Report

Primary nitrogen dioxide emissions from road traffic: analysis of monitoring data

Report to Department for the Environment, Food and Rural Affairs; Scottish Executive; Welsh Assembly Government; Department of the Environment for Northern Ireland

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Executive Summary

Monitoring data from the London Marylebone Road site indicates that nitrogen dioxide concentrations have increased in recent years (2003 and 2004) rather than decreasing as expected in line with decreasing oxides of nitrogen emissions. It has been suggested that this increase might be associated with a change in the proportion of the oxides of nitrogen emitted from motor vehicles as nitrogen dioxide. The aim of the work described in this report was to determine whether the increase in the proportion of oxides of nitrogen emitted as nitrogen dioxide was limited to London Marylebone Road or was indicative of a more general trend across the country.

Monitoring data from roadside sites at London Marylebone Road, Bury Roadside and Exeter Roadside sites was analysed to provide estimates of the proportion of the oxides of nitrogen effectively released from road vehicles as nitrogen dioxide (the "primary nitrogen dioxide emission factor"). Typical estimated primary nitrogen dioxide emission factors were approximately 0.1. The primary nitrogen dioxide emission factor at London Marylebone Road increased substantially over the period 2000-2004 from approximately 0.1 to approximately 0.2. The trend in primary emission factor was less clear at the Bury Roadside and Exeter Roadside sites.

There was some diurnal variation in the primary nitrogen dioxide emission factor at London Marylebone Road: the emission factor was greatest during the daytime. There was also some weekly variation in the emission factor: the highest emission factors were observed on weekdays.

Source apportionment analysis of the data for London Marylebone Road was carried out for those hours during 2003 and 2004 when the limit value of 200 $\mu g\ m^{-3}$ was exceeded. The background contribution and the secondary contribution from nitric oxide emissions reacting with ozone were small compared to the primary nitrogen dioxide component. The proportion of oxides of nitrogen emitted as nitrogen dioxide during the exceedence hours was similar to that for other hours of the year.

The analysis of data from London Marylebone Road, Bury Roadside and Exeter Roadside was possible because roadside ozone concentration measurements were available at those sites. A one-dimensional model of the transfer and reactions of ozone in the surface boundary layer was developed so that monitoring data could be analysed in the same way for other roadside sites where ozone concentrations are not measured. The model was validated by comparing the primary nitrogen dioxide emission factor A calculated using measured and modelled ozone concentrations at London Marylebone Road and Bury Roadside.

There was a substantial increase (>0.015 per year) in the factor A at the following sites:

- Brighton Roadside;
- Bristol Old Market;
- Camden Kerbside;
- Hove Roadside;
- London A3 Roadside;
- London Marylebone Road;
- Southwark Roadside.

The factor A remained the same (trend <0.005 per year) at the following sites:

- Bury Roadside
- Dumfries
- Glasgow Kerbside
- Stockton on Tees Yarm
- Norwich Roadside

The average value of factor A over all sites increased during the period 2000-2004:

2000	0.08
2001	0.09
2002	0.11
2003	0.12
2004	0.14

The one dimensional model may also be used to predict nitrogen dioxide concentrations at roadside sites from oxides of nitrogen concentrations. It might thus be useful for dispersion modelling and climate mapping purposes. The model performance is similar to that of the semi-empirical model developed for AQEG when compared on a like for like basis for the estimation of annual average nitrogen dioxide concentrations from annual average measurements of oxides of nitrogen concentrations. However, the new model has the advantage that it is based on a mathematical representation of the physical and chemical processes in the surface boundary layer. It may also be used to provide predictions of hourly average nitrogen dioxide concentrations.

Contents

1 Introduction

The Air Quality Strategy for England, Scotland, Wales and Northern Ireland set concentration objectives for a range of pollutants. For nitrogen dioxide, the objectives are:

> 40 μg m^{-3} as an annual mean to be achieved by December 31 2005;

and

> 200 μg m^{-3} as an hourly mean not to be exceeded more than 18 times in a year to be achieved by December 31 2005.

The annual mean objective has been exceeded in recent years, including 2003 and 2004, at many places where there are houses close to major roads. The hourly objective has been exceeded at rather fewer relevant locations where members of the public are present. Table 1 shows the measured annual mean nitrogen dioxide concentration and the number of exceedences of the hourly objective for five roadside or kerbside sites. The sites shown in Table 1.1 were selected because the measured concentrations were amongst the highest in the UK.

Table 1.1: Annual mean nitrogen dioxide concentrations and number of exceedences of 200 μg m^{-3} at selected roadside and kerbside monitoring sites

Annual mean, μg m^{-3}	2000	2001	2002	2003	2004
London Marylebone Road	93	84	81	107	110
Glasgow Kerbside	72	71	74	75	68
Bristol Old Market	55	54	-	71	54
Camden Kerbside	63	66	64	65	66
London Cromwell Road 2	80	76	72	76	80
Number of exceedences of 200 μg m^{-3}					
London Marylebone Road	108	60	2	471	529
Glasgow Kerbside	18	54	38	36	15
Bristol Old Market	7	0	-	6	0
Camden Kerbside	0	0	0	2	8
London Cromwell Road 2	13	2	0	6	3

Table 1.1 shows that there has been a sharp increase in the annual mean nitrogen dioxide concentration and the number of exceedences of the hourly objective at Marylebone Road in 2003 and 2004.

Motor vehicle exhausts emit a mixture of oxides of nitrogen into the atmosphere. The major part (about 90%) is emitted as nitric oxide, but a substantial part is emitted directly as nitrogen dioxide. The nitric oxide emitted reacts in the atmosphere over time with ozone in the atmosphere to form nitrogen dioxide so that at a roadside location oxides of nitrogen are present:

- as nitrogen dioxide emitted from vehicle exhausts (the "primary" nitrogen dioxide);
- as nitrogen dioxide formed by reaction of nitric oxide emitted from vehicle exhausts in the atmosphere (the "secondary" nitrogen dioxide);
- as unreacted nitric oxide.

Close to a busy road, the major part of the oxides of nitrogen in the atmosphere is associated with local emissions from traffic on the road: a smaller part is associated with emissions from other, more distant background sources. The primary nitrogen dioxide emission from vehicles can make a substantial contribution to total nitrogen dioxide concentrations close to many major roads. A reliable estimate of the proportion of primary nitrogen dioxide in vehicle emissions is therefore required in order to develop measures to control nitrogen dioxide concentrations near roads.

It is difficult to measure the proportion of nitrogen dioxide in vehicle emissions directly and so there are few reliable data. Clapp and Jenkin developed a technique to estimate the proportion of nitrogen dioxide in local emissions from ambient concentration monitoring data. They plotted the annual average total oxidant ([Ox]=[O_3+NO_2]) concentration against annual average total oxides of nitrogen ([NOx]=[NO+NO_2]) concentration for a range of mostly urban background monitoring stations and obtained a relationship of the form:

$$[Ox] = A[NO_x] + B$$

The method has been used by the Air Quality Expert Group (AQEG) to analyses recent data from London monitoring stations. Fig. 1.1 shows a plot of annual average total oxidant concentrations against oxides of nitrogen concentrations taken from the AQEG report.

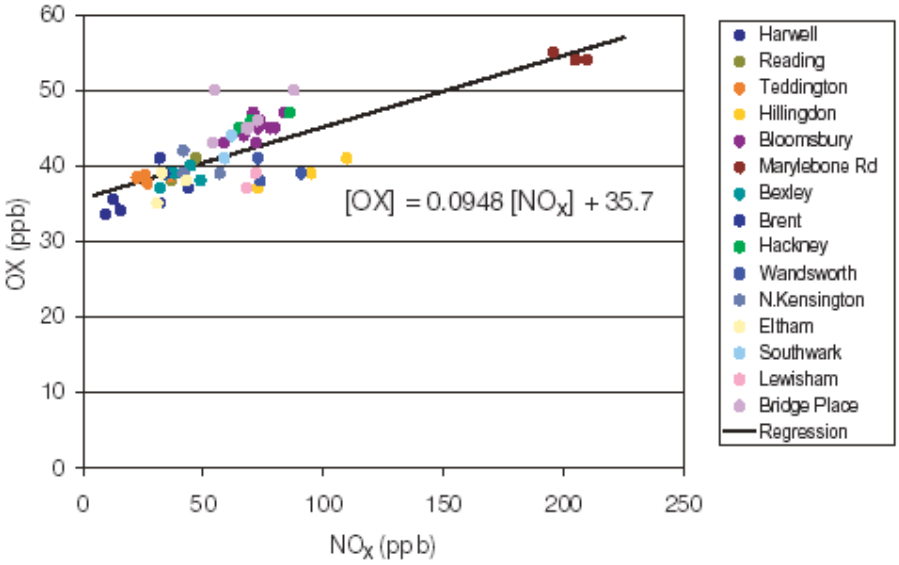

Fig. 1.1:Plot of annual average total oxidant concentrations against oxides of nitrogen concentrations taken from the AQEG report

The method is developed further in Section 2 of this report and used to estimate the apparent proportion, A, of the oxides of nitrogen emitted as nitrogen dioxide at roadside sites on an hour by hour basis in order to determine the extent of temporal trends in the apparent primary emission.

The application of the analysis requires measurements of ozone, nitric oxide and nitrogen dioxide concentrations. Ozone concentration measurements are made at few roadside sites in Automatic Urban and Rural Network; Marylebone Road, Bury Roadside and Exeter Roadside. A model is developed in Section 3 of this report to estimate ozone concentrations at the roadside from measurements at urban background sites. The estimated ozone concentrations can then be used to determine the proportion of oxides of nitrogen emitted as nitrogen dioxide at other roadside sites The performance of the model is demonstrated by comparison of modelled and measured ozone concentrations at the Marylebone Road and Bury Roadside sites. The use of the modelled ozone concentrations to predict the factor A is also demonstrated. The model is then applied at range of UK sites.

Dispersion models are widely used to predict roadside oxides of nitrogen concentrations for local authority review and assessment. The model developed in Section 3 has the potential to provide a simple non-empirical method to estimate roadside nitrogen dioxide concentrations from oxides of nitrogen concentrations predicted by dispersion models. The ability of the model to predict roadside nitrogen dioxide concentrations is assessed in section 4.

2 Analysis of monitoring data

2.1 BASIS OF THE ANALYSIS METHOD

Consider a simple box model containing a unit volume of air moving from location 0 (a background location) to location 1, near a road. A mass balance for nitrogen dioxide over that volume may be represented by:

$$[NO_2]_1 = [NO_2]_0 + E_{NO_2} + R_{NO_2} - D_{NO_2}$$

where

$[NO_2]_1$ and $[NO_2]_1$ are the concentrations of nitrogen dioxide at 1 and 0 respectively;

E_{NO2} is the net increase in concentration resulting from emissions into the volume;
R_{NO2} is the net increase in concentration resulting from chemical or photochemical reaction;
D_{NO2} is the net reduction in concentration resulting from deposition.

Similarly, the mass balances for nitric oxide and ozone are:

$$[NO]_1 = [NO]_0 + E_{NO} + R_{NO} - D_{NO}$$

$$[O_3]_1 = [O_3]_0 + E_{O_3} + R_{O_3} - D_{O_3}$$

The most important reactions are the reaction of ozone and nitric oxide to form nitrogen dioxide:

$$NO + O_3 \rightarrow NO_2$$

and the photodissociation of nitrogen dioxide:

$$NO_2 + h\vartheta \rightarrow NO + O_3$$

There are many other chemical and photochemical reactions taking place in the atmosphere that contribute to a lesser extent to oxides of nitrogen and ozone concentrations. The increase in concentration resulting from reactions, R, may be split into two components, R' corresponding to the two reactions above and R'' associated with other reactions:

$$R = R' + R''$$

The stochiometry of the reactions requires that:

$$R'_{O_3} = R'_{NO} = -R'_{NO_2}$$

Then:

$$[NO]_1 + [NO_2]_1 = [NO]_0 + [NO_2]_0 + E_{NO} + E_{NO2} + R''_{NO} + R''_{NO2} - D_{NO} - D_{NO2}$$

Putting

$$[NO_x] = [NO] + [NO_2]$$

$$[NO_x]_1 = [NO_x]_0 + E_{NOx} + R''_{NO} + R''_{NO2} - D_{NO} - D_{NO2}$$

Assume then that A represents the proportion of oxides of nitrogen emitted as nitrogen dioxide and that the emission of ozone is zero:

$$[O_3]_1 + [NO_2]_1 = [O_3]_0 + [NO_2]_0 + AE_{NOx} + R''_{O3} + R''_{NO2} - D_{O3} - D_{NO2}$$

Putting

$$[Ox] = [O_3] + [NO_2]$$

$$[Ox]_1 = [Ox]_0 + AE_{NOx} + R''_{O3} + R''_{NO2} - D_{O3} - D_{NO2}$$

Substituting for E_{NOx}

$$[Ox]_1 = [Ox]_0 + A\left([NO_x]_1 - [NO_x]_0 - R''_{NO} - R''_{NO2} + D_{NO} + D_{NO2}\right) + R''_{O3} + R''_{NO2} - D_{O3} - D_{NO2}$$

Rearranging:

$$[Ox]_1 = \left\{[Ox]_0 - A\left([NO_x]_0 + R''_{NO} + R''_{NO2} - D_{NO} - D_{NO2}\right) + R''_{O3} + R''_{NO2} - D_{O3} - D_{NO2}\right\} + A[NO_x]_1$$

The terms within the brackets {} may be lumped together as a constant B:

$$[Ox]_1 = A[NO_x]_1 + B$$

This relationship corresponds with that used by AQEG. If the reaction terms, R'' and the deposition terms D are ignored, then B may be considered to represent a "regional oxidant" concentration, which includes the contribution from background oxidant concentrations.

Alternatively the equation may be arranged as follows:

$$[Ox]_1 - [Ox]_0 = A\left([NO_x]_1 - [NO_x]_0\right) - A\left(R''_{NO} - D_{NO}\right) + \left(R''_{O3} - D_{O3}\right) + (1 - A)\left(R''_{NO2} - D_{NO2}\right)$$

$$[Ox]_1 - [Ox]_0 = A\left([NO_x]_1 - [NO_x]_0\right) + B^*$$

This equation forms the basis for the method of analysis used in this report. B^* excludes the background oxidant concentrations and represents the net effect of other reactions and deposition.

The equation can also be rearranged as :

$$[NO_2]_1 = [NO_2]_0 + \left([O_3]_0 - [O_3]_1\right) + A\left([NO_x]_1 - [NO_x]_0\right) + B^*$$

The nitrogen dioxide concentration at the roadside can thus be apportioned in terms of the background contribution, the contribution from the oxidation of nitric oxide by ozone (the "secondary" nitrogen dioxide), the contribution from nitrogen dioxide emitted from local road vehicles (the "primary" nitrogen dioxide and a small "residual" contribution arising as net result of deposition and other chemical reactions.

2.2 APPLICATION OF THE METHOD

There are three roadside monitoring stations in the UK where continuous automatic oxides measurements of nitric oxide, nitrogen dioxide and ozone concentrations are made:

- London Marylebone Road;
- Bury Roadside;
- Exeter Roadside

Values of the total oxidant concentration, $[Ox]_1$ and oxides of nitrogen concentration, $[NOx]_1$ may be calculated for each hour of the year. Background monitoring sites may be identified in each case to provide estimates of $[Ox]_0$ and $[NOx]_0$. Thus the London Bloomsbury or North Kensington sites can provide estimates of background concentrations near the London Marylebone Road roadside site.

A simple estimate of the apparent hour-by-hour proportion, A of vehicle emissions emitted as nitrogen dioxide may be made if it is assumed that B* is small:

$$A_s = \frac{[Ox]_1 - [Ox]_0}{[NOx]_1 - [NOx]_0}$$

The value of A calculated in this way becomes indeterminate when $[NOx]_1$-$[NOx]_0$ approaches zero. The simple method is therefore limited to those hours where there is a significant increase in the roadside oxides of nitrogen concentration above the background. An arbitrary lower limit of 100 ppb has been applied here. The value of A calculated in this way shows substantial hour by hour variations. An **average** value of A may be calculated as:

$$A_{av} = \frac{\sum_i [Ox]_1 - [Ox]_0}{\sum_i [NOx]_1 - [NOx]_0}$$

where i represents a set of hours. The set of hours may include, for example, all hours over a 30 day or 365 day period.

Regression analysis may be used to estimate both A and B*.

$$A_{reg} = \frac{S_{xy}}{S_{xx}}$$

$$B^* = \frac{1}{I}\sum_i [Ox]_1 - [Ox]_0 - \frac{A_{reg}}{I}\sum [NOx]_1 - [NOx]_0$$

where

$$S_{xy} = \sum_i \left([Ox]_1 - [Ox]_0\right)\left([NOx]_1 - [NOx]_0\right) - \frac{1}{I}\sum_i \left([Ox]_1 - [Ox]_0\right)\sum_i \left([NOx]_1 - [NOx]_0\right)$$

$$S_{xx} = \sum_i \left([NOx]_1 - [NOx]_0\right)^2 - \frac{1}{I}\left(\sum_i \left([NOx]_1 - [NOx]_0\right)\right)^2$$

2.3 LONDON MARYLEBONE ROAD

Fig.2.1 shows the calculated simple hourly estimates of A for London Marylebone Road for the period 2001-2004. Data from London North Kensington were used to provide estimates of background concentrations. A lower limit of 100 ppb was applied to the incremental oxides of nitrogen concentration. Calculated values for a 50 ppb cut-off are also shown. The general trend is similar, although using the 50 ppb cut off leads to a wider range in calculated values of A. The value of A increases sharply through 2003 from approximately 0.1 to 0.2.

Fig.2.2 shows 30 day average estimates of A calculated using the average method and the regression method. The estimates of A are similar. In both cases the value of A increases in 2003 from approximately 0.1 in 2000, 2001 and 2002 to 0.23 in January 2004.

Fig. 2.3 shows the difference in total oxidant concentration between Marylebone Road and North Kensington plotted against the difference in oxides of nitrogen concentrations for a typical month (January 2004). The linear regression line through the points is also shown. The intercept with the oxidant change axis (-1.4 ppb), corresponding to B*, is small.

The calculated estimates of A are not very sensitive to the choice of the background site. Fig.2.4 shows the values of A calculated by the regression method using background data from the North Kensington, Bloomsbury, Westminster and Brent monitoring sites. Fig. 2.5 shows regression estimates of A made with upwind and downwind rural monitoring data. The upwind and downwind data were selected on the basis of wind direction from (Lullington Heath, Harwell, Wicken Fen and Rochester).

The calculated estimates of B* are also relatively insensitive to the choice of background monitoring site. Fig.2.6 shows a time series of 30 day average estimates of B* for Marylebone Road based on background data from North Kensington and upwind and downwind rural sites. There appears to be little obvious trend in the estimates. The values of B* based on the north Kensington background data are generally smaller than those based on the rural monitoring data. Table 2.1 shows annual average estimates of B*.

Table 2.1: Annual average estimates of B* for London Marylebone Road with London North Kensington and upwind and downwind rural background data

Year	North Kensington	Upwind	Downwind
2000	-0.5	1.6	2.6
2001	0.2	4.7	3.2
2002	0.2	3.8	3.4
2003	-1.2	0.3	1.1
2004	-0.4	0.7	1.3

There appears to be some diurnal variation in the primary nitrogen dioxide emissions factor, A. Fig.2.7 shows the estimated values of A calculated by regression analysis for each hour for the years 2000-2004 , grouped by hour of the day, based on North Kensington background data. The estimated value of A is lowest in the early hours of the morning and increases to a maximum around midday. The proportional reduction in A between daytime and early morning in 2003 and 2004 appears to be smaller than in earlier years.

There also appears to be some variation in A with the day of the week. Fig.2.8 shows the estimated values of A calculated by regression analysis for each hour for the years 2000-2004 , grouped by day of the week, based on North Kensington background data. The estimated value of A is lowest on Sunday and highest during weekdays, Monday to Friday. The proportional reduction in A between weekdays and Sunday in 2003 and 2004 appears to be smaller than in earlier years.

Figs. 2.9 and 2.10 show the contribution from background nitrogen dioxide and secondary nitrogen dioxide as a fraction of the measured nitrogen dioxide concentration at Marylebone Road for each hour of 2003 and 2004 when the measured concentration was greater than 200 $\mu g\ m^{-3}$. The difference between the measured concentration and the combined background and secondary contributions may be allocated to the primary emission of nitrogen dioxide, if it is assumed that other chemical reactions and deposition are small. Figs 2.9 and 2.10 show that the background and secondary nitrogen dioxide contributions combined contribute less than half of the measured nitrogen dioxide concentration for most of the exceedence hours.

The estimated primary contribution based on an average value of A derived by regression analysis of all hourly data for 2003 is also shown in Figs 2.9 and 2.10. The estimate of the total nitrogen dioxide concentration (i.e. the background plus secondary plus estimated primary contribution) corresponds well with the measured concentrations. It is concluded that the primary contribution as a fraction of emitted oxides of nitrogen during the exceedence hours is similar to that during other hours in the year.

2.4 BURY ROADSIDE

Fig.2.11 shows a time series of 30-day estimates of the primary emission factor , A, derived from the Bury Roadside and Bolton background monitoring data. There is no obvious trend in the calculated primary emission factors.

Fig.2.12 shows the diurnal variation in the calculated values of A. The fraction of the oxides of nitrogen emitted as nitrogen dioxide appears to be smallest during the early hours of the morning.

Fig.2.13 shows the weekly variation in the calculated values of A. There does not appear to be a consistent trend in the data.

2.5 EXETER ROADSIDE

Fig. 2.14 shows a time series of 30-day estimates of the primary emission factor , A, derived from the Exeter Roadside and Plymouth Centre background monitoring data. There is no obvious trend in the calculated primary emission factors.

Fig.2.15 shows a time series of the 30-day estimates of the residual B^*. The calculated residual was relatively large in 2000 and 2004.

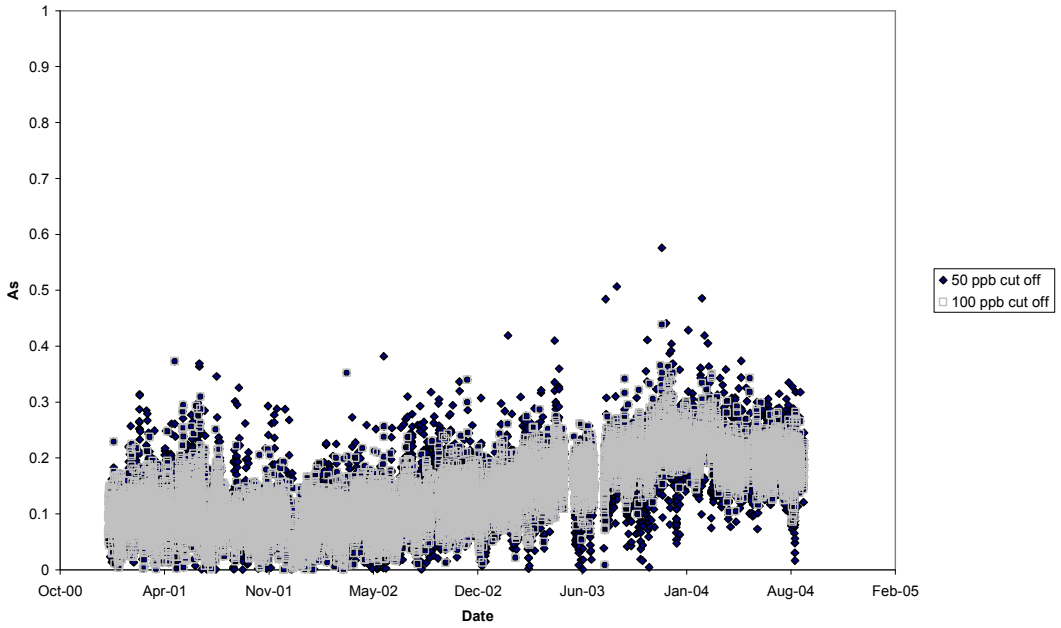

Fig. 2.1: Simple estimate of primary nitrogen dioxide emissions for London Marylebone Road. London North Kensington background data.

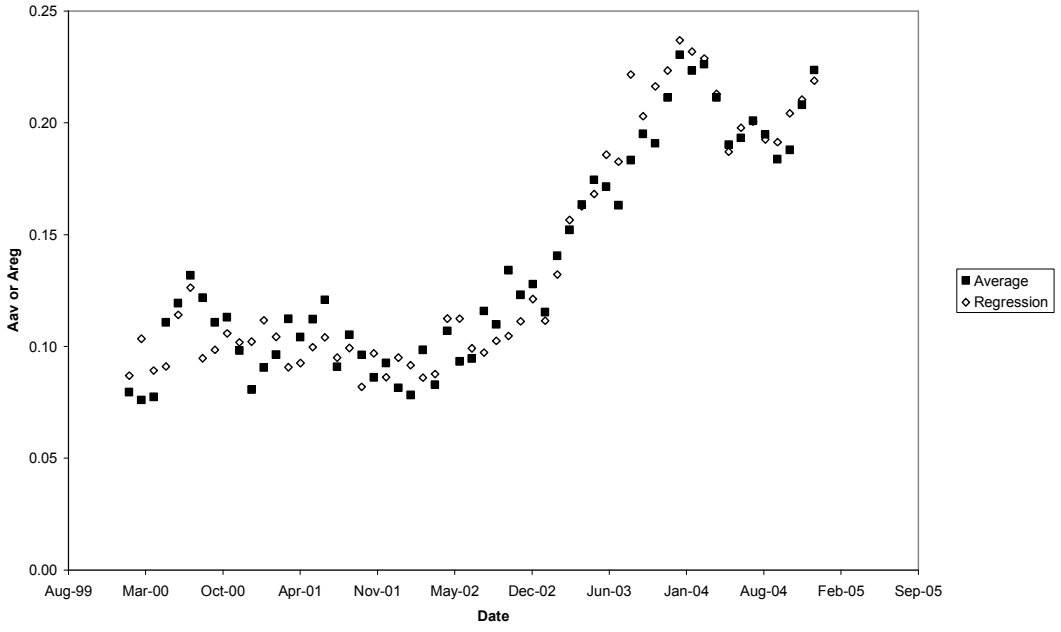

Fig. 2.2: 30 day average estimates of primary nitrogen dioxide emissions for London Marylebone Road calculated using the average and regression methods. London North Kensington background data.

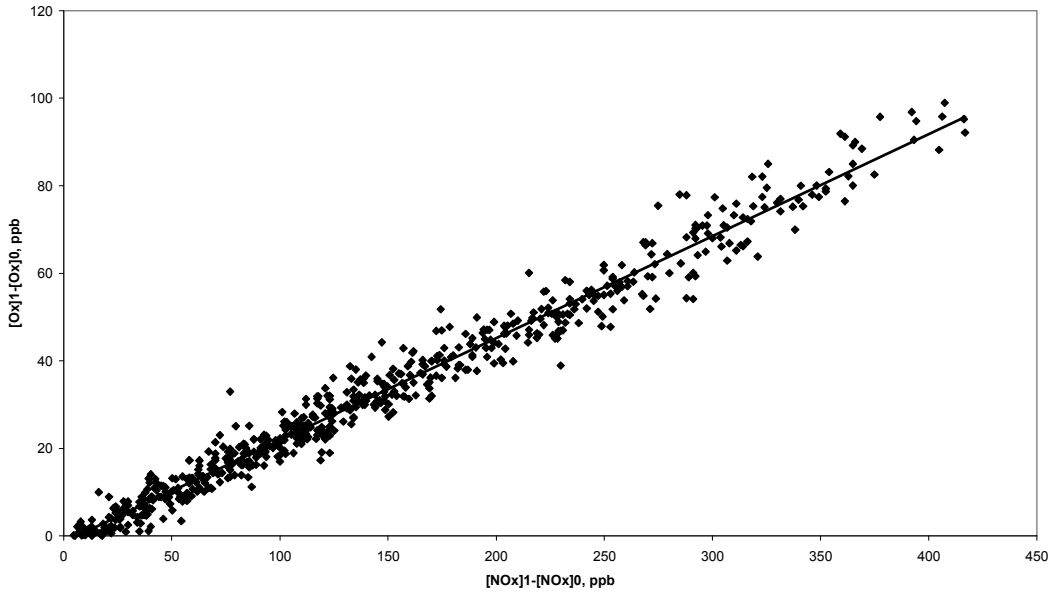

Fig.2.3: Plot of total oxidant difference $[Ox]_1$-$[Ox]_0$ against oxides of nitrogen difference $[NO_x]_1$-$[NO_x]_0$ for all hours of January 2004 for Marylebone Road compared with North Kensington

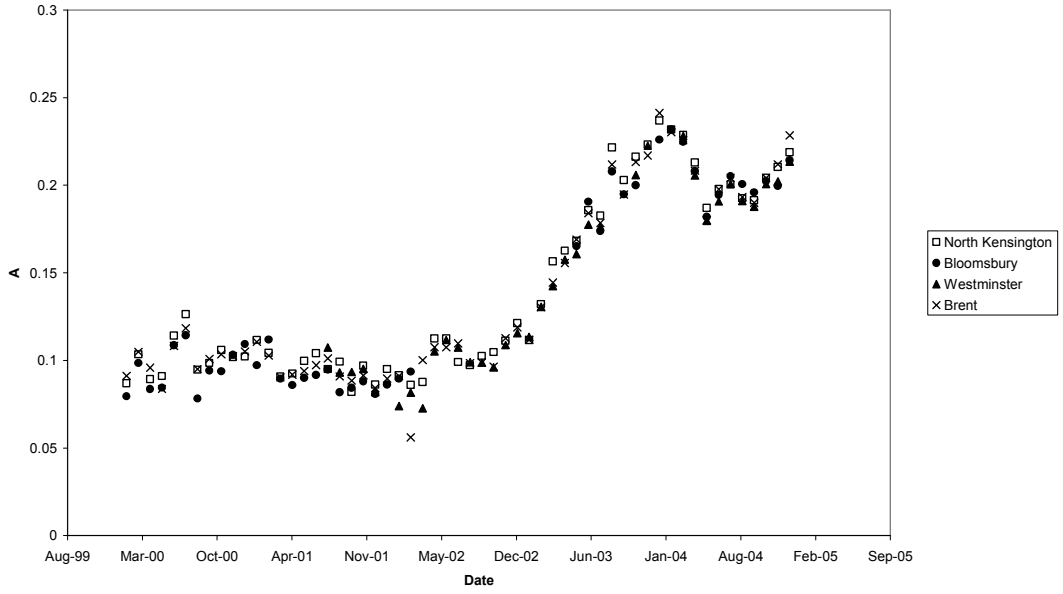

Fig.2.4: 30 day average estimates of primary nitrogen dioxide emission factor, A, for London Marylebone Road calculated using the regression methods. Background data from North Kensington, Bloomsbury, Westminster and Brent.

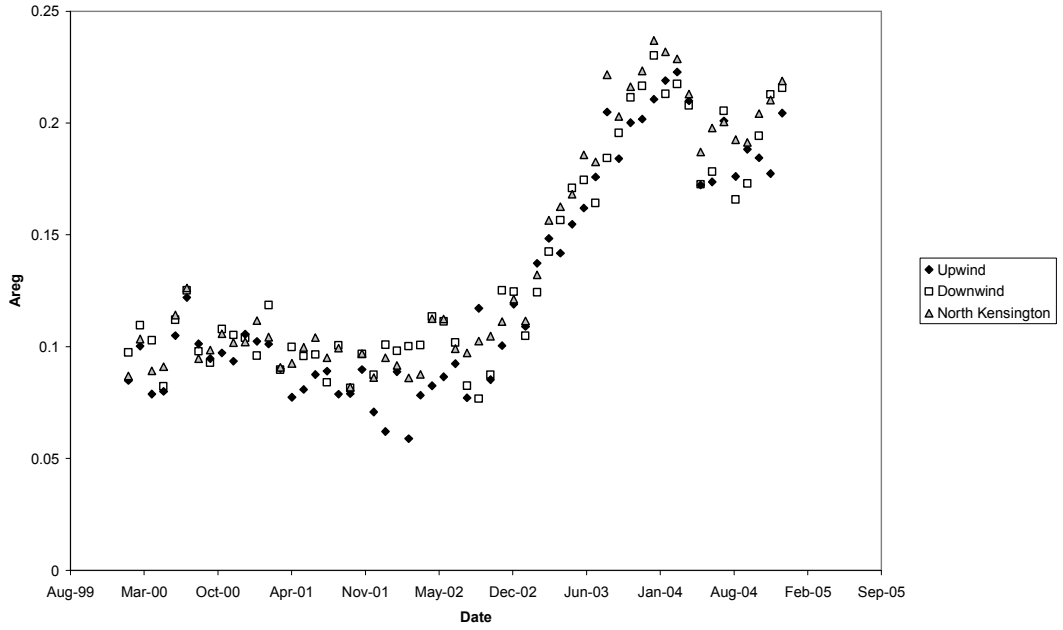

Fig.2.5: 30 day average estimates of primary nitrogen dioxide emission factor, A, for London Marylebone Road calculated using the regression methods. Background data from North Kensington, and upwind and downwind rural sites.

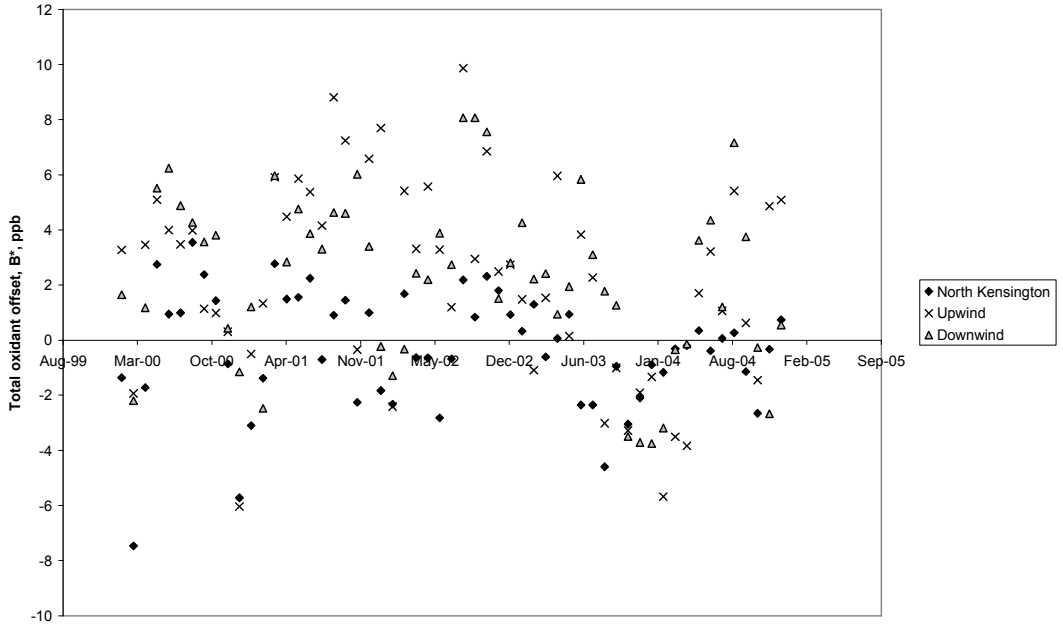

Fig. 2.6: 30 day average estimates of the residual, B^*, for London Marylebone Road calculated using the regression methods. Background data from North Kensington, and upwind and downwind rural sites.

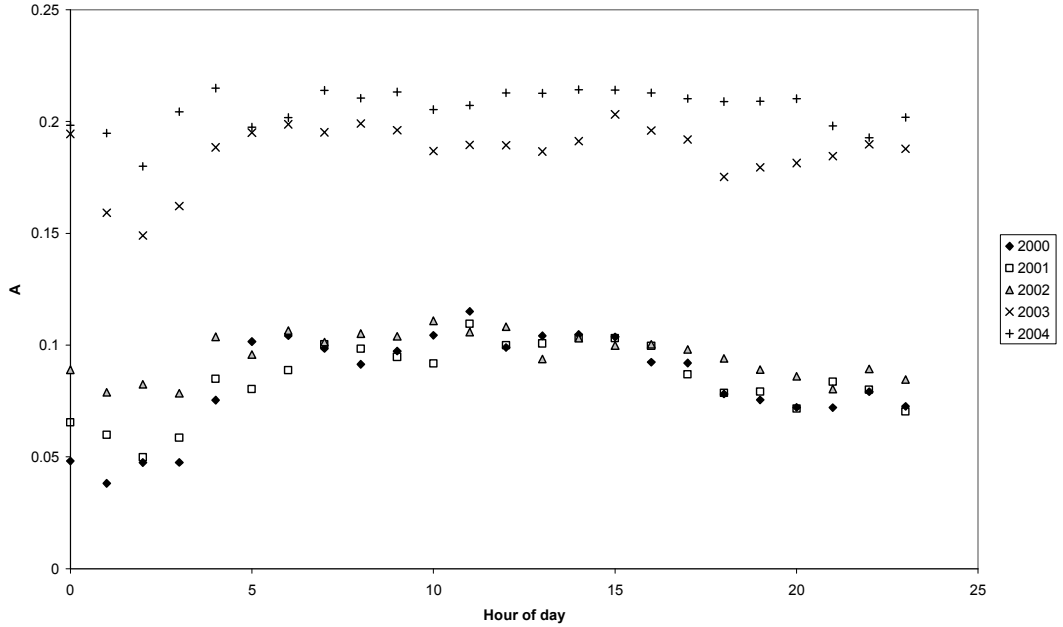

Fig. 2.7:Diurnal variation in estimates of the primary nitrogen dioxide emission factor, A for London Marylebone Road. Background data from London North Kensington

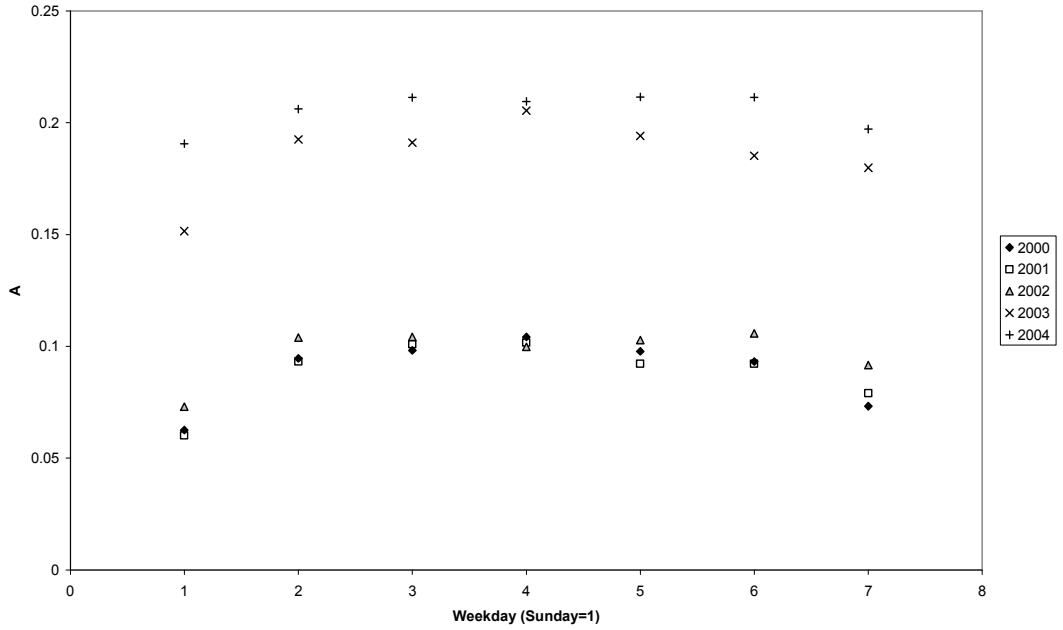

Fig. 2.8:Weekly variation in estimates of the primary nitrogen dioxide emission factor, A for London Marylebone Road. Background data from London North Kensington

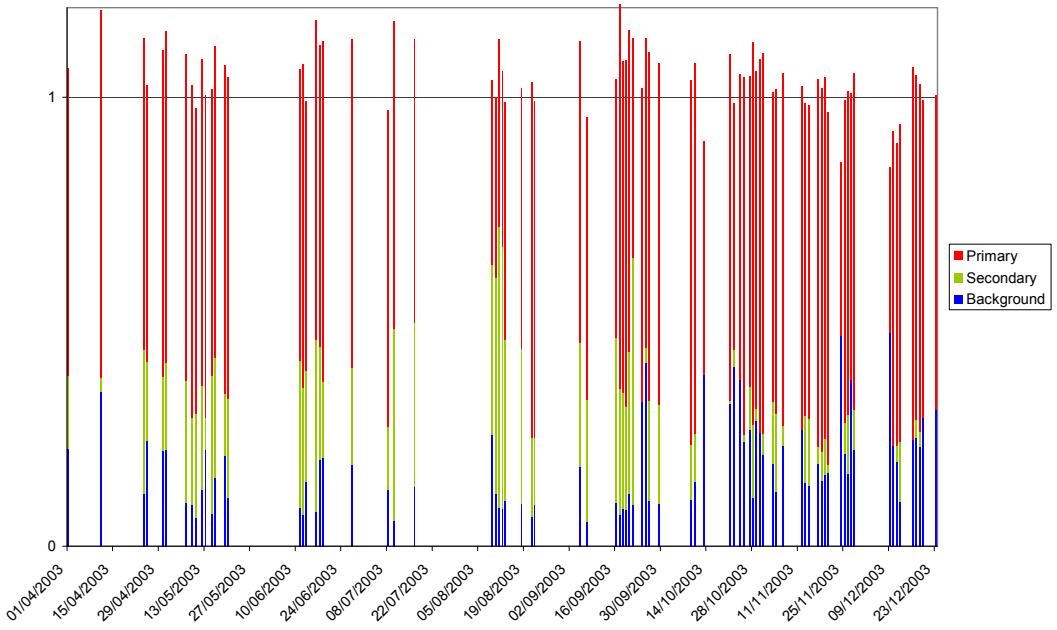

Fig. 2.9:Apportionment of nitrogen dioxide concentrations for hours with nitrogen dioxide concentrations in excess of 200 μg m^{-3} in 2003

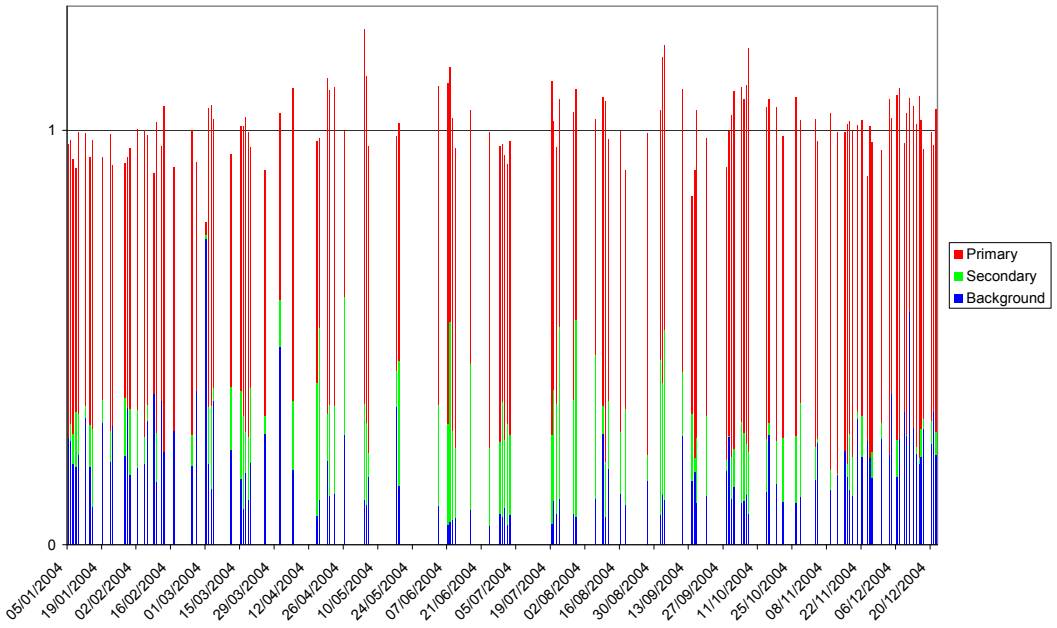

Fig. 2.10:Apportionment of nitrogen dioxide concentrations for hours with nitrogen dioxide concentrations in excess of 200 μg m^{-3} in 2004

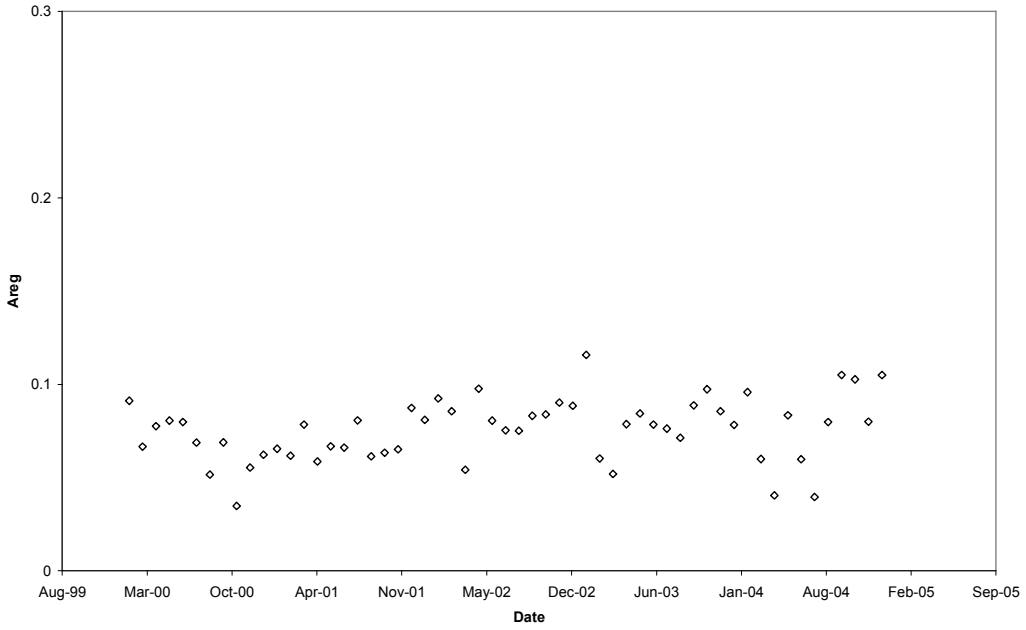

Fig.2.11: Time series of 30 day average regression estimates of A for Bury Roadside, using background data from Bolton

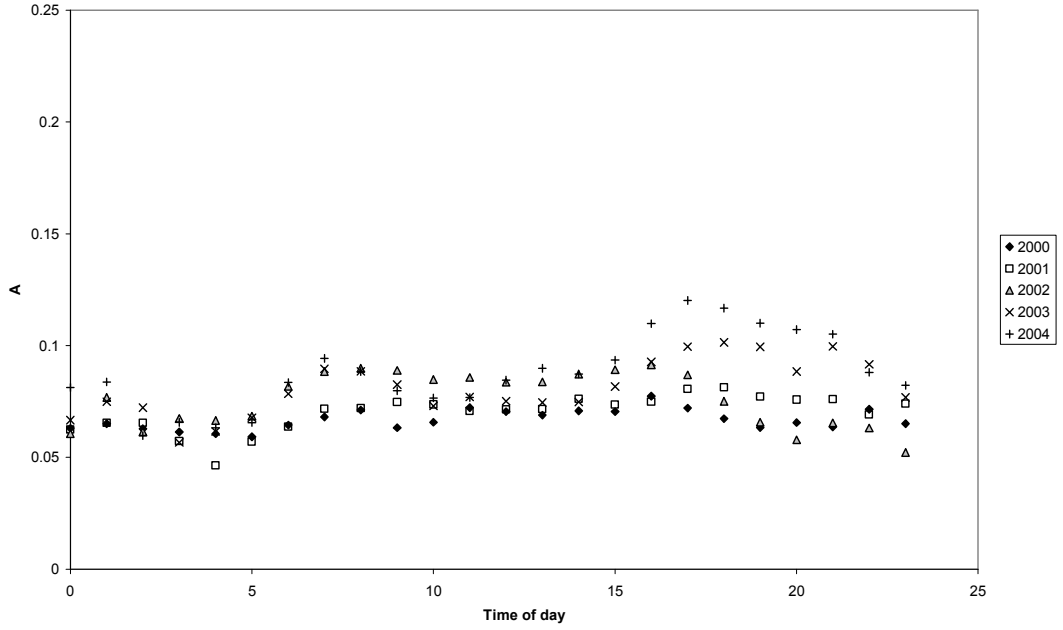

Fig. 2.12: Diurnal variation in regression estimates of A for Bury Roadside, using background data from Bolton

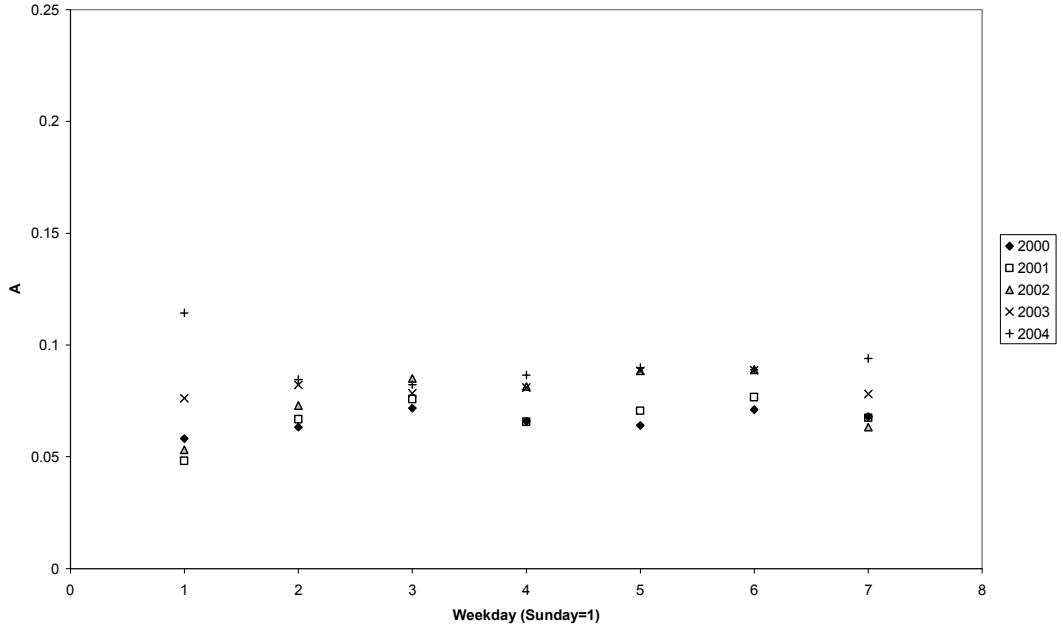

Fig. 2.13: Weekly variation in regression estimates of A for Bury Roadside, using background data from Bolton

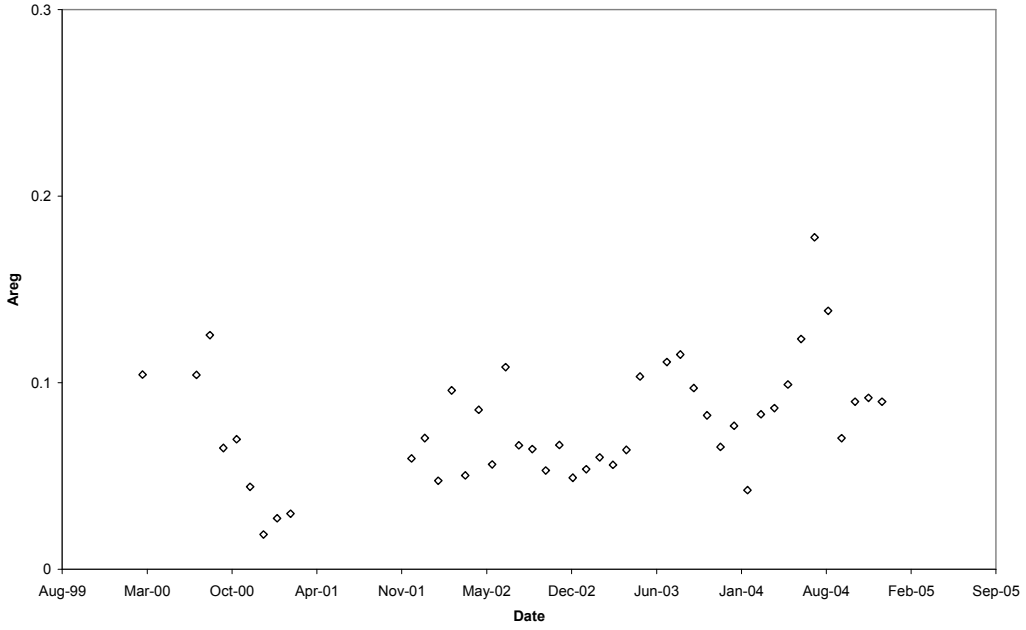

Fig.2.14: Time series of 30 day average regression estimates of A for Exeter Roadside, using background data from Plymouth centre

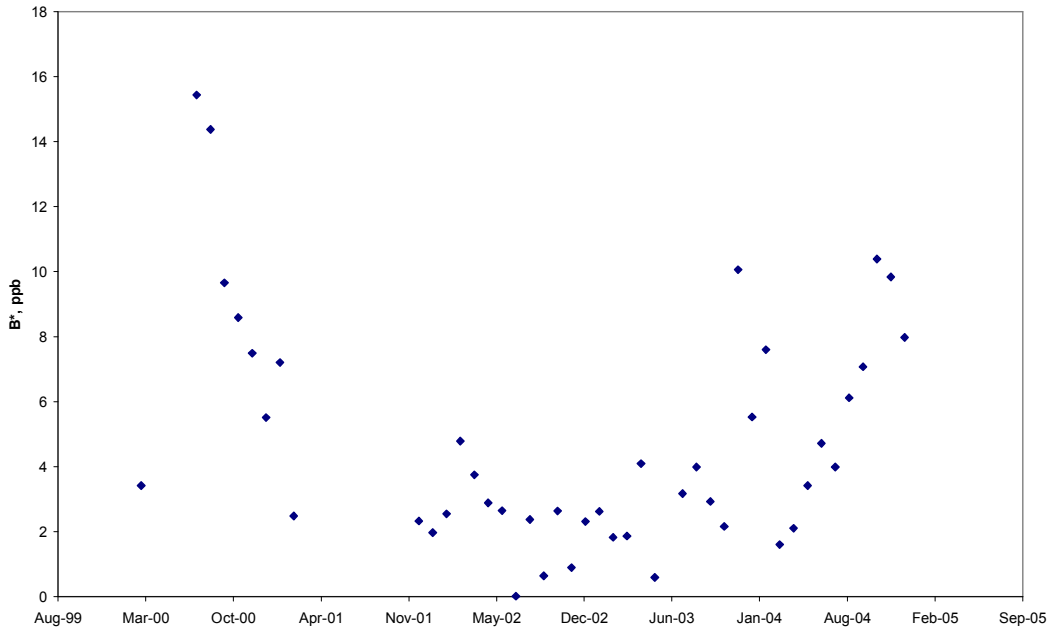

Fig.2.15: Time series of 30 day average regression estimates of B* for Exeter Roadside, using background data from Plymouth centre

3 Modelled ozone concentrations

3.1 INTRODUCTION

The estimates of the fraction of the oxides of nitrogen emitted by road vehicles as nitrogen dioxide made in Section 2 relied on measurements of ozone concentrations at the roadside sites. Measurements of ozone are made at only three roadside monitoring stations (London Marylebone Road, Bury Roadside and Exeter Roadside). Nitrogen dioxide and nitric oxide concentrations are made at several other sites throughout the United Kingdom. A simple model to predict roadside ozone concentrations is developed in this section and applied to roadside monitoring sites.

3.2 MODEL DEVELOPMENT

The transfer of ozone through the surface boundary layer (the surface stress layer) may be represented by means of mass balance over a vertical element of the boundary layer:

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

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 ozone and nitric oxide to form nitrogen dioxide;
J is the rate of photodissociation of nitrogen dioxide to nitric oxide and ozone;
Φ is a stability function.

For stable atmospheric conditions(0<z/L<1) (Pasquill and Smith,1983):

$$\phi = (1 + 5.2\frac{z}{L})$$

where L is the Monin-Obukhov length

For unstable conditions (0>z/L>-4):

$$\phi = (1 - 14\frac{z}{L})^{-0.5}$$

The rate of reaction, k_1, depends on temperature, T (K) (J Abbott et al, 2002):

$$k_1 = 1.8 \times 10^{-18} \exp\left(\frac{-1370}{T}\right) \qquad \text{m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The rate of photodissociation depends on the solar zenith angle, θ, and the cloud cover fraction ,C:

$$J = 0.011 \times (\cos\theta)^{0.397} \exp\left(\frac{-0.183}{\cos\theta}\right)\left(1 - \frac{C}{2}\right) \qquad s^{-1}$$

The solar zenith angle was calculated using the method recommended by Finlayson-Pitts and Pitts (1999).

Similar differential equations are used to represent the mass balance of nitric oxide and nitrogen dioxide:

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

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

The following conditions are applied at the upper boundary of the surface stress layer, assumed to be at one tenth of the atmospheric boundary layer height:

$$[O_3] = [O_3]_0$$
$$[NO] = [NO]_0$$
$$[NO_2] = [NO_2]_0$$

The following conditions are applied at the lower boundary at $z=z_0$, where z_0 is the surface roughness (typically 1.5 m in urban areas):

$$[NO] = [NO]_1$$
$$[NO_2] = [NO_2]_1$$
$$\frac{ku^* z}{\phi}\frac{\partial[O_3]}{\partial z} = \frac{[O_3]}{(r_b + r_c)}$$

where r_b is the resistance to ozone transfer in the laminar sublayer and r_c is the resistance at the surface (r_b+r_c=500 s m^{-1}).

The simultaneous differential equations are solved numerically for each hour of the year to provide $[O_3]=[O_3]_1$ at $z=z_0$. Hourly sequential meteorological data for 2000-2004 for Heathrow or Waddington was used to provide measurements of wind speed and cloud cover. The ADMS preprocessor was then used to estimate the friction velocity, Monin-Obukhov length and the boundary layer height for each hour.

3.3 MODEL VALIDATION

Fig.3.1 shows modelled and measured ozone concentrations for January 2004 for London Marylebone Road. The model follows the trend in the measured concentrations reasonably well.

Figs 3.2 and 3.3 show the measured ozone concentration at London Marylebone Road plotted against the modelled ozone concentration for each hour of January 2004 and June

2003 respectively. The model provides reasonable estimates of the measured hourly ozone concentrations, generally in the range +/-5 ppb.

Fig. 3.4 shows estimated values of the 30-day average primary nitrogen dioxide emissions factor A for London Marylebone Road, based on background data from London North Kensington. It shows estimates based on:

- Measured ozone concentrations;
- Modelled ozone concentrations made using meteorological data from London Heathrow;
- Modelled ozone concentrations based on "typical" meteorological conditions with a friction velocity of 0.4 m s^{-1}, neutral atmospheric stability, 50 % cloud cover a temperature of 10 ^{o}C and a boundary layer height of 800 m.

The estimates of the primary emission factor A are similar in each case.

Fig.3.5 shows estimated values of the 30-day average primary nitrogen dioxide emissions factor A for Bury Roadside, based on background data from Bolton. It shows estimates based on:

- Measured ozone concentrations;
- Modelled ozone concentrations made using meteorological data from Waddington;
- Modelled ozone concentrations based on "typical" meteorological conditions with a friction velocity of 0.4 m s^{-1}, neutral atmospheric stability, 50 % cloud cover a temperature of 10 ^{o}C and a boundary layer height of 800 m.

The estimates of the primary emission factor A are similar in each case.

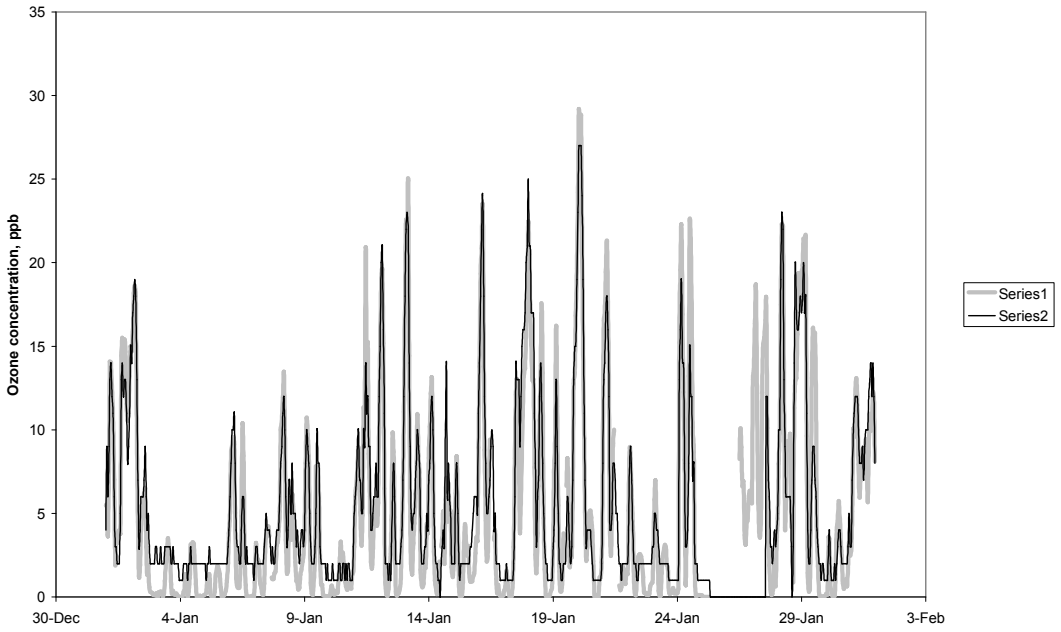

Fig.3.1: Comparison of modelled (Series 1) with measured (Series 2) ozone concentrations at London Marylebone Road for January 2004. London North Kensington background data. Heathrow meteorological data

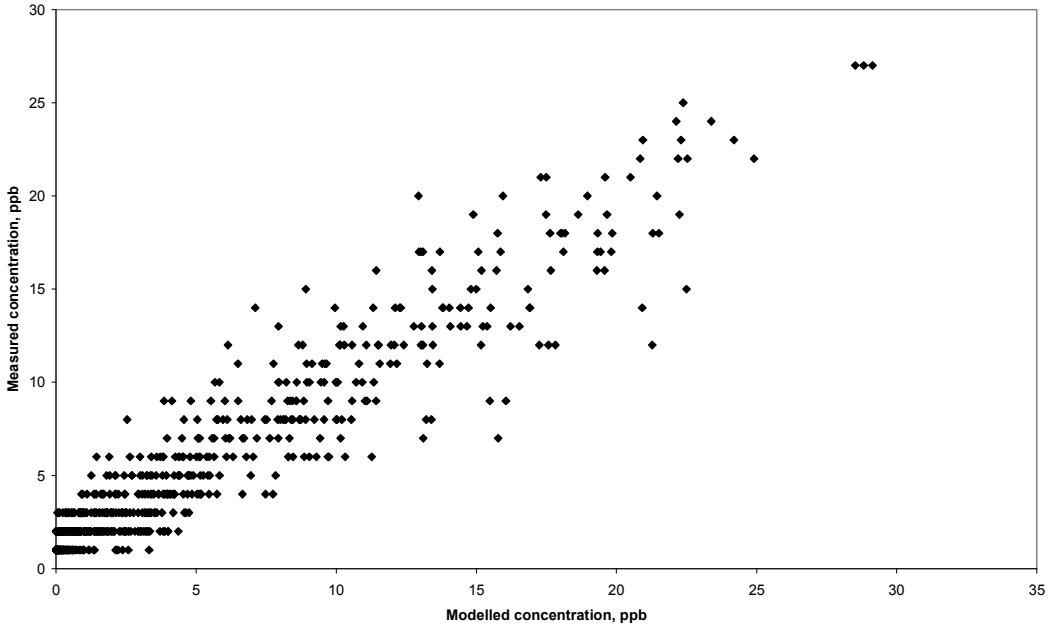

Fig. 3.2: Comparison of modelled and measured ozone concentrations at Marylebone Road, January 2004

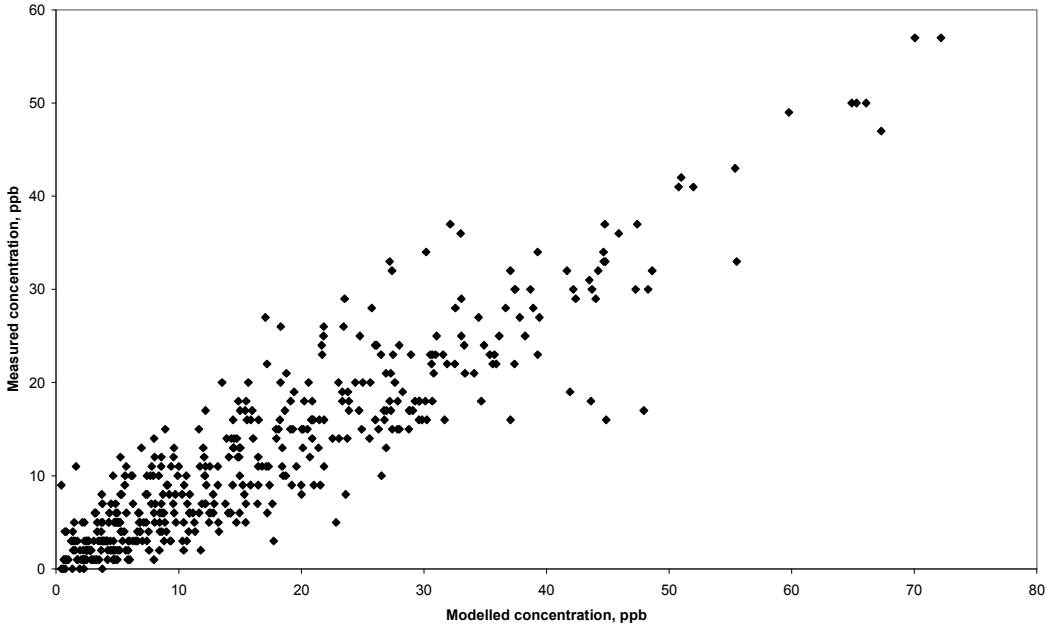

Fig. 3.2: Comparison of modelled and measured ozone concentrations at Marylebone Road, June 2003

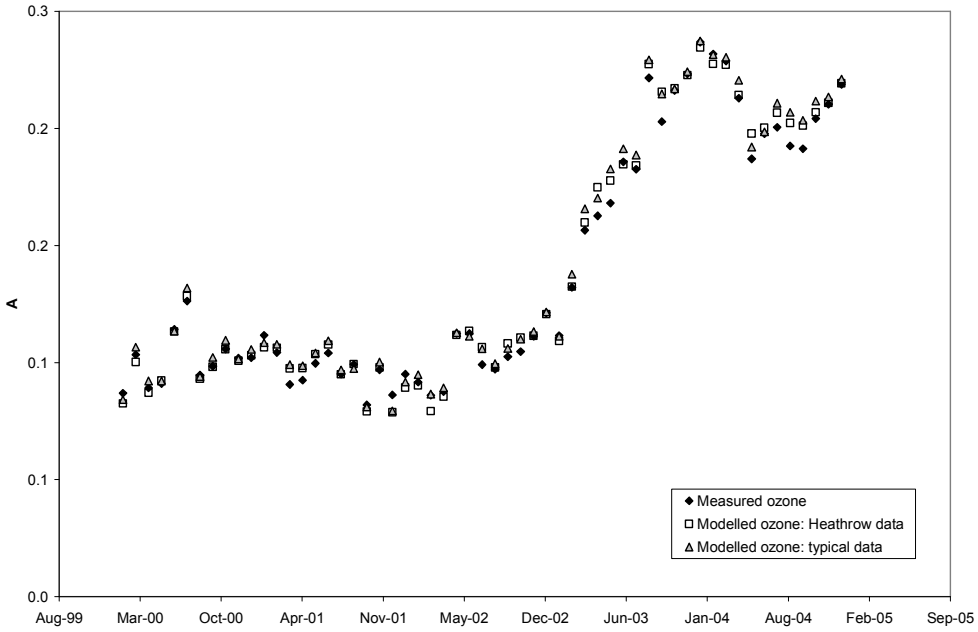

Fig.3.3: 30 day average estimates of primary nitrogen dioxide emission factor, A, for London Marylebone Road calculated using the regression methods with measured roadside ozone and with modelled ozone concentrations using Heathrow meteorological data and "typical" weather conditions.. Background data from North Kensington.

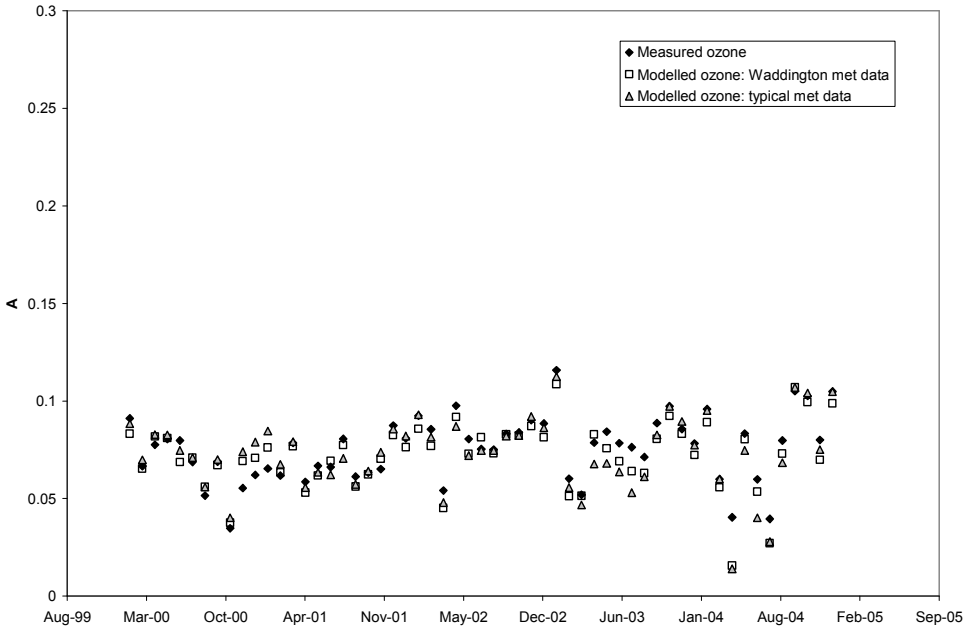

Fig.3.4: 30 day average estimates of primary nitrogen dioxide emission factor, A, for Bury Roadside calculated using the regression methods with measured roadside ozone and with modelled ozone concentrations using Waddington meteorological data and "typical" weather conditions.. Background data from Bolton.

3.4 MODEL APPLICATION

The primary emission factor A was estimated for roadside and kerbside monitoring stations throughout the United Kingdom. Measured ozone concentrations were used where these data were available at London Marylebone Road, Bury Roadside and Exeter Roadside. Modelled ozone concentrations were used at other sites. Table 3.1 summarises the background sites and meteorological data used in each case.

Table 3.1: Summary of model input data

Site	Background site	Modelled (1) or measured (0) ozone	Heathrow (1) or Waddington (2) meteorological data
Bath Roadside	Bristol Centre	1	1
Brighton Roadside	Lullington Heath	1	1
Bristol Old Market	Bristol Centre	1	1
Bury Roadside	Bolton	0	
Cambridge Roadside	Wicken Fen	1	1
Camden Kerbside	London N. Kensington	1	1
Dumfries	Glasgow Centre	1	2
Exeter Roadside	Plymouth Centre	0	
Glasgow Kerbside	Glasgow Centre	1	2
Haringey Roadside	London Hackney	1	1
Hounslow Roadside	London Brent	1	1
Hove Roadside	Lullington Heath	1	1
London A3 Roadside	London Teddington	1	1
London Bromley	London Lewisham	1	1
London Cromwell Road 2	London N. Kensington	1	1
London Marylebone Road	London N. Kensington	0	
Norwich Roadside	Norwich Centre	1	1
Oxford Centre	Harwell	1	1
Southwark Roadside	London Southwark	1	1
Stockton-on-Tees Yarm	Middlesbrough	1	2
Sutton Roadside	London Sutton	1	1
Tower Hamlets Roadside	London Hackney	1	1

Table 3.2 shows the estimated annual average primary nitrogen dioxide emission factor A for each site for the years 2000-2004. Note that estimates for 2004 include unratified data for October –December 2004. The predicted annual average factor is in the range 0.03-0.25. The factor has remained approximately the same (<0.005 change per year) throughout the period for the following sites:

- Bury Roadside
- Dumfries
- Glasgow Kerbside
- Stockton on Tees Yarm
- Norwich Roadside

There was a substantial increase (>0.015 per year) in the factor A at the following sites:

- Brighton Roadside;
- Bristol Old Market;
- Camden Kerbside;
- Hove Roadside;
- London A3 Roadside;
- London Marylebone Road;
- Southwark Roadside.

The trend is less obvious at the other sites: however, the general trend shows an increase at each of the other sites. Table 3.2 shows the trend in factor A calculated by regression of the annual values.

The trend in A appears to be influenced by geographical factors. There is no change in A at sites in England, north of Norwich and in Scotland. All sites in England, south of Norwich show some increase in A.

Table 3.3 shows annual average values of the offset B^* for each of the sites. There appears to be little obvious pattern in the calculated values.

Table 3.2: Estimated values of A for roadside and kerbside sites

	2000	2001	2002	2003	2004	Slope of trend line (increase per year)
Bath Roadside	0.07	0.12	0.13	0.14	0.13	0.014
Brighton Roadside	0.08	0.06	0.10	0.11	0.13	0.015
Bristol Old Market	0.07	0.06		0.14	0.12	0.018
Bury Roadside	0.07	0.07	0.08	0.08	0.09	0.005
Cambridge Roadside	0.06	0.09	0.11	0.09	0.10	0.008
Camden Kerbside	0.07	0.08	0.10	0.11	0.15	0.019
Dumfries		0.14	0.13	0.13	0.14	0.000
Exeter Roadside	0.06	0.04	0.05	0.07	0.09	0.009
Glasgow Kerbside	0.10	0.11	0.10	0.10	0.10	-0.001
Haringey Roadside	0.07	0.07	0.08	0.08	0.12	0.011
Hounslow Roadside	0.05	0.06	0.15			0.050
Hove Roadside	0.09	0.08	0.16	0.17	0.17	0.025
London A3 Roadside	0.03	0.05	0.09	0.13	0.13	0.028
London Bromley	0.12		0.14	0.16	0.25	0.029
London Cromwell Road 2	0.18	0.15	0.17	0.19	0.22	0.012
London Marylebone Road	0.10	0.09	0.10	0.19	0.21	0.032
Norwich Roadside	0.15	0.09	0.11	0.13	0.15	0.004
Oxford Centre	0.11	0.10	0.12	0.13	0.14	0.009
Southwark Roadside	0.05	0.07	0.07	0.13	0.14	0.024
Stockton-on-Tees Yarm		0.09	0.08	0.06	0.07	-0.008
Sutton Roadside	0.06	0.07	0.08			0.010
Tower Hamlets Roadside	0.10	0.10	0.09	0.13	0.14	0.011

95% percentile confidence interval less than +/- 0.01 in each case.
Value of A calculated on a minimum of 100 hours in each case.

Table 3.3: Estimated values of B^* for roadside and kerbside sites

	2000	2001	2002	2003	2004	Slope of trend line (increase per year)
Bath Roadside	1.2	-0.5	-0.6	0.6	-0.3	-0.18
Brighton Roadside	4.7	3.7	3.9	4.4	4.1	-0.04
Bristol Old Market	2.3	5.2		2.2	1.3	-0.51
Bury Roadside	4.2	0.9	-0.2	1.9	2.9	-0.14
Cambridge Roadside	5.8	4.2	4.5	4.6	3.6	-0.41
Camden Kerbside	1.7	2.1	2.8	1.6	1.8	-0.03
Dumfries		1.9	1.8	1.0	1.4	-0.24
Exeter Roadside	9.6	3.3	3.0	4.2	6.6	-0.50
Glasgow Kerbside	3.2	1.5	3.3	2.3	1.5	-0.26
Haringey Roadside	0.7	1.2	1.2	1.3	1.2	0.11
Hounslow Roadside	3.8	4.9	6.4			1.30
Hove Roadside	4.9	4.3	2.7	3.1	4.4	-0.21
London A3 Roadside	5.0	3.6	3.6	5.0	4.6	0.05
London Bromley	3.4		1.9	2.5	2.6	-0.20
London Cromwell Road 2	0.3	0.9	-0.2	-1.5	-1.0	-0.51
London Marylebone Road	0.8	0.9	0.6	-1.6	-0.7	-0.55
Norwich Roadside	0.4	1.6	1.8	2.3	2.0	0.38
Oxford Centre	4.3	3.4	3.0	2.7	4.6	-0.01
Southwark Roadside	2.3	1.8	1.1	0.5	1.3	-0.34
Stockton-on-Tees Yarm		-0.2	-0.7	3.2	0.8	0.70
Sutton Roadside	2.0	2.6	2.1			0.03
Tower Hamlets Roadside	0.7	1.3	0.8	-0.3	-0.4	-0.38

95% percentile confidence interval less than +/- 0.6 ppb in each case.
Value of B^* calculated on a minimum of 100 hours in each case.

4 Modelled nitrogen dioxide concentrations

4.1 INTRODUCTION

Dispersion models are widely used to predict oxides of nitrogen concentrations near roads. Various methods are then used to predict nitrogen dioxide concentrations from the predicted oxides of nitrogen concentrations. The model developed in Section 3 can be readily adapted to predict nitrogen dioxide concentrations from modelled or measured oxides of nitrogen concentrations. The model has the advantage that it has a more mechanistic basis than the more empirical methods currently used: on the other hand, it is simpler to implement than more complex numerical models. The performance of the model is assessed her by comparison with measured concentrations near roads.

4.2 MODEL DEVELOPMENT

The model is identical to that used to estimate roadside ozone concentrations except that the surface boundary conditions:

$$[NO] = [NO]_1$$
$$[NO_2] = [NO_2]_1$$

are replaced by:

$$[NO] + [NO_2] = [NO_x]_1$$
$$\frac{\partial [NO_2]}{\partial r} = \frac{A}{1-A}\frac{\partial [NO]}{\partial r}$$

where A is the fraction of the oxides of nitrogen emitted as nitrogen dioxide.

4.3 MODEL VALIDATION

4.3.1 Site specific values of the primary nitrogen dioxide emission factor, A

The model was used to annual average predict nitrogen dioxide concentrations at each of the roadside or kerbside monitoring stations. Background sites were as shown in Table 3.1. The values of A were taken from Table 3.2. Fig. 4.1 shows the measured nitrogen dioxide concentration plotted against the modelled concentration for all sites. Table 4.1 lists the measured and modelled annual average concentrations. Table 4.2 lists the measured and modelled numbers of exceedence of the 200 $\mu g\ m^{-3}$ hourly limit value. Table 4.3 lists the number of hours in each year for each site over which the comparison of modelled and measured concentrations was made. In general, the model provides reasonable estimates of the measured nitrogen dioxide concentrations. The standard error in the annual average concentration over all sites and years was 4.7 $\mu g\ m^{-3}$.

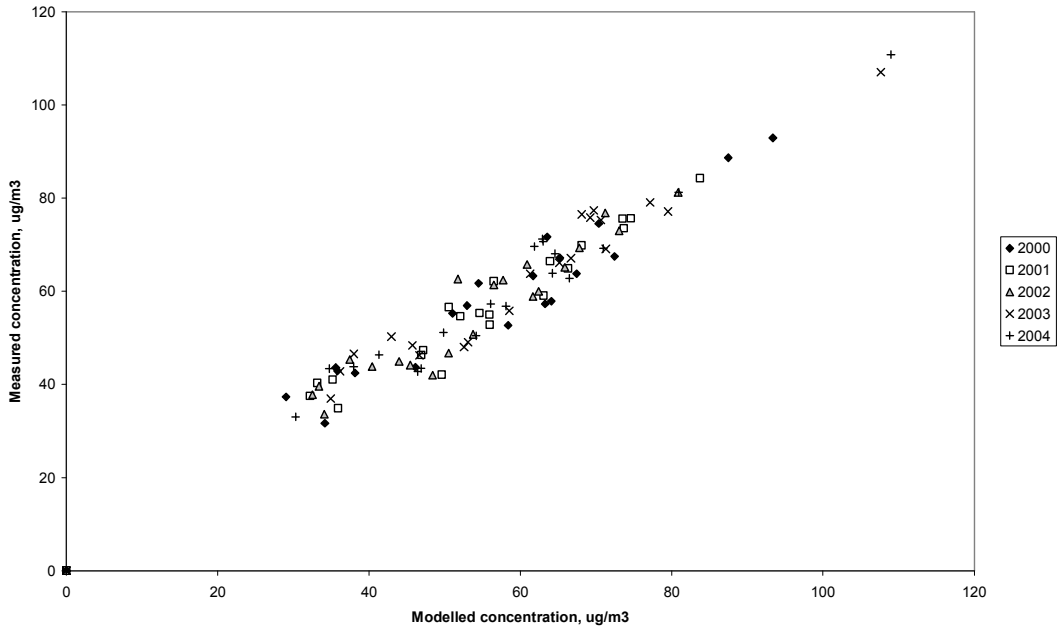

Fig. 4.1:Model predictions of nitrogen dioxide concentrations using site specific values of the primary nitrogen dioxide emission factor , A

4.3.2 Annual average values of the the primary nitrogen dioxide emission factor, A

The model predictions set out in 4.3.1 were made using site specific estimates of the primary nitrogen dioxide emission factor, A derived from the analysis in Section 3. Fig. 4.2 compares the annual average concentration predicted using national average values of the factor A:

2000	0.08
2001	0.09
2002	0.11
2003	0.12
2004	0.14

The modelled and measured concentrations are listed in Table 4.4. In general, use of the national average estimates of A leads to some deterioration in model performance, although the method still provides reasonable estimates. The standard error in the annual average concentration over all sites and years was 6.5 μg m^{-3}. Note that the use of national average estimates of the factor A leads to an underestimate of the measured nitrogen dioxide concentrations at London Marylebone Road in 2003 and 2004, because the proportion of the oxides of nitrogen emitted as primary nitrogen dioxide is greater at this site than the national average (see Table 3.2).

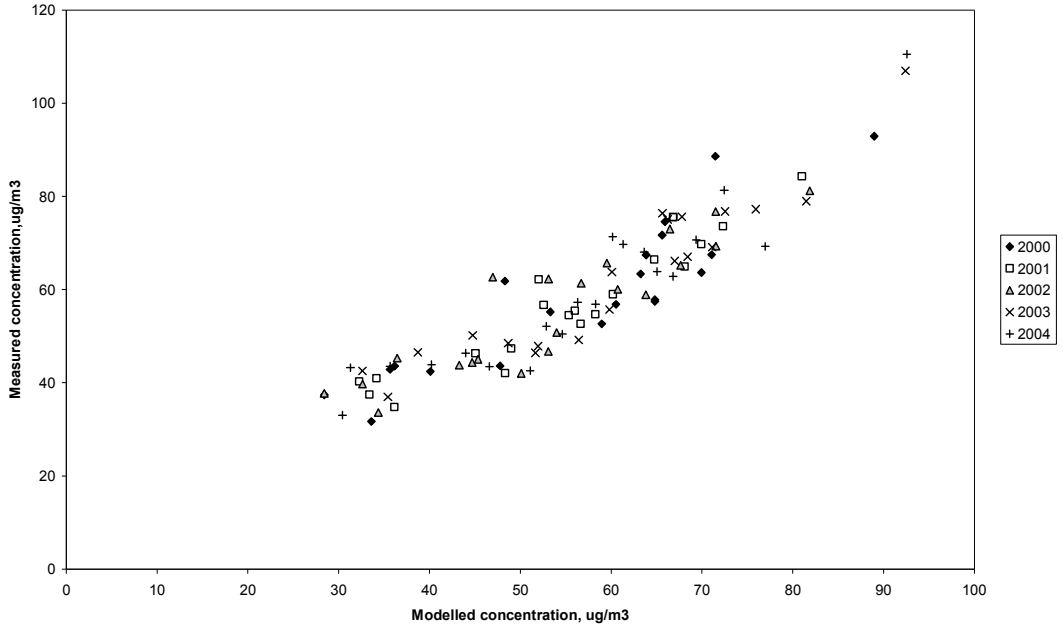

Fig. 4.2:Model predictions of nitrogen dioxide concentrations using national average values of the primary nitrogen dioxide emission factor , A

4.3.3 Annual average concentrations

Fig. 4.2 shows the modelled annual average nitrogen dioxide concentrations based on hourly average oxides of nitrogen, nitrogen dioxide and ozone concentrations. Fig. 4.3 shows the modelled annual average concentration based on the annual average oxides of nitrogen concentration at the roadside site and annual average oxides of nitrogen, nitrogen dioxide and ozone concentrations at the background site. Roadside receptors are influenced by traffic emissions when the wind direction is from the road towards the receptor. It was assumed that the wind direction for a typical site is from the road towards the receptor for half of the time. Typical meteorological conditions with friction velocity of 0.4 m s^{-1}, neutral atmospheric stability, 50% cloud cover, boundary layer height of 800 m and zenith angle of 77^{o} were assumed. Comparison of Fig. 4.3 with Fig. 4.2 indicates that use of the model with annual average inputs rather than hour by hour calculation does not lead to significant deterioration in model predictions.

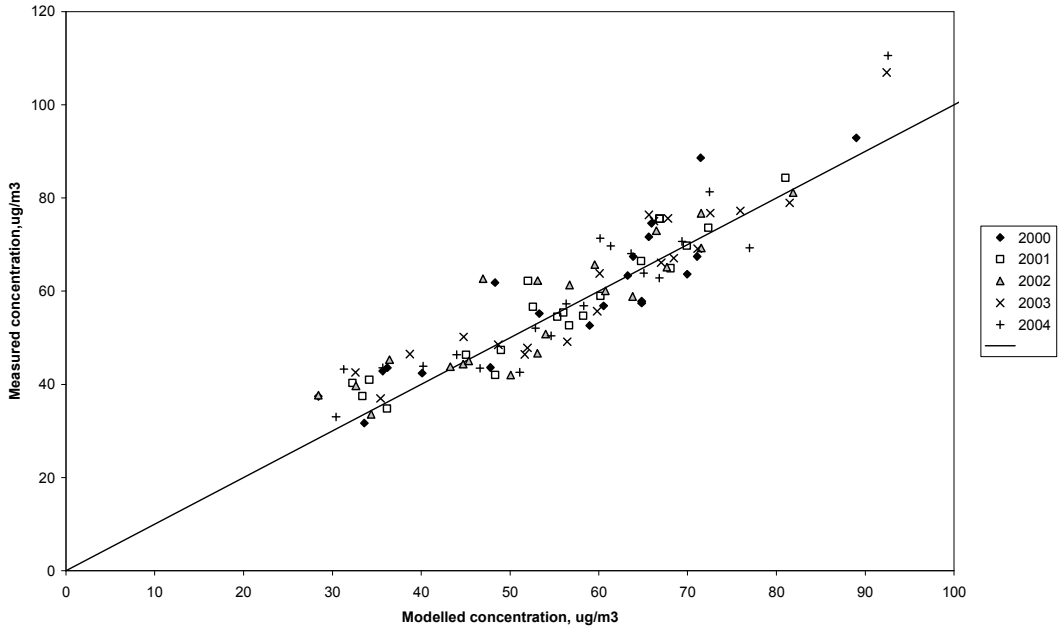

Fig. 4.3: Model predictions of nitrogen dioxide concentrations using national average values of the primary nitrogen dioxide emission factor , A , annual average concentration measurements and typical meteorological data

4.3.4 AQEG

The performance of the model may be compared to that based on the AQEG approach.

$$[Ox]_1 = [Ox]_0 + A\left([NO_x]_1 - [NO_x]_0\right)$$

where A are the annual average estimates of the primary nitrogen dioxide emission factor listed in 4.3.2.

The roadside nitrogen dioxide concentration was then calculated using the empirical fit 2 given by AQEG:

$$\frac{[NO_2]_1}{[Ox]_1} = 8.962\times10^{-2} + 1.474\times10^{-2}[NOx]_1 - 1.290\times10^{-4}[NOx]_1^2 + 5.527\times10^{-7}[NOx]_1^3 - 8.906\times10^{-10}[NOx]_1^4$$

Modelled nitrogen dioxide concentrations are compared with measured concentrations in Fig 4.4. Comparison of Fig. 4.3 and Fig. 4.4 indicates that the performance of the mechanistic model developed here and that of the empirical data fit employed by AQEG are similar.

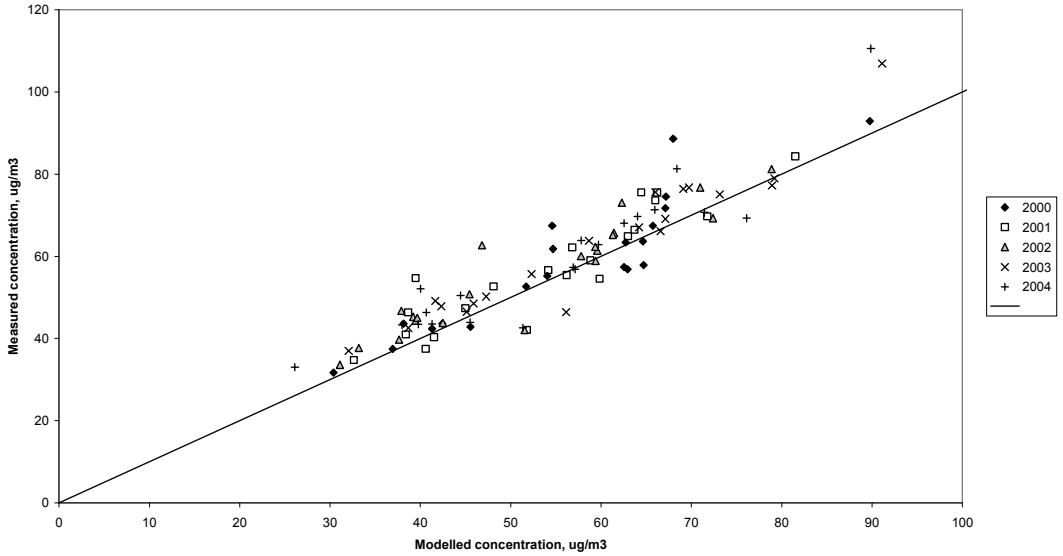

Fig. 4.4: Model predictions of nitrogen dioxide concentrations using national average values of the primary nitrogen dioxide emission factor , A and the AQEG fit 2.

4.3.5 Local Authority Review and Assessment Technical Guidance

Local Authority Review and Assessment Technical Guidance TG(03) provides a simple empirical relationship for predicting roadside nitrogen dioxide concentrations from roadside oxides of nitrogen concentrations and background oxides of nitrogen and nitrogen dioxide concentrations.

$$F = -0.068 \ln[NOx]_1 + 0.53$$

$$[NO_2]_1 = [NO_2]_0 + F\left([NOx]_1 - [NOx]_0\right)$$

Fig. 4.5 compares the predictions made using this relationship and measured nitrogen dioxide concentrations. Generally the TG(03) method underestimates the measured concentrations in recent years. The data points are more widely scattered than those shown in Figs 4.3 and 4.4.

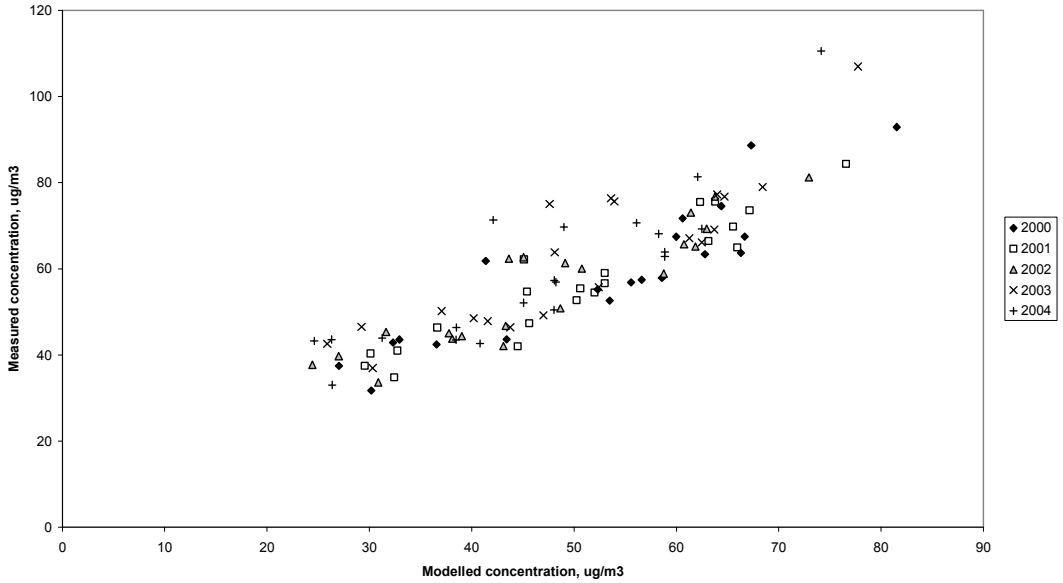

Fig. 4.5: Model predictions of nitrogen dioxide concentrations using the Technical Guidance method.

Table 4.1: Modelled and measured annual average nitrogen dioxide concentrations, μg m^{-3}: site specific values of A

	Modelled					Measured				
	2000	2001	2002	2003	2004	2000	2001	2002	2003	2004
Bath Roadside	63	63	62	61	58	57	59	60	64	57
Brighton Roadside	36	32	33	38	36	43	37	40	47	44
Bristol Old Market	64	55		69	56	58	55		76	57
Bury Roadside	64	68	68	70	63	72	70	69	77	71
Cambridge Roadside	36	35	37	43	38	44	41	45	50	44
Camden Kerbside	62	64	61	65	65	63	66	66	66	68
Dumfries		47	45	53	47		46	44	48	43
Exeter Roadside	38	56	40	46	41	42	55	44	48	46
Glasgow Kerbside	70	74	71	77	71	75	76	77	79	69
Haringey Roadside	58	56	54	59	54	53	53	51	56	50
Hounslow Roadside	51	51	52			55	57	63		
Hove Roadside	29	33	33	36	35	37	40	38	43	43
London A3 Roadside	53	52	57	68	62	57	55	61	77	70
London Bromley	65		51	53	50	67		47	49	51
London Cromwell Road 2	87	75	73	80	81	89	76	73	77	81
London Marylebone Road	93	84	81	108	109	93	84	81	107	111
Norwich Roadside	34	36	34	35	30	32	35	34	37	33
Oxford Centre	54	57	58	71	63	62	62	62	75	71
Southwark Roadside	67	66	62	67	64	64	65	59	67	64
Stockton-on-Tees Yarm		50	48	47	46		42	42	46	43
Sutton Roadside	46	47	44			44	47	45		
Tower Hamlets Roadside	72	74	66	71	67	67	74	65	69	63

Table 4.2: Numbers of modelled and measured exceedences of 200 μg m^{-3} nitrogen dioxide concentrations: site specific values of A

	Modelled					Measured				
	2000	2001	2002	2003	2004	2000	2001	2002	2003	2004
Bath Roadside	4	4	4	7	4	0	0	1	0	0
Brighton Roadside	1	0	7	1	0	0	0	2	0	0
Bristol Old Market	2	0		5	2	5	0		6	0
Bury Roadside	11	21	6	27	10	5	11	0	1	0
Cambridge Roadside	1	0	4	0	1	0	0	0	0	0
Camden Kerbside	7	11	0	6	5	0	0	0	0	8
Dumfries		1	1	1	0		0	0	1	1
Exeter Roadside	0	0	1	1	0	0	0	3	0	0
Glasgow Kerbside	12	18	38	15	12	14	53	28	20	10
Haringey Roadside	0	0	0	1	3	0	0	0	0	0
Hounslow Roadside	1	0	4			0	0	4		
Hove Roadside	0	0	0	1	1	0	0	0	0	0
London A3 Roadside	17	7	5	26	9	0	0	4	16	2
London Bromley	0		0	0	0	0		0	0	0
London Cromwell Road 2	23	9	7	10	17	7	1	0	4	3
London Marylebone Road	40	32	23	391	493	85	47	2	418	501
Norwich Roadside	0	0	0	0	0	0	0	0	0	0
Oxford Centre	28	17	26	53	28	1	0	0	17	6
Southwark Roadside	0	0	0	3	0	0	0	0	1	0
Stockton-on-Tees Yarm		4	1	3	1		0	1	1	0
Sutton Roadside	0	3	0			0	0	0		
Tower Hamlets Roadside	5	1	4	2	5	2	5	2	5	3

Table 4.3: Numbers of hours with valid data for model validation.

	2000	2001	2002	2003	2004
Bath Roadside	5450	6332	7297	6556	6898
Brighton Roadside	3097	6103	5911	5363	6354
Bristol Old Market	5318	4006		4303	6795
Bury Roadside	7387	7460	7073	6574	6609
Cambridge Roadside	4668	6197	6128	4317	5253
Camden Kerbside	6808	7496	571	3392	4946
Dumfries		4260	5630	2742	5488
Exeter Roadside	5291	1788	5961	5259	6069
Glasgow Kerbside	5310	6756	6927	3292	6626
Haringey Roadside	5064	3812	6277	5727	6205
Hounslow Roadside	6301	6037	5884		
Hove Roadside	4978	6010	5599	5471	5779
London A3 Roadside	6881	6738	6484	5863	7122
London Bromley	2648		4765	5490	5800
London Cromwell Road 2	6829	7399	7601	7043	7893
London Marylebone Road	7144	7240	8056	7271	7970
Norwich Roadside	5912	5499	6126	6117	6173
Oxford Centre	6233	6306	7245	6355	6045
Southwark Roadside	6658	6933	5552	5030	5622
Stockton-on-Tees Yarm		6802	5520	5553	4455
Sutton Roadside	5166	6190	1951		
Tower Hamlets Roadside	5501	3752	6688	6938	6668

Table 4.4: Modelled and measured annual average nitrogen dioxide concentrations, $\mu g\ m^{-3}$: national average values of A

	Modelled					Measured				
	2000	2001	2002	2003	2004	2000	2001	2002	2003	2004
Bath Roadside	65	60	61	60	58	57	59	60	64	57
Brighton Roadside	36	33	33	39	36	43	37	40	47	44
Bristol Old Market	65	56		68	56	58	55		76	57
Bury Roadside	66	70	72	76	69	72	70	69	77	71
Cambridge Roadside	36	34	36	45	40	44	41	45	50	44
Camden Kerbside	63	65	60	67	64	63	66	66	66	68
Dumfries		45	45	52	47		46	44	48	43
Exeter Roadside	40	58	43	49	44	42	55	44	48	46
Glasgow Kerbside	66	67	72	81	77	75	76	77	79	69
Haringey Roadside	59	57	54	60	55	53	53	51	56	50
Hounslow Roadside	53	53	47			55	57	63		
Hove Roadside	28	32	28	33	31	37	40	38	43	43
London A3 Roadside	61	55	57	66	61	57	55	61	77	70
London Bromley	64		53	56	53	67		47	49	51
London Cromwell Road 2	71	67	66	73	72	89	76	73	77	81
London Marylebone Road	89	81	82	92	93	93	84	81	107	111
Norwich Roadside	34	36	34	35	30	32	35	34	37	33
Oxford Centre	48	52	53	66	60	62	62	62	75	71
Southwark Roadside	70	68	64	68	65	64	65	59	67	64
Stockton-on-Tees Yarm		48	50	52	51		42	42	46	43
Sutton Roadside	48	49	45			44	47	45		
Tower Hamlets Roadside	71	72	68	71	67	67	74	65	69	63

5 Conclusions

Monitoring data from roadside sites at London Marylebone Road, Bury Roadside and Exeter Roadside sites was analysed to provide estimates of the proportion of the oxides of nitrogen effectively released from road vehicles as nitrogen dioxide (the "primary nitrogen dioxide emission factor"). Typical estimated primary nitrogen dioxide emission factors were approximately 0.1. The primary nitrogen dioxide emission factor at London Marylebone Road increased substantially over the period 2000-2004 from approximately 0.1 to approximately 0.2. The trend in primary emission factor was less clear at the Bury Roadside and Exeter Roadside sites.

There was some diurnal variation in the primary nitrogen dioxide emission factor at London Marylebone Road: the emission factor was greatest during the daytime. There was also some weekly variation in the emission factor: the highest emission factors were observed on weekdays.

Source apportionment analysis of the data for London Marylebone Road was carried out for those hours during 2003 and 2004 when the limit value of 200 $\mu g\ m^{-3}$ was exceeded. The background contribution and the secondary contribution from nitric oxide emissions reacting with ozone were small compared to the primary nitrogen dioxide component. The proportion of oxides of nitrogen emitted as nitrogen dioxide during the exceedence hours was similar to that for other hours of the year.

The analysis of data from London Marylebone Road, Bury Roadside and Exeter Roadside was possible because roadside ozone concentration measurements were available at those sites. A one-dimensional model of the transfer and reactions of ozone in the surface boundary layer was developed so that monitoring data could be analysed in the same way for other roadside sites where ozone concentrations are not measured. The model was validated by comparing the primary nitrogen dioxide emission factor A calculated using measured and modelled ozone concentrations at London Marylebone Road and Bury Roadside.

There was a substantial increase (>0.015 per year) in the factor A at the following sites:

- Brighton Roadside;
- Bristol Old Market;
- Camden Kerbside;
- Hove Roadside;
- London A3 Roadside;
- London Marylebone Road;
- Southwark Roadside.

The factor A remained the same (trend <0.005 per year) at the following sites:

- Bury Roadside
- Dumfries
- Glasgow Kerbside
- Stockton on Tees Yarm
- Norwich Roadside

The average value of factor A over all sites increased during the period 2000-2004:

2000	0.08
2001	0.09
2002	0.11
2003	0.12
2004	0.14

The one dimensional model may also be used to predict nitrogen dioxide concentrations at roadside sites from oxides of nitrogen concentrations. It might thus be useful for dispersion modelling and climate mapping purposes. The model performance is similar to that of the semi-empirical model developed for AQEG when compared on a like for like basis for the estimation of annual average nitrogen dioxide concentrations from annual average measurements of oxides of nitrogen concentrations. However, the new model has the advantage that it is based on a mathematical representation of the physical and chemical processes in the surface boundary layer. It may also be used to provide predictions of hourly average nitrogen dioxide concentrations.

6 References

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