A New Approach to Deriving NO$_2$ from NO$_x$ for Air Quality Assessments of Roads

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Contents

1   Introduction

1.1   The assessment of the air quality impacts of emissions from road traffic relies upon the application of air quality models. These models predict the dispersion and dilution of primary pollutants, translating emissions in grammes per second to concentrations in microgrammes per cubic metre. These road traffic concentrations are then added to the local background to give the total concentrations, which decline as a function of distance from the road. Complications arise in the case of pollutants that undergo chemical transformations in the atmosphere. This applies in the case of nitrogen oxides (NO_x) (the sum of nitric oxide (NO) and nitrogen dioxide (NO_2)). The emissions occur primarily as NO, but this is transformed in the atmosphere to NO_2, principally by reaction with ozone[1]. The reaction with ozone changes the proportion of NO_2 and this has to be allowed for in the modelling. There is the added complexity of background NO and NO_2 mixing with freshly emitted NO and NO_2. Prediction of NO_2 concentrations is thus not straightforward.

1.2   The principal interest when assessing NO_x emissions from road traffic is the concentrations of NO_2 at the roadside, as it is the NO_2 that is associated with adverse health effects, not the NO_x. It is thus necessary to predict the transformation of NO to NO_2. There are various approaches to this, ranging from the application of complex chemical models, through the use of simple chemical models, to empirically based models. The annual mean concentration of NO_2 is the principal focus for air quality assessment, as NO_2 averaged over this period is more likely to exceed the air quality objective than the 1-hour concentration. This can be derived by running the dispersion models to predict hour by hour concentrations of NO_x and then applying the chemical or empirical models to predict hour by hour NO_2 concentrations, and then averaging over a year. An alternative approach is to derive annual mean NO_x concentrations and then use an empirical approach to calculate the annual mean NO_2. In both cases, it is necessary to take account of the mixing of fresh emission, which have a low NO_2 to NO_x ratio with background air with a higher NO_2 to NO_x ratio. Given the intrinsic limitations of all these approaches there is no 'best' way to calculate annual mean NO_2 at roadside locations.

1.3   This report examines the empirical approaches that have been widely applied to the transformation of annual mean NO_x concentrations to annual mean NO_2. They have

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[1] The actual chemistry is far more complicated and, amongst other things, has to allow for the photolytic decomposition of NO2 to form NO and ozone, and the development of a photo-stationary state during daylight hours.

been used in the Design Manual for Roads and Bridges (DMRB) screening model, which is used by the Highways Agency to assess the air quality impacts of trunk road schemes, and more widely for assessments of concentrations alongside roads as part of the reviews and assessments being carried out by local authorities, as well as being applied to the results of more sophisticated models.

2   Limitations of Current Empirical Approach

2.1   The empirical conversion of annual mean NO_x to annual mean NO_2 relies on the relationship between NO_2 and NO_x found in measured data. A typical data set from which such relationships are derived is presented in Figure 1. This shows data from the national automatic urban and rural network (AURN) monitoring sites, sites operated for the Highways Agency by TRL, and a site operated by Salford MBC alongside the M60, within the years 1997-2001. The overall picture is of a considerable scatter in the data, with no clear-cut relationship. For instance, at a NO_x concentration of 200 $\mu g/m^3$ the NO_2 concentration can range between 40 and 75 $\mu g/m^3$. A single regression line fitted to the full data set clearly has considerable limitations as a means of deriving NO_2 from NO_x, especially at the higher NO_x concentrations. The use of a single best fit relationship has nevertheless been applied to the modelling methodology set out in the DMRB (2000), as well as being proposed by Pratt and Dalton (Pratt & Dalton, 2000). These relationships are shown in Figure 2, together with the same data as presented in Figure 1.

2.2   The first step taken to improve the empirical approach was to examine the data in relation to site type. It is immediately apparent that there is a clear distinction between roadside/kerbside sites and rural/urban background sites (see Figure 1). The latter lie above the former in general, reflecting the higher ratio of NO_x to NO_2 at sites further from the source. This distinction was developed and used as the basis for converting NO_x to NO_2 in guidance to local authorities carrying out reviews and assessments of air quality (DETR, 2000). The roadside and background relationships are shown in Figure 2. However, an immediate difficulty arises with this approach when modelling roads, as it is necessary to determine at what point the relationship moves from being roadside/kerbside to background. This transition point will give rise to a discontinuity in concentrations on moving away from the road. This was partly tackled in the spreadsheet version of the DMRB (Casella Stanger, 2000), by assuming a gradual transition from one curve to the other over the first 30 m from the edge of the road. The result of this, however, is to produce a zone out to 20 m from the edge of the road where concentrations are relatively constant before declining to

the local background (Figure 3). This does not match the monitoring data, which show a rapid decrease over the first 20 m, as illustrated in the results of a transect survey carried out alongside the M25 motorway (Figure 3) (Hickman et al, 2002).

3   A New Empirical Approach

3.1   The empirical approach described above has been developed further to provide a better match to the observations. The new approach is based on an idea first proposed by Stedman et al (2001), which involved splitting roadside NO_2 into two components, 1) a background component brought into the area from outside and 2) a component directly related to the fresh NO_x emissions. The empirical analysis suggested that the latter could be represented as a fixed proportion of the road traffic $NO_{x(road)}$, this proportion being 16%. The approach was thus to add background $NO_{2(background)}$ to the road traffic $NO_{2(road)}$, derived from road traffic $NO_{x(road)}$, to give total NO_2.

3.2   The additional development of the Stedman approach has involved testing the method more widely and modifying it to allow for a variable contribution to be made by road traffic NO_x to the road traffic NO_2. The modification is designed to reflect the decreasing amount of ozone available to oxidise the NO to NO_2 at higher NO_x concentrations. The variable proportion of $NO_{2(road)}$ in the fresh $NO_{x(road)}$ has been derived from an analysis of the ratio $NO_{2(road)}$ / $NO_{x(road)}$ against total NO_x at roadside monitoring sites throughout the UK (Figure 4). Results for 28 roadside/kerbside sites over three years 1999-2001, were available for this analysis[2]. The roadside contributions, $NO_{2(road)}$ and $NO_{x(road)}$, at these sites have been determined by subtraction of estimated background concentrations for the monitoring year, derived from the national 1x1 km grid background maps (Stedman, 2002)[3]. The scatter in the data in Figure 4, will be due in large part to the subtraction of two large numbers, each of which has an uncertainty associated with it[4]. The best-fit relationship shows that the ratio of $NO_{2(road)}$ to $NO_{x(road)}$ reduces from around 0.25 at 50 $\mu g/m^3$ total NO_x, tending towards 0.1 at higher concentrations (Figure 4). The tendency towards a ratio of 0.1, i.e. 10% of $NO_{x(road)}$ is $NO_{2(road)}$, is consistent with the analysis of total oxidants as a function of total NO_x (Clapp & Jenkin, 2001). The relationship in Figure 4 ($NO_{2(road)}$ = -0.068 ln $NO_{x(total)}$ + 0.53) has been used to convert the road contribution

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[2] The definition of roadside is not restricted to that normally used of 1-5 m, but includes sites out to about 30 m from very busy roads, e.g. the Hillingdon site, which is classified as suburban is in practices dominated by the M4 emissions, and is thus classified as roadside for the purposes of this analysis.

[3] In the case of the motorway sites, the background was taken as the average of the two 1x1 km grid squares located 4 km to either side of the motorway. This is to avoid double counting (see DEFRA (2002))

[4] This occasionally gave rise to negative road contributions, which is clearly not possible in practice. These values were excluded from the analysis.

of $NO_{x(road)}$ to $NO_{2(road)}$, rather than a fixed factor of 0.16. The $NO_{2(road)}$ calculated in this way is then added to the local background $NO_{2(background)}$ to give the total $NO_{2(total)}$. The steps involved in the new method are set out in Box 1.

3.3   The performance of the new empirical method is illustrated in Figure 5, which shows the calculated NO_2 plotted against the measured NO_2 for the 28 roadside sites. There is no systematic difference in the performance from one year to another over the three years. Figure 6 shows the performance of the TG4(00) method, using the roadside curve[5]. The new method performs better, especially at higher concentrations. There is still scatter about the 1:1 line, thus the new approach is not capturing all the factors affecting roadside NO_2 concentrations[6]. Table 1 provides details of the sites for which the new method is not performing well. This shows that 24 out of the 69 data points depart from the measured value by more than ±10%. There appears to be some systematic variation, with the NO_2 conversion at motorway sites being more likely to have been over-estimated, while more congested town centre roads are more likely to be under-estimated. It is possible that this is due to a greater proportion of NO_2 in the road traffic NO_x emissions from more congested traffic in town centres. Support for this view is provided by the tendency for the sites showing an under-estimate of NO_2 to have a higher $NO_{2(road)}$ to $NO_{x(road)}$ ratio (Table 1).

3.4   The new approach differs from previous approaches, which used just one or two relationships to fit the data, in that it involves fitting a unique relationship for each site. The shapes of the resultant curves are illustrated in Figure 7, for 4 different background concentrations. The monitoring data have also been grouped by background concentration. Each group of data should lie between the relevant lines, e.g. the low data points should lie between the 15-32.5 μg/m³ lines. There is reasonable agreement between the measured data and the model, although scatter is still evident.

3.5   The performance of the model has also been tested on an independent data set. The Environmental Research Group at King's College London has made available the 1999 and 2000 results for the networks it operates across the south-east of England on behalf of local authorities. The predicted NO_2 concentrations for these sites using the new method are plotted against the measured values in Figure 8[7]. The performance is

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[5] No allowance has been made for the gradation from roadside to background as applied within the Stanger spreadsheet version of the DMRB.

[6] Some of the scatter will be due to the uncertainty in the background concentrations required for the calculations and the uncertainty in the NO_x and NO_2 measurements.

[7] One outlier has been excluded. The measured concentration was 121 μg/m³, while the predicted value was 76.9 μg/m³.

similar to that for the sites from which the method was developed, confirming the validity of the new approach (Figure 5).

3.6   The principal advantage of the new method is that it readily accommodates the transition from the roadside to background locations, providing a more realistic fit to monitoring data. This is seen in Figure 3 where concentrations calculated using the new approach are plotted against the measured data at different distances from the M25 motorway. The fall-off of NO_x concentrations with distance has been derived from the DMRB model.

3.7   The new method implies, albeit at the annual mean level, a rapid conversion of fresh NO emissions to NO_2, to give a fixed proportion of NO_2 within the fresh road traffic NO_x. This proportion is dependent on the total NO_x concentration. The total NO_x concentration could be acting as a surrogate for the amount of ozone available for transformation of NO to NO_2. There is then no further conversion of fresh NO to NO_2, just a mixing of background NO and NO_2 and road traffic NO and NO_2. The ratio of NO_2 to NO_x will vary with distance from the road due to the mixing process, not chemical transformation. This is unlikely to represent the true behaviour of discrete parcels of roadside air as they mix with background air and are subject to chemical reactions dependent on ambient conditions (especially solar intensity and ozone concentrations).

4   Conclusions

4.1   A new empirical approach to the derivation of annual mean NO_2 from annual mean NO_x for roadside locations has been developed. The new method allows for a smooth transition from lower NO_2:NO_x ratios at the roadside to higher ratios in background air. It has been developed from an examination of monitoring data for 28 roadside monitoring sites over a three year period that form part of the national network, together with results from motorway sites. The method has been tested by application to an independent data set for roadside sites operated by local authorities across the south-east of England. The vast majority of the concentrations predicted using the new method are within ±15% of the true value. There appears though to be a tendency for the method to over-predict NO_2 for motorway locations and under-predict for more congested town-centre locations. At this stage there is insufficient information to refine the method further.

4.2 The new approach to NO_x to NO_2 conversion has been incorporated in the revised DMRB (2002). It is also incorporated in the Guidance provided to local authorities for the next round of review and assessment (Defra 2002).

5   References

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DMRB (2002) A spreadsheet version of the revised screening model is available at www.highways.gov.uk/contracts/index.htm#2

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Stedman J R, Goodwin J W L, King K, Murrells T P and Bush T J (2001) An empirical model for predicting urban roadside nitrogen dioxide concentrations in the UK, Atmos. Env. 35, 1451-1463.

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6   Acknowledgements

Box 1: A new approach to deriving NO$_2$ from NOx for road traffic sources

The new empirical method to convert annual mean NO$_x$ to NO$_2$ at roadside locations involves the following steps:

1. Obtain the annual mean background NO$_{2(background)}$ and NO$_{x(background)}$ concentrations for the area. These can be derived from the national 1x1 km background maps or from local monitoring at background sites.

2. Calculate the annual mean contribution due to the road, NO$_{x(road)}$, at the location of interest. This could be from any suitable model.

3. Convert the NO$_{x(road)}$ to NO$_{2(road)}$ using the equation

    NO$_{2(road)}$ = ((-0.068 x Ln(NO$_{x(total)}$))+0.53) x NO$_{x(road)}$
    where NO$_{x(total)}$ = NO$_{x(background)}$ + NO$_{x(road)}$, and Ln is log to the base e

4. Add the NO$_{2(road)}$ to the NO$_{2(background)}$ to get the NO$_{2(total)}$ at the location of interest.

Table 1 Sites where calculated NO_2 is outside $\pm 10\%$ of measured NO_2 using the new method.

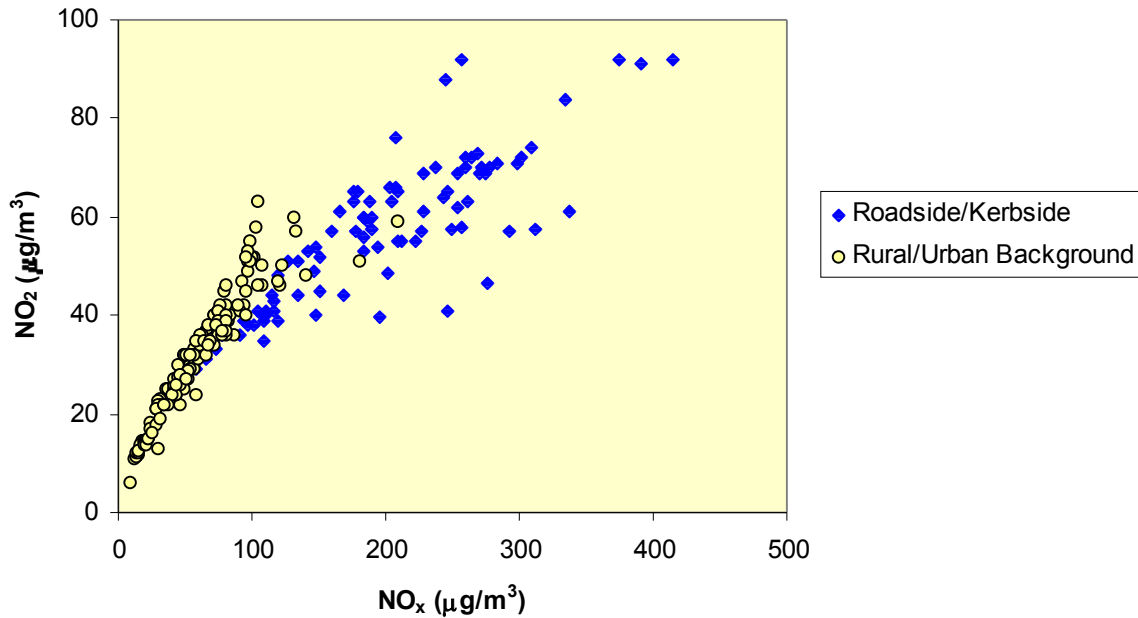| Site	Year	Measured ($\mu g/m^3$)		Calculated NO_2 ($\mu g/m^3$)	Difference Calculated/Measured		Ratio $NO_{2(road)}$: $NO_{X(road)}$
		NO_x	NO_2		$\mu g/m^3$	%	
London Bromley	1999	179.8	65.0	54.5	+10.5	84%	0.27
London Bromley	2001	166.4	61.2	51.6	+9.6	84%	0.27
London Bromley	2000	176.0	63.1	53.3	+9.8	85%	0.26
Dumfries	2001	101.4	38.3	32.5	+5.8	85%	0.29
Exeter Roadside	2001	103.3	42.1	36.6	+5.5	87%	0.29
Oxford Centre	2000	183.6	61.2	53.3	+7.9	87%	0.24
Bath Roadside	2001	177.9	57.4	50.1	+7.3	87%	0.23
London Cromwell Road 2	1999	256.3	91.8	80.3	+11.6	87%	0.23
Southwark Roadside	2001	176.0	65.0	57.0	+8.0	88%	0.26
London Cromwell Road 2	2000	244.9	88.0	77.7	+10.3	88%	0.23
Oxford Centre	2001	183.6	59.3	52.9	+6.4	89%	0.22
Bristol Old Market	2000	210.4	55.5	61.9	-6.5	112%	0.11
London Hillingdon	2000	141.6	47.8	53.7	-5.9	112%	0.06
M4 Theale 2	2000	201.8	48.7	54.7	-6.0	112%	0.13
M4 Theale 2	2001	168.5	44.3	50.0	-5.7	113%	0.13
M60 Kirkhams	2000	133.9	44.1	50.4	-6.3	114%	0.06
Bristol Old Market	1999	221.9	55.5	64.2	-8.7	116%	0.10
M60 Salford	2000	248.7	57.4	66.6	-9.2	116%	0.10
Norwich Roadside	2000	59.3	28.7	34.7	-6.1	121%	0.48
Cheltenham	2001	99.2	31.0	39.2	-8.2	126%	0.05
M60 Salford	1999	311.8	57.4	73.8	-16.4	129%	0.07
M25 Staines	2001	196.0	39.7	58.7	-18.9	148%	0.01
M25 Staines	1999	276.2	46.6	69.3	-22.7	149%	0.03
M25 Staines	2000	246.8	41.0	65.4	-24.4	160%	0.01

Figure 1   NO$_2$ vs NO$_x$ for national network sites 1997-2001, Highways Agency sites 1999-2000 and Salford MBC M60 site 1999-2000.
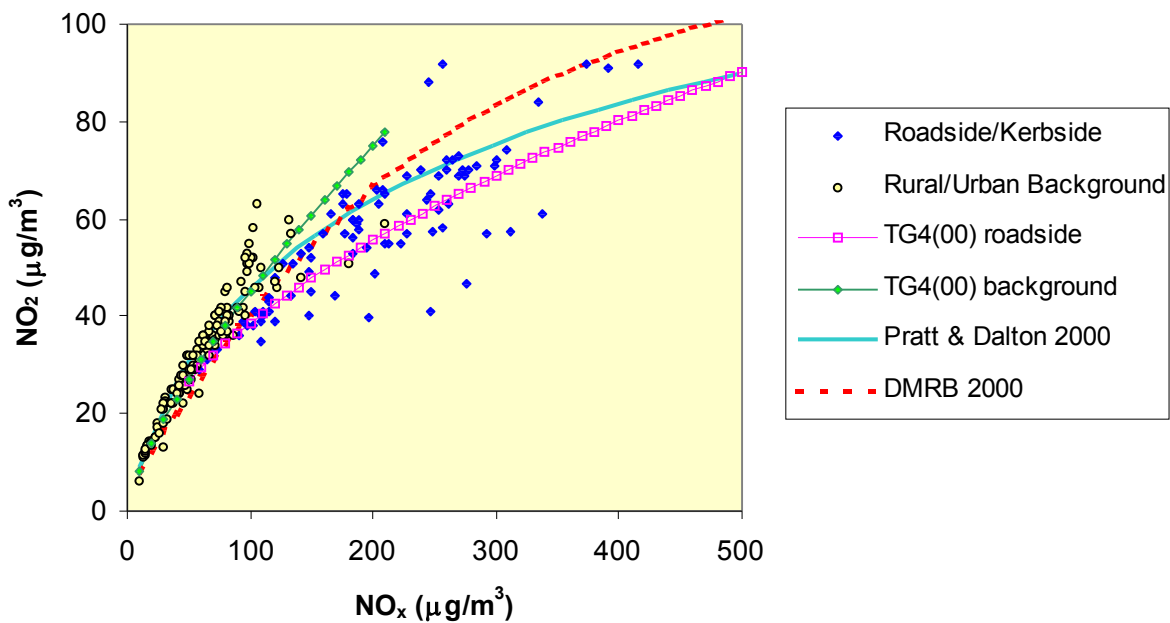

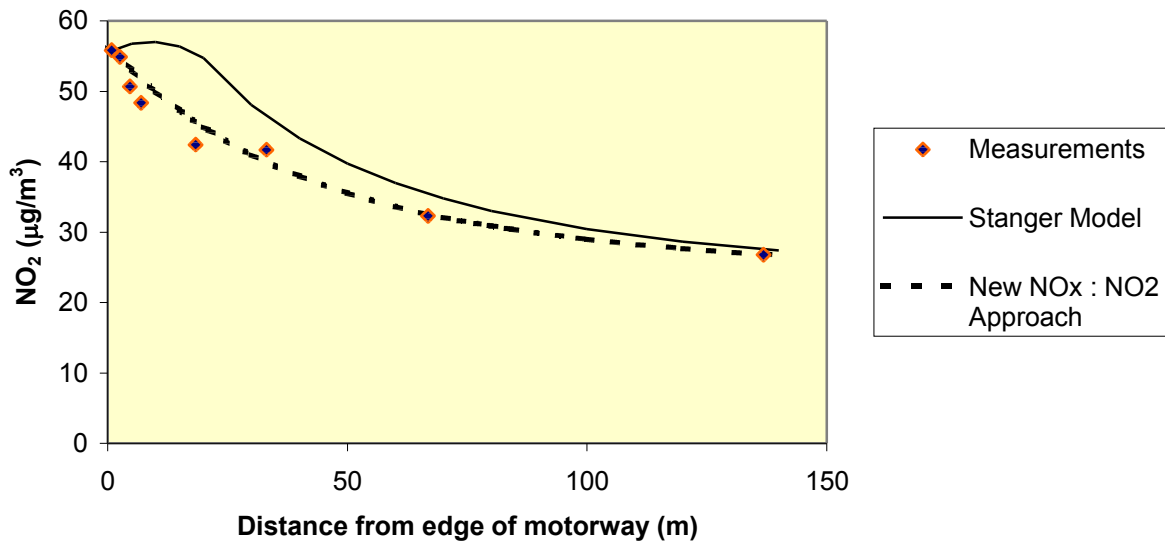**Figure 2**   Relationships used to derive NO$_2$ from NO$_x$. Also shown are the data points from Figure 1.

Figure 3 NO$_2$ monitoring data for a transect away from the M25 motorway and equations fitted using the Casella Stanger spreadsheet approach to NO$_x$ conversion to NO$_2$ and the new approach. Modelled NO$_x$ fall-off with distance from the DMRB. Values normalised to match the measured roadside value.

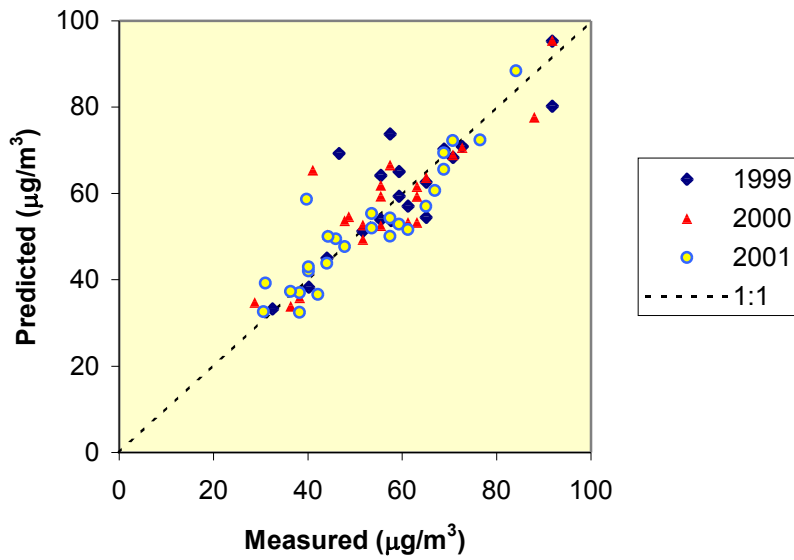**Figure 4** Ratio of NO$_{2(road)}$ to NO$_{x(road)}$ versus total NO$_x$. The line represents the best-fit equation.

Figure 5 Predicted NO$_2$ using the new approach versus measured NO$_2$ at roadside/kerbside sites.
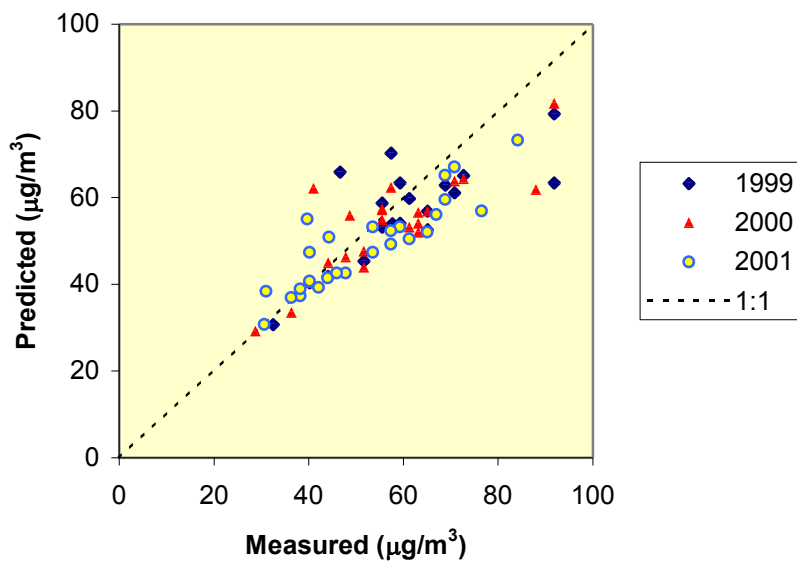
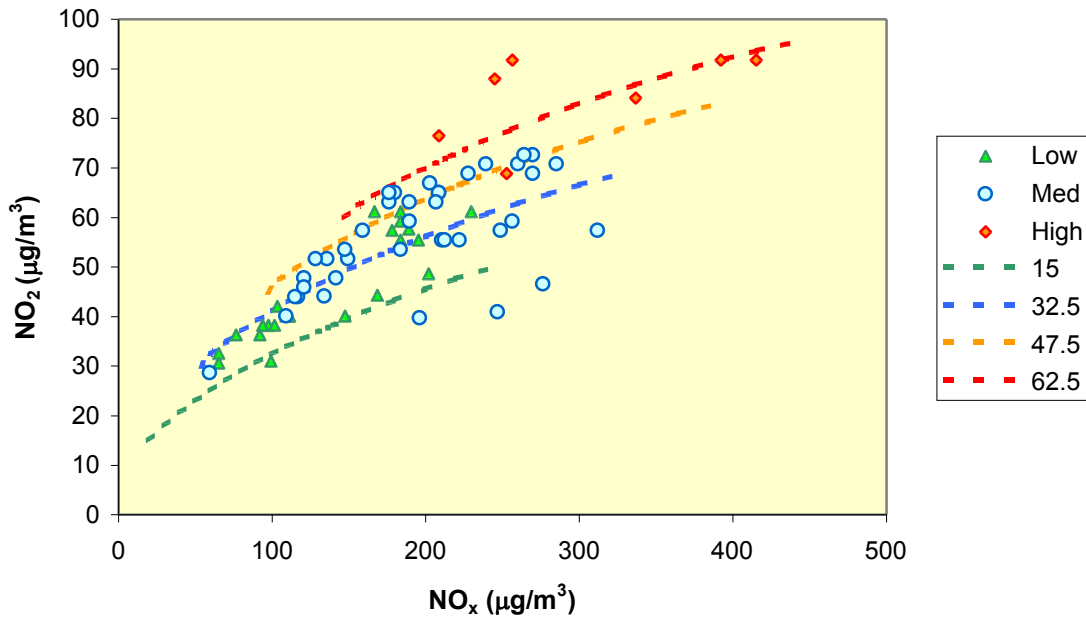**Figure 6** Predicted NO$_2$ using the TG4(00) roadside equation versus measured NO$_2$ at roadside/kerbside sites.

Figure 7   Measured NO_2 and NO_x at roadside/kerbside sites grouped by local background NO_2: Low = 15-32.5 $\mu g/m^3$, Medium = 32.5-47.5 $\mu g/m^3$, High = 47.5-62.5 $\mu g/m^3$. The lines represent predicted concentrations for a given background NO_2 and increasing road NO_x contribution.
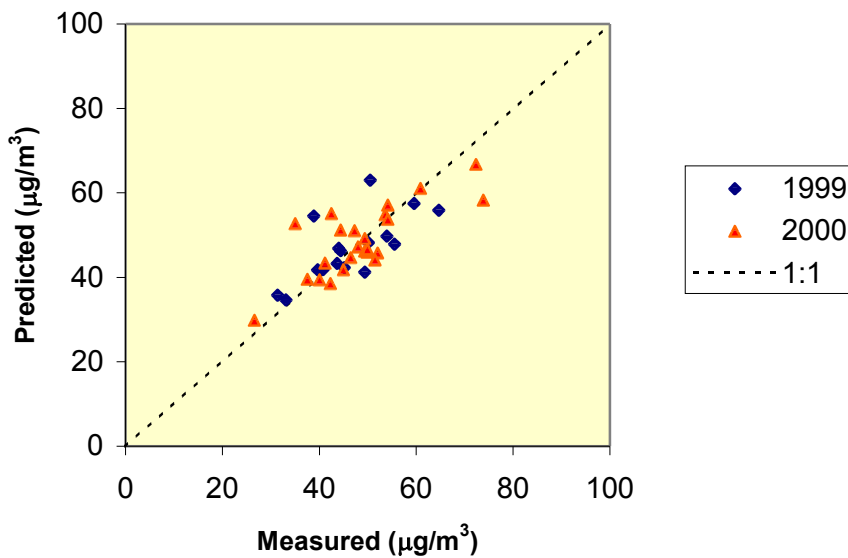

Figure 8   Predicted NO_2 using the new approach versus measured NO_2 at roadside/kerbside sites operated by local authorities in the south-east of England.