehicles are, in fact, significantly higher than the corresponding emissions from Euro 1 or Euro 2 vehicles. The analysis also shows that the difference in the emissions of NO2 between Euro 1 and Euro 2 vehicles is not significant for the sample of vehicles studied.

This observation is reasonably consistent with the expected change in NO_2 if it were reduced in proportion to the NO_x legislation, although the wide confidence limits make any direct comparison rather tenuous. Nevertheless, the indicated trend implies that the more stringent Euro 1 and Euro 2 regulations have had some effect on reducing primary emissions of NO_2 as well as NO_x levels.

(iii) Comparison of petrol-engined cars and diesel-engined vans:

The effect on emissions of the type of engine used (diesel or petrol) and the size of the vehicles cannot be easily separated since these factors are dependent upon one another. For example, the diesel vans are larger than the petrol cars. Therefore a more general comparison of diesel vehicles v petrol vehicles was conducted, so the overall effect was partly one of size and partly the type of engine used. Whilst the effect of petrol car size on NOx is examined separately.

It was found that the diesel vehicles emit significantly greater NO_2 emissions than petrol vehicles. This could be partly due to the greater availability of oxygen present in the exhaust of the diesel vehicles examined. The diesel vehicles were all large vans which, by virtue of their larger mass when compared with the petrol cars examined, would tend to produce more exhaust emissions by virtue of their greater fuel use. This effect, for the vehicles studied, would be expected to more than offset the greater fuel efficiency of the diesel engines.

(iv) Effect of speed, cycle type and start temperature (FT-IR only):

Higher average speeds generally produce higher exhaust temperatures therefore a positive correlation between speed and NO_2 emissions would be expected. The examination of the independent effect of speed on NO_2 confirms this to be the case (See Appendix A). Nevertheless, it should be noted that the scatter in results is very high. This is expected since average cycle speed is not a good indicator of emissions on an individual cycle-to-cycle basis. Surprisingly the NO_2/NOx ratio decreases at higher speed which implies that the NOx emission is increasing at a faster rate than NO_2 at higher speeds.

The effect of higher speeds on NO_2 emissions appears to be more pronounced for the raw sample than the dilute sample on the EURO 0 vehicles. This can be seen over the constant 90 and 113 kph cycles. The remaining cycles have relatively low average speeds. The NO_2 levels appear to be very low for cycles with low average speeds particularly when these are started from a low engine temperature. This would imply that temperature has a very pronounced effect. NO_2 levels are generally less for vehicles conforming to older types of legislation, for example, during the raw sampling tests for EURO 0 vehicles. The overall effect of start temperature across all the FT-IR measurements was not found to be statistically significant (See Appendix A).

(v) Effect of petrol vehicle size on NO_2 emissions (FT-IR only):

As a general rule NO_2 emissions would be expected to increase as a function of vehicle size simply because more emissions are generally produced from larger engines and vehicles due to their greater fuel use. However, other factors such as technology and maintenance could also be influential. This

could explain why the results for the medium sized cars gave higher NO_2 levels than the small or larger vehicle categories. Another issue is that the level of certainty of this ranking is low since the 95% confidence limits of the three categories overlap.

(vi) NO_2 emissions from trucks and buses

Exhaust emission regulations have required manufacturers to gradually reduce NO_x emissions from heavy trucks and buses as well as light vehicles. Although there has been no legislation to reduce NO_2 directly, it might be assumed that if NO_x is reduced, the NO_2 will probably also reduce. However, the truck and bus results do not show this, in fact for the raw sample, over most of cycles, the NO_2 emissions generally increased for vehicles conforming to newer standards. The only exceptions to this was the bus when driven over the FIGE motorway and FIGE rural cycles, the former cycle being less important for buses.

For the dilute sample, which may better represent the processes by which exhaust gas exits the exhaust and mixes in the atmosphere, there is no clear relationship between NO_2 emissions and legislation. However, the EURO 1 trucks appeared to emit the highest, and the EURO 1 bus the lowest NO_2 emissions for the FIGE cycles. A basic statistical analysis of the measured data generally confirms that legislation has not influenced primary NO_2 emissions from trucks and buses when this data is averaged. The 95% confidence limit bands between the 3 legislative categories mainly overlap, which indicates there is no significant difference in heavy vehicle NO_2 emissions in relation to legislation using FT-IR measurements of the dilute sample. This is in contrast to the light vehicle study which indicated that the older EURO 0 vehicles emit the highest NO_2 levels.

(vii) Primary NO_2 and roadside concentrations and implications of the results for air pollution modelling

The consideration of primary nitrogen dioxide emissions in a pollution modelling study has been demonstrated to have a significant effect on the results. Hypothetically, the analysis has shown the potential for nitrogen dioxide concentrations to be significantly underestimated where no allowance is made for primary emissions, and two realistic case studies show differences of up to 30% in an urban context and 15% near to a motorway between results obtained with and without the inclusion of primary emissions.

In practice, though, the neglect of primary emissions by most models is unlikely to lead to such errors. This is because most models make an initial estimate of the concentration of total oxides of nitrogen and, from that, estimate the corresponding nitrogen dioxide concentration using relationships derived empirically from observations of the two pollutants. Obviously, any empirical relationship of that type will automatically include the effects of primary nitrogen dioxide emissions. In the less common cases, however, where models estimate nitrogen dioxide from oxides of nitrogen emissions using fundamental chemical principles, the composition of the emissions will be of importance.

It has also been seen that the difference between nitrogen dioxide concentrations derived with and without an allowance for primary emissions can vary considerably depending on the traffic conditions. This is clearly apparent by comparing the two examples given above - primary nitrogen dioxide emissions were estimated to contribute up to 30% of the atmospheric concentration in an urban area and up to 15% near to a motorway. Even at a single location (the motorway example), the airborne nitrogen dioxide attributable to primary emissions varied between about 10% and 17% of the total concentration depending on the flow, speed and composition of the traffic.

It would therefore be possible to improve the accuracy of air pollution models for nitrogen dioxide by incorporating routines to deal explicitly with the primary emissions. This would be particularly relevant for models that attempt to simulate the chemical processes involved. It is likely that this would only be appropriate for detailed modelling exercises. In a more general context such as the screening approach presented in Volume 11 of the Design Manual for Roads and Bridges, the

potential errors from this omission are small compared with other generalizations that are made concerning, for example, the meteorological conditions and the traffic composition.

4.2 PARTICULATE MATTER

The results of the particle measurements are presented below. Initially, the total mass of particulate matter is examined in terms of the vehicle category, driving cycle, and technology level. Differences between the mass measurements obtained using the standard filter paper method and a TEOM instrument are also examined. The reproducibility of particle size distributions is presented, and the results of particle size measurements are given for different vehicles, driving cycles, and vehicle technologies.

4.2.1   Total particulate matter

(i) Driving cycle and technology effects

Figure 26 shows the mass emission rates of total particulate matter, based on the filter measurements, for the four vehicle categories tested (*i.e.* cars, vans, trucks, and buses) and for the different drive cycles employed[7]. The results for each vehicle category are mean values for all the vehicles tested within that category. The figure also differentiates between the results obtained from measurements taken on both the raw and diluted exhaust gas.

A fairly prominent driving cycle effect was evident in the emissions from passenger cars (tested at 25°C); emissions were generally higher over the low-speed urban cycles (up to 19mg/km) and high-speed motorway cycles (up to 14mg/km) than over the cycles typical of suburban or rural driving (less than 5mg/km in most cases). For the vans, trucks and buses, PM emissions exhibited ranges of 63-183mg/km, 682-1402mg/km, and 169-386mg/km respectively. PM emissions from these three categories of vehicle generally exhibited a lesser dependence on speed, although the vans also had higher mass emissions over the driving cycles with the lowest and highest speeds, and emissions from the trucks and buses tended to decrease with increasing cycle speed.

It can be seen that there was generally a poor level of agreement between the measurements on the raw and diluted exhaust gas from passenger cars, with the raw exhaust measurements tending to be higher at lower cycle speeds, and the dilute exhaust measurements tending to be higher at higher cycle speeds. For the other vehicle categories the agreement was much better overall.

Total mean particulate mass emissions for the four vehicle categories are presented in terms of technology level in Figure 27. The results for the passenger cars are average values for three vehicles. For vans, trucks, and buses, only one vehicle of each technology level was tested.

As might have been expected, particulate mass emission rates from the newer-technology vehicles tended to be the lowest. In particular, the emission rates from the Euro 1and Euro 2 trucks and buses were substantially lower that the emissions from the Euro 0 vehicles. The emission rate of the Euro 1 truck was, depending on the driving cycle, between around 3 and 7 times lower than its Euro 0 counterpart, whereas the emission rate for the Euro 2 truck was between around 8 and 17 times lower than that of the Euro 0 vehicle. The emission rate of the Euro 1 bus was also around 3 times lower than that of the Euro 0 bus, though there was no clear further improvement concerning the Euro 2 bus. The emissions from the three vans tested showed a steady decrease with improved technology over most of the driving cycles employed, but the emissions from passenger cars were rather variable.

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[7] To allow greater discrimination between driving conditions, the heavy duty cycles were subdivided. The Millbrook bus cycle formed the basis for the inner London and outer London cycles, while the urban, suburban and motorway cycles were each part of the FIGE cycle.
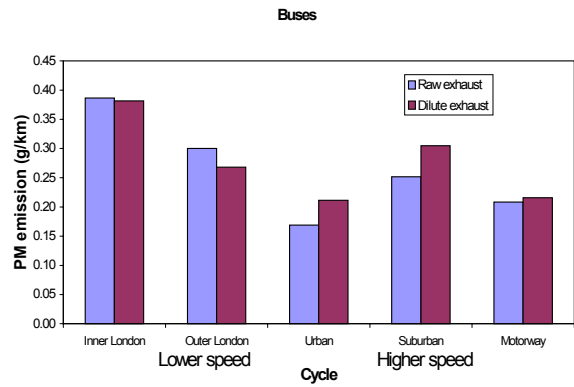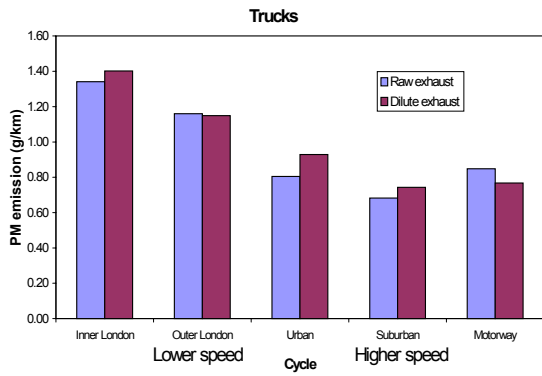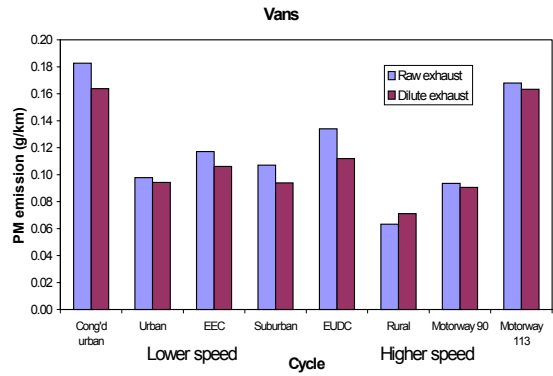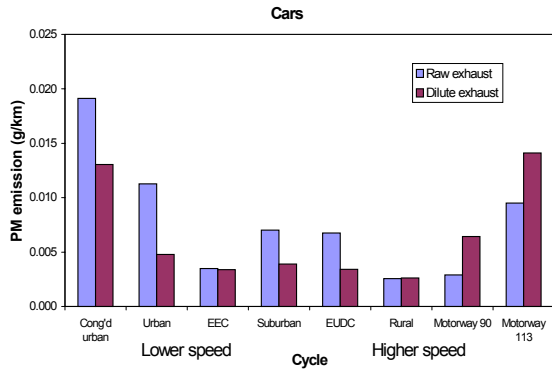
Figure 26: Mean emissions of total particulate matter by vehicle category, based on filter measurements
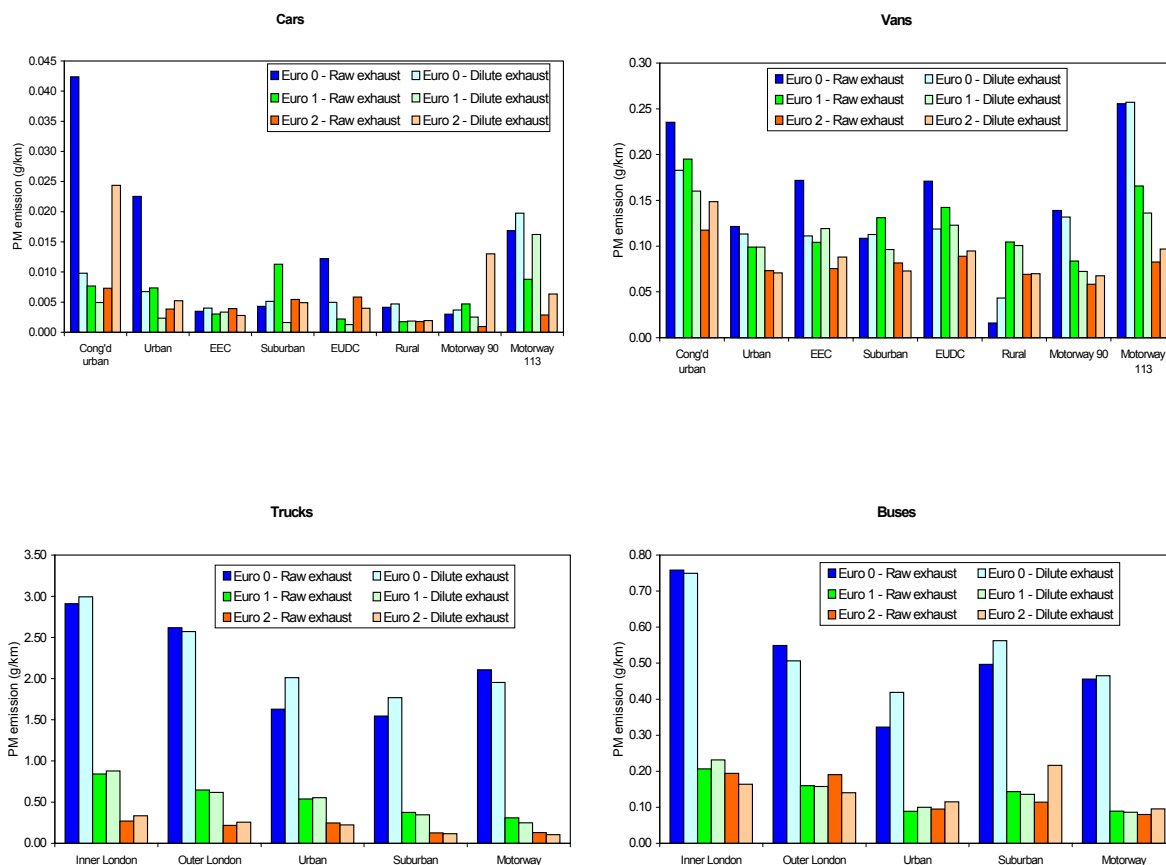
Figure 27: Emissions of total particulate matter by vehicle technology level, based on filter measurements

(ii) Comparison between filter paper and TEOM measurements

Comparisons between the gravimetric measurement of total particulate matter and the aggregate TEOM measurements for all the vehicles tested are shown in Figure 28. It can be seen from the left-hand graph in Figure 28 that, although the correlation coefficient (R^2) was high and indicated a good level of agreement between the results from the two types of measurement, the high value appeared to be largely conditioned by the results obtained for the highest-emitting vehicles. When these results were removed (right-hand graph of Figure 28), it can be seen that the correlation was substantially poorer, and the value of the correlation coefficient was greatly reduced. Overall, it was found that the total of the TEOM measurements was only within 5% of the filter measurement in 16% of the tests, and within 10% of the filter measurement in 26% of the tests. In 37% of the tests, the TEOM measurement was not within 100% of the filter measurement. Whether particulate matter was sampled from the raw exhaust or the dilute exhaust made little difference to the strength of the relationship between the TEOM and filter data. However, neither method seemed systematically to over- or under estimate, and the regression lines fitted to the data were very close to a 1:1 relationship.
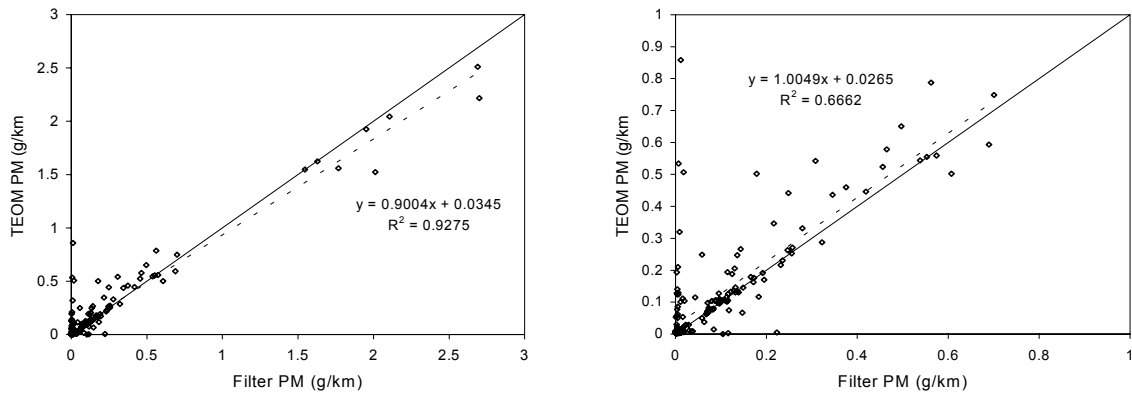
Figure 28: Total particulate measure measured gravimetrically (filter) vs sum of TEOM measurements

NB. The graph on the left includes all the measurements for all vehicles, whereas in the graph on the right the top 4% approximately of measurements (those for which the filter PM was >1.0g/km) are excluded. The solid line in each graph indicates a 1:1 ratio, and the dotted line is the regression plot in each case).

4.2.2 Particle size distributions

(i) Reproducibility

The importance of sampling conditions in the measurement of particle size distributions was emphasised earlier in this Report. However, further investigation of sampling parameters was beyond the scope of the research. Instead, particle size distributions were measured at a location equivalent to that occupied by the filter during normal gravimetric measurements. Hence, as the precise sampling conditions for the particle size measurements were not strictly controlled, the results presented here cannot be compared directly with those in other studies. During the raw and dilute exhaust gas tests, the size distribution measurements were conducted under the same (*i.e.* dilute) conditions[8]. This allowed for an assessment of the reproducibility of the size distributions, and thus provided an indication of the stability of the adopted measurement approach.

Figure 29 shows the repeat size distribution measurements for vehicle 1. It should be noted that both scales are logarithmic[9]. The results are reasonably typical of the sample of petrol-engined passenger cars tested.

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[8] As noted previously, the particle concentrations in the raw exhaust frequenctly exceeded the maximum acceptable for the ELPI instrument.

[9] The axes show dN/dlog (Dp), which is a measure of the number of particles in a given size range between successive values of Dp_{50}, which is the particle cut-off diameter.
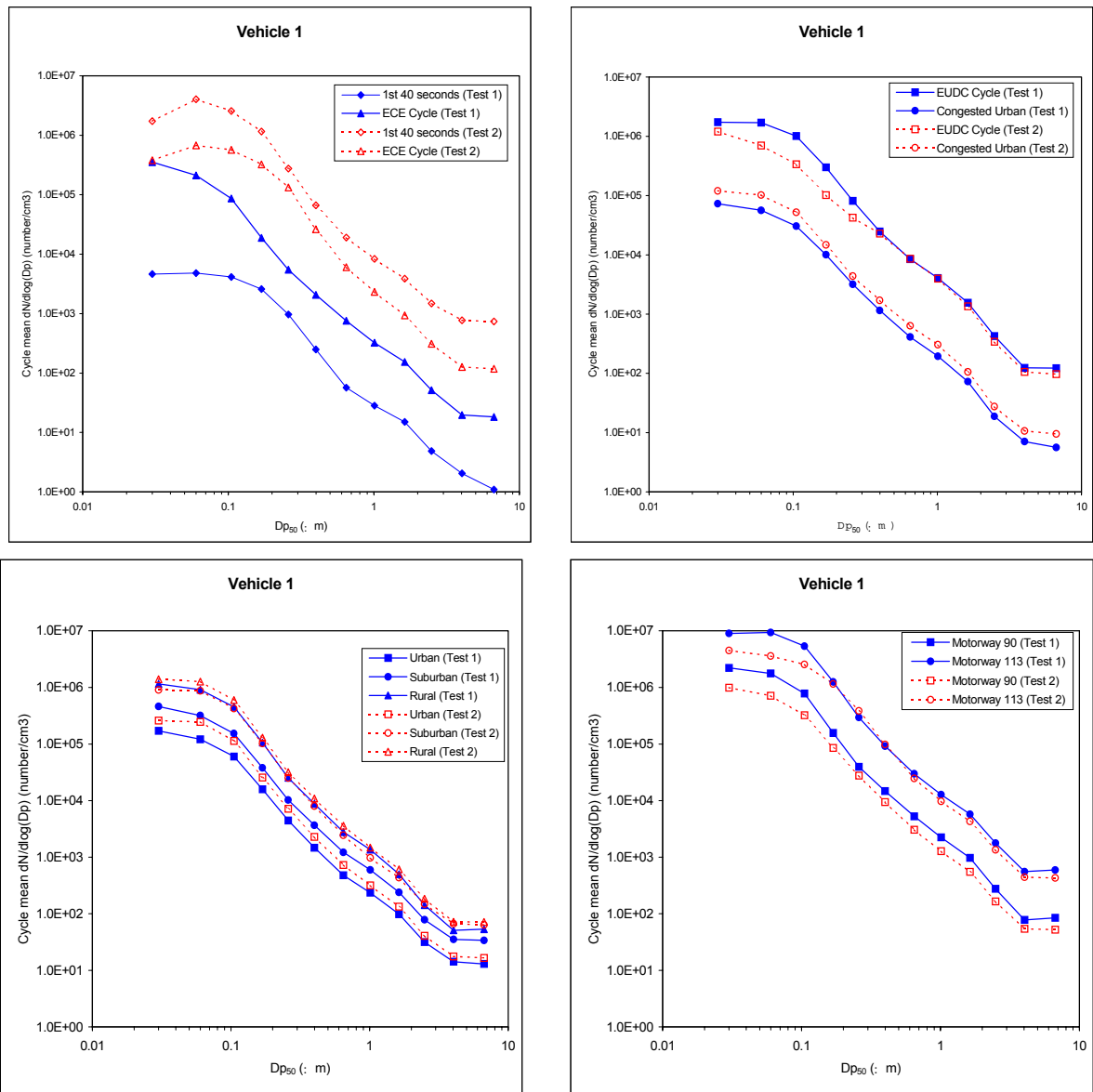
Figure 29: Reproducibility of ELPI number concentration measurements under different driving conditions for vehicle #1. Dp_{50} is the particle cut-off diameter

It can be seen that the reproducibility under cold start conditions (the first graph in Figure 29) was generally much poorer than under hot-start conditions. Otherwise, no strong links between the driving cycle and the reproducibility of the size distributions were evident. The measurements on some vehicles consistently showed a good level of reproducibility, whilst the measurements on others showed a consistently poor level of reproducibility. With some vehicles the reproducibility was good over some cycles but poor over others.

Although the size distributions measured for the diesel-engined vans also showed a poor level of reproducibility for drive cycles involving cold starts, the values measured for the hot-start cycles generally exhibited a higher degree of reproducibility than those for passenger cars. For trucks and buses (all hot-start cycles), the measurements showed a mixed degree of reproducibility.

(ii) Effects of vehicle category

Figure 30 shows cycle mean particle size distributions for the various vehicle categories studied. The size distributions are compared over driving cycles with a similar mean speed, with vehicles starting from hot in all cases.
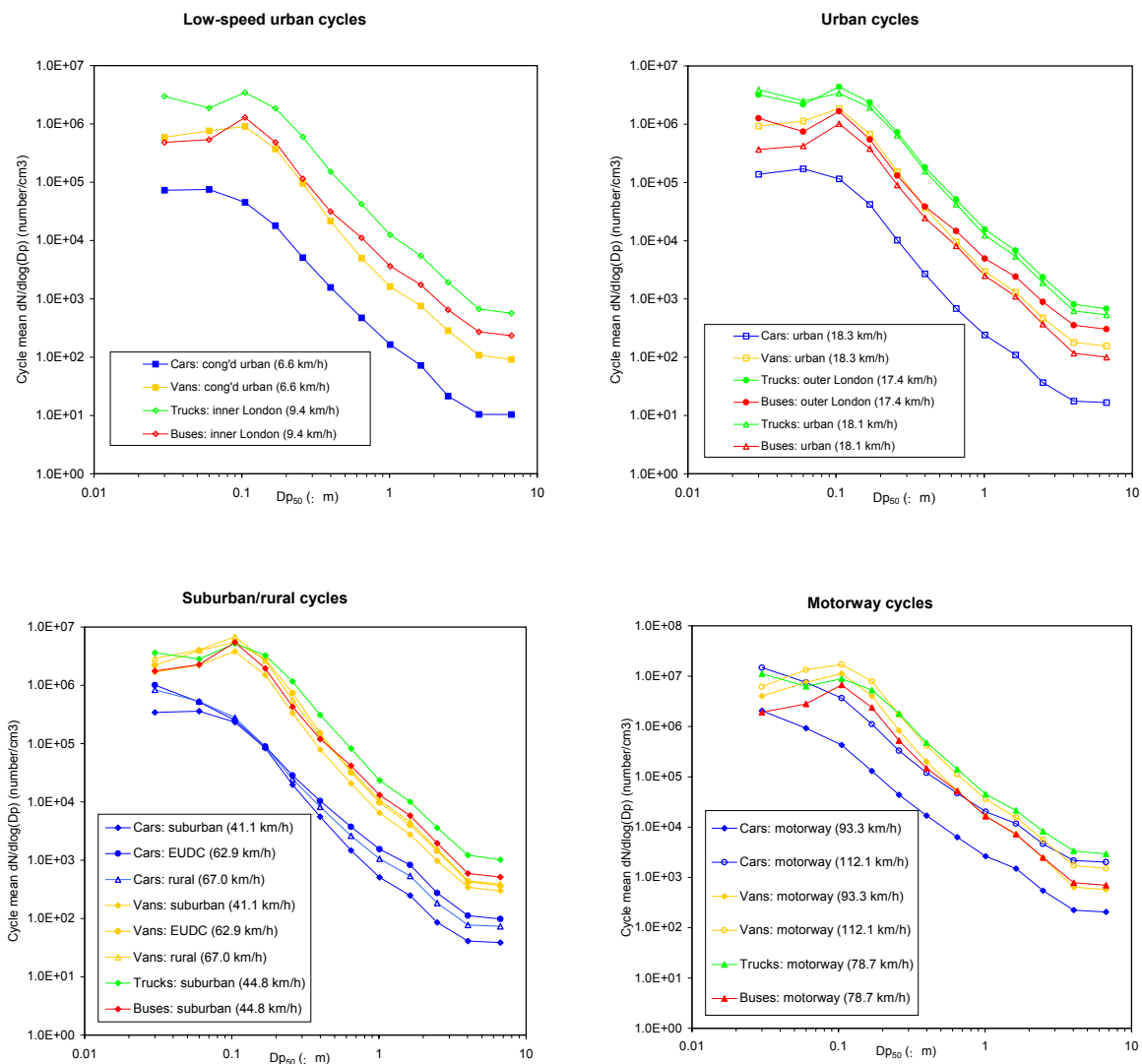
Figure 30: Mean particle number concentrations for the four vehicle categories under a range of driving conditions

It can be seen that for all cycles except the motorway cycle, with the highest mean speed, particulate emissions from the passenger cars were typically an order of magnitude lower than the corresponding concentrations found for the other vehicle categories. This was found to be broadly true across the entire range of particulate sizes studied. However, it should be remembered that the passenger cars were all powered by petrol engines, whilst the other vehicles were powered with diesel engines.

The size distributions of the vehicle categories appear to merge with increasing cycle speed. For the drive cycles simulating motorway conditions, the particle size distributions for the passenger cars overlapped with those for the other vehicle categories, and for the smallest particle size bin, passenger cars actually had the highest emissions of all the vehicle categories. For the urban cycles, trucks gave the greatest particle numbers.

(iii) Effects of driving cycle

Individual vehicles, and vehicles of a given category, exhibited substantially different particle size distributions when driven over different test cycles (Figure 31). Total particle concentrations are plotted as a function of cycle speed in Figure 32, which shows that, for all four vehicle categories particle concentration in each size range generally increased with increasing cycle speed. The distinctions between the different driving cycle was generally clearer for cars and vans, although a wider range of speeds were used with these vehicles.
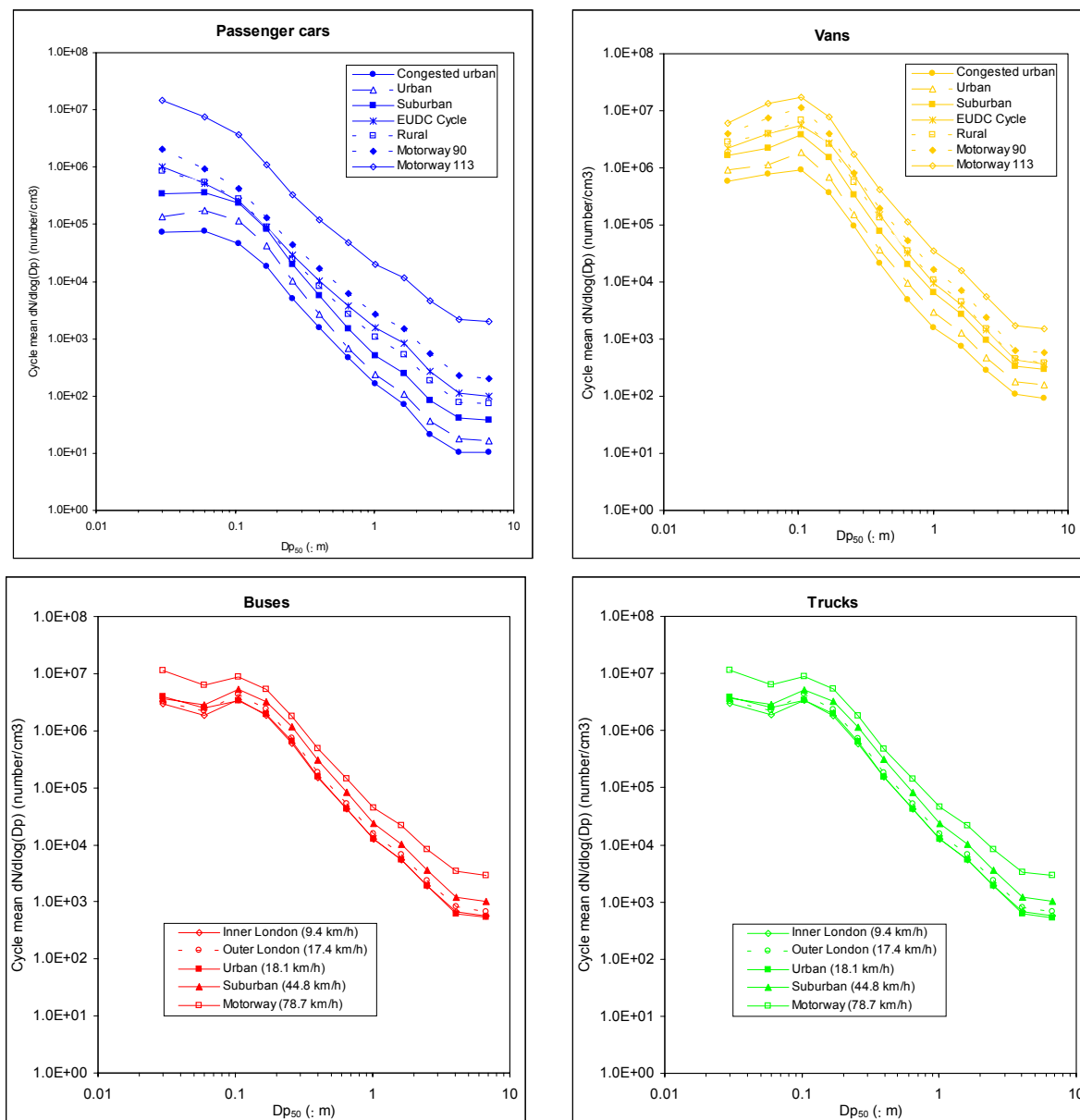
Figure 31: Particle size distributions measured under different driving conditions for four vehicle categories. Hot start at 25°C ambient
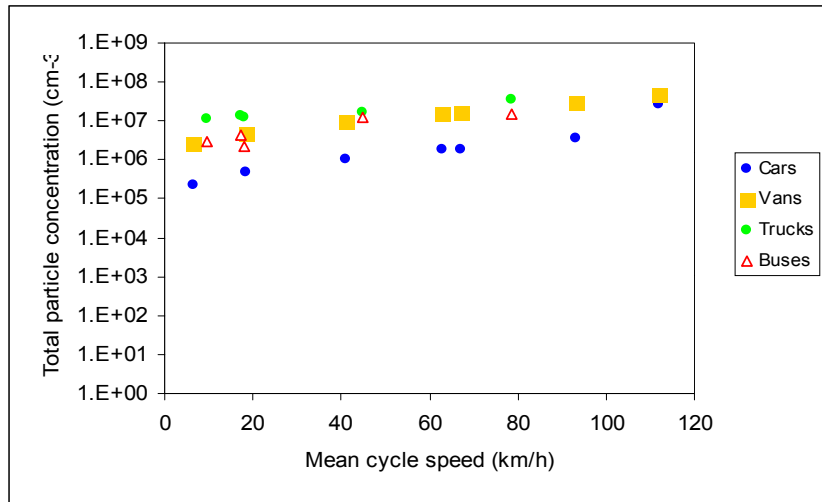
Figure 32: Total particle number concentration as a function of cycle speed for the four categories of vehicle

(iv) Effects of variations in ambient temperature

The particle size distributions for the three passenger cars tested at different ambient temperatures are presented in Figure 33. Figure 33 simply illustrates that changes in ambient temperature generally had a smaller effect of the size distributions than changes in the driving cycle.
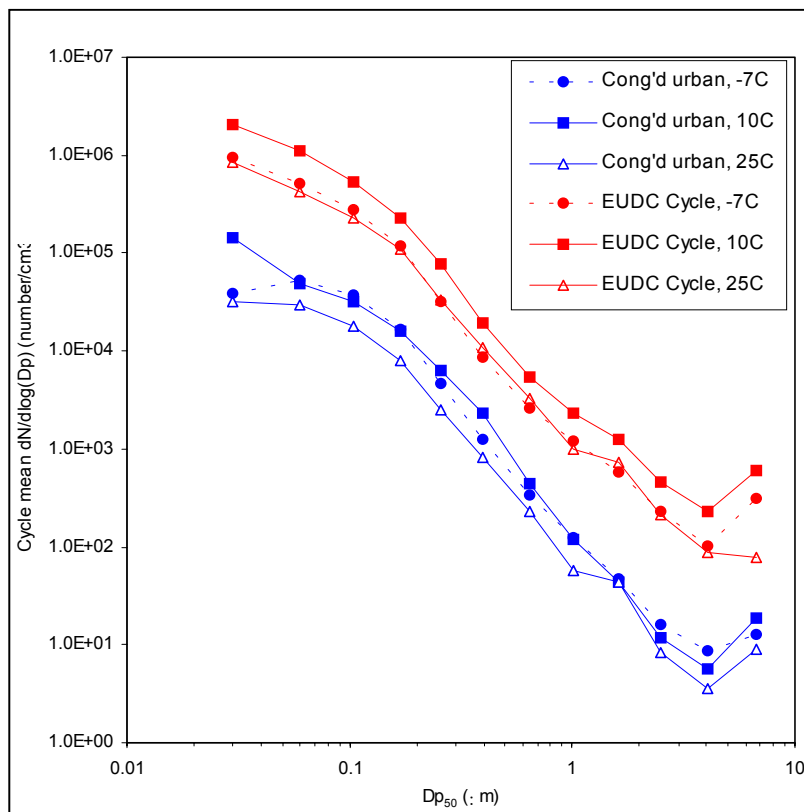
Figure 33: Particle number concentrations for passenger cars #4-6 measured over TRL Congested Urban and EUDC cycles (both hot-start) at ambient temperatures of -7°C, 10°C, and 25°C

(v) Effects of vehicle technology level

Within each vehicle category tested, particle size distributions were examined as a function of vehicle technology level. The distributions, averaged over all driving cycles, for the Euro 0, Euro 1, and Euro 2 vehicle(s) in the different categories are shown in Figure 34.
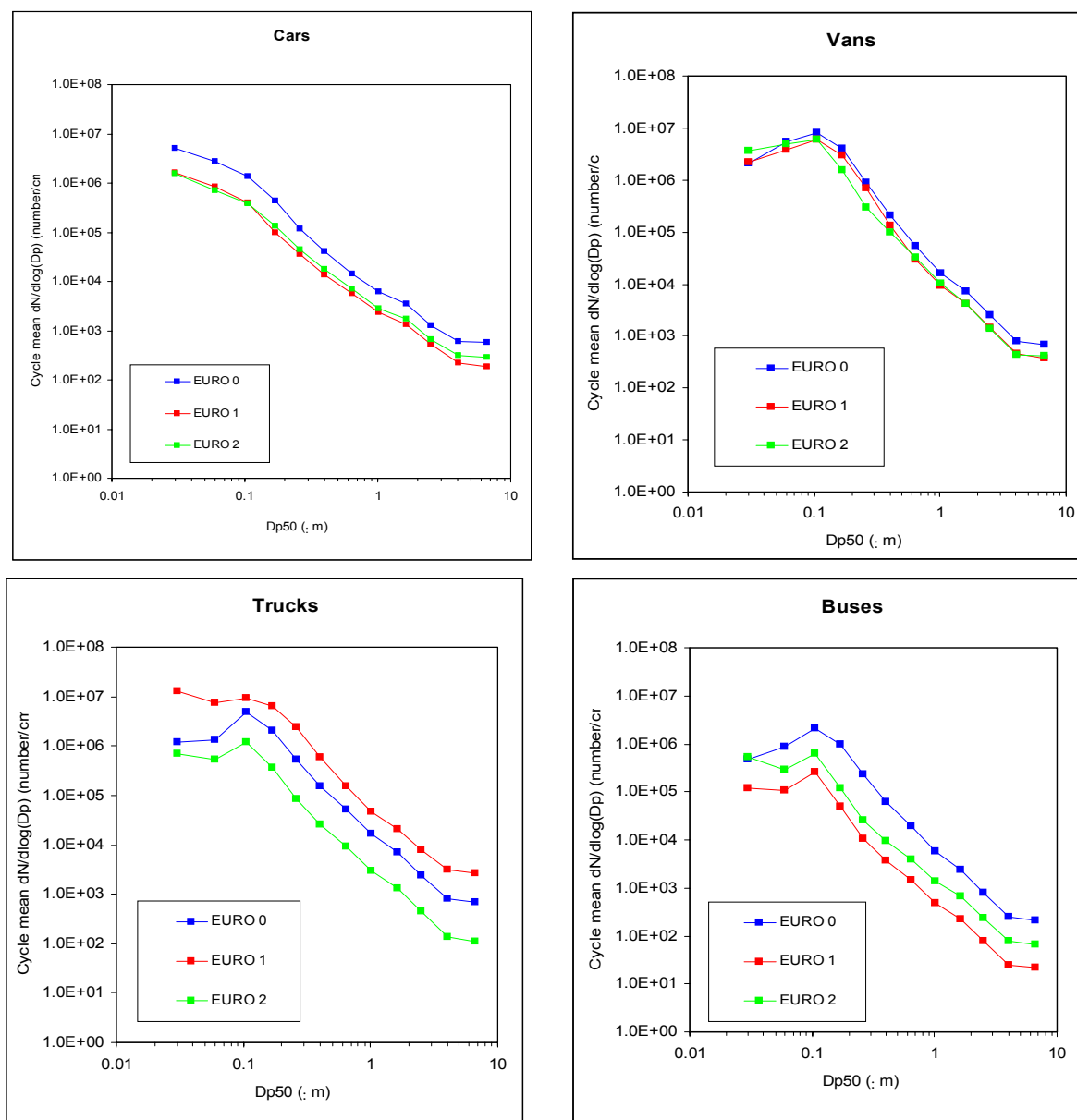
Figure 34: Particle size distributions, averaged over all driving cycles, for the Euro 0, Euro 1, and Euro 2 vehicles in each category

The results were rather mixed. When averaged over all the test cycles, there was very little difference between the size distributions for Euro 1 and Euro 2 passenger cars, with the distribution of Euro 0 being slightly higher. The three vans tested exhibited very similar mean particle size distributions. Of the three trucks tested, the Euro 1 vehicle had the highest number concentrations across the size range, and the Euro 2 vehicle the lowest. In the case of the buses, the Euro 0 vehicle had the highest number concentrations, and the Euro 1 vehicle the lowest.

The size distributions obtained for passenger cars showed some dependency (across the size range) upon the driving cycle used. For example, the number concentrations measured over the Urban Congested, Urban, and Suburban cycles were highest for the Euro 2 vehicles, and lowest for the Euro 1 vehicles. Over the EUDC and Motorway 113 cycles, the size distributions for the Euro 1 and Euro 2 vehicles were similar, with the Euro 0 vehicles having higher number concentrations across the size range. Over the Rural and Motorway 90 cycles the highest number concentrations were observed for the Euro 0 vehicles, and the lowest for the Euro 1 vehicles.

The size distributions observed for the three vans tested were very similar over most of the driving cycles. Over the Congested Urban and EUDC cycles, the Euro 2 vehicle emitted slightly fewer particles in the size range above 100nm.

The three buses tested exhibited similar particle size distributions over the Inner London and Outer London driving cycles, although over the Outer London cycle the Euro 2 vehicle emitted the highest number concentrations in the smallest size range. Over the Urban, Suburban and Motorway cycles, the Euro 0 bus had the highest number concentrations, and the Euro 1 vehicle the lowest.

4.2.3   Summary and discussion

The study provided a large amount of detailed information relating to particle size distributions over a range of transient driving cycles. It was found that a driving cycle effect was evident in the mass emissions of total particulate matter from the petrol-engined cars, with emissions generally being higher over the cycles relating to urban and motorway driving than over the cycles relating to suburban and rural driving. Emissions from the diesel-engined vans, trucks and buses generally exhibited a lesser dependence on speed, although emissions from the trucks and buses tended to decrease with increasing cycle speed.

There was generally a poor level of agreement between the measurements on the raw and diluted exhaust gas from passenger cars, with the raw exhaust measurements tending to be higher at lower cycle speeds, and the dilute exhaust measurements tending to be higher at higher cycle speeds. For the other vehicle categories the agreement was much better. The large differences between the raw and dilute samples observed for passenger cars, which were all petrol-engined, are most likely due to the emission rates of these vehicles being very low and close to the overall accuracy of the measurement technique, which would inevitably reduce the repeatability. For the other vehicle categories (all diesel), the emission rates were higher and there was a better agreement between the samples taken from the raw and dilute exhaust gas.

Particulate mass emission rates from the newer-technology vehicles tended to be the lowest. In particular, the emission rates from the Euro 1 and Euro 2 trucks and buses were substantially lower that the emissions from the Euro 0 vehicles. The emissions from the three vans tested showed a steady decrease with improved technology over most of the driving cycles employed, but the emissions from passenger cars were rather variable and no firm conclusions could be drawn from the results for these vehicles.

Comparisons between gravimetric measurement of total particulate matter and aggregated TEOM measurements for all the vehicles tested showed a good correlation over the full mass range, but for filter masses of less than 1g/km the correlation was substantially poorer. Whether particulate matter was sampled from the raw exhaust or the dilute exhaust made little difference to the strength of the relationship between the TEOM and filter data.

The reproducibility of the size distribution measurements was generally found to be poor under cold start conditions. Otherwise, the measurements generally showed an acceptable level of reproducibility.

For all cycles except the motorway cycle, with the highest mean speed, particle number concentrations from the (petrol) passenger cars were typically an order of magnitude lower than the corresponding concentrations found for the other (diesel) vehicle categories. This was found to be broadly true across the entire range of particle size studied. The size distributions of the vehicle categories appeared to merge with increasing cycle speed. For all four vehicle categories particle concentration in each size range generally increased with increasing cycle speed. This implies that substantially more particles will be emitted at higher speeds, as not only are more particles per unit volume being produced, but the volume of gas being produced is also larger. However, further work is required to confirm this observation, as the results may well be a measurement artefact. For example, it has been shown previously that increased particle numbers are associated with low-dilution of the exhaust gas, and low dilution is associated (under laboratory conditions at least) with high-speed cycles. The distinction between the different driving cycle was generally clearer for cars and vans, although a wider range of speeds were used with these vehicles. For the three cars tested at different ambient temperatures, changes in ambient temperature generally had a smaller effect of the size distributions than changes in the driving cycle.

When averaged over all the test cycles, there was very little difference between the size distributions for Euro 1 and Euro 2 passenger cars, with the distribution of Euro 0 being slightly higher. The three vans tested exhibited very similar mean particle size distributions. Of the three trucks tested, the Euro 1 vehicle had the highest number concentrations across the size range, and the Euro 2 vehicle the lowest. In the case of the buses, the Euro 0 vehicle had the highest number concentrations, and the Euro 1 vehicle the lowest. The size distributions obtained for all categories of vehicle showed a dependency (usually across the entire size range) upon the driving cycle used, but no systematic emission behaviour was apparent.

These results imply that although the total mass of particulate matter measured gravimetrically in the regulated test is decreasing with improvements in vehicle technology, especially for diesel vehicles, it does not necessarily follow that there will be a decrease in the numbers of fine and ultrafine particles being emitted.

4.3 HYDROCARBON AND OTHER ORGANIC EMISSIONS

Hydrocarbon emissions were measured using gas chromatography analysis. A comparison of the effects of emissions legislation on HC emissions was carried out for Euro 0, Euro 1 and Euro 2 specification passenger cars, vans, trucks and buses. For each vehicle type, these effects were examined for two or three different drive cycles: for passenger cars and vans, these were the TRL congested urban cycle, the ECE cycle and the EUDC cycle, whilst for trucks the urban, suburban and motorways cycles were used, and for buses the inner and outer London cycles. This study begins with an assessment of the effects of drive cycle and legislation/technology levels on total hydrocarbon emissions, before an examination of the composition of the HC emissions, and how the composition varies with drive cycle, legislation/technology level, and vehicle type.

4.3.1   Measurements of Total HC emissions

Total hydrocarbon emissions can be determined from the speciated gas chromatography data by summing the mass emissions of each individual compound to give a total value. In this study this was achieved by summing the 170 organic species identified by the method. Theoretically, although this does not represent the total hydrocarbon species present in the exhaust emissions, for practical purposes it does represent a very close approximation to the total mass emitted.

The results of this analysis are presented in Table 11.

Table 11: Total hydrocarbon emissions (measured using Gas Chromatography) for each vehicle type and drive cycle configuration

Vehicle type	Drive cycle	Total HC emissions (mg/km) by technology level / emissions legislation		
		Euro 0	Euro 1	Euro 2
Passenger cars	Congested urban	3441.3	438.5	310.3
	ECE	1966.2	684.4	513.5
	EUDC	796.5	53.0	40.8
Vans	Congested urban	408.9	402.0	257.4
	ECE	326.0	287.9	151.5
	EUDC	102.7	88.60	44.1
Trucks	Urban	945.3	450.2	466.0
	Suburban	730.9	230.0	163.8
	Motorway	1105.9	174.4	132.5
Buses	Inner London	935.3	459.9	276.8
	Outer London	635.1	269.2	189.3

The measurements of total HC emissions show that, as might be expected, total emissions were lower for vehicles fitted with more advanced technology to comply with stricter legislation. Hence, emissions from Euro 0 vehicles are the highest, and those from Euro 2 vehicles are the lowest (the only exception to this was the Euro 2 truck which was found to have slightly higher HC emissions than the Euro 1 truck).

In addition to this, a strong relationship between drive cycle and total HC emissions was also found. For all passenger cars and vans, emissions were consistently lowest when operating in the Extra Urban Drive Cycle, and for buses emissions were lowest during the outer London cycle. For both the Euro 1 and Euro 2 trucks, emissions were found to be lowest during the motorway drive cycle however, this cycle was found to responsible for very high emissions from the Euro 0 truck.

As might be expected, an important feature of these results is the very high levels of HC emissions from Euro 0 passenger cars compared to all of the other vehicles. For example, total HC emissions from Euro 0 cars in the Extra Urban Drive Cycle (EUDC) are more than fifteen times higher than emissions from Euro 1 cars, and almost twenty times higher than emissions from Euro 2 vehicles. Emissions from Euro 0 cars were also found to be more than six times greater than emissions from Euro 0 vans.

The comparatively high HC emissions from the Euro 0 passenger cars are consistent with expectations for petrol-engined vehicles of this type. Prior to the introduction of catalyst technology (usually associated with the implementation of Euro 1 legislation), petrol engines were often equipped with mechanical carburettors to facilitate fuel/air mixing. In comparison to fuel injection systems, carburettors do not mix fuel and air with a high degree of accuracy. Consequently, the engines of such vehicles tended to be set up to run with a rich fuel/air mixture leading to high levels of unburnt fuel emissions. The introduction of catalytic converters to petrol-engined vehicle designs, was accompanied by other engineering changes to ensure a greater control over the fuel supply to the cylinders. This effectively meant that carburettors were replaced with fuel injection systems which immediately affect a reduction in the proportion of the unburnt HC emissions. In addition to this, the

role of the catalytic converter in the vehicle exhaust system is to oxidise hydrocarbon compounds to carbon dioxide and water, further reducing HC emissions.

The reason that the Euro 0 diesel engined vehicles have relatively low HC emissions is in part due to the fact that fuel injection systems were fitted to these vehicles, and that the high air:fuel ratios indiesel engines promote good fuel combustion.

4.3.2   Speciation by Gas Chromatography

Gas chromatography measurements were used to measure the emissions of almost all volatile organic compounds in the exhaust gases of the test vehicles. The technique is set up to identify the presence of the 170 different organic compounds that make up the bulk of organic emissions. However, for the purpose of this study only 17 of the most important compounds was selected for further analysis. The choice of compounds was based on a combination of source strength and toxicity or other potential environmental effects. The compounds chosen have been subdivided by homologous series and are listed below:

Alkanes:	methane, propane
Alkenes:	ethene (ethylene), 1,3-butadiene
Alkynes:	ethyne (acetylene)
Aldehydes:	formaldehyde (methanal), acetaldehyde (ethanal), acrolein (propenal)
Ketones:	acetone (propanone)
Monocyclic aromatics:	benzene, toluene (methyl benzene), m-, o-, and p-xylenes (dimethyl benzenes), ethyl benzene
Polycyclic aromatics:	naphthalene
Ethers:	MTBE

The results of GC analysis have been used to determine the effects of vehicle type, legislation, and drive cycle type on levels of each of the seventeen compounds listed above.

4.3.3   Light duty vehicles

(i) Passenger cars

The effects of more stringent legislation on a range of passenger car HC emissions (averaged over the three cars tested in each legislative class) can be seen in Figures 35, 36 and 37. Levels of ethene, ethyne, formaldehyde and monocyclic aromatic compounds are dramatically lower for Euro 1 than they are for Euro 0. For example, in the congested urban cycle it can be seen that emissions of ethene drop from 260.3 mg/km for Euro 0 vehicle to 17.3 mg/km for Euro 1 vehicles (equating to a fifteen-fold reduction). Similarly it can be seen that m- and p-xylene emissions dropped from 221.9 mg/km to 23.5 mg/km. Moving from Euro 1 to Euro 2 produces further reductions, but these are on a much smaller scale. Ethene emissions decreased from 17.3 mg/km to 11.5 mg/km whilst m- and p-xylene decreased from 23.5 mg/km to 7.1 mg/km. Certain HC compounds were found to be produced in very small amounts, regardless of whether the vehicles were Euro 0, Euro 1 or Euro 2 spec. These compounds included propane, acetaldehyde, MTBE and naphthalene. However, even these compounds show a similar progression from Euro 0 to Euro 2.

For all three driving cycles, methane emissions were found to decrease significantly going from Euro 0 vehicles (192.4 mg/km in the congested urban cycle) to Euro 1 vehicles (92.5 mg/km), and to virtually stabilise at this level for Euro 2 vehicles (90.5 mg/km). However, as a proportion of total HC emissions, it can clearly be seen that, for all driving cycles, the relative contribution attributable to

methane increased with the introduction of stricter legislation (see Figure 41). For example, in the congested urban cycle, methane emissions accounted for 5.6% of total HC emissions for Euro 0 cars, 21.1% for Euro 1 cars and 29.2% for Euro 2 cars. This is because the efficiency with which catalytic converters oxidise methane is lower than for the other compounds.

For Euro 0 cars, toluene was the dominant HC pollutant, whilst for Euro 1 and 2 cars in both the EUDC and congested urban cycles, its importance drops significantly, and methane becomes the most abundant HC compound emitted. For example, in the congested urban cycle, the proportion of toluene drops from 10.2% for Euro 0 cars to 5.2% for Euro 2 cars. In the ECE cycle, the amount of toluene emitted as a proportion of all HC emissions remains relatively stable at between 9 and 10%.

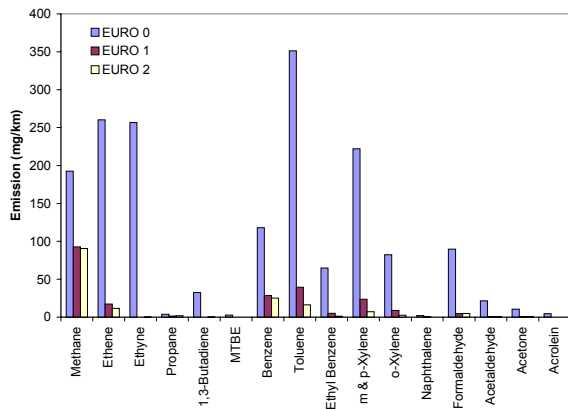Also noticeable is the relative importance of ethene, ethyne, and monocyclic aromatic compounds for Euro 0 cars.

Figure 35: Passenger car HC emissions – TRL congested urban cycle
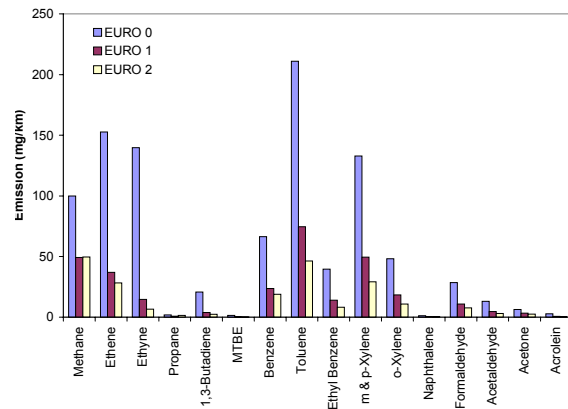
Figure 36: Passenger car HC emissions – ECE cycle
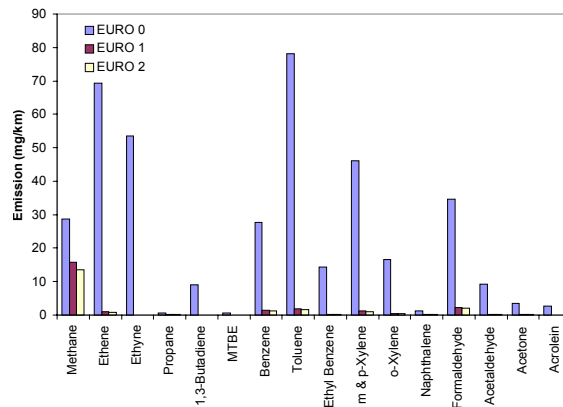
Figure 37: Passenger car HC emissions – EUDC cycle
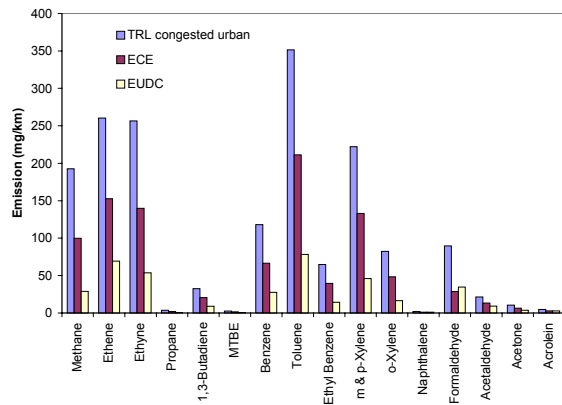
Figure 38: Euro 0 Passenger car HC emissions
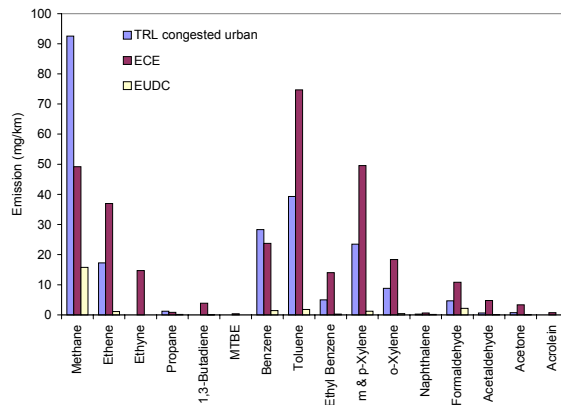
Figure 39: Euro 1 Passenger car HC emissions
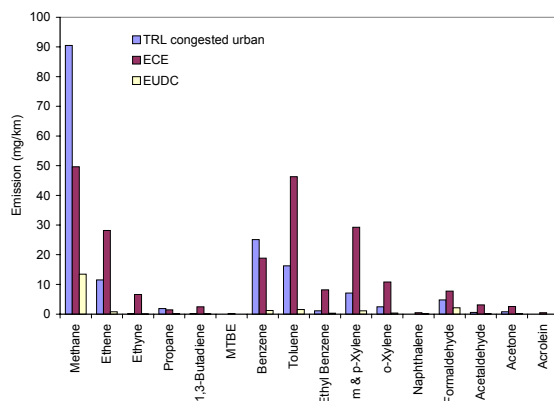
Figure 40: Euro 2 Passenger car HC emissions
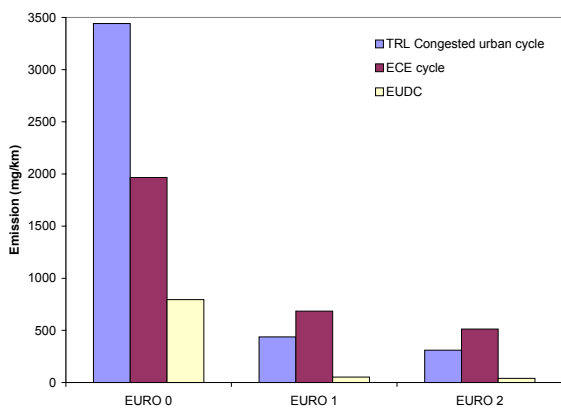
Figure 41: Passenger car methane emissions as a proportion of total HC emissions

It can be seen from Figures 38, 39 and 40 that for Euro 0 passenger cars, HC emission levels were consistently highest when the vehicle was operating in the congested urban cycle, and lowest in the EUDC. The only exception to this finding was formaldehyde; emissions of this compound were highest in the congested urban cycle, but levels in the ECE cycle were found to be marginally lower than those in the EUDC. For Euro 1 and Euro 2 passenger cars, only emissions of methane and benzene were greatest in the congested urban cycle, whilst for all other HC compounds, emission levels were found to be greatest during the ECE cycle.

(ii) Vans

As with passenger cars, HC emissions from vans tend to decrease with increasing levels of emissions technology associated with the advent of more stringent legislation (see Figures 42, 43, and 44) although the changes observed are not as clearly defined as those found for the passenger car emissions. The decrease between Euro 0 and Euro 1 is not as dramatic as that observed for passenger cars. THe reason for this is that emission rates from diesel-engined vehicles are lower than for petrol-engined vehicles, so consequently smaller reductions are needed to meet tighter standards.

For Euro 0 and Euro 1 vans, formaldehyde is the dominant pollutant for all three driving cycles. Ethene and acetaldehyde are the next two most significant contributors after formaldehyde for all levels of technology and for all drive cycles.

It is interesting to note that the relative importance of monocyclic aromatic compounds in HC emissions is much lower for the vans studied than it is for the passenger cars. For the passenger cars, the proportion of HC emissions consisting of monocyclic aromatics was found to vary between 10.4% and 26.4% depending on technology level and drive cycle. For the diesel-powered vans, the proportion was in the range 4.0% to 9.3%. After examining the specifications for the two fuels used in this study, it was found that 27.7% of the unleaded petrol was composed of aromatic compounds, whilst for diesel, the value was 28.7%. As can be seen from these figures, for the diesel fuel, the proportion of aromatic hydrocarbon emissions differs significantly from the aromatic content of the fuel. It should also be noted that emissions of all monocyclic aromatic compounds (except benzene) were higher from the Euro 2 van than they were from the Euro1 van.

Figure 42: HC emissions from Euro 0, Euro 1 and Euro 2 vans – TRL congested urban cycle
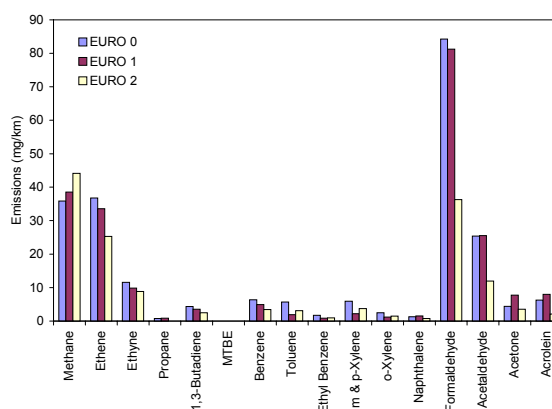
Figure 43: HC emissions from Euro 0, Euro 1 and Euro 2 vans – ECE cycle
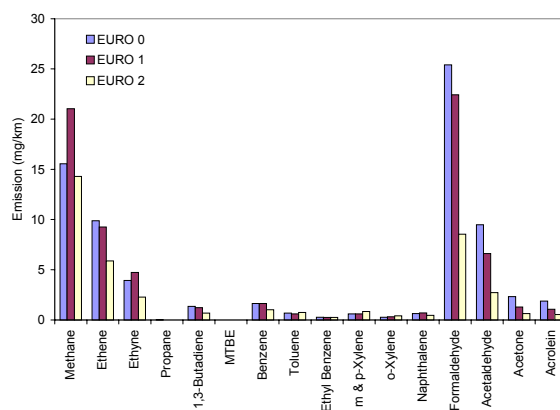
Figure 44: HC emissions from Euro 0, Euro 1 and Euro 2 vans – EUDC cycle
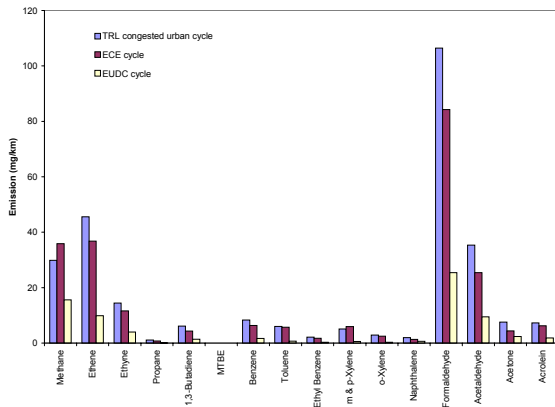
Figure 45: HC emissions for three drive cycles – Euro 0 van
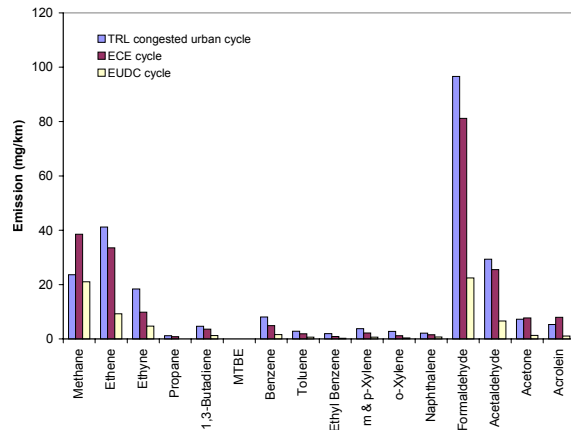
Figure 46: HC emissions for three drive cycles – Euro 1 van
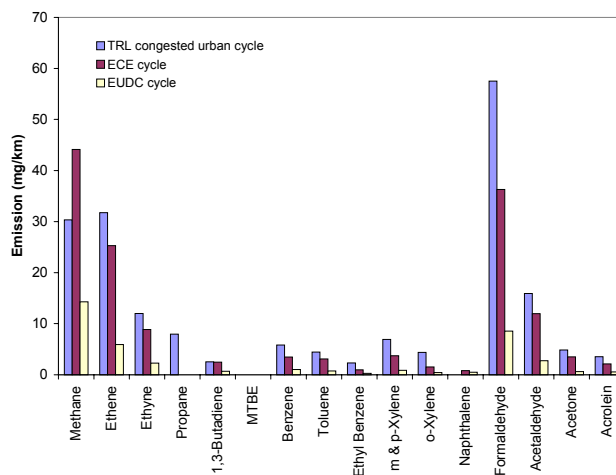
Figure 47: HC emissions for three drive cycles – Euro 2 van

4.3.4 Heavy duty vehicles

(i) Trucks

For all three legislation/technology levels, and for all three drive cycles, the most abundant HC emissions from trucks were found to be ethene and formaldehyde. This follows the pattern found for the diesel-engined vans, although the relative emission of methane by the heavy duty vehicles was significantly lower. The difference in levels between Euro 0 emissions and Euro 1 emissions was found to be much more significant than the difference between Euro 1 and Euro 2. Whilst the general trend was for emission of each constituent component to decrease as the legislation became more strict, levels of ethene, formaldehyde, acetaldehyde and acrolein were found to be higher from the Euro 2 vehicle compared to the Euro 1.

For the Euro 0 truck, emissions of ethene, ethyne, benzene, formaldehyde, acetaldehyde, acetone and acrolein were found to be highest when the vehicle was operating under the motorway cycle. This differs from the Euro 1 and Euro 2 trucks, where it was found that all HC emissions were lowest when the vehicle was following the motorway cycle, and highest in the urban cycle.
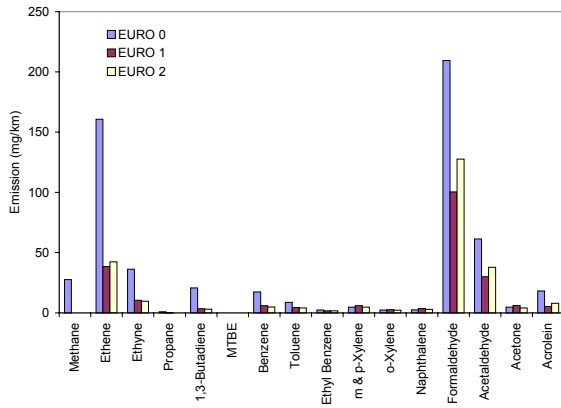
Figure 48: HC emissions from Euro 0, Euro 1 and Euro 2 trucks – urban cycle
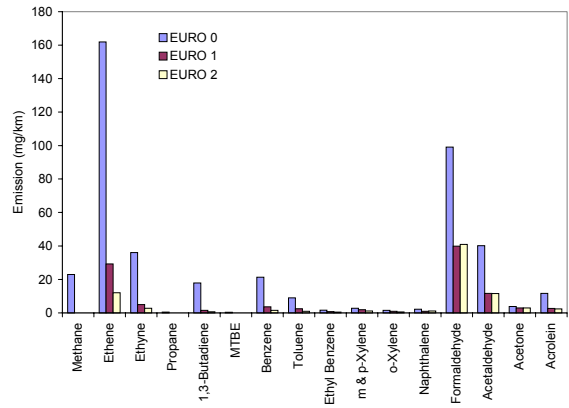
Figure 49: HC emissions from Euro 0, Euro 1 and Euro 2 trucks – suburban cycle
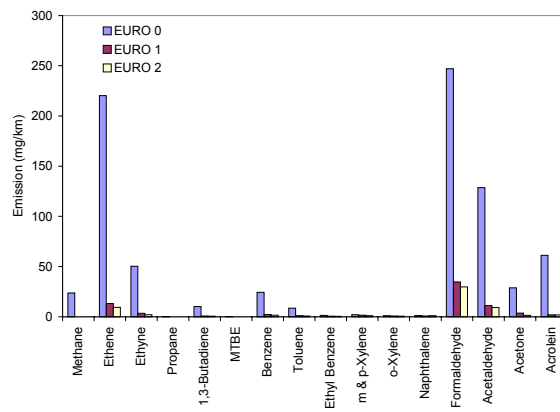
Figure 50: HC emissions from Euro 0, Euro 1 and Euro 2 trucks – motorway cycle
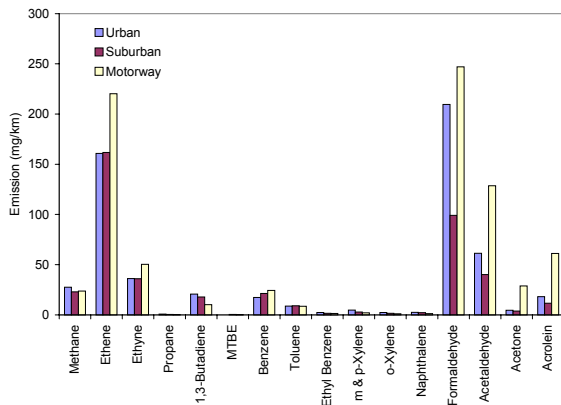
Figure 51: HC emissions for three drive cycles – Euro 0 truck
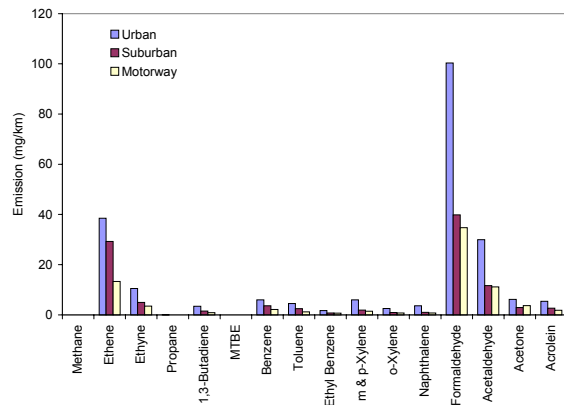
Figure 52: HC emissions for three drive cycles – Euro 1 truck
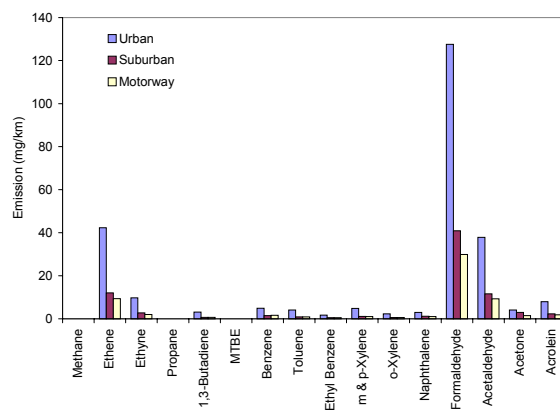
Figure 53: HC emissions for three drive cycles – Euro 2 truck

4.3.5 Buses

The data obtained from buses follows the expected trend of lower emissions with stricter legislation. As can be seen from Figures 54 and 55, HC emissions from buses (like vans and trucks) are dominated by formaldehyde and ethene. Whilst overall HC emission levels have reduced as the legislative requirements have become more stringent, the proportion of formaldehyde and ethene in HC emissions has increased. For the outer London cycle, formaldehyde emissions accounted for 18.5% of Euro 0 HC emissions, 28.8% of Euro 1 HC emissions, and 29.9% of Euro 2 HC emissions. Ethene emissions as a proportion of total HC emissions were found to rise from 8.3% for Euro 0 to 14.9% for Euro 1, before dropping back to 12.8% for Euro 2. Similar trends were found for the inner London cycle.

Bus emissions were generally found to be higher during the congested driving cycle (in this case, the inner London cycle). For example, levels of formaldehyde emissions during the inner London cycle were found to be 66.1% higher for Euro 0, 64.4% higher for Euro 1, and 30% higher for Euro 2, when compared to emissions from the corresponding vehicles during the outer London cycle.
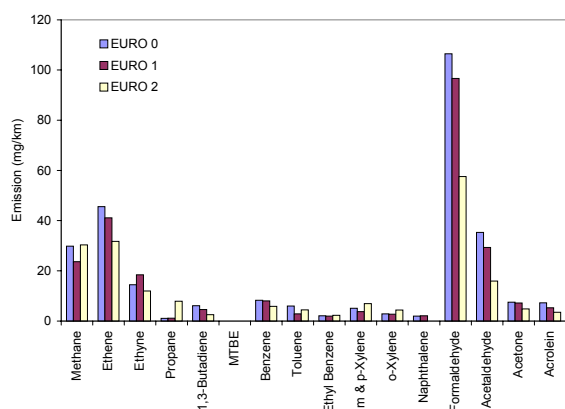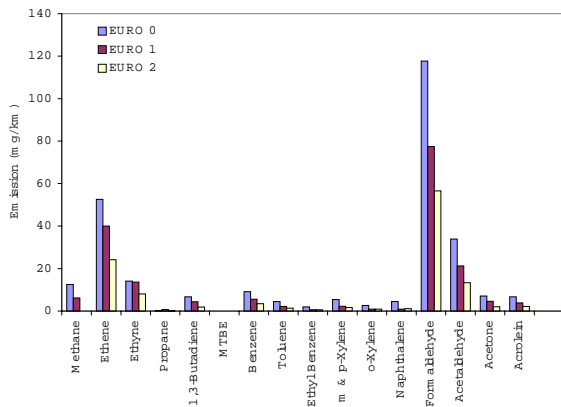
Figure 54: HC emissions from Euro 0, Euro 1 and Euro 2 – outer London cycle
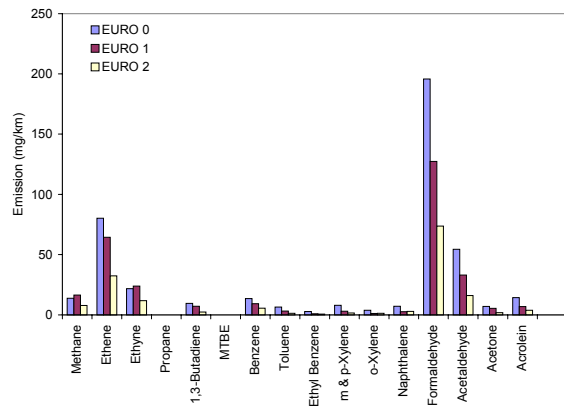
Figure 55: HC emissions from Euro 0, Euro 1 and Euro 2 – inner London cycle
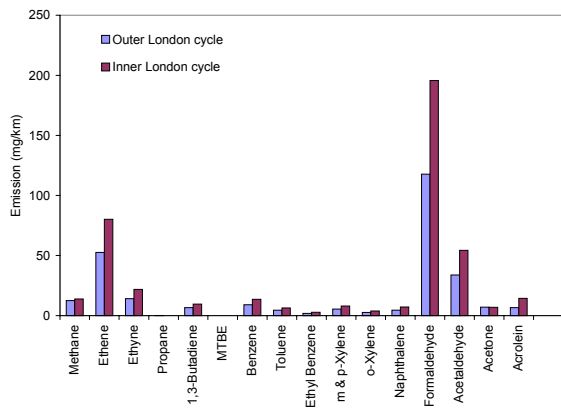
Figure 56: HC emissions for two drive cycles – Euro 0 bus
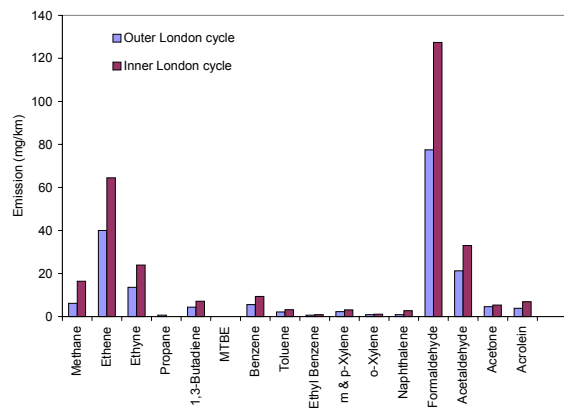
Figure 57: HC emissions for two drive cycles – Euro 1 bus
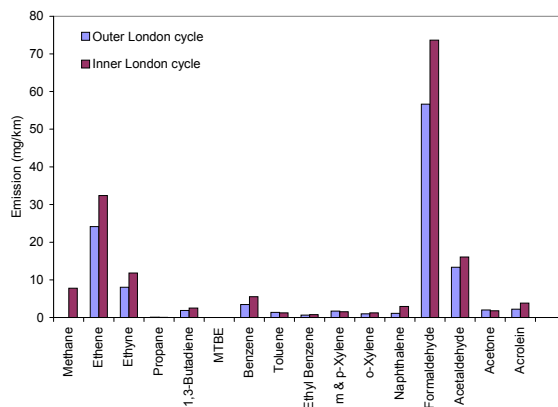
Figure 58: HC emissions for two drive cycles – Euro 2 bus

4.3.6   Summary and discussion

As was expected, levels of HC emissions were generally found to be highest from the Euro 0 petrol-engined passenger cars. The introduction of Euro 1 legislation that brought with it the universal fitment of catalytic converters to petrol vehicles resulted in a very large drop (upto a fifteen-fold

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reduction) in the abundance of organic compounds emitted. The reduction in emissions from Euro 1 to Euro 2 cars was found to be much smaller.

The GC speciation study identified toluene as the organic compound emitted in greatest abundance from the Euro 0 cars, whilst methane dominated Euro 1 and Euro 2 passenger car emissions. Although methane emission levels were found to drop as the legislation became more strict, its proportion of total HC emissions actually increased. This can be explained by the fact that it is difficult for catalytic converters to oxidise methane to carbon dioxide and water.

Total HC emissions from the Euro 0 diesel-engined vehicles (vans, trucks and buses) were in general, lower than from the cars. Consequently, the decrease in emission levels between Euro 0 and Euro 1 diesel vehicles was much less significant than it was for petrol vehicles. For the vans, the decrease in HC emissions between Euro 1 and Euro 2 vehicles was found to be more significant than the decrease between Euro 0 and Euro 1. The GC speciation study indicated that the most abundant organic emissions from trucks and buses were formaldehyde and ethene. For vans, these two compounds, along with methane were emitted in greatest abundance.

Emission rates were found to be dependent on driving cycle – in general, emissions decreased as the average cycle speed increased. The most significant exception to this finding was for the Euro 0 truck, where emissions were highest during the high-speed motorway cycle.

5   SUMMARY AND RECOMMENDATIONS

5.1 GENERAL

Measurements of a wide range of unregulated compounds were carried out on a selection of road vehicles. Although the exhaust components measured are not directly subject to emission control standards, many of them are important environmental contaminants. They included nitrogen dioxide which causes respiratory damage and is an important contributor to photochemical smog, many individual organic species including known and suspected carcinogens and reactive compounds that are involved in atmospheric reactions producing ozone, and the size distributions of the particulate emissions, the small fractions of which are considered to be most damaging to health.

The vehicles used in the test programme included cars, LGVs, HGVs and buses manufactured to conform with the three different levels of emission control introduced during the 1980s and 1990s. They therefore represented most of the vehicles in operation at the time of the study. Because rates of emission vary depending on the way a vehicle is operated, the tests were conducted over a variety of driving cycles simulating driving conditions from those in congested urban traffic through to freely flowing motorway traffic.

The measurements of some of the compounds, notably nitrogen dioxide and particulates, are highly dependent on the sampling and analytical procedure used. A number of different methods were included to try to demonstrate and understand some of the difficulties involved. Nitrogen oxides were measured in both raw and diluted exhaust (the dilution may affect the rate and extent to which nitric oxide is oxidised to nitrogen dioxide during sampling), and by the standard chemiluminescence method and Fourier transform infra red spectrometry (the chemiluminescence method derives the nitrogen dioxide concentration from the difference between those of nitric oxide and total oxides of nitrogen and is therefore prone to significant errors). Particles were also measured in raw and dilute exhaust (dilution causes the formation of nuclei mode particles from semi-volatile exhaust components), by the standard gravimetric method after collection on a filter, using a tapered element oscillating microbalance (TEOM) which provided a continuous measurement of the PM_{10} mass, and using an electrical low pressure impactor (ELPI) which gave the numbers of particles in each of 12 size ranges from 30 nm to 10 μm. Organic compounds were analysed by gas chromatography, using a flame ionization detector.

The results of the emission tests were examined for the effects of the various sampling methods, the influence of the different types of driving cycle and of the type of vehicle.

5.2 NITROGEN DIOXIDE EMISSIONS

The nitrogen dioxide data were analysed statistically, using a technique that can identify the independent effects of each variable in a multivariate system after allowing for those of the other variables. The method was used to examine the dependency of the emission rate of nitrogen dioxide, and of the ratio of nitrogen dioxide to total oxides of nitrogen on five independent variables: the average cycle speed, the emission standard of the vehicle, the start temperature of the test, the fuel (petrol or diesel) and the sampling method. For nitrogen dioxide emissions, it was shown that:

- There was a statistically significant relationship with the fuel type, the emission standard and the cycle speed, but not with the test temperature or sampling method.

- Nitrogen dioxide emissions from diesel vehicles were higher than from petrol vehicles.

- Emissions from Euro 0 vehicles were higher than from Euro 1 vehicles, which were in turn higher than from Euro 2 vehicles. The difference between Euro 0 and Euro 1 was highly significant; that between Euro 1 and Euro 2 was less significant.

- Average rates of emission showed a statistically significant increase with increasing cycle speed.

And for the ratio of nitrogen dioxide to total oxides of nitrogen emissions:

- There was a statistically significant relationship with the method of sampling, the fuel type and the average cycle speed, but not with the emission standard or test temperature.

- The ratio was higher for petrol vehicles than for diesels.

- The ratio was higher when a dilute sample was used than for the raw exhaust.

- The ratio decreased as the average speed of the test cycle increased.

5.3 PARTICULATE EMISSIONS

- The particulate data were not analysed in this formal way, but were nevertheless examined in relation to the same vehicle and operational variables.

- Total particulate mass varied with the average cycle speed, with the highest emissions tending to be during cycles with the lowest speeds. For cars and LGVs, emissions increased again during the high-speed, motorway cycles.

- There were differences between the results from raw and diluted exhaust, but they were neither systematic nor significant.

- Emissions from Euro 0 vehicles in all classes were higher than from Euro 1 and Euro 2 vehicles, but only HGVs showed a systematic reduction from Euro 1 to Euro 2.

- Emissions from the diesel vehicles were higher by an order of magnitude or more than those from petrol vehicles.

- There was a good overall agreement between the particulate mass measured by the filter measurement and the aggregated results from the TEOM. Variations between the two methods did not show a systematic bias.

- The particle size distributions for all vehicle types were broadly similar, with highest numbers emitted in the smallest size classes (30 to about 150 nm).

- For all types of vehicle there was a tendency for particle numbers to increase in all size classes as the average cycle speed increased.

- Tests on cars at different ambient temperatures showed relatively small differences.

- The influence of the emission standard varied for the different types of vehicle. For cars, particle numbers were highest from the Euro 0 class but there was little difference between Euro 2 and Euro 3. LGVs showed little difference between any of the Euro standards. The Euro 1 HGV

produced the highest numbers of particles across the whole size range, and the Euro 2 HGV the lowest. In the case of buses, the Euro 0 vehicle emitted the highest number and the Euro 1 vehicle the lowest. These results imply that the reductions in particle mass that are generally seen with the newer technology vehicles do not necessarily correspond with reductions in the numbers of very fine particles emitted (the small particles contribute very little to the mass, but the highest numbers).

5.4 EMISSIONS OF ORGANIC COMPOUNDS

The organic compound analysis identified 170 individual species including saturated and unsaturated aliphatic hydrocarbons, monocyclic and polycyclic aromatic hydrocarbons and oxygenated compounds such as aldehydes, ketones and ethers. An initial assessment was made of total emissions by summing those of the individual compounds. This revealed significant improvements, in most cases, according to the vehicles' emission standards. With only one exception, emissions from Euro 2 vehicles were lowest and those from Euro 0 vehicles highest. It also showed the effectiveness of the three-way catalyst in reducing hydrocarbon emissions: those from the Euro 0 (non-catalyst) cars were higher than from the Euro 1 and 2 (catalyst) cars by factors of up to 20, depending on the driving cycle. Substantial differences were also apparent for the different driving cycles: for example, the emissions from Euro 1 HGVs were 450, 230 and 175 mg/km for the urban, suburban and motorway cycles respectively.

Seventeen of the compounds were selected, on the basis of their abundance and environmental importance, and subjected to a more detailed analysis. Dependencies with the emission standard and driving cycle were shown for each of the classes of vehicle tested.

- For cars, there was a very large decrease in emissions from Euro 0 to Euro 1 and a general, though smaller decrease from Euro 1 to Euro 2.

- Emissions were compared for three driving cycles, and were shown for almost all compounds to reduce significantly as the average cycle speed increased.

- Although methane emissions from Euro 1 and Euro 2 cars were lower than from Euro 0 cars, they represented a significantly higher proportion of the total. This is because the catalyst is less efficient at oxidising methane than most other compounds.

- The effect of the emission standard on LGV emissions varied for different compounds. For example, over the urban part of the legislative test cycle, methane emissions increased from Euro 0 to Euro 1 and from Euro 1 to Euro 2 (the LGVs were diesel engined, so this is not related to the catalyst effect noted above); formaldehyde emissions decreased in the same sequence and toluene emissions were higher in both the Euro 0 and Euro 2 than the Euro 1 class.

- Emissions of all compounds except methane reduced as the average cycle speed increased. Methane emissions were highest for a standard urban cycle with a higher average speed than the congested urban cycle.

- HGV emissions generally reduced in the sequence Euro 0 - Euro 1 - Euro 2, with the greatest change between Euro 0 and Euro 1. For a few compounds (e.g. ethene and formaldehyde), Euro 2 emissions were higher than Euro 1.

- For the Euro 1 and Euro 2 HGVs, emissions of almost all compounds reduced with increasing cycle speed. For Euro 0 vehicles, however, the highest emissions were often found for the high speed motorway cycle.

- Emissions of all compounds by the buses showed a systematic decrease in the transition from Euro 0 to Euro 2 standards.

- Emissions of all compounds were higher for the slow speed inner London cycle than for the higher speed outer London cycle.

5.5 THE EFFECT OF PRIMARY NITROGEN DIOXIDE EMISSIONS ON AIRBORNE CONCENTRATIONS

In addition to the emission measurement programme, a main objective of this work was to investigate the effects of primary emissions of nitrogen dioxide on roadside concentrations. In principle, the nitrogen dioxide found in the air near to roads will be a mixture of that emitted directly by the traffic and that which is produced by the atmospheric oxidation of nitric oxide emissions. Where there is a major source of nitric oxide, the latter of these is usually limited by the availability of oxidising agents (mainly ozone) in the air.

How these effects combine was examined in a modelling exercise in which pollution concentrations for two typical traffic situations were simulated. One example considered urban traffic in Leicester and the other considered motorway traffic on the M25. Traffic emissions of total oxides of nitrogen and, separately, of nitrogen dioxide were estimated from the traffic flow and speed data using functions based on the emission rates measured in this study. These were then input to a dispersion model, and nitrogen dioxide concentrations were calculated in two ways:

- Assuming that all of the traffic emissions were nitric oxide. This will disperse from the roads under the influence of the local wind conditions and some will be converted to nitrogen dioxide. However, the extent of the nitric oxide conversion will be limited by the oxidising capacity of the air.

- Assuming the emissions to be a mixture of nitric oxide and nitrogen dioxide in the proportions indicated by this emission test programme. The nitric oxide will behave in the same way as before, being dispersed and partially oxidised. In addition, though, there will be input from the primary nitrogen dioxide that will also disperse, but that will not consume atmospheric oxidants. This will tend to produce higher concentrations than the first case, and the difference between the two results gives a measure of the effect of the primary nitrogen dioxide emissions.

The results of these calculations showed the primary emissions to have a significant impact on the concentrations near to the roads. In the urban example, the difference in concentration with and without allowance for primary nitrogen dioxide was typically in the range between 15 and 25% at locations within about 50 m of the roads. Differences for the motorway example were lower, but still of the order of 5 to 15%.

The data from the motorway example were further examined to investigate the influence of the traffic conditions on the primary emission input to nitrogen dioxide concentrations. The variables studied were the total traffic flow, the proportion of goods vehicles in the traffic and the average speed of the traffic. The flow obviously affects the total emission output, while the speed and types of vehicle have both been shown to influence the proportion of primary nitrogen dioxide emitted. When these variables were examined independently, they showed a rather poor correlation with both the predicted nitrogen dioxide concentrations and with the primary contribution (represented by the ratio between the calculations made with and without the primary emissions contribution). However, when a multiple regression procedure was used to test the effect of the variables in combination, they were able to explain a good deal of the variability in the pollution results.

5.6 RECOMMENDATIONS

1. The findings discussed in this report are based on limited results, in most cases using only a single vehicle to represent its class. They demonstrate the principles of the issues that have been examined, but cannot necessarily be taken to be quantitatively representative. Consideration should be given to a further, more extensive test programme.

2. As primary nitrogen dioxide emissions have been shown to contribute significantly to roadside concentrations, consideration should be given to the introduction of standards specifically to limit nitrogen dioxide emissions in addition to those limiting total oxides of nitrogen. However, for the vehicles tested in this work, the proportion of nitrogen dioxide in the exhaust was shown to be statistically independent of the Euro standard. This suggests that the tightening of limits for total oxides of nitrogen are equally effective in reducing both nitric oxide and nitrogen dioxide emissions.

3. Similarly, size related standards for particulates, based on number rather than mass should be studied. In this case, there was no evidence that mass based limits were effective in reducing the number of particles emitted.

4. Standards for individual organic compounds should be considered, focusing on those that are environmentally important because of their reactivity, toxicity or carcinogenicity. As for nitrogen dioxide, though, these results suggest that the current procedure of restricting total hydrocarbon emissions is more or less equally effective in reducing most organic species. One exception appears to be methane, whose proportional (though not absolute) contribution may be increasing in the exhaust of catalyst equipped cars.

5. An issue that was not addressed in this study is the use of particulate traps for diesel engined vehicles. Some, at least, use nitrogen dioxide to promote trap regeneration, and the engine's production of nitrogen dioxide is specially increased for that purpose. With the increasing use of traps, an investigation of this process and its potential effects should be considered.

6   ACKNOWLEDGEMENTS

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APPENDIX A: STATISTICAL ANALYSIS OF THE FACTORS AFFECTING PRIMARY NO_2 AND NO_2/NO_x RATIO

A general linear statistical model has been applied to the measured data for the *light duty vehicles only* in order to examine the relationship between different independent variables on primary NO_2 and the NO_2/NO_x ratios. The independent variables examined were the average cycle speed, emission standard, start temperature, sampling method, fuel[10], and size of vehicle. Section A.1 below provides an overview of the analysis adopted and an interpretation of the results obtained. Sections A.2 and A.3 provide details of the outputs from the statistical model for the calculations made for NO_2 and NO_2/NO_x ratios respectively.

A.1 OVERVIEW OF RESULTS OF THE STATISTICAL ANALYSIS

Fuel, emission standard and average cycle speed were identified as being the most significant variables affecting NO_2 emissions, whilst fuel, sampling method and speed were found to be the most significant variables influencing the NO_2/NOx ratio. (NB. Details of the multiple regression statistics results are provided in sections A.2 and A.3). However, it should be noted that even when taking these variables into account there is still a considerable degree of unexplained variance in the measured values of primary NO_2 and NO_2/NO_x ratios. This is possibly the result of poor repeatability in the emission measurements, or that several of the independent variables are simultaneously influencing the measured results.

One method of clarifying relationships in a multi-variable analysis is to eliminate the effects of all but one of the significant variables. For example, to clarify the relationship between average cycle speed on NO_2 emissions, the effect of the next most significant variable (fuel) is first removed. This is achieved by adjusting each NO_2 value so the relative effect of using different fuels is zero (i.e. the gradient of the linear regression line of NO_2 v fuel type is zero). The NO_2 values on the graph for average cycle speed are then adjusted by the same amount and similarly for the other variables. This process is continued until the only significant variable that remains is speed.

This form of analysis has been repeated to isolate the effect of all the significant variables on NO_2 and NO_2/NO_x emissions. In each analysis the adjusted NO_2 values are called 'NO_2 residuals'. The difference between any two residual values predicts the independent effect of changing the variable being examined. For example, where the variable is average cycle speed, the slope of the graph represents the independent effect. It follows that the absolute values of the individual residuals should be ignored for the purpose of this analysis.

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[10] More specifically fuel is used as shorthand for differentiating between diesel and petrol fuelled vehicles

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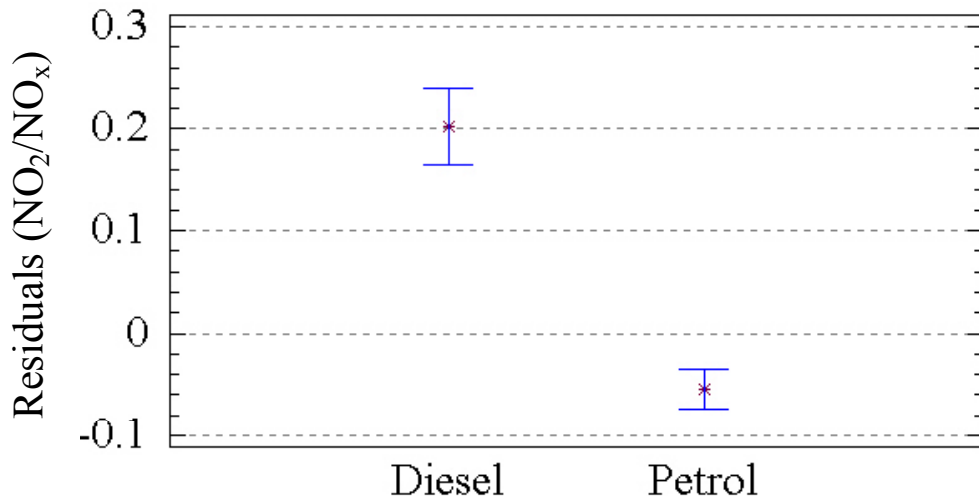
Figure A1: Effect of fuel type on NO$_2$/NO$_x$ ratio

Figure A1 shows a comparison of the NO$_2$/NO$_x$ ratios for diesel and petrol vehicles once the other independent variables have been eliminated. On average the Diesel vehicles show NO$_2$/NO$_x$ ratios that are 0.25 greater than petrol vehicles with 99% confidence levels of approximately +/- 0.04 for diesel and +/-0.02 for Petrol. The relatively large difference between the average values in relation to the size of the confidence limits indicates that the difference in NO$_2$/NO$_x$ between diesel and petrol is highly significant. This difference is further confirmed from the ANOVA (analysis of variance) test where the P-value is less than 0.01 this shows the data to be statistically different at the 99% confidence level. (NB. The values of P are given in sections A.2 and A.3 of this appendix).
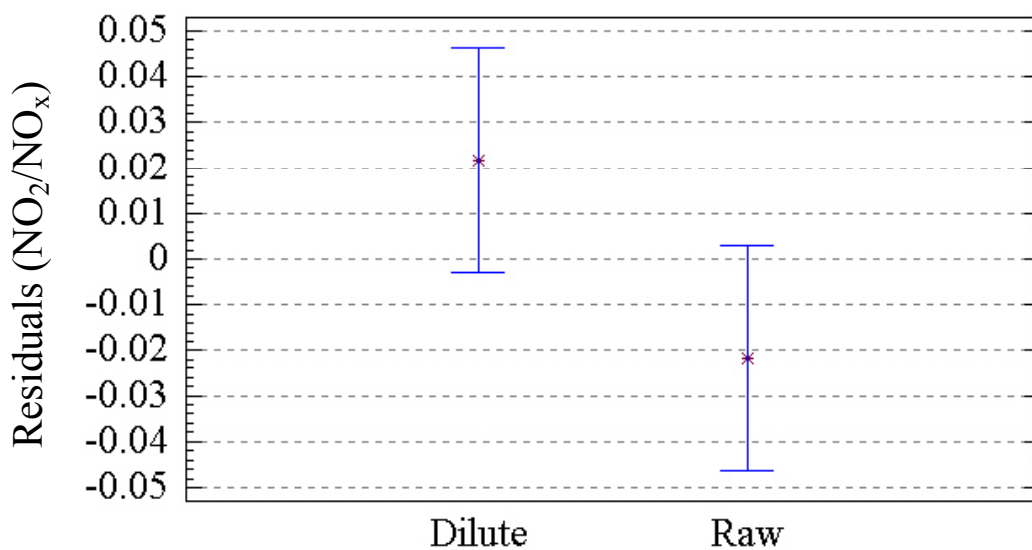
Figure A2: Effect of sampling method on NO$_2$/NO$_x$ ratio

The independent effect of using raw and dilute sampling methods on the NO_2/NO_x ratio is shown in Figure A2. The results show that, on average, the dilute method of sampling increases NO_2/NO_x ratios by 0.044 compared to raw sampling with 99% confidence levels of +/- 0.05 in each case. The ANOVA test shows the P-value is 0.0155 indicating a significant difference between raw and dilute sampling on NO_2/NO_x at the 95% confidence level. The overlap of the confidence limits and the slightly higher P value indicates that the level of significance is somewhat less than that of fuel, the absolute difference is also relatively small.
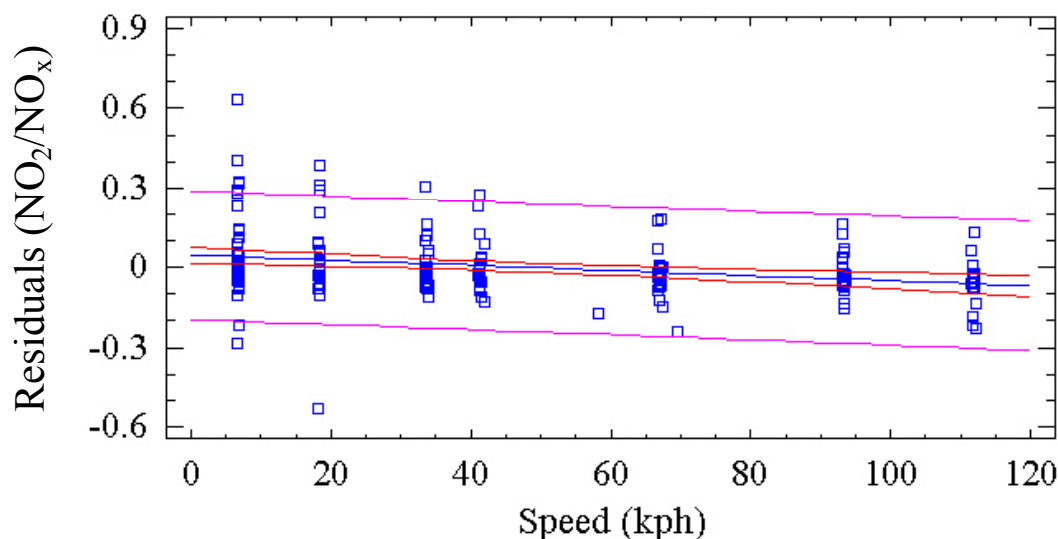
Figure A3: Effect of speed on NO_2/NO_x

The independent effect of the average cycle speed on primary NO_2/NOx ratios is shown in Figure A3. A linear regression model fitted to the speed data indicates that NO_2/NOx decreases at higher speeds11 although the overall effect is small in relation to that of fuel. The 99% confidence limits associated with the mean values at any given speed are denoted by the inner bands, on Figure A3. The statistical analysis showed that the P-value deduced from the ANOVA analysis is less than 0.01, indicating that there is a statistically significant relationship between the NO_2/NOx and speed at the 99% confidence level. However, it can be seen from the figure that a considerable degree of variability in the data remains even when the effects of speed are taken into account and the effects of other variables are eliminated. The standard deviation of the errors produced using the regression line is 0.12. The 95% confidence boundaries associated with the determination of new observations are shown on the figure as the outer boundary lines.

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[11] $NO_2/NO_x = 0.046 - 0.00096*Speed(km/h)g$
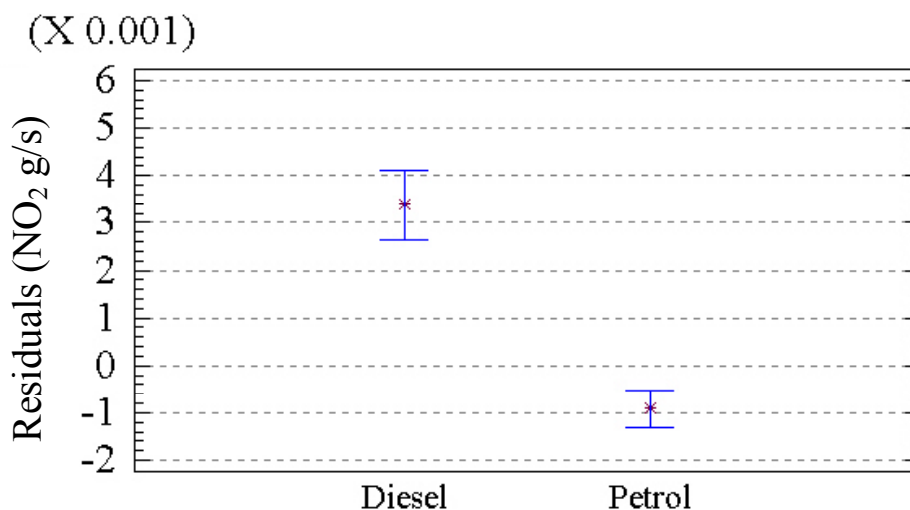
Figure A4: Effect of fuel type on NO_2

A comparison of the effect of using diesel v petrol fuelled vehicles on NO_2 emissions is shown in Figure A4. On average the diesel vehicles gave NO_2 emissions that are 4.4 g/sec greater than petrol vehicles with 99% confidence levels of approximately +/- 1.5 for diesel and +/-0.9 for petrol. Again since the P-value in the ANOVA table for NO_2 is less than 0.01, it can be concluded that the observed differences in primary NO_2 for the different fuels are statistically significant at the 99% confidence level.
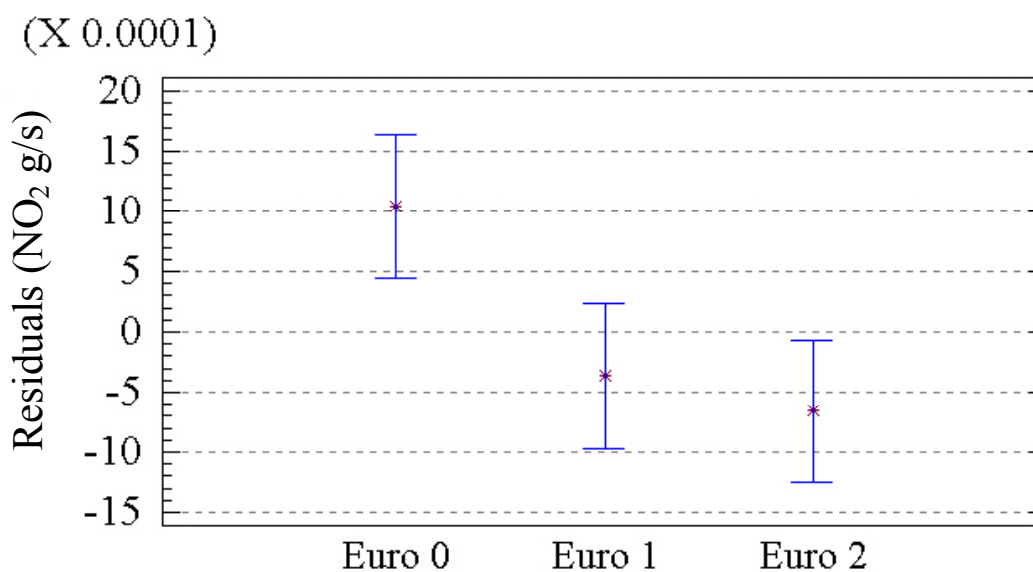
Figure A5: Effect of legislation on NO_2 emissions

The influence of the vehicle type approval level (legislation) on NOx is shown in Figure A5. On average the Euro 0 vehicles exhibit 14 g/sec greater primary NO_2 than Euro 1 vehicles and 17 g/km greater than the Euro 2 vehicles tested. The confidence limits are approximately +/- 6 g/sec in each case, suggesting that whilst Euro 0 vehicles emit significantly more NO_2 than the other vehicle types, the difference between Euro 1 and Euro 2 is far less significant. For this data set, the ANOVA P-value is less than 0.01 suggesting there is a statistically significant relationship between NO_2 and vehicle legislation category at the 99% confidence level.
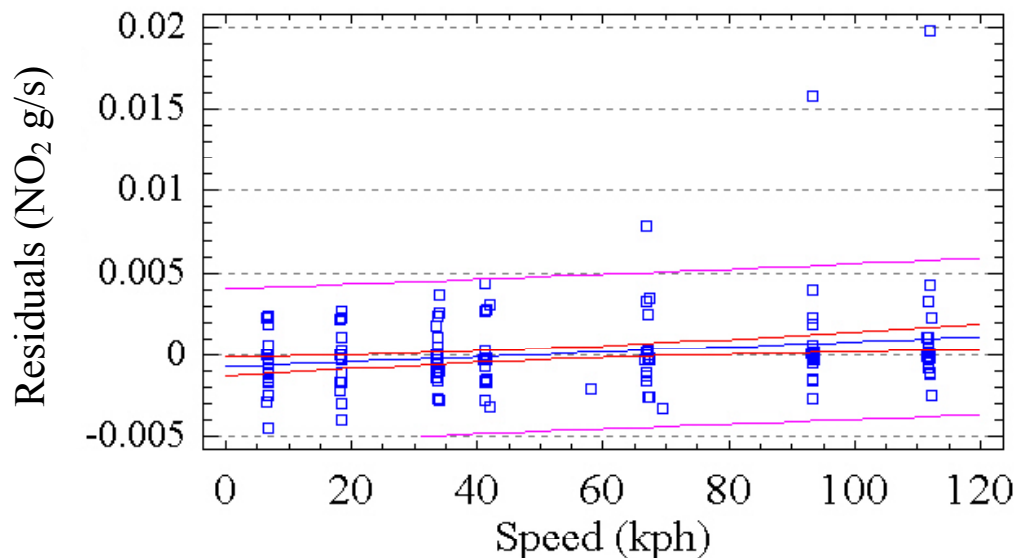
Figure A6: Effect of speed on NO$_2$ emissions

The independent effect of the average cycle speed on the NO$_2$ emissions is shown in Figure A6. The regression line and 99% confidence boundaries associated with the means at any given speed are shown on the figure. The P-value in the ANOVA analysis is less than 0.01, confirming this relationship is statistically significant at the 99% confidence level. The slope of the regression line indicates that NO$_2$ increases[12] by approximately 1.5 mg/sec on average between an average cycle speed of 7 and 120 km/h, although clearly this effect is relatively small in relation to the observed effects of both fuel and legislation. The standard error of the estimate shows the standard deviation of NO$_2$ to be 2.4 mg/sec. This is quite large in relation to average change over the speed range. The regression line, as fitted, explains only 4.8% of the variability in NO$_2$, suggesting that effects other than average speed are more influential on NO$_2$ emissions.

A.2 SUMMARY

The results of the analysis to examine the independent effect of variables on NO$_2$/NOx and NO$_2$ are summarised in Tables A1 and A2 respectively. The most significant factor, which could be identified influencing NO$_2$/NO$_x$, was fuel, followed by average cycle speed, then the method of sampling (raw v dilute). The most significant factor influencing primary NO$_2$ was legislation, followed by fuel then average cycle speed.

The effect of start temperature, vehicle size and legislation were not found to significantly influence the NO$_2$/NO$_x$ ratio, and the start temperature, vehicle size and sampling method were not found to significantly influence the NO$_2$ emissions.

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[12] NO$_2$ (g/km) = -0.0007412 + 0.0000153*Speed(km/h)

Table A1: Summary of the influence of significant variables on primary NO$_2$/NO$_x$ ratio

Independent Variable	Average Difference	Confidence limits	P value
Fuel (diesel v petrol vehicles)	0.250	+/- 0.04	<0.01
Dilute v Raw Sampling	0.044	+/-0.05	0.0155
Average cycle speed (7 v 120 kph)	0.108	+/-.0025 to +/-0.05	<0.01

Table A2: Summary of the influence of significant variables on primary NO$_2$

Independent Variable	Average Difference (mg/km)	Confidence limits (mg/km)	P value
Fuel type (diesel vs petrol vehicles)	4.40	+/-1.5 and +/- 0.9	<0.01
Legislation (Euro 0 vs Euro 2)	17.00	+/-6	<0.01
Average cycle speed (7 km/h v 120 km/h)	1.72	+/-1 to +/-2	<0.01

A.3 STATISTICAL ANALYSIS FOR NO$_2$

General Linear Models

Number of dependent variables: 1
Number of categorical factors: 3
Number of quantitative factors: 2

A.3.1 Primary NO$_2$ - Analysis of variance using all variables

```
-------------------------------------------------------------------------
Source          Sum of Squares Df      Mean Square    F-Ratio  P-Value
-------------------------------------------------------------------------
Model           0.000737843    6       0.000122974    21.25    0.0000
Residual        0.00104723     181     0.0000057858
-------------------------------------------------------------------------
Total (Corr.)   0.00178507     187
```

Type III Sums of Squares

```
--------------------------------------------------------------------------
Source          Sum of Squares      Df      Mean Square   F-Ratio    P-Value
--------------------------------------------------------------------------
```

fuel	**0.000573487**	**1**	**0.000573487**	**99.12**	**0.0000**
Sampling	0.0000164817	1	0.0000164817	2.85	0.0932
Standard	**0.000105542**	**2**	**0.0000527711**	**9.12**	**0.0002**
Speed	**0.0000556818**	**1**	**0.0000556818**	**9.62**	**0.0022**
Temperature	0.00000121106	1	0.00000121106	0.21	0.6479
Residual	0.00104723	181	0.0000057858		

Total (corr)	0.00178507	187	

A.3.2: Effect of legislation on NO_2 emissions

General Linear Models

Number of dependent variables: 1
Number of categorical factors: 1
Number of quantitative factors: 0

Analysis of Variance for RESIDUALS

Source	Sum of Sq.	Df	Mean Square	F-Ratio	P-Value
Model	0.000103176	2	0.0000515879	8.96	0.0002
Residual	0.00106513	185	0.00000575746		

Total (cor.)	0.00116831	187	

Type III Sums of Squares

Source	Sum of Sq.	Df	Mean Square	F-Ratio	P-Value
Standard	0.000103176	2	0.0000515879	8.96	0.0002
Residual	0.00106513	185	0.00000575746		

Total (cor.)	0.00116831	187	

Expected Mean Squares

Source	EMS
Standard	(2)+Q1
Residual	(2)

F-Test Denominators

Source	Df	Mean Square	Denominator
Standard	85.00	0.00000575746	(2)

Variance Components

```
-------------------------------------------------------------------------
Source                  Estimate
-------------------------------------------------------------------------
Residual                0.00000575746
-------------------------------------------------------------------------
```

R-Squared   = 8.83122 percent
R-Squared (adjusted for d.f.) = 7.84562 percent
Standard Error of Est.   = 0.00239947
Mean absolute error   = 0.0013189
Durbin-Watson statistic = 0.725654 (P=0.0000)

Residual Analysis

Estimation   Validation
n   188
MSE   0.00000575746
MAE   0.0013189
MAPE
ME   -1.66091E-19
MPE

A.3.3: Effect of speed on NO2

Regression Analysis - Linear model: Y = a + b*X

Dependent variable: RESIDUALS
Independent variable: Speed

Parameter	Standard Estimate	Error	T Statistic	P-Value
Intercept	-0.000741273	0.00029653	-2.49982	0.0133
Slope	0.0000153242	0.00000495609	3.09199	0.0023

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Model	0.0000547391	1	0.0000547391	9.56	0.0023
Residual	0.00106496	186	0.00000572558		
Total (Cor.)	0.0011197	187			

Correlation Coefficient   = 0.221105
R-squared   = 4.88874 percent
R-squared (adjusted for d.f.) = 4.37738 percent

Standard Error of Est.　　　　　= 0.00239282
Mean absolute error　　　　　　　= 0.00132435
Durbin-Watson statistic　　　= 0.724607 (P=0.0000)
Lag 1 residual autocorrelation　= 0.632953

A.3.4　Effect of Fuel on NO2 emissions

General Linear Models

Number of dependent variables:　　　　1
Number of categorical factors:　1
Number of quantitative factors:　0

Analysis of Variance for NO2

Source	Sum of Squ.	Df	Mean Square	F-Ratio	P-Value
Model	0.00056805	1	0.00056805	86.82	0.0000
Residual	0.00121702	186	0.00000654313		

Total (Corr.)　　0.00178507　187

Type III Sums of Squares

Source	Sum of Squ	Df	Mean Square	F-Ratio	P-Value
fuel	0.00056805	1	0.00056805	86.82	0.0000
Residual	0.00121702	186	0.00000654313		

Total (cor.)　0.00178507　187

Expected Mean Squares

Source	EMS
fuel	(2)+Q1
Residual	(2)

F-Test Denominators

Source	Df	Mean Square	Denominator
fuel	186.00	0.00000654313	(2)

Variance Components

```
Source                  Estimate
-------------------------------------------------------------------------------
Residual           0.00000654313
-------------------------------------------------------------------------------


R-Squared                    = 31.8222 percent
R-Squared (adjusted for d.f.)    = 31.4557 percent
Standard Error of Est.    = 0.00255796
Mean absolute error          = 0.00134065
Durbin-Watson statistic = 0.754163 (P=0.0000)
```

Residual Analysis

```
Estimation     Validation
n            188
MSE          0.00000654313
MAE          0.00134065
MAPE
ME           -1.34949E-18
MPE
```

A.4 STATISTICAL ANALYSIS FOR NO2/NOX RATIO

A.4.1.   NO2/NOx Ratio - Analysis of variance on all variables

Source	Sum of Squ.	Df	Mean Square	F-Ratio	P-Value
Model	2.43382	6	0.405636	27.41	0.0000
Residual	2.67811	181	0.0147962		
Total (Corr.)	5.11193	187			

Type III Sums of Squares

Source	Sum of Squ.	Df	Mean Square	F-Ratio	P-Value
Sampling	**0.0902238**	**1**	**0.0902238**	**6.10**	**0.0145**
fuel	**2.00199**	**1**	**2.00199**	**135.30**	**0.0000**
Standard	0.0676864	2	0.0338432	2.29	0.1045
Temperature	0.000682152	1	0.000682152	0.05	0.8302
Speed	**0.199603**	**1**	**0.199603**	**13.49**	**0.0003**
Residual	2.67811	181	0.0147962		

A.4.2   Effect of sampling on NO_2/NO_x

General Linear Models

Number of dependent variables: 1
Number of categorical factors: 1
Number of quantitative factors: 0

Analysis of Variance for RESIDUALS

Source	Sum of Squ.	Df	Mean Square	F-Ratio	P-Value
Model	0.0881522	1	0.0881522	5.97	0.0155
Residual	2.7467	186	0.0147672		
Total (Corr.)	2.83485	187			

Type III Sums of Squares

```
--------------------------------------------------------------------------------
Source          Sum of Squares      Df              Mean Square  F-Ratio  P-Value
--------------------------------------------------------------------------------
Sampling        0.0881522           1       0.0881522     5.97   0.0155
Residual        2.7467              186     0.0147672
--------------------------------------------------------------------------------
Total (cor.)    2.83485             187
```

Expected Mean Squares

```
--------------------------------------------------------------------------------
Source          EMS
--------------------------------------------------------------------------------
Sampling        (2)+Q1
Residual        (2)
--------------------------------------------------------------------------------
```

F-Test Denominators

```
--------------------------------------------------------------------------------
Source          Df      Mean Square    Denominator
--------------------------------------------------------------------------------
Sampling        186.00          0.0147672      (2)
--------------------------------------------------------------------------------
```

Variance Components

```
--------------------------------------------------------------------------------
Source          Estimate
--------------------------------------------------------------------------------
Residual        0.0147672
--------------------------------------------------------------------------------
```

R-Squared   = 3.10959 percent
R-Squared (adjusted for d.f.)   = 2.58867 percent
Standard Error of Est.   = 0.12152
Mean absolute error   = 0.0794061
Durbin-Watson statistic = 1.10691 (P=0.0000)

Residual Analysis

```
--------------------------------
Estimation    Validation
n             188
MSE           0.0147672
MAE           0.0794061
MAPE
ME            4.74281E-18
MPE
```

A.4.3. Effect of speed on NO2/NOx ratio

Regression Analysis - Linear model: Y = a + b*X

Dependent variable: NO2/NOx RESIDUALS
Independent variable: Speed

Parameter	Estimate	Standard Error	T Statistic	P-Value
Intercept	0.0463457	0.0150593	3.07754	0.0024
Slope	-0.000958097	0.000251696	-3.80657	0.0002

Analysis of Variance

Source	Sum of Squ.	Df	Mean Square	F-Ratio	P-Value
Model	0.213974	1	0.213974	14.49	0.0002
Residual	2.74667	186	0.0147671		

| Total (Corr.) | 2.96065 | 187 | | | |

Correlation Coefficient = -0.268836
R-squared   = 7.22727 percent
R-squared (adjusted for d.f.) = 6.72849 percent
Standard Error of Est.   = 0.12152
Mean absolute error   = 0.0793716
Durbin-Watson statistic = 1.1061 (P=0.0000)
Lag 1 residual autocorrelation = 0.446617

A.4.4 Effect of Fuel on NO_2/NO_x ratio

General Linear Models

Number of dependent variables: 1
Number of categorical factors: 1
Number of quantitative factors: 0

Analysis of Variance for RESIDUALS

Source	Sum of Squ.	Df	Mean Square	F-Ratio	P-Value
Model	2.0881	1	2.0881	141.33	0.0000
Residual	2.74813	186	0.0147749		

| Total (Corr.) | 4.83624 | 187 | | | |

Type III Sums of Squares

```
------------------------------------------------------------------------
Source          Sum of Squ.   Df     Mean Square   F-Ratio      P-Value
------------------------------------------------------------------------
fuel            2.0881        1      2.0881  141.33  0.0000
Residual        2.74813       186    0.0147749
------------------------------------------------------------------------
Total (cor.)    4.83624       187
```

Expected Mean Squares

```
------------------------------------------------------------------------
Source          EMS
------------------------------------------------------------------------
fuel            (2)+Q1
Residual        (2)
------------------------------------------------------------------------
```

F-Test Denominators

```
------------------------------------------------------------------------
Source          Df      Mean Square    Denominator
------------------------------------------------------------------------
fuel            186.00         0.0147749       (2)
------------------------------------------------------------------------
```

Variance Components

```
------------------------------------------------------------------------
Source              Estimate
------------------------------------------------------------------------
Residual            0.0147749
------------------------------------------------------------------------
```

R-Squared   = 43.1762 percent
R-Squared (adjusted for d.f.)   = 42.8707 percent
Standard Error of Est.   = 0.121552
Mean absolute error   = 0.0790616
Durbin-Watson statistic   = 1.11006 (P=0.0000)

Residual Analysis

```
Estimation    Validation
n             188
MSE           0.0147749
MAE           0.0790616
MAPE
ME            -1.02755E-16
MPE
```