AIR QUALITY EXPERT GROUP

Trends in Primary Nitrogen Dioxide in the UK

Prepared for:

Department for Environment, Food and Rural Affairs;

Scottish Executive; Welsh Assembly Government; and

Department of the Environment in Northern Ireland

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The Air Quality Expert Group (AQEG) was set-up in 2001, to provide independent scientific advice on air quality, in particular the air pollutants contained in the Air Quality Strategy (AQS) for England, Scotland, Wales and Northern Ireland and those covered by the EU Directive on ambient air quality assessment and management (the Air Quality Framework Directive). AQEG replaces the Airborne Particles Expert Group, who published their report on 'Source apportionment of airborne particulate matter in the UK' in January 1999.

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- to give advice to ministers on levels, sources and characteristics of air pollutants in the UK;
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- to analyse trends in pollutant concentrations;
- to assess current and future ambient concentrations of air pollutants in the UK; and
- to suggest potential priority areas for future research aimed at providing a better understanding of the issues that need to be addressed in setting air quality objectives.

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Executive summary

Urban concentrations of nitrogen oxides (NO_x (NO_x = NO + NO_2)) showed a downward trend since the early 1990s, associated mainly with reduced emissions from road traffic. While the nitrogen dioxide (NO_2) concentration declined, its decrease was not so marked as that of nitric oxide (NO), so that the ratio NO_2/NO_x showed an increase. Nitrogen oxides are emitted from combustion sources, such as road vehicles, mainly as NO, which reacts with ozone (O_3) in the atmosphere to form NO_2. Some NO_2 is directly emitted, but it was generally accepted that this fraction was small (approximately 5%). The partitioning in the atmosphere between NO and NO_2 changes as the concentration of NO_x falls, so that an increase in NO_2/NO_x would be expected. It was against this background that the Air Quality Expert Group (AQEG) prepared its first report, *Nitrogen Dioxide in the United Kingdom*, which included an examination of the trends in NO_x and NO_2 concentrations up to the end of 2001. The increases observed in this ratio at many roadside sites since 1998, though, were greater than expected.

This phenomenon is the subject of this further report on NO_2 in the UK, which investigates the changes taking place through an analysis of road vehicle emissions, data from monitoring sites and modelling, with the aim of identifying the causes and predicting likely future trends in NO_2 concentrations. The origins of the increasing NO_2/NO_x ratio have been analysed in some detail and various mechanisms have been invoked to explain the observed behaviour, including (i) increasing primary emissions of NO_2 from the increased market penetration of diesel cars and the retrofitting of pollution control devices, such as catalytically regenerative traps fitted to London buses, and (ii) increasing background O_3. The increasing trend in the NO_2/NO_x concentration ratio has become more marked in recent years, making it harder to meet the UK air quality objectives and EU limit values for NO_2.

The number of emissions measurements on different vehicle types is relatively limited. They indicate that the fraction of NO_x emitted as NO_2 (f-NO_2) is considerably in excess of 5%, with values in the range 20 – 70% for Euro III diesel cars. Heavy duty vehicles and buses show a smaller f-NO_2, but the fitting of diesel particulate filters to buses substantially increases the fraction of NO_2 in vehicle exhaust gases. In 2005, over 90% of Transport for London buses were operating with such traps.

Estimates of emissions to 2010 have been made both for London and for other UK urban areas, using projections of the fleet mix and estimates of emissions of both NO_x and NO_2 from the different vehicle types. These calculations show a continuing fall in NO_x emissions but almost constant, or even slightly increasing, values for NO_2 emissions over the period 2002 – 2005 and slight falls in NO_2 emissions over the period 2005 – 2010 with large uncertainty ranges.

Monitoring data in London over the period 2002 – 2006 show greater than anticipated increases in the annual mean NO_2/NO_x concentration ratio at 44 roadside and kerbside sites and at 24 out of 28 urban background sites in the London Air Quality Network. Increases were also observed at a number of Defra Automatic Urban and Rural Network (AURN) roadside and kerbside sites outside London and at a few urban background and urban centre sites. There are also, however, a significant number of sites outside the London conurbation where no clear trend was observed. It has not proved possible to rationalise these differences, because of inadequate quantitative information on vehicle emissions. Similar differences were also observed in peak hourly mean NO_2 concentrations, with some sites, particularly those within the London conurbation, showing substantial increases in the number of exceedences of 200 µg m^{-3} and others showing no clear trend. Greater increases than anticipated in the NO_2/NO_x concentration ratio have also been observed across Europe.

AQEG undertook computer modelling studies for London using five different models to try to understand the observed behaviour. The models all showed that the observed increases in the NO_2/NO_x concentration ratio could be explained by a 5% absolute increase in the percentage of NO_x emitted as NO_2, f-NO_2, (e.g. from 10% to 15%) over the period 2002 – 2005.

Increases in NO_2/NO_x ratios could be due to increased penetration of Euro-III diesel vehicles fitted with oxidation catalysts or the fitting of catalytically regenerative particle traps to buses, particularly in London. It is difficult to ascribe the increases solely to increased penetration of Euro-III diesel vehicles given the observation of increases in the NO_2/NO_x concentration ratio at only some roadside and kerbside sites outside London. It may be that London is particularly sensitive to direct NO_2 emissions, because of its size and emission density, but it is difficult, on this basis, to understand why the concentration ratio behaves so differently in, for example, Glasgow. However, it must be recognised that considerably more analysis has been carried out for the sites in London than elsewhere in the UK, in part because of the greater availability of data in London.

Inverse modelling of NO_2 concentrations for London sites has provided an important link between empirically-derived NO_2/NO_x emission ratios (or f-NO_2) and information from vehicles emissions testing. Within the limitations of the analysis, there is consistency in f-NO_2 values between the two estimates for major vehicle types. A statistical analysis of the observations at the London Marylebone Road site, and comparison with the timing of the retrofit scheme for London buses, shows that the fitting of catalytically regenerative particle traps provides a plausible explanation of the observations, although emissions from other diesel vehicles probably also contribute to the increase in f-NO_2 inferred at this and other sites.

A statistical analysis showed that concentrations of particulate matter ($PM_{2.5}$) decreased and PM_{coarse} increased at Marylebone Road around the time buses were fitted with particle filters. However, the analysis was compromised because the $PM_{2.5}$ instrument was not part of the national QA/QC procedures until 2003. As a result it is not known with confidence how $PM_{2.5}$ or PM_{coarse} concentrations have changed due to the introduction of particle filters on Transport for London buses. An analysis of the impact of the London bus retrofit scheme on PM concentrations therefore warrants further investigation.

Other possible explanations for the observed changes in NO_2/NO_x concentration ratio were also investigated, including increases in the background concentration of O_3, and were ruled out. It was not possible to eliminate direct emissions of nitrous acid (HONO), although direct NO_2 emission provides the more plausible explanation. It is recommended that direct emissions of HONO are further investigated, especially since it is plausible that this has contributed to PM concentration changes.

Projections of future concentrations of NO_2 show that the expected increases in the primary NO_2 emission percentage between 2004 and 2010 are likely to increase the extent of exceedences of an annual mean NO_2 concentration of 40 µg m^{-3} relative to projections based on no change in primary NO_2 percentage. It is unclear, however, exactly how the balance between NO_x emission reductions and increases in primary NO_2 percentages will influence the achievement of objectives and limit values in 2010 and beyond, because of the uncertainty associated with estimates of future primary NO_2 emissions. Current evidence suggests that reductions in total NO_x emissions will be sufficient to result in an overall reduction in the extent of exceedences in 2010 relative to 2004. In view of the difficulties in predicting future concentrations, AQEG recommends the compilation of a separate emissions inventory for NO_2 within the National Atmospheric Emissions Inventory, to facilitate more reliable predictions of NO_2 emissions and concentrations. Meanwhile AQEG recommends that local authorities, and any other users of the future-year adjustment factors, currently provided by Defra to adjust monitoring data, should exercise caution, as actual decreases in NO_2 concentrations at some sites may be considerably smaller than those calculated using these adjustment factors.

Chapter 1

Introduction

1. Combustion processes in air generate both nitric oxide (NO) and nitrogen dioxide (NO_2). Emissions measurements, over many years, showed that the major species emitted was NO with a small NO_2/NO_x[1] ratio of approximately 5%. Nitrogen dioxide is formed in the atmosphere by oxidation of NO, for example, by reaction with ozone (O_3). It has thus been considered as a secondary pollutant, with only a small fraction of its ambient concentration deriving from primary emissions.

2. The first report by the Air Quality Expert Group (AQEG), *Nitrogen Dioxide in the United Kingdom*, showed that, although NO_x concentrations at urban background and urban centre sites had declined substantially since the mid-1990s, there had been a much more modest fall in NO_2. This was due in part to the expected increase in partitioning between NO_2 and NO_x as NO_x concentrations fall, but the increase was greater than expected. Three possible causes of the additional increase in the observed NO_2/NO_x ratio were identified:

   - an increase in the emissions of primary NO_2 arising from increased market penetration of diesel cars
   - an increase of primary NO_2 from the use of some mobile source pollution control technologies, such as the catalytically regenerative traps which had, for example, been retro-fitted to London buses
   - an increase in the hemispheric background O_3 concentration, leading to increased oxidation of NO to NO_2.

   Increases in primary emissions of NO_2 can have a pronounced effect on NO_2 concentrations close to pollution sources, such as roads. The major areas of exceedence of the NO_2 annual mean Air Quality Strategy objective, identified in the first AQEG report, were close to roads, especially in London. Thus increases in the NO_2/NO_x ratio at roadside locations cause particular concern.

3. These changes have continued since the first report. Figure 1.1 illustrates the implications. It shows trends in annual mean NO_x and NO_2 averaged over six urban background sites (1993 – 2005) and eight roadside and kerbside sites (1998 – 2005). The NO_x levels have steadily declined, with the decline being somewhat steeper at the roadside sites, as expected from the control of vehicle emissions. The NO_2 concentrations at urban background sites also decline over this period, but at roadside sites the expected decline is not evident.

4. This pattern is consistent with significant increases in the NO_2/NO_x ratio observed at several roadside and kerbside monitoring sites and also, in London, at urban background sites. The first AQEG report showed that exceedences of the annual mean NO_2 concentration of 40 $\mu g\ m^{-3}$ were likely to remain in 2010, especially in London, despite the emissions reductions policies. It also commented that these projections might be optimistic, because of the trend of an increasing proportion of NO_x being emitted as NO_2.

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[1] Nitrogen oxides (NO_x) = NO + NO_2

5. Nitrogen dioxide exceedences have been the primary cause of declarations of Air Quality Management Areas, with 174 declarations for NO_2 and 71 for particulate matter (PM_{10}). In the light of these problems, the projected difficulties in future years in meeting the Air Quality Strategy objective for NO_2, and the observations of increasing NO_2/NO_x concentration ratios, Defra asked AQEG to:

   - Examine information on NO_x emissions from road vehicles, with particular reference to (a) the fraction of NO_x emitted as NO_2, (b) the effects of different pollution abatement measures on primary NO_2 and (c) future changes in emissions ratios.
   - Analyse data available from NO_2 monitoring networks to determine the extent of the increasing trend in the NO_2/NO_x ratio observed at some sites. The primary target should be annual mean measurements over the period 2002 – 2005, but the hourly mean should also be examined.
   - Conduct modelling studies to determine whether the observed increase in the NO_2/NO_x ratio could be ascribed to an increase in primary NO_2 and, if so, what the primary source of this increase is. The AQEG was also asked to examine other possible causes of the increased concentration ratio, such as increasing background O_3.

6. These issues are addressed in Chapters 2-4. This report should be read in conjunction with the AQEG report, *Nitrogen Dioxide in the United Kingdom*[2], which contains the necessary background and historical information. Note that throughout this report, the concentration of NO_x is given in units of $\mu g\ m^{-3}$ and is calculated as if all the NO had been oxidised to NO_2. Strictly the unit should be written as $\mu g\ m^{-3}$ *as* NO_2, but this is shortened to $\mu g\ m^{-3}$. A full explanation of this convention is given in Box 1.1 of the AQEG report, *Nitrogen Dioxide in the United Kingdom*.

7. In this report a distinction is drawn between the fraction of NO_x emitted from an emissions sources as NO_2, termed **f-NO_2** and the ratio of NO_2 to NO_x in ambient air, termed **NO_2/NO_x ratio**.

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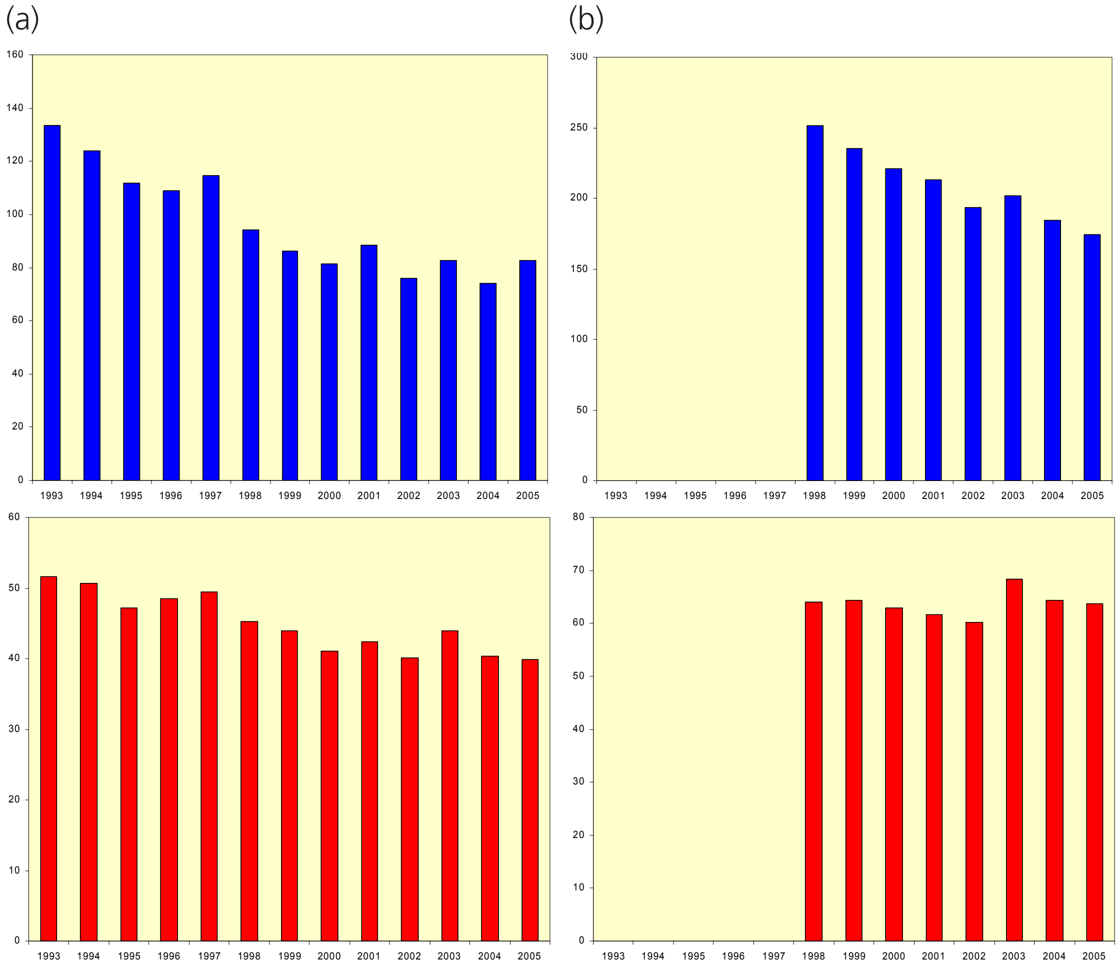
[2] This report can found at http://www.defra.gov.uk/environment/airquality/publications/nitrogen-dioxide/index.htm

Figure 1.1: Trends in annual mean nitrogen oxides (blue) and nitrogen dioxide (red) concentrations in µg m^{-3} at (a) six urban background sites and (b) eight roadside/kerbside sites.



Chapter 2

2 Primary nitrogen dioxide exhaust emissions

2.1 What is the evidence to support the use of an f-NO_2 of 5% for road vehicle exhaust emissions?

8. Since the early 1970s, NO_x exhaust emissions have generally declined, and the proportion of primary NO_2 in vehicle exhaust (f-NO_2) has been estimated to be between 0% and 10% by volume. A value of 5% has been widely accepted and applied to emission inventories and dispersion modelling approaches incorporating first principal chemistry schemes (McCrae *et al.*, 2002). This 5% value was derived from relatively few tests on vehicles without complex exhaust after-treatment systems, and it is questionable if it was ever robust, or indeed if it is applicable to modern vehicles.

9. These measurements were recorded on diluted exhaust using a chemiluminescence detector (CLD), and were expressed in units of mass.

10. Evidence of an f-NO_2 of more than 5% has been available since the early 1990s, particularly in relation to the primary NO_2 emissions associated with the diesel engines, and more recently as a consequence of the use of a range of exhaust after-treatment systems. The gradual introduction of tighter emissions limits for new vehicles has generally resulted in a reduction in total NO_x emissions per vehicle. However, reductions in average NO_x emissions, whilst complying with the various Euro-standards, have often been limited due to priority afforded to seeking reductions in particulate emissions. There has thus been a trade-off between the improvements in NO_x and PM emissions. Evidence on the impact of tighter NO_x exhaust emission limits on the primary NO_2 component remains limited. It is for this reason that there have been few proposals to change the f-NO_2 used in emission inventories and air pollution modelling.

11. The fundamentals of NO_x and primary NO_2 formation in combustion were discussed in AQEG's first report "*Nitrogen Dioxide in the United Kingdom*". An overview is provided again in a technical annex (Annex 1) to this report that also discusses the different types of exhaust after-treatment technologies fitted to diesel vehicles that can potentially influence f-NO_2.

2.2 What are the likely proportions of primary nitrogen dioxide from road vehicles, and how are these changing with new powertrain and exhaust after-treatment technologies?

12. The proportion of primary NO_2 in vehicle exhaust has been investigated during the last ten years, but robust evidence has remained limited and uncertain. However, it is evident that primary NO_2 emissions are higher from diesel vehicles, whose penetration within the UK vehicle fleet is continuing to increase. In addition, f-NO_2 has been shown to be higher from various exhaust after-treatment technologies, entering the market after 1992 (see Annex 1 for some examples). Furthermore, the introduction of leaner burn petrol engine technologies such as the gasoline direct injection (GDI), are associated with increased NO_x formation. All of the evidence, therefore, suggests that the 5% primary NO_2 factor is a significant underestimation.

13. The measurement of regulated pollutants in vehicle exhaust is defined and controlled under Type Approval legislation. However, the measurement of unregulated pollutants such as NO_2 is not currently covered by the regulations (see section 2.9). Therefore, existing measurement campaigns have failed to follow consistent sampling and measurement protocols (Latham *et al.*, 2001). This issue introduces considerable uncertainty into the derivation of primary NO_2 emission factors and ratios from existing measurements.

14. Due in part to the measurement of relatively high roadside NO_2 concentrations, which could not be fully explained by the availability of oxidants, the Department for Transport (DfT) TRAMAQ programme, devised in 1997, incorporated an investigation of primary NO_2 emissions. The TRAMAQ project attempted to derive emission factors for primary NO_2, but also aimed to investigate the influence of the measurement protocol and sampling regime. The first AQEG report on NO_2 (AQEG, 2004) provided a summary of this Transport Research Laboratory (TRL) research project. The evaluation included tests on 18 vehicles (nine petrol cars, three diesel vans, three heavy goods vehicles (HGVs) and three buses) covering pre-Euro I, Euro I and Euro II legislation classes.

15. Tests were conducted over a range of real-world driving cycles[3], using two measurement techniques (CLD and Fourier Transform Infra-Red (FTIR)) and various sampling methods (raw exhaust, diluted exhaust, unheated and heated sampling lines). The conclusions of the study were as follows:

    - There were statistically significant relationships between f-NO_2 and the fuel type, the emission standard and the cycle speed, but not the test temperature or sampling method.
    - Sampling raw rather than dilute exhaust resulted in lower measured primary NO_2. This has an implication for the way in which measurements are undertaken, and the necessity for a consistent approach.

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[3] A description of the most common real world and Type Approval drive cycles may be found in Barlow *et al.* (2006).

- Measured f-NO_2 ranged from 8% to 40%.
- Absolute NO_2 emissions from diesel vehicles were higher than those from petrol vehicles.
- For light-duty petrol vehicles, NO_2 emissions from pre-Euro I vehicles were significantly higher than those from Euro I vehicles which were, in turn, higher than those from Euro II vehicles. The difference between pre-Euro I and Euro I was highly significant, whilst that between Euro I and Euro II was less significant.
- Exhaust emission regulations have required manufacturers to gradually reduce NO_x emissions from heavy-duty vehicles (HDVs) as well as light-duty vehicles (LDVs). 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 results for HGVs and buses did not show this. In fact, for the raw sample, and over most cycles, NO_2 emissions generally increased for vehicles conforming to newer emission standards.
- Higher average speeds generally produce higher exhaust temperatures and hence higher NO_x emissions, therefore a positive correlation between speed and NO_2 emissions might be expected if f–NO_2 is unaffected by speed. The examination of the independent effect of speed on NO_2 confirmed this to be the case. Nevertheless, it should be noted that the scatter in results was very high. This is expected, since average cycle speed is a less robust determinant of emissions for post-Euro I vehicles. However NO_x emissions still appeared to increase more significantly than NO_2 emissions, at higher speeds. Therefore the f-NO_2 decreases with increasing vehicle speed. Whilst this speed dependency was evident in this TRAMAQ study, subsequent measurement programmes have not always supported this observation.

2.3 What do the results from the most recent measurement programmes tell us about the proportion of primary nitrogen dioxide from modern light-duty vehicles?

16. The results from independent test programmes remain uncertain, due to the absence of agreed measurement protocols and vehicle sample selection methods. Therefore, primary NO_2 emission data remain uncertain.

17. Since the completion of the TRAMAQ primary NO_2 study, several other measurement campaigns have been undertaken in the UK. The majority of these have been commissioned by the Department for Transport (DfT) (involving measurement and analysis programmes undertaken by the organisations TRL, AEA-Technology, Perkins, Ricardo and Millbrook), but other notable studies have been commissioned by fleet operators such as Transport for London (TfL) (again undertaken by Millbrook). The following sections provide a summary of some of the results from a selection of these measurement campaigns.

2.3.1 Light-duty vehicle emissions: petrol cars

18. Ricardo, as part of a project for DfT, measured emissions from six Euro III petrol cars (Ricardo, 2003). The f-NO_2 was found to be around 5%, with a range of between 2% and 10%. This was similar to estimates obtained in the past, despite changes in technology. Euro III petrol cars are dominated by vehicles running very close to stoichiometric, and are routinely fitted with a three-way catalyst. These vehicles produce moderate amounts of 'engine-out' NO_x, with a low percentage of primary NO_2, which is itself reduced by the catalyst. It is thought that the catalyst, whilst reducing NO_x, has led to little change in f-NO_2.

19. Some manufacturers are trying to improve fuel economy by using lean-burn petrol technology (e.g. GDI). The consequence of the higher air:fuel ratio is that there is more oxygen in the burnt mixture, and consequently exhaust NO_x levels can increase. These engines are running at similar cylinder temperatures and pressures to non-GDI vehicles, and consequently the engine out f-NO_2 shows little change, although in absolute terms NO_2 increases.

20. In order to ensure that GDI vehicles conform to low NO_x standards, remedial technology has to be fitted. This can comprise a NO_x sensor, a NO_x storage/reduction catalyst and appropriate controlling software. The use of this after-treatment strategy is not thought to increase the primary NO_2 emission significantly.

2.3.2 Light-duty vehicle emissions: diesel cars

2.3.2.1 Department for Transport funded programmes

21. Compared with the relatively limited changes in the fundamental technologies used for petrol cars, significant developments have taken place over the last decade in small diesel engine design and emission control. These include the following:

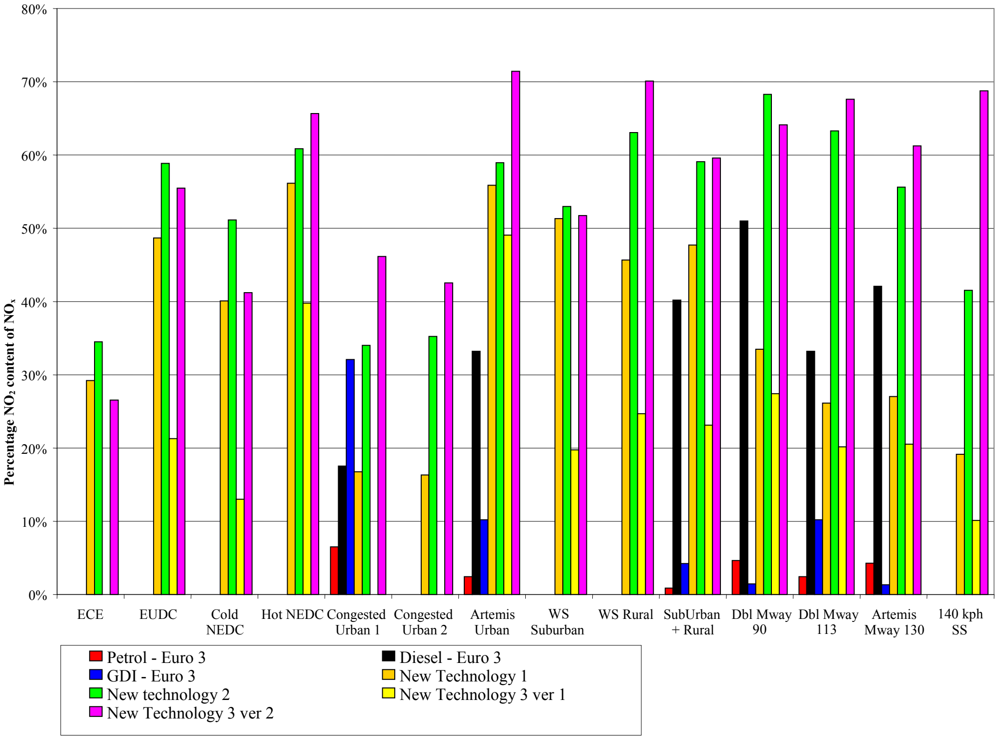
    - Pressures for injection systems have increased very markedly.
    - Injection timing is now dominated by electronically operated solenoids rather than mechanically operated ones. The former can inject the fuel in several stages for each combustion cycle.
    - Exhaust gas recirculation (EGR) is now common, primarily introduced as a control for NO_x. Evidence suggests that EGR can increase hydrocarbons and carbon monoxide (CO) emissions, and thus with introduction of tighter Euro-III CO limits the use of oxidation catalysts has become widespread.

22. All these factors potentially affect NO_x and the f-NO_2. However, the general trend has been for overall lower engine-out NO_x and primary NO_2, as combustion temperatures and efficiencies have increased. However, pressure on particulate emissions particularly (and to a lesser extent hydrocarbon and CO emissions) has led to the common practice of installing oxidation catalysts, to oxidise exhaust constituents (which contain significant amounts of unused oxygen). Oxidation catalyst can increase the proportion of primary NO_2 as discussed in Annex 1 of this report.

23. Data for Euro III diesel passenger cars can be taken from the analysis (by AEA-Technology) of data measured by Ricardo (2003)[4]. In a more recent DfT-funded study assessing the effect of emerging technologies on unregulated emissions, four diesel vehicles, fitted with three different abatement technologies, were studied. It is important to note that as these tests were carried out on a small number of vehicles, they may not be representative of the national fleet. The study showed that, for two of the four vehicles, the f-NO_2 was in the 50% to 70% range, and in the 20% to 50% range for the other two vehicles. The results from this study, together with data for petrol and diesel Euro III car from the Ricardo study, are shown in Figure 2.1.

24. The red bars in Figure 2.1 represent the proportion of NO_X that is emitted as NO_2 from Euro III petrol vehicles. The figures confirm that recent technology has had little impact on the f-NO_2 previously observed for pre-Euro III cars. Similarly, the black columns show the Ricardo data for the Euro III diesels cars without further emissions abatement fitted. Whilst the f-NO_2 depends on the precise driving cycle, it is typically 30 to 40%. The blue columns relate to Ricardo data for a GDI. However, a new data set for a more recently manufactured GDI gave the f-NO_2 as 0%. Together these primary NO_2 emissions from petrol GDI appear to bracket the other petrol vehicles, one vehicle having a higher and the other a lower f-NO_2.

Figure 2.1: The f-NO_2 of some emerging diesel technologies together with data for Euro III petrol, diesel and gasoline direct injection technology for a range of drive cycles.



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[4] This was a parallel study on diesel cars to the Euro III petrol car study discussed in section 2.3.1.

25. The f-NO_2 values for the other four diesel vehicles tested, i.e. those fitted with differing emerging emissions abatement technologies, were more than 50% in some cases.

2.3.2.2 Transport for London funded programmes

26. All new vehicle types entering the TfL bus fleet are subjected to emission tests to confirm compliance with emission legislation, and to validate the effectiveness of any retrofit exhaust after-treatment equipment. In addition to the management of the London bus fleet, TfL also operates a number of light commercial vehicles. Emission tests have been undertaken for a number of vehicle types on a chassis dynamometer, and involve measurements over the New European Driving Cycle (NEDC) and the Forschungsinstitut Geräusche und Erschütterungen (FIGE) cycles. Table 2.1 provides a summary of emission tests on a selection of vehicles from this fleet, but also includes measurements on a typical London black cab. The measurements were undertaken as part of the Low Emission Zone (LEZ) feasibility study, and are reported here only for the FIGE cycle, with the results further sub-divided into various operational modes, including urban, suburban and motorway.

27. Robust analysis of these data is limited by the small sample sizes. This is highlighted by the tests on the two London black cabs. Tests on the earlier TX1 exhibited increasing NO_x emissions and fuel consumption with higher average cycle speeds, with little speed related impact on primary NO_2 emissions. However, tests on the later TX2 model showed similar emissions of NO_x under urban and motorway conditions, yet a three-fold increase in the primary NO_2 component. Primary NO_2 emissions from the Euro-II taxis ranged from 8% to 20%. Primary NO_2 emissions from the light good vehicles (LGVs) ranged from 20 to 38%.

2.4 Does vehicle speed influence the fraction of primary nitrogen dioxide?

28. An earlier study by TRL investigated the primary NO_2 and NO_x emissions from a range of pre-Euro III vehicles at different drive cycles and reported some simple speed-related emission functions for both NO_x and NO_2 that allows the speed-dependence of f-NO_2 to be seen for some vehicle types (Latham *et al.*, 2001). From these functions, one can derive plots showing the variation of f-NO_2 with average speed (Figure 2.2) for pre-Euro III diesel LGVs, HGVs and buses. There are inherent uncertainties in the absolute f-NO_2 values and comparisons between the different plots should be made with caution due to the limited number of vehicles tested, but there is a consistent trend tending to show a decrease in f-NO_2 with increasing average speed over the range 40-90 kph. Given these vehicles are with older technology, this trend is entirely consistent with the fundamental behaviour of NO_2 formation within diesel engines, discussed in Annex 1. The decrease in f-NO_2 with decreasing speed shown at low speeds cannot be explained, but might be due to complications arising from gear shift.

29. Some independent support for a decrease in f-NO_2 with increased speed for older vehicles comes from the study of Jenkin (2004b). In that study, the interpretation of observed local oxidant contributions at Marylebone Road in 1998 and 1999, in conjunction with the vehicle flow and NO_x emission estimates of Carslaw and Beevers (2004), required a speed dependence to be assigned to f-NO_2 for diesel fuelled vehicles, such that f-$NO_2 = 0.996\ v^{-0.6}$, where v is the mean vehicle speed over the range 30 to 60 km hr^{-1}. This is consistent with NO_2 accounting for 12.9% of NO_x emissions from diesel vehicles travelling at a mean speed of 30 km hr^{-1}, decreasing to 8.5% at 60 km hr^{-1} (Figure 2.2).

30. In contrast to the conclusion reached in the earlier TRL TRAMAQ study, those data from the more recent Millbrook and Ricardo studies exhibit limited speed dependency (Figure 2.3). In contrast to the earlier analysis, which was based upon Pre-Euro I, Euro I and Euro II vehicles, these more recent data indicate that speed has little effect on emissions from more recent Euro III and Euro IV legislation classes.

Figure 2.2: The trends in f-NO_2 with average speed for pre-Euro III diesel vehicles calculated from the speed relationships in Latham *et al.* (2001).

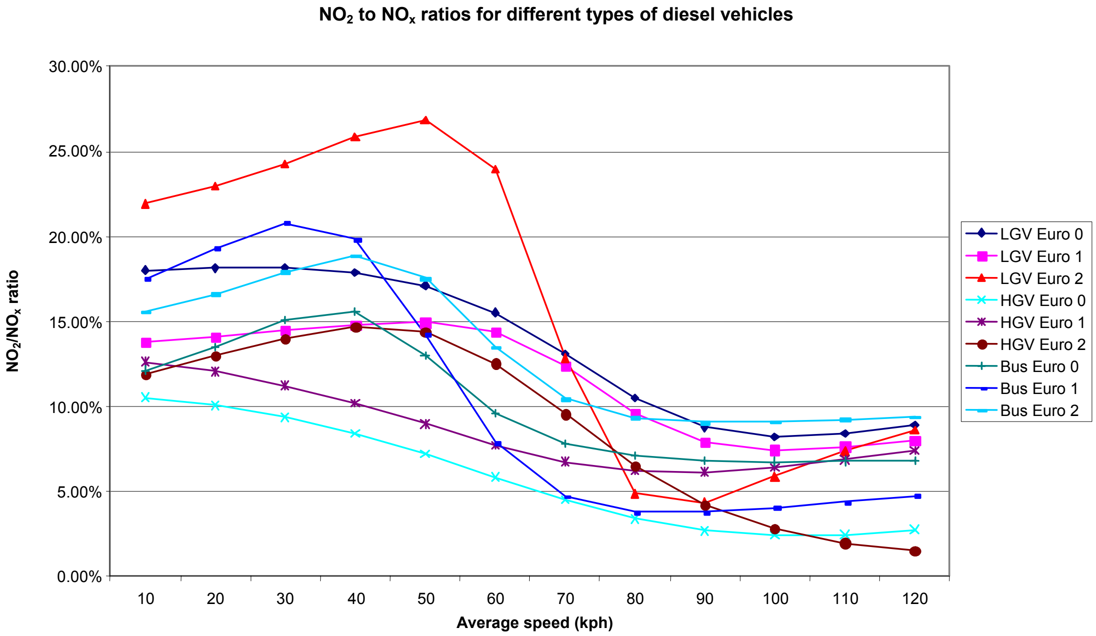
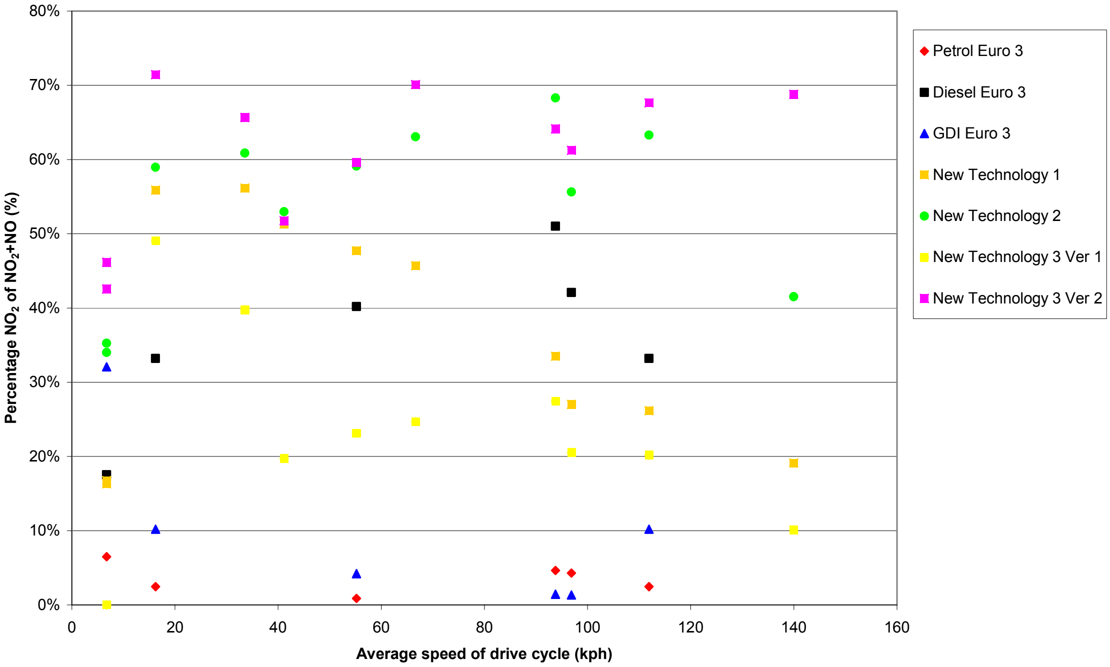


Figure 2.3: The f-NO_2 from Figure 2.1 plotted against mean drive cycle speed.



31. Figure 2.3 shows the data from Figure 2.1 plotted against the mean cycle speed. For the two vehicles with the highest f-NO_2 (the purple and bright green columns of Figure 2.1) it is seen in Figure 2.3 that the ratio shows little dependency on speed.

32. The TfL LGV measurements (Table 2.1) show a tendency for the highest NO_x emission and fuel consumption to be associated with the highest cycle speeds. However, corresponding measurements of primary NO_2 show little relationship between cycle speed and the f-NO_2.

33. In a more recent DfT sponsored research programme on emissions from Euro III light duty diesel vehicles, test data from Ricardo showed a similar lack of strong dependence of f-NO_2 on speed, and if anything tended to show a trend of increasing f-NO_2 with increasing speed. This might be due to competition between opposite trends in engine-out NO_2 emissions and the effects of after-treatment such as oxidation catalysts on these newer vehicles complicating the speed dependence of f-NO_2.

Table 2.1: Light commercial vehicles and taxis tested over the Forschungsinstitut Geräusche und Erschütterungen (FIGE) cycle, and operated using ultra low sulphur diesel (Transport for London, 2006).

Make and model	Type	Engine type, after-treatment system and test inertia	Euro class	NO_x (g/km)	CO_2 (g/km)	FTIR tailpipe primary NO_2 (g/km)	FTIR tailpipe f-NO_2 (%)
Lti, TXI	Taxi	Nissan IDI engine, standard, 1930 kg	Euro II	0.968 (urban) 1.327 (suburban) 1.693 (motorway) 1.471 (total)	193.4 (urban) 185.0 (suburban) 230.0 (motorway) 209.9 (total)	0.074 (urban) 0.098 (suburban) 0.096 (motorway) 0.094 (total)	7.5 (urban) 8.5 (suburban) 7.0 (motorway) 7.6 (total)
Lti, TX2	Taxi	Nissan IDI, Standard (includes oxicat) 1930 kg	Euro II	1.215 (urban) 1.072 (suburban) 1.246 (motorway) 1.201 (total)	179.5 (urban) 154.0 (suburban) 181.8 (motorway) 173.5 (total)	0.092 (urban) 0.217 (suburban) 0.307 (motorway) 0.244 (total)	6.2 (urban) 20.5 (suburban) 24.1 (motorway) 20.0 (total)
Mercedes-Benz, Sprinter	LGV	Standard, 3590 kg	Euro III	1.939 (urban) 1.446 (suburban) 1.513 (motorway) 1.540 (total)	286.5 (urban) 252.8 (suburban) 255.1 (motorway) 257.8 (total)	0.403 (urban) 0.262 (suburban) 0.186 (motorway) 0.244 (total)	29.1 (urban) 25.2 (suburban) 18.4 (motorway) 22.6 (total)
Mercedes-Benz, Sprinter	LGV	Standard, 4600 kg	Euro III	2.127 (urban) 1.523 (suburban) 1.504 (motorway) 1.588 (total)	304.5 (urban) 260.1 (suburban) 254.4 (motorway) 262.2 (total)	0.380 (urban) 0.238 (suburban) 0.176 (motorway) 0.227 (total)	26.2 (urban) 23.3 (suburban) 18.7 (motorway) 21.7 (total)
Ford, Transit SWB	LGV	Standard (includes oxicat), 2150 kg	Euro III	0.392 (urban) 0.367 (suburban) 0.466 (motorway) 0.424 (total)	165.4 (urban) 149.3 (suburban) 185.8 (motorway) 171.2 (total)	0.114 (urban) 0.112 (suburban) 0.090 (motorway) 0.102 (total)	30.0 (urban) 32.8 (suburban) 20.3 (motorway) 25.7 (total)
Ford, Transit Connect	LGV	Standard (includes oxicat), 1810 kg	Euro III	0.509 (urban) 0.499 (suburban) 0.618 (motorway) 0.572 (total)	137.9 (urban) 125.8 (suburban) 157.4 (motorway) 146.1 (total)	0.157 (urban) 0.177 (suburban) 0.244 (motorway) 0.206 (total)	31.1 (urban) 36.3 (suburban) 40.1 (motorway) 37.7 (total)

34. With the currently available evidence, the following qualitative conclusions can best be drawn on the speed-dependence of f-NO_2:

• Petrol light duty vehicles	No dependence on speed
• Pre-Euro III diesel vehicles	Decreases in f-NO_2 with increasing speed
• Euro III, IV, V diesel vehicles	Slight increase in f-NO_2 with increasing speed
• Diesel vehicle with oxidation catalyst	Slight increase in f-NO_2 with increasing speed
• Diesel vehicle with diesel particulate filter	Speed-dependence unknown

35. These conclusions, however, are based on limited measurements and do require further verification.

2.5 Do the UK light duty vehicles primary nitrogen dioxide estimates agree with those from international studies?

36. International measurement campaigns generally support the measurements undertaken in the UK, and confirm that primary NO_2 emissions are associated with the leaner fuel combustion technologies. In addition, they support the hypothesis of an increasing f-NO_2 from Euro I to Euro IV LDVs, and also generally confirm a corresponding reduction in NO_x emissions. The results from some of these other test programmes are summarised below.

2.5.1 Emission measurements from Laboratory of Applied Thermodynamics, Aristotle University, Thessaloniki

37. A campaign of primary NO_2 measurements was undertaken at the Laboratory of Applied Thermodynamics (LAT) – (Geivanidis and Samaras, 2006). This included tests on four vehicles (Table 2.2) using a fast-response CLD (<4ms in NO mode and <8ms in NO_x mode), measuring raw exhaust. Measurements were undertaken over various test cycles, including the cold urban drive cycle (UDC), the extra urban drive cycle (EUDC), the hot UDC, and the ARTEMIS urban, road and motorway cycles. In addition, steady-state tests were performed on three vehicles and one engine using a fast-response CLD (separate channels for NO and NO_x) and a conventional CLD (switching between NO and NO_x modes).

Table 2.2: Vehicles and tests undertaken by the Laboratory of Applied Thermodynamics, Aristotle University, Thessaloniki.

Vehicle type	Test type
Honda Accord 2.2 i-CTDi (diesel, Euro IV, manufactured year: 2005)	(i) pre catalyst + main oxidation catalyst (OEM configuration) (ii) pre catalyst only (iii) pre-catalyst + catalyzed trap (SiC, 300cpsi, V=4l)
VW Golf Tdi (diesel, Euro II, manufactured year: 1996	(i) oxidation catalyst (OEM configuration) (ii) no after treatment
Toyota Corolla TS 1.8 (petrol, Euro III, manufactured year: 2003)	(i) pre-catalyst + main 3 way catalyst (OEM configuration)
Renault Laguna 1.9 dCi (diesel, Euro III, manufactured year: 2001)	(i) pre catalyst + main oxidation catalyst (OEM configuration)

38. Figures 2.4 and 2.5 show the results from the LAT measurement programme, for transient cycles and steady-state conditions, respectively.

39. For the Honda Accord, the removal of the main catalyst resulted in a substantial decrease of the f-NO_2. Similar results were achieved with the removal of the platinum-coated diesel particulate filter (DPF). For the Renault Laguna, the f-NO_2 was found in the range 5% to approximately 30%. For the VW Golf a 5% to 25% f-NO_2 was measured for the original configuration of the aftertreatment system (similar to Laguna). The f-NO_2 was substantially increased after the removal of the oxidation catalyst (30 to 60%). Finally, in the case of the petrol fuelled Toyota Corolla, an unexpectedly high NO_2 fraction was observed.

Figure 2.4: f-NO_2 from transient tests, undertaken by Laboratory of Applied Thermodynamics, Aristotle University, Thessaloniki. For each test the average temperature recorded at the exhaust outlet is provided (Geivanidis and Samaras, 2006).

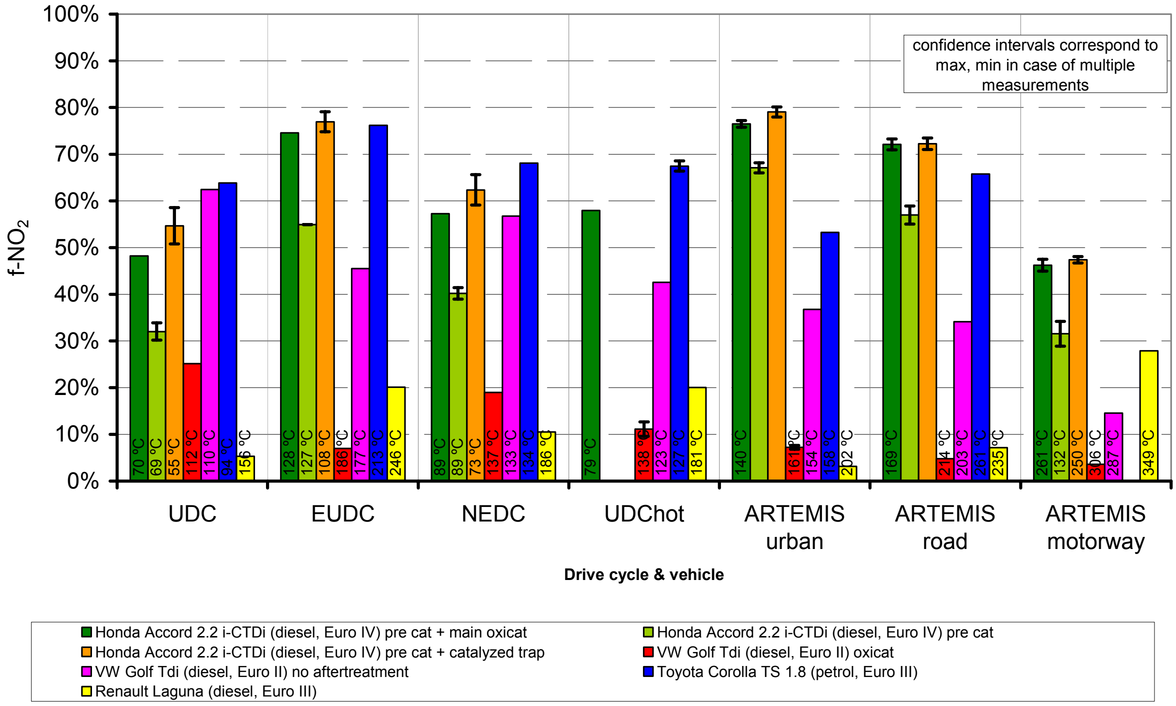
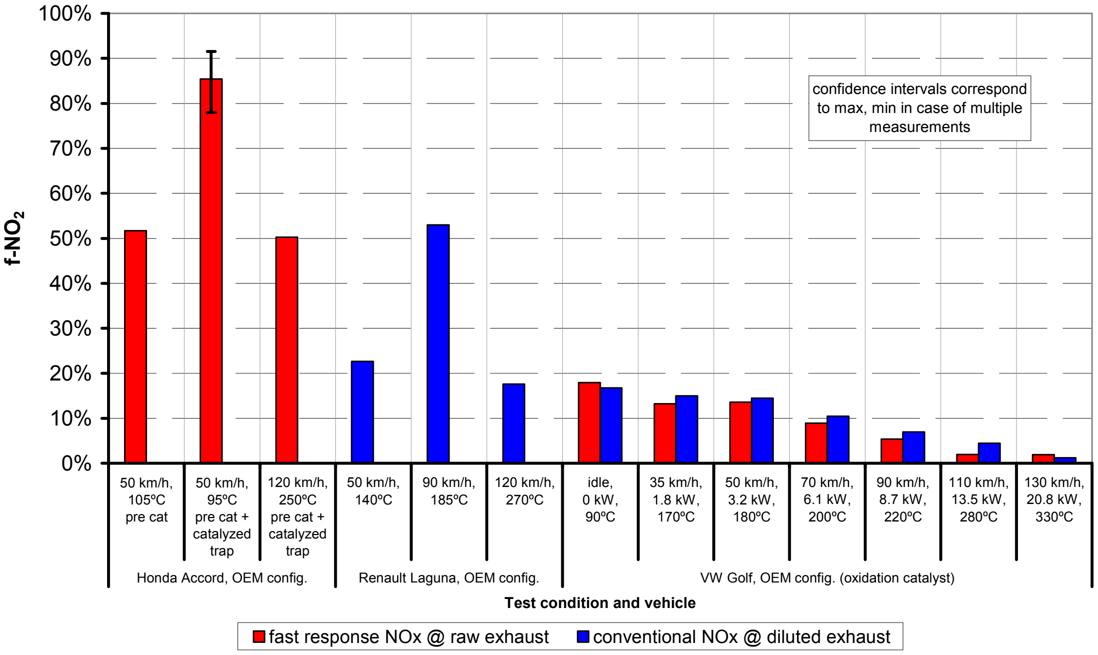


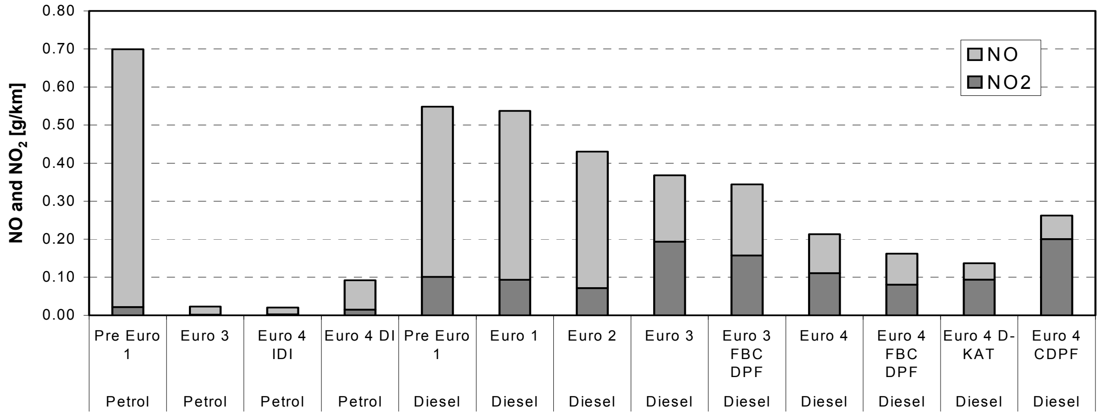
Figure 2.5: f-NO_2 from steady-state tests, undertaken by Laboratory of Applied Thermodynamics, Aristotle University, Thessaloniki. For each test the average temperature recorded at the exhaust outlet is provided (Geivanidis and Samaras, 2006).



2.5.2 Emission measurements from TNO and EMPA

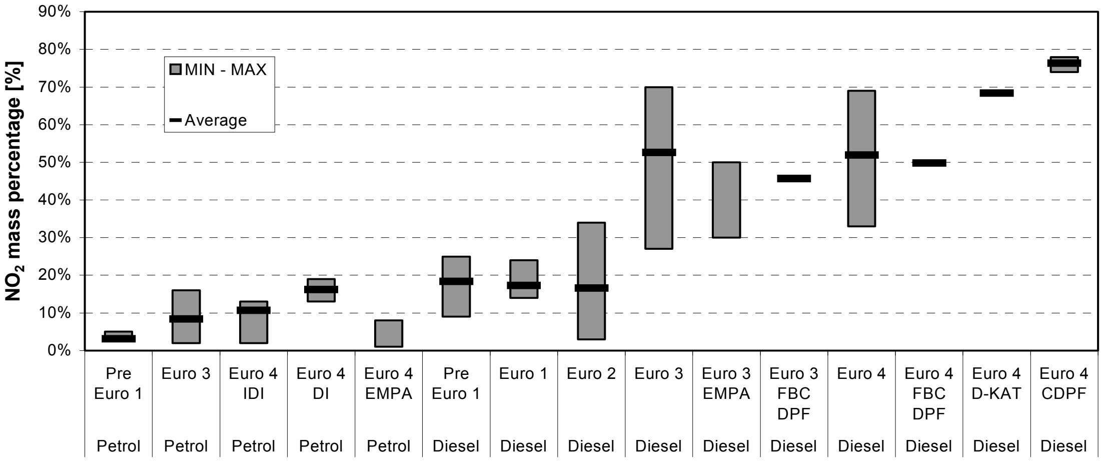
40. Sixty-nine passenger cars were tested during 2005 and 2006 by TNO and EMPA (Gense *et al.*, 2006). Measurements of primary NO_2 were undertaken using a CLD, sampling from the raw exhaust using heated sampling lines, and real-world driving cycles. Figure 2.6 demonstrates the significant reductions in total NO_x for the most recent emission legislative classes.

Figure 2.6: A summary of nitrogen dioxide and nitric oxide emissions measured by TNO and EMPA (Gense *et al.*, 2006).



41. Figure 2.7 provides a summary of the primary NO_2 fraction. Both the NO_2 emission and the NO_2 fraction are higher for diesel cars than for petrol cars. For petrol cars, the f-NO_2 ranges from a few percent to about 20%, while for diesel cars the fraction ranges from about 5% to almost 80%. For diesel cars, there is a large step in the f-NO_2 from Euro II to Euro III. While the average fraction of Pre-Euro I to Euro II does not vary much and is about 15% to 20%, the Euro III diesel cars have a considerably higher NO_2 fraction, of the order of 50%. Even though the total NO_x emission gradually decreases from Pre-Euro I to Euro IV, the absolute NO_2 emission also increases sharply from Euro II to Euro III and remains high for Euro IV. A summary of the international experience on light-duty primary NO_2 emissions is provided by Hoermandinger (2007).

Figure 2.7: f-NO_2, as recorded by TNO and EMPA (Gense *et al.*, 2006).



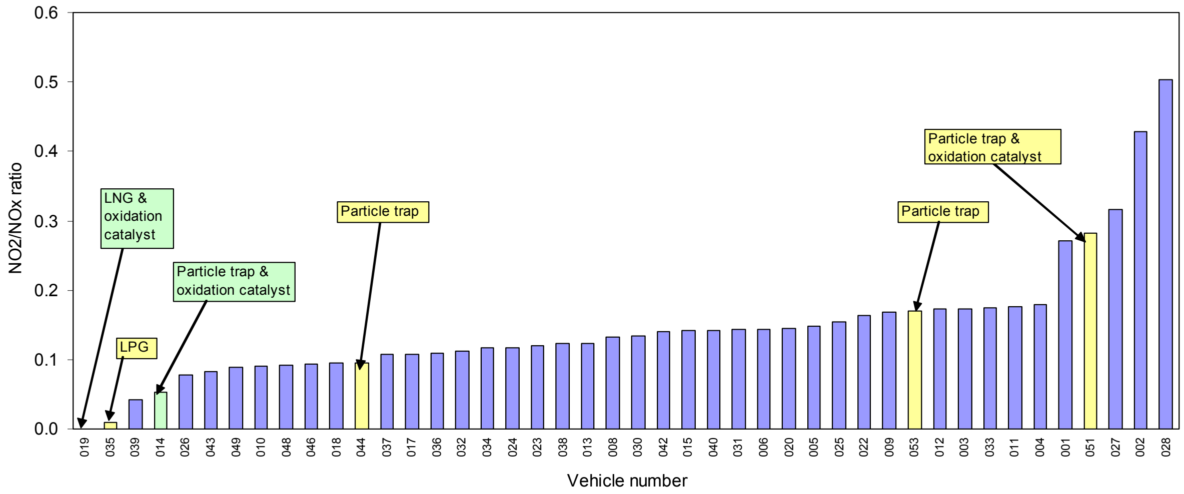
2.6 What do the results from the most recent measurement programmes tell us about the fraction of primary nitrogen dioxide from modern heavy-duty vehicles?

42. Heavy-duty diesel technology tends to lag behind diesel passenger car technology, with an early emphasis on exhaust after-treatment for emission control. The early practice of combining charge cooling and turbocharging allowed higher power for a given smoke level, or less smoke for a given power, therefore possibly reducing particulate mass emissions. Charge cooling reduces NO_x emissions due to the lower charge temperatures. Turbocharging produces a greater charge density, a leaner mixture, and thus gas temperatures are lower, reducing the tendency for dissociation and oxidation of nitrogen to occur in the combustion reaction. The higher efficiency achieved via turbocharging should also result in lower fuel consumption. With respect to variable geometry turbocharging, additional charge air can be programmed to eliminate the momentary smoke puff that usually occurs during sudden accelerations. Variable geometry turbocharging also allows the pressure between the exhaust and intake manifolds to be varied achieving more exhaust gas recirculation, thus lowering NO_x emissions. It is difficult to isolate the effect of turbocharging on emissions, since this will enable other changes in the fuel injection or valve timing which allows a better trade off between the various emissions and power.

43. The high injection pressure, electronically operated unit injectors and computer controlled fuelling system which became available for most Euro III HGVs, appeared earlier in passenger cars. Hence, observations on primary NO_2 from HDVs are not so robust. Significant differences do exist between light- and heavy-duty diesel emission controls, most notably the infrequent use of oxidation catalysts on HDVs.

44. The principal recent source of HDV primary NO_2 data was the DfT-funded TRAMAQ project, undertaken by TRL and Millbrook (Latham *et al.*, 2004). Whilst this project was primarily charged with the investigation of the impact of traffic management on exhaust emissions, it included a series of measurements for primary NO_2. Figure 2.8 summarises the f-NO_2 results from this programme of measurements on 50 vehicles. The f-NO_2 varied between 0% and 50%, though for 70% of vehicles the fraction was between around 8% and 18% (the median value was 13%). Examples of vehicles with specific known after-treatment are highlighted. The two highest f-NO_2 were recorded from vehicles 002 and 028, which were a 2-axle rigid Euro II truck and a single decker Euro III bus, respectively. Neither of these diesel vehicles were fitted with a DPF. Full details of vehicle specifications used within this study are available in Latham *et al.* (2004).

Figure 2.8: The f-NO_2 values derived from the Transport Research Laboratory TRAMAQ study on 50 heavy-duty vehicles (Latham *et al.*, 2004).



45. The fitting of a particulate trap may have implications for NO_2 emissions. For catalyst-based DPFs the catalytic action is achieved by oxidising a portion of the NO in the exhaust to NO_2, which is then used to aid oxidation of the soot collected in the filter (further details on effects of catalyst based DPF systems on primary NO_2 are given in the Technical Annex 1 to this report). The results in the TRAMAQ final report are not conclusive. Two of the buses fitted with particle traps (vehicles 51 and 53) were amongst the highest NO_2 emitters, although the third bus fitted with a trap (vehicle 44) was one of the lowest emitters. The f-NO_2 of these three vehicles followed the NO_2 emissions, i.e. was above average for two vehicles and below average for the third.

2.6.1 London transport emission measurements

46. The London TfL bus fleet comprised some 7,952 vehicles, as of March 2006, of which 6,892 were in operation at any one time in order to fulfill network requirements. During 2005/06, TfL buses travelled some 454 million kilometres. Prior to the introduction of any new vehicle type into this fleet, TfL commissions chassis dynamometer tests to ensure that exhaust emissions of these vehicles are well within the requirements of the emission legislation (TfL, 2006). The emission tests are conducted over a dedicated real-world bus cycle, the Millbrook London transport bus (MLTB) cycle. The standard test programme involves three repeated hot-start tests. Prior to July 2005, the majority of emission tests commissioned by TfL were based on the measurement of regulated emissions, but recently TfL has enhanced the test programme such that it now also includes NO_x speciation as well as particulate sizing. Table 2.3 provides some results from this programme, showing emissions of both regulated pollutants and primary NO_2 for Euro III and Euro IV buses. The f-NO_2 was derived using the mass-based NO_2 measurements from the CLD, and the mass based NO_x derived from the analysis of the emission test bag samples. Again, the sample sizes are relatively small, but it is evident that the f-NO_2 for Euro III buses is of the order of 38%, whilst the proportion for Euro IV buses is significantly lower (less than 10%). All vehicles in Table 2.3 were operated on Ultra low sulphur diesel (ULSD), but only the Euro III vehicles were equipped with particulate traps. The Euro IV vehicles were only equipped with selective catalytic reduction (SCR), as post-SCR exhaust temperatures are thought not to be sufficent for the optimal operation of the Eminox particulate traps (further details on SCR systems are given in the Technical Annex 1 to this report). Finally, data from Johnson Matthey would suggest that the performance of the Euro III with the combined retrofit SCR and particulate trap relates to a relatively early development SCR calibration. Subsequent improvements in the retrofit SCR systems can now give even lower NO_x (3.7 g km^{-1}) and NO_2 (1.9 g km^{-1}) emissions for this vehicle. In addition, these data illustrate the effectiveness of particulate traps and SCR technologies, achieving lower PM emissions from Euro III buses with particulate traps than Euro IV buses without filters, and lower PM and NO_x from SCR equipped buses compared to those Euro IV buses tested. Again these conclusions must be treated with caution, given the relatively small sample size.

Table 2.3: An extract from the Transport for London exhaust emission database, showing the f-NO_2, based on volumetric chemiluminescence data (Transport for London, 2007).

Bus type	Tailpipe NO_x (g km^{-1})	f-NO_2 tailpipe (%)	PM (g km^{-1})
Euro III buses fitted with DPF			
Volvo B7TL Double Deck	12.42	53.4	0.014
Scania Double Deck	10.58	39.3	0.008
Optare Solo Single Deck	5.43	24.3	0.014
Mercedes-Benz Citaro G Artic	12.98	35.0	0.024
Euro III buses fitted with DPF and SCR			
Dennis Dart single deck	5.33	46.0	0.007
Dennis Dart single deck	4.89	54.3	0.015
Euro IV buses without DPF			
Dennis Enviro 400 double deck	7.26	3.7	0.052
Dennis Dart single deck	8.6	7.7	0.029

47. It is, therefore, evident that TfL have invested heavily in new vehicles, powertrains and exhaust after treatment, and that uniquely they also undertake emission tests to appraise vehicle performance before vehicle models enter into the London fleet. Whilst the introduction of particulate traps to the TfL bus fleet has resulted in an increase in the f-NO_2, the TfL fleet represent just one source of DPF equipped vehicles in London. A relatively large number of DPF equipped HGVs are also operated in London, as recorded through the Reduced Pollution Certificate (RPC) process (see Section 2.10.3).

48. It is also important to consider the reductions in legislated emissions arising from the TfL particulate trap programme. It is estimated that between 2000 and 2005, that some 375 tonnes of PM, 2,710 tonnes of CO and 845 tonnes of hydrocarbon emissions have been saved as a result of this particulate trap programme (TfL, 2007). In addition TfL have committed to the introduction of hybrid vehicles from 2012, which will result in reductions in NO_x emissions from individual vehicles.

2.7 Do the results from UK heavy goods vehicles measurement programmes agree with international studies?

49. As part of the 2005 Dutch in-use compliance programme for HDVs, the Dutch Ministry of Environment sponsored supplementary tests on primary NO_2 (Riemersma, 2005). TNO were commissioned to undertake these tests, in which on-road measurements of NO_x and NO were recorded during typical 30-minute bus journeys. Table 2.4 provides a summary of some of the vehicles tested, and Figure 2.9 provides a summary of the derived NO_2 emissions. The first two bars in Figure 2.9 are for Euro II vehicles without a PM filter (red), the subsequent six bars are for Euro II buses retrofitted with a Continuously Regenerating Trap (CRT®), and the final two bars are for Euro III buses with Original Equipment Manufacturers (OEM) filters.

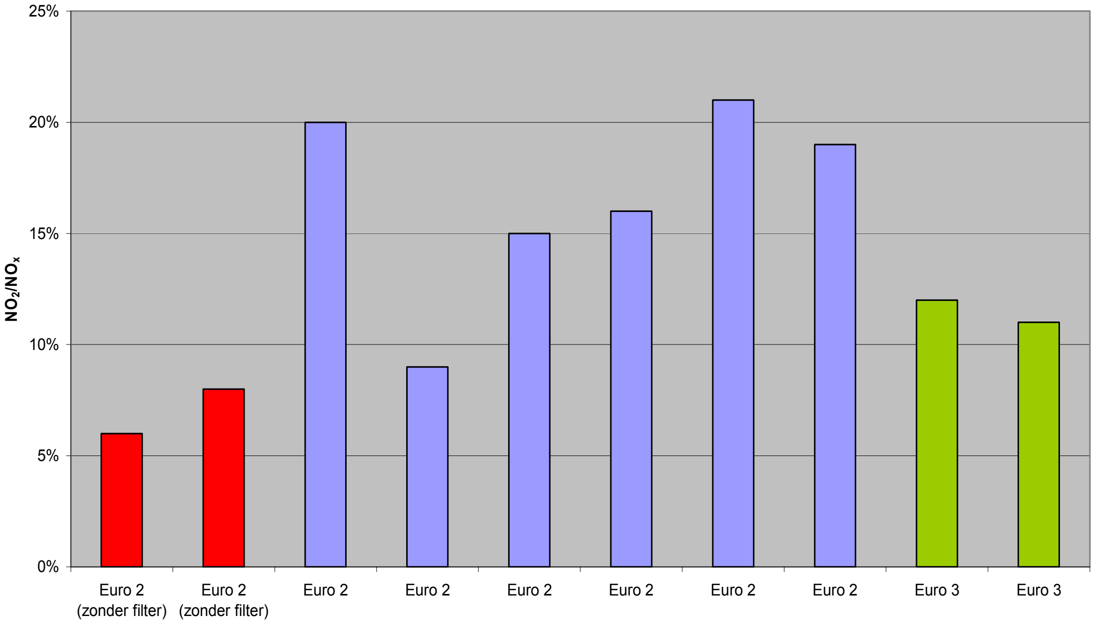
Table 2.4: Test matrix for the supplementary primary nitrogen dioxide measurements from the Dutch 2005 in-use compliance test programme.

Bus ID	Operator	Manufacturer	Engine type	Category	Filter type[1]
1	HTM	DAF	GS 200	Euro II	None
2	HTM	Mercedes	O 405 N	Euro II	None
3	n/a	n/a	n/a	n/a	n/a
4	HTM	DAF	GS 200	Euro II	CRT®
5	HTM	DAF	GS 200	Euro II	CRT®
6	HTM	Mercedes	O 405 N	Euro II	CRT®
7	HTM	Mercedes	O 405 N	Euro II	CRT®
8	HTM	Mercedes	O 405 N	Euro II	CRT®
9	GVU	DAF	PE183C	Euro III	DPX™
10	Connexxion	Volvo	8700 BLE	Euro III	OEM
11	Connexxion	Volvo	8700 BLE	Euro III	OEM
12	n/a	n/a	n/a	n/a	n/a
13	n/a	n/a	n/a	n/a	n/a

[1] CRT (continuously regenerating trap) is a registered trademark of Johnson Matthey. DPX™ is a registered trademark of BASF.

50. The f-NO_2 for Euro II buses without DPFs ranged from 6% to 8%, Euro III vehicles retrofitted with CRT® ranged from 9 to 22%, whilst Euro III vehicles equipped with OEM DPF systems averaged 12%. These data are significantly lower than those recorded from the TfL measurement programme. This variation may result from differences in the test conditions and DPF types between the TfL and Dutch test methodology and vehicle samples. In particular NO_2 formation is affected by exhaust gas temperature and the amount of PM or soot accumulated on the filter. The MLTB is a relatively high temperature test cycle, with the higher speed coming first and an average speed of 14 km/h. This would tend to remove soot from the filter early in the test, as well as promoting high levels of NO_2 from the catalyst (Tremayne, 2006).

Figure 2.9: f-NO_2 results from the 2005 Dutch in-use compliance programme.



2.8 Can tunnel studies be used to validate primary nitrogen dioxide emission factors?

51. Due to the limited dispersion and dilution conditions in a tunnel environment, pollutant concentrations tend to be higher than in normal ambient air. In addition, external influences are reduced – these being particularly important in the case of atmospheric NO_2 formation. Therefore, tunnels provide unique real-world experiment chambers for the estimation of transport emissions. Road tunnels have been widely used for the derivation of exhaust emissions, but infrequently used for the estimation of primary NO_2 (Sjodin and Cooper, 2001). During 2005 and 2006 TRL, funded by the Transport Research Foundation (TRF), applied this technique to a UK road tunnel (Boulter *et al.*, 2007).

52. Measurements were conducted in the Hatfield and Bell Common tunnels, during winter and summer periods during 2005 and 2006. In each tunnel, atmospheric concentrations of NO, NO_2 and O_3 were measured continuously at three main sites: near to the tunnel entrance, near to the mid point, and near to the exit. In order to provide greater spatial resolution of NO_2 concentrations, measurements were also conducted inside the tunnel using passive diffusion tubes. Traffic parameters and meteorological parameters were also recorded continuously.

53. The measurements have shown that the NO_2 generated in the second half of the tunnels is probably all primary in origin, with little or no contribution from atmospheric reactions. However, in longer tunnels where the air has a longer residence time, there may be a significant NO_2 contribution from the reactions of NO with oxygen. Such phenomena ought to be investigated in longer tunnels.

54. A range of total fleet-weighted NO_x and NO_2 emission factors were derived, each incorporating different assumptions relating to the formation of NO_2. Emission factors for different vehicle categories were subsequently derived using multiple regression analysis. Rather different emission factors were obtained in the two tunnels. In the Hatfield tunnel the NO_x emission factors for rigid HGVs (5.37 g vehicle^{-1} km^{-1}) and articulated HGVs (3.37 g vehicle^{-1} km^{-1}) were much higher than those for cars/small vans (0.27 g vehicle^{-1} km^{-1}) and large vans (1.17 g vehicle^{-1} km^{-1}). One of the most significant findings of the study was the much larger emission factor for HDVs in the Bell Common tunnel (around 17 g vehicle^{-1} km^{-1}) compared with the Hatfield tunnel. In addition, the NO_2/NO_x proportion for such vehicles was lower in the Bell Common tunnel. These findings may have been due to the difference in road gradient (0% in Hatfield, around +2% in Bell Common), and calculations with an emission model indicated that the overall ratio between the NO_x emission factor at +2% road gradient and that at level grade was approximately 2. Consequently, although the gradient has an important effect, it does not fully explain the difference between the HGV emission factors in the two tunnels. It is possible that the HGVs in the Bell Common tunnel are generally heavier than those in the Hatfield tunnel, although no information was available to allow this to be tested. The largest NO_2/NO_x proportions (16-25%) were obtained for light-duty vehicles in the Hatfield tunnel, which was a rather surprising result given that a substantial proportion of the light-duty vehicle fleet is composed of vehicles with petrol engines, which have previously been found to have a relatively low NO_2/NO_x proportion. The NO_2/NO_x proportions for HGVs were 9-11% in the Hatfield tunnel and 6% in the Bell Common tunnel. These data are subject to ongoing analysis.

2.9 Should limits be set for the emission of primary nitrogen dioxide?

55. Whilst the existing exhaust emission legislation has sought step-wise reductions in NO_x mass emissions, the changing proportion of primary NO_2 emissions associated with new engine and exhaust after-treatment technologies raises the need to control primary NO_2 emissions.

56. The California Air Resources Board (CARB) undertook a consultation exercise in March 2006 to seek the adoption of proposed amendments to the Verification Procedure, Warranty and In-Use Compliance Requirements for In-Use Strategies to Control Emissions from Diesel Engines. The proposed amendments included a revised limit on emissions of NO_2, which are currently suspended[5].

57. The proposal re-defined the NO_2 limit, expressing it as an emissions increase associated with the verified control technology (as opposed to an absolute NO_2 level). The proposal sets an NO_2 limit of 30% (relative to the baseline NO_x) which would become effective in January 2007. From 2009, the NO_2 limit would be further tightened to 20%. The proposal also includes new preconditioning requirements for technologies, where NO_2 emissions may be influenced by the presence of soot and/or ash.

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[5] In 2002, CARB developed a verification procedure for diesel exhaust after-treatment retrofits. This set a primary NO_2 limit of 20% of the total baseline NO_x. This limit proved too restrictive, and in 2004, was suspended for a period of 3-years. For more information on this ruling, see http://www.arb.ca.gov/regact/verpro06/verpro06.htm

58. Consideration should therefore be given to the necessity of establishing European limits on primary NO_2 emissions. If adopted, these limits must be complementary to, and not replace the existing limits on NO_x. However, essential to the establishment of a limit for primary NO_2, is the development of a consistent measurement protocol. Given the uncertainties and costs imposed by the establishment of a legislative emission limit for NO_2, consideration should also be given to the benefits of tighter NO_x control, which would undoubtedly result in an overall reduction in the mass of both NO_x and primary NO_2.

2.10 How will the development of the vehicle fleet affect primary nitrogen dioxide emissions?

59. Currently the UK National Atmospheric Emissions Inventory (NAEI) does not estimate emissions of primary NO_2. Only emissions of NO_x are estimated for all sources. In the past there has been a lack of primary NO_2 emissions data available for both for transport and industrial sectors.

60. A change in composition of the road transport fleet in future years is likely to have an impact on national primary NO_2 emissions. The assumptions in the NAEI's road transport emission projections base case of relevance to the primary NO_2 emissions issue are discussed in this section.

2.10.1 The percentage of light duty vehicle sales that are diesel

61. The NAEI road transport projections assume that the share of diesel cars in the new car market will continue to grow as it has been doing since 2000, from levels of around 24% in 2002 to reach 42% of all new car sales by 2010, after which it is assumed to remain constant. This assumption was recommended by DfT (pers comm., 2004, and WebTag[6]) and took account of the views of the motor industry groups at the time the projections were undertaken. This rate of growth in diesel car sales has been the basis of the emission projections and air quality forecasting calculations done since 2004, but in fact, diesel cars already accounted for 36.6% of the cars sold in the UK in 2005 according to DfT's vehicle licensing statistics on new registrations (DfT, 2006); the anticipated projected growth to 2005 was originally expected to be 33%. Thus diesel car sales appear to be growing faster than expected and may extend beyond the projected estimate of 42% by 2010 if the trend continues. The growth in diesel car sales is partly driven by the industry's voluntary agreement to reduce CO_2 emissions from new cars and its associated marketing strategy, combined with improved consumer perception of diesel cars in terms of driveability and performance. As diesel cars have a higher f-NO_2 than petrol cars (approximately 10% compared to approximately 5%), it is likely that with increasing diesel car sales, the fleet-weighted f-NO_2 will increase and possibly at a rate faster than currently forecast if the trend continues beyond 42% by 2010.

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[6] These data are also reported in the DfT's WebTag: http://www.webtag.org.uk/

62. Currently, 90% of LGVs on the road are diesel vehicles. This figure is not expected to change in the near future. The NAEI projections assume that some new diesel cars are fitted with DPFs to reduce PM emissions, even though they are not required to do so by current legislation. On the advice of DfT (pers comm., 2004), the assumptions outlined in Table 2.5 are made about the proportions of new diesel cars sold each year that are fitted with a DPF. Current national emission projections and air quality forecasting have been based on these assumptions, and it is recommended that these figures be re-assessed with DfT and the motor industry to check whether they are still valid or should be revised in light of current trends.

Table 2.5: Percentage of new diesel cars sold in the UK each year fitted with a diesel particulate filter.

Year	% diesel cars with DPFs
2000	0
2001	5
2002	10
2003	15
2004	20
2005	20
2006+	20

63. The increasing numbers of DPFs, and in particular diesel oxidation catalysts (DOCs), being fitted to diesel cars are likely to have a large impact on primary NO_2 emissions.

2.10.2 Retrofits of diesel particulate filters on heavy-duty vehicles in the national fleet

64. Euro IV standards for HDVs do not mandate the fitting of particulate traps to vehicles. However, according to DfT, operators of commercial fleets have received grants to have an increasing number of HDVs fitted with DPFs, thus enabling them to qualify for a 'Reduced-Pollution Certificate'. The NAEI projections use estimates from DfT (pers comm. 2004) of the number of HDVs retrofitted with DPFs, as shown in Table 2.6. Again, current national emission projections and air quality forecasting have been based on these assumptions, and it is recommended that these figures are also re-assessed with DfT and the motor industry to check whether they are still valid or should be revised in light of current trends.

Table 2.6: Number of buses and heavy-duty vehicles fitted with diesel particulate filters in the UK[7].

Year	HDVs with DPFs	HDVs in the fleet fitted with particulate traps (%)
2000	4000	0.8
2001	6000	1.2
2002	8000	1.6
2003	10000	2.0
2004	12000	2.3
2005+	14000	2.7

65. The DPFs are fitted to Euro II and Euro III vehicles, with data from the Energy Savings Trust CleanUp programme, estimating that approximately 55% of grants for DPFs awarded to buses.

2.10.3 The London bus fleet development

66. Information is available from TfL on the numbers of buses operating to different Euro standards, and the numbers fitted with particulate traps (TfL, 2003). The figures, shown in Table 2.7, suggest a significantly newer bus fleet operating in London compared with the average for the UK.

Table 2.7: The proportion of buses in London falling within each Euro standard and the proportion fitted with particulate traps (Data based on measurements during the March of each year).

Emission class	2002 (%)	2003 (%)	2004 (%)	2005 (%)	2006 (%)
Pre–Euro & Euro I	22	16	10	4	0
Euro II	38	28	11	5	0
Euro II + DPF	31	27	35	38	41
Euro III + DPF	9	29	44	53	59
% DPF	39	56	79	91	100

67. Compiling a national inventory of primary NO_2 emissions from road transport requires either NO_2 emission factors or at least values of f-NO_2 for different vehicle categories that can be used in conjunction with existing NO_x emission factors. Table 2.8 provides a summary of f-NO_2 values for different vehicle classes and Euro standards, as compiled from data available to ERG during 2005 to early-2006. These f-NO_2 values formed the initial basis of an inventory of primary NO_2 emissions from road transport. In fact, as discussed in Technical Annex 1, the situation is more complex because within each of the Euro classes, at least from Euro III onwards, the main types of after-treatment systems listed in Table 2.8 may employ a range of different technological approaches (e.g. catalyst materials, DPF regeneration systems). These approaches may have a different effect on f-NO_2 and the problem, as discussed in Annex 1, lies in knowing the mix of these technologies in the national fleet. However, the figures in Table 2.8 demonstrate an early attempt at compiling an NO_2 emission inventory.

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[7] It is recognised that the number of vehicles fitted with DPFs are likely to be underestimated, as retrofits which are undertaken without Reduced Pollution Certificates are not always visible in the statistics.

68. There would be interests among modellers (e.g. for local planning and for use with review and assessment air quality modelling tools) to have guidance on trends in f-NO_2 with time for main classes of vehicles (light duty and heavy duty vehicles and buses with and without DPFs) reflecting the development of the national vehicle fleet. Annex 2 to this report provides simple f-NO_2 curves for these main vehicle classes calculated from a combination of those factors in Table 2.8 and alternative factors for Euro IV and IV+ heavy duty vehicles discussed in Section 2.12, and the NAEI's fleet turnover model as at least interim guidance for treatment of primary NO_2 emissions in models.

Table 2.8: Typical f-NO_2 for different vehicle classes, as developed by Environmental Research Group, King's College, London and used within the London Atmospheric Emissions Inventory (Beevers, 2006).

Vehicle category	2-wheelers	Petrol cars	Diesel cars	HGV	Bus	Petrol LGV	Diesel LGV
Pre Euro I	0.04	0.04[1]	0.105[2]	0.14[1]	0.175[1]	0.04	0.22[1]
Euro I	0.04	0.04	0.105	0.14	0.175	0.04	0.22
Euro II	0.04	0.04	0.105	0.14	0.175	0.04	0.22
Euro III	0.04	0.04	speed related (0.2 to 0.4)[3]	0.14	0.175	0.04	speed related (0.2 to 0.4)[3]
Euro IV+	0.04	0.04	speed related (0.2 to 0.4)	0.14	0.175	0.04	speed related (0.2 to 0.4)[3]
Oxidation catalyst	-	-	speed related (0.2 to 0.4)	-	0.35[3]	-	-
Particle trap	-	-	0.23	0.48[3]	0.43	-	0.23
Selective catalytic reduction	-	-	-	-	0.43	-	-

[1] (Latham *et al.*, 2001), [2] (Richards *et al.*, 2002), [3] (Carslaw, personal comm.)

2.11 Initial predictions of primary nitrogen dioxide emissions in London

69. Initial estimates of primary NO_2 emissions from vehicles have been made for London for the area covered by the London Atmospheric Emissions Inventory (LAEI): up to and including the M25 motorway. The estimates were calculated as a proportion of NO_x emissions and vary by vehicle type, vehicle age and, in the case of new diesel cars (Euro III+) and LGVs, vehicle speed. The f-NO_2 values were taken from a combination of published papers and early emissions tests made by TfL and DfT, and were part of a collaborative study between ERG (Environmental Research Group, King's College, London) and ITS (Institute of Transport Studies, University of Leeds), for TfL.

70. The vehicle class assumptions are summarised in Table 2.8. Note that the assumptions used for bus and HGV particle traps, oxidation catalysts and SCR are sourced from TfL vehicle tests. Those relating to diesel car Euro III +, diesel cars with oxidation catalysts and diesel LGV Euro III + are sourced from DfT vehicle tests.

2.11.1 Emission time series – all London

71. Using the above factors an emissions time series has been calculated between the years 2002 to 2010 for total NO_x and NO_2 emissions (tonnes per year) by vehicle type, see Figure 2.10 and Figure 2.11, respectively. These factors scale the NO_x emissions calculated using the same method as for the LAEI and are based upon comprehensive vehicle counts and speed estimates that vary by both hour of the day and by road link. The emissions from approximately 6,346 road links are calculated separately, plus additional minor road estimates, to give total emissions for each year. The time series are based upon the LAEI 2003, with back calculation to 2002 and forward calculations using vehicle-km changes which include major London developments such as the extension to the Congestion Charging Zone (CCZ) as well as vehicle stock projections which are both London specific (buses and taxis) and include the effect of a London LEZ scenario.

Figure 2.10: Total nitrogen oxides emissions in London by vehicle type.

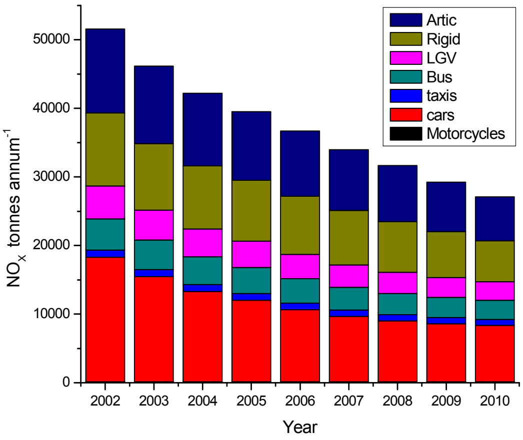


Figure 2.11: Total nitrogen dioxide emissions in London by vehicle type.

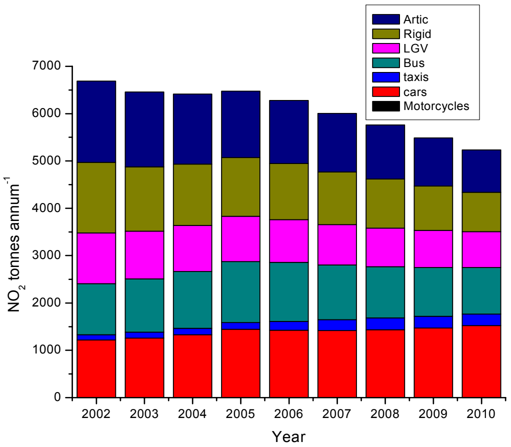


Figure 2.12: The percentage composition of primary nitrogen dioxide in NO_x for all vehicle types in London.

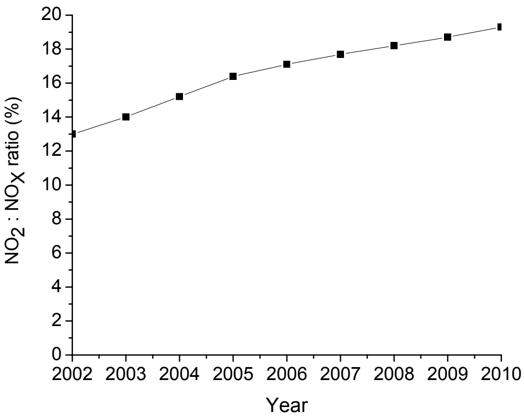
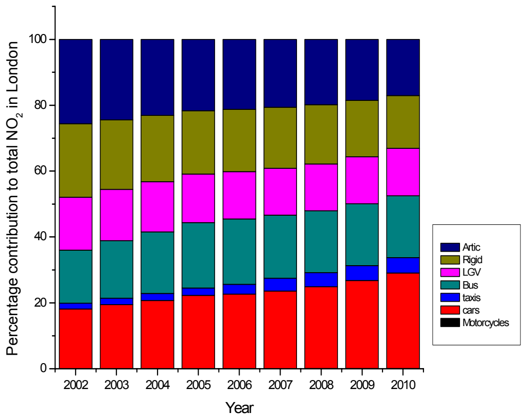


Figure 2.13: The percentage contribution to total London nitrogen dioxide emissions by vehicle type.



2.11.2 Results – all London

72. The emissions calculations show that in London road transport NO_x emissions totals show a steady decline between 2002 and 2010 and overall reduce by 48%. The same cannot be said for NO_2 emissions, however, which show little decline between 2002 and 2005 but beyond this date are predicted to fall. This is indicative of, on the one hand, an increasing proportion of vehicle primary NO_2, and on the other the steady reduction of the absolute NO_x emissions from all vehicles.

73. Figure 2.12 shows the f-NO_2 from all vehicles combined and how this is predicted to change through time. The fraction increases from 13% to 19.3% between 2002 and 2010. Within these overall totals the estimate for individual vehicle types show that the biggest increases in f-NO_2 values are buses: 24% in 2002 rising to 35% in 2010; cars, 7% in 2002 rising to 18% in 2010; taxis, which increase from 11% to 28% over the same period and finally LGVs that increase from 22% in 2002 to 28% in 2010. This is in contrast with predictions for HGVs, which remain at 14% between 2002 and 2010.

74. Figure 2.13 provides the proportion that each vehicle type contributes to the total NO_2 emissions in London. Here one can see the increasing importance of both cars and taxis, and the relatively unchanged contribution from the bus fleet. The increase in contribution from cars is a likely consequence of the increased use of diesel vehicles in the car fleet. The increase associated with taxis, which are all diesel, is the effect of newer vehicles entering the fleet. Note that whilst taxis contribute little to NO_2 emissions overall in London, large spatial differences are likely to exist and in the case of central London, where taxis represent a large proportion of vehicle km travelled, their contribution is likely to be higher. This analysis does not include any consideration of the impact of the Mayor's Taxi Emission Strategy, which is aimed at ensuring that all taxis meet a minimum of Euro III for NO_x and PM by July 2008.

75. Despite the small changes in the f-NO_2 for HGVs the model predicts that they still represent 33% of the total NO_2 emissions in 2010. Again large regional differences are likely and possibly the most important factor in this result is the M25 motorway, which is not only a considerable source of NO_x but also carries large quantities of HGV traffic. Despite this however it identifies a key concern in the prediction of direct NO_2 in future and that relates to whether there will be widespread use of particle traps on the newest Euro IV and Euro V HGVs. If this were the case the HGV f-NO_2 and subsequent total NO_2 emissions would rise and contribute an even larger total of NO_2 emissions in London.

2.11.3 Emissions time series – Central London

76. To understand further the local differences in London the above emissions time series have been reanalysed using only emissions from central London. Central London in this case is an area equal to 25 km^2 and is a combination of the CCZ plus an additional area to the west. These results are summarised in Figure 2.14 to Figure 2.17.

Figure 2.14: Total nitrogen oxides emissions in Central London by vehicle type.

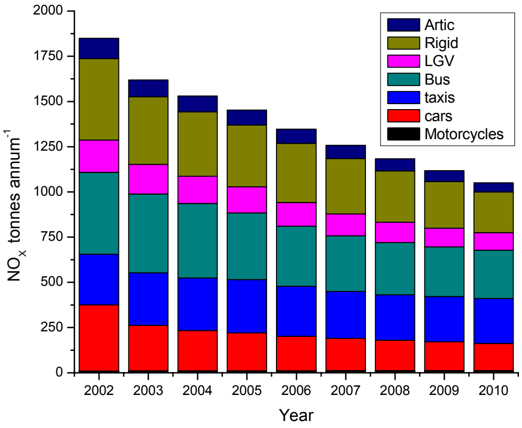
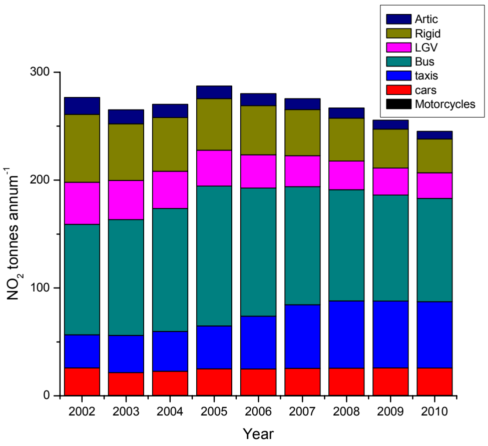


Figure 2.15: Total nitrogen dioxide emissions in Central London by vehicle type.



2.11.4 Results – Central London

77. Figure 2.14 shows that in central London a similar trend in NO_x emissions exists to that of London as a whole, although, at 43% the reduction is smaller. Emissions of NO_2 also show similar trends with no reduction in emissions up to 2005. Indeed Figure 2.15 shows that predictions of NO_2 emissions peak in 2005 before beginning a downward trend driven by a reduction in NO_x emissions towards 2010. Figure 2.16 also shows that in central London the average f-NO_2 started higher at 15% in 2002 increasing to over 23% by 2010. However, the most striking differences between central London and London as a whole is the considerable role played by buses as a source of NO_2 emissions and towards 2010 the increasing role of taxis. These vehicle types dominate the emissions of NO_2, with the role of both cars, LGVs and HGVs, greatly diminished. The importance of buses and taxis combined is also shown in Figure 2.17 where they make up 64% of total NO_2 emissions. Furthermore their contribution does not fall below 48% for whole period studied.

Figure 2.16: The percentage of nitrogen dioxide emitted as primary nitrogen dioxide by all vehicle types in Central London.

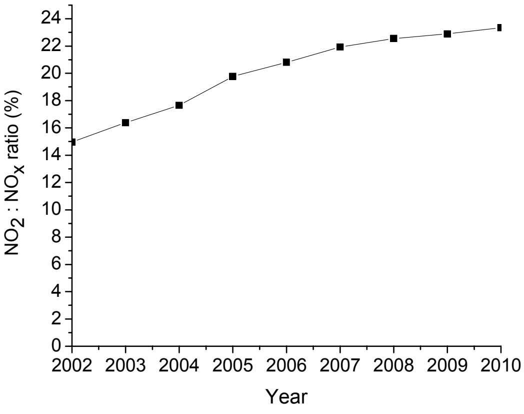
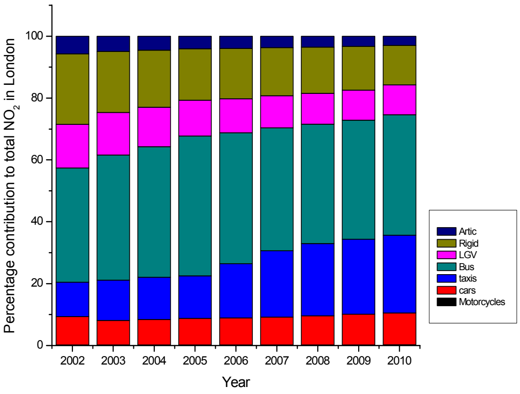


Figure 2.17: The percentage contribution to Central London nitrogen dioxide emissions by vehicle type.



2.12 An analysis of nitrogen oxides and nitrogen dioxide emissions from road transport in other UK urban areas

78. Data in the NAEI was used to assess NO_x and NO_2 emissions from road transport in UK urban areas. This follows a similar approach to that in Section 2.11, using the same values of f-NO_2 as in Table 2.8 except for Euro IV and IV+ (usually referred to as Euro V) heavy duty vehicles where lower values were used on the basis that many of these vehicles are or will be fitted with SCR emitting lower fractions of NO_x as primary NO_2. It was assumed that the majority of Euro IV+ HDVs are fitted with SCR with an average f-NO_2 of 0.08 based on the information of TfL; for Euro IV HDVs, an intermediate value between Euro III and IV+ of 0.10 was assumed on the basis that many, but not all vehicles are fitted with SCR. The analysis indicates that those trends estimated for London are also evident in other urban areas.

79. Annual NO_x and NO_2 emissions were calculated for the years 2002 to 2010 for road transport in UK urban areas by vehicle type (Figure 2.18 and Figure 2.19).

Figure 2.18: Annual UK nitrogen oxides emissions for road transport in urban areas by vehicle type, 2002 – 2010.

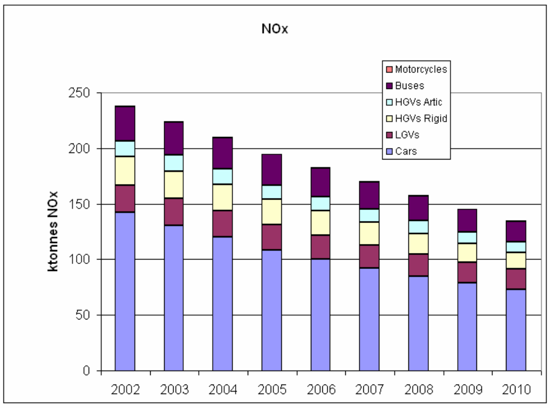
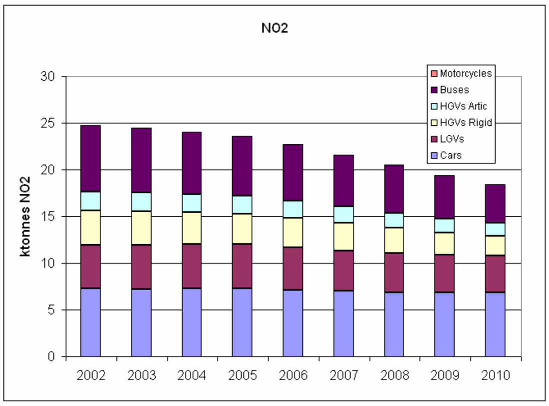


Figure 2.19: Annual UK nitrogen dioxide emissions for road transport in urban areas by vehicle type, 2002 – 2010.



80. The NAEI uses traffic forecasts from the July 2004 central traffic forecasts for Great Britain from the Department for Transport (DfT, 2004) and based on DfT's FORGE model taking into account the ten-year plan for transport. The rate at which new vehicles penetrate the fleet and old ones are removed, are calculated by a fleet turnover model based on average survival rates and figures from DfT's Vehicle Market Model (VMM) on new car sales. The survival rates are based on averages of historical survival rates over the last 10 years. It has been assumed that diesel car sales will grow to 42% by 2010. This is significantly higher than the estimate given in the earlier AQEG NO_2 report (AQEG, 2004).

81. The emission calculations show that in urban areas, road transport NO_x emissions decline from 238 kt to 135 kt between 2002 and 2010 respectively (Figure 2.18), a decrease of 43%. In contrast, urban UK NO_2 emissions from road transport are predicted to decrease by only 28% over the same period. (Figure 2.19). This slower decline is as a net result of an overall trend in increasing f-NO_2 (see Figure 2.20) for all vehicles in combination with declining NO_x emissions.

82. In 2002, the overall fleet average f-NO_2 value for urban UK road transport (Figure 2.20) was approximately 10% and this is predicted to increase to 13% by 2010. This is rather slower than the rate of increase in f-NO_2 predicted for London and reflects the slower rate of penetration of newer diesel vehicles in the national fleet fitted with abatement technologies associated with higher f-NO_2 than is predicted for London. For the UK, these data are further disaggregated into LDV and HDV in Technical Annex 2.

83. Figure 2.21 shows the proportion that each vehicle type contributes to the total NO_2 emissions in urban areas. The analysis shows that cars and LGVs will be of increasing importance in the future. This is as a result of the increasing numbers of diesel cars and LGVs conforming to Euro III and Euro IV emission standards in the fleet associated with higher f-NO_2. The analysis has shown that HGVs and buses are of less importance as their contribution to total NO_2 emissions in urban areas is predicted to fall over time. This is because the NAEI forecasts at present assume that there is no widespread use of particulate traps on Euro IV and IV+ vehicles. This assumption obviously has large implications on the total NO_2 emissions predicted in urban areas.

Figure 2.20: Estimated ratio of urban emissions in the UK of nitrogen dioxide to nitrogen oxides.

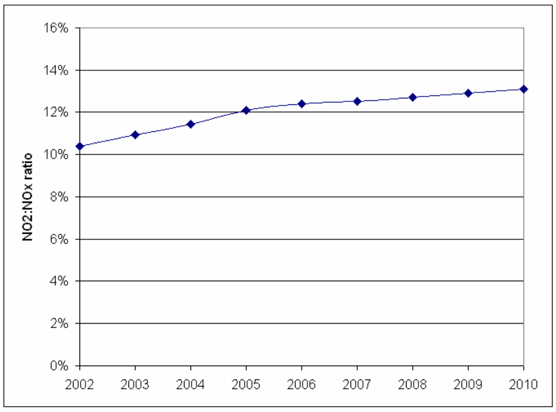
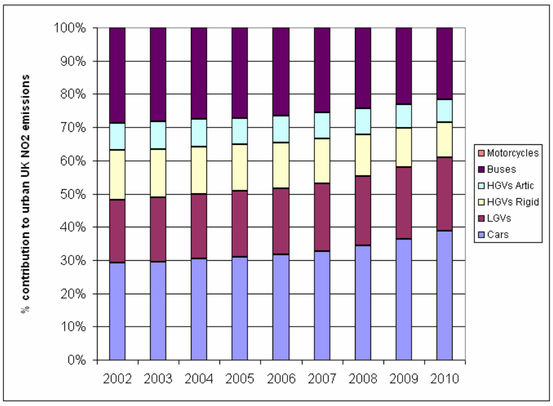


Figure 2.21: Contribution to urban UK nitrogen dioxide emissions by vehicle class.



2.13 Summary and key points

84. Evidence suggests that whilst the fleet average NO_x emissions are reducing, that the fleet average f-NO_2 is increasing. The widely-adopted 5% fraction appears to be an underestimate for both light (specifically diesel engined cars and light commercial vehicles) and heavy vehicles, with the results from the most recent UK and international measurement programmes suggesting f-NO_2 values of between 8% and 40%. These higher primary NO_2 proportions are associated with diesel engine technology, the growth in the proportion of diesel vehicles in the fleet and the increasing use of oxidation catalysts.

85. Whilst the focus of this review was on f-NO_2, consideration should also be given to tracking changes in the emission of other nitrogen species, such as ammonia (NH_3) (associated with SCR), nitrous acid (HONO) (associated with diesel combustion) and nitrous oxide (N_2O) (associated with de-NO_x technologies frequently used with stationary applications).

86. Whilst the proportion of primary NO_2 emissions appears to be underestimated in existing emission models, it must be recognised that the total mass of NO_x continues to reduce with the newest technologies. This is also reflected in a reduction in the total mass of NO_2. However, the reduction in particulate mass has received more emphasis than NO_x emissions. Therefore engine-out NO_x emissions have remained relatively high in comparison with PM emissions.

87. Whilst the measurement of regulated pollutants are subject to strict Type Approval procedures, there are no prescriptive methods for the measurement of primary NO_2. Nitrogen oxides emissions are routinely measured from diluted exhaust gas streams, with samples collected in Tedlar bags. These samples are subsequently subjected to analysis using CLDs. Reactions within the sampling bag can modify the partition between NO and NO_2. Furthermore, the dilution of the exhaust stream with air can potentially introduce additional NO_x and O_3 into the sample. This can be offset by the purification and/or measurement of the dilution air. Furthermore, the rapid cooling of the exhaust sample can again modify the partition between NO and NO_2. Given these insights, a procedure that analyses exhaust gas rapidly upon emission (on-line measurement) might be considered the most accurate and reliable. Rapid sampling and analysis would limit chemical production and loss of NO_2. Whilst chemiluminescence continues to be the most widely used analytical technique for the measurement of NO_x and NO_2, FTIR continues to be used in UK emissions measurement programmes, as it remains one of the few techniques for measuring NO_2 directly. However, simultaneous measurement of NO and NO_x using paired CLDs[8] has proven to be feasible. Although the latter is not a direct measurement of NO_2, it remains widely used in UK and European vehicle emission test programmes. Finally, sample conditioning using heated sample lines will limit interferences with water vapour. However, concerns remain in relation to potential interferences with ammonia in the exhaust gas (associated with SCR/de-NO_x equipped vehicles) and also with HONO (observed increases in the exhaust from some modern diesel vehicles). Measurements of these technologies using CLDs could lead to significant errors in the absolute NO_2 emission.

88. Consideration should be given for the further evaluation of primary NO_2 measurement protocols, incorporating continuous measurements using CLD, FTIR and the relatively new application of non-dispersive ultra-violet. It is essential that future measurements are undertaken using techniques that are free from interferences. Furthermore, it is recommended that lessons learnt from the EU PARTICULATES project and the DfT-coordinated Particulates Measurement Programme (PMP) should be considered. Under these programmes, the measurements of particulate emissions were only considered representative when the exhaust stream was subject to significant dilution. This dilution simulates the rapid dilution of the exhaust stream upon emission into ambient air at the rear of the vehicle. Given that this same dilution occurs in the case of primary NO_2, a case for dilution prior to the measurement of primary NO_2 should be considered.

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[8] CLD may be configured with two optical benches and photomultiplier detectors which can measure both NO_x and NO simultaneously. Alternately CLD may be equipped with a single channel, which switches between the measurement of NO_x and NO.

89. Higher average speeds generally produce higher exhaust temperatures and higher NO_x emissions, and therefore a positive correlation between speed and NO_2 emissions might be expected. However, studies that examined the change in NO_2 emissions with drive cycle suggest a more complex relationship depending on the type of exhaust after-treatment technology fitted to the vehicle. Older, pre-Euro III diesel vehicles with conventional diesel engined technology tend to show a decrease in f-NO_2 with increasing speed, but more recent technologies fitted to more modern diesel vehicles including oxidation catalysts and DPFs show less of a speed-dependence or even a tendency for f-NO_2 to increase with speed. However, there remains a high degree of variability between emission results from different sources so that trends in f-NO_2 with speed or drive cycle remain highly uncertain. Additional investigations on the choice of the emission test cycle, the representativeness of test cycles to real world operational conditions and average speed on the engine-out and post after-treatment f-NO_2 are recommended.

90. Measurement of f-NO_2 for Euro III light-duty petrol vehicles range from between 2% and 10%, whilst those for similar diesel vehicles range from 20% to 70%. The highest emissions are those associated with diesel engines, and the use of the new generation of highly reactive oxidation catalysts. Measurements on London taxis suggest a primary NO_2 proportion of 7%. The f-NO_2 for Euro III light commercial vehicles range from 22% to 38%.

91. Measurements from international programmes confirm a gradual reduction in NO_x mass emissions from Euro I to Euro IV cars. However, the f-NO_2 is reported to be between 5% and 15% for Euro I vehicles, increasing to 10% to 80% for Euro IV vehicles. However, the robustness of these f-NO_2 estimates remains uncertain, due to the use of inconsistent sampling protocols and limited sample sizes.

92. Measurements on HDVs have highlighted the relatively high primary NO_2 emissions associated with a range of exhaust after-treatment systems, particularly the CRT® technology. For Euro III buses fitted with DPF, f-NO_2 range from 24% to 53%. However limited data from TfL also indicates that the fraction of primary NO_2 is significantly lower for Euro IV vehicles, at between 4% and 7%. This is explained by the use of SCR, which negates the need for the use of oxidation catalysts for Euro IV emission compliance.

93. It is thus recommended that additional tests are undertaken to investigate primary NO_2 emissions from Euro IV and potential Euro V after-treatment technologies. These tests should also consider the process of optimising exhaust after-treatment technologies to specific in-use duty-cycles. This optimisation process is already undertaken by various fleet operators, such as TfL.

94. Investigations on the influence of fuel quality have indicated an increase in f-NO_2 with conventional fuel sulphur content reductions. In addition, considerable uncertainty surrounds both NO_x and f-NO_2 emissions from alternative fuels, such as bio-fuels and powertrains, such as hybrids. Consideration should thus be given to the assessment of the impact on NO_x and NO_2 emissions associated with changes in conventional fuels and the introduction of alternative fuels and powertrains. Whilst biodiesel is associated with some carbon dioxide (CO_2) benefits, some evidence suggests higher overall NO_x emissions, when compared to conventional fuels. In contrast, initial trials of hybrid buses in London have indicated significant NO_x emission reductions, of the order of 15% when compared to the existing Euro IV vehicle stock.

95. Given the measured increase in f-NO_2 in vehicle exhaust, an evaluation of the CARB proposals, which are introducing stringent f-NO_2 Type Approval exhaust emission limits, should be undertaken. The benefits of setting new limits on NO_2 or f-NO_2, against the existing policy of setting increasingly more stringent limits on NO_x should be evaluated.

96. The use of tunnel studies to validate road transport emission factors has been widely employed. Recent UK-based studies have been used to derive estimated NO_x and NO_2 emissions. Subsequently these studies have been used to estimate the proportion of primary NO_2. For cars/small vans and LGVs the f-NO_2 has been estimated between 16 and 25% for the Hatfield and Bell Common Tunnels. For HGVs a value of 11% was estimated from the Hatfield Tunnel, and a much lower value of 6% estimated from the Bell Common Tunnel. These studies remain a potentially valuable way in validating road transport emission factors.

97. The use of these higher f-NO_2 values has been evaluated in relation to the general increase in roadside NO_2 concentrations, particularly within the Greater London area. A good correlation is evident between these higher primary NO_2 fractions and the increase in ambient roadside NO_2.

Chapter 3

What do measurements tell us?

3.1 Can the nitrogen oxides and nitrogen dioxide trends at national network sites be explained by changes in nitrogen oxides emissions?

Measured NO_x concentrations have declined in line with emission changes but NO_2 concentrations have not declined as expected, particularly at the roadside and some sites have shown increases in recent years.

98. Ambient concentrations of NO_x and NO_2 were expected to have shown a decline in recent years due to the continuing decline in urban NO_x emissions, largely as a result of the reductions in emissions from traffic associated with the Euro standards. Figure 3.1a illustrates trends in annual mean NO_x and NO_2 between 1998 and 2005 at a selection of roadside and kerbside monitoring sites. While most of the sites show a decline in NO_x, NO_2 concentrations show little change or an increase in NO_2. Figure 3.1b shows that the ambient NO_2/NO_x ratio has increased at some sites by more than would be expected due to the decrease in NO_x on its own. Nitrogen oxides concentrations at London Marylebone Road increased to 2000 and have since declined. Nitrogen dioxide concentrations changed in line with NO_x until 2003 when they showed a large increase. Nitrogen oxides concentrations have declined steadily at Bury Roadside and NO_2 concentrations have remained roughly constant. There has been very little change in NO_x at Oxford Centre Roadside but NO_2 concentrations have increased. A contrast is provided by the Glasgow Kerbside site, where there have been small declines in both NO_x and NO_2 concentrations.

99. The trends in ambient NO_x, NO_2 and O_3 concentrations at selected national network monitoring sites have been explored using a combination of a site-specific projection model for NO_x (Stedman *et al.*, 2001) and the oxidant partitioning model (Jenkin, 2004a).

100. Figure 3.2 shows an example for the London Bloomsbury background site. (The 1996 data presented in these plots is provisional; total oxidant is expressed as μg m^{-3}, as NO_2.) The figure shows that there has been a decline in measured annual mean NO_x concentration at this site and that the site-specific projection model provides a good fit to this trend. The site-specific projections of NO_x have been calculated both backwards and forwards in time from a base year of 1998 using sector specific emission projections from the NAEI and a source apportionment of local sources derived from the mapped inventory. Nitrogen dioxide and O_3 projections have been calculated from a combination of these NO_x projections and estimates of regional and local oxidant concentrations using the oxidant partitioning model to assign the total oxidant between NO_2 and O_3. The regional oxidant concentration has been assumed to remain constant except for in the recent photochemically active years of 2003 and 2006 for which an additional 2 ppb has been added. The local oxidant has been assumed to be a proportion of the total NO_x concentration, the value of f-NO_2 has been held constant at the values derived by Jenkin (2004a) from monitoring data up to and including 2001 (14% in central London and about 9% elsewhere). Thus the model seeks to model the expected decline in NO_2 concentrations as NO_x is controlled in the absence of any changes in f-NO_2. Deviations for the expected behaviour could be due to real world changes in f-NO_2. It is clear that the model provides a reasonably good description of the trends in measured total oxidant, NO_2 and O_3 at this site. Thus the measured NO_2 concentration has followed the expected decline as NO_x has declined and the proportion of total oxidant present as O_3 has increased.

Figure 3.1a: Annual mean nitrogen oxides (solid lines) and nitrogen dioxide (broken lines) at selected national network roadside and kerbside monitoring sites (μg m^{-3}).

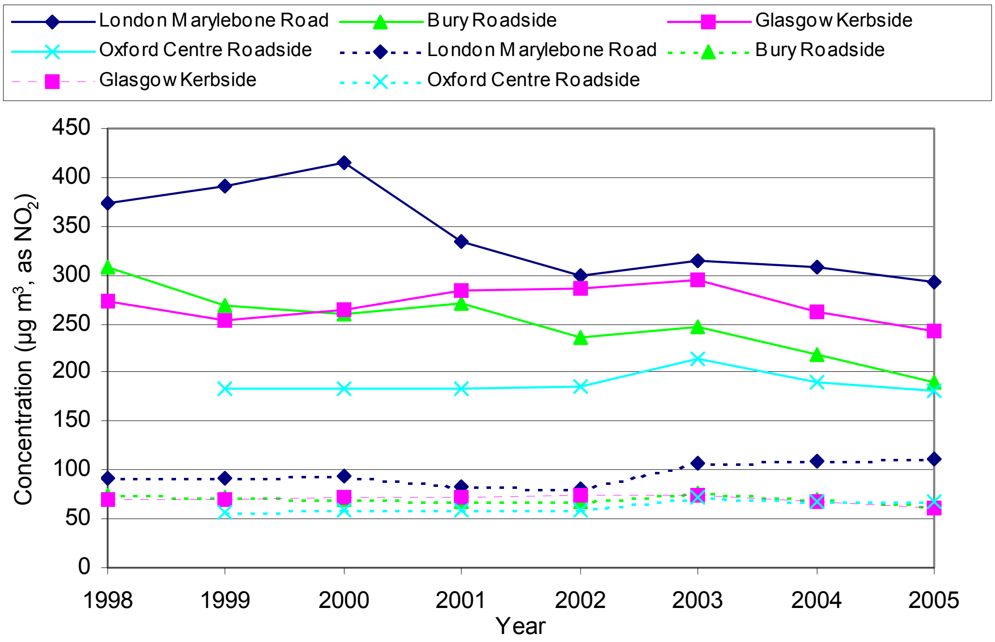
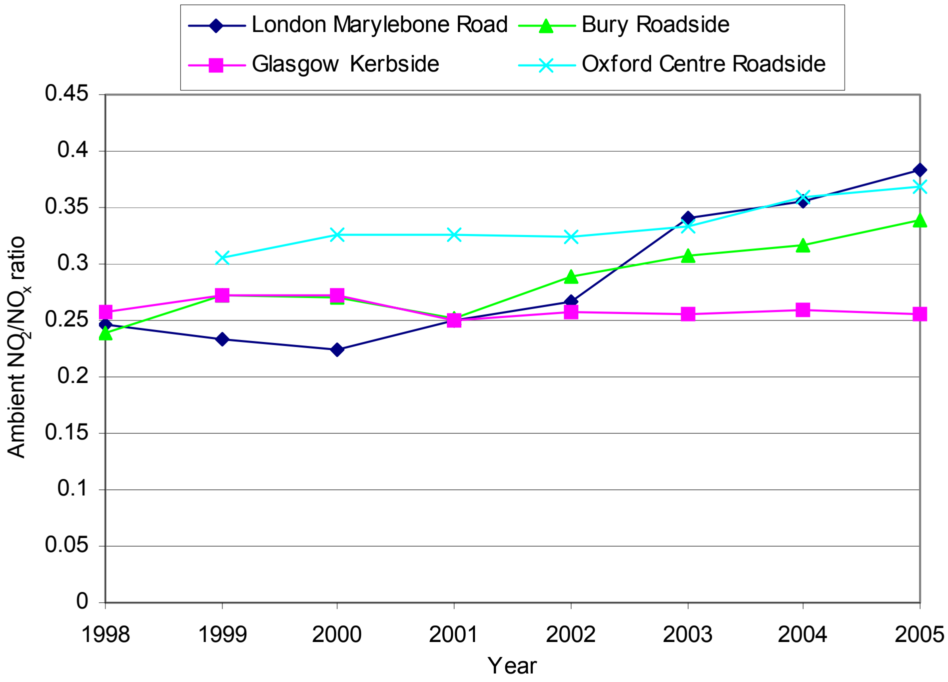


Figure 3.1b: Ambient annual mean nitrogen dioxide/nitrogen oxides concentration ratios at selected national network roadside and kerbside monitoring sites.



101. Figures 3.3 and 3.4 show similar plots for the Cardiff Centre and Leeds Centre sites. The trends in ambient NO_x are well described by the emission inventory based projections, as are the trends in NO_2 and O_3 by the oxidant partitioning model. It is generally the case that the trends in ambient NO_2 at background monitoring sites can be explained by a combination of the trends in NO_x and the changes in the partitioning of oxidant as NO_x has declined. The plots for the background sites also illustrate the expected impact of the higher regional oxidant concentrations in 2003 and 2006, which is relatively small.

102. The picture is more mixed for roadside monitoring sites. Figure 3.5 shows that at Haringey Roadside the modelled trend in NO_x is in good agreement with the measured decline in concentrations and that this change in NO_x is reflected in the more gentle decrease in NO_2. There is no clear evidence from this analysis of any other factors other than the change in the partitioning of the oxidant having a large influence on ambient NO_2 at this site.

103. The ambient NO_2 concentrations at the Camden Kerbside site (Figure 3.6) have not shown the expected decline as NO_x concentrations have reduced. Nitrogen dioxide concentrations remained roughly constant from 1996 to 2002 and were higher than this in 2005 and 2006. Similarly there are indications that total oxidant and NO_2 concentrations have shown an unexpected increase at Bury Roadside in recent years, while the O_3 concentration has remained in line with expectations (Figure 3.7). Such increases would be consistent with an increase in f-NO_2. This site also illustrates rather well that in a high NO_x environment the increases in regional oxidant are largely reflected in the NO_2 concentrations rather than the O_3 concentration.

104. The model results for the London A3 Roadside site are illustrated in Figure 3.8 and suggest that the oxidant partitioning model over-predicted NO_2 before 2003 and has since shown better agreement. This would be consistent with a recent increase in f-NO_2 from levels lower than assumed in the model (about 9%).

105. Figure 3.9 shows the results of this analysis for London Marylebone Road. This analysis suggests that ambient annual mean NO_x concentrations showed roughly the expected decline between 1998 and 2002 and have remained approximately constant since then. Ozone concentrations have been reasonably well predicted by the model with a small over-prediction throughout. Nitrogen dioxide concentrations were, however, predicted well to up 2002, after which there was a sharp increase. This plot suggests that this increase was not related to a change in the partitioning of oxidant because O_3 concentrations have not declined over this period. The most likely explanation for the increase in NO_2 at this site is thought to be an increase in the proportion of NO_x emitted as NO_2 (f-NO_2) and this is discussed further in the sections below.

Figure 3.2: Site-specific predictions of nitrogen oxides, nitrogen dioxide and ozone at London Bloomsbury (μg m^{-3}).

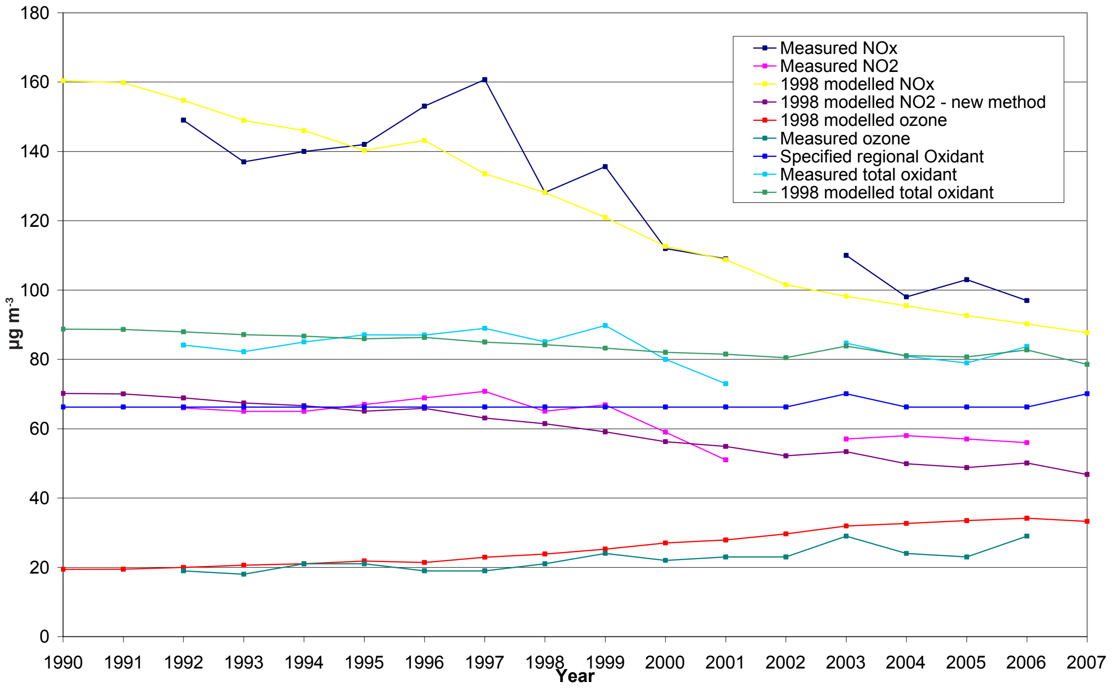


Figure 3.3: Site-specific predictions of nitrogen oxides, nitrogen dioxide and ozone at Cardiff Centre (µg m^{-3}).

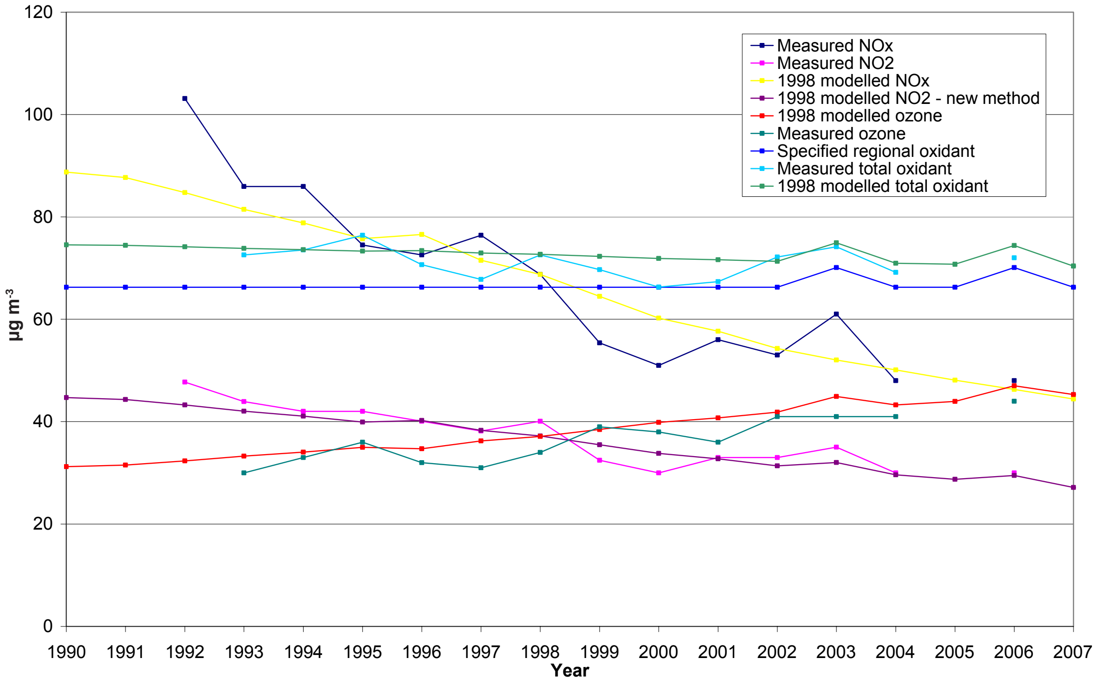


Figure 3.4: Site-specific predictions of nitrogen oxides, nitrogen dioxide and ozone at Leeds Centre (µg m^{-3}).

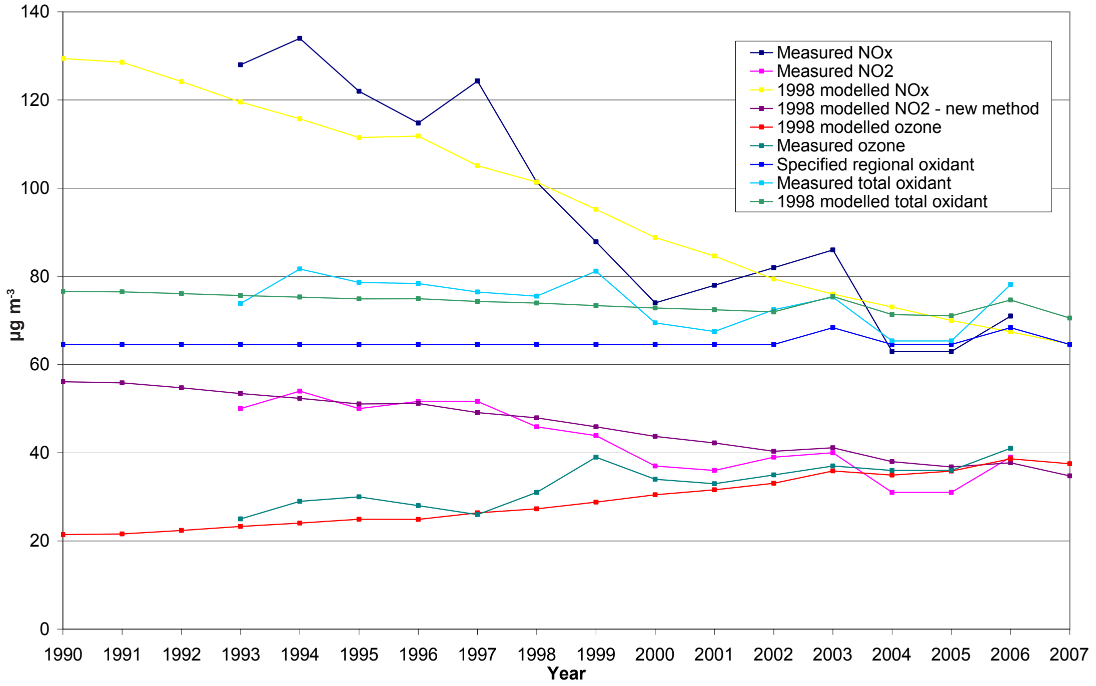


Figure 3.5: Site-specific predictions of nitrogen oxides, nitrogen dioxide and ozone at Haringey Roadside (μg m^{-3}).

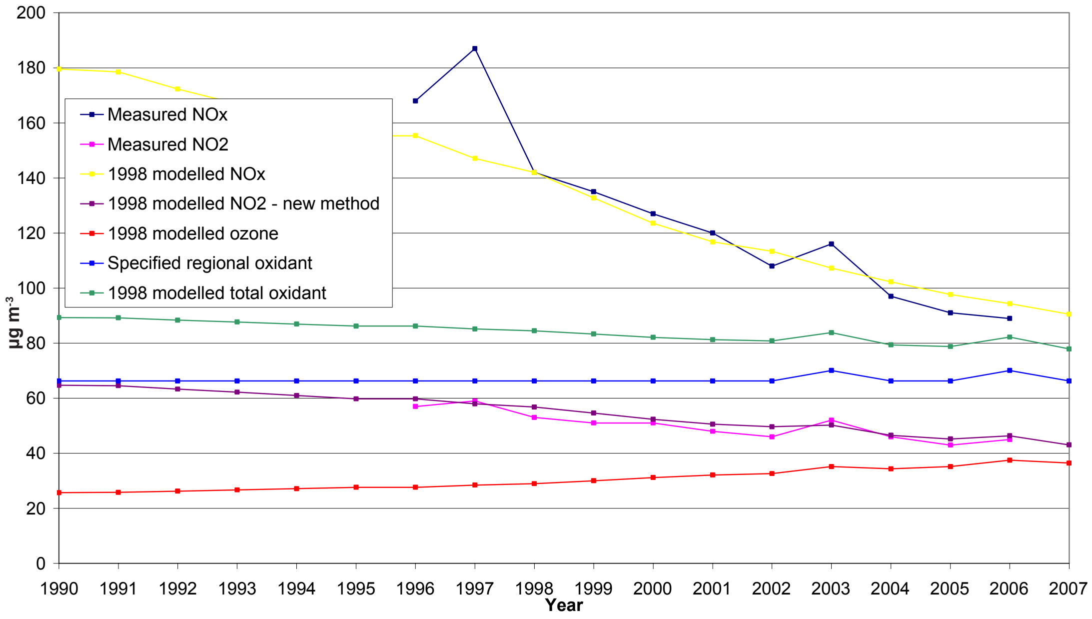


Figure 3.6: Site-specific predictions of nitrogen oxides, nitrogen dioxide and ozone at Camden Kerbside (μg m^{-3}).

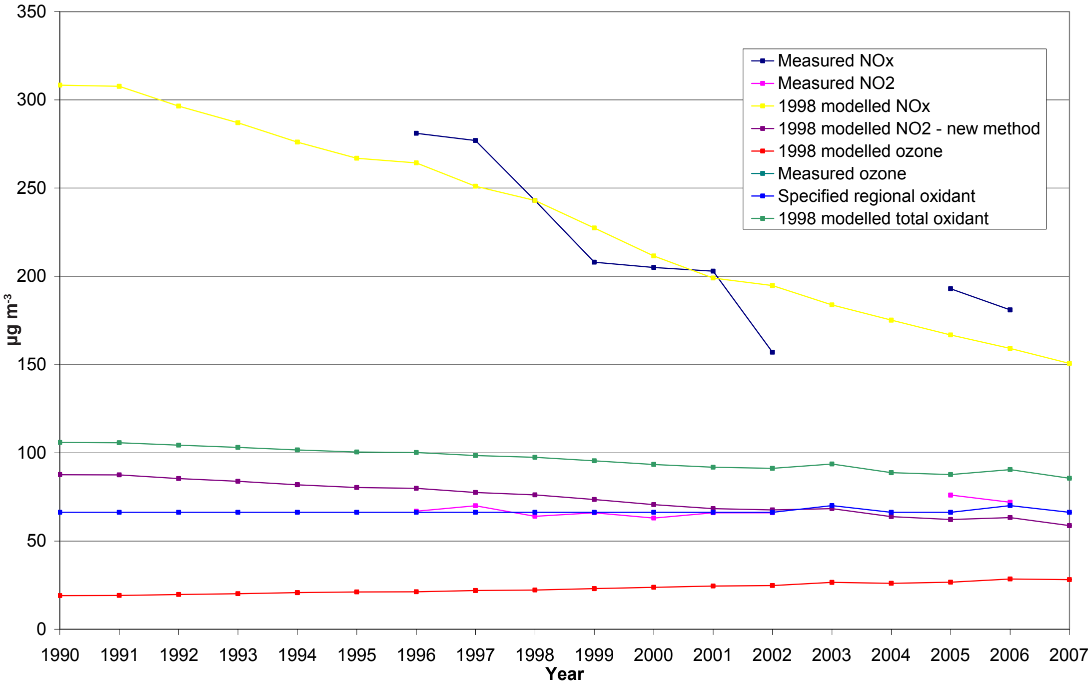


Figure 3.7: Site-specific predictions of nitrogen oxides, nitrogen dioxide and ozone at Bury Roadside (µg m^{-3}).

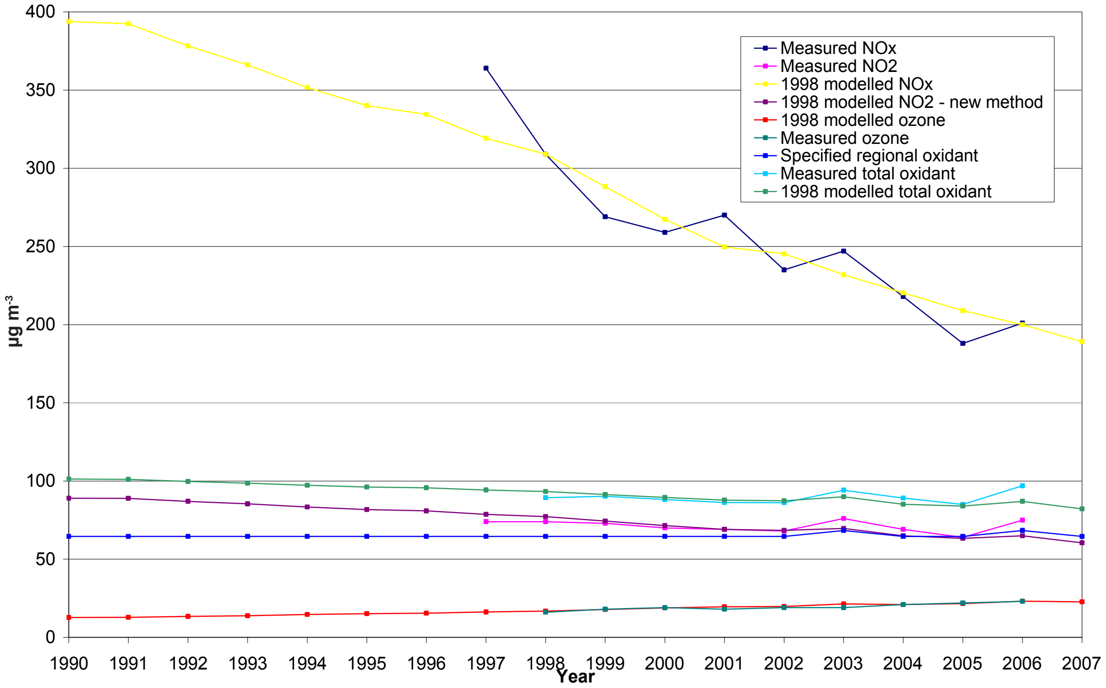


Figure 3.8: Site-specific predictions of nitrogen oxides, nitrogen dioxide and ozone at London A3 Roadside (µg m^{-3}).

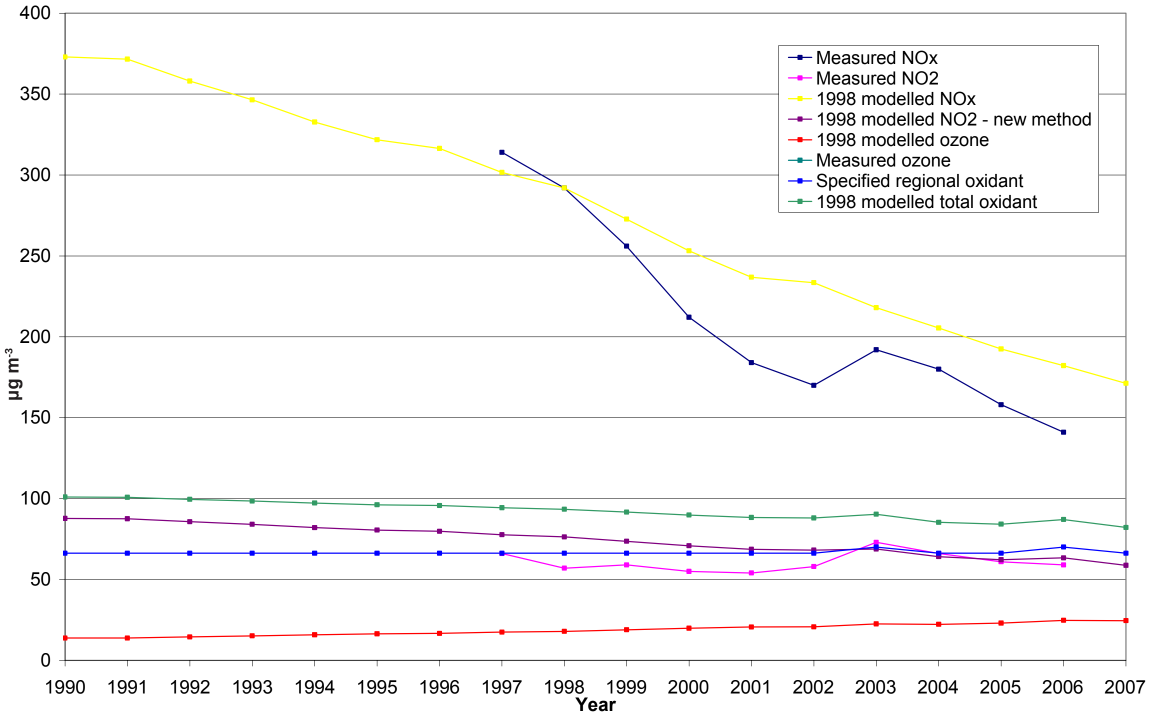
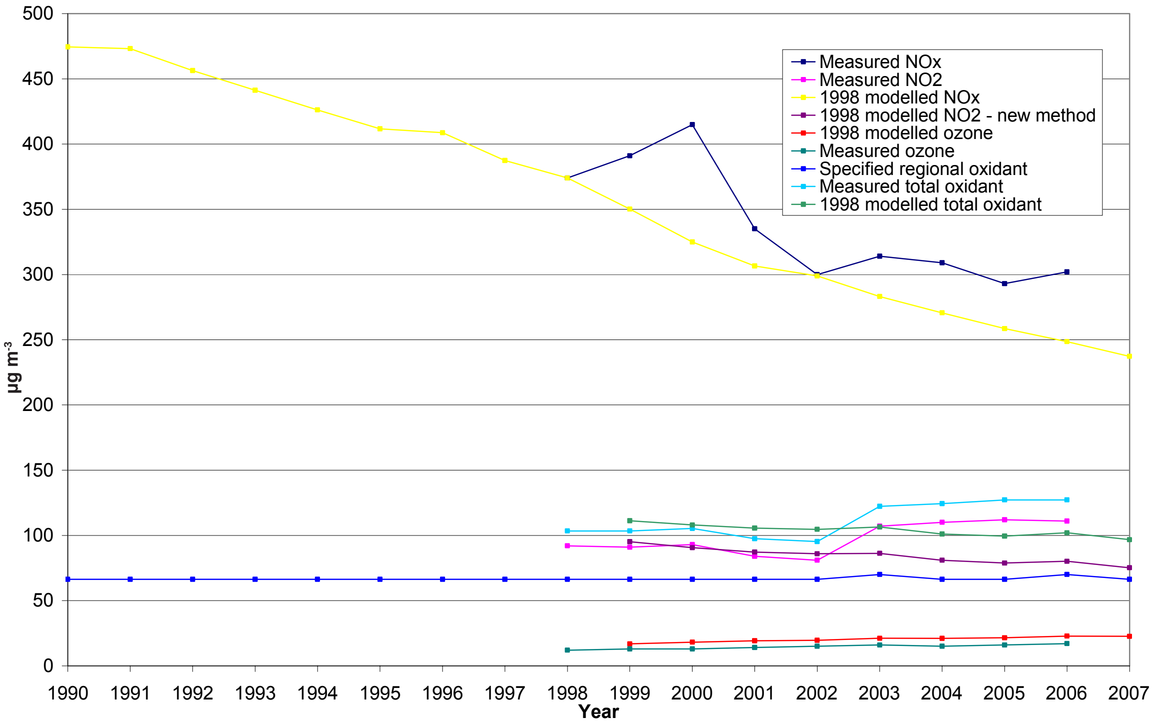


Figure 3.9: Site-specific predictions of nitrogen oxides, nitrogen dioxide and ozone at London Marylebone Road (µg m^{-3}).



3.2 What are the trends at all roadside national network sites?

Overall there seems to have been no decrease in roadside NO_2 concentrations as roadside NO_x concentrations have declined in line with NO_x emissions at many sites. There has been a rather dramatic increase in NO_2 concentrations at some sites, while ambient NO_2 concentrations have declined in line with roadside NO_x concentrations at some other sites.

106. Tables A3.1 to A3.4 in Annex 3 provide a summary of statistics for measured NO_x and NO_2 concentrations at roadside national network sites. These data for all sites are consistent with the data presented for individual sites above. Annual mean and 98th percentile NO_2 concentrations show little indication of a downward trend since 1997 and show an increase at a number of sites. There are large increases in 98th percentile at Marylebone Road and Oxford Centre Roadside and a dramatic rise in the number of hours above 200 µg m^{-3} between 2002 and 2005 at Marylebone Road (all 2005 data are provisional). The number of sites with more than 18 hours above 200 µg m^{-3} has remained roughly constant but the degree of exceedence at Marylebone Road was much larger in 2003, 2004 and 2005 than in previous years.

107. The measured annual NO_2/NO_x ratio at all national network monitoring sites is listed in Table A2.5 for the years from 2002 to 2005. This ratio increases at many sites by a greater degree than might be expected due to the reductions in annual mean NO_x concentration over this period. The changes in ratio between 2002 and 2004 are summarised in Table 3.1 by site type. There were clear average increases at kerbside, roadside and suburban sites; the average increase was much smaller at other site types. Sites in Table A2.5 have been highlighted in yellow if they clearly show no increase in ratio and in blue if they show a clear increase in ratio. An increase in ratio is to be expected at sites with a decrease in NO_x concentration. Further modelling analysis is required to confirm whether the observed increases in ambient NO_2/NO_x ratio are greater than would have been expected. Such analysis has been carried out using modelling methods developed by Jenkin (2004a), Abbott *et al.* (2006) and Carslaw and Beevers (2005). This is discussed further below.

Table 3.1: Summary of increases in measured nitrogen dioxide/nitrogen oxides ratios at a) national network and b) London Air Quality Network sites between 2002 and 2004 annual means.

a)

Site type	Mean change in ratio	Standard deviation	Number of sites
Kerbside	0.040	0.037	3
Roadside	0.035	0.019	17
Urban background	0.015	0.030	20
Urban centre	0.016	0.045	19
Urban industrial	0.012	0.030	3
Suburban	0.035	0.009	3
Rural	-0.024	0.021	5

b)

Site type	Mean change in ratio	Standard deviation	Number of sites
Kerbside	0.036	0.035	8
Roadside	0.041	0.035	36
Urban background	0.024	0.031	28
Suburban	0.006	0.052	10

108. The increase in NO_2/NO_x ratios seen at the roadside, kerbside and suburban sites are likely to be statistically significant but those seen at urban background sites are not significant. A more detailed treatment of the London Air Quality Network (LAQN) data is given in Section 3.3.1 below.

3.3 What can we learn by considering total oxidant (i.e., ozone and nitrogen dioxide) at urban roadside and urban background locations?

Examination of plots of NO_2, O_3 and total oxidant against NO_x suggest that there has been an increase in f-NO_2 at Marylebone Road and a smaller increase at Bury Roadside. There has been little change in NO_x concentration at Exeter Roadside but the increase in ambient NO_2/NO_x ratio suggests that f-NO_2 has also increased at this site. In contrast the increase in observed ambient NO_2/NO_x ratio at Leeds Centre over recent years can be explained by the reduction in NO_x concentration.

109. A detailed analysis of the relationships between ambient concentrations of O_3, NO and NO_2, using Automatic urban rural network (AURN) data from 56 sites up to 2001, has previously been carried out by Jenkin (2004a). As described in detail in Box 3.1, there is a strong chemical coupling between the NO_x species and O_3. Because of this, the consideration of NO, NO_2 and O_3 as a set of species, rather than NO and NO_2 alone, can provide additional information to assist the interpretation of how the level of NO_2 varies with NO_x. Consistent with the definition explained in Box 3.1, NO_2 and O_3 are collectively considered as oxidant (OX).

110. The method of Jenkin (2004a) involves first defining how the level of OX varies with NO_x. This was shown to be made up of a background (NO_x-independent) contribution, which is equivalent for all locations in a given region, and a local (linearly NO_x-dependent) contribution. The local contribution results mainly from primary NO_2 emissions, and therefore can vary from one location to another because of differences in vehicle fleet composition and driving conditions. The contributions of NO_2 and O_3 to OX are then determined from empirical [NO_2]/[OX][9] vs. [NO_x] curves derived from fitting to data for groups of sites with particular characteristics.

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[9] [ ] denotes concentration, i.e. [NO_2] is NO_2 concentration.

Box 3.1 The chemical coupling of nitrogen oxides and ozone

As described in more detail in AQEG (2004), NO_2, NO and O_3 are chemically coupled, typically on the timescale of minutes, by the following reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$NO_2 + \text{sunlight} (+O_2) \rightarrow NO + O_3 \qquad (2)$$

Because of this, "oxidant (OX)" is often used as a collective term for NO_2 and O_3. Consequently, the above reactions partition NO_x between its component forms of NO and NO_2, and OX between its component forms of O_3 and NO_2, but conserves both NO_x and OX. As a result, OX derived from background O_3 is partitioned between the forms of NO_2 and O_3, with a progressively greater proportion in the form of NO_2 as NO_x increases as a result of received emissions. Similarly, OX derived from emitted NO_2 is subsequently partitioned between the forms of NO_2 and O_3, with a progressively greater proportion in the form of O_3 as NO_x decreases with dilution. The emission of an elevated fraction of NO_x in the form of NO_2 therefore has a direct impact on ambient concentrations of both NO_2 and O_3 in urban areas.

Regional-scale chemical processes

The photochemical processing of emitted NO_x and volatile organic compounds (VOC) on local-to-regional scales leads to the conversion of NO to NO_2 and therefore the formation of OX. As indicated above, this is partitioned between the forms of NO_2 and O_3, with the relative contributions depending on the level of NOx at the given location. The photochemical processing is driven by reactions of free radicals, which can be generated from the photolysis of O_3, and from its reactions with emitted alkenes. Consequently, the emission of an elevated fraction of NO_x in the form of NO_2 also has a secondary impact on OX formation.

As described in more detail in AQEG (2004), historical observations made at urban roadside locations and in tunnels are consistent with a small fraction (0.5 – 1%) of oxidised nitrogen being emitted in the form of nitrous acid (HONO). Although this is a small fraction, it is potentially significant from a chemistry point of view, because HONO photolyses efficiently to generate free radicals, thereby promoting VOC oxidation and additional NO-to-NO_2 conversion:

$$HONO + \text{sunlight} \rightarrow OH + NO \qquad (3)$$

Given that HONO is known to be generated by surface reactions of NO_2 with water vapour and with semi-volatile exhaust organics, it is probable that an increase in the primary NO_2 emissions fraction is also accompanied by an increase in the fractional emission of HONO, although there have been no investigations to test this.

It is also noted that the enhanced generation of free radicals by the above processes also increases the oxidation rate of NO_x to nitric acid (HNO_3), through reactions mediated by energy transfer involving nitrogen and oxygen, represented as M, that remain chemically unchanges in the reactions. This has a potential influence on the generation of nitrate aerosol following uptake of HNO_3, or its reaction with ammonia (NH_3) to form ammonium nitrate (NH_4NO_3) aerosol:

$$OH + NO_2\ (+M) \rightarrow HNO_3\ (+M) \quad (4)$$

$$HNO_3 + NH_3 \leftrightarrows NH_4NO_3 \quad (5)$$

In addition, nitrate aerosol is generated by the direct thermal reaction of NO_2 and O_3, by the following mechanism, which is mainly operative in the absence of light and at low NO concentrations:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (6)$$

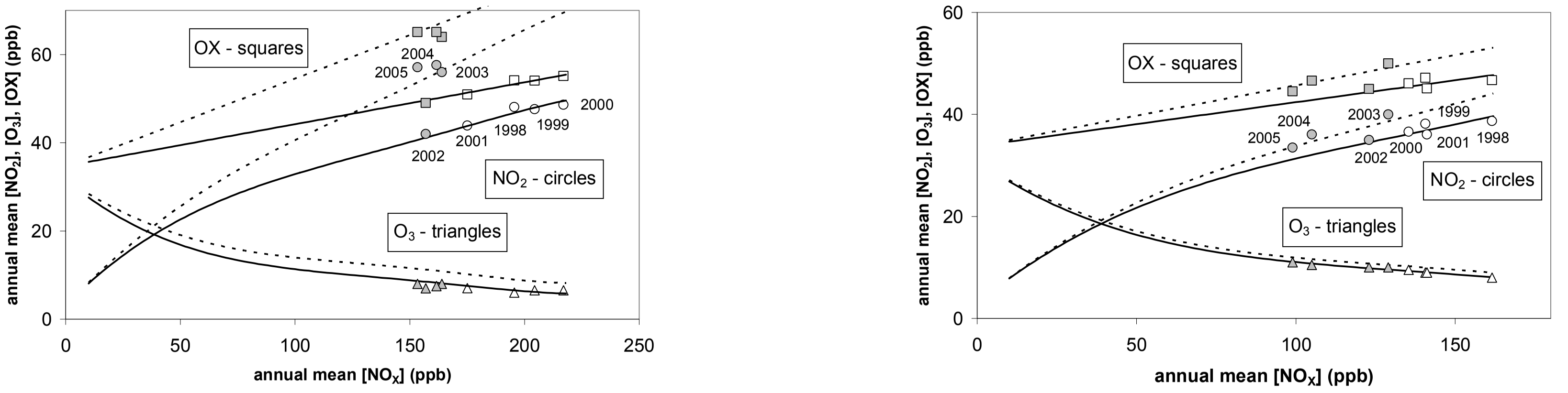
$$NO_3 + NO_2\ (+M) \leftrightarrows N_2O_5\ (+M) \quad (7)$$

$$N_2O_5 + H_2O\ (+\text{ aerosol surface}) \rightarrow 2\ HNO_3\ (\text{aerosol}) \quad (8)$$

An increase in the ambient concentrations of NO_2 and O_3 in the wider urban area, arising from emission of a greater fraction of NO_x as NO_2, therefore increases the efficiency of oxidation of NO_x to nitrate aerosol by this night-time mechanism.

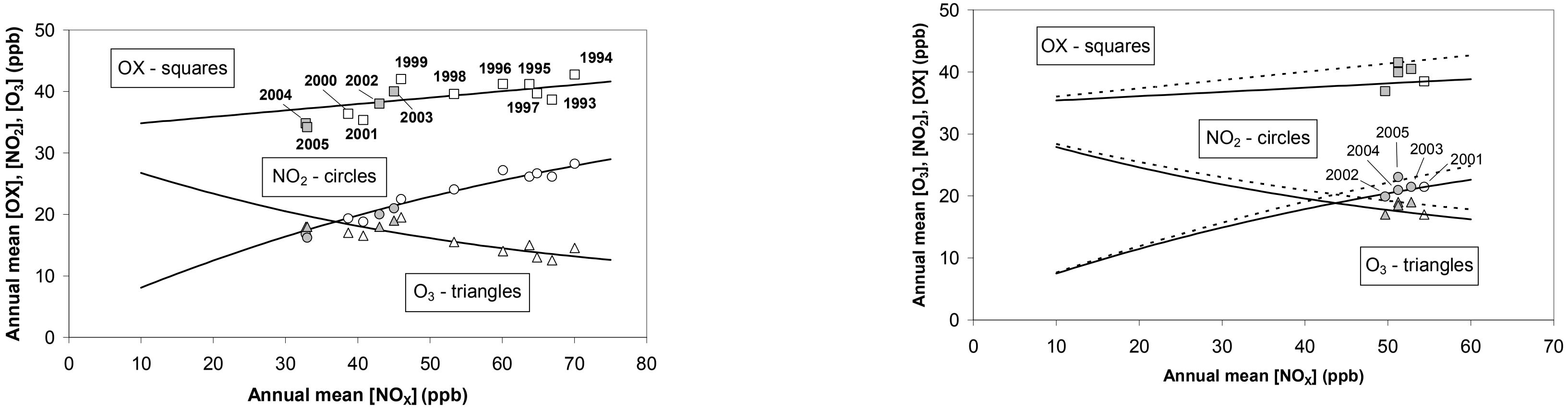
111. Figure 3.10a shows the time series of annual mean data for OX, O_3 and NO_2 at Marylebone Rd over the period 1998-2005. The solid lines are the inferred NO_x dependence of OX, O_3 and NO_2 based on the semi-empirical method of Jenkin (2004a), using AURN data up to 2001. As shown in Figure 3.10a, these provide a good description of the corresponding data in the time series, and a prediction of how OX, O_3 and NO_2 would respond to changing NO_x mixing ratio. The data are consistent with the local OX contribution (i.e., primary NO_2) being 9.5% of NO_x (f-NO_2 = 9.5%). The 2002 annual mean data are also well described by the previous prediction. In contrast, the data in 2003-2005 demonstrate a significant discontinuity, consistent with an abrupt increase in f-NO_2 to 17.9% in 2003, 18.8% in 2004 and 19.8% in 2005. The broken lines in Figure 3.10a are revised predictions of how OX, O_3 and NO_2 would respond to changing NO_x, based on the 2005 OX mixing ratio, and assuming that the relative partitioning of OX into O_3 and NO_2 remains unchanged. The revised prediction is reasonable, but underestimates [NO_2] by about 3 ppb in 2005 (approximately 54 ppb compared with approximately 57 ppb), and thus overestimates [O_3] by the same amount (approximately 11 ppb compared with 8 ppb). Indeed, the predicted increase in O_3 mixing ratio is not apparent in any of the data from 2003-2005, indicating that the precise OX partitioning has also changed. A probable explanation for this is that the incremental increase in OX is due to additional emission as NO_2, which has an annual average lifetime prior to photolysis of about 8 minutes. Consequently, the sampled air at the kerbside location is typically too young for full partitioning of this increment to occur, such that OX increase is manifested almost entirely as NO_2. It should be noted, however, that the increased air mass age as dilution into the urban background occurs should result in incremental increases in both O_3 and NO_2 not dissimilar to those inferred by the broken lines in Figure 3.10a. Thus, at 50 ppb NO_x, NO_2 is predicted to increase by 2.9 ppb (22.6 to 25.5 ppb) and O_3 is predicted to increase by 2.2 ppb (16.9 to 19.1 ppb), as a result of the observed increase in the f-NO_2 from 9.5% to 19.8%.

Figure 3.10: Annual mean mixing ratios of ozone, nitrogen dioxide and oxidant at a) Marylebone Rd. b) Bury Roadside, c) Leeds Centre and d) Exeter Roadside for the period 1998-2005. Solid lines are the inferred nitrogen oxides-dependence of ozone, nitrogen dioxide and oxidant, based on the semi-empirical method of Jenkin (2004a), using AURN data up to 2001 (including the displayed open points). Broken lines are the revised nitrogen oxides dependences, based on the 2005 data, assuming the relative partitioning of oxidant into ozone and nitrogen dioxide remains unchanged.



a) Marylebone Road

b) Bury Roadside



c) Leeds Centre

d) Exeter Roadside

112. Figure 3.10b shows the same analysis for Bury Roadside, which displays some of the same features. The analysis of the data up to 2001 (Jenkin, 2004a) is consistent with the local OX contribution (i.e., primary NO_2, f-NO_2) being 8.6%. The 2002 annual mean data are also well described by the previous prediction. Once again, the subsequent data demonstrate significant, but smaller, increase in f-NO_2 to 11.9% of NO_x, based on the average of the 2003-2005 data. The broken lines in Figure 3.10b are corresponding revised predictions of how OX, O_3 and NO_2 would respond to changing NO_x, based on the 2003-2005 OX mixing ratios, and assuming that the relative partitioning of OX into O_3 and NO_2 remains unchanged. Similarly to the Marylebone Road analysis, the revised prediction slightly underestimates [NO_2] on average, and predicts a small increase in [O_3] which is not apparent in the data at this roadside location.

113. Plots of OX, NO_2 and O_3 trends in data are shown in Figure 3.10c and 3.10d for Leeds Centre and Exeter Roadside in relation to the oxidant partitioning model predictions. The Leeds centre NO_2 data fall close to the prediction for the whole time series, even though a large drop in NO_x between 2003 and 2004 has resulted in a notable increase in NO_2/NO_x (i.e. this is not apparently due to an increase in primary NO_2). On the other hand, the 2005 data for Exeter Roadside suggest an increase in NO_2/NO_x with no notable change in NO_x from previous years, consistent with an increase in f-NO_2. It should also be noted that no change in NO_2/NO_x in conjunction with an increase in NO_x at a given site might indicate an increase in primary NO_2.

3.3.1 Data for sites in London confirm the results of the analyses for data from the national networks

114. Data for national network sites in London can be supplemented with data from the LAQN. Figure 3.11a presents the annual mean NO_x data from 24 long-running roadside and kerbside LAQN sites, expressed relative to their 2006 values. The presence of a downwards trend of about -6% per year is apparent from the 'all sites' line. The corresponding annual mean NO_2 concentration data from these same sites is presented in Figure 3.11b, also on a relative basis. This plot shows a much reduced downwards trend of about -1% per year with little apparent trend over the period from 2000 onwards. Figure 3.11c shows how the ratio of the annual mean NO_2 to annual mean NO_x concentration has changed, also expressed relative to that ratio in the year 2006. Ratios have doubled over the 1995 to 2006 period.

Figure 3.11a: Annual mean nitrogen oxides concentrations expressed relative to the 2006 value at 24 long-running London Air Quality Network roadside and kerbside sites from 1995 – 2006. (Note the provisional nature of the 2006 data).

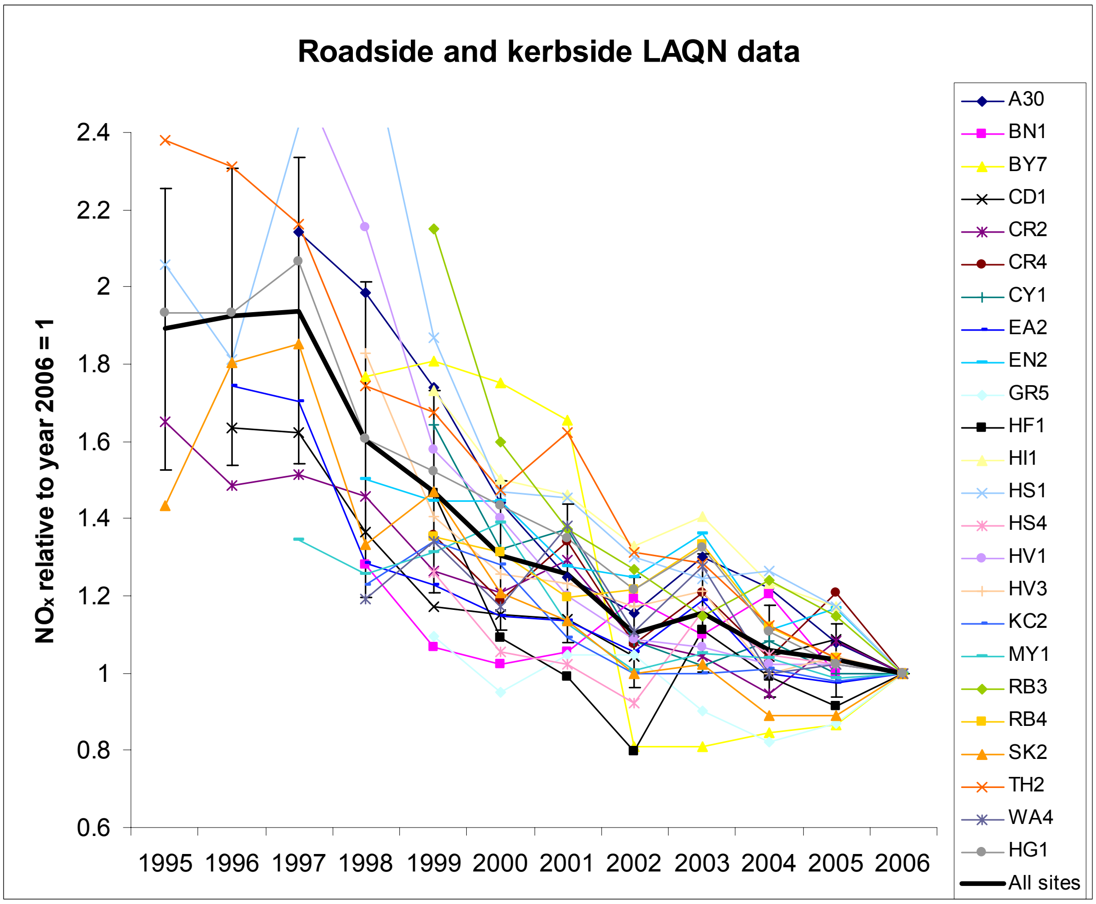


Figure 3.11b: Annual mean nitrogen dioxide concentrations expressed relative to the 2006 value at 24 long-running London Air Quality Network roadside and kerbside sites from 1995 – 2006. (Note the provisional nature of the 2006 data).

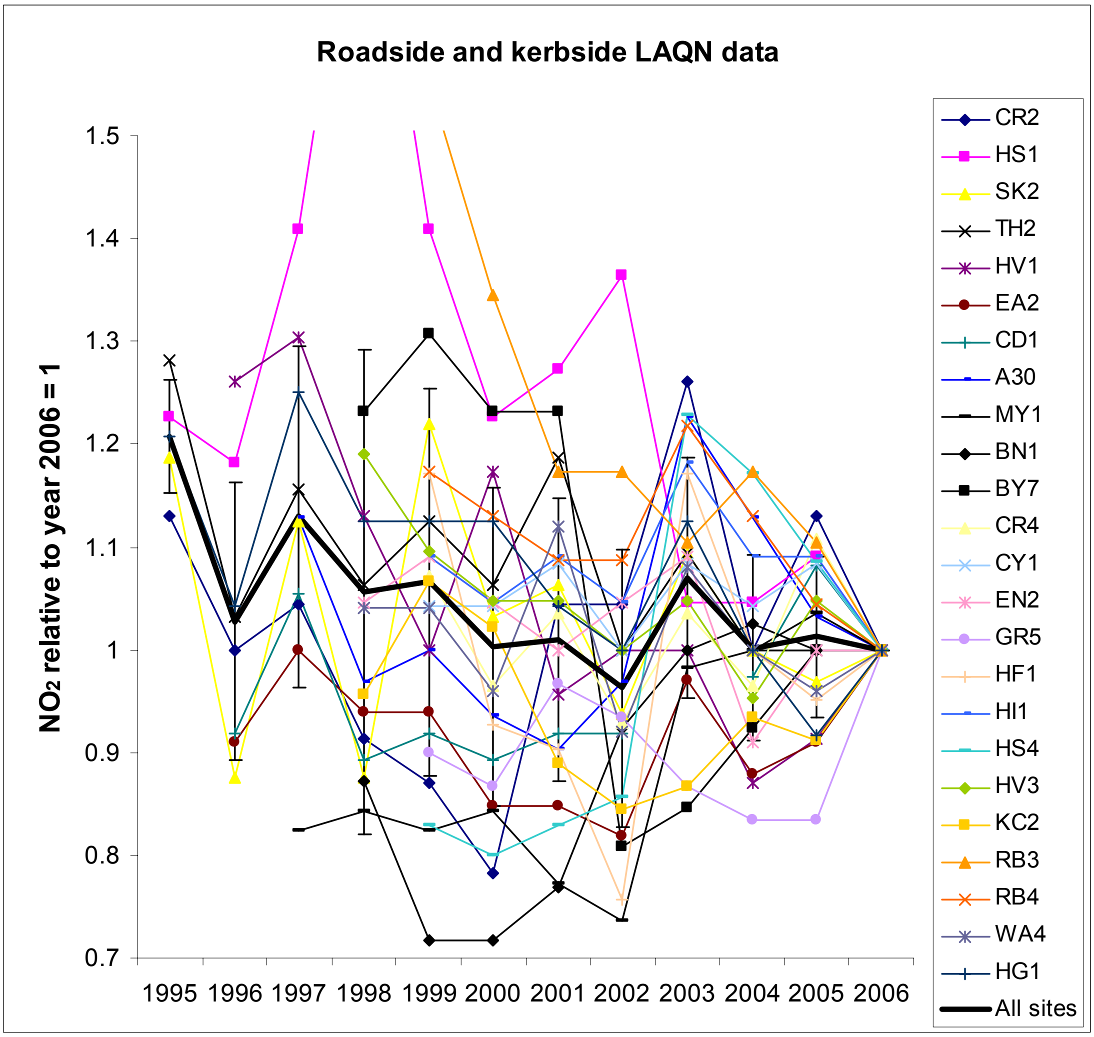
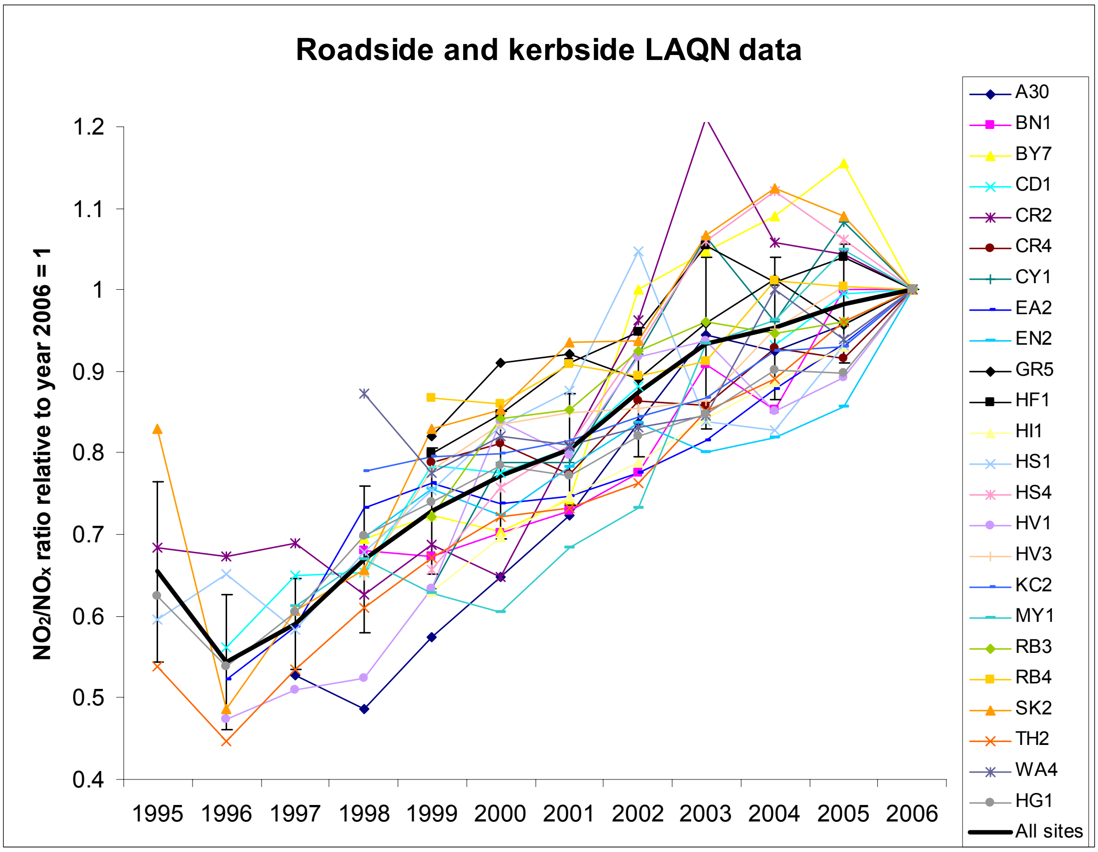


Figure 3.11c: Annual mean nitrogen dioxide/nitrogen oxides concentration ratios expressed relative to the 2006 value at 24 long-running London Air Quality Network roadside and kerbside sites from 1995 – 2006. (Note the provisional nature of the 2006 data).



115. Clearly much of this observed increase in NO_2/NO_x ratios at these roadside and kerbside sites will have been due to the changing NO and NO_2 partitioning within NO_x as concentrations of NO_x decline. Figure 3.11c shows a slight steepening in the slope of the plot from 2002 onwards indicating that other effects may be occurring. To highlight this, Figure 3.12a shows the NO_2 – NO_x partitioning as a function of NO_x expressed as in Figure 3.10, for the above roadside and kerbside sites for the 1995 – 2001 period (diamond points). The thick line shows the average NO_2/NO_x concentration ratios for 10 ppb (19.1 µg m^{-3}, as NO_2) NO_x concentration bins. This line shows that NO_2/NO_x concentration ratios generally increase with decreasing NO_x concentrations exactly as described in the First AQEG report.

116. The corresponding NO_2 – NO_x partitioning as a function of NO_x for the 2002 – 2006 period is shown as the thin line in Figure 3.12a and this is entirely different in shape from that of the earlier period. As a result the lines diverge from each other at NO_x concentrations above about 120 µg m^{-3}, as NO_2. The 2002 – 2006 NO_2 and NO_x data, therefore, belong on a different NO_2 – NO_x partitioning curve, implying a marked change in the formation of NO_2 from NO_x through its direct emission. Interestingly, the roadside site Haringey 1 HG1 has annual mean NO_x concentrations for much of the 2000s that are below the 120 µg m^{-3}, as NO_2 divergence point and shows little evidence of an abrupt change in the NO_2 – NO_x

partitioning. This behaviour is illustrated further in Figure 3.5 above. It is possible that the difference in observed behaviour for the more polluted roadside sites reflects the increasing proportion of buses and HGVs at these sites and argues against the cause of the abrupt change as being widespread across London. Alternatively, secondary NO_2 plays a much larger role at background and the less polluted roadside sites than at the more polluted locations and thus the impact of any increase in primary NO_2 is much less evident at these monitoring sites.

117. In Figure 3.12b, the NO_2 – NO_x partitioning is examined at a range of 34 urban background LAQN sites. The evidence is that at these sites the data from 2002 – 2006 are barely different from those from the 1995 – 2001 period. Again, this argues against a widespread change in the direct emission of NO_2 across London.

Figure 3.12a: Scatter plot showing how the nitrogen dioxide/nitrogen oxides concentration ratio varies with annual mean nitrogen oxides concentration for 24 London Air Quality Network roadside and kerbside sites. Diamonds show 1995 – 2001 data and triangles, 2002 – 2006 data. The thick line joins the average nitrogen dioxide/nitrogen oxides concentrations ratios for sites allocated to 10 ppb nitrogen oxides bins. Note the provisional nature of the 2006 data.

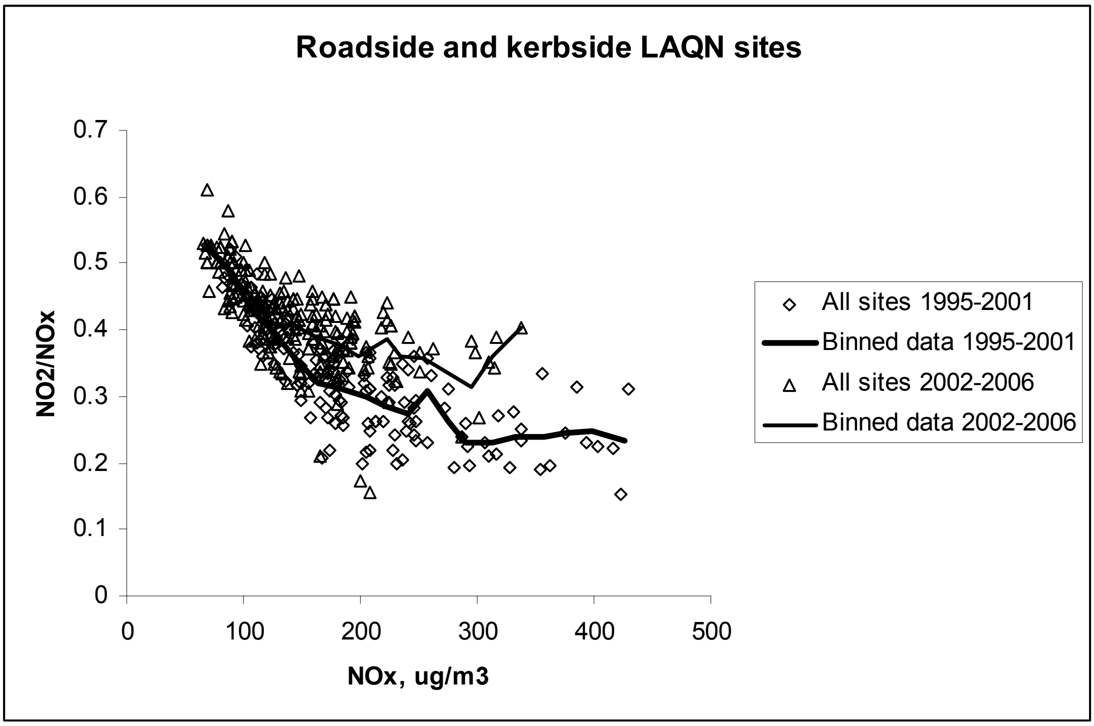
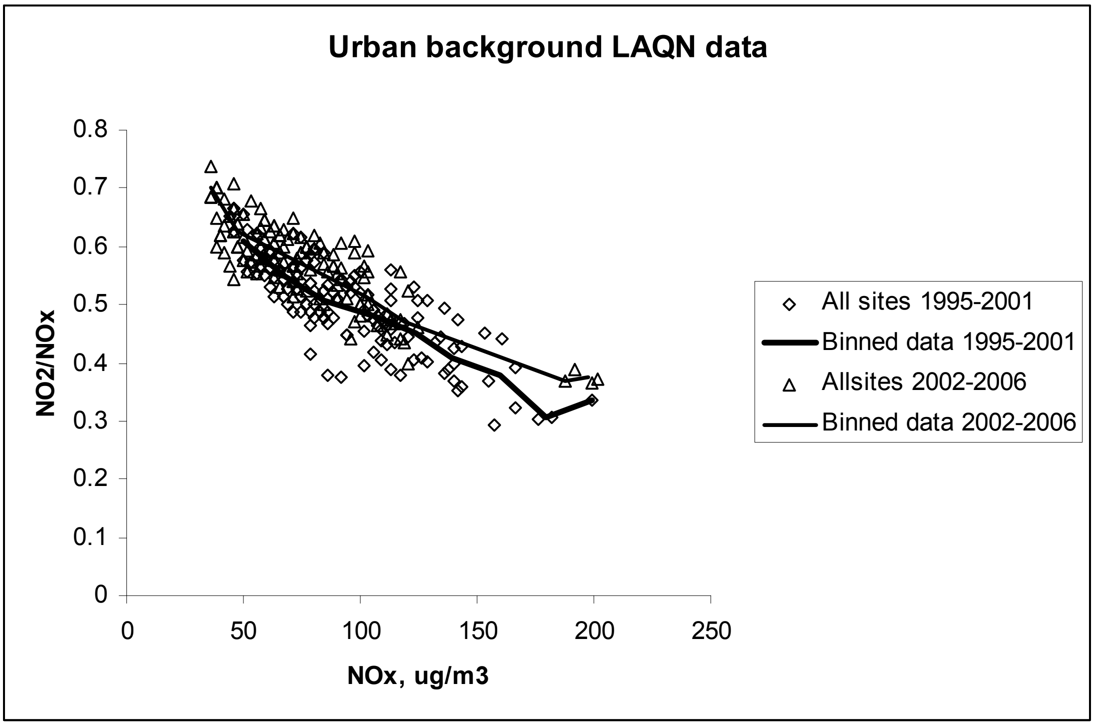


Figure 3.12b: Scatter plot showing how the nitrogen dioxide/nitrogen oxides concentration ratio varies with annual mean nitrogen oxides concentration for 34 London Air Quality Network urban background sites. Diamonds show 1995 – 2001 data and triangles, 2002 – 2006 data. The thick line joins the average nitrogen dioxide/nitrogen oxides concentrations ratios for sites allocated to 10 ppb nitrogen oxides bins. Note the provisional nature of the 2006 data.



118. Table 3.2 lists the number of sites with more than 18 hours exceeding 200 µg m^{-3} from 1997 to 2005. This table suggests an initial decline in the number of sites with exceedences followed by a rise. The table also shows the site with the highest number of measured exceedences. This was Marylebone Road in 1998, 1999 and 2003. Redbridge 2 (Ilford Broadway) had the largest number of exceedences in 2000, 2001 and 2002 (and subsequently ceased operation). The site with the largest number of exceedences in 2004 and 2005 was the newly established site at Lambeth 4 (Brixton Road).

Table 3.2: Summary statistics for national network and London Air Quality Network sites in London. 2006 data are provisional.

Year	Number of sites with more than 18 hours > 200 µg m^{-3} (percentage of sites)	Number of sites	Number of hours > 200 µg m^{-3} at highest site	Highest site
1997	16 (55%)	29	69	Camden 1
1998	1 (3%)	33	70	Marylebone Road
1999	1 (3%)	40	60	Marylebone Road
2000	4 (12%)	33	846	Redbridge 2
2001	3 (8%)	40	824	Redbridge 2
2002	2 (4%)	55	957	Redbridge 2
2003	7 (10%)	67	471	Marylebone Road
2004	7 (10%)	72	3874	Lambeth 4
2005	11 (13%)	87	3744	Lambeth 4
2006	12 (14%)	88	3752	Lambeth 4

119. Data from the LAQN for the period from 2002 to 2004 has been examined in some detail (see Table A3.5 in Annex 3 and Table 3.1 for data discussed in these paragraphs). Annual average NO_x levels at the eight kerbside sites in the LAQN increased slightly from 2002 to 2003 and then fell back to 2004. Over this same period NO_2/NO_x ratios increased steadily at all but one site (Camden 1 – Swiss Cottage). The greatest increase from 0.27 to 0.36 was recorded at the Marylebone Road site.

120. Annual average NO_x levels at the 36 roadside sites increased between 2002 and 2003 before dropping back in 2004. Over this same period, NO_2/NO_x ratios increased at all but two sites (Havering 1 – Rainham, Greenwich 7 – Blackheath). The greatest increase was noted at a roadside site was from 0.366 to 0.495 at the Hillingdon 2 – Hillingdon Hospital site.

121. Annual average NO_x levels at the 28 urban background sites in the LAQN increased between 2002 and 2003 before dropping back in 2004. Over this same period, NO_2/NO_x ratios increased steadily at all but four sites (Castle Point 1 – Town Centre, Enfield 3 – Salisbury School Ponders End, Waltham Forest 1 – Perth Terrace, Lambeth 3 – Loughborough Junction). The greatest increase from 0.452 to 0.560 was reported for the Bloomsbury – AURN site.

122. There was no significant change in the NO_2/NO_x ratio between 2002 and 2004 over the ten suburban sites. The average increase in the NO_2/NO_x ratio from 2002 to 2004 over all the 66 LAQN sites was 0.031 ± 0.037.

3.3.2 Summary of analysis of monitoring data

123. The increases in the NO_2/NO_x ratios during the 2002 – 2005 period were first noticed at 44 roadside and kerbside sites in London. In addition, evidence of increasing annual mean NO_2/NO_x ratios between 2002 and 2004 has been found at 24 out of the 28 urban background sites in the LAQN. Increases in NO_2/NO_x ratios have therefore been widespread across London.

124. Increased NO_2/NO_x ratios have been observed at eight out of the 13 roadside and kerbside national network sites outside of London over the same period, at one out of 23 urban background sites and three out of 16 urban centre sites. Examples of roadside and kerbside sites outside of London that have seen NO_2/NO_x concentration ratio increases include: Bath, Brighton, Bury, Dumfries, Hove, Inverness, Oxford and Wrexham.

125. There are a number of national network sites outside of London where no changes have been observed over the 2002 – 2005 period in NO_2/NO_x ratios. There have been no significant changes in the annual mean NO_2/NO_x ratios at any of the rural sites. Some urban sites do not have long enough records to be sure either way. At 13 out of 23 urban background sites, eight out 16 urban centre sites and three out of 13 roadside and kerbside AURN sites there is clear evidence that NO_2/NO_x concentration ratios have remained unchanged. Examples of kerbside and roadside sites outside of London where NO_2/NO_x ratios have remained unchanged include: Cambridge, Glasgow and Yarm.

126. We have not been able to investigate the reasons why monitoring data for roadside and kerbside sites is consistent with an increase in f-NO_2 at some sites outside London while no increase has been observed at other sites. This is due to a lack of detailed local information on the site-to-site variation in the mix of vehicle technologies and fuels (such as the proportion of diesel Euro III cars and buses fitted with catalytically regenerative particle traps), which would be expected to influence f-NO_2. Predictions of f-NO_2 for London and for urban areas of the UK have been provided in Sections 2.11 and 2.12. The differing trends in ambient NO_2/NO_x ratios observed at roadside and kerbside sites across the UK suggest that f-NO_2 may show considerable variation from site to site depending on local traffic conditions and technology mix.

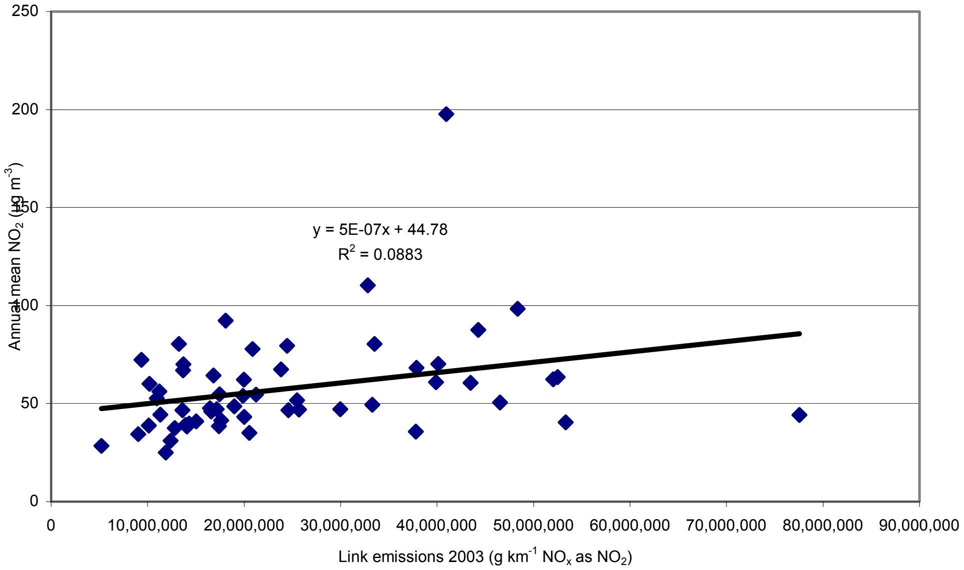
3.4 Is there a relationship between roadside nitrogen dioxide concentrations and traffic count data?

Yes. Some of the highest measured concentrations and locations with increases may be associated with higher bus counts.

127. An analysis of traffic count data has been carried out to identify factors that may be of relevance in determining which monitoring sites have the highest roadside NO_2 concentrations. Census points have been assigned to 53 national network and LAQN and associated site locations in London and the South East. Measurement statistics have been compared with daily traffic count data by vehicle type from 2000 to 2004 and roadlink emission estimates for 2003 from the NAEI.

128. Figure 3.13a shows that there is little relationship between measured annual mean NO_2 concentrations and NO_x emissions from all traffic. There is also little relationship with emissions from car, LGV or HGV vehicle classes. Figure 3.13b, however, shows that annual mean concentrations are more closely correlated with estimates of emissions from buses. The monitoring sites at Lambeth 4, Marylebone Road, Lewisham 2 (Old Kent Road) and Ealing 6 (Hanger Lane) are highlighted. The site at Lambeth 4 has by far the highest measured concentrations and, interestingly, the fifth highest bus count of all major roads in the UK (4752 annual average daily flow in 2004). Marylebone Road has the second highest annual mean NO_2 concentration and a relatively high bus count. The relationship with bus count is, however, not repeated at all sites including the outliers at Ealing 6 (Hanger Lane) and Lewisham 2.

Figure 3.13a: A comparison of annual mean nitrogen dioxide concentrations and estimated road link traffic nitrogen oxides emissions from the National Atmospheric Emissions Inventory for roadside sites in London and the south east.



129. Table A2.6 shows the correlation coefficients for these 53 roadside monitoring sites between measured parameters in 2004 and traffic count and emissions estimates for 2003. This confirms the closer relationship between bus counts and annual mean and 98th percentile NO_2 concentration than for the other traffic classes. While the count data for most traffic classes correlate well with each other the bus count show only a weak correlation with motorcycle counts and poor correlation with all other classes.

Figure 3.13b: A comparison of annual mean nitrogen dioxide concentrations and estimated road link bus nitrogen oxides emissions from the National Atmospheric Emissions Inventory for roadside sites in London and the south east.

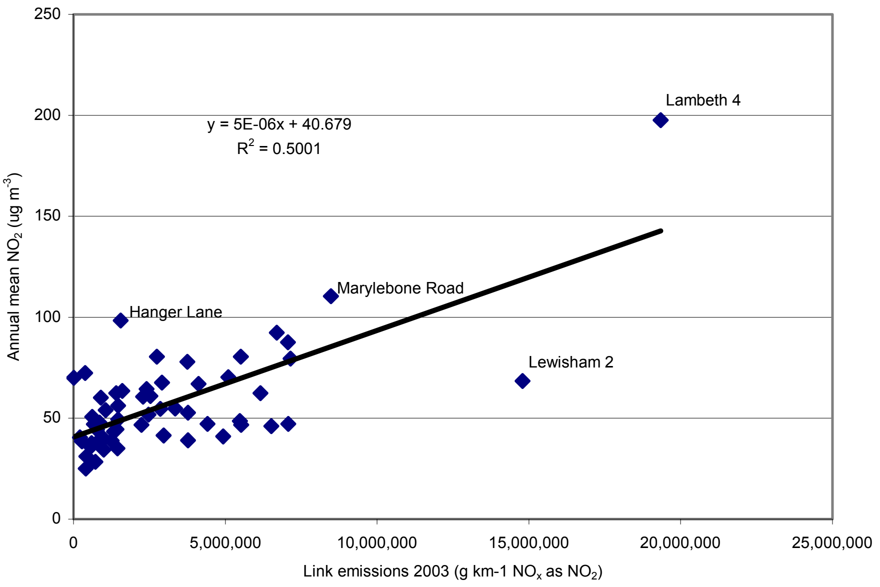
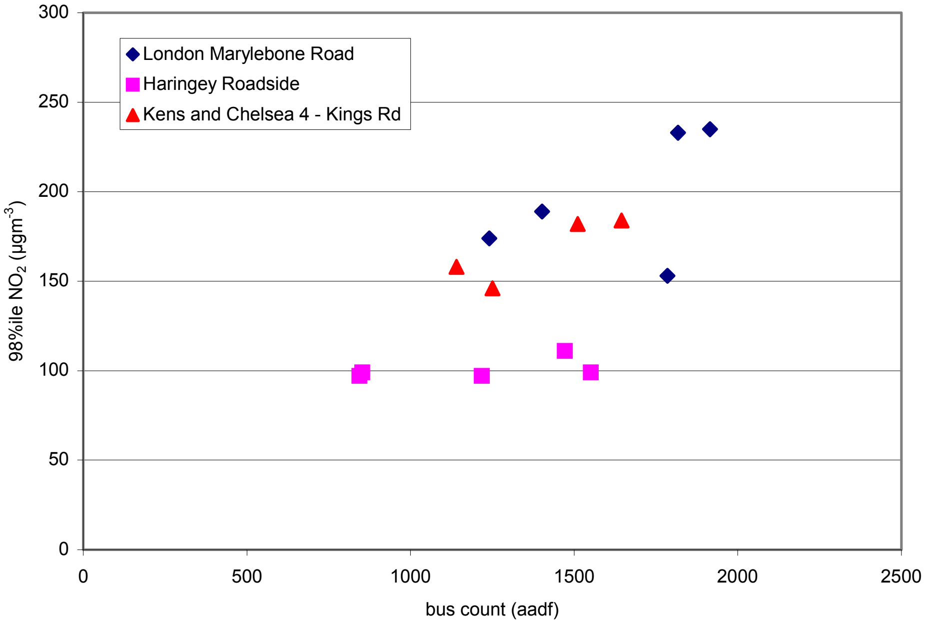


Figure 3.14: 98th Percentile nitrogen dioxide concentrations and bus counts for different years 2000 – 2004.

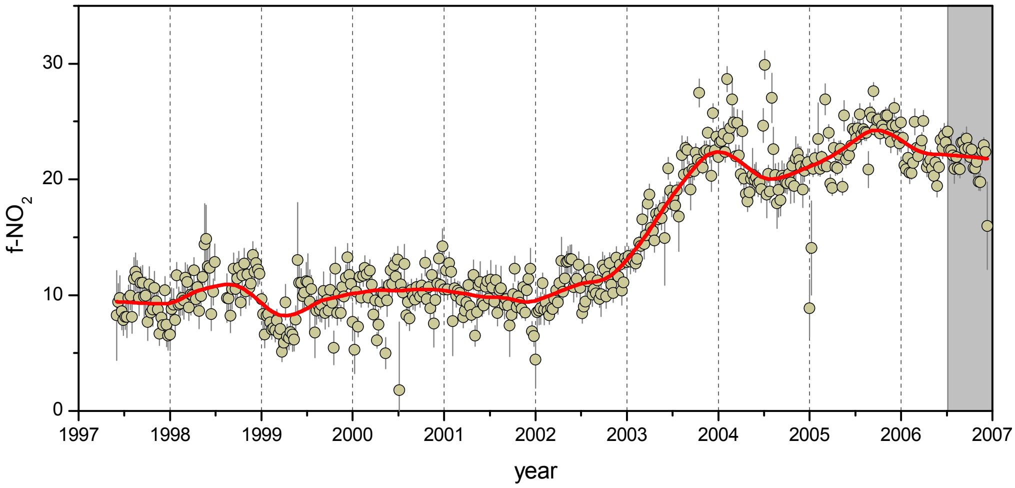


130. We have also examined the change in traffic count data from 2000 to 2004 and the changes in NO_2 concentrations. Both the concentrations and the bus counts have increased at Marylebone Road and Kensington and Chelsea 4 (Kings Road). The bus count has also increased at Haringey 1 (Town Hall) but the NO_2 concentration has remained roughly constant (Figure 3.14). It is possible that an increase in f-NO_2 at Haringey Roadside has been offset by a reduction in total NO_x concentrations at this site.

131. Box A3.1, Annex 3 and Carslaw and Beevers (2005) describe a method of estimating road vehicle f-NO_2 from the modelling of ambient concentration data. This model has been applied to 37 monitoring sites in the LAQN for 2004. Previous work had considered earlier years. On average it is estimated that the mean f-NO_2 is 18.3% (range 7.4 to 30.3%) at these sites. In 2002, for example, it is estimated that the mean level in London was about 13.0%. Individual site data are shown in Table A2.7. Emissions data were used from LAEI calculations for 2004 (Sean Beevers, personal communication).

132. Figure 3.15 shows the estimated weekly f-NO_2 at Marylebone Road derived using the method of Carslaw and Beevers (2005). The ratio remained roughly constant from 1997 to late 2002. This was followed by a steep increase to the end of 2003 with a subsequent more gentle increase during 2004 and 2005 and finally followed by a gentle decrease from mid 2005. Figure 3.16 shows the trend in the estimated NO_2/NO_x emission ratio at London roadside and kerbside sites from 1997 to 2005. There is therefore little evidence to suggest that f-NO_2 has continued to increase from the beginning of 2004. Annex 3, Figure A3.1 shows the estimated trends in f-NO_2 at the individual sites in London. There is considerable variation in f-NO_2 between the sites and in the timing and gradient of the trends. Almost all sites show an increase over the period and a number of sites show steepest increases between 2002 and 2004, in common with the London Marylebone Road monitoring sites.

Figure 3.15: Estimated weekly nitrogen dioxide/nitrogen oxides emission ratio (f-NO_2) at Marylebone Road derived using the method of Carslaw and Beevers (2005). Error bars are shown at 2σ. Data for the second half of 2006 are provisional.

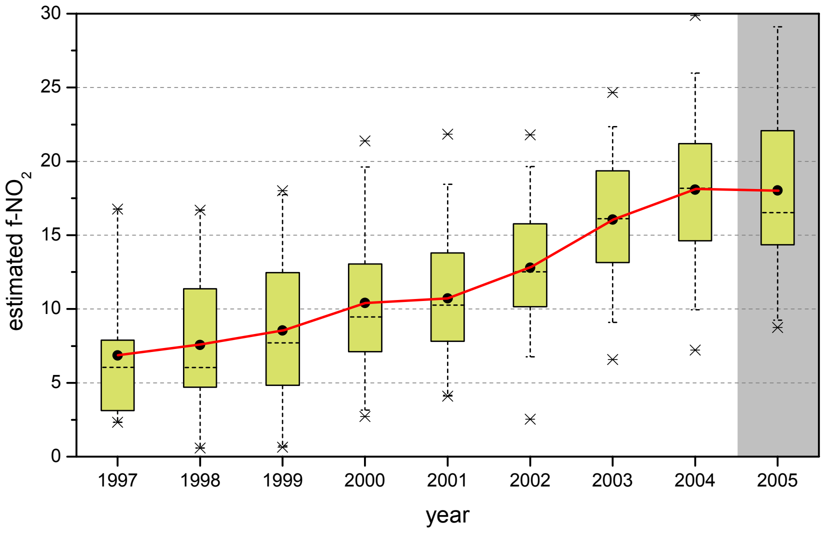


133. Based on individual site data, a multiple regression has been used to estimate the mean f-NO_2 for different vehicle types. The regression links the estimated NO_2 concentration due to primary NO_2 (i.e. the primary NO_2 fraction multiplied by the increment in NO_x concentration above a suitable background site) with the estimated concentration of NO_x due to different vehicle types. The latter has been estimated using the NO_x emission estimates provided by ERG expressed as a fraction of the NO_x concentration estimate above background. The following model was obtained:

$$[NO_2]_{primary} = 0.39\ (\pm 0.02)[NO_x]_{buses} + 0.12\ (\pm 0.05)[NO_x]_{HGVs} + 0.18\ (\pm 0.05)[NO_x]_{cars+LGVs} - 1.35\ (\pm 0.76)$$

This suggests f-NO_2 values of around 39% for buses, 12% for HGVs and 18% for cars and LGVs considered together.

Figure 3.16: Trend in the estimated nitrogen dioxide/nitrogen oxides emission ratio (f-NO_2) at London roadside and kerbside sites (1997-2005). The solid circles connected by the line show the mean in each year. The box shows the 25th and 75th percentiles. Note that most data for 2005 are provisional.



134. Figure 3.17(a) shows the results of applying the regression at the 37 sites. In general there is excellent agreement between the two data sets (r^2=0.96). However, it is also clear that there is an outlier with a very high level of primary NO_2. This is the Lambeth 4 site. Because the multiple regression could be adversely affected by the outlier, the multiple regression was applied without Lambeth 4 (Figure 3.17 (b)). Here, the relationship is still good (r^2=0.85). The individual vehicle specific f-NO_2 percentages for both models are shown in Table 3.3. These results show that the ratios calculated are not sensitive to the inclusion of Lambeth 4: both models provide a very good explanation of the estimated f-NO_2 for different vehicles.

Figure 3.17: a) Estimated primary nitrogen dioxide derived from the analysis of measurements vs. multiple regression model for all 37 monitoring sites, b) for all sites except Lambeth 4, shown as the outlier in a).

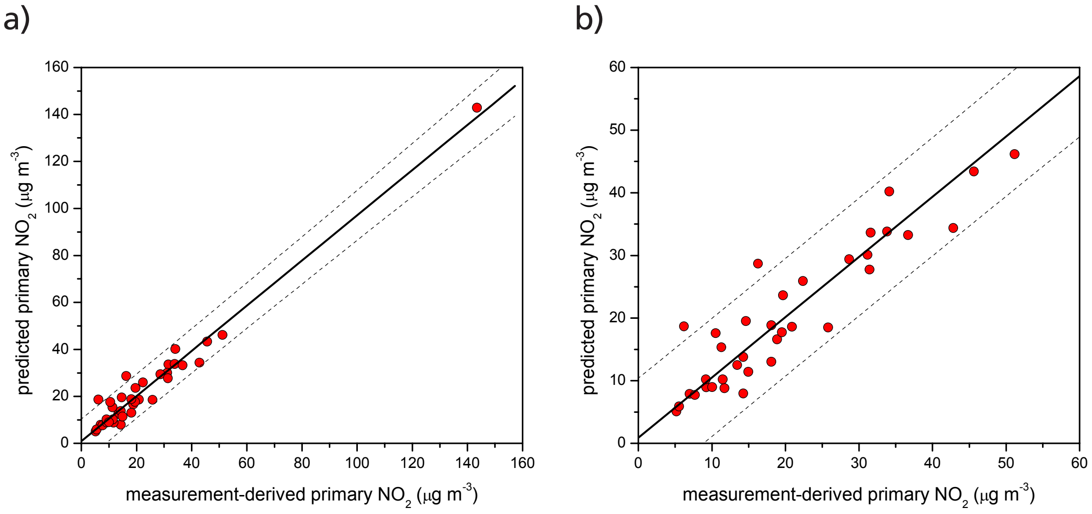


Table 3.3: Mean nitrogen dioxide/nitrogen oxides emission ratio (f-NO_2) results estimated from the multiple regression model with and without the Lambeth 4 site.

Scenario	Car + LGV	HGV	Bus
All sites	18.1 ± 5.2	12.4 ± 5.1	38.6 ± 2.4
Without Lambeth 4	18.3 ± 5.3	11.9 ± 5.4	37.5 ± 4.8

135. Thus estimates of road vehicle f-NO_2 from derived from a combination of measured concentrations in London and emission inventory estimates of NO_x emissions for different vehicle classes suggest that f-NO_2 is greatest for buses, with lower values for cars and LGVs and HGVs.

136. The estimated f-NO_2 values for HGVs, buses and cars + LGVs can be used to estimate the mean contribution made by these vehicles to the NO_x and NO_2 along a sample of 37 roads in London. Using the roadside increments in NO_x concentration at the 37 sites shown in Table A2.7 it can be shown that each vehicle type accounts for the following proportions of NO_x: HGVs = 31%, buses = 26% and car + LGV = 43%. For NO_2 the following proportions were derived: HGVs = 18%; buses = 46%; car + LGV = 36%. On this basis, buses account for the least NO_x road emissions at these sites and the majority of road NO_2 emissions. These estimates have been derived from an analysis at 37 monitoring sites and the results could be considered as reasonably representative of London as a whole, given the range of road types and traffic conditions represented by these sites.

3.5 Can we use change-point detection to understand the reasons for observed changes in nitrogen dioxide and particulate matter concentrations at roadside monitoring sites?

Yes. Some of the more noticeable changes in concentrations appear to be associated with changes in traffic management or vehicle fleet composition.

137. An approach has been developed to detect abrupt changes to the concentration of NO_2 and other species in ambient time series data (Carslaw *et al.*, 2006). Such changes can arise for various reasons, for example, the rapid introduction of a new technology or a traffic management measure. The method is based on a cumulative sum technique (CUSUM), which is a simple but effective approach for detecting small changes in time series (see Barratt, 2005). The technique has been further developed here to include a quantification of the uncertainty in the timing of the change-point (the uncertainty level) and the uncertainty interval associated with it. The uncertainty quantification has been derived using randomisation and bootstrap re-sampling techniques. These methods are appropriate where the uncertainty distribution is non-normal as is the case for most air pollutant concentration distributions. The technique has been applied to two sites: Marylebone Road (kerbside) in central London and the Oxford Centre (roadside) site.

138. Figure 3.18 shows the time series of NO_x and NO_2 concentrations at the Oxford Centre site and the associated CUSUMS. Figure 3.18(b) shows that three change-points were identified for NO_x and two for NO_2, which are shown with their uncertainty levels and intervals in Table 3.4. Of particular note are the two change-points identified for NO_2 in June 1999 and August 2002. To investigate the possible reasons for these change-points, the trend in f-NO_2 for the road was calculated as described in Box A3.1 and Carslaw and Beevers (2005), shown in Figure 3.19. In the analysis, Harwell was used as a background site and meteorological data from Heathrow Airport were used. Two notable increases in primary NO_2 seem to have occurred: during the latter half of 1999 (although there are some data points missing due to low data capture) and also in the latter half of 2002. The timing of these points ties in well with the CUSUM analysis of NO_2, which suggests increases in primary NO_2 at these points as an important factor affecting observed concentrations. There are two likely causes of these changes. The change in 1999 is likely to be associated with the introduction of the Oxford "bus gate" in June 1999, where bus numbers increased considerably while flows of other vehicle types reduced (Roger Pitman, Oxford City Council, personal communication). The second change-point could be due to the increased use of CRT® on some Oxford buses. Information is available from the Oxford Bus Company[10] suggests that 89% of their buses are fitted with CRT®. Their programme of fitting buses began in 2001. From emissions data presented, the most significant reduction in hydrocarbons, CO and PM occurred between 2001/02 and 2002/03, consistent with the change points identified. Nevertheless, full information on the numbers of these buses used along that specific road is not known and hence there remains some uncertainty associated with the causes of change-point in NO_2.

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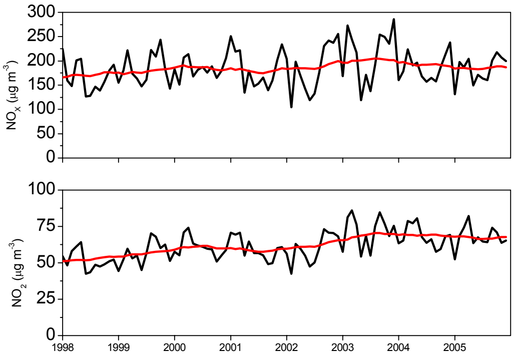
[10] (http://www.oxfordbus.co.uk/air/pollutants.pdf)

Figure 3.18: a) Monthly time series of nitrogen oxides and nitrogen dioxide at Oxford Centre (1998-2005) b) Cumulative Sums calculated for nitrogen oxides and nitrogen dioxide at the Oxford centre site (1998-2005). The vertical dashed lines show change-points that are statistically significant at the 95% confidence level. The histograms highlight the uncertainties associated with the timing of the change-point, normalised such that the area under them is equal to 100.

a)



b)

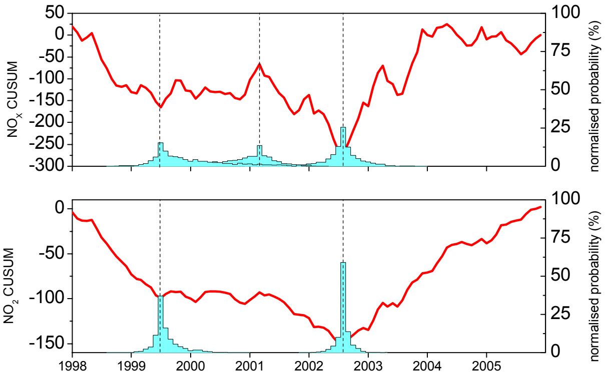


Figure 3.19: Estimated trend in the monthly f-NO$_2$ at Oxford Centre roadside site.

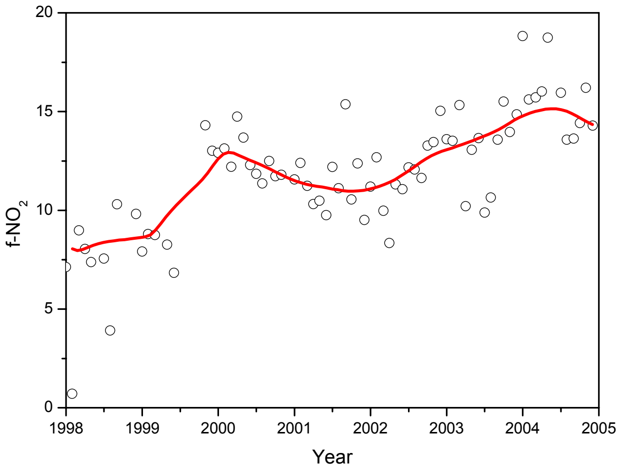


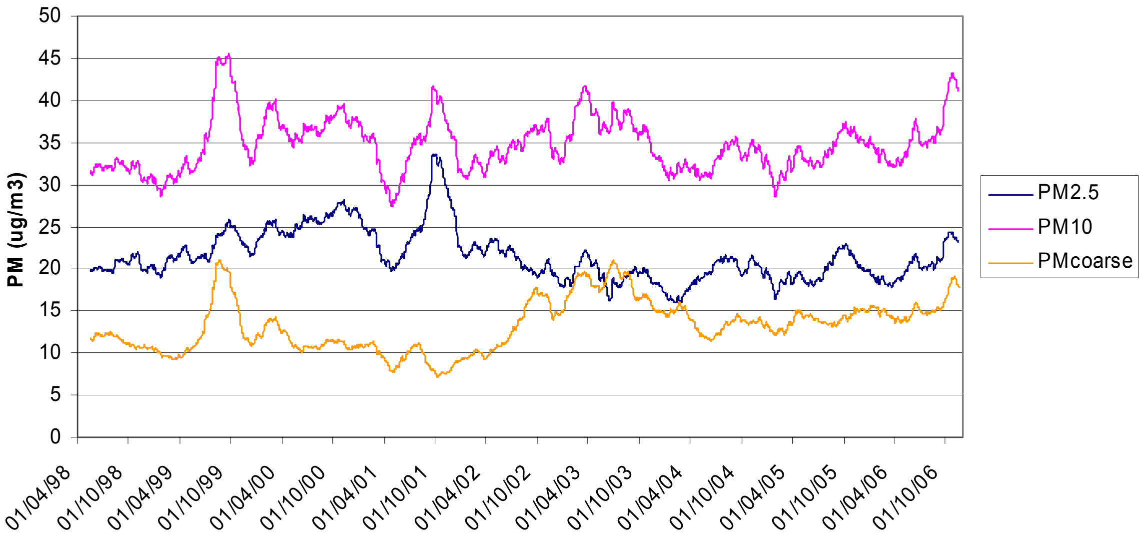
Table 3.4: Change-points identified for nitrogen oxides and nitrogen dioxide with a confidence level greater than 95%.

Species	Date	Confidence level	Confidence interval
NO_x	Jun. 99	96.2	Feb. 99 – Jul. 01
	Mar. 01	95.2	Nov. 99 – Oct. 01
	Aug. 02	97.2	Oct. 01 – Feb. 03
NO_2	Jul. 99	100.0	Mar. 99 – Dec. 00
	Aug. 02	100.0	Apr. 02 – Nov. 02

139. It is possible that the fitting of traps to reduce PM emissions from buses has lead to an increase in f-NO_2. It is therefore instructive to consider the trends in PM, NO_x and NO_2 at Marylebone Road. Figure 3.20 shows 90-day rolling mean concentrations of PM_{10}, $PM_{2.5}$ and PM_{coarse} for the Marylebone Road, London site from March 1998 onwards. A linear regression analysis of these data showed that all three PM components exhibited statistically significant trends as follows (calculated from the 90-day rolling mean concentrations):

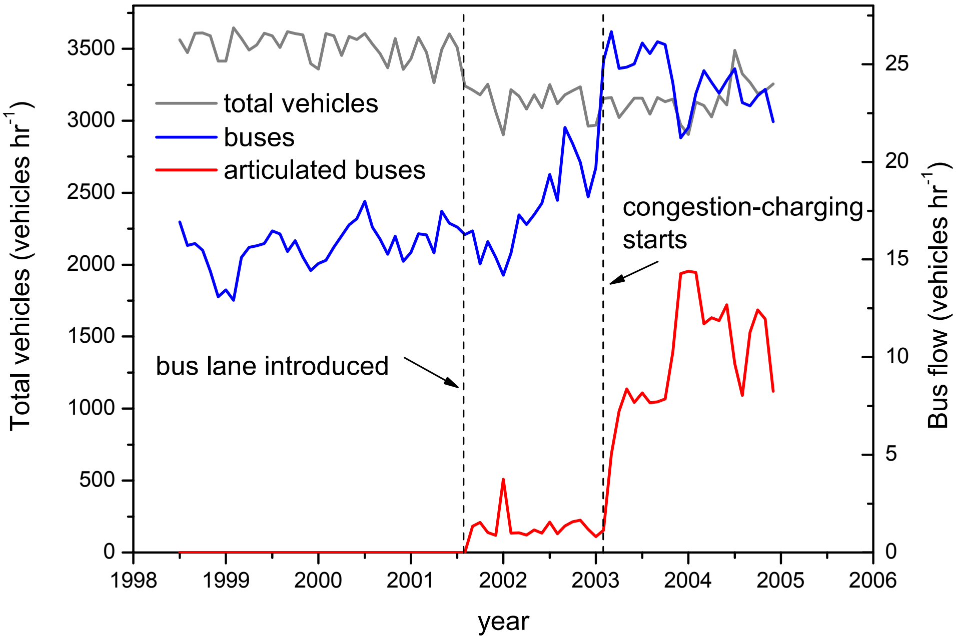
$PM_{2.5}$:	downwards trend of -0.50 ± 0.02 μg m^{-3} $year^{1}$
PM_{10}:	upwards trend of +0.03 ± 0.02 μg m^{-3} $year^{1}$
PM_{coarse}:	upwards trend of +0.53 ± 0.02 μg m^{-3} $year^{1}$

Figure 3.20: Long-term trends in 90-day running mean PM_{10}, $PM_{2.5}$ and PM_{coarse} at Marylebone Road, London (μg m^{-3}, TEOM). 2006 data are provisional.



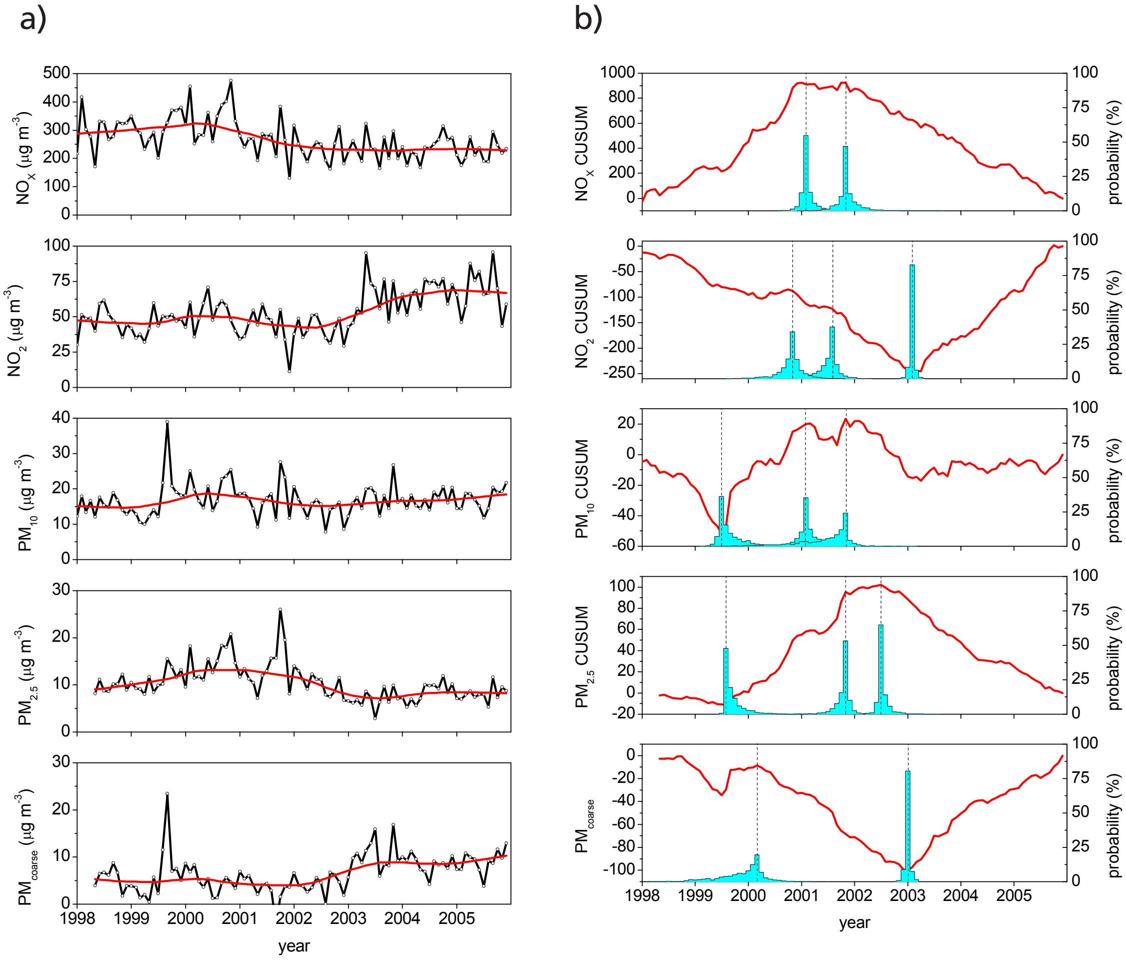
140. Figure 3.21 shows the flows of different vehicle types along Marylebone Road as recorded by an automatic traffic counter. The bus flows are shown only for the bus lanes because they can be unambiguously identified due to its strict enforcement. Figure 3.21 shows that total bus flows increased during 2002 and increased markedly close to the time of the introduction of the London congestion charging scheme.

Figure 3.21: Vehicle flows at Marylebone Road recorded by the automatic traffic counter. The total vehicle flow is that for all six lanes. The bus and articulated bus flows are those for the bus lanes only.



141. The trends in NO_x, NO_2 and PM at Marylebone Road have been investigated further in the time series concentrations and CUSUM analysis results shown in Figure 3.22. In addition to NO_x and NO_2, it has also been possible to consider different particle concentrations (as measured by TEOM): PM_{10}, $PM_{2.5}$ and PM_{coarse} (defined as $PM_{2.5-10}$). To increase the influence made by the road on the concentration of these species background concentrations have been subtracted. In the case of NO_x and NO_2 the North Kensington site was used and for the particle concentrations Harwell was used. For NO_2, a highly statistically significant change-point (an increase in NO_2) was detected in February 2003 coinciding with when congestion charging commenced (see Table 3.5). At this time, bus numbers (with catalytically regenerative particle traps) increased as shown by Figure 3.21. A change-point was also detected for $PM_{2.5}$ in June 2002 with a 95% confidence interval from April-August 2002, where concentrations decreased. This change-point might be associated with the TfL programme of fitting traps to buses, which commenced before congestion charging. However, the timing of the change-point detected for a decrease in $PM_{2.5}$ is less certain that the timing of the increase in NO_2.

Figure 3.22: a) monthly mean increment in concentration above a background site for nitrogen oxides, nitrogen dioxide, PM_{10}, $PM_{2.5}$ and PM_{coarse}. The red line is a locally weighted regression smoothing fit. b) Cumulative sums calculated for each species. The vertical dashed lines show change-points that are statistically significant at the 95% confidence level. The histograms highlight the uncertainties associated with the timing of the change-point, normalised such that the area under them is equal to 100.



142. Figure 3.22 gives a strong indication that PM_{coarse} increased markedly at the beginning of 2003. Along with the change-point for NO_2 around this time, the uncertainty interval is narrow (the 95% confidence interval is from December 2002 to February 2003, as shown in Table 3.5). Currently, the factors leading to this increase are uncertain. However, the timing of the change is very close to that for NO_2, which might suggest a similar cause. Furthermore, Carslaw *et al.* (2006) show that the increase in PM_{coarse} pre and post congestion charging is most closely associated with the increase in bus flows along Marylebone Road. A contributory factor could be the increase use of articulated buses, which are considerably heavier than conventional buses. Heavier vehicles are known to result in increased emissions of non exhaust particle emissions (e.g. resuspended material, tyre and brake wear). More discussion of the possible causes of these and other change points can be found in Carslaw *et al.* (2006).

143. The proportion of London buses fitted with catalytically regenerative particle traps increased from 39% in 2002 to 79% in 2004 (see section 2.10.3). A more sudden change took place in February 2003 when the bus flow along Marylebone Road increased as shown in Figure 3.21. The change point analysis presented here suggests a decrease in $PM_{2.5}$ in June 2002, which may have been associated with the fitting of catalytically regenerative particle traps to buses. The analysis also clearly identifies more sudden increases in NO_2 and PM_{coarse} in early 2003 coinciding with the increase in bus flow. It is worth noting that $PM_{2.5}$ concentrations did not increase at this time.

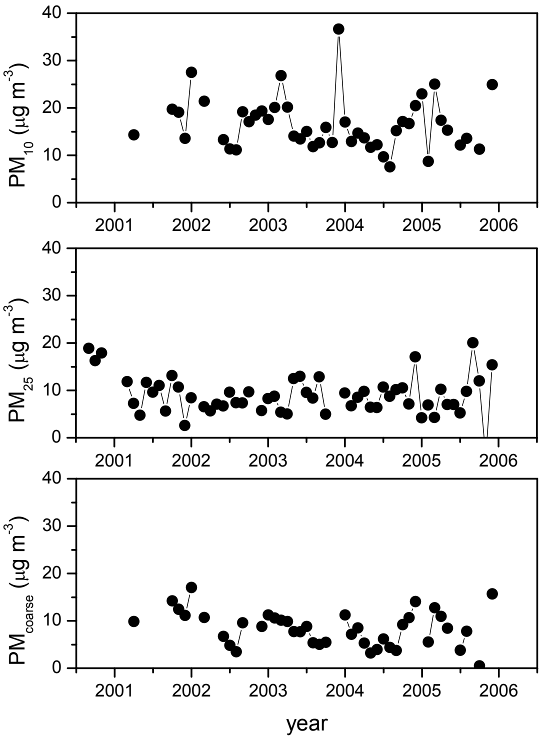
Table 3.5: Estimated change-point dates with associated confidence levels and confidence intervals for monthly concentrations of nitrogen oxides, nitrogen dioxide, PM_{10}, $PM_{2.5}$ and PM_{coarse}. Only change-points with a confidence level of greater than 95% are shown.

Species	Date	Confidence level	Confidence interval
NO_x	Feb 01	100.00	Nov. 00 – Jun. 01
	Nov. 01	99.79	Jul. 01 – May 02
NO_2	Nov. 00	100.00	May 00 – Apr. 01
	Aug. 01	100.00	Oct. 00 – Nov. 01
	Feb. 03	100.00	Jan. 03 – Mar. 03
PM_{10}	Jul. 99	99.70	Jun. 99 – Jun. 00
	Feb. 01	99.47	May 00 – Dec. 01
	Nov. 01	99.79	Nov. 99 – Jun. 02
$PM_{2.5}$	Aug. 99	100.00	Aug. 99 – May 00
	Nov. 01	100.00	Jun. 01 – Jun. 02
	Jun. 02	100.00	Apr. 02 – Aug. 02
PM_{coarse}	Mar. 00	100.00	Dec. 99 – Apr. 00
	Jan. 03	100.00	Dec. 02 – Feb. 03

144. Since the publication of the draft version of this report, concerns were raised over the TEOM measurements of $PM_{2.5}$ prior to 2003 (Fuller, 2006). These concerns relate to the instrument not being part of national quality control and quality assurance procedures prior to 2003 (i.e. there is no documentation relating to its operation) and the fact that time series of $PM_{2.5}$ TEOM measurements do not reflect trends observed at several other sites in London. While it is difficult to fully establish whether the change-points identified for $PM_{2.5}$ and PM_{coarse} are real or related to some instrument problem, it is prudent to treat these results with caution.

145. Due to the concerns over the TEOM $PM_{2.5}$ measurements, time series of PM_{10}, $PM_{2.5}$ and PM_{coarse} have also been derived using gravimetric partisol instruments using daily mean concentrations. Only months where data capture was greater than 50% were used and urban background concentrations were subtracted using data from the North Kensington site. Time series of these data are shown in Figure 3.23. There were insufficient data to run the change-point analysis on $PM_{2.5}$ and PM_{coarse} using the same methods as for the TEOM instrument. However, from a visual inspection of Figure 3.23 there are no obvious, consistent changes to the concentrations of $PM_{2.5}$ and PM_{coarse}. If these data are assumed to represent PM concentrations at this site, then it would be concluded that there was neither a reduction in $PM_{2.5}$ (assumed to be most likely due to buses) nor an increase in PM_{coarse}. The effect of fitting catalytic particle filters to buses (and other vehicles) on concentrations of PM is therefore a topic that warrants further investigation.

Figure 3.23: a) Monthly mean increment in concentration above North Kensington for gravimetric PM_{10}, $PM_{2.5}$ and PM_{coarse}. Only months with data capture greater than 50% are shown.



3.6 Have measurements consistent with increases in f-NO_2 also been observed in other European Countries?

146. An expert meeting was held in Bonn at the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety on 15 September 2005. This meeting considered first analyses of the causes of the air quality development and impacts of different technologies on NO_2 emissions of motor vehicles. The meeting concluded that:

    - In Germany, NO_2 concentrations near many heavily polluted roads have hardly decreased over the past years – they have even increased at some sites.
    - The explanation that direct NO_2 emissions in vehicle exhaust make a relevant contribution to roadside NO_2 concentrations is supported by many experts.

147. An EU level workshop was held in Brussels on 19 September 2006 on the impact of direct emissions of NO_2 from road vehicles on NO_2 concentrations (EU, 2006). This workshop considered the status of air quality legislation and the vehicle emissions regulations currently under development, the evidence from ambient NO_2 concentrations and the contribution of road sources and the current status and future outlook on vehicle technology and emissions abatement technology. A number of points were made at the workshop are summarised in Box 3.2.

148. Evidence was presented at the workshop of an increasing trend in f-NO_2 in several member states including Germany, The Netherlands and the United Kingdom.

149. An analysis of monitoring data for Baden Wurtemberg in Germany suggests that the primary NO_2 fraction, f-NO_2 has increased from about 5% to about 20% over the period from 1995 to 2005 (Kessler *et al.*, 2006). This has been linked with an increase in the number of modern diesel cars fitted with oxidation catalysts.

150. Hueglin *et al.* (2006) have examined data from a roadside monitoring site situated on a motorway in Switzerland. They also found a much smaller downward trend in ambient NO_2 concentrations than in ambient NO_x at this site. They conclude that this indicates an increase in f-NO_2 from 14% in 1992 to 23% in 2004.

151. Monitoring data from across the EU is available from Airbase (2007). Ambient monitoring data for a selection of roadside sites in different member states have been down loaded and are presented in Figure 3.24. Roadside annual mean concentrations of NO_x, NO_2 and, if available, O_3 have been plotted for sites in the Czeck Republic (Prague), France (Paris), Germany (Stuttgart and Karlsruhe in Baden Wurtemberg), The Netherlands (Haarlem and Utrecht) and Spain (Barcelona). The monitoring data are consistent with an increase in f-NO_2 at some of the sites in these member states and the evidence is more mixed in others. In selecting these monitoring sites we have chosen those with relatively high ambient NO_2 concentrations and data capture to provide a reasonable geographical coverage.

152. The graph for Prague (Figure 3.24a) republic shows little clear trend in NO_x or NO_2 concentrations over the period from 2000 to 2004, although there is some evidence of an increase in O_3 concentrations. There is a clear decrease in NO_x concentrations at the sites in Paris (Figure 3.24b) over the period from 1995 to 2005 but there is little change in or an increase in NO_2. The data for Baden Wurtemburg (Figure 3.24c) show a similar trend, with perhaps more evidence of an increase in NO_2 in recent years. Figure 3.24d shows that O_3 concentrations have increased at the roadside as NO_x concentrations have declined but there has been little change in NO_2 at these sites in the Netherlands. The data for Barcelona shows a mixed picture with one site showing a decrease in NO_2 as NO_x has declined but another showing an increase in NO_2 (Figure 3.24e).

Box 3.2 Summary of EU workshop on the impact of direct emissions of nitrogen dioxide from road vehicles on nitrogen dioxide concentrations

- Observations and projections of ambient NO_2 concentrations suggest that there will be widespread non-compliance with the existing limit values when they enter into force in 2010.
- While the concentrations of ambient NO_x are on a downward trend, concentrations of NO_2 have often been static or even rising. Atmospheric chemistry alone cannot account for this behaviour. The short-term limit on NO_2 was not exceeded in the past but it now is.
- The development of ambient NO_2 concentrations as observed near roadsides can be explained by an increasing contribution of direct emissions of NO_2 specifically from diesel-powered vehicles, both light-duty and heavy-duty. Instead of the 5% share of NO_2 in the emitted NO_x typically assumed in standard atmospheric pollution models, modern diesel cars can be as high as 30-80%. This trend in ambient concentrations of NO_2 is expected to continue and to exacerbate any non-compliance with ambient limit values in 2010.
- Nitrogen dioxide is not the only nitrogen species of pollutant to give rise to concern:
  - Nitrous acid is emitted in a constant ratio to NO_x or NO_2.
  - Nitrous oxide has been found to be formed in de-NO_x technology in stationary applications.
  - The rising share of NO_2 in NO_x may have implications on the O_3 chemistry even in a situation of decreasing overall NO_x levels.
- The rising direct NO_2 emissions from diesel vehicles are caused by the use of exhaust aftertreatment equipment, including oxidation catalysts (mostly since the introduction of Euro III standards for light-duty vehicles) and retrofitted CRT® on urban buses. This equipment has been introduced in order to address other types of health-related air pollution (CO, hydrocarbons and PM) but it is now seen to create problems related both to the health impact from NO_2 and to the legal compliance of Member States in view of EU limit values.

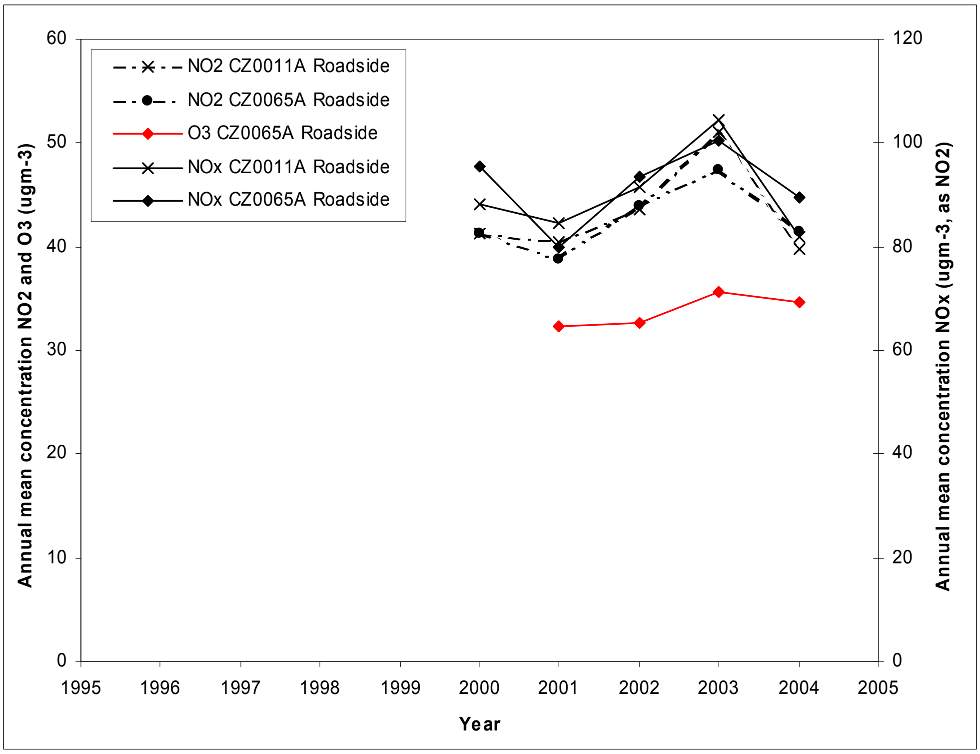
- The introduction of low-sulphur fuel may also act to increase the efficiency of the oxidation catalyst, thereby exacerbating the NO_2 problem.
- Where CRT® have been retrofitted, this was sometimes done on old buses (Euro I/II). Due to the high raw NO_x emissions, a higher share of NO_2 in these cases has a higher impact than for Euro V/VI vehicles.
- Nitrogen dioxide is mostly not seen as a pressing issue in the USA at the moment. The current USA limit values on NO_2 are not following the WHO advice to the same extent as those in the EU. However, they are based on less recent evidence than those in the EU. Diesel cars are expected to enter the US market but they will have to meet Tier II Bin 5 limit values, which are much stricter in terms of NO_x than even the currently discussed Euro VI standard. Retrofitted CRT® on urban buses may be more of an issue in the USA. California plans to take steps to constrain the NO_2/NO_x ratio in its diesel retrofit program in two steps.

153. Overall the evidence collected suggests that the trends in ambient NO_x, NO_2 concentrations and primary NO_2 emissions across Europe are similar to those in the UK described in this report. This situation has been found to be similar in a number of areas:

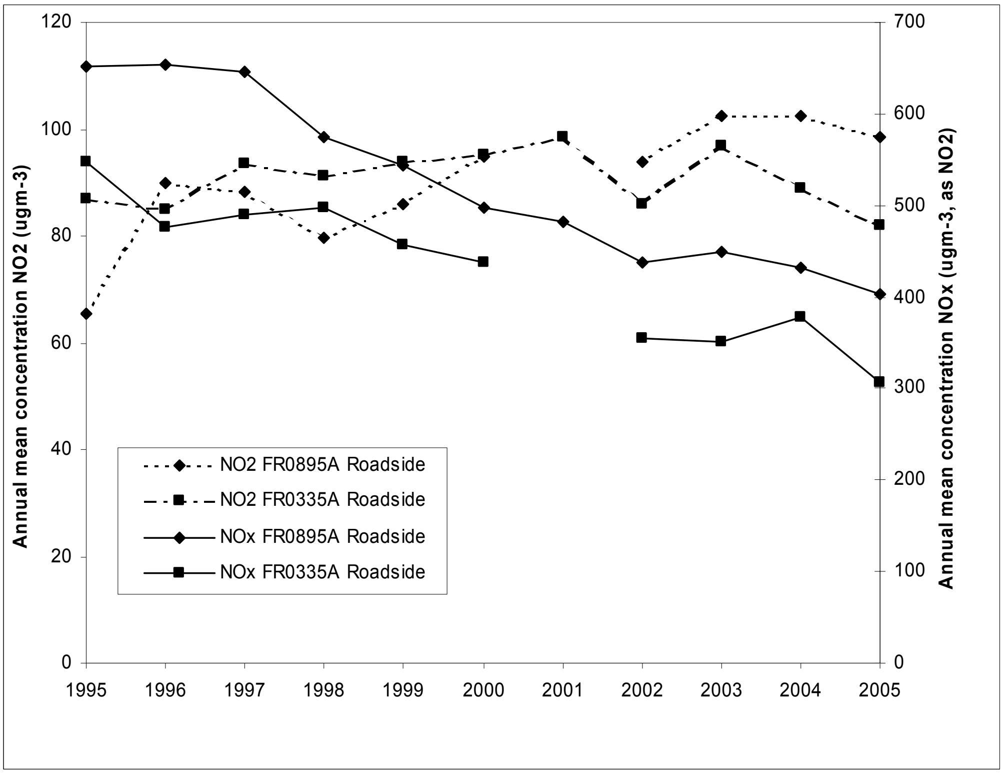
    - The indications of increases in f-NO_2 are strongest at roadside monitoring sites with high NO_x concentrations.
    - The pattern of changes in f-NO_2 is not consistent across all sites and ranges from large increases to no increase and is dependent on local traffic conditions and fleet composition.
    - The most likely reason for the widespread increase in f-NO_2 is thought to be the increasing number of light-duty diesel vehicles fitted with strong oxidation catalysts.
    - There is also evidence of a more dramatic increase in f-NO_2 at monitoring sites influenced by the increased use of catalytically regenerative particle traps on heavy-duty diesel vehicles.

Figure 3.24: Ambient monitoring data for selected roadside monitoring sites across Europe.

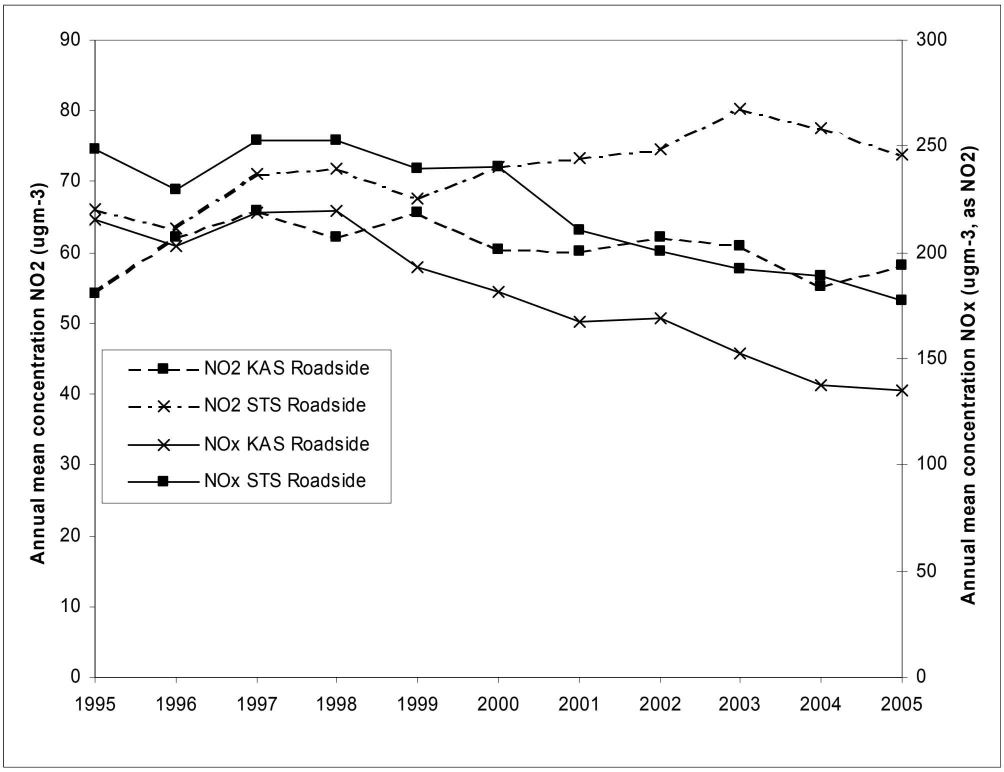
a) Prague, Czech republic



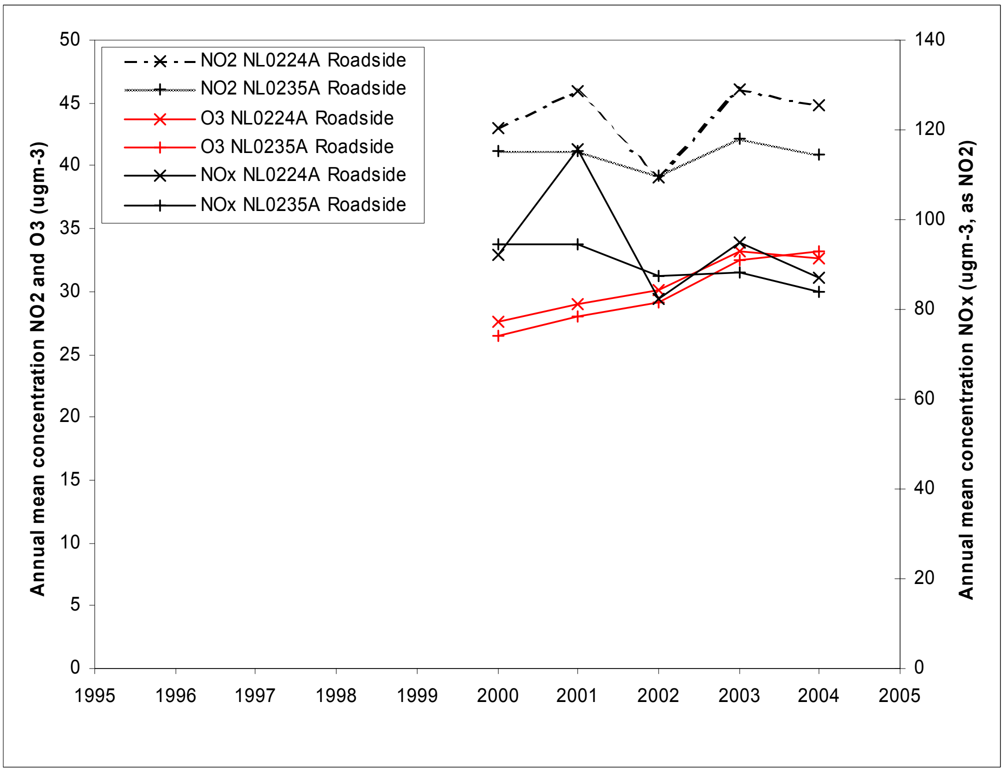
b) Paris, France



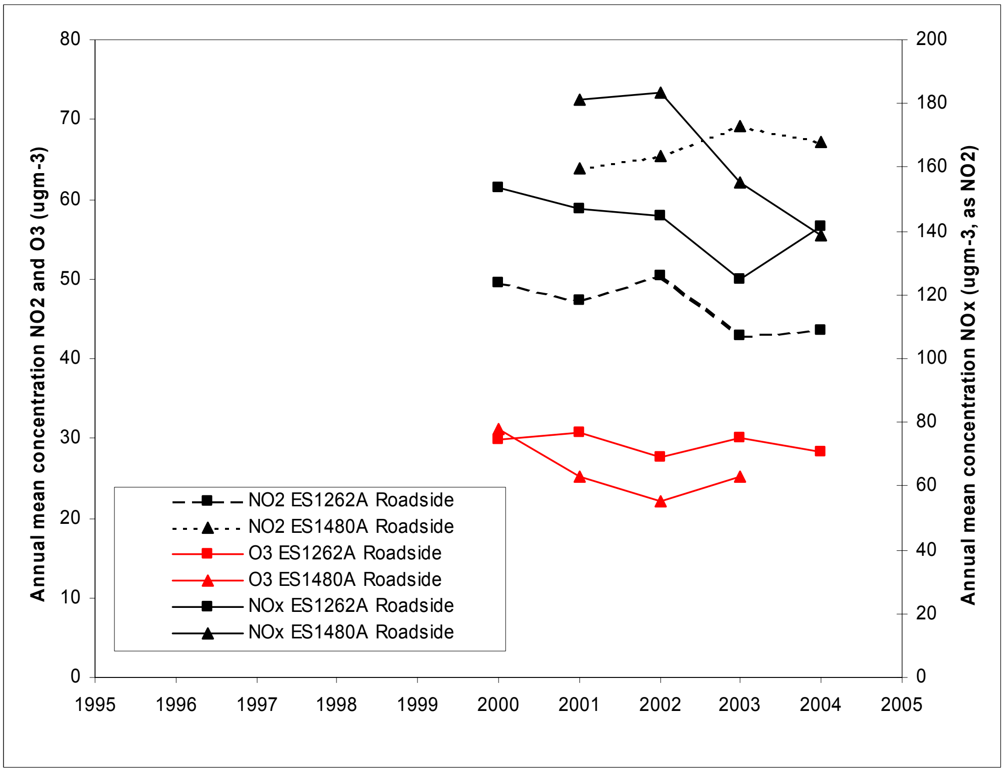
c) Stuttgart, Karlsruhe, Baden-Wurtemburg, Germany



d) Vlaardingen, Utrecht, The Netherlands



e) Barcelona, Spain



Chapter 4

Air quality modelling section

4.1 Can we show from first principles using models, that an increase in direct emissions of nitrogen dioxide can explain the observed changes in the partitioning between nitrogen dioxide and nitrogen oxides?

Yes, air quality models show that a modest increase, by 5% or so, in the direct emissions of NO_2 from urban road traffic can explain the observed changes in the partitioning between NO_2 and NO_x.

154. To answer this question, five air quality modelling approaches have been used to examine the influence of direct NO_2 emissions on NO_2 and NO_x concentrations in London. Because the NO_2/NO_x ratio depends on a range of factors including the NO_x concentration, all of the modelling teams were asked to investigate the influence of direct NO_2 emissions keeping all other factors the same, including the total NO_x emissions. That is to say, they were asked to use their base case model for 2002 and to report the influence of an absolute 5% increase in the direct emissions of NO_2 as a percentage of the total urban road traffic emissions (f-NO_2), say from 10% to 15%. The sensitivity case may be taken to represent an absolute 5% increase in direct emissions across-the-board or could represent a stronger increase in a particular sub-sector of urban road traffic.

155. The five modelling approaches are as follows:

- The constrained chemical model of Carslaw and Beevers (2005).
- The oxidant partitioning model (Jenkin, 2004a).
- LRCTM (London Routine Column Trajectory Model) model (Derwent, 1999).
- ADMS-Urban (Carruthers *et al.*, 2006).
- NETCEN model (Abbott *et al.*, 2006).

Annex 4 contains a summary description of the modelling approaches together with a detailed tabulation of the model results. Each model adopts a different formulation and addresses different air quality situations as described in AQEG (2004).

4.1.1 Modelled effect of a 5% absolute increase in primary nitrogen dioxide emissions at roadside and kerbside locations in London

156. Roadside and kerbside sites in London were modelled using the approach of Carslaw and Beevers (2005), see Annex 4, Box A4.1. A base case was set up for 2002 for 44 roadside and kerbside sites in the LAQN. The average annual mean model results for these sites for NO_2 and NO_x were 30.6 ppb and 78.1 ppb, respectively. An additional 5% primary NO_2 emission was added at each site to that previously estimated for the total road traffic f-NO_2, with total road traffic NO_x emissions remaining unchanged at their 2002 values. The resulting changes in the NO_2 and NO_x concentrations and their ratios are shown in Annex 4, Table A4.1. Average annual mean model NO_2 concentration increased to 32.9 ppb and the modelled annual mean NO_2/NO_x ratio increased from 0.409 to 0.437.

157. Annual average observed NO_x levels at the 44 LAQN roadside and kerbside sites increased between 2002 and 2003 before dropping back in 2004. Annual mean NO_2/NO_x ratios were observed to increase from 0.352 to 0.387 at the kerbside sites and from 0.394 to 0.434 at the roadside sites over this same period. The average increase in the annual mean NO_2/NO_x ratio was 0.040 ± 0.035 for the roadside and kerbside sites combined. This compares closely with the results from the Carslaw and Beevers (2005) model which gave an increase of 0.028 in NO_2/NO_x ratios for an absolute 5% increase in f-NO_2.

4.1.2 Results from the oxidant partitioning model of Jenkin (2004a)

158. Annual mean monitoring data from 56 urban UK sites reporting co-located measurements of O_3 and NO_x have previously been analysed to provide a method of describing NO_2/NO_x partitioning as a function of NO_x (Jenkin, 2004a), see Annex 4, Box A4.2. This analysis considered data up to 2001 and recommended site-dependent expressions to describe the NO_2/NO_x ratio for all 56 sites. These expressions have been used to calculate annual mean NO_2 concentrations, and NO_2/NO_x partitioning, based on the measured NO_x concentrations for the years 2002-2005, where the required data are available.

159. Annex 4, Table A4.2 presents a summary of the results, which indicate that the previously recommended expressions in AQEG (2004) provide a reasonable description of the annual mean NO_2 concentrations and NO_2/NO_x ratios in 2002, but underestimate these quantities in 2003-2005. Also presented are the results obtained for an illustrative increase of 5% in f-NO_2 at all sites. The corresponding results overestimate the annual mean NO_2 concentrations and the NO_2/NO_x ratios in 2002, but provide a good description of these quantities in 2003-2005. Although it is probable that the changes in the f-NO_2 have, in practice, varied from one site to another, this calculation suggests that an increase of approximately 5% is broadly appropriate for the years 2003-2005.

4.1.3 Modelled effect of a 5% absolute increase in f-NO_2 at urban background and suburban locations in London

160. The LRCTM model (Derwent 1999), see Annex 4, Box A4.3, was used to estimate the change in the ratio of the annual mean NO_2/NO_x concentrations at 33 urban background and 11 suburban sites in the LAQN network. A base case was set up with 20% f-NO_2 and the annual mean NO_2/NO_x ratios were estimated for each site. A sensitivity case was then modelled with an increase in the f-NO_2 to 25% from road traffic sources with no change in the total NO_x emissions. Annex 4, Table A4.3 presents the ratios in the base case and in the sensitivity case.

161. Annual mean NO_2/NO_x ratios increased across the urban background and suburban sites from 0.629 to 0.640 in the model calculations with an increase in f-NO_2. Overall, observed annual mean NO_2/NO_x ratios increased by 0.024 ± 0.031 at the urban background LAQN sites between 2002 and 2004 and there was no significant change at the suburban LAQN sites. This suggests that an absolute increase in direct NO_2 emissions of about 5% from urban road traffic is broadly appropriate for what has been observed at urban background sites between 2002 and 2004 in London.

4.1.4 ADMS-Urban calculations of impacts of changing priority nitrogen dioxide emissions in London

162. In this ADMS study, see Annex 4 Box A4.4, a baseline calculation and future projections of NO_x, NO_2, and O_3 for 10% f-NO_2 described in Carruthers *et al.* (2006), have been repeated for higher f-NO_2 percentages of both 15% and 20%. Tables A3.5 to A3.7 show calculated annual average NO_x, annual average NO_2 and 99.8th percentile of NO_2. Increasing f-NO_2 from 15% to 20% of urban road traffic NO_x emissions, increased the average NO_2/NO_x ratios at 23 London AURN sites from 0.450 to 0.487. This increase in ratio of 0.037 compares closely to that observed between 2002 and 2004.

163. Most of the increase in NO_2 emitted directly impacts on the annual average NO_2 concentrations with a relatively small percentage of the increase in available oxidant being converted to O_3. Small quantities of additional oxidant are generated by photochemical reactions of VOCs. At roadside sites, for example, Marylebone Road and Cromwell Road, the increases in NO_2 concentration are large, with the NO_2 concentration for the 2010 projection for 20% f-NO_2 being as large as the 2001 concentration for a 10% f-NO_2.

4.1.5 Modelling the Automatic Urban Rural Network sites using the NETCEN (2005) model

164. Roadside and kerbside sites in the national AURN network were similarly modelled using the NETCEN model, see Annex 4, Box A4.5. A base case was set up for 2002 for 21 roadside and kerbside sites in the AURN. The average annual mean model results for these sites for NO_2 and NO_x were 27.9 ppb and 77.8 ppb, respectively. An additional 5% primary NO_2 emission was added at each site to that previously estimated for the total road traffic f-NO_2, with total road traffic NO_x emissions remaining unchanged at their 2002 values. The resulting changes in the NO_2 and NO_x concentrations and their ratios are shown in Annex 4, Table A4.9. Average annual mean NO_2 concentrations increased to 30.0 ppb and the annual mean NO_2/NO_x ratio increased from 0.36 to 0.39.

165. Annual average NO_x levels measured at the 21 AURN roadside and kerbside sites similarly increased between 2002 and 2003 before dropping back in 2004. Annual mean NO_2/NO_x ratios were observed to increase from 0.36 to 0.39 at the roadside and kerbside sites kerbside sites over this same period. This result compares closely with the modelled change for a 5% increase f-NO_2.

4.2 What other plausible explanations are there for the observed changes in the partitioning between nitrogen dioxide and nitrogen oxides observed in London?

Apart from a change in direct emissions of NO_2, there appears to be one other plausible explanation of the abrupt changes in London's air quality and that is direct emission of HONO. Several additional alternative explanations have been ruled out of further consideration in the paragraphs below.

166. The first AQEG report *Nitrogen Dioxide in the United Kingdom* explained that the presence of NO_2 in urban areas was the consequence of either direct emission of NO_2 into the urban atmosphere or of the conversion of NO into NO_2 in the urban atmosphere. In principle then, alternative explanations to direct NO_2 emission and based on the conversion by atmospheric chemistry processes of NO into NO_2 do exist. The issue is whether they are plausible and whether they can be ruled out of further consideration.

167. We have used air quality modelling to investigate a number of alternative explanations to direct NO_2 emissions based on heightened NO to NO_2 conversion, involving the following atmospheric chemistry processes:

- background (hemispheric) O_3 concentrations
- oxidation of VOCs.

168. The first leads to NO_2 formation as a result of the reaction of O_3 with emitted NO, which can be enhanced if the background O_3 concentration has increased. The second leads to NO-to-NO_2 conversion as result of reactions of peroxy radical intermediates with NO. This category of process can be enhanced by increased availability of reactive VOCs in the urban environment, or by an increased source strength of the free radical intermediates which drive their oxidation. We have therefore considered sensitivity to the following:

- VOC availability
- diene-catalysed processes (free radical source)
- direct emission and photolysis of HONO (free radical source).

169. In Figure 4.1, LRCTM results are presented for the 1 km x 1 km grid square centred on the North Kensington AURN (KC1) site. In the base case model, the annual mean model NO_2 and NO_x concentrations were found to be 20.4 and 36.0 ppb respectively in close agreement with the observed 2002 values of 20.6 and 34.1 ppb. The model-derived annual mean NO_2/NO_x ratio was 0.565 compared to the observed value of 0.605. Increasing f-NO_2 by an absolute 5% from 20% to 25% increased the model NO_2/NO_x ratio from 0.565 to 0.581. Figure 4.1 shows the results of sensitivity experiments to test the influence of the above processes on the model NO_2/NO_x ratio.

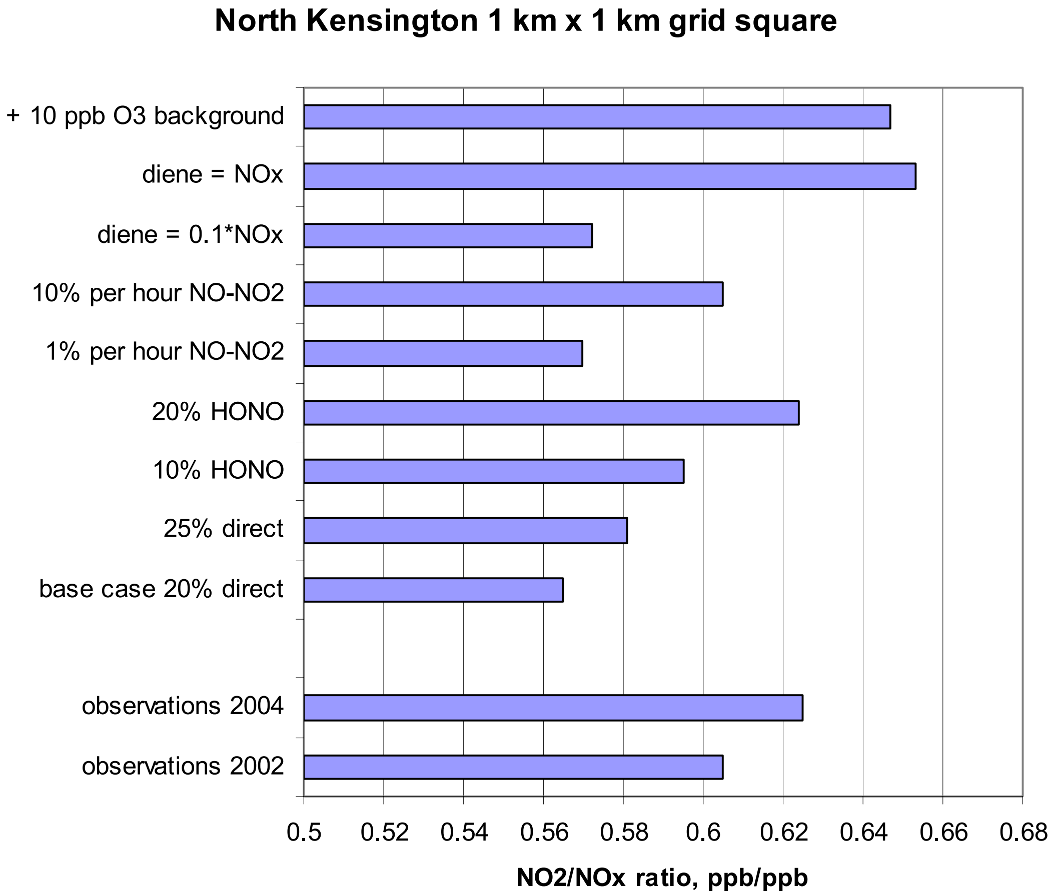
170. The first sensitivity test investigated changes in the hourly concentrations of background O_3 used to set the initial level of O_3 at the start of each trajectory calculation. Increasing each hourly O_3 concentration by 10 ppb produced an increase in the NO_2/NO_x ratio from 0.565 to 0.647, see Figure 4.1. This shows that model NO_2/NO_x ratios at the North Kensington site are sensitive to assumptions concerning background O_3 levels. However, there is no suggestion from the baseline monitoring at the Mace Head station that background O_3 levels in air masses entering the British Isles have increased abruptly over the 2002 – 2005 period to the extent that would be required to explain the observed increase in NO_2/NO_x ratio at the North Kensington site. It is concluded that background O_3 concentrations could be ruled out of further consideration.

171. A second sensitivity test involved peroxy radical driven processes during VOC oxidation. Jenkin (2004a) in his analyses with the oxidant partitioning model has pointed out that there is evidence of fast peroxy radical driven processes influencing the production of oxidant (NO_2 and O_3) in certain urban areas and at certain times. This has been simulated by adding a NO to NO_2 conversion process to the base case model with a first order loss coefficient of 1% and 10% per hour for NO, see Figure 4.1. Including such an imaginary peroxy radical-driven NO to NO_2 conversion process, increases the NO_2/NO_x ratio at the North Kensington site.

172. Based on historical observations of VOC concentrations at London sites, it is estimated that enhanced NO-to-NO_2 conversion at these rates would require increases in availability of reactive VOC (e.g. isoprene) of the order of 10% and a factor of two, respectively. However, there is no evidence that reactive VOC availability has abruptly changed during the 2002 – 2005 period. Isoprene concentrations have in fact been falling rapidly (-28% per year) at the Marylebone Road site over the period 1998 – 2004, as have other reactive hydrocarbons: trans but-2-ene (-18% per year), cis but-2-ene (-19% per year), but-1-ene (-19% per year), trans pent-2-ene (-17% per year) and cis pent-2-ene (-17% per year). Peroxy-radical driven processes, stimulated by increased VOC availability, could therefore be ruled out of further consideration.

173. Incorporation of free radical formation from a diene-catalysed oxidation route, following the suggestion of Shi and Harrison (1997), also led to enhanced NO_2/NO_x ratios, see Figure 4.1. Assuming that motor traffic emitted a conjugated diene that reacted with NO_2 with the rate coefficient of that of NO_2 with cyclohexa-1,3-diene from Jenkin *et al.* (2005) and with the peroxy radical driven chemical mechanism given by Shi and Harrison (1997), Figure 4.1 shows that this mechanism is certainly feasible in London's atmosphere under appropriate conditions. However, for the conjugated dienes to explain what has been seen at the North Kensington site, diene emissions from urban road traffic would have to approach those of NO_x on a mass per vehicle km basis. This is not considered plausible for the current vehicle fleet, furthermore, this emission rate would have had to have been achieved as an abrupt change over the 2002 – 2005 period. Conjugated diene-driven processes could therefore be ruled out of further consideration[11].

Figure 4.1: Ratio of annual mean nitrogen dioxide/nitrogen oxides concentrations at the London North Kensington site in the observations for 2002 and 2004 and in selected model sensitivity experiments with the London Routine Column Trajectory Model.



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[11] Note also that cyclohexa-1,3-diene + O_3 rate coefficient is 1000 times greater than that with NO_2, such that reaction with O_3 is by far the major fate of emitted cyclohexa-1,3-diene under most atmospheric conditions.

174. As described in more detail in AQEG (2004), historical observations made at urban roadside locations such as Marylebone Road, London and in tunnels are consistent with a small fraction (0.5 – 1%) of oxidised nitrogen being emitted in the form of HONO (e.g., Kurtenbach *et al.* (2001); Martinez-Villa *et al.* (2006)). Although this is a small fraction, it is potentially significant from a chemistry point of view because HONO photolyses efficiently to generate free radicals, thereby promoting VOC oxidation and additional NO-to-NO_2 conversion. Given that HONO is known to be generated by particle surface reactions of NO_2 with water vapour and with surface-adsorbed semi-volatile exhaust organic compounds (e.g., Gutzwiller *et al.*, 2002), it is probable that an increase in the primary NO_2 emissions fraction is also accompanied by an increase in the fractional emission of HONO. Although there have been no investigations to test this to date, it is feasible that DPF that oxidise "soot" particles could lead to increased direct emissions of HONO. In addition to its potential role as a free radical precursor, HONO is detected as NO_2 by the chemiluminescence analysers operated by the Defra AURN and LAQN networks (see AQEG, 2004), and therefore can also contribute directly to the apparent NO_2 signal.

175. Figure 4.1 confirms that a significant elevation in direct HONO emissions causes significant impacts on NO_2/NO_x ratios. Studies with the UK photochemical trajectory model (PTM) and LRCTM confirm that HONO once photolysed in the urban atmosphere will act as an oxidant source (by stimulating VOC oxidation) and a HNO_3 source (by stimulating NO_x oxidation). Some of the HNO_3 will form fine particle ammonium nitrate by reaction with NH_3 and coarse particle nitrate by displacement reactions on sea-salt and wind-blown dust particles. It is entirely feasible, therefore, that diesel vehicles fitted with particle filters could lead to increased HONO emissions and this may contribute to the abrupt changes in NO_2 and NO_x air quality observed in London during the period 2002 – 2005. This possibility is worthy of further consideration. However, there is currently no evidence from motor vehicle emission testing for such a change in direct HONO emissions.

4.3 What are the knock-on effects anticipated for urban ozone and other pollutants if there has indeed been an increase in the direct emissions of nitrogen dioxide or nitrous acid?

Increases in both urban O_3 and particulate nitrate are anticipated if there has been an increase in the direct emissions of NO_2 and HONO, respectively, from urban road traffic.

176. Up until now, any increase in urban O_3 concentrations has been explained by a decrease in the capacity for urban areas to destroy O_3 through reactions with NO_x. Reducing urban emissions of NO through the fitting of exhaust gas catalysts to petrol-engined motor vehicles will have led to a diminution of urban O_3 destruction. During the late 1990s, urban O_3 levels have started to rise and, if present trends continue, are anticipated to rise towards those observed in the suburban and rural areas surrounding our towns and cities. However, this reduced 'NO_x-titration' is not the only process affecting urban O_3 levels. The steadily increasing penetration of diesel vehicles into urban road traffic has led to an increasing direct emission of NO_2. This acts as an urban source of oxidant and will over the urban background scale lead to increasing urban O_3 concentrations though the well-characterised oxidant partitioning processes. Increasing direct emissions of HONO will also lead to additional regional scale O_3 and nitrate particle formation as is characterised in the following paragraphs.

4.3.1 Simulation of regional scale oxidant (ozone and nitrogen dioxide) formation

177. In conjunction with the NERC TORCH project, a PTM has been used to simulate regional scale O_3 formation during late July and August 2003, a period which included the best recent example of a regional-scale photochemical event. The model is based on that of Derwent *et al.* (1996), with recent updates described by Utembe *et al.* (2005) and Johnson *et al.* (2006). It simulates the chemical development in a well-mixed boundary layer air parcel being advected along multi-day trajectories prior to arrival at a given receptor site. The air parcel picks up emissions of NO_x, CO, sulphur dioxide, methane and non-methane VOC, which are processed using a detailed description of the chemical and photochemical transformations leading to the formation of O_3 and other secondary pollutants.

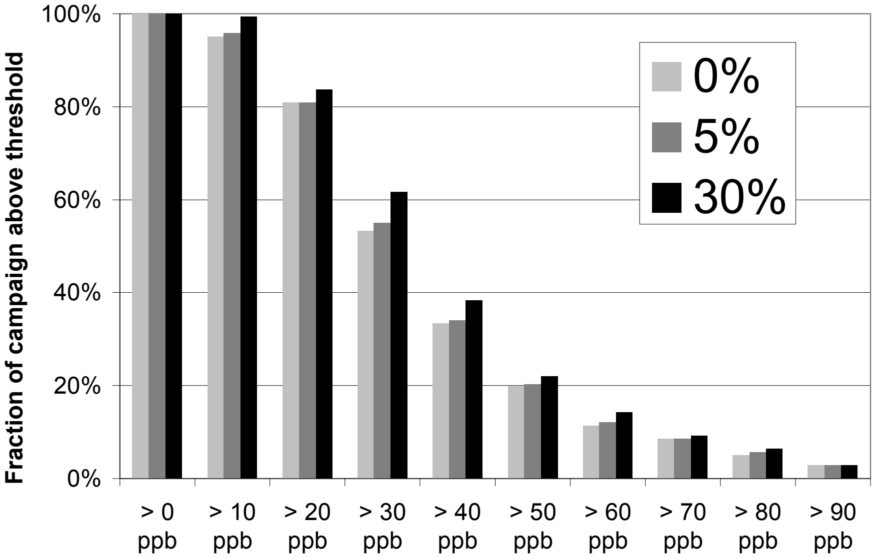
178. The model was used to simulate the chemical development over a 96 hour period along 150 trajectories arriving at the rural campaign site of the TORCH-2003 campaign at Writtle in Essex. The trajectories corresponded to arrival times of 0000, 0600, 1200 and 1800 hr for the period 26 July – 31 August 2003. The model broadly recreates the observed distribution statistics, including the generally elevated mixing ratios (i.e. greater than approximately 60 ppb) which occurred during the anticyclonic period (i.e., the photochemical episode), in the period from 3-12 August.

4.3.1.1 The impact of varying the f-NO_2

179. The effect of varying the f-NO_2 over the range 0 – 30% on the simulated campaign mean mixing ratios of O_3 and OX was investigated. The results demonstrate an approximately linear dependence over this range, with the respective campaign mean O_3 and OX mixing ratios increasing (from 37.5 ppb and 43.9 ppb in the absence of primary NO_2) by 0.433 ppb and 0.417 ppb for each 5% increment in the f-NO_2. The marginally smaller dependence for OX is a result of a slightly increased oxidation rate of NO_x as the f-NO_2 increases, such that the mean NO_2 mixing ratio actually decreases by 0.016 ppb for each 5% increment in the f-NO_2. This is matched by a corresponding increase in the nitrate aerosol concentrations, formed from NO_2 oxidation by the processes described earlier in Box 3.1.

180. The simulated increment in the OX mixing ratio as a function of [NO_x], resulting from a 5% increase in the f-NO_2, was investigated in detail for the entire campaign. Generally, the impact on the NO_2 mixing ratio was very small, such that the OX increments are manifested as increases in the O_3 mixing ratio. The results indicate that, outside the anticyclonic period, the normalised increment Δ[OX]/[NO_x] is approximately 5% on average, consistent with the additional OX being a direct consequence of the increased NO_2 emission. However, the increments for the conditions of the anticyclonic period are generally greater than those in the remainder of the campaign, with the normalised increment, Δ[OX]/[NO_x], being approximately 8.5% on average, approximately 13% based on the afternoon (i.e., 1800 h) data alone, and 31% for the single event with the highest increment. Because the values are greater than the direct 5% contribution, this indicates that notable secondary OX formation results from the enhanced regional-scale chemical processing that the additional NO_2 emission promotes.

Figure 4.2: Simulated percentages of the TORCH-2003 campaign with ozone mixing ratios greater than the given threshold, for primary nitrogen dioxide emissions fractions of 0%, 5% and 30%.



181. An increase in the f-NO_2 therefore has a potential knock-on effect on regional scale photochemical O_3 formation. The impact on the campaign O_3 statistics caused by increases in the f-NO_2 of 5% and 30% are presented in Figure 4.2, in terms of the fraction of the time period for which threshold mixing ratios were exceeded. At the extreme ends of the ranges, the influence of increased primary NO_2 is small on the time above thresholds. However, there is a modest sensitivity at the threshold mixing ratios in the centre of the range.

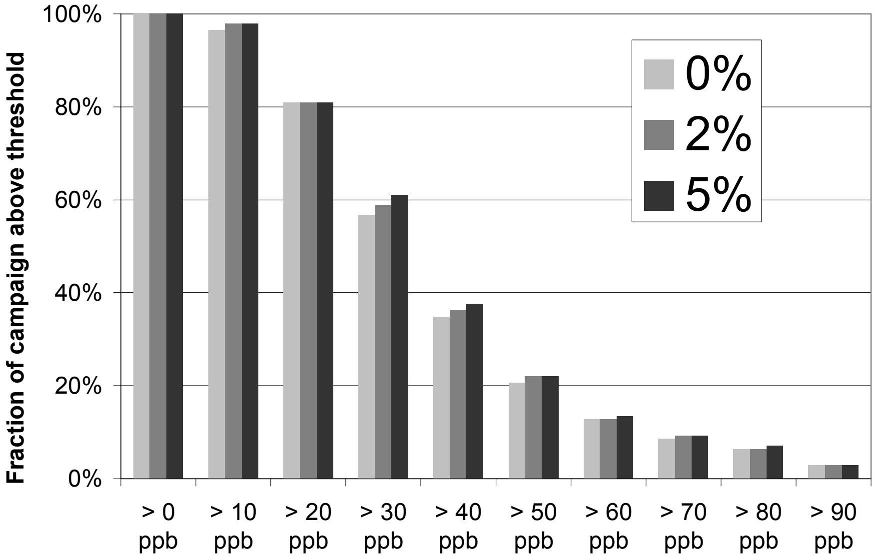
4.3.1.2 The impact of varying the primary nitrous acid emissions fraction

182. The effect of varying the primary HONO emissions fraction (f-HONO) over the range 0 – 5% of NO_x on the simulated campaign mean mixing ratios of O_3 and OX was also investigated. The results demonstrate an approximately linear dependence over this range, with the respective campaign mean O_3 and OX mixing ratios being 1.51 ppb and 1.15 ppb greater as a result of a 5% f-HONO. The smaller dependence for OX is a result of an increased oxidation rate of NO_x as the HONO emissions fraction increases, such that the NO_2 mixing ratio decreases by 0.36 ppb over the simulated range. This is indicative of a notable increase in nitrate aerosol formation from NO_2 oxidation by the processes described earlier in Box 3.1.

183. The simulated increment in the OX mixing ratio as a function of $[NO_x]$, resulting from a 5% f-HONO, was also investigated in detail for the entire campaign. In almost all cases, small decreases in $[NO_2]$ were simulated (typically 5%), such that the OX increments approximate to the simulated increases in the O_3 mixing ratio. The results indicate that the increments during the anticyclonic period are generally greater than those in the remainder of the campaign, with the normalised increment, $\Delta[OX]/[NO_x]$, being approximately 32% on average, approximately 50% based on the afternoon (i.e., 1800 h) data alone, and 81% for the single event with the highest increment. Given that the increased HONO emissions have no direct impact on OX, the simulated increments result exclusively from enhanced regional-scale chemical processing promoted by the HONO emissions. During the remainder of the campaign, $\Delta[OX]/[NO_x]$ is approximately 10%, on average.

184. Emission of a small fraction of NO_x in the form of HONO therefore has a potential knock-on effect on regional scale photochemical O_3 formation. The impact on the campaign O_3 statistics caused by a 2% and 5% f-HONO are presented in Figure 4.3, in terms of the fraction of the time period for which threshold mixing ratios were exceeded. Once again, there is modest sensitivity to emission of HONO at the threshold mixing ratios in the centre of the range.

Figure 4.3: Simulated percentages of the TORCH-2003 campaign with ozone mixing ratios greater than the given threshold, for f-HONO of 0%, 5% and 30%.



4.3.2 Estimation of the impact of increased direct emissions of nitrogen dioxide on annual mean ozone concentrations within London using the London Routine Column Trajectory Model model

185. The knock-on effects of increased direct emissions of NO_2 on O_3 in London have been investigated using the LRCTM model. Annex 4, Table A4.4 presents the observed annual mean O_3 concentrations in 2002 for 19 urban background, five suburban, one roadside and two kerbside sites in the LAQN. Also shown are the LRCTM model results for a base case f-NO_2 of 20% for urban road traffic and a sensitivity case with 25% f-NO_2. Annual mean O_3 concentrations are anticipated to have increased by about 0.24 ppb across the 27 sites.

4.3.3 Estimation of the impact of increased direct emissions of nitrogen dioxide on annual mean ozone concentrations within London using the ADMS-URBAN model

186. In this ADMS study, a baseline calculation and future projections of NO_x, NO_2, and O_3 for 10% f-NO_2 described in Carruthers *et al.* (2006), has been repeated for both 15% and 20% f-NO_2. Annex 4, Table A4.8 shows calculated annual average O_3 mixing ratios. Broadly speaking, annual mean O_3 concentrations appear to increase by about 0.5 ppb for an absolute 5% increase in f-NO_x from urban road traffic.

4.4 What percentage of urban road traffic nitrogen oxides emissions that are direct emissions of nitrogen dioxide should be assumed in the national policy modelling for 2010, 2015 and 2020 in London and elsewhere in the UK?

In the absence of robust predictions of future primary NO_2 emissions percentages, it is not possible to make recommendations for national modelling for 2010.

187. To illustrate these questions roadside NO_2 concentrations in 2010 have been calculated for a range of different f-NO_2 percentages using the oxidant partitioning model. The baseline assessment has the same f-NO_2 percentages as in the 2004 base year calculations, this varies with location from 10 – 15%. Table 4.1 shows the results of the assessment in terms of the percentage of urban road length estimated to have annual mean NO_2 concentration above 40 µg m^{-3} in 2010. It is known that the oxidant partitioning model may not produce fully realistic results at values of f-NO_2 above 25%, it is expected that the model would be more likely to over predict ambient NO_2 at higher f-NO_2 percentages. Example results from the NETCEN primary NO_2 model suggest that the results from the oxidant partitioning model should be reasonably robust in the range estimated here.

Table 4.1: The percentage of urban major road length predicted to be above 40 µg m^{-3} annual mean nitrogen dioxide in 2010 for different f-NO_2 percentages (shown in brackets).

	2004 base year (10 – 15%)	2010 (10 – 15%)	2010 (15 – 22.5%)	2010 (20 – 30%)	2010 (25 – 37.55%)	2010 (30 – 45%)
London	84%	46%	52%	57%	62%	67%
Rest of England	31%	11%	14%	16%	18%	20%
Scotland	22%	6%	8%	9%	10%	12%
Wales	13%	6%	7%	8%	8%	9%
Northern Ireland	8%	0%	1%	1%	2%	3%
Total	35%	15%	17%	19%	21%	24%

188. The reduction in NO_x emissions between 2004 and 2020 is predicted to reduce the extent of exceedences from 35% to 15% of major road length if the primary NO_2 percentage is held at 2004 values. Increasing the f-NO_2 percentage to a range from 30 – 45% is expected to lead to an increase in the extent of exceedences in 2010 relative to the projections for 2010 with unchanged primary NO_2 percentage. The reduction in total NO_x emissions still results in a reduction in the extent of exceedences.

189. It is unclear exactly how this balance between NO_x emission reductions and increases in primary NO_2 percentages will influence the achievability of objectives and limit values in 2010 and beyond. This is because there are currently no robust predictions of future primary NO_2 emissions percentages.

4.5 Are future exceedences of the EU hourly limit value for nitrogen dioxide likely to continue in London up to the year 2010 and beyond?

Exceedences of the EU hourly limit value for NO_2 are expected to continue at kerbside and roadside sites up to 2010 and beyond.

4.5.1 Estimated future exceedences of the EU hourly limit value for nitrogen dioxide at Marylebone Road

190. The model described in Annex 4, Box A4.1 has been used to project the likely number of exceedences of the 200 $\mu g\ m^{-3}$ hourly Limit Value for NO_2 for different assumptions for the decline in NO_x concentration, the f-NO_2 and meteorological year. The base case NO_x reduction of 5% yr^{-1} assumed is consistent with observed trends and predictions to 2010 (AQEG, 2004). It is further assumed that the uncertainty in this reduction is ± 25%. The model uncertainty in predicting hourly NO_2 was calculated to be ± 14.0 $\mu g\ m^{-3}$ (1 σ), based on model performance over the period 1998-2004. Future projections were made of NO_2 and O_3 concentrations at Marylebone Road for a large range of assumptions using a Monte Carlo technique. Hourly background concentrations of NO_x were also assumed to decline at 5% yr^{1} and NO_2 and O_3 concentrations also calculated using the method described in Annex 4, Box A4.1.

191. Figure 4.4a shows the projected number of hours each year where NO_2 is greater than 200 $\mu g\ m^{-3}$. In this plot, projections have been based on 2004 meteorology and a f-NO_2 level of 22% by volume, corresponding to the value calculated at the end of 2004. The uncertainty in these predictions, shown for the -5% yr^{-1} decline in NO_x, is shown to increase until 2008 and then decrease. The decrease in uncertainty after 2008 is because there is an increasing chance that there are no hours where NO_2 is greater than 200 $\mu g\ m^{-3}$. These results also highlight that the decline in the risk of exceeding the Limit Value is at a slower rate than the increase from 2002-4. Based on 2004 meteorology and projected decreases in NO_x it is likely that the Limit Value will not be met.

192. Figure 4.4b shows the effect of the assumptions for primary NO_2 on future hourly NO_2 concentrations. Projections were made from 2004 based on a -5% yr^{-1} decline in total NO_x concentration. Road vehicle f-NO_2 levels from 20 to 30% by volume were considered. This plot highlights the high level of sensitivity to future assumptions for the primary NO_2 emission level. In particular, Figure 4.4b shows that if f-NO_2 levels increase beyond the 22% observed at the end of 2004, the number of hours where NO_2 is greater than 200 $\mu g\ m^{-3}$ increases considerably. For example, if f-NO_2 was to reach 26%, it would take another four years for the number of hours to decline below that observed in 2004. Data for 2005 does indeed reflect this effect: 853 hours were above 200 $\mu g\ m^{-3}$ and the level of f-NO_2 is estimated to be approximately 25%. Furthermore, it is clear that if primary NO_2 were to increase beyond 2004 levels, the risks of exceeding the 2010 limit would increase considerably.

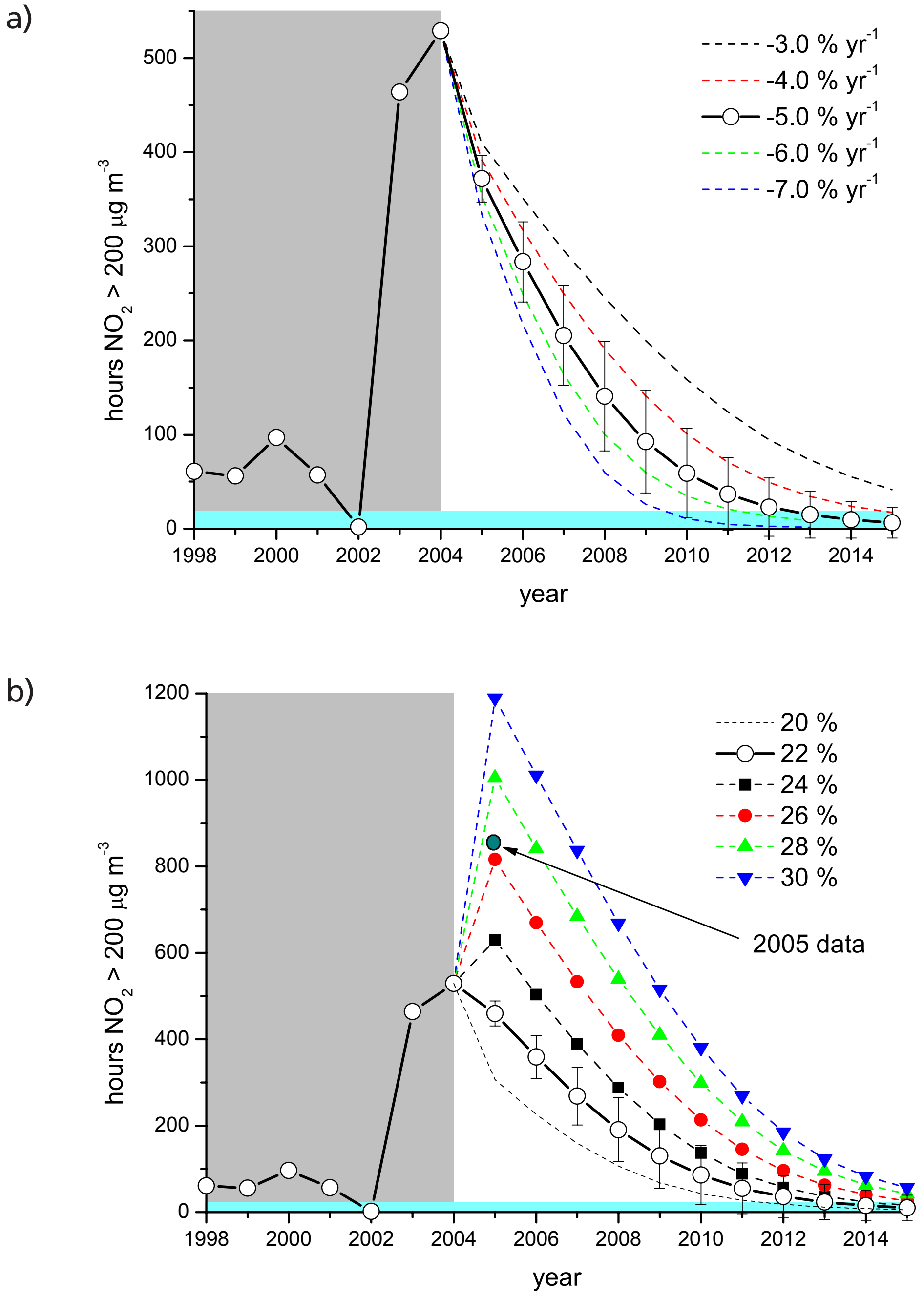
193. It is estimated that there would have been 10 ± 4 (2 σ) hours greater than 200 µg m^{-3} NO_2 in 2004 if f-NO_2 had remained equal to historically typical values of 10% by volume. Therefore, it is very likely that the hourly Limit Value would have been met in 2004 if the f-NO_2 had remained at 10% by volume. These results also suggest that the potential delay in meeting the Limit Value due to increased f-NO_2/NO_x values is substantial. For example, if NO_x concentrations continue to decline at historically typical rates and the f-NO_2 were to remain at 22% by volume, then it is estimated that the EU Limit Value would not be met until 2014; a delay of 10 years. Any further increase in the ratio beyond 22% would delay compliance still further.

194. The analysis above was based on projecting forward from 2004. However, the inter-annual variation in meteorology is also an important consideration; particularly for high percentile concentrations of NO_x and NO_2. Furthermore, each year is also influenced by different concentrations of background O_3, for example, in 2003 when background oxidant levels were high. The influence of inter-annual variations in meteorology has been considered by projecting forward from each one of the years 1998-2004 up to 2015. These simulations were used to calculate the probability that there will be an exceedence of the 2010 Limit Value for different assumptions of f-NO_2 and NO_x reduction. Table 4.2 shows the results of these simulations. It is clear from these results that the inter-annual variation in meteorology has an important affect on the probability that the limit value will be exceeded. For example, for a 20% f-NO_2 assumption and a 5% yr^{1} reduction in NO_x, the probability of not meeting the limit varies from 8% (2002 meteorology) to 72% (2004 meteorology). Years that result in a low probability are 1998 and 2002, whereas years that might be considered as “worst-case” are 2003 and 2004.

Table 4.2: Probability (%) that the hourly concentration of nitrogen dioxide will be greater than 200 μg m^{-3} for at least 18 hours each year in 2010. Numbers in bold text show probabilities greater than 75%.

	Primary NO_2 (% by vol.)											
Primary NO_2	**20%**		**22%**		**24%**		**26%**		**28%**		**30%**	
NO_x reduction (% yr^{-1})	-5%	-4%	-5%	-4%	-5%	-4%	-5%	-4%	-5%	-4%	-5%	-4%
1998	11.4	33.2	15.8	41.8	20.6	55.0	32.2	67.8	37.4	74.8	48.8	**79.8**
1999	33.8	70.4	47.0	**78.2**	55.4	**85.4**	64.0	**90.6**	64.0	**92.2**	71.4	**94.8**
2000	43.8	**75.4**	55.8	**85.6**	65.4	**92.2**	72.0	**95.8**	**80.8**	**97.6**	**83.4**	**98.8**
2001	41.0	**75.4**	57.0	**87.0**	63.0	**92.4**	73.0	**97.2**	**78.6**	**98.4**	**82.8**	**99.2**
2002	8.2	22.0	18.2	47.2	29.6	71.4	50.6	**80.0**	64.2	**92.0**	71.2	**97.8**
2003	68.2	**95.8**	**82.6**	**99.0**	**91.0**	**99.2**	**95.4**	**99.8**	**97.2**	**100.0**	**99.0**	**100.0**
2004	71.8	**96.0**	**87.8**	**99.6**	**95.8**	**100.0**	**98.8**	**99.8**	**99.6**	**100.0**	**99.8**	**100.0**

Figure 4.4: a) Values in the shaded grey area show measured number of hours where nitrogen dioxide is greater than 200 μg m^{-3}. The effect of different nitrogen oxides reduction projections are shown from 2004-2015 assuming a primary nitrogen dioxide ratio of 22% by volume. Error bars (1 σ) are only shown on the -5% yr^{-1} projection for clarity. b) Projected hours where nitrogen dioxide is greater than 200 μg m^{-}3 for different percentage primary nitrogen dioxide assumptions, based on -5% yr^{-1} nitrogen oxides reduction. Provisional data for 2005 are also highlighted. Error bars (1 σ) are only shown on the 22% by volume primary nitrogen dioxide for clarity.



Chapter 5

5 Conclusions

5.1 Recent trends in nitrogen dioxide and nitrogen oxides concentrations

195. During the last 10 – 15 years, there has been a steady downward trend in long term average urban NO_x concentrations in the UK that has been accompanied by a steady decrease in urban background NO_2 concentrations. This trend in NO_x has been attributed to the decreasing emissions of NO_x from urban road traffic. The downward trends in annual mean NO_2 concentrations have not been as steep as those in NO_x and this is due, in part, to the changing partitioning between NO_2 and NO_x as NO_x levels fall, with a greater proportion of NO_x being oxidised to NO_2 by the available O_3. It was against this background that AQEG prepared its first report on 'Nitrogen Dioxide in the United Kingdom'.

196. Since 1998 many roadside sites have not seen a downward trend in NO_2 concentrations. This has been accompanied by a marked increase in the annual mean NO_2/NO_x ratio, above that expected from the previous understanding of NO_2/NO_x ratios at roadside locations. These increases arose towards the end of the 1990s, and became more marked between 2002 and 2004, and as far as AQEG can tell, have been maintained through 2005 and 2006.

197. The recent greater than expected increases in NO_2/NO_x ratios were first noticed at 44 roadside and kerbside sites in London. In addition, evidence of increasing annual mean NO_2/NO_x ratios between 2002 and 2004 has been found at 24 out of the of the 28 urban background sites in the LAQN. Unexpected increases in NO_2/NO_x ratios have therefore been widespread across London.

198. Increased NO_2/NO_x ratios greater than would be expected due to the fall in NO_x concentrations have been observed at 8 out of the 13 roadside and kerbside Defra AURN sites outside of London over the same period, at one out of 23 urban background sites and three out of 16 urban centre sites. Examples of roadside and kerbside sites outside of London that have seen NO_2/NO_x ratio increases include: Bath, Brighton, Bury, Dumfries, Hove, Inverness, Oxford and Wrexham.

199. There are a number of Defra AURN sites outside of London where no changes in NO_2/NO_x ratios have been observed over the 2002 – 2005 period. There have been no significant changes in the annual mean NO_2/NO_x ratios at any of the rural sites. Some urban sites do not have long enough records to be sure either way. At 13 out of 23 urban background sites, eight out of 16 urban centre sites and three out of 13 roadside and kerbside AURN sites there is clear evidence that NO_2/NO_x ratios have remained unchanged. Examples of kerbside and roadside sites outside of London where NO_2/NO_x ratios have remained unchanged include: Cambridge, Glasgow and Yarm. Due to a lack of information on the particular mix of vehicle technologies and fuel found at these sites, AQEG has been unable to investigate why there has been no increase at these sites.

200. In addition to the above increases in annual mean NO_2/NO_x ratios, significant increases have also been observed in peak hourly mean NO_2 concentrations. During the 1990s, steady declines were observed in the 98-percentile hourly mean NO_2 concentration at most urban sites, together with a related decline in the number of hours in each year when 200 µg m^{-3} (105 ppb) was exceeded. For many Defra AURN sites, these trends have continued through to 2005, for example: Brighton and Hove, Bury, Cambridge, Dumfries, Glasgow, Inverness, Norwich and Yarm. At other sites, there has been a dramatic increase in 98-percentile concentrations and 200 µg m^{-3} (105 ppb) exceedences, particularly at roadside and kerbside sites including; Bath, Bristol, Oxford, London A3, London Cromwell Road 2 and London Marylebone Road.

5.2 Possible causes for the observed trends

201. At first, these changes were attributed to the 2003 pollution year which was characterised by the intense summer heat-wave and the unusual persistence of easterly winds. However, the changes in NO_2/NO_x ratios have persisted beyond 2003 and explanations other than changes in meteorology must be sought. Detailed site-specific information on factors such as vehicle technologies and fuel use are required to support the kind of analysis necessary to investigate possible causes for the change in NO_2/NO_x ratios. Such information is most commonly available for the London area and therefore the analysis carried out in this report and the conclusions that are drawn are necessarily largely focused on London.

202. The first report of AQEG 'Nitrogen Dioxide in the United Kingdom' identified three mechanisms by which NO_2/NO_x ratios could be influenced in the future when generating forecasts of the exceedences of NO_2 air quality objectives and limit values. The AQEG warned of the steadily increasing fraction of diesel cars in urban traffic and the significance of their direct emissions of NO_2. The AQEG noted the steadily increasing hemispheric scale O_3 background and pointed out that this may have consequences for annual mean NO_2/NO_x ratios. The AQEG also drew attention to the USA experience of the potential impact of certain mobile source pollution control technologies, such as catalytically regenerative particle traps for diesel vehicles, that could lead to increased direct emissions of NO_2 into the urban atmosphere.

203. A simple explanation for the observed increases in NO_2/NO_x ratios is an increase in the direct emissions of NO_2 as a fraction of the emission of NO_x into the urban atmosphere. AQEG identified two main sources of urban NO_2: firstly, oxidation by regional background O_3 of emitted NO; and, secondly, direct emission of NO_2 into the urban atmosphere. Ozone concentrations in large cities are reduced below the background rural value because of the large concentrations of NO. This effect is more pronounced in London because of its size and extent, so that, in central London, much of the atmosphere's capacity to oxidise NO to NO_2 has been exhausted in the suburban areas. Direct emission therefore becomes a relatively much more important source of NO_2, particularly at some roadside and kerbside sites. In other UK conurbations, depending on their size and emission densities, both sources operate side-by-side. The f-NO_2 has been steadily increasing in London following the increasing fraction of motor vehicles with diesel engines. By 2002, the fraction of direct emissions of NO_2 had risen from about 7% in 1997 to about 11% in 2001.

204. Computer modelling studies for London have shown that if f-NO_2 had increased in absolute terms by 5%, say from 10% to 15%, between 2002 and 2005, then annual mean NO_2/NO_x ratios would increase from about 0.41 to 0.44 at roadside and kerbside locations. This is approximately what has been seen across the LAQN and at the Defra AURN roadside and kerbside sites in London. This increase between 2002 and 2005 in f-NO_2 is significant in comparison to that anticipated over the period from 1997 to 2001.

205. Accepting that an increase in direct emissions of NO_2 is a plausible explanation for the increases in NO_2/NO_x ratios seen in London between 2002 and 2005, then what has been the root cause? The AQEG considered two possibilities: the increasing penetration of new EURO-III diesel light-duty vehicles fitted with oxidation catalysts, and the fitting of catalytically regenerative particle traps to the London bus fleets. Emission measurements provide evidence that the new EURO-III diesel vehicles have direct NO_2 emissions that are up to 50% of total NO_x emissions. This is significantly higher than the 7 – 11% normally assumed for urban road traffic over the 1997 – 2001 period. Buses fitted with catalytically regenerating traps emit substantially more of their NO_x emissions as NO_2 because the latter is used as an oxidant for removal of the black carbon particles caught in the particle trap.

206. In considering the potential impacts of the new EURO-III diesel vehicles and the fitting of catalytically regenerative particle traps to London's bus fleets, AQEG took a number of issues into account. Over the period 2002 – 2005, a number of other factors influenced London's air quality in addition to the exceptional meteorology experienced in 2003. A CCZ was introduced during February 2003. Associated with this, there was a substantial increase in bus traffic to meet the demand for this mode of travel. Furthermore, a large number of changes in traffic flows resulted from the implementation of red routes, bus lanes and adjustments in traffic light operations.

207. If the new EURO-III diesel vehicles with their oxidation catalysts are the sole explanation for the increases in NO_2/NO_x ratios, then it is not clear why the changes were first noticed in London and only at some roadside and kerbside sites across the rest of the United Kingdom. An explanation could be that direct NO_2 emissions are such a central feature of London's NO_2 air quality, that London is especially sensitive to direct NO_2 emissions because of its size and emission density. It is difficult to understand why NO_2/NO_x ratios, in, for example, Glasgow have remained much the same during the 2002 – 2005 period despite its size and emission density.

208. Fitting catalytically-regenerative particle traps to London's buses is certainly a plausible explanation of some of the increases observed in London. The timing of the retrofit scheme fits in with the observations at the roadside and kerbside sites. For example, a CUSUM[12] analysis of the London Marylebone Road NO_2 data, points to the presence of a change-point around February 2003.

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[12] Cumulative sum technique used for detecting small changes in time series (see Section 3.6).

209. If the changes derive from the fitting of traps to London buses in order to decrease emissions of $PM_{2.5}$ and PM_{10}, then it would be anticipated that a similar change analysis would show similar change point decreases in PM concentrations. Unfortunately such an analysis is compromised because the TEOM $PM_{2.5}$ instrument at Marylebone Road was not part of the national QA/QC proceedures prior to 2003. An analysis of the impact of the fitting of catalytic particle regenerative traps to buses warrants further investigation.

210. The AQEG has considered a range of other possible explanations for the observed changes in NO_2 to NO_x concentration ratios. It ruled out other plausible explanations of the observed changes, including increases in the regional background levels of O_3, the fast peroxy radical chemistry, and the diene-catalysed NO_x chemistry. However, direct emission of HONO could not be ruled out and should be given further consideration. On balance, an increase in direct NO_2 emissions is considered to be a more plausible explanation of what has been seen, rather than an increase in direct emissions of HONO.

211. The AQEG considers that a change in the percentage of road traffic NO_x emissions that are directly emitted as NO_2 is the simplest explanation of the observed changes in NO_2 to NO_x concentration ratios observed in London between 2002 and 2005. Evidence from measurements of NO_2 and NO_x emissions from EURO-III light-duty diesel vehicles with oxidation catalysts and heavy-duty vehicles fitted with catalytically regenerative particle traps, give us some confidence that this is indeed a likely explanation.

5.3 Implications of a change in road traffic nitrogen oxides emitted as nitrogen dioxide

212. There are a number of important implications arising from the conclusions of this report at both the UK and local levels. At the UK level, the effects of increasing primary NO_2 emissions have not been accounted for within the scenarios carried out for the review of the Air Quality Strategy. Clearly, this may have implications for achievement of the air quality objectives and limit values, particularly at roadside sites.

213. An examination of the impact of an increase in primary NO_2 percentage from 2004 levels of 10-15% to up to 30-45% in 2010 suggests that the extent of exceedences of an annual mean NO_2 concentration of 40 $\mu g\ m^{-3}$ would be significantly increased relative to projections based on no change.

214. Overall, however, reductions in total NO_x emissions are still expected to lead to a reduction in the extent of exceedences in 2010 relative to 2004. The exact extent of exceedence of objectives and limit values in 2010 and beyond is hard to predict with a high degree of certainty as this will depend on the balance between NO_x emission reductions and changes in primary NO_2 percentages. This is because currently available predictions of future primary NO_2 emissions percentages are subject to considerable uncertainty.

215. Prediction of the degree of exceedence of the 1-hour NO_2 objective and limit value at the roadside is sensitive to the assumed primary NO_2 percentage. Predictions for Marylebone Road suggest that reductions in total NO_x emissions are likely to lead to a reduction in 1-hour exceedences of 200 µg m^{-3} in 2010, relative to measured concentrations in 2004 and 2005. However, the objective of no more than 18 exceedences per year will be exceeded for many years to come.

216. At the local level, there are implications for local authorities concerning judgements that are made regarding future expected improvements to NO_2 concentrations. For the purpose of completing their 'reviews and assessments', authorities are advised to use 'year-adjustment factors' to correct monitoring data from the current year to some time in the future. These adjustment factors have been calculated from the expected changes in emissions in future years, taking into account changes in activity (such as traffic movements) and emissions factors (such as vehicle technologies and fuel standards). These adjustment factors do not take account of increasing primary NO_2 emissions. The outcome is that the use of these factors may overestimate the reduction in NO_2 concentrations, at some roadside locations.

217. There is no simple way to include the effect of primary NO_2 emissions into the adjustment factors. In addition, the trends in NO_x and NO_2 concentrations do not appear to be consistent across the UK, and AQEG has not been able to resolve this disparity.

218. AQEG recommends that local authorities (and any other users) should exercise caution in applying these adjustment factors. This is particularly the case where current annual mean concentrations of NO_2 exceed the objectives by a small margin. On the basis of the analyses of trends in NO_2 concentrations described in this report, the actual decrease in NO_2 concentrations at some sites may be considerably lower than expected.

219. Finally, this report raises implications for the choices of vehicle technologies in future years, particularly with regard to PM reduction methods that may increase primary NO_2 emissions. In this regard, the AQEG draws attention to the conclusions of its first report which highlighted that NO_2 should not be considered in isolation from other pollutants, and that trade-offs would be likely.

5.4 Recommendations for further work

220. There is an urgent need for the development of emissions inventories for NO_2 for transport sources. Currently, the lack of inventories is a major weakness in the current and future assessment of concentrations of NO_2 in the UK.

221. The AQEG were left with a number of unanswered questions and issues that form the basis for recommendations for further work. These are to establish:

    - the contributions to increased NO_2/NO_x concentration ratios arising from diesel vehicles with catalytically regenerating particle traps and from EURO-III diesel vehicles with oxidation catalysts, both in London and elsewhere in the United Kingdom;
    - why the NO_2/NO_x ratios are changing at some UK roadside sites, but not others;
    - the impact of the fitting of catalytically regenerating particle traps on $PM_{2.5}$ concentrations and on secondary nitrate particle formation;
    - the part played by direct emissions of HONO;
    - a separate emission inventory for NO_2 within the NAEI to be updated regularly in the light of new data, which would then allow more reliable future predictions of NO_2 concentrations;
    - an expanded analysis, with periodic updating, of the extent to which the behaviour seen in the United Kingdom has been experienced elsewhere in Europe. This should improve our understanding of the cause and effect relationships.

222. The AQEG was not able to unambiguously detect a change in particle concentrations at Marylebone Road due to the fitting of particle filters to buses. A reduction in particle emissions and hence particle concentrations would be expected because particle filters effectively reduce particle mass emissions. Further work is recommended to establish whether the fitting of particle abatement technologies to road vehicles has a measurable effect on particle concentrations.

Abbreviations

AQEG	Air Quality Expert Group
ARTEMIS	European 5th framework project – Assessment of transport emissions and inventory systems. Sponsored by DGTREN
AURN	Automatic urban rural network
CADC	Common ARTEMIS drive cycle. The cycled can be subdivided into an urban, road and motorway cycle
CARB	Californian Air Resources Board
CCZ	Congestion charging zone
CDPF	Catalyzed diesel particulate filter
CLD	Chemiluminescence detector
CO	Carbon monoxide
CO_2	Carbon dioxide
CRT	Continuously regenerating trap. The CRT® system is a patented Johnson Matthey technology. It comprises an oxidation catalyst followed by a DPF
CUSUM	Cumulative sum technique
D-Kat or D-Cat	The D-CAT package includes the DPNR (Diesel PM and NO_x Reduction) system, which is a combination of a diesel particulate filter with a NO_x adsorber-catalyst
Defra	Department for Environment, Food and Rural Affairs
DfT	Department for Transport
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
EGR	Exhaust gas recirculation
ERG	Environmental Research Group, Kings College, London
EUDC	Extra urban drive cycle
Euro I, II, III, IV, V etc	Euro emission standards
FBC	Fuel borne catalyst
FIGE	Forschungsinstitut Geräusche und Erschütterungen
f-NO_2	Fraction of primary NO_2
FORGE	FORGE is the DfT highway supply module of the National Transport Model. It models the congestion and pollution impacts of traffic growth and investment policies on the road network

FTIR	Fourier Transform Infra-Red
GDI	Gasoline direct injection
HDV	Heavy Duty Vehicle
HGV	Heavy Goods Vehicles
HNO_3	Nitric acid
HONO	Nitrous acid
IDI	Indirect injection
ITS	Institute of Transport Studies, University of Leeds
LAT	Laboratory of Applied Thermodynamics, University of Thessaloniki
LAEI	London Atmospheric Emission Inventory
LAQN	London Air Quality Network
LDV	Light Duty Vehicles
LEZ	Low Emission Zone
LGV	Light Goods Vehicles
LRCTM	London Routine Column Trajectory Model
MLTB	Millbrook London Transport bus cycle. A real world test cycle, derived from in-service measurements over route 159
NAEI	National Atmospheric Emission Inventory
NEDC	New European Driving Cycle
NH_3	ammonia
NO	nitrogen monoxide (otherwise known as nitric oxide)
NO_2	nitrogen dioxide
NO_x	nitrogen oxides ($NO + NO_2$)
N_2O	Nitrous oxide
O_3	ozone
OEM	Original equipment manufacturer
OX	oxidant
PARTICULATES	European 5th framework project, PARTICULATES. Sponsored by DGTREN
PM	Particulate matter
PM_{10}	Airborne particulate matter passing through a sampling inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter and which transmits particles of below this size

$PM_{2.5}$	Airborne particulate matter passing through a sampling inlet with a 50% efficiency cut-off at 2.5 μm aerodynamic diameter and which transmits particles of below this size
PM_{coarse}	Fraction of the measured particle mass concentration determined from PM_{10} minus $PM_{2.5}$
PMP	Particulates measurement programme, coordinated by the Department for Transport
PSA Group	Peugeot Société Anonyme, later to be changed to PSA Peugeot Citroën. A French automobile and motorcycle manufacturer; sold under the Peugeot and Citroën marques
PTM	Photochemical trajectory model
RPC	Reduced Pollution Certificate
SCR	Selective Catalytic Reduction
TfL	Transport for London
TRAMAQ	DfT Traffic management and air quality research programme
TRF	Transport Research Foundation
TRL	Transport Research Laboratory
UDC	Urban drive cycle
ULSD	Ultra low sulphur diesel
VOC	Volatile organic compound
VMM	Vehicle market model

References

Abbott, J. *et al.* (2006). Primary nitrogen dioxide emissions from road traffic: analysis of monitoring data. AEA Technology, National Environmental Technology Centre. Report AEAT/ENV/R/1925.

Airbase (2007). http://air-climate.eionet.europa.eu/databases/airbase/

Ambs, J.L. and McClure, T.B. (1994). The influence of oxidation catalysts on NO_2 in diesel exhaust. SAE paper 932494.

AQEG (2004). Nitrogen dioxide in the United Kingdom. First report of the Air Quality Expert Group. Defra, London. The report can be found at: http://www.defra.gov.uk/environment/airquality/aqeg/nitrogen-dioxide/index.htm

Barratt (2005). Assessment of recent trends in NO_2 using CUSUM analysis methods. Environmental research Group, King's College London. March 2005. Report available from http://www.erg.kcl.ac.uk/erg/asp/MonitoringReports.asp

Barlow, T.J., Latham, S., McCrae, I.S. and Boulter, P.G. (2006). A reference book of driving cycles for use in the measurement of road vehicle emissions. TRL project report UPR/IE/054/06. TRL, Wokingham.

Beavers, S. (2006). Primary NO_2 emissions in London. Paper submitted to AQEG, 26/5/06. Environmental Research Group, Kings College, London.

Boulter, P.G., McCrae, I.S. and Green, J. (2007). Primary NO_2 emissions from road vehicles in the Hatfield and Bell Common tunnels. TRL project report UPR/IE/040/07. TRL, Wokingham.

Carruthers, D.J., Williams, M. and Johnson, K.L. (2006). Modelling of Current and Future Concentrations of PM, NO_x and O_3 in London using ADMS-Urban. Report prepared for Defra and the Devolved Administrations.

Carslaw, D. (2006). Personal communication with Sean Beavers of ERG.

Carslaw, D.C. and Beevers, S.D. (2004). Investigating the potential importance of primary NO_2 emissions in a street canyon. Atmospheric Environment. Vol, 38, pp. 3585-3594.

Carslaw, D.C. and Beevers, S.D. (2005). Estimations of road vehicle primary NO_2 exhaust emission fractions using monitoring data in London. *Atmospheric Environment*, **38**, 3585-3594.

Carslaw, D.C., Ropkins, K. and Bell, M.C. (2006). Change-Point Detection of Gaseous and Particulate Traffic-Related Pollutants at a Roadside Location. *Environmental Science and Technology*. Vol. 40. Issue 22. 6912-6918.

Czwewinski, J., Petermann, J-L., Comte, P. and Mayer, A. (2006). NO-NO_2 of diesel engines with different catalysts and differing measuring systems. Paper submitted to the Transport and Air Pollution conference, Reims, 12-14 June 2006. INRETS report 107, pp191-198. AFHB and TTM.

Derwent, R.G. (1999). Oxides of nitrogen and ozone in the London routine column trajectory model. Meteorological Office, Bracknell.

Derwent, R.G., Jenkin, M.E. and Saunders, S.M. (1996). Photochemical creation potentials for a large number of reactive hydrocarbons under European conditions. *Atmospheric Environment*, **30**, 181-199.

DfT (pers comm., 2004-2005). There are a number of references to information, data and advice provided by experts in the Department for Transport in personal communications by telephone and e-mail. These are largely based on expert judgement, sometimes in consultation with industry, and cannot be referenced to any particular documentation. The source of most of the information came from within Cleaner Fuels and Vehicles Division of DfT.

DfT (2004). The Future of Transport: a network for 2030. The Department of Transport. Cm6234. The Stationery Office, Norwich.

DfT (2006). Vehicle Licensing Statistics: 2005, Transport Statistics Bulletin (SB(06)25). Department for Transport, London.

EU (2006). http://forum.europa.eu.int/Public/irc/env/cafe_baseline/library?l=/cafe_ambient_quality/workshop_vehicles&vm=detailed&sb=Title

Fuller, G. (2006). King's College London, personal communication.

Geivanidis, S. and Samaras, S. (2006). Evaluation of the actual NO_2/NO_X ratio of recent vehicle technologies. Laboratory of Applied Thermodynamics, Thessaloniki, 5/04/2006.

Gense, R., Vermeulen, R., Weilenmann, M. and McCrae, I. (2006). NO_2 emissions from passenger cars. Paper to be presented at the Transport and Air Pollution conference, Reims, 12-14 June 2006. INRETS report 107, pp175-182. TNO, EMPA and TRL. TNO Automotive, Delft.

Gutzwiller, L., Arens, F., Baltensperger, U., Gäggeler, H.W., Amman, M. (2002). Significance of semivolatile diesel exhaust organics for secondary HONO formation. *Environmental Science and Technology*, **36**, 677-682.

Hoermandinger, G. (2007). The issue of NO_2 from cars: Overview of the 2006 workshop. International conference on Transport and Environment: A global challenge technological and policy solutions. Milan, 19-21 March 2007. Full details of the 2006 DG Environment workshop may be found at: http://forum.europa.eu.int/Public/irc/env/cafe_baseline/library?l=/cafe_ambient_quality/workshop_vehicles&vm=detailed&sb=Title

Hueglin, C., Buchmann, B. and Weber, R.O. (2006). Long-term observation of real-world road traffic emission factors on a motorway in Switzerland. *Atmospheric Environment*, **40**, 3696-3709.

Jenkin, M.E. (2004a). Analysis of sources and partitioning of oxidant in the UK-Part 1: the NO_x-dependence of annual mean concentrations of nitrogen dioxide and O_3. *Atmospheric Environment*, **38**, 5117-5129.

Jenkin, M.E. (2004b). Analysis of sources and partitioning of oxidant in the UK. Part 2: contributions of nitrogen dioxide emissions and background ozone at a kerbside location in London. *Atmospheric Environment*, **38**, 5131-5138.

Jenkin, M.E., Sulbaek Anderson, M.P., Hurley, M.D., Wallington, T.J., Taketani, F., Matsumi, Y. (2005). A kinetics and mechanistic study of the OH and NO_2 initiated oxidation of cyclohexa-1,3-diene in the gas phase. *Physical Chemistry Chemical Physics*, **7**, 1194-1204.

Johnson, D., Utembe, S.R., Jenkin, M.E., Derwent, R.G., Hayman, G.D., Alfarra, M.R., Coe, H. and McFiggans, G. (2006). Simulating regional scale secondary organic aerosol formation during the TORCH 2003 campaign in the southern UK. *Atmosheric Chemistry and Physics*, **6**, 403-418.

Kessler, C., Niederau, A. and Scholz, W. (2006), Estimation of NO_2/NO_x relations of traffic emissions in Baden-Württemberg from 1995 to 2005. 2nd conf. Environment & Transport, incl. 15th conf. Transport and Air Pollution. Reims, France, 12-14 June 2006. Proceedings no107, Vol. 2, Inrets ed., Arceuil, France, 2006, p. 101-105.

Kurtenbach, R., Becker, K.H., Gomes, J.A.G., Kleffmann, J., Loerzer, J.C., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A. and Platt, U. (2001). Investigation of emissions and heterogeneous formation of HONO in a road traffic tunnel. *Atmospheric Environment*, **35**, 3385-3394.

Latham, S., Kollamthodi, S., Boulter, P.G., Nelson, P.M. and Hickman, A.J. (2001). Assessment of primary NO_2 emissions, hydrocarbon speciation and particulate sizing on a range of road vehicles. TRL Project report PR/SE/353/2001. TRL, Wokingham.

Latham, S., Boulter, P. and Barlow, T. (2004). The effects of traffic management schemes on emissions from heavy-duty vehicles. TRL Project report PR/SE/960/04. TRL, Wokingham.

Martinez-Villa, G., Ame, D.L., Green, D. and Clemitshaw, K.C. (2006). Observations of nitrous acid (HONO) at a street-canyon kerbside site in central London. *Atmospheric Environment*.

McCrae, I.S., Latham, S. and Hickman, A.J. (2002). Primary NO_2 vehicle exhaust emission. Transport and Air Pollution Symposium, Graz, 10-21 June 2002. TRL Paper PA3863/02. Transport Research Laboratory, Wokingham.

Millbrook (2005). The effects of emerging vehicle technologies on certain vehicle emissions not currently regulated. Millbrook Proving Ground Ltd & AEA Technology, December 2005. CFV project S0426/T4. Report number MBK 05/0832.

Ricardo (2003). Emission factors for cars, Q40240/VSE Project S0135/VB. March 2003.

Richards, P., Terry, B. and Pye, D. (2002). Experience of fitting London black cabs with fuel borne catalyst assisted diesel particulate filters – Part 2 Non-regulated emissions measurements. Society of Automotive Engineers 2002-01-2785.

Riemersma, I. (2005). Dutch In-Use Compliance Programme for Trucks (2005) performed by TNO. Sponsored by the Dutch Ministry of Environment. Personal communication with Ian McCrae, 1/11/05.

Samaras, Z. (2006). LAT primary NO_2 emission test data. Personal communication with Ian McCrae, 8/4/06.

Shi, J.P. and Harrison, R. (1997). Rapid NO_2 formation in diluted petrol-fuelled engine exhaust – a source of NO_2 in winter smog episodes. *Atmospheric Environment*, **31**, 3857-3866.

Sjodin, A. and Cooper, D. (2001). Overview of road tunnel exhaust emission measurement studies for validation of vehicle exhaust emission models. Deliverable 46(2) of the 5FP ARTEMIS project. Report L00/78. IVL, Gothenberg.

SMMT (2006). http://www.smmt.co.uk

Soltic, P. and Weilenmann, M. (2003). NO_2/NO emissions of gasoline passenger cars and light-duty trucks with Euro-II emission standard. *Atmospheric Environment*, **38**, 5207-5216.

Soltic, P. and Rutter, J. (2003). Comparison of the NO_2/NO_x emissions of heavy-duty Euro-III diesel engines with and without a CRT® system. EMPA paper TAP 03-60 Paper presented at the Transport and air pollution symposium, Avignon, 2003.

Stedman, J.R., Bush, T.J., Murrells, T.P. and King, K. (2001). Baseline PM_{10} and NO_x projections for PM_{10} objective analysis. AEA Technology, National Environmental Technology Centre. Report AEAT/ENV/R/0726.

TfL (2003). Personal communication between Tim Murrells, Netcen & Transport for London, June 2003.

TfL (2006). TfL exhaust emission data. Personal communication between Anna Rickard (TfL) and Ian McCrae (TRL), 5/4/06.

TfL (2007). TfL exhaust emission data. Personal communication between Anna Rickard (TfL) and Ian McCrae (TRL), 16/4/07.

Tremayne, G. (2006). Consultation response on the draft report 'Trends in primary NO_2 in the UK'. Johnson Matthey written response to Defra, 7 November 2006.

Utembe, S.R., Jenkin, M.E., Derwent, R.G., Lewis, A.C., Hopkins, J.R. and Hamilton, J.F. (2005). Modelling the ambient distribution of organic compounds during the August 2003 ozone episode in the southern UK. *Faraday Discussions*, **130**, 311-326.

Annex 1

Sources of primary nitrogen dioxide emissions from vehicle exhausts and implications to the development of emission inventories

A1.1 Fundamentals of nitrogen dioxide formation in combustion

Nitrogen oxides are formed in all combustion systems where a fuel is burned in air. The fundamentals of NO_x formation in combustion were described in detail in AQEG's first report *"Nitrogen Dioxide in the United Kingdom"*. That report explained that NO_x is mainly released from combustion in the form of NO (greater than 95%) because of the high temperature conditions, but under certain combustion conditions, a significant amount of NO_x may be released as NO_2. These are conditions where the fuel and air are not well mixed, allowing cooler regions in the combustion environment where the combustion chemistry is quenched, and where there is an excess of oxygen. These conditions can be found in a compression-ignition diesel engine which works under excess air conditions (a lean air:fuel ratio) and with lower exhaust temperatures. Older diesel engines in particular suffered from relatively poor air-fuel mixing and, especially under light engine loads and low engine speeds (where cooler regions are more widespread in the combustion chamber), as much as 30% of NO_x could be emitted as NO_2. Improved design in diesel fuel injection systems (particularly the move from mechanical to electronic systems that were introduced during the late 1990s) and fuel atomisation in the chamber of modern diesel engines have improved air-fuel mixing, so have contributed to a reduction in the amounts of NO_x being emitted as NO_2 directly from the engine ("engine-out" emissions).

In a petrol engine, the air-to-fuel ratio is closer to stoichiometric, that is the relative amount of fuel and oxygen is just of the right balance, such that neither is in excess over the other. Furthermore, the petrol fuel and air are relatively well-mixed. The lack of excess oxygen and the well-mixed combustion environment means that conditions are less favourable for generating primary NO_2 in a petrol engine.

While a diesel engine has a higher propensity in forming engine-out primary NO_2 emissions compared with a petrol engine, the problem is compounded by the effects of certain exhaust after-treatment systems, primarily aimed at reducing other pollutant emissions, leading to further conversion of NO to NO_2 in the exhaust. The most common NO_x emission abatement systems were described in AQEG (2004). These abatement systems and systems used to control other pollutant emissions from diesel engines are discussed here in the context of their effects on f-NO_2.

A1.2 Effect of exhaust after-treatment systems on primary nitrogen dioxide emissions from diesel engines

Diesel oxidation catalysts are fitted on many light duty diesel vehicles. They are relatively inexpensive and durable catalyst devices and were originally fitted to diesel exhausts to reduce CO and hydrocarbon emissions, for which they are very effective, but they are also found to make a modest reduction in PM emissions. With increased pressure on manufacturers to reduce PM emissions from diesel vehicles, they have made a valuable contribution to the attainment of early Euro emission standards for PM without recourse to particulate filters. Diesel oxidation catalysts work by oxidising CO and hydrocarbons to CO_2 on the catalyst surface. However, this same process oxidises NO to NO_2 so that although diesel oxidation catalysts have little impact on total NO_x emissions, they have the disbenefit of increasing the fraction of NO_x emitted as NO_2 (higher f-NO_2). The efficiency of conversion of NO to NO_2 on the catalyst can depend on the activity of the catalyst agent. A high platinum loading increases the efficiency of oxidation of CO and hydrocarbons, but also increases the efficiency of converting NO to NO_2. Combining palladium with platinum on the catalyst surface has been found to reduce the oxidation of NO to NO_2 whilst little sacrificing the efficiency of oxidation of hydrocarbons. Developments on the optimisation of the catalyst formulation for reducing the f-NO_2 are ongoing.

Diesel Particulate Filters are being fitted on an increasing number of new diesel vehicles in order to meet tighter limits on PM emissions. Many existing diesel vehicles in the heavy duty fleet are also being retrofitted with DPFs, especially those in captive fleets. There are a number of different types of DPFs, but all require some type of technology to regenerate the filter otherwise it quickly becomes clogged with soot particles. The differences in design are based on the way the DPFs are regenerated. The types most commonly used in the UK and Europe are of the continuously regenerating type, such as the CRT®, that regenerate the trap by oxidising the soot trapped on the filter with NO_2. Nitrogen dioxide oxidises soot on the filter at a lower temperature than does oxygen. The CRT® is currently the most widely used DPF in the UK, and is currently fitted to buses in the London TfL fleet. These systems use an oxidation catalyst to deliberately oxidise the NO in the exhaust to NO_2 which then oxidises the soot on the filter. Not all the NO_2 is required all the time to regenerate the trap, so the result is that a higher proportion of the emitted NO_x (which overall is affected little by the filter system) is in the form of NO_2. These types of DPFs can be optimised to reduce the amount of "excess NO_2" (or NO_2 slip) by, for example, modifying catalyst loading or formulation. However, not all retrofit DPFs may be optimised.

The NO_2 is a product of the oxidation catalyst component of a CRT® upstream of the filter, not the filter itself. There are other types of DPFs that do not rely on NO_2 as a regenerating agent. For example, some use a thermal oxidation regeneration process, using back-pressure and time sensors to initiate regeneration on demand by raising filter inlet temperature, through short periods of additional fuelling. These systems have been designed mainly for heavy duty applications. Other filter regeneration designs used mainly for off-road or stationary engines include electric-heater and fuel-burner-assist regeneration systems. Because these use essentially thermal strategies for regenerating the filters without the use of NO_2, these types of DPFs are likely to produce lower NO_2 levels (i.e. lower f-NO_2) than the CRT® type, possibly to levels of Euro I-III diesel vehicles without a DPF, although there are no data in the literature to confirm this. Other types of thermal management strategies exist to minimise NO_2 from catalyst-based DPFs.

Fuel-borne catalysts (FBC) have been shown to have a beneficial effect on PM, NO_x and NO_2 emissions, and are typically most widely used by the PSA group. Fuel-borne catalysts should be distinguished from fuel additives, whereby fuel additives are mixed within the fuels distributed at service stations or after-market addition with a dose not optimised for the vehicle, whilst FBC are added into the fuel on-board the vehicle. The most effective FBC technologies require that the fuel dosing to be determined through feedback from the engine-out emission.

Used in conjunction with a diesel particulate filter, FBCs offer an alternative way of regenerating the filter at low temperatures without recourse to NO_2. Fuel-borne catalysts are dosed as fuel additives usually comprising of oxides of metals or other inorganic agents such as iron, cerium and strontium. The FBCs mix with the soot particles and catalyse their oxidation on the filter at lower exhaust temperatures than would otherwise be required. Unlike the CRT-based DPF, no NO_2 is involved in the regeneration process. Studies have shown that not only are PM emissions substantially reduced from a FBC-DPF system, but NO_x and NO_2 emissions are also reduced. Where NO_x speciation tests were carried out on some systems, the studies found that NO_2 emissions were actually reduced more than NO_x implying a reduction in the NO_2/NO_x ratio of the emissions, i.e. lower f-NO_2. However, the choice additive has been subject to ongoing investigations. The early use of copper was withdrawn as it catalysed dioxin formation within the trap. The knock-on effects of other catalysts such as cerium, are currently subject to review.

Selective Catalytic Reduction can be applied to diesel exhausts to reduce NO_x emissions, either as an OEM fit or as a retrofit solution. They have been fitted to some large marine diesel engines for a number of years, and are now finding their way into the automotive sector. Selective Catalytic Reduction de-NO_x systems use NH_3 to reduce NO_x emissions on the surface of a catalyst. For a mobile diesel engine, a derivative of NH_3 such as urea is injected into the exhaust stream. Further details of SCR technology were given in AQEG (2004). Selective Catalytic Reduction has mostly been applied to heavy duty diesel engine exhausts and although still relatively uncommon in the fleet, tighter NO_x emission limits on these vehicles are likely to see an increasing number of SCR systems fitted on diesel heavy duty vehicle exhaust in the future in order to meet future emission standards. Combined SCR-CRT after-treatment systems have been developed to simultaneously reduce both PM and NO_x emissions from heavy duty diesel exhausts. Selective Catalytic Reduction is effective in reducing both NO_x and NO_2 emissions and as shown in Section 2.6, tests have suggested that NO_2 emissions may be reduced to a greater extent than total NO_x emissions, leading to a reduction in the NO_2/NO_x ratio, i.e. lower f-NO_2.

A1.3 Implications for developing emission inventories of nitrogen dioxide

With such a range of diesel exhaust after-treatment technologies currently available and still emerging, each aimed at reducing the regulated pollutant emissions, but each having different impacts upon primary NO_2 emissions, it is becoming increasingly challenging to develop a primary NO_2 emissions inventory for diesel vehicles in the national fleet. Methods for controlling NO_x and PM emissions have been driven by legislation and inventories for these pollutants could be based on the legislated limit values and the reductions required to achieve them. Moreover, the choice of technology has until recently been quite limited. This has meant that simply knowing the year of introduction of the different Euro emission standards and past, current and predicted new vehicle sales, linked to vehicle licensing data (new registrations) has been an adequate way of estimating the number or proportion of vehicles in the fleet having different levels of NO_x and PM emissions. This is because the Euro emission standards that a vehicle complies with can be linked to its year of first registration. With NO_2 not being a regulated pollutant and with so many different technologies affecting f-NO_2, the link between primary NO_2 emissions and a vehicle's Euro standard is not so strong. This means that from the point of view of developing an inventory for primary NO_2 emissions, the limitations lie in not only understanding how f-NO_2 is affected by technology, but in knowing the technology mix out in the fleet, for example, the proportion of diesel vehicles fitted with oxidation catalysts, SCR and, importantly, different types of DPF available. Even within a technology class, such as diesel oxidation catalysts, different equipment manufacturers may use different catalyst coatings with different propensity to form NO_2 on the surface.

One further complicating factor is that even with an individual vehicle, the f-NO_2 is dictated not just by the engine-out emission of NO_x, but by the way in which the vehicle is operated (its duty cycle). The operation of a vehicle influences the engine-out and exhaust temperatures that also dictate the effectiveness of many exhaust gas after-treatment systems. Whilst NO_2 emissions are not currently included in Type Approval testing, the effectiveness of exhaust-gas after treatment systems may not be adequately represented in standard legislative testing. Finally it should also be noted that changes in fuel formulation, particularly the reduction in the sulphur content of diesel has been associated with an increase in oxidation catalyst efficiency, thus exacerbating the f-NO_2.

At a national level, the problem in compiling a primary NO_2 inventory that such ranges in technology represents, may be possible to overcome to an extent by conducting surveys with different vehicle and equipment manufacturers and suppliers or the relevant trade associations to gain an appreciation of their uptake in the national fleet, and the way in which these vehicles are operated. But knowing the mix of technologies in more localised traffic will be far more difficult where the only indicator available on ascertaining a vehicle's likely emission performance is usually the vehicle's registration and an indication of average speed.

Annex 2

Interim guidance on UK fleet-average projections in values of f-NO_2 for use in models

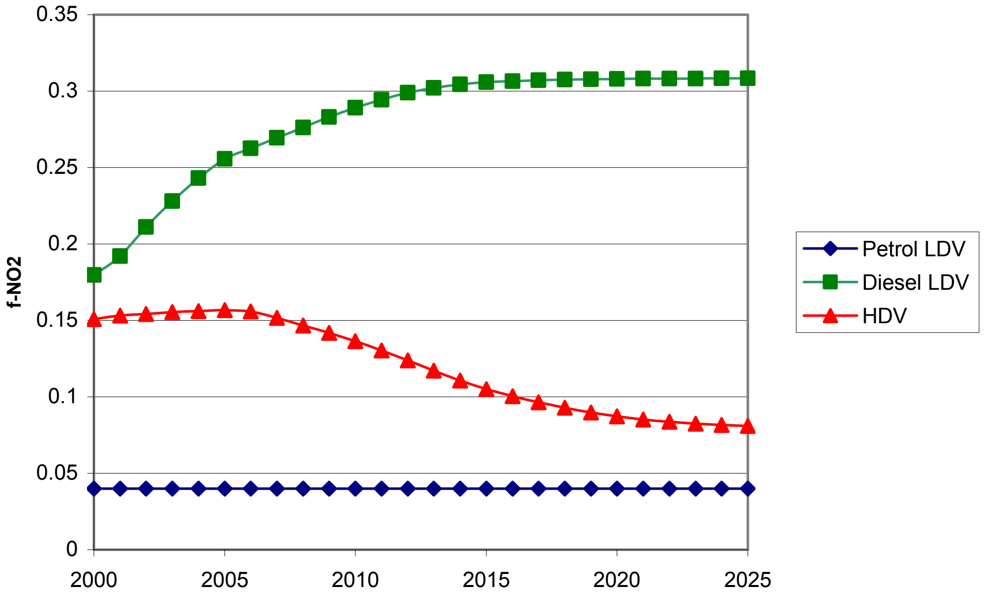
There are various modelling toolkits and databases of emission factors for modelling and projecting NO_x emissions from traffic based on the development of the national vehicle fleet. These are based on the penetration rates of cleaner vehicles meeting the tighter Euro standards and the survival rates of older vehicles in the fleet calculated in the NAEI's road transport emissions forecasting model (see Section 2.10). Projected values of f-NO_2 for the national fleet are not currently included in these modelling tools and emission factor databases. Modellers engaged in local planning and air quality assessments would find it useful to have some simple f-NO_2 values for use in combination with the NO_x emission factors and traffic information to enable the prediction of primary NO_2 emissions from traffic on local road networks as the fleet evolves.

The NAEI road transport emissions model has been used to develop projected UK-averaged values of f-NO_2 for petrol and diesel light duty and heavy duty diesel vehicle flows using the same fleet turnover assumptions. The trends in f-NO_2 from 2000 to 2025 are shown in Figure A2.1 and tabulated in Table A2.1. The purpose of these figures is to provide interim guidance to modellers on national fleet-averaged values of f-NO_2 for use in models. The fleet-average f-NO_2 values are based on the same assumptions of f-NO_2 for specific vehicle types and Euro standards discussed in Section 2.12 and represented by Figure 2.20. The flat trend in f-NO_2 for petrol LDVs reflects the constant factor of 0.04 in Table 2.8 for these vehicles. The increase in f-NO_2 for the diesel light duty fleet with time reflects the penetration of newer Euro standards in the national diesel LDV fleet, associated with higher f-NO_2. These figures are based on the current projected growth of diesel car sales reaching 42% by 2010. If, as current trends are suggesting, the rate of growth in diesel car sales occurs faster than this and extends beyond 42% by 2010, the penetration of higher Euro standards in the diesel car fleet will mean that the growth in f-NO_2 will occur at a faster rate than indicated in Figure A2.1 and Table A2.1. Average values of f-NO_2 for the heavy duty fleet show a downward trend from 2006 reflecting the penetration of Euro IV and IV+ vehicles with SCR emitting lower f-NO_2 These figures refer to assumptions concerning the composition of the national fleet. Where it is known that a high proportion of buses (or for example HGVs associated with certain supermarket chains and local authority fleets) in a local area are fitted with DPFs of the CRT-type, then the specific f-NO_2 figure of 0.4 in Table 2.8 should be used.

Table A2.1: Proportion of nitrogen oxides emitted as nitrogen dioxide (f-NO_2) in the national fleet for petrol and diesel light duty and heavy duty diesel vehicles based on the projections of the National Atmospheric Emissions Inventory.

f-NO_2	2000	2005	2010	2015	2020	2025
Petrol LDV	0.040	0.040	0.040	0.040	0.040	0.040
Diesel LDV	0.180	0.256	0.289	0.306	0.308	0.308
HDV	0.151	0.157	0.136	0.105	0.087	0.081
Bus with CRT-DPF	0.40	0.40	0.40	0.40	0.40	0.40

Figure A2.1: Proportion of nitrogen oxides emitted as nitrogen dioxide (f-NO_2) in the national fleet for petrol and diesel light duty and heavy duty diesel vehicles based on the projections of the National Atmospheric Emissions Inventory.



Annex 3

Supplementary information to Chapter 3 – What do the measurements tell us?

Table A3.1.

	Annual Mean NO_x µg m^{-3}, as NO_2 (20°C 1013mb)								
Site/Year	1997	1998	1999	2000	2001	2002	2003	2004	2005
Bath Roadside	261	253	228	194	178	168	167	151	179
Brentford Roadside								155	147
Brighton Roadside					91	83	90	82	82
Bristol Old Market	338	227	221	209				150	171
Bury Roadside		309	269	259	270	235	247	218	189
Cambridge Roadside				110	111	112	116	111	113
Camden Kerbside	277	243	208	205	203				191
Dumfries					102	101	100	92	90
Exeter Roadside	150	120	109	97	104	95	101	98	98
Glasgow Kerbside		272	253	264	284	287	294	263	242
Haringey Roadside	187	142	135	127	120	108	116	97	88
Hounslow Roadside		260	189	150	148	132			
Hove Roadside		109		77	94	69	71	73	64
Inverness						49	51	48	44
Lincoln Roadside		301	274						
London A3 Roadside		292	256	212	184	170	192	180	158
London Bromley			179	176	165	81	81	84	83
London Cromwell Road 2			256	245	208	191	192	193	189
London Marylebone Road		374	391	415	335	300	314	309	292
Norwich Roadside		73	66	58	65	61	62	54	
Oxford Centre Roadside			183	184	184	185	213	189	182
Southwark Roadside				188	176	154	159	138	137
Stockton-on-Tees Yarm					148	129	139	120	110
Sutton Roadside	148	116	116	108	115				
Tower Hamlets Roadside	299	247	238	209	228	186	182	159	146
Wrexham						50	51	40	38

Table A3.2.

	Annual mean NO_2 µg m^{-3} (20°C 1013mb)								
Site/Year	1997	1998	1999	2000	2001	2002	2003	2004	2005
Bath Roadside	63	62	61	54	57	56	60	55	64
Brentford Roadside								54	48
Brighton Roadside					36	37	43	41	39
Bristol Old Market	60	57	55	55				54	60
Bury Roadside		74	73	70	68	68	76	69	64
Cambridge Roadside				41	39	43	46	42	45
Camden Kerbside	70	64	66	63	66				75
Dumfries					38	38	38	37	36
Exeter Roadside	45	39	39	38	41	38	41	40	43
Glasgow Kerbside		70	69	72	71	74	75	68	62
Haringey Roadside	59	53	51	51	48	46	52	46	41
Hounslow Roadside		72	60	52	54	58			
Hove Roadside		35		36	39	33	37	38	36
Inverness						22	23	23	21
Lincoln Roadside		72	69						
London A3 Roadside		57	58	55	53	58	73	66	61
London Bromley			65	63	61	41	42	47	49
London Cromwell Road 2			93	88	76	72	75	80	79
London Marylebone Road		92	91	93	84	80	107	110	112
Norwich Roadside		33	33	29	31	30	33	29	
Oxford Centre Roadside			56	60	60	60	71	68	67
Southwark Roadside				63	65	58	67	62	60
Stockton-on-Tees Yarm					40	39	43	37	34
Sutton Roadside	49	41	43	39	44				
Tower Hamlets Roadside	71	65	70	65	69	61	67	61	61
Wrexham						24	25	21	19

Table A3.3.

	NO$_2$ 98%ile µg m^{-3} (20°C 1013mb)								
Site/Year	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**
Bath Roadside	130	128	122	109	122	120	126	118	138
Brentford Roadside								122	117
Brighton Roadside					76	84	92	86	86
Bristol Old Market	136	134	118	122				122	143
Bury Roadside		138	132	128	134	128	147	130	128
Cambridge Roadside				88	80	86	96	88	90
Camden Kerbside	153	130	136	117	126				160
Dumfries					109	101	107	101	103
Exeter Roadside	99	94	92	88	90	88	96	101	118
Glasgow Kerbside		168	166	153	160	145	168	157	149
Haringey Roadside	136	107	105	99	97	97	111	99	92
Hounslow Roadside		159	117	101	107	128			
Hove Roadside		90		90	94	86	96	101	88
Inverness						65	74	74	73
Lincoln Roadside		178	168						
London A3 Roadside		103	122	105	111	118	149	134	138
London Bromley			126	117	117	84	92	99	107
London Cromwell Road 2			162	155	139	130	141	145	151
London Marylebone Road		183	176	189	174	153	235	233	256
Norwich Roadside		76	76	67	71	73	78	73	
Oxford Centre Roadside			132	136	130	132	168	153	157
Southwark Roadside				107	115	105	128	107	115
Stockton-on-Tees Yarm					101	96	103	88	84
Sutton Roadside	117	92	97	94	103				
Tower Hamlets Roadside	157	120	132	136	134	115	138	118	118
Wrexham						67	71	65	57

Table A3.4.

	Sum of Exceedences >200 µg m^{-3} NO_2								
Site/Year	1997	1998	1999	2000	2001	2002	2003	2004	2005
Bath Roadside	0	2	2	0	0	1	0	0	3
Brentford Roadside								8	2
Brighton Roadside					0	3	0	0	0
Bristol Old Market	5	5	5	7				0	22
Bury Roadside		6	0	5	11	0	1	0	3
Cambridge Roadside				0	0	0	0	0	1
Camden Kerbside	36	6	7	0	0				13
Dumfries					0	0	2	0	1
Exeter Roadside	1	0	0	0	0	3	0	0	0
Glasgow Kerbside		65	46	18	54	38	36	14	17
Haringey Roadside	32	0	1	0	0	0	0	0	2
Hounslow Roadside		6	0	0	0	4			
Hove Roadside		0		0	0	0	0	0	1
Inverness						0	0	0	0
Lincoln Roadside		41	14						
London A3 Roadside		0	6	0	0	6	16	8	28
London Bromley			0	0	0	0	0	0	1
London Cromwell Road 2			12	13	2	0	6	3	8
London Marylebone Road		71	64	108	60	2	471	542	828
Norwich Roadside		0	0	0	0	0	0	0	
Oxford Centre Roadside			4	2	0	0	23	6	12
Southwark Roadside				0	0	0	2	0	0
Stockton-on-Tees Yarm					0	1	1	0	0
Sutton Roadside	12	0	0	0	3				
Tower Hamlets Roadside	41	10	11	3	6	2	6	3	0
Wrexham						0	0	0	1
NB roadside only									
count	7	15	17	19	21	20	19	21	21
count > 18 days	3	3	2	1	2	1	3	1	3

Table A3.5: The annual average nitrogen dioxide/nitrogen oxides ratios observed at a) national network, b) London Air Quality Network sites for different site types. **For the national network sites are coloured yellow if they clearly show no significant increase in ratio between 2002 and 2005 and blue if they show an increase in ratio.**

a)

Site	Site type	Ratio 2002	Ratio 2003	Ratio 2004	Ratio 2005	Ratio 2004 – Ratio 2002
London Harlington	Airport			0.528	0.528	
Camden Kerbside	Kerbside				0.394	
Glasgow Kerbside	Kerbside	0.258	0.255	0.259	0.256	0.001
London Marylebone Road	Kerbside	0.267	0.341	0.356	0.382	0.089
Bath Roadside	Roadside	0.333	0.359	0.364	0.358	0.031
Brentford Roadside	Roadside			0.348	0.333	
Brighton Roadside	Roadside	0.446	0.478	0.500	0.476	0.054
Bristol Old Market	Roadside			0.360	0.351	
Bury Roadside	Roadside	0.289	0.308	0.317	0.339	0.027
Cambridge Roadside	Roadside	0.384	0.397	0.378	0.398	-0.006
Dumfries	Roadside	0.376	0.380	0.402	0.400	0.026
Exeter Roadside	Roadside	0.400	0.406	0.408	0.439	0.008
Haringey Roadside	Roadside	0.426	0.448	0.474	0.473	0.048
Hove Roadside	Roadside	0.478	0.521	0.521	0.563	0.042
Inverness	Roadside	0.449	0.451	0.479	0.477	0.030
London A3 Roadside	Roadside	0.341	0.380	0.367	0.386	0.025
London Bromley	Roadside	0.506	0.519	0.560	0.563	0.053
London Cromwell Rd 2	Roadside	0.377	0.391	0.415	0.422	0.038
Oxford Centre Roadside	Roadside	0.324	0.333	0.360	0.368	0.035
Southwark Roadside	Roadside	0.377	0.421	0.449	0.438	0.073
Stockton-on-Tees Yarm	Roadside	0.302	0.309	0.308	0.309	0.006
Tower Hamlets Roadside	Roadside	0.328	0.368	0.384	0.415	0.056
Wrexham	Roadside	0.480	0.490	0.525	0.500	0.045

Site	Site type	Ratio 2002	Ratio 2003	Ratio 2004	Ratio 2005	Ratio 2004 – Ratio 2002
London Bexley	Suburban	0.564	0.567	0.603	0.571	0.040
London Eltham	Suburban	0.638	0.644	0.681	0.630	0.043
London Hillingdon	Suburban	0.398	0.419	0.420	0.425	0.021
Aberdeen	Urban Background	0.587	0.585	0.591	0.585	0.004
Barnsley Gawber	Urban Background	0.556	0.568	0.629	0.541	0.073
Birmingham Tyburn	Urban Background				0.515	
Bournemouth	Urban Background	0.680	0.710	0.704	0.692	0.024
Brighton Preston Park	Urban Background				0.647	
Canterbury	Urban Background	0.621	0.647	0.621	0.586	0.000
Coventry Memorial Park	Urban Background	0.677	0.676	0.647	0.647	-0.030
Cwmbran	Urban Background	0.714	0.655	0.680	0.654	-0.034
Derry	Urban Background	0.625	0.680	0.682	0.667	0.057
Edinburgh St Leonards	Urban Background			0.694	0.694	
Glasgow City Chambers	Urban Background	0.461	0.485	0.485	0.469	0.024
Liverpool Speke	Urban Background			0.622	0.615	
London Brent	Urban Background	0.569	0.567	0.592	0.579	0.023
London N. Kensington	Urban Background	0.606	0.595	0.625	0.597	0.019
London Teddington	Urban Background	0.655	0.640	0.671	0.597	0.016
London Westminster	Urban Background	0.544		0.590	0.571	0.045
Manchester Town Hall	Urban Background	0.606	0.587	0.606	0.597	0.000
Port Talbot	Urban Background	0.594	0.629	0.656	0.633	0.063
Portsmouth	Urban Background	0.650	0.634	0.632	0.605	-0.018
Reading New Town	Urban Background			0.610	0.575	
Sandwell West Bromwich	Urban Background	0.617	0.591	0.628	0.659	0.011
Southend-on-Sea	Urban Background	0.676	0.641	0.667	0.622	-0.009
Stockport Shaw Heath	Urban Background	0.576		0.610	0.585	
Sunderland Silksworth	Urban Background				0.667	
Thurrock	Urban Background	0.545	0.559	0.565	0.538	0.019
Walsall Alumwell	Urban Background	0.544	0.512	0.512	0.532	-0.032
West London	Urban Background	0.584	0.598	0.630	0.588	0.045
Wigan Centre	Urban Background				0.543	

Site	Site type	Ratio 2002	Ratio 2003	Ratio 2004	Ratio 2005	Ratio 2004 – Ratio 2002
Birmingham Centre	Urban Centre	0.576	0.532	0.660	0.623	0.084
Bradford Centre	Urban Centre	0.457	0.425	0.443	0.500	-0.014
Glasgow Centre	Urban Centre	0.451		0.514	0.500	0.064
Hull Freetown	Urban Centre		0.569	0.600	0.563	
Leeds Centre	Urban Centre	0.476	0.465	0.492	0.492	0.016
Leicester Centre	Urban Centre	0.593	0.552	0.563	0.559	-0.031
London Bloomsbury	Urban Centre			0.592	0.553	
London Hackney	Urban Centre	0.475	0.467	0.511	0.533	0.036
London Lewisham	Urban Centre	0.455	0.470	0.490	0.490	0.035
London Southwark	Urban Centre	0.517		0.554	0.557	0.037
London Wandsworth	Urban Centre	0.468	0.512	0.478	0.470	0.009
Newcastle Centre	Urban Centre	0.556	0.561	0.558	0.571	0.002
Norwich Centre	Urban Centre	0.641	0.595	0.600	0.657	-0.041
Nottingham Centre	Urban Centre	0.522	0.554	0.565	0.532	0.042
Plymouth Centre	Urban Centre	0.650	0.622	0.614	0.595	-0.036
Rotherham Centre	Urban Centre	0.493	0.461	0.538	0.523	0.046
Sheffield Centre	Urban Centre	0.436	0.448	0.517	0.526	0.081
Southampton Centre	Urban Centre	0.493	0.486	0.500	0.463	0.007
Stoke-on-Trent Centre	Urban Centre	0.545	0.525	0.517	0.485	-0.028
Swansea	Urban Centre	0.456	0.466	0.378	0.442	-0.078
Wolverhampton Centre	Urban Centre	0.528	0.523	0.604	0.528	0.076
Billingham	Urban Industrial	0.526	0.508	0.547	0.540	0.021
Grangemouth	Urban Industrial		0.564	0.630	0.533	
Middlesbrough	Urban Industrial	0.634	0.610		0.694	
Salford Eccles	Urban Industrial	0.567	0.506	0.540	0.565	-0.027
Sheffield Tinsley	Urban Industrial	0.427	0.418	0.471	0.432	0.044

Site	Site type	Ratio 2002	Ratio 2003	Ratio 2004	Ratio 2005	Ratio 2004 – Ratio 2002
Aston Hill	Rural			0.763	0.770	
Eskdalemuir	Rural				0.792	
Harwell	Rural	0.764	0.770	0.769	0.803	0.005
High Muffles	Rural				0.773	
Ladybower	Rural	0.890	0.860	0.852	0.819	-0.038
Lullington Heath	Rural	0.863	0.817	0.823	0.831	-0.040
Market Harborough	Rural			0.837	0.859	
Rochester	Rural	0.773	0.708	0.727	0.673	-0.046
Somerton	Rural			0.829	0.790	
St Osyth	Rural		0.784	0.810	0.806	
Wicken Fen	Rural	0.723			0.693	
Yarner Wood	Rural			0.839	0.891	
Narberth	Remote	0.758	0.838	0.757	0.758	-0.001

b)

Site name	Site type	Ratio 2002	Ratio 2003	Ratio 2004
Camden 1 - Swiss Cottage	Kerbside	0.423		0.400
Dartford Roadside - St Clements	Kerbside	0.365	0.371	0.408
Redbridge 3 - Fullwell Cross	Kerbside	0.398	0.415	0.408
Sutton 4 - Wallington	Kerbside	0.344	0.393	0.413
Barnet 1 - Tally Ho Corner	Kerbside	0.339	0.396	0.378
Croydon 5 - Norbury	Kerbside	0.292	0.322	0.348
Marylebone Rd - Baker St	Kerbside	0.268	0.341	0.355
Redbridge 2 - Ilford Broadway	Kerbside	0.384	0.406	
Bromley 7 - Central	Roadside	0.510	0.521	0.554
Watford Roadside	Roadside	0.511	0.507	0.522
Enfield 2 - Church Street	Roadside	0.497	0.481	0.507
Richmond 1 - Castlenau	Roadside	0.483	0.496	0.510
Havering 1 - Rainham	Roadside	0.471	0.484	0.436
Wandsworth 4 - High Street	Roadside	0.458	0.459	0.524
Havering 3 - Romford	Roadside	0.383	0.393	0.429
Greenwich 7 - Blackheath	Roadside	0.488	0.402	0.394
Lewisham 2 - New Cross	Roadside	0.357	0.431	0.437
Croydon 4 - George Street	Roadside	0.461	0.455	0.503
Haringey 1 - Town Hall	Roadside	0.428	0.449	0.472
Enfield 4 - Derby Road, Upper Edmonton	Roadside	0.433	0.437	0.446
Redbridge 4 - Gardner Close	Roadside	0.408	0.413	0.444
Greenwich 5 - Trafalgar Road	Roadside	0.439	0.469	0.487
Crystal Palace 1 - C Palace Parade	Roadside	0.345	0.424	0.393
Broxbourne Roadside	Roadside	0.374	0.407	0.418
Lambeth 1 - Christchurch Road	Roadside	0.432	0.453	0.463
Lambeth 2 - Vauxhall Cross	Roadside	0.438	0.484	
Hillingdon 1 - South Ruislip	Roadside	0.330	0.359	0.384
Croydon 2 - Purley Way	Roadside	0.308	0.382	0.330
Ealing 2 - Acton Town Hall	Roadside	0.346	0.366	0.383
Dartford Roadside 3 - Bean Interchange	Roadside	0.340	0.396	0.414
Camden 3 - Shaftesbury Avenue	Roadside	0.414	0.437	0.455
Southwark 2 - Old Kent Road	Roadside	0.377	0.423	0.443
Hounslow 4 - Chiswick High Rd	Roadside	0.378	0.421	0.443
Greenwich Bexley 6 - A2 Falconwood	Roadside	0.314	0.333	0.364
Hillingdon 2 - Hillingdon Hospital	Roadside	0.366	0.496	0.495
Gravesham Roadside - A2	Roadside	0.305	0.346	0.376
A3 - AURN	Roadside	0.349	0.392	0.369
Hackney 6 - Old Street	Roadside	0.358	0.407	0.416
Tower Hamlets 2 - Mile End Rd	Roadside	0.329	0.367	0.383
Kens and Chelsea 2 - Cromwell Rd	Roadside	0.377	0.394	0.415
Islington 2 - Holloway Road	Roadside	0.341	0.371	0.413

Site name	Site type	Ratio 2002	Ratio 2003	Ratio 2004
H and F 1 - Hammersmith Broadway	Roadside	0.318	0.368	0.352
Kens and Chelsea 3 - Knightsbridge	Roadside	0.372	0.387	0.399
Kens and Chelsea 4 - Kings Rd	Roadside	0.335	0.374	0.413
Mole Valley 2 - Lower Ashstead	Suburban	0.647	0.606	0.642
Bexley 5 - Bedonwell	Suburban	0.678	0.676	0.674
Barking & Dagenham 1 - Rush Green	Suburban	0.657	0.587	0.633
Enfield 1 - Bushhill Park	Suburban	0.600	0.573	0.523
Bexley 2 - Belvedere	Suburban	0.580	0.577	0.633
Richmond 2 - Barnes Wetlands	Suburban	0.539	0.633	0.662
Haringey 2 - Priory Park	Suburban	0.593	0.572	0.602
Croydon 6 - Euston Road	Suburban	0.521	0.527	0.524
Hounslow 2 - Cranford	Suburban	0.590	0.576	0.546
Hillingdon - AURN	Suburban	0.400	0.415	0.422
Castle Point 1 - Town Centre	Urban Background	0.719	0.685	0.694
Teddington - AURN	Urban Background	0.655	0.640	0.673
Mole Valley 3 - Dorking	Urban Background	0.563	0.577	0.585
Harrow 1 - Stanmore	Urban Background	0.609	0.578	0.629
Greenwich 4 - Eltham	Urban Background	0.630	0.641	0.642
Brent 1 - Kingsbury (AURN)	Urban Background	0.566	0.565	0.601
Bexley 1 - Slade Green (AURN)	Urban Background	0.576	0.561	0.600
Enfield 3 - Salisbury School Ponders End	Urban Background	0.599	0.557	0.585
Waltham Forest 1 - Dawlish Road	Urban Background	0.609	0.555	0.588
Redbridge 1 - Perth Terrace	Urban Background	0.569	0.565	0.591
Tower Hamlets 1 - Poplar	Urban Background	0.621	0.619	0.639
Lambeth 3 - Loughborough Junct	Urban Background	0.594	0.618	0.589
Kens and Chelsea 1 - North Kensington	Urban Background	0.605	0.598	0.625
Thurrock	Urban Background	0.542	0.560	0.569
Barnet 2 - Finchley	Urban Background	0.548	0.540	0.556
Ealing 1 - Ealing Town Hall	Urban Background	0.524	0.524	0.565
Tower Hamlets 3 - Bethnal Green	Urban Background	0.582	0.620	0.593
Islington 1 - Upper Street	Urban Background	0.601	0.599	0.617
West London - AURN	Urban Background	0.589	0.600	0.622
Westminster - AURN	Urban Background	0.547	0.614	0.596
City of London 1 - Senator House	Urban Background	0.569	0.595	0.591
Southwark 1 - Elephant and Castle	Urban Background	0.521	0.551	0.557
Bloomsbury - AURN	Urban Background	0.452	0.560	0.595
Hackney 4 - Clapton	Urban Background	0.471	0.470	0.516
Lewisham 1 - Catford	Urban Background	0.454	0.471	0.492
Wandsworth 2 - Town Hall	Urban Background	0.464	0.517	0.478
Brent 3 - Harlesden	Urban Background	0.414	0.440	0.461
Heathrow Airport	Urban Background	0.437	0.441	0.445

Table A3.6: Correlation coefficients for 53 roadside monitoring sites.

	NO_x annual mean	NO_2 annual mean	98 %ile	Exceedences	Count all	Count - car	Count - bus	Count - LGV	Count HGVr[1]	Count HGVa[2]	Count motor bike	NO_x all	NO_x car	NO_x bus	NO_x LGV	NO_x HGVr[1]	NO_x HGVa[2]	NO_x motor bike
NO_x annual mean	1.00																	
NO_2 annual mean	0.96	1.00																
98 %ile	0.94	0.98	1.00															
Exceedences	0.75	0.78	0.78	1.00														
Count – all	0.35	0.26	0.24	0.11	1.00													
Count – car	0.32	0.22	0.21	0.08	1.00	1.00												
Count – bus	0.57	0.67	0.66	0.64	0.14	0.10	1.00											
Count – LGV	0.28	0.21	0.18	0.10	0.93	0.91	0.12	1.00										
Count – HGVr[1]	0.27	0.17	0.17	-0.01	0.81	0.80	-0.05	0.70	1.00									
Count – HGVa[2]	0.06	0.00	0.02	-0.05	0.58	0.56	-0.14	0.63	0.49	1.00								
Count – motorbike	0.49	0.54	0.50	0.20	0.56	0.51	0.43	0.55	0.40	0.09	1.00							
NO_x all	0.38	0.30	0.28	0.17	0.75	0.72	0.17	0.77	0.69	0.51	0.46	1.00						
NO_x car	0.25	0.16	0.14	0.06	0.95	0.95	0.05	0.87	0.77	0.64	0.44	0.76	1.00					
NO_x bus	0.61	0.71	0.69	0.66	0.13	0.08	0.99	0.10	-0.05	-0.18	0.47	0.18	0.02	1.00				
NO_x LGV	0.32	0.26	0.22	0.13	0.90	0.87	0.18	0.98	0.67	0.58	0.60	0.79	0.86	0.18	1.00			
NO_x HGVr[1]	0.33	0.25	0.24	0.03	0.75	0.74	0.03	0.65	0.97	0.39	0.49	0.67	0.70	0.05	0.64	1.00		
NO_x HGVa[2]	0.08	0.02	0.03	-0.04	0.59	0.56	-0.12	0.66	0.51	1.00	0.11	0.54	0.64	-0.15	0.61	0.42	1.00	
NO_x motor bike	0.39	0.41	0.39	0.15	0.72	0.68	0.30	0.71	0.57	0.36	0.91	0.64	0.66	0.31	0.72	0.59	0.37	1.00

[1] Heavy goods vehicle – rigid

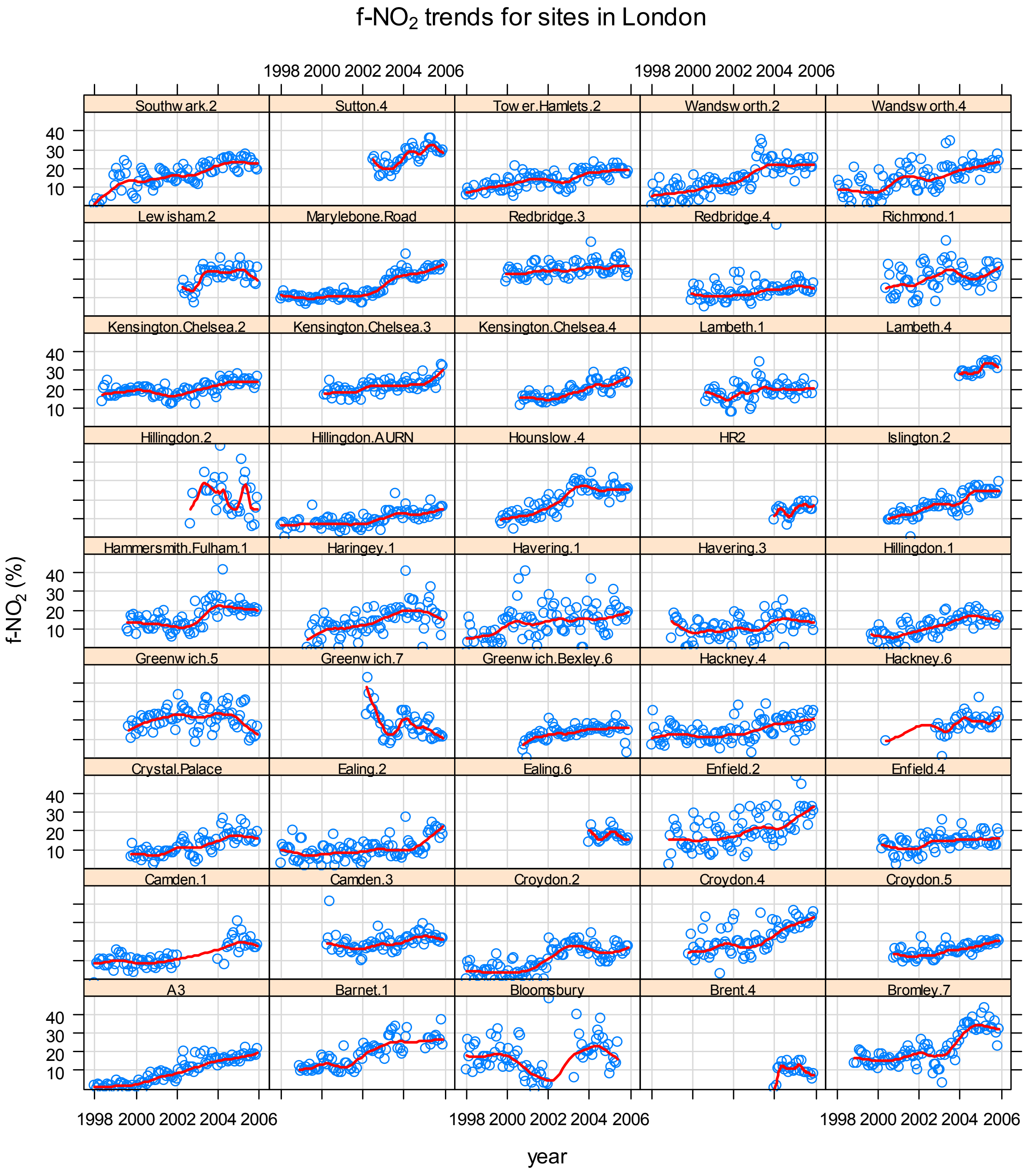
[2] Heavy goods vehicle – articulated

Table A3.7: London sites used to estimate primary nitrogen dioxide fractions by vehicle type (vehicle NO_x emissions provided by Sean Beevers, ERG).

Site	Annual mean NO_x ($\mu g\ m^{-3}$)	Annual mean NO_2 ($\mu g\ m^{-3}$)	Estimated primary NO_2 (% by vol.) (f-NO_2)	Road NO_x ($\mu g\ m^{-3}$)	Road primary NO_2 ($\mu g\ m^{-3}$)	Bus NO_x ($\mu g\ m^{-3}$)	HGV NO_x ($\mu g\ m^{-3}$)	Car + LGV NO_x ($\mu g\ m^{-3}$)
Greenwich Bexley 6 – A2 Falconwood	121.6	44.2	14.3	93.9	13.4	3.4	44.9	45.6
Brent 4 – Ikea	250.6	63.5	8.2	198.7	16.3	4.2	97.2	97.4
Bromley 7 – Central	84.4	46.7	30.3	47.0	14.3	13.0	10.3	23.7
Camden 1 – Swiss Cottage	168.8	67.5	17.7	110.8	19.7	36.2	22.0	52.6
Camden 3 – Shaftesbury Avenue	158.7	72.3	20.7	100.8	20.9	21.0	23.6	56.2
Croydon 2 – Purley Way	131.1	43.3	10.5	108.0	11.3	8.6	58.8	40.6
Croydon 4 – George Street	104.6	52.7	26.1	72.3	18.9	33.7	13.8	24.8
Croydon 5 – Norbury	185.4	64.4	14.8	151.4	22.4	25.0	70.6	55.8
Crystal Palace 1 – C Palace Parade	123.5	48.6	15.6	93.9	14.6	31.8	24.0	38.1
Ealing 2 – Acton Town Hall	142.9	54.8	7.4	84.0	6.2	33.2	12.6	38.1
Ealing 6 – Hanger Lane	354.5	98.3	15.4	297.3	45.6	3.9	151.1	142.3
Enfield 2 – Church Street	77.0	39.1	15.9	32.6	5.2	11.3	9.2	12.1
Greenwich 5 – Trafalgar Road	97.1	47.1	22.3	52.4	11.7	14.1	16.4	21.8
Greenwich 7 – Blackheath	128.5	50.6	14.3	80.1	11.5	3.6	42.2	34.3
Hackney 6 – Old Street	145.9	60.6	21.1	85.6	18.1	10.3	34.7	40.7
H'smith and Fulham 1 – H'smith Broadway	224.6	79.5	20.5	154.3	31.6	50.7	36.7	66.8
Haringey 1 – Town Hall	97.3	46.0	15.1	46.0	7.0	14.5	13.7	17.7
Harrow 2 – North Harrow Roadside	127.9	44.4	10.4	100.9	10.5	16.2	23.8	60.9
Havering 1 – Rainham	87.7	38.3	10.2	54.5	5.5	2.0	31.1	21.3
Havering 3 – Romford	90.7	38.9	14.5	53.1	7.7	7.3	13.2	32.6
Hillingdon 1 – South Ruislip	122.4	46.9	16.2	88.0	14.3	9.7	26.4	51.9
Hounslow 4 – Chiswick High Rd	175.9	77.9	23.6	143.2	33.8	60.9	35.0	47.2
Islington 2 – Holloway Road	169.9	70.2	23.0	112.0	25.8	16.0	42.7	53.3
Kens and Chelsea 2 – Cromwell Rd	194.0	80.5	23.1	135.1	31.2	27.7	30.0	77.4
Kens and Chelsea 3 – Knightsbridge	219.4	87.6	21.1	161.4	34.1	57.7	34.8	69.0

Site	Annual mean NO_x (µg m^{-3})	Annual mean NO_2 (µg m^{-3})	Estimated primary NO_2 (% by vol.) (f-NO_2)	Road NO_x (µg m^{-3})	Road primary NO_2 (µg m^{-3})	Bus NO_x (µg m^{-3})	HGV NO_x (µg m^{-3})	Car + LGV NO_x (µg m^{-3})
Kens and Chelsea 4 – Kings Rd	223.6	92.4	21.5	170.5	36.7	77.6	27.6	65.3
Lambeth 1 – Christchurch Road	116.4	53.9	18.0	83.4	15.0	4.8	36.1	42.5
Lambeth 4 – Brixton Road	567.7	197.7	26.5	540.6	143.4	262.9	109.3	168.4
Lewisham 2 – New Cross	156.8	68.3	23.3	123.1	28.7	58.0	38.0	27.1
Redbridge 3 – Fullwell Cross	163.7	66.9	26.3	119.7	31.4	47.9	19.8	52.0
Redbridge 4 – Gardner Close	111.5	49.4	13.0	71.2	9.2	3.5	36.2	31.5
Richmond 1 – Castlenau	81.3	41.4	19.1	47.9	9.2	21.1	2.6	24.3
Southwark 2 – Old Kent Road	125.8	62.3	21.0	93.0	19.5	25.9	31.5	35.6
Sutton 4 – Wallington	195.2	80.5	25.8	165.8	42.8	49.8	56.4	59.6
Tower Hamlets 2 – Mile End Rd	158.9	60.9	16.1	112.1	18.1	17.7	42.9	51.6
Wandsworth 4 – High Street	89.7	47.1	18.2	55.1	10.0	13.8	21.3	20.1
Marylebone Rd – Baker St	310.9	110.4	20.8	246.3	51.2	42.8	80.1	123.4

Figure A3.1: Estimated trends in f-NO_2 at individual monitoring sites in London.



Annex 4

Details of the modelling approaches and tabulation of the modelling results to supplement Chapter 4

A4.1 Carslaw and Beevers (2005) model

Box A4.1: Description of the Carslaw and Beevers (2005) model

Estimating f-NO_2 from ambient measurements in London

Carslaw and Beevers (2005) describe the development of a simple constrained chemical model to estimate the proportion of NO_x emitted as NO_2 (f-NO_2) at roadside sites where O_3 is not measured. Briefly, the increment in NO_x and NO_2 concentration at roadside site above a nearby background site is partitioned into NO_2 that is chemically derived through the reaction between NO and O_3 and that which is emitted directly by road vehicles. The model is constrained by assuming that the difference between roadside and background NO_x concentrations each hour is due to NO_x emissions from road vehicles adjacent to the roadside monitoring site. A simple set of chemical equations is used to describe the time-dependent change in NO, NO_2 and O_3 concentrations as vehicle plumes are mixed with background air. By running many simulations that vary f-NO_2 from road traffic and the time available for the NO–O_3 reaction to take place (τ), the best agreement between modelled hourly NO_2 concentrations and measured roadside concentrations is sought. It should be noted that τ strictly includes micro-mixing effects because vehicle exhaust plumes do not mix instantaneously with ambient air. In practice, several hundred combinations of the NO_2/NO_x emissions ratio and τ are considered before the best single combination, resulting in the minimum error between modelled and measured NO_2 concentrations, is identified. The technique assumes that the increment in NO_2 concentration above a local background site is controlled by the availability of O_3 and directly emitted NO_2 only. The formation of NO_2 through other routes (e.g. through reactions with VOCs) is assumed to be negligible. The approach yields estimates of hourly NO_2 and O_3, as well as an estimate of the road transport f-NO_2 for vehicles using Marylebone Road. The model has been extensively compared with f-NO_2 derived through the total oxidant method.

Table A4.1: Base case nitrogen oxides and nitrogen dioxide concentrations for 2002 at the roadside and kerbside sites in the London Air Quality Network and the effect of adding an additional 5% primary nitrogen dioxide to each site.

		Base case		Base case + 5% primary NO_2	
Site	NO_x (ppb)	NO_2 (ppb)	f-NO_2	NO_2 (ppb)	f-NO_2
A3	90.5	32.4	0.358	35.5	0.393
Bloomsbury	49.5	23.2	0.470	24.3	0.492
Barnet 1	108.7	37.8	0.348	41.9	0.386
Bromley 7	42.9	22.4	0.522	23.3	0.543
Camden 1	92.9	35.5	0.382	37.9	0.408
Camden 3	84.3	36.9	0.438	39.2	0.465
Croydon 2	81.6	25.2	0.309	28.1	0.345
Croydon 4	57.1	27.2	0.475	28.7	0.501
Croydon 5	116.3	35.2	0.303	39.6	0.341
Crystal Palace 1	70.7	26.4	0.374	28.5	0.404
Ealing 2	77.7	28.3	0.364	30.3	0.390
Enfield 2	47.8	24.7	0.517	25.6	0.535
Enfield 4	57.7	26.0	0.452	27.3	0.473
Greenwich Bexley 6	84.8	27.1	0.320	29.9	0.353
Greenwich 5	64.6	29.6	0.457	31.3	0.484
Greenwich 7	53.0	27.0	0.510	28.2	0.532
H'smith & Fulham 1	96.0	32.3	0.337	35.4	0.369
Haringey 1	58.5	25.6	0.438	26.8	0.458
HIillingdon	68.1	27.6	0.405	29.7	0.435
Hillingdon 1	71.0	24.6	0.347	26.9	0.378
Hillingdon2	89.7	34.2	0.381	36.4	0.405
Hackney 4	52.9	26.0	0.492	27.3	0.516
Hackney 6	91.5	35.0	0.383	37.2	0.407
Hounslow 4	80.8	31.6	0.392	34.3	0.425
Havering 1	50.3	23.8	0.472	25.0	0.496
Havering 3	57.2	22.6	0.395	24.1	0.422
Islington 2	108.4	37.7	0.348	41.1	0.380
Kens & Chelsea 2	99.8	39.2	0.393	42.3	0.424
Kens & Chelsea 3	119.8	46.1	0.385	50.1	0.418
Kens & Chelsea 4	130.4	45.9	0.352	50.3	0.386
Lambeth 1	66.5	30.1	0.453	32.0	0.481
Heathrow Airport	56.5	28.8	0.509	30.1	0.532
Lewisham 1	59.2	27.9	0.472	29.5	0.499
Lewisham 2	64.0	25.1	0.391	27.0	0.421
Marylebone Rd 1	157.0	43.7	0.279	49.5	0.316
Redbridge 3	92.5	37.3	0.403	40.3	0.435
Redbridge 4	70.8	28.3	0.399	30.0	0.424
Richmond 1	46.6	24.0	0.514	25.0	0.536

Site	NO_x (ppb)	Base case NO_2 (ppb)	f-NO_2	Base case + 5% primary NO_2 NO_2 (ppb)	f-NO_2
Southwark 2	80.6	32.0	0.398	34.4	0.427
Sutton 4	101.5	36.5	0.360	40.1	0.395
Tower Hamlets 2	96.1	33.3	0.346	36.5	0.379
Wandsworth 2	61.8	28.8	0.467	30.5	0.494
Wandsworth 4	51.0	24.0	0.471	25.2	0.495
Mean	**78.1**	**30.6**	**0.409**	**32.9**	**0.437**

A4.2 The Oxidant Partitioning Model (Jenkin, 2004a)

Box A4.2: The oxidant partitioning model (Jenkin, 2004a)

Annual mean monitoring data from 56 urban UK sites reporting co-located measurements of O_3 and NO_x have previously been analysed to provide a method of describing NO_2/NO_x partitioning as a function of NO_x (Jenkin, 2004a). It was demonstrated that consideration of O_3, NO and NO_2 as a set of chemically coupled species (rather than NO and NO_2 alone) provides additional information to assist the prediction and interpretation of how the level of NO_2 varies with that of NO_x. The method involves defining (i) linear expressions describing how the level of "oxidant", OX (equal to the sum of O_3 and NO_2) varies with the level of NO_x, and (ii) algebraic expressions describing how the fractional contribution of NO_2 to OX (i.e. NO_2/OX) varies with NO_x. The product of these two quantities yields the dependence of NO_2 levels as a function of NO_x. The advantage of this semi-empirical approach (usually termed the "oxidant partitioning model") is that it allows the derived NO_2 vs NO_x relationships to be rationalised in terms of sources of OX and well-understood chemical processes. In this way it also enables predictions that take account of possible changes in the magnitudes of OX sources, such as the background O_3 level or the fractional contribution of NO_2 to NO_x emissions (i.e. "primary NO_2").

Table A4.2: Observed and calculated summary statistics for annual mean nitrogen oxides and nitrogen dioxide concentrations (µg m^{-3}) and nitrogen dioxide/nitrogen oxides ratios in 2002-2005, for sites used in the development of the oxidant partitioning model (Jenkin, 2004a).

Year	Number of sites	Observed mean (1σ) NO_x	 NO_2	 NO_2/NO_x	Calculated mean (1σ) NO_2 (a)	 (b)	 NO_2/NO_x (a)	 (b)
2002	48	71.5 (47.1)	34.9 (11.2)	0.540 (0.099)	34.2 (10.8)	36.2 (12.8)	0.530 (0.091)	0.553 (0.086)
2003	43	78.1 (51.4)	38.1 (15.1)	0.532 (0.088)	36.1 (11.2)	38.3 (13.4)	0.513 (0.091)	0.538 (0.086)
2004	45	69.7 (49.1)	35.5 (15.7)	0.558 (0.095)	33.6 (11.7)	35.4 (13.7)	0.540 (0.100)	0.563 (0.095)
2005	36	74.3 (48.2)	37.4 (16.0)	0.543 (0.086)	35.2 (11.5)	37.5 (13.2)	0.523 (0.091)	0.547 (0.086)

Notes

(a) Calculated using the observed NO_x and the site dependent semi-empirical method of Jenkin (2004a), which was based on an analysis of data up to 2001; (b) Calculated using the observed NO_x and the site dependent semi-empirical method of Jenkin (2004a), with the local oxidant contribution increased by 0.05 ppb/ppb NO_x, consistent with an illustrative increase of 5% in primary NO_2 emissions.

A4.3 The London Routine Column Trajectory Model (Derwent, 1999)

Box A4.3: The London Routine Column Trajectory model (Derwent, 1999)

The LRCTM Model (Derwent, 1999) adopts a Lagrangian approach in which air parcels are advected with the wind field from the outlying rural areas into the London area, over a regular emissions grid mesh, and into the arrival point. A travel time of 6 hours has been chosen so that under all meteorological conditions and whatever the arrival point, all air parcels start off outside the Greater London area and finish within it. The air parcels themselves are given some vertical structure and consist of a stack of twenty layers from the ground surface to the top of the atmospheric boundary layer. Wind shears are neglected and the wind field is taken to be constant with height. In this way, each column of layers defining an air parcel remains well-defined throughout the travel time without being stretched apart and its integrity destroyed.

As the air column moves over the emissions grid, following the trajectory path, the time-development of the concentrations of the three model species NO, NO_2 and O_3 can be represented by the differential equations given below:

$$\partial[NO]/\partial t = P_{NO} - L_{NO}\,[NO] + \partial/\partial z\,(\,K\partial\,[NO]/\partial z\,) \qquad (1)$$

$$\partial[NO_2]/\partial t = P_{NO2} - L_{NO2}\,[NO_2] + \partial/\partial z\,(\,K\partial[NO_2]/\partial z\,) \qquad (2)$$

$$\partial[O_3]/\partial t = P_{O3} - L_{O3}\,[O_3] + \partial/\partial z\,(\,K\partial[O_3]/\partial z\,) \qquad (3)$$

In these equations (1)-(3), the P terms describe the production of the pollutant in question from emissions and chemistry and the L terms, the loss of the species by chemistry and surface removal. The terms containing K describe the turbulent vertical exchange of pollutant throughout the air column. Horizontal exchange has been implicitly neglected because, in the Lagrangian approach, horizontal advection terms are not required as the air column is moving with the advecting wind flow.

Meteorological data from Heathrow Airport and regional O_3 background concentrations from Sibton, Lullington Heath and Harwell were employed for each hour of the year using 1995 data. Emission of NO_x at 1 km x 1 km spatial resolution were taken for road traffic and other sources within the Greater London area from the LAEI inventory for 2000 and for source in the south-east region from the NAEI. Rate coefficients for the NO + O_3 and NO + NO + O_2 reactions were taken from published chemical kinetic data evaluations. The photolysis rate data for NO_2 were calculated at each point in time in each trajectory from the local solar zenith angle using a two-stream scattering method. Dry deposition removed NO_2 and O_3 from the base of each column using a dry deposition velocity approach.

Table A4.3: Observed and model annual mean nitrogen dioxide and nitrogen oxides concentrations in ppb at urban background and suburban London Air Quality Network sites, together with the nitrogen dioxide/nitrogen oxides ratios in the model base case and in a sensitivity case with an additional 5% direct nitrogen dioxide emission.

Code	Observed		Modelled		NO_2/NO_x	NO_2/NO_x
	NO_2, ppb	NO_x, ppb	NO_2, ppb	NO_x, ppb	base case	+5% case
Bloomsbury	22.9	50.7	21.5	38.4	0.559	0.576
Barnet 2	22.2	37.4	17.2	28.5	0.605	0.619
Barnet 3	22.2	43.9	16.4	26.0	0.630	0.643
Brent 1	15.2	26.9	15.0	22.7	0.661	0.670
Brent 3	26.9	64.8	18.0	29.6	0.608	0.621
BW1	16.5	25.1	11.0	15.2	0.724	0.730
Bexley 1	16.4	28.5	14.2	21.8	0.650	0.660
C’ of London 1	26.4	46.3	22.5	41.8	0.539	0.557
DC1	16.4	32.3	8.7	11.3	0.765	0.767
Ealing 1	19.6	37.5	17.6	28.6	0.616	0.627
Enfield 3	17.6	29.3	14.8	22.6	0.657	0.667
Greenwich 4	15.3	24.3	15.1	24.2	0.623	0.635
Hackney 4	24.3	51.5	17.3	27.5	0.630	0.641
HM1	14.6	26.3	13.7	20.0	0.683	0.691
Harrow1	14.8	24.3	14.7	22.3	0.658	0.668
Islington 1	23.3	38.9	19.5	32.7	0.597	0.611
Ken’ & Chels’ 1	20.6	34.1	20.4	36.0	0.565	0.581
Lambeth 3	20.1	33.9	18.2	31.1	0.585	0.599
H’row Airport 2	29.0	66.3	28.4	53.3	0.532	0.539
Lewisham 1	26.1	57.6	16.8	28.0	0.601	0.615
Mole Valley 3	13.1	23.2	9.4	12.9	0.727	0.731
Redbridge 1	18.9	33.2	15.8	24.9	0.636	0.648
SA1	13.7	25.3	9.8	12.9	0.754	0.757
Southwark 1	24.2	46.5	19.9	35.2	0.564	0.580
Sutton 2	19.9	31.6	14.5	22.6	0.643	0.653
Teddington	13.3	20.3	14.4	22.3	0.645	0.654
T’ Hamlets 1	20.7	33.3	18.8	32.3	0.582	0.598
Thurrock 1	18.6	34.4	11.1	15.7	0.703	0.710
TR1	15.4	40.9	12.3	18.2	0.675	0.684
Wandsworth 2	27.0	58.1	18.3	31.2	0.585	0.600
West London	23.8	40.5	20.7	37.0	0.560	0.576
WH1	13.5	21.8	17.0	27.0	0.631	0.643
Westminster	22.6	41.3	21.5	39.7	0.541	0.558
B’king+D’ham1	16.5	25.1	14.4	22.2	0.649	0.659
Bexley 2	16.8	29.0	14.2	21.6	0.659	0.667
Bexley 5	15.8	23.3	14.5	22.0	0.657	0.666
Croydon 6	18.3	35.1	15.1	24.3	0.622	0.634
Enfield 1	16.8	28.0	14.2	21.1	0.673	0.683

Code	Observed		Modelled		NO_2/NO_x	NO_2/NO_x
	NO_2, ppb	NO_x, ppb	NO_2, ppb	NO_x, ppb	base case	+5% case
Haringey 2	18.9	31.9	16.5	25.5	0.648	0.658
Hillingdon	23.7	59.1	18.4	32.2	0.573	0.589
Hounslow 2	22.5	38.1	19.5	34.8	0.562	0.576
Mole Valley 2	13.7	21.1	13.5	20.7	0.651	0.661
Richmond 2	16.2	30.1	17.3	28.4	0.610	0.622
Sutton 3	16.1	29.1	14.7	23.5	0.625	0.636
Average	**19.3**	**35.9**	**16.3**	**26.6**	**0.629**	**0.640**

Table A4.4: Observed and model annual mean ozone concentrations in ppb for 27 London Air Quality Network sites and the results of a sensitivity case with an additional absolute 5% increase in direct nitrogen dioxide emissions from urban road traffic.

Code	Observed O_3 ppb	Model O_3 ppb	Model O_3 +5% ppb	Model O_3 increase ppb
Brent 1	17.7	16.1	16.3	0.22
Bexley 1	19.2	16.7	16.9	0.21
City of London 1	14.3	12.8	13.2	0.33
DC1	19.5	19.8	19.8	0.05
Ealing 1	14.8	14.9	15.1	0.26
Enfield 3	20.3	16.3	16.5	0.24
Greenwich 4	18.7	16.3	16.6	0.23
Hackney 4	14.4	14.9	15.1	0.25
HM1	19.8	16.8	17.0	0.19
K'ton & Chelsea 1	16.3	13.6	13.9	0.30
Lewisham 1	13.4	15.5	15.7	0.26
Redbridge1	18.3	15.8	16.0	0.26
SA1	18.8	19.1	19.2	0.09
Southwark1	16.8	13.9	14.2	0.31
Teddington	23.1	16.7	16.9	0.20
Tower Hamlets 1	18.3	14.4	14.7	0.30
Thurrock 1	19.8	18.5	18.6	0.14
Wandsworth 2	13.3	14.7	15.0	0.28
WH1	21.0	15.1	15.3	0.28
Haringey 2	16.3	15.2	15.5	0.24
Hillingdon	12.8	14.5	14.8	0.27
Hounslow 2	14.9	14.0	14.3	0.25
Richmond 2	11.0	15.1	15.3	0.26
Sutton 3	20.5	16.6	16.8	0.21
Watford 1	16.7	17.3	17.5	0.19
M'bone Road 1	7.4	13.0	13.3	0.32
Richmond7	20.6	16.6	16.8	0.21
Average	**17.0**	**15.7**	**15.9**	**0.24**

A4.4 ADMS – Urban (Carruthers *et al.*, 2006)

Box A4.4. ADMS-Urban

ADMS-Urban is routinely used to calculate current and projected concentrations of NO_x, NO_2, and O_3 across London both at receptor points and as air quality maps. The model has been described in detail elsewhere (e.g. AQEG (2004) (NO_2 Report) and Carruthers *et al.* (2006)). In essence it consists of a Gaussian type dispersion model nested within a straight-line trajectory model. Particular features of note for the current study are inclusion of the Generic Reaction Set for the treatment of chemical reactions within the urban area, a street canyon model and a flexible input which allows the percentage of NO_x emitted as NO_2 to be specified on a road by road basis. Inputs to the model are emissions (NO_x, VOCs) for London for 2001 from the London Atmospheric Emissions Inventory (LAEI 2001), hourly sequential meteorological data for Heathrow and hourly averaged rural background concentrations taken from Harwell, Rochester, Wicken Fen and Lullington Heath dependent on the prevailing wind directions.

Table A3.5: Annual Average nitrogen oxides (ppb) at London Automatic Urban Rural Network sites calculated using ADMS-Urban for different percentages of emissions of primary nitrogen dioxide.

Site	2001			2010			2020		
	10%	15%	20%	10%	15%	20%	10%	15%	20%
A3	82.71	82.70	82.68	43.62	43.61	43.60	34.90	34.89	34.88
Bexley	44.48	44.47	44.47	32.51	32.51	32.50	28.01	28.01	28.00
Bloomsbury	78.07	78.05	78.04	49.98	49.97	49.96	43.64	43.63	43.62
Brent	31.88	31.88	31.87	21.61	21.61	21.61	18.17	18.16	18.16
Bromley	62.19	62.18	62.16	39.64	39.63	39.63	32.85	32.84	32.84
Camden	89.29	89.27	89.26	57.93	57.92	57.91	48.66	48.65	48.65
Cromwell Road	123.5	123.5	123.5	77.70	77.69	77.67	65.49	65.48	65.47
Eltham	43.13	43.12	43.11	28.83	28.82	28.82	24.38	24.37	24.37
Hackney	57.20	57.19	57.18	38.27	38.26	38.26	32.06	32.05	32.04
Haringey Roadside	63.75	63.74	63.73	42.85	42.84	42.84	35.88	35.88	35.87
Hillingdon	72.53	72.52	72.50	40.74	40.73	40.73	31.93	31.92	31.92
Hounslow	61.50	61.49	61.48	37.40	37.39	37.39	30.27	30.26	30.26
Lewisham	61.73	61.72	61.71	40.70	40.70	40.69	33.75	33.75	33.74
Marylebone Road	177.9	177.8	177.8	113.7	113.6	113.6	91.96	91.94	91.93
North Kensington	52.11	52.10	52.09	36.96	36.95	36.95	32.00	32.00	31.99
Southwark Backg'nd	63.82	63.80	63.79	42.34	42.33	42.33	36.45	36.44	36.44
Southwark Roadside	99.27	99.25	99.23	62.10	62.09	62.08	50.49	50.48	50.47
Sutton Roadside	39.21	39.20	39.20	26.66	26.66	26.66	22.33	22.33	22.32
Sutton Suburban	37.53	37.52	37.52	25.35	25.35	25.34	21.31	21.31	21.31
Teddington	33.66	33.66	33.65	23.32	23.31	23.31	19.08	19.08	19.07
Tower Hamlets	78.28	78.27	78.25	49.47	49.46	49.45	40.46	40.46	40.45
Wandsworth	67.55	67.54	67.53	44.03	44.02	44.01	36.51	36.51	36.50
West London	53.15	53.14	53.14	37.16	37.16	37.15	32.06	32.05	32.05
Average	**68.45**	**68.44**	**68.43**	**44.04**	**44.03**	**44.02**	**36.64**	**36.63**	**36.62**

Table A4.6: Annual Average nitrogen dioxide (ppb) at London Automatic Urban Rural Network sites calculated using ADMS-Urban for different percentages of emissions of primary nitrogen dioxide.

Site	2001			2010			2020		
	10%	15%	20%	10%	15%	20%	10%	15%	20%
A3	30.42	33.60	36.77	21.60	23.01	24.40	18.78	19.84	20.88
Bexley	22.17	23.53	24.87	17.40	18.38	19.35	15.54	16.38	17.21
Bloomsbury	32.91	35.78	38.62	26.30	27.92	29.50	24.34	25.70	27.04
Brent	18.96	19.73	20.48	14.96	15.38	15.79	13.25	13.58	13.89
Bromley	27.21	29.38	31.53	20.94	22.17	23.37	18.48	19.45	20.41
Camden	34.89	38.36	41.78	28.44	30.46	32.44	25.89	27.51	29.09
Cromwell Road	40.20	45.40	50.54	32.37	35.45	38.47	29.64	32.15	34.62
Eltham	21.01	22.34	23.66	16.38	17.19	17.98	14.56	15.23	15.88
Hackney	27.61	29.49	31.35	22.25	23.35	24.43	19.93	20.81	21.66
Haringey Roadside	29.66	31.85	34.01	24.06	25.35	26.62	21.58	22.60	23.60
Hillingdon	30.18	32.86	35.49	22.59	23.81	25.00	19.52	20.38	21.21
Hounslow	26.67	28.81	30.92	20.59	21.68	22.76	17.94	18.77	19.58
Lewisham	27.53	29.67	31.78	21.84	23.10	24.33	19.37	20.37	21.34
Marylebone Road	47.65	55.62	63.54	38.74	43.57	48.36	35.02	38.81	42.54
North Kensington	26.23	27.87	29.48	21.90	22.94	23.94	20.08	20.93	21.76
Southwark Background	28.41	30.63	32.82	22.84	24.16	25.46	20.90	22.00	23.07
Southwark Roadside	36.29	40.26	44.17	28.90	31.21	33.48	25.77	27.56	29.31
Sutton Roadside	19.53	20.69	21.84	15.35	16.07	16.77	13.53	14.11	14.68
Sutton Suburban	18.93	20.03	21.11	14.75	15.42	16.08	13.02	13.57	14.10
Teddington	17.22	18.17	19.10	13.55	14.16	14.75	11.83	12.30	12.76
Tower Hamlets	32.76	35.66	38.53	25.95	27.57	29.15	23.06	24.30	25.52
Wandsworth	29.39	31.79	34.15	23.28	24.69	26.06	20.74	21.85	22.93
West London	25.95	27.65	29.33	21.41	22.48	23.52	19.60	20.47	21.33
Average	**28.34**	**30.83**	**33.30**	**22.45**	**23.89**	**25.30**	**20.10**	**21.25**	**22.37**

Table A4.7: 99.8th percentile of hourly average nitrogen dioxide (ppb) at London Automatic Urban Rural Network sites calculated using ADMS-Urban for different percentages of emissions of primary nitrogen dioxide.

Site	2001			2010			2020		
	10%	15%	20%	10%	15%	20%	10%	15%	20%
A3	89	106	127	69	81	91	65	74	84
Bexley	90	106	123	77	87	99	74	84	94
Bloomsbury	90	106	123	75	86	96	71	79	89
Brent	79	87	96	67	73	80	63	68	74
Bromley	87	106	122	70	80	92	66	74	83
Camden	94	109	127	78	89	99	75	82	92
Cromwell Road	93	111	130	77	88	99	72	80	90
Eltham	86	101	119	70	80	91	65	74	83
Hackney	89	100	113	74	83	91	70	76	83
Haringey Roadside	95	107	120	78	85	95	74	80	88
Hillingdon	92	107	128	76	87	98	68	76	84
Hounslow	77	89	102	66	72	81	59	66	72
Lewisham	79	90	104	67	75	81	63	69	75
Marylebone Road	111	133	156	89	104	121	83	93	107
North Kensington	77	84	94	68	74	82	64	69	77
Southwark B'ground	83	96	110	69	78	86	64	72	80
Southwark Roadside	92	110	125	75	85	97	68	76	87
Sutton Roadside	73	86	97	61	69	77	58	64	71
Sutton Suburban	71	84	96	61	69	76	58	64	71
Teddington	68	79	88	58	66	73	55	61	66
Tower Hamlets	96	113	133	78	87	101	71	80	91
Wandsworth	79	92	105	67	73	82	62	67	74
West London	72	84	95	64	71	78	60	66	73
Average	**85**	**99**	**114**	**71**	**80**	**90**	**66**	**74**	**82**

Table A4.8: Annual Average ozone (ppb) at London Automatic urban rural network sites calculated using ADMS-Urban for different percentages of emissions of primary nitrogen dioxide.

Site	2001			2010			2020		
	10%	15%	20%	10%	15%	20%	10%	15%	20%
A3	10.63	11.13	11.66	15.90	16.38	16.87	17.77	18.23	18.70
Bexley	15.20	15.63	16.08	18.31	18.70	19.10	19.58	19.95	20.34
Bloomsbury	8.62	9.19	9.79	12.76	13.34	13.96	14.00	14.59	15.21
Brent	16.68	17.06	17.46	20.24	20.59	20.97	21.59	21.95	22.32
Bromley	12.22	12.72	13.25	16.44	16.90	17.39	18.12	18.57	19.03
Camden	7.38	7.91	8.49	10.97	11.54	12.15	12.51	13.09	13.70
Cromwell Road	5.77	6.29	6.85	9.16	9.78	10.43	10.54	11.18	11.86
Eltham	16.12	16.52	16.93	19.57	19.92	20.29	20.85	21.20	21.55
Hackney	11.39	11.91	12.46	15.21	15.72	16.25	16.83	17.33	17.85
Haringey Roadside	9.96	10.50	11.07	13.80	14.34	14.91	15.51	16.04	16.61
Hillingdon	9.67	10.16	10.69	14.62	15.12	15.66	16.75	17.25	17.77
Hounslow	12.38	12.87	13.38	16.50	16.96	17.45	18.36	18.80	19.27
Lewisham	11.73	12.24	12.77	15.62	16.11	16.62	17.31	17.78	18.28
Marylebone Road	3.85	4.30	4.79	6.43	6.97	7.55	7.83	8.40	9.02
North Kensington	12.05	12.56	13.10	15.33	15.84	16.38	16.60	17.12	17.65
Southwark B'ground	11.41	11.93	12.48	15.17	15.68	16.21	16.43	16.94	17.47
Southwark Roadside	7.30	7.84	8.43	11.14	11.75	12.39	12.97	13.58	14.23
Sutton Roadside	17.11	17.49	17.87	20.47	20.80	21.15	21.79	22.10	22.43
Sutton Suburban	17.45	17.81	18.17	20.83	21.15	21.47	22.10	22.40	22.71
Teddington	18.45	18.76	19.09	21.65	21.92	22.21	22.94	23.20	23.48
Tower Hamlets	8.63	9.19	9.78	12.78	13.35	13.95	14.65	15.21	15.81
Wandsworth	10.65	11.18	11.74	14.67	15.19	15.74	16.35	16.86	17.39
West London	12.49	12.99	13.52	15.86	16.36	16.88	17.11	17.61	18.13
Average	**11.61**	**12.09**	**12.60**	**15.37**	**15.84**	**16.35**	**16.89**	**17.36**	**17.86**

A4.5 The NETCEN primary Nitrogen Dioxide model (Abbott *et al.*, 2006)

Box A4.5: The NETCEN primary nitrogen dioxide model

The NETCEN model is a one-dimensional steady-state finite difference model of the surface stress layer of the atmospheric boundary layer. It solves the following differential equations for the O_3, NO and NO_2 concentrations ($[O_3]$, [NO], $NO_2]$) for each hour of the modelled year:

$$\frac{\partial}{\partial z}\left(\frac{ku^{*}z}{\phi}\frac{\partial[O_3]}{\partial z}\right)-k_1[NO][O_3]+J[NO_2]=0$$

$$\frac{\partial}{\partial z}\left(\frac{ku^{*}z}{\phi}\frac{\partial[NO]}{\partial z}\right)-k_1[NO][O_3]+J[NO_2]=0$$

$$\frac{\partial}{\partial z}\left(\frac{ku^{*}z}{\phi}\frac{\partial[NO_2]}{\partial z}\right)+k_1[NO][O_3]-J[NO_2]=0$$

where z is the vertical dimension;
u* is the friction velocity;
k is von Karman's constant, 0.4;
k_1 is the rate of reaction between O_3 and NO to form NO_2;
J is the rate of photodissociation of NO_2 to NO and O_3;
Φ is a stability function.

The friction velocity, stability function and reaction rate constants are calculated for each hour from meteorological data. The concentrations at the upper boundary of the surface stress layer are set equal to hourly measured values at appropriate background sites.

The vertical flux of O_3 at the lower boundary is set equal to the dry deposition:

$$\frac{ku^{*}z}{\phi}\frac{\partial[O_3]}{\partial z}=\frac{[O_3]}{(r_b+r_c)}$$

where r_b is the resistance to O_3 transfer in the laminar sublayer and r_c is the resistance at the surface.

The total concentration of $[NO]+[NO_2]$ at the lower boundary is set equal to the measured NO_x concentration.

The vertical fluxes of NO_2 and NO at the lower boundary are related by the fraction of the NO_x emitted as NO_2, A:

$$\frac{\partial[NO_2]}{\partial z}=\frac{A}{1-A}\frac{\partial[NO]}{\partial z}$$

Table A4.9: Base case nitrogen oxides and nitrogen dioxide concentrations for 2002 at the roadside and kerbside sites in the Automatic Urban Rural Network and the effect of adding an additional 5% primary nitrogen dioxide to each site.

	Best estimate of A	valid hours	NO_x ppb	NO_2, ppb			NO_2/NO_x		
				Measured	Modelled	Modelled A+5%	Measured	Modelled	Modelled A+5%
Bath Roadside	0.13	7901	88	30	32	34	0.35	0.37	0.39
Brighton Roadside	0.10	7214	44	20	17	18	0.46	0.38	0.42
Bristol Old Market									
Bury Roadside	0.08	7660	123	35	36	40	0.28	0.29	0.32
Cambridge Roadside	0.11	6786	59	23	19	21	0.39	0.33	0.36
Camden Kerbside	0.10	615	98	33	31	33	0.34	0.32	0.34
Dumfries	0.13	6053	53	23	24	25	0.42	0.45	0.47
Exeter Roadside	0.05	6834	50	22	21	23	0.44	0.42	0.45
Glasgow Kerbside	0.10	7282	150	39	37	42	0.26	0.24	0.28
Haringey Roadside	0.08	6808	57	26	28	28	0.45	0.50	0.50
Hounslow Roadside	0.15	6547	69	31	27	29	0.45	0.39	0.41
Hove Roadside	0.16	6910	36	18	16	17	0.51	0.45	0.48
London A3 Roadside	0.09	7353	89	31	29	32	0.35	0.32	0.36
London Bromley	0.14	4815	42	25	27	27	0.58	0.64	0.63
London Cromwell Road 2	0.17	8036	100	38	38	41	0.38	0.38	0.41
London Marylebone Road	0.10	8340	157	42	42	48	0.27	0.27	0.31
Norwich Roadside	0.11	7118	32	17	18	19	0.52	0.55	0.58
Oxford Centre	0.12	8252	97	31	28	32	0.32	0.29	0.33
Southwark Roadside	0.07	6016	81	30	32	34	0.37	0.40	0.42
Stockton-on-Tees Yarm	0.08	6149	67	21	25	27	0.31	0.37	0.41
Sutton Roadside	0.08	2213	45	22	24	24	0.49	0.52	0.53
Tower Hamlets Roadside	0.09	7002	97	34	35	37	0.34	0.35	0.38
Average			**78**	**28**	**28**	**30**	**0.36**	**0.36**	**0.39**