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An empirical approach for the prediction of annual mean nitrogen dioxide concentrations in London

David C. Carslaw*, Sean D. Beevers, Gary Fuller

Environmental Research Group, King's College London, London SE1 7EH, UK Received 16 March 2000; received in revised form 23 May 2000; accepted 30 May 2000

Abstract

Annual mean limits for NO₂ concentrations have been set in the European Union, which will be most challenging to meet in large urban conurbations. In this paper, we discuss techniques that have been developed to predict current and future NO₂ concentrations in London, utilising ambient data. Hourly average NO_x (NO + NO₂) and NO₂ concentrations are used to calculate NO_x frequency distributions. By defining relationships between the annual mean NO_x and NO₂ at different sites, it is possible to investigate different NO_x reduction strategies. The application of the frequency distribution approach to monitoring sites in London shows that given the likely change in emissions by 2005, it is unlikely that much of central and inner London will meet the objective. The approaches used suggest that meeting the objective in central London will be the most challenging for policy makers requiring NO_x concentrations as low as 30 ppb, compared with values closer to 36-40 ppb for outer London. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The Air Quality Strategy for England, Scotland, Wales and Northern Ireland sets out the UK Governments' approach to tackling air pollution for eight key pollutants (DETR, 1999a, b). The strategy sets limits and objectives for these pollutants and the times scales by which they are to be met. Two objectives for NO₂ are being considered: an annual mean objective of 21 ppb ($40 \,\mu g \,m^{-3}$) not to be exceeded in any calendar year and a 1-h limit value of 105 ppb ($200 \,\mu g \,m^{-3}$) not to be exceeded more than 18 times in each calendar year. The 21 ppb limit is consistent with the European Union Directive 96/62/EC Framework Directive for NO₂ to be achieved by 1 January 2010. The UK aims however to meet this objective by 31 December 2005. The annual mean objective is considered more stringent than the 1-h objective, and this is borne out by pollution measurements in London (SEIPH, 2000).

The need to meet the annual mean objective has led to considerable interest in the development of techniques to predict future concentrations of NO₂, particularly in urban areas. Many modelling approaches are currently used to predict NO₂ concentrations such as Gaussian, Lagrangian and Eulerian models (Derwent, 1999; Owen et al., 1999). These models require significant data input and resources. Furthermore, it can be difficult to develop deterministic models that are accurate at the time scales and spatial scales of urban pollution, i.e. down to scales of seconds and metres. An alternative approach is the use of empirical models derived from ambient measurements of pollution. This approach is potentially very attractive; being both simple and easy to apply. Empirical models also make use of monitoring data, which are often only used in a retrospective sense through comparisons with air quality guidelines and standards. London is unique in the UK for having such a high density of monitoring sites and lends itself to the development of alternative techniques based on the use of ambient data.

^{*} Corresponding author.

E-mail address: david.carslaw@kcl.ac.uk (D.C. Carslaw).

In this paper we have adopted a new approach to formulating relationships between NO_x and NO_2 for urban background locations. Urban background locations are defined here as sites that are at least 25 m away from a major road source, or at least are not dominated by a single source in the immediate vicinity of the monitoring site. These sites therefore tend to represent the pollution climate over an area of approximately 1 km^2 .

Through the development of such models, we hope to determine the following:

- the relationship between annual means of NO_x and NO₂ in a large urban area;
- the effect of NO_x reductions on annual mean NO₂ concentrations;
- the extent to which NO_x concentrations must be reduced in order to meet the annual mean NO₂ objective;
- the extent of exceedences of the annual mean NO₂ objective across London by the end of 2005.

2. Monitoring data

2.1. Automatic monitoring data

London is unique in the UK in having a large number of high-quality automatic monitoring sites for the measurement of NO_x and NO_2 . At the beginning of the year 2000 NO_x and NO_2 were measured at over 60 monitoring sites within the area bounded by London's orbital motorway. Fig. 1 shows the area covered by Greater London and the orbital motorway. The sites are operated by the UK Department of the Environment Transport and the Regions (DETR) or by local authorities and are part of either the UK Automatic Urban and Rural Network or the London Air Quality Monitoring Network (LAQN). All instruments measure concentrations of NO_x and NO by chemiluminescence. The instruments are tested on a weekly or fortnightly basis using traceable low-concentration NO cylinders to derive correction factors for NO_x and NO measurements. NO_2 is subsequently calculated as the difference between the corrected values of NO_x and NO. More extensive instrument performance tests are carried out either 3 or 6 monthly by external audit bodies. These tests include linearity of response, response time, flow, NO₂ converter efficiency and checks on the stability of the gas source used for fortnightly calibrations.

The uncertainty associated with air quality measurements was estimated by Stevenson et al. (1998) for the UK Automatic Urban Network and by SEIPH (1997) for the LAQN. These studies suggest that a working uncertainty of around 10% (2σ) should be considered when discussing high values and long-term averages of NO₂.

3. NO_2 vs. NO_x curves

3.1. Hourly NO_2 vs. NO_x curves

The relationship between hourly NO_x and NO_2 concentrations can be investigated by plotting each hourly



Fig. 1. The location of urban background monitoring sites in the London area.

value of NO_x against the corresponding NO₂ concentration in a scatter plot, as shown for the Bloomsbury site in Fig. 2. Fig. 2 shows that for any value of NO_x there can be a wide range of NO₂ concentrations. Derwent and Middleton (1996) found that the relationship between NO_x and NO₂ could be usefully summarised by plotting NO₂ against NO_x in different NO_x 'bins'. The mean NO₂ concentration is averaged according to different ranges of NO_x concentration, in Derwent and Middleton's case 0–10, 10–20 ppb, etc. Fig. 3(a) shows the effect of summarising data in this way for the Bloomsbury site in 1998. The first part of the curve in Fig. 3(a) between 0 and approximately 100 ppb NO_x shows a steep NO₂ gradient, which can be interpreted as the region in which



Fig. 2. The NO_x - NO_2 relationship for the Bloomsbury site (1998) based on hourly data.

there is generally enough ozone (O_3) present to convert NO to NO₂, i.e. a NO_x-limited regime. As the NO_x concentration increases further, the gradient of the curve decreases markedly, corresponding to conditions where little O₃ remains due to titration by NO. Under these conditions, little conversion from NO to NO₂ occurs, i.e. O₃-limited conditions. This regime continues until the gradient once again steepens and NO₂ concentrations increase. At high NO_x concentrations that occur typically during winter time episodes the tri-molecular reaction between NO and O₂ is thought to occur, resulting in increased NO₂ conditions (Bower et al., 1994). The shape of NO₂ vs. NO_x curves exemplified by Fig. 3(a) is seen at all monitoring sites and for all years. However, the precise relationship is always both year and site-dependent.

3.2. Derivation of annual mean NO₂ concentrations

The annual mean concentration of NO₂ at a monitoring site can be derived by calculating the NO₂ concentration from the NO₂ vs. NO_x relationship for each hourly value of NO_x, and then averaging the results. Alternatively, the annual mean can be calculated by first sorting the data into NO_x bins, and calculating the mean NO₂ concentration for each bin, $\overline{NO_2(i)}$. The bin averages are multiplied by the number of points in each bin, F(i) (the frequency distribution of points in the bins). Finally, the annual mean NO₂ concentration is calculated by dividing by the number of observations, $N_{obs} = \sum_{i=n}^{i=n} F(i)$:

$$NO_2 = \frac{\sum_{i=1}^{i=n} NO_2(i)F(i)}{N_{obs}},$$
(1)

where *i* is a NO_x interval, e.g. 10–15 ppb and *n* is the interval that contains the highest measured NO_x concentration.



Fig. 3. (a) The hourly NO_x - NO_2 relationship at Bloomsbury for 1998 showing the bin averaged NO_2 concentrations after sorting into 5 ppb NO_x bins and (b) the corresponding NO_x frequency distribution F(i) showing the number of points averaged in each bin.

The frequency distribution approach, Eq. (1), can be derived from and is equivalent to the usual definition of an annual mean. When using Eq. (1), the bin means are evaluated separately before combining them, and this may cause slight numerical discrepancy. Later in this paper, Eq. (1) is adapted to predict future annual means, and in order to do this, sparsely populated bin may be omitted. The equation would no longer exactly equal the full annual mean, but if such omitted bins are few in number, their effect on the accuracy of the equation will be small. For example, the annual mean NO₂ concentration at the Bloomsbury site was calculated by multiplying the NO₂ vs. NO_x relationship in Fig. 3(a) by the frequency distribution shown in Fig. 3(b) and dividing by the number of hourly measurements. Eq. (1) is efficient to use because it reduces N_{obs} observations in a year to n bin means and n populations F(i) in each bin. Taking the Bloomsbury site as an example, 8760 observations are reduced to 105 bins for 1998 data. It should be noted that no attempt is made to fit a line through the data in Fig. 3(a) using an appropriate polynomial equation: the corresponding NO_x bin values are simply multiplied together. At high NO_x concentrations, there may only be one measurement in each bin, with neighbouring bins remaining empty. However, this does not affect the process described. The frequency distribution approach avoids the cumbersome process of curve-fitting large data sets.

3.3. Annual mean NO_2 vs. NO_x relationships

A more useful relationship than the hourly relationship discussed in the previous section for predicting NO_2 concentrations would be that between the annual mean NO_x and NO_2 concentrations. One potential approach to developing such a relationship would be to plot the annual mean NO_x against the annual mean NO_2 for all urban background sites in London. Even in London, the number of appropriate sites is limited. For example, the use of 13 monitoring sites would yield a plot with 13 points with a significant degree of scatter. Stedman et al. (1997) and Stedman (1998) have adopted this approach for sites across the UK, but have combined data from many different urban areas to do so.

Derwent (1999) using a Lagrangian trajectory model for predicting NO_x and NO_2 concentrations in London, has explored the effect on NO_2 of reducing NO_x concentrations. As NO_x concentrations were reduced, NO_2 concentrations were shown to move down NO_2 vs. NO_x curves following the same relationship. The assumption that points follow the same NO_2 vs. NO_x relationship seems reasonable as for example, points with high concentrations of NO_x (and little O_3 available) move down the curve to a higher $NO_2 : NO_x$ ratio, where more O_3 is available. This approach assumes that every hourly NO_x concentration is reduced by the same proportion and does not consider scenarios that are more complex.



Fig. 4. The effect on the NO_x frequency distribution, F(i), at the Bloomsbury site as NO_x concentrations are reduced in 10% intervals from 0 to 80% reduction (1998).

Using the techniques described in the previous section, involving the NO₂ vs. NO_x relationship and the frequency distribution to calculate annual mean NO₂, the effect of NO_x reduction at different monitoring sites across London has been explored. Different NOx reductions have been considered by re-calculating the hourly values of NO_x for different percentage reductions in NO_x from 0 to 80% in 5% intervals, reducing the annual mean NO_x accordingly, and then sorting to find the new frequency distribution. The revised frequency distributions $F'(NO_x)$ for NO_x can be multiplied by the NO₂ vs. NO_x relationship to provide a new estimate of the annual mean NO₂ concentration, using Eq. (1). Fig. 4 shows how the frequency distribution changes with reductions in NO_x . There are several points to note when considering the effect of successive NO_x reductions on the frequency distribution. First, the shape of the relationship becomes increasingly narrow and tall as NO_x values migrate to lower concentrations, with increased reductions in NO_x. Second, as the NO_x concentration is reduced an increased number of points move to the NO_x-limited regime. The process therefore calculates the annual mean NO2 concentration that corresponds to the reduced NO_x concentration. The process can be repeated to recalculate new annual mean NO2 concentrations and their corresponding NO_x concentrations for each NO_x reduction scenario considered. The result is a new relationship (Fig. 5) relating the reduced annual means of NO_{x} and NO_{2} concentrations, instead of the hourly relationship derived by Derwent and Middleton (1996). The new relationship, despite relating annual mean concentrations of NO_x and NO₂, implicitly includes the full sponding annual mean NO2 concentration. distribution of concentrations measured each hour of the year. At high concentrations of NO_x and for small reductions in NO_x it is possible for a few points to move down

to a bin that is empty, i.e. where no measurements exist. These points, which are few in number, can be ignored as they do not affect the annual mean concentration prediction in a significant way. The value of N_{obs} in Eq. (1) is revised accordingly before calculating the annual mean NO₂ concentration.

3.4. Analysis of background monitoring sites in London

Annual mean NO_2 vs. NO_x relationships have been calculated for the urban background monitoring sites in Fig. 1. For each monitoring site, NO_2 vs. NO_x relationships have been calculated using the technique described in the previous section. Fig. 6 shows the relationship between NO_x and NO_2 for urban background sites across London for 1998. Fig. 6 shows that the relationship supports the original idea of directly relating emissions of NO_x to NO_2 concentrations by Stedman et al. (1997). However, the relationship is non-linear enough to affect the predictions of NO2 from NOx. Fig. 6 also shows a spread in the relationships derived with the central London sites Bloomsbury and Bridge Place having higher NO₂ concentrations for a particular concentration of NO_x . Conversely, outer London sites such as Enfield and Sutton have lower NO₂ concentrations for a particular value of NO_x . An analysis of other years shows that the relative ordering of these relationships Fig. 6. Derived annual mean relationships between NO_x and NO₂ (1998) for (a) central and inner London monitoring sites and (b) outer London monitoring sites.

was consistent from one year to the next, i.e. central and inner London sites always have a higher $NO_2:NO_x$ ratio. The observation that monitoring sites can be ordered in this way is based on data from relatively few sites and additional analysis of more monitoring sites over more years is required to further support this idea. Some spread in the curves is also expected simply because of measurement uncertainty and the broad definition of an urban background site.

The statement that central London sites have a higher NO₂ concentration than inner and outer London locations for a particular value of NO_x needs some qualification. To illustrate this point, the Bloomsbury site, situated close to the centre of London, can be considered in more detail. During 1998, the annual mean NO_x concentration was 67 ppb and NO₂ was 34 ppb. For a location surrounded by lower emissions, e.g. a single road in a rural area, to have the same value of NO_x as Bloomsbury, it would have to be much closer to the emissions source. However, being closer to the source of NO_x would mean that there would be less time for NO to be converted to NO₂ through reaction with O₃, therefore

Fig. 5. The relationship between the annual mean NO_x and NO₂ at the Bloomsbury site for 1998. The plot shows the effect of generating extra points by successive NO_x reductions, sorting for the new frequency distribution, and re-calculating the corre-

Annual mean NO_X (ppb)

40

35

30

25

20

15

10

5

0

0 10 20 30 40 50 60 70 80

Annual mean NO₂ (ppb)

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leading to an annual mean NO₂ concentration lower than 34 ppb. The same argument applies to locations in inner or outer London or indeed any smaller city or town; the location would have to be *closer* to a source of NO_x, leading to lower NO₂ concentrations than seen at Bloomsbury. The high NO₂ : NO_x ratio is therefore only seen in central London at higher annual mean NO_x concentrations, from approximately 40–80 ppb. An analysis of other monitoring sites in London and other urban areas of the UK confirmed that at no time has an annual mean NO_x concentration of around 67 ppb corresponded to an annual mean NO₂ concentration as high as 34 ppb (Broughton et al., 1997, 1998).

4. Reduction in NO_x required to meet 21 ppb NO_2

For monitoring sites that currently exceed the 21 ppb objective, an analysis has been carried out to determine the NO_x concentration that must be reached in order that the NO₂ objective is met. This step is a useful link in determining the likely reduction in emissions required to meet the NO₂ objective. It is easier to consider NO_x concentrations than NO₂ concentrations as NO_x can be more readily related to changes in emissions. Three sites have been assessed in detail over 7 or more years: Bridge Place, Bloomsbury and West London. These sites have been chosen as all of them have been in operation continuously at least since the beginning of 1992. Table 1 shows the percentage reduction in NO_x concentration

required to meet the NO_2 objective. The two central London sites (Bloomsbury and Bridge Place) require the greatest reduction in NO_x of between 42 and 61% depending on the year being considered. Despite decreases in emissions in urban areas in the UK since 1993, little variation is seen in the calculated NO_x reduction required at the Bloomsbury site.

Table 1 also gives an estimate of the corresponding NO_x concentration for 21 ppb NO_2 at each site. These values are reasonably consistent from one year to the next, with the exception of 1997 for the Bloomsbury and Bridge Place sites, where lower reductions in NO_x are required. Bloomsbury requires the lowest NO_x concentration to reach 21 ppb NO_2 , ranging between 29.6 and 35.9 ppb (mean 31.7 ppb). The other sites in inner London will apparently meet the objectives with higher NO_x concentrations, typically in the range 36–38 ppb.

5. NO₂ predictions for 2005

5.1. Pollution climate mapping of NO_x concentrations

A mapping technique originally devised by Stedman et al. (1997) has been used to successfully provide a simple and effective way of predicting background concentrations across the UK on a 1 km² basis. Stedman et al. (1997) found that the concentration at a background location could be assumed to consist of two components: an underlying "rural" background and a contribution

Table 1

 NO_x reduction required to meet the annual mean NO_2 objective of 21 ppb at urban background monitoring sites

Year	Bridge place (Central London)	Bloomsbury (Central London)	West London (Inner London)	Kensington (Inner London)	Tower Hamlets (Inner London)	Ealing (Outer London)
Percenta	ge NO_x reduction requ	vired to meet 21 ppb No	\mathcal{O}_2			
1998	42	55	33	18	21	21
1997	45	58	42	31	30	35
1996	52	60	37	30	28	32
1995	51	59	39	_	_	_
1994	51	56	48	_	_	_
1993	53	59	50	_	_	_
1992	61	61	53	—	—	—
Annual m	uean NO _x concentratio	n corresponding to 21	opb NO ₂			
1998	31.7	30.7	35.4	33.8	33.8	36.9
1997	38.5	35.9	41.1	40.0	38.0	38.0
1996	32.8	32.2	40.0	37.4	36.4	39.5
1995	33.8	30.7	39.5			
1994	34.8	32.2	36.4			
1993	33.8	29.6	36.4			
1992	34.8	31.2	39.5			
Mean	$34.3 \pm 4.2 \ (2\sigma)$	$31.7 \pm 4.0 \; (2\sigma)$	$38.5 \pm 4.4 \; (2\sigma)$	36.9	35.9	38.0

Background NO_x (ppb) =
$$kE$$
 + rural NO_x (ppb) + C,
(2)

where k is a constant and E is the total emission of NO_x in the $5 \times 5 \text{ km}^2$ area in tonnes per year from nearground-level emissions sources, i.e. excluding major industrial point source emissions, and C is a constant equal to zero in this formulation of Eq. (2).

The underlying rural concentrations of NO_x were derived by first estimating the rural NO₂ concentration field using 32 diffusion tube measurements of NO2 from sites on the UK. Acid Deposition Secondary Network (Stedman et al., 1997). The NO_x concentration was then derived by multiplying the estimated NO₂ concentrations by a factor of 1.2; the ratio of NO_x to NO_2 observed at the rural Lullington Heath site on the south coast of England, measured using a chemiluminescent monitor. To obtain the value k in Eq. (2), the difference between the measured concentration at a site and the underlying rural concentration was plotted against the $5 \times 5 \text{ km}^2$ emissions, E, and a linear interpolation was applied, forcing the regression line through the origin. The method described above assumes, therefore, that the difference between the NO_x measured at a background site and the underlying rural concentration is a result of emissions from the $5 \times 5 \text{ km}^2$ area.

We have applied the principles of the mapping technique to London alone, using all urban background sites within the Greater London area, i.e. the sites bounded by the outline of London in Fig. 5. Fig. 7 shows the

0

0

1

 $5 \times 5 \text{ km}^2$ emissions of NO_x plotted against the annual mean NO_x concentration recorded at each site. Some scatter in the plot is expected since the emissions distribution in a $5 \times 5 \text{ km}^2$ area is not equally homogeneous around each site and because of uncertainties in measurements and emissions estimates. However, by considering enough sites it is possible to establish typical or average conditions. A linear regression analysis of the data shown in Fig. 7 yields a line with gradient 13.0 and an intercept of 22.5 for 1998. Plotting the data in this way is equivalent to the method used by Stedman (1998), except no attempt has been made to subtract the underlying rural concentration. A value of 22.5 ppb appears to be too high compared with an estimated value of underlying rural NO_x concentration of 8 ppb for 1998 derived from the diffusion tube network. We therefore interpret the intercept as consisting of two components: an underlying rural concentration of 8 ppb and a contribution from the rest of London that is not accounted for in the $5 \times 5 \text{ km}^2$ area (14.5 ppb). It is necessary therefore to adopt a modified approach for large urban areas, where emissions from outside the $5 \times 5 \text{ km}^2$ area affect local concentrations. The constant, C, in Eq. (2), which is the "other urban contribution", is therefore equal to 14.5 ppb in our application of the approach to London for 1998.

Eq. (2) allows estimates to be made of future concentrations by modifying the values of the three products independently. The value of k can be assumed constant as it relates to dispersion; E can be re-calculated based on an appropriate inventory; the rural NO_x can be adjusted downwards according to UK national NO_x emission forecasts, and the other London contribution can be reduced in line with total NO_x emissions in London. The application of the above approach to London alone has



Fig. 7. Emissions over a 25 km^2 area centred on urban background monitoring sites in London plotted against the annual mean NO_x concentration for 1996–1998.

3

4

2

NO_x emission (kt per 25 km²yr⁻¹)

Table 2 Pollution climate mapping for urban background locations in London^a

Year	Relationship	R^2
1996	$NO_x = 12.8.E + 30.1$	0.91
1997	$NO_x = 13.4.E + 34.8$	0.89
1998	$NO_x = 13.0.E + 22.5$	0.89

^aNote: *E* is the $5 \times 5 \text{ km}^2$ emission area.

many advantages. First, London has its own detailed emissions inventory (Buckingham et al., 1997). Second, there are sufficient monitoring sites for London to be treated separately. Third, there is a consistent "dilution" of emissions by meteorology across London, compared with considering the entire area of the UK and the relationships implicitly take account of complex mixing, urban heat island effects and changes in surface roughness. Emissions in London are dominated by groundlevel road transport sources unlike many other more industrial urban locations in the UK, which lends itself to the approach. Another advantage of the approach is that predictions are constrained by actual measurements and it is in effect self-calibrating. Furthermore, the predictive capability of the approach is determined more by identifying the *relative* contribution of emissions sources in London and by the relative change expected in the future.

The same analysis has been applied to 1996 and 1997 data and the results are shown in Table 2. Table 2 shows that the gradient is reasonably constant from one year to the next (12.8–13.4). The gradient represents the effect of meteorology, with a low value indicating more dilution than a high value. The relatively high r^2 values should be interpreted with caution as only 13 sites were used for the analysis. The relationships are however consistent from one year to the next and give some confidence in the validity of the technique as a method of calculating annual mean NO_x concentration in a large urban area.

5.2. A London NO_2 map for 2005

The London-specific pollution climate mapping approach has been applied to the year 2005 to estimate the likely scale of exceedences of the NO_2 objective. It has been assumed for the purposes of calculating future emissions that non-road traffic sources of NO_x remain constant between 1998 and 2005. Non-road traffic sources of NO_x are dominated by commercial and domestic natural gas use and these sources change slowly over time compared with the comparatively rapid changes in vehicle emissions technology. Based on the difference in total NO_x emissions between 1998 and 2005 for near-ground-

Table 3

Predictions of NO_x and NO_2 at monitoring sites across London for 2005 based on 1998 meteorology

Location	NO _x (ppb)	NO ₂ (ppb)
Bloomsbury	42.4	26.2
Bridge Place	39.6	24.2
Bexley	18.1	12.4
Brent	18.5	12.6
Ealing	25.2	15.8
Greenwich	17.9	12.3
Enfield	16.5	11.5
Kensington	30.4	18.0
Southwark	34.0	22.6
Sutton	19.4	13.0
Tower Hamlets	24.3	16.8
West London	34.0	21.0

level sources, the "other London" contribution, has been reduced by 33%. The underlying rural NO_x concentration was assumed to be 5 ppb in 2005, reduced in line with anticipated total UK NO_x reduction projections. The London mapping approach was applied to estimate 1 km^2 concentrations of annual mean NO_x. From these NO_x predictions it was possible to estimate the annual mean NO2 concentration based on the techniques described previously. Table 3 shows the predictions of NO_x and NO2 at the different urban background monitoring sites in London, with those sites exceeding the annual mean NO₂ objective shown in bold type. The Bloomsbury site is predicted to exceed the objective by more than 5 ppb, whereas the West London site is predicted to equal the objective. The highest NO2 concentration predicted in central London is 27 ppb, some 6 ppb over the objective, and a few kilometres from the Bloomsbury site. The distribution of NO₂ across London is shown in Fig. 8, which shows two areas where the objective is exceeded: in central London and west towards Heathrow Airport. It should be noted that the area around Heathrow Airport is currently the subject of further analyses using more detailed and specific emissions data.

6. Discussion

6.1. Implications for urban background locations in London

The predictions of NO_2 concentrations at urban background locations in London have produced interesting results that have implications as to how the reduction in NO_x in London should be tackled. The predictions indicate that the reductions in emissions expected, by 2005,



Fig. 8. NO_2 concentrations predicted across London in 2005 assuming 1998 meteorology and chemistry. The shaded areas represent regions where the annual mean objective of 21 ppb is predicted to be exceeded.

are insufficient in order to meet the NO_2 objective at urban background locations. Failure to meet the objective at urban background locations presents a very different challenge for decision makers compared with exceedences restricted to the immediate vicinity of major roads. Traffic management on single roads might reasonably tackle the latter situation. However, a much more widespread approach will be required to tackle exceedences over larger areas.

The application of the technique suggests that the NO_x concentration required to meet 21 ppb NO₂ differs depending on the location in London: central London areas require much larger NO_x reductions than outer and inner London locations. This situation is not simply a feature of the fact that central London has the highest concentrations, but more a feature of NO₂ vs. NO_x chemistry. The predictions show for example, that to achieve the objective in central London *lower* NO_x concentrations (as low as 29.6 ppb) will be required compared with outer London. We interpret this finding as reflecting the unique location of these sites in the middle of a very large conurbation. Trajectories arriving at these locations always have to travel over areas of NO_x emissions, regardless of their origin. An air parcel arriving at

central London therefore has more time for atmospheric chemistry to occur, even when the general availability of O₃ is low as a result of scavenging by NO. Such trajectories are also likely to be affected more by direct emissions of NO₂, particularly from road traffic. Furthermore, when emissions in London are low enough to result in annual mean NO₂ concentrations of 21 ppb, London will represent a very large but relatively dilute source of NO_x emissions, thus increasing the availability of O₃ to convert NO to NO₂. The empirical model therefore appears to implicitly take account of factors that can be difficult to model in a deterministic way. For example, a trajectory model would have to ensure the correct amount of mixing over a large and complex urban area and also represent the chemistry correctly. Such approaches can be limited by the availability of suitable initial model conditions, require the detailed parameterisation of the key processes and hence are computationally expensive. The NO₂ to NO_x ratio when the concentration of NO₂ reaches 21 ppb is approximately 75%, which is similar to the ratio of annual mean NO_2 to NO_x in rural locations in southeast England today.

The approaches employed here are attractive from the point of view of simplicity and can make use of ambient data, which are often only compared with air pollution guidelines and standards. However there are limitations to these techniques, including the assumption that every hour of NO_x is changed by the same proportion when generating the additional points. It could not therefore take account of more complex NO_x reduction strategies. Nevertheless, in a large urban area such as London where the concentrations of NO_x are dominated by road traffic, reasonably uniform reductions in NO_x can be expected, as the reduction in emissions are dominated by national strategies to reduce emissions. This analysis is specific to a particular monitoring site and it can be difficult to extrapolate the results to other locations. However, the representativeness issue can be tackled by taking account of many monitoring sites in different NO_x environments. As the availability of sites increases, better and more representative models can be built.

The techniques described in this paper do not currently take account of any future changes in atmospheric conditions that might lead to different conversion rates between NO and NO₂. There is some evidence that there has been an upward trend in mean O₃ concentrations over the past decade (PORG, 1997; Collins et al., 2000). Derwent (1999) has explored the implications of increases in tropospheric O_3 on the annual mean concentration of NO₂ in London, by testing the implications of a 10 ppb increase in O_3 for every hour of the year on annual mean NO₂ concentrations. Modelling results for a transect across central London showed that a 10 ppb increase in O_3 would result in a 7 ppb increase in annual mean NO_2 (Derwent, 1999). Although the assumption of a significant increase in O_3 concentrations for every hour of the year is unrealistic, the analysis does highlight that estimates of annual mean NO₂ made in this paper are potentially underestimated.

7. Conclusions

A technique has been developed for the prediction of annual mean NO₂ concentrations in London using monitoring data. The technique relies on developing a relationship between annual mean NO_x and NO_2 using site-specific NO_2 vs. NO_x hourly relationships and frequency distributions. Analysis of data in London shows that the concentration of NO_x that must be reached in order that the annual mean NO₂ objective of 21 ppb is met is lowest in central London. Concentrations as low as 30 ppb NO_x are predicted to be required, which is lower than that required in smaller cities or towns or outer areas of London. Combined with a pollution climate mapping technique specific to urban areas, these predictions indicate that a significant proportion of central London will exceed the objective by the end of 2005, the date by which the objective must be met. A map has been produced, which shoes the distribution of NO₂

concentrations across London in 2005. These results highlight the challenge faced by policy makers in developing strategies to reduce emissions of NO_x in a very large and complex urban area.

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