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Estimations of road vehicle primary NO_2 exhaust emission fractions using monitoring data in London

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Abstract

Hourly mean concentration data for nitrogen oxides (NO_X), nitrogen dioxide (NO_2) and ozone (O_3) have been used to derive a method for estimating the mean primary NO_2 fraction from vehicle exhausts in London. A set of simple chemical equations has been used to explain the differences in NO_2 concentrations between background and roadside site pairs and to estimate the proportion of NO_2 that is likely to be derived from primary NO_2 vehicle emissions and the NO_2 formed through the reaction of nitric oxide (NO) with O_3. These results suggest that there is a wide range of primary NO_2 emission fractions observed on different roads in London. The estimates ranged from 3.2 to 23.5 vol% with a median value of 10.6 vol% for the 43 measurement sites considered. A median primary NO_2 fraction of 10.6% accounts for an average of 21% of the observed NO_2 concentration at roadside sites. The range in calculated primary NO_2 fractions explains much of the variation in annual mean NO_2 concentrations between monitoring sites in London. The estimated primary NO_2 fraction is considerably higher than the 5.0 vol% typically used in modelling studies that aim to predict ambient NO_2 concentrations. These results have implications for the assessment of NO_2 concentrations in London and whether London will meet the limit values set by the European Union. Further work is required to explain the wide range of primary NO_2 fractions estimated in terms of road traffic composition and activity.

Keywords: Nitrogen dioxide; Dispersion modeling; Air quality assessment; Ozone; EU Daughter Directive

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1. Introduction

In the UK, it is projected that many areas will not meet the EU Daughter Directive limit for an annual mean NO_2 concentration of $40\,\mu g\,m^{-3}$ by 2010. In particular, it is clear that to meet the limits in London will be most difficult (AQEG, 2004). Although there is uncertainty regarding the extent to which areas of London will meet the NO_2 limit, all assessments show that the annual limit for NO_2 will be exceeded at both background and roadside locations. As the area of exceedence reduces there will be an increased interest in the assessment of concentrations close to roads. The prediction of ambient concentrations in this environment can be difficult since small-scale effects, particularly those related to complex dispersion, increasingly influence concentrations. Furthermore, being closer to the source also requires a good understanding of the magnitude and temporal variation of emissions.

It is clear from recent work that the magnitude of directly emitted NO_2, i.e. primary NO_2 from road

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vehicle exhausts is important (Latham et al., 2001; Carslaw and Beevers, 2004c). However, little is understood of the variation of primary NO_2 emissions across a large urban area such as London. This lack of information is a weakness in the prediction methods for NO_2, which often resort to using 'typical' proportions of primary NO_2 in vehicle exhausts. Most commonly it is assumed that NO_2 accounts for 5.0% by vol of the total NO_X in vehicle exhausts (e.g. PORG, 1997; Berkowicz, 2000). If primary NO_2 emissions are significantly higher than 5.0 vol%, as suggested by recent studies, either some of the models used will underestimate NO_2 concentrations or they will wrongly account for observed concentrations perhaps through some form of model adjustment. To understand the contribution made by primary NO_2 emissions to ambient concentrations close to roads, it is necessary to delineate between the different origins of NO_2.

In London, recent analyses of hourly monitoring data from a busy central London kerbside site (Marylebone Road) suggest that the mean primary NO_2 fraction is considerably higher than 5.0% (Carslaw and Beevers, 2004b; Jenkin, 2004b). Results from these studies also highlight the potential importance of diesel vehicles, which were estimated to have a mean primary NO_2 fraction of 12.7% (Carslaw and Beevers, 2004b) and 11.8% (Jenkin, 2004b). Both studies used the gradient in total oxidant (defined as NO_2+O_3) at the Marylebone Road site, to derive the estimates of primary NO_2 fractions. The 'total oxidant approach', however, requires measurements of NO_2, NO_X and O_3 to estimate the potential contribution made by primary NO_2. In London, despite the large number of roadside monitoring sites (see Section 2.1), only one roadside site measures NO_X, NO_2 and O_3. The total oxidant approach can only, therefore, be used at background locations where O_3 measurements are generally available and which tend to be influenced by many different source types. Alternative approaches are therefore required if estimates of the primary NO_2 fraction are to be made at roadside monitoring sites.

Even though the chemical formation of NO_2 close to NO_X emission sources follows straightforward and well-understood chemistry, shown by Eqs. (1) and (2), the actual amount of NO converted to NO_2 in the ambient environment is difficult to determine in practice. The reaction rate of Eq. (1) assumes that NO is fully mixed instantaneously with O_3, bringing both gases in molecular contact with one another so that the reactions can take place. However, plumes do not mix instantaneously in ambient air and the efficiency with which they do so is determined by both mechanical and thermal atmospheric turbulence. Studies of plume mixing rates show that mixing on the microscale is important (Fraigneau et al., 1996a, b; Brown and Woodfield, 2004). The timescales of turbulence and NO_2 formation from chemistry through the NO–O_3 reaction are similar and therefore, it cannot be assumed that the reaction rate of Eq. (1) is relevant to near-field dispersion in an urban area. The reaction rate indicated by Eq. (1) maybe erroneous for air masses close to the source where mixing is incomplete. It can be difficult to determine therefore the contribution that NO–O_3 chemistry makes to NO_2 concentrations close to the source.

$$NO + O_3 \rightarrow NO_2 + O_2, \tag{1}$$

$$NO_2 + hv(+O_2) \rightarrow NO + O_3. \tag{2}$$

Since policy makers are interested in the contributory factors affecting ambient NO_2 concentrations, it is important to develop an understating of the sources of ambient NO_2 in the urban environment. Different policies might be adopted, e.g. if a significant fraction of the observed NO_2 concentrations was the result of primary NO_2 compared with the case where NO_2 is almost entirely secondary in origin. In this paper, a method is developed to determine the primary NO_2 fraction in road vehicular emissions through the analysis of comprehensive air pollution monitoring data available in London.

2. Analysis of data

2.1. Source of data and site characteristics

London has a large number of continuous monitoring sites that measure NO_X, NO_2 and O_3 most of which form part of the London Air Quality Network (Fuller et al., 2003). Measurements are made using a range of commercially available chemiluminescence NO_X instruments from a range of manufacturers. Continuous hourly O_3 measurements are made using the UV photometry technique. All measurements undergo quality control and assurance procedures with each measurement traceable to national metrological standards provided by the National Physical Laboratory (Fuller et al., 2003). The NO_X and NO_2 sites cover a wide range of environments from rural locations in outer London to heavily trafficked kerbside central London locations. Fig. 1 shows the locations of both roadside (<5 m from the kerb) and kerbside (<1 m from the kerb) NO_X/NO_2 sites and the locations of background sites, which in addition measure O_3. Further information relating to these sites including site photographs can be found at the Environmental Research Group website (www.erg.kcl.ac.uk). A total of 43 sites were used in the analysis (40 roadside and kerbside sites and 3 intermediate sites located between background and roadside), together with 7 background sites.

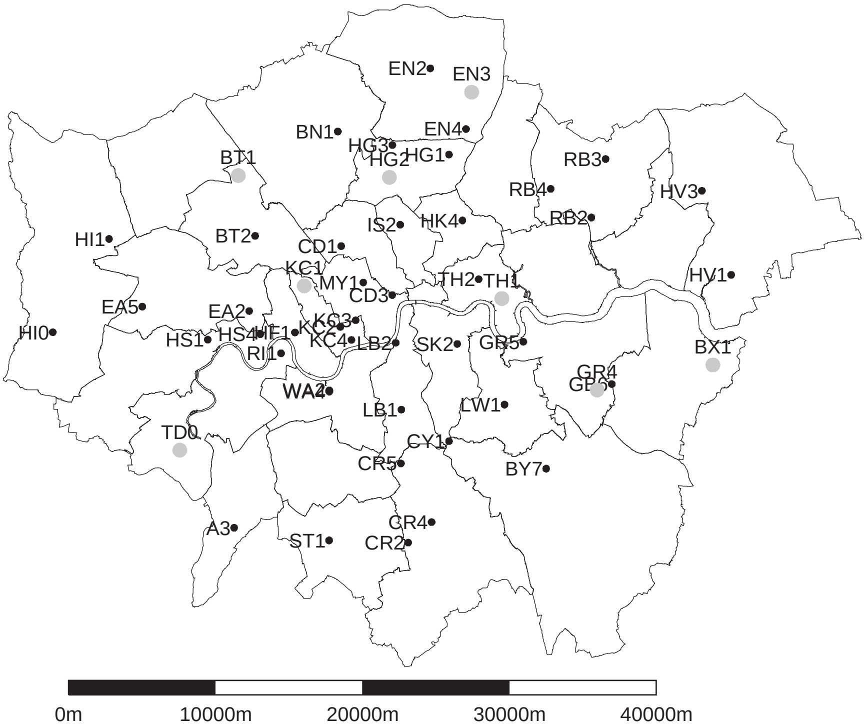

Fig. 1. Location of monitoring sites used in the analysis. Filled black circles show the location of roadside sites and filled grey circles show the location of the background sites.

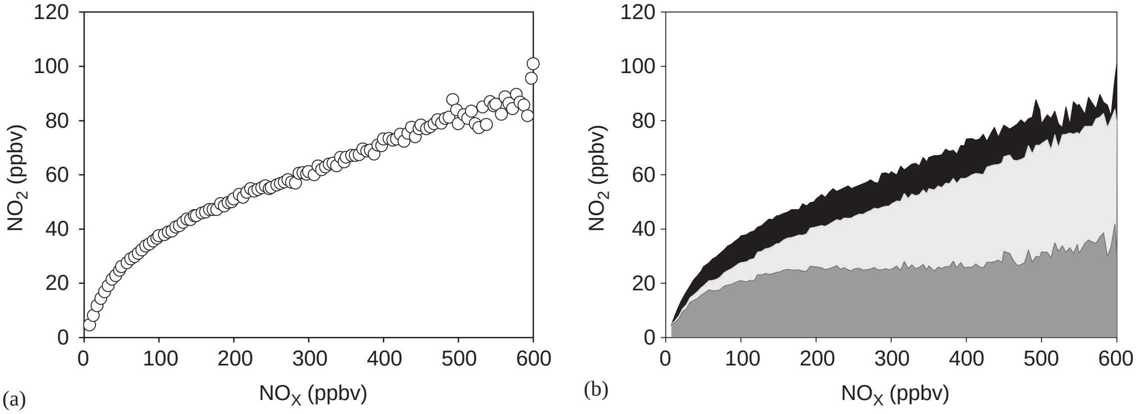

Fig. 2. (a) NO_X–NO_2 relationship for Marylebone Road (1998–2002), (b) NO_X–NO_2 relationship for Marylebone Road highlighting the principal contributors to the NO_2 concentration. The black shading, light grey and dark grey shows the estimated contribution from local NO–O_3 chemistry, primary NO_2 emissions and background air.

2.2. Methodology

The method developed in this study relies on the use of simple chemical equations to replicate the observed variation in the relationship between NO_X and NO_2 at roadside monitoring sites. The relationship between NO_X and NO_2 can usefully be described by considering the mean NO_2 concentration for different NO_X intervals. Fig. 2a shows such a relationship for Marylebone Road between 1998–2002. At NO_X concentrations below ca. 100 ppbv, the NO_2 concentration rises sharply because of the availability of O_3 to react with NO. At concentrations of NO_X between approximately 0–100 ppbv, the rate of increase of NO_2 declines sharply and the relationship between NO_X and NO_2 becomes almost linear. Plotting the data in this way also acts as a useful data reduction technique. Fig. 2b shows the same relationship, but attempts to delineate between three different major sources of NO_2 based on Carslaw and Beevers (2004c) using the total oxidant approach. First, there is a contribution from the background sources, which contribute to almost 50% of the observed NO_2. Second, there is a contribution from primary NO_2 emissions from vehicular traffic on Marylebone Road. Finally, there is a contribution from the reaction between NO and O_3 in the vicinity of the street. Fig. 2b shows that at concentrations of $NO_X <$ ca. 100 ppbv, the roadside increment in NO_2 i.e. that in addition to the background concentration, is dominated by local chemistry. Conversely, as NO_X increases towards 600 ppb, the contribution from primary NO_2 emissions dominates the roadside increment. These two controlling influences on the roadside increment of NO_2 concentrations provide the basis for the estimation of the primary NO_2 fraction from vehicle emissions.

A set of simple chemical equations has been originally used for the purpose of predicting NO_2 concentrations in street canyons. These equations have been used as part of the OSPM (Operational Street Pollution Model) developed by Berkowicz (2000). The rate of change of the concentrations of NO, NO_2 and O_3 can be expressed by Eqs. (3)–(5) (Palmgren et al., 1996):

$$\frac{d[NO]}{dt} = -k[NO][O_3] + J[NO_2] + \frac{[NO]_V}{\tau} + \frac{[NO]_B - [NO]}{\tau}, \tag{3}$$

$$\frac{d[NO_2]}{dt} = k[NO][O_3] - J[NO_2] + \frac{[NO_2]_V}{\tau} + \frac{[NO_2]_B - [NO_2]}{\tau}, \tag{4}$$

$$\frac{d[O_3]}{dt} = -k[NO][O_3] + J[NO_2] + \frac{[O_3]_B - [O_3]}{\tau}, \tag{5}$$

$$[NO_2] = 0.5\left(B - (B^2 - 4\left([NO_X](A + [O_3]_B) + \frac{B}{k\tau}\right)\right), \tag{6}$$

where for Eq. (6):

$$A = [NO_2]_V + [NO_2]_B, \tag{7}$$

$$B = [NO_X] + A + [O_3]_B + \frac{1}{k}\left(J + \frac{1}{\tau}\right). \tag{8}$$

In Eqs. (3)–(5) J is the photo-dissociation coefficient of NO_2, k is the rate coefficient for the reaction between NO and O_3, calculated as in the OSPM model (Berkowicz, 2000). $[NO]_V$ and $[NO_2]_V$ are the concentrations of NO and NO_2 due to vehicle emissions. Eqs. (3)–(5) above are also adequate for quantifying the degree of chemical processing of NO_2 between a roadside and a background site. Instead of τ representing the mean time an air parcel is in a street canyon, it can also describe the mean time available for atmospheric chemistry to occur between a roadside and background location. Using Eq. (4) as an example, the last two terms take account of the mixing of the vehicle emissions and exchange with background air. If it is assumed that equilibrium is achieved then Eqs. (3)–(5) can be set to zero and solved analytically for NO_2 as shown by Eq. (6). For the current application the following was assumed for Eq. (6): $[NO_X]$ is the monitored hourly roadside concentration, $[NO_2]_B$, $[O_3]_B$ the monitored hourly background concentrations of NO_2 and O_3, $[NO_2]_V$ is the calculated primary NO_2 concentration from road vehicles that is given by $NO_2(p)([NO_X]–[NO_X]_B)/100$, where $NO_2(p)$ is defined as the percentage primary NO_2 by vol. in the vehicle exhaust. The contribution from primary NO_2 emissions is therefore related to the NO_X increment above the background concentration of NO_X.

As shown in Fig. 2b, the observed difference between the NO_2 concentration close to roads and a background site can be thought of as consisting of two principal origins: that which originates from primary NO_2 emissions and that derived through local NO–O_3 chemistry in the vicinity of the road. In principle, NO_2 could be formed through reactions involving VOCs. However, since the typical separation of a roadside and a background site in London is only a few kilometres, there is generally insufficient time available for these reactions to become important and they can be neglected. As previously discussed in Section 1, the amount of NO_2 formed though the NO–O_3 reaction is dependent on the efficacy with which the emissions mix with background air and the time available for the reactions to take place. In terms of Eq. (6), these two controlling influences of the roadside NO_2 increment are given by $[NO_2]_V$ i.e. the primary NO_2 fraction and τ, which represents the time available for the NO–O_3 reaction to take place.

Datasets were assembled for each of the 43 sites consisting of hourly measurements of NO_X and NO_2 from a roadside monitoring site and NO_X, NO_2 and O_3 from a nearby background-monitoring site. Hourly data were only used if measurements were available for all species for a particular hour. Previous work (Carslaw and Beevers, 2004b) has shown that the primary NO_2 fraction expressed as a percent by volume, $NO_2(p)$, varies by day of the week and is estimated to be lower on Saturdays and Sundays as a result of less heavy goods vehicles on those days. For this reason consideration was given to weekdays only, where variation in $NO_2(p)$ between each day is small. Because the monitoring sites were commissioned at different start dates, data were processed from January 2000 onwards. This choice of start date ensured a dataset of three years of hourly measurements for most sites and a consistent set of conditions e.g. meteorology, for the calculations.

Each dataset was processed using specific values for $NO_2(p)$ and τ, which were applied to the entire hourly dataset. $NO_2(p)$ and τ were varied over a pre-defined range e.g. $NO_2(p)$ from 5.0% to 15.0% in 0.1% intervals and τ from 10 to 100 s in 5 s intervals, to yield many sets of hourly results with different values assumed for $NO_2(p)$ and τ. Each of the sets of hourly results was processed to yield a predicted NO_X–NO_2 relationship that was then compared with the measured relationship and the RMS error calculated. By varying $NO_2(p)$ and τ, it was found that good agreement between the measured and predicted NO_X–NO_2 relationships could be attained for narrow ranges of $NO_2(p)$ and τ. Fig. 3 shows an example of the error surface for the estimated mean NO_2 and the influence of $NO_2(p)$ and τ. The variation along the x-axis shows the clearly strong influence that the value of $NO_2(p)$ has on the results. The plot shows that there is a relatively narrow range of values of $NO_2(p)$ for which the calculated error is small. By contrast, the variation due to τ is weak beyond approximately 100 s. However, as τ is reduced to below 100 s, the calculated error increases significantly. This result is expected since the reaction between NO and O_3 is rapid and typically takes tens of seconds to occur. A closer examination of the results from such plots reveals that there is a unique value of $NO_2(p)$ and τ that results in a minimum error. The lowest point on the surface shown in Fig. 3 corresponds to a $NO_2(p) = 10.0\%$ and $\tau = 80$ s, which provides the best estimate of the primary NO_2 fraction for this hour and this site. More generally, the location of the minimum error is assumed to represent the best estimate of the $NO_2(p)$.

Fig. 4a shows the best fit between the observed and the modelled NO_X–NO_2 relationship for Marylebone Road. There is a good agreement between observations and predictions across the full NO_X range from approximately 10 to 900 ppbv. The good agreement between observations and predictions is also shown in Fig. 4b, which considers hourly values. Differences between the hourly modelled and observed NO_2 concentrations arise for several reasons. First, it is likely that $NO_2(p)$ is variable on an hourly basis and cannot be fully described by a single value. Second, errors are likely to be introduced by assuming a constant value for τ, since concentrations of NO_2 at roadside locations will be affected by sources over a range of distances therefore affecting the time available for chemistry. These effects are minimized, however, by considering concentrations very close to a single source i.e. a road, where the influence from that source is strong. Furthermore, the method is concerned with the increment in concentrations of NO_X and NO_2 above background, which will be dominated by the effect of the road closest to the monitoring site.

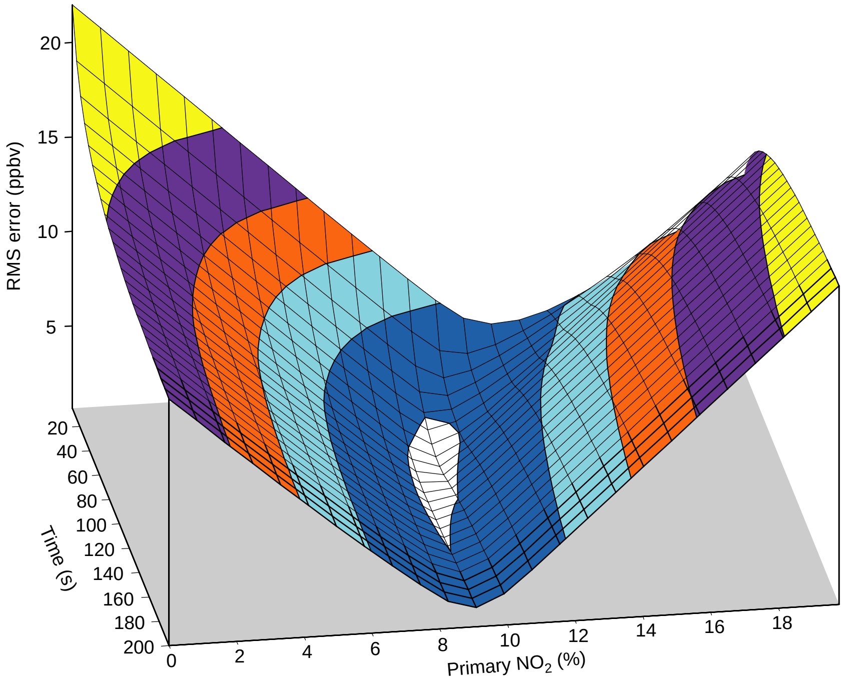

Fig. 3. The dependence of the calculated error from fitting measured and fitted NO_X–NO_2 relationships on the assumed primary NO_2 fraction and the time available for chemistry, τ. The error surface related to measurements from Marylebone Road at 9.00 am using data between 1998 and 2002.

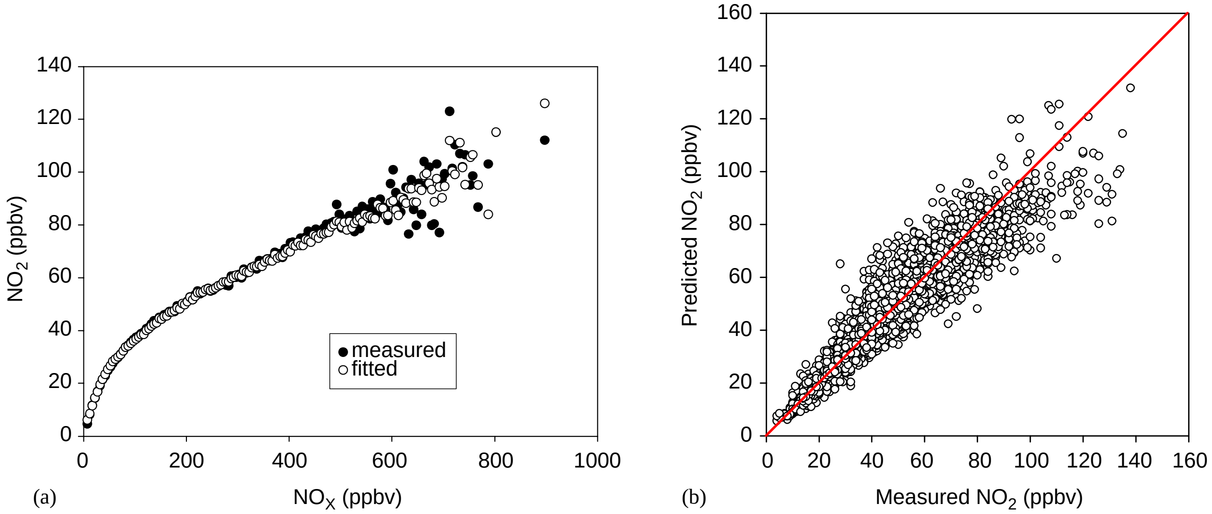

Fig. 4. (a) Measured and fitted NO_X–NO_2 relationship for Marylebone Road for weekdays between 1998 and 2002, (b) measured and predicted hourly mean NO_2 concentrations for Marylebone Road (2001).

Table 1
Estimated primary NO_2 fraction using four different background sites (1998–2002)

Background site	Distance from Marylebone Road (km)	Angle of background site with respect to Marylebone Road (degrees)	Calculated primary NO_2 fraction for all wind directions (% by vol)	Calculated primary NO_2 fraction for upwind conditions (% by vol)	Background concentration (ppbv)		
					NO_X	NO_2	O_3
Kensington	4	270	9.5	9.3	39.0	22.3	16.4
Tower Hamlets	9	100	9.1	10.5	38.2	23.0	17.1
Teddington	17	230	10.0	9.9	24.6	15.2	22.2
Rochester	56	100	9.6	11.6	15.2	11.2	24.8

2.3. Dependence on choice of background site

The choice of background site is clearly an important factor to be considered in the method developed above. However, in the case of NO_2 predictions, the choice of a background site that has NO_2 concentrations that are too high or too low is compensated for to some extent by the chemistry of NO_2. For example, if a background site was chosen where the concentration of NO_2 was too low, the corresponding O_3 concentration at that site would tend to be higher. The use of such a site in the method developed would result in higher rate of NO_2 formation because of the additional availability of O_3, or τ would be estimated to be higher to allow more time for the chemistry to occur and give best agreement with the measurements. Nevertheless, more reliable results would be expected with the most appropriate choice of background site.

Table 1 shows the dependence of the calculated primary NO_2 fraction at Marylebone Road on the choice of background site. Four sites were chosen for the comparison, two in inner London, one in outer London and one outside London. These sites are between 4 and 56 km from Marylebone Road and cover a range of environments from an urban background site to a rural site. The background sites also cover a wide range of NO_X, NO_2 and O_3 concentrations as shown in Table 1. The primary NO_2 fraction calculated using these different sites does, however, cover a small range from 9.1 to 10.0 vol% i.e. within ±6% of the value estimated using the total oxidant approach, described in Section 2.4. These results demonstrate, therefore, that the calculated primary NO_2 fraction is not particularly sensitive to the choice of background site and even produces good estimates using a rural site 56 km from Marylebone Road.

The primary NO_2 emission ratios have also been calculated for a selected range of wind directions. The background sites are located at different directions with respect to Marylebone Road as shown in Table 1. Kensington and Teddington are both west of Marylebone Road and also upwind of the prevailing south-westerly wind direction. Tower Hamlets and Rochester are both east of Marylebone Road. The primary NO_2 fraction was estimated for wind directions when the different background sites were upwind of Marylebone Road. A wind sector $\pm 45^\circ$ was chosen to represent conditions when the upwind criterion was met. Table 1 shows that selecting only upwind conditions for each of the site pairs results in very similar estimates of the primary NO_2 ratio for Kensington and Teddington compared with using all wind directions. However, higher estimates were obtained for the Tower Hamlets (10.5 vs. 9.1 vol%) and the Rochester (11.6 vs. 9.6 vol%) site pairs. The higher ratios calculated for Tower Hamlets and Rochester might be the result of meteorological conditions that prevail when these sites are upwind of Marylebone Road i.e. when the wind is from an easterly direction. The easterly wind conditions frequently occur during periods of high photochemical activity and anticyclonic conditions. During these conditions it is possible that there are other photochemical sources of NO_2 that do not result in the removal of ozone, which could become important over the distance scales shown in Table 1 for these sites (9 and 56 km).

2.4. *Comparison with the total oxidant approach*

The method described in Section 2.2 can be compared with an alternative approach that uses the measurements of O_3 at the Marylebone Road site. As described in Section 1, it is possible to derive an estimate of the local primary NO_2 emissions by considering how the difference in total oxidant (NO_2+O_3) varies with NO_X. The slope of such a relationship provides a useful and direct estimate of the local primary NO_2 fraction. A useful comparison to make between the two methods is to consider the diurnal profile of the calculated oxidant slope. This approach is valuable since it is able to confirm whether the clear diurnal pattern of the 'observed' variation of the NO_2:NO_X ratio of emissions derived using the total oxidant approach can be derived using the current technique which does not use roadside O_3 measurements. Fig. 5a shows a comparison of the total oxidant approach and the approach developed in Section 2.2. In general, the agreement between the two approaches is very good by hour of the day. The mean oxidant slope integrated over the whole daily period is very similar in each case (9.4% for the total oxidant approach and 9.5% for the modelling approach). Fig. 5b shows the diurnal profile of the observed and the predicted O_3 concentration, which shows good agreement between the two. These results indicate that there is reasonable partitioning between the calculated NO_2 from primary NO_2 emissions and the NO_2 that is derived through the NO–O_3 reaction.

A comparison has also been made of the mean weekday oxidant slope at five sites shown in Table 2, which all measure O_3 in addition to NO_X and NO_2. All sites can be considered to be intermediate between roadside and background and are influenced by nearby roads, with the exception of Marylebone Road, which is a kerbside site. The oxidant slope was derived by plotting daily mean NO_X vs. NO_2+O_3 and applying a regression analysis to derive the slope, consistent with the approach of Clapp and Jenkin (2001). The results in Table 2 show that there is good agreement between the

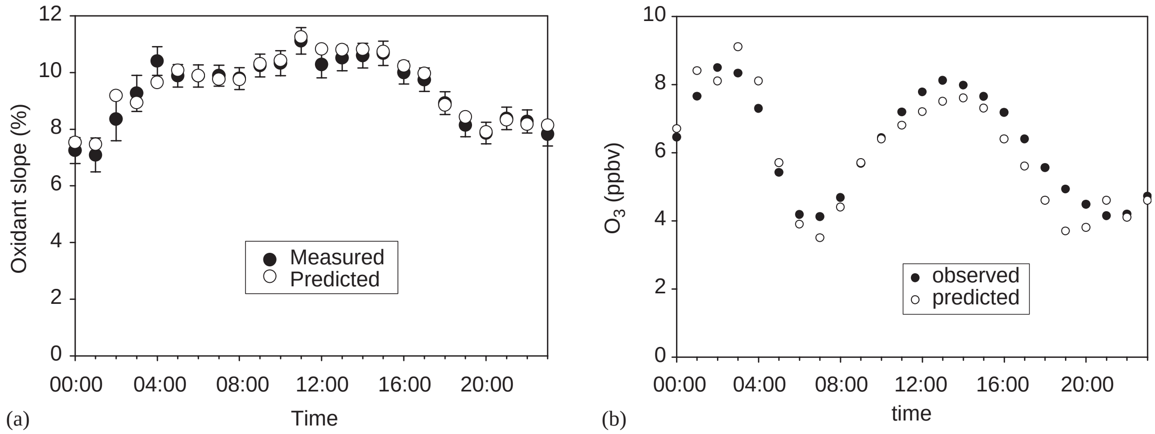

Fig. 5. (a) Comparison between the diurnal variation in primary NO_2 estimated using the total oxidant approach (filled circles) and the fitted NO_X–NO_2 relationship approach (hollow circles) at Marylebone Road (1998–2002). (b) Comparison between measured and modelled diurnal variation in O_3 (1998–2002).

Table 2
Comparison between estimated primary NO_2 fractions using the total oxidant approach and the modelling approach for data between 2000 and 2002

Monitoring site	Total oxidant approach[a]	Current method
Marylebone Road	9.1 ± 0.4	9.5
Wandsworth 2	10.3 ± 1.1	10.6
Hackney 4	10.4 ± 1.0	9.7
Lewisham 1	10.1 ± 1.9	10.6
Hillingdon	5.2 ± 0.6	3.4

[a] Error at $\pm 1\sigma$.

total oxidant approach and the modelling approach that does not need roadside ozone measurements to derive the estimated primary NO_2 fraction.

3. Results and discussion

3.1. Estimated primary NO_2 fraction at roadside sites

Estimates of $NO_2(p)$ were made at 43 sites shown in Fig. 1 and Table 3. Different roadside–background site pairs were identified based on several criteria including the proximity of the roadside site to the background site, data availability and the error derived when comparing the measured and derived NO_X–NO_2 relationships. In practice, several background sites were used for each roadside site to identify the site that yielded least error compared with measurements. The results in Table 3 highlight a large range in calculated $NO_2(p)$ values from 3.2 to 23.5 vol% with a median value of 10.6 vol%. No significant difference was found between sites situated in different areas of London e.g. central and inner London cf. outer London.

The estimated values of $NO_2(p)$ and τ shown in Table 3 were used to calculate an hourly time series of predicted NO_2 concentrations that could be compared with observed values. The resultant r^2 value of the comparison is shown in Table 3. In general, the agreement between measurements and predictions is very good with a mean $r^2 = 0.86$. Consideration of the hourly predictions in more detail shows that the agreement was good by hour of the day and by season and that good predictions could be achieved for high percentile values of NO_2. The calculated values of $NO_2(p)$ seem therefore to provide a good description of the NO_2 concentrations at almost all of the 43 monitoring sites. The Croydon 2 site and the Brent 2 site showed anomalous results that yielded poor agreement with the measurements ($r^2 = 0.66$). In the case of Croydon 2, almost all the NO_2 could be explained without the need for local chemistry, which is clearly not possible. However, in the case of Croydon 2 it has been observed over several years that the annual mean NO_2 concentration is very low for the observed annual mean NO_X concentration. Further work is required to investigate and explain the poor agreement at these sites.

The effectiveness of the technique might be expected to depend on wind direction. First, the wind direction will determine whether the emissions from a particular road are blown towards the monitoring station. Many of the 43 sites considered are situated in street canyons, or situations where the dispersion is complex, making it difficult to always clearly identify the wind directions where the monitoring site is influenced by the road source. Second, there will be periods when background site would be upwind of the roadside site and other periods where the roadside site would be downwind of the background site, as discussed in Section 2.3. Overall, the most important factor influencing the estimated primary NO_2 emission ratios appears to be the magnitude of the contribution made by the road above the background concentration. In cases where this contribution is high, the signal from the road source is clear and the efficacy of the fitting technique is dominated by the influence of the road source.

Almost all of the 43 monitoring sites considered in the analysis are located in complex environments close to road junctions or situations where the flow of traffic is interrupted in some way e.g. by traffic control signals. Two sites have however been identified as being located where traffic is mostly free-flowing and where the traffic speed is high: the A3 and Hillingdon sites. At these two locations the estimated $NO_2(p)$ is 3.9 and 3.2% respectively, which is much lower than the median value of 10.6% for all sites. Lower values of $NO_2(p)$ for fast moving traffic appears to be consistent with other work that has aimed to quantify $NO_2(p)$ e.g. Jenkin (2004a) and Latham et al. (2001). However, further detailed work is required to establish how $NO_2(p)$ varies with traffic composition and activity data.

Fig. 6a shows the variation in the mean NO_X with NO_2 measured concentrations at the 43 sites over the periods covered in Table 3. It is clear that even with long-term averages of NO_X and NO_2, there is a large degree of variation in the concentration of NO_2 for a particular concentration of NO_X. Using the method described in Section 2.2, annual mean NO_2 concentrations were re-calculated assuming a consistent set of conditions with $NO_2(p) = 10.0\%$ for each site, as shown in Fig. 6b. Although some scatter remains in Fig. 6b, it is significantly reduced compared with Fig. 6a. Also shown in Fig. 6b is a best-fit line which has been calculated based on the typical annual mean values of different variables (k, the reaction rate coefficient between NO and $O_3 = 3.7 \times 10^{-4}\,\mathrm{ppb\,s^{-1}}$; J, the photolysis rate of $NO_2 = 2.2 \times 10^{-3}\,\mathrm{s^{-1}}$ (Jenkin, 2004a); $NO_2(p) = 10.0\%$ and a mean value of τ of 89 s). In addition, Fig. 6b shows

Table 3
Estimated primary NO_2 fractions at roadside sites in London

LAQN Site name	Site code	Background site	Estimated primary NO_2 (%)	r^2 (a)	τ (s)	NO_X (ppbv) (b)	NO_2 (ppbv) (b)	Estimated primary NO_2 (ppbv)	Start date	End date
A3	A3	TD0 (Teddington)	3.9	0.88	96	115	30	3.4	Jan-00	Dec-02
Barnet 1	BN1	BT1 (Brent 1)	14.7	0.80	26	105	34	12.2	Jul-00	Dec-02
Brent 2	BT2	BT1	5.8	0.66	154	168	37	8.2	Jun-01	Dec-02
Bromley 7	BY7	GR4 (Greenwich 4)	13.5	0.93	78	78	30	6.9	Jan-00	Dec-02
Camden 1	CD1	KC1 (Kensington 1)	9.9	0.86	123	107	36	6.9	Jan-00	Dec-02
Camden 3	CD3	KC1	16.6	0.92	87	98	39	10.4	Apr-00	Dec-02
Croydon 2	CR2	TD0	6.7	0.66	18	95	24	4.9	Jan-00	Dec-02
Croydon 4	CR4	TD0	15.5	0.87	98	67	29	6.7	Jul-00	Dec-02
Croydon 5	CR5	TD0	11.3	0.91	74	128	36	11.7	Oct-00	Dec-02
Crystal Palace	CY1	GR4	6.3	0.85	64	86	27	3.7	Jan-00	Dec-02
Ealing 2	EA2	KC1	5.5	0.88	52	86	29	2.7	Jan-00	Dec-02
Ealing 5	EA5	KC1	8.1	0.88	33	87	29	3.9	Jul-00	Dec-02
Enfield 2	EN2	EN3 (Enfield 3)	13.9	0.91	62	53	25	3.2	Jul-00	Dec-02
Enfield 4	EN4	EN3	9.1	0.90	97	67	28	3.2	Jul-00	Dec-02
Greenwich-Bexley 6	GB6	GR4	9.7	0.94	31	99	28	6.7	Oct-00	Dec-02
Greenwich 5	GR5	GR4	19.3	0.89	68	67	29	7.4	Jan-00	Dec-02
Hammersmith and Fulham 1	HF1	KC1	11.1	0.87	39	119	37	9.1	Jan-00	Dec-02
Haringey 1	HG1	HG2 (Haringey 2)	8.0	0.92	86	66	27	2.6	Jul-00	Dec-02
Haringey 3	HG3	HG2	15.8	0.95	59	72	29	5.2	Jul-00	Dec-02
Hillingdon (c)	HI0	TD0	3.2	0.83	96	82	28	1.5	Jan-00	Dec-02
Hillingdon 1	HI1	TD0	5.4	0.81	52	80	25	3.1	Jul-00	Dec-02
Hounslow 1	HS1	TD0	8.0	0.83	105	89	32	4.1	Jan-00	Dec-02
Hounslow 4	HS4	TD0	11.7	0.87	44	93	31	8.1	Jul-00	Dec-02
Havering 1	HV1	BX1 (Bexley 1)	13.9	0.76	56	65	27	4.7	Jan-00	Dec-02
Havering 3	HV3	BX1	3.3	0.82	43	63	23	1.1	Jul-00	Dec-02
Islington 2	IS2	KC1	11.9	0.90	48	116	37	9.3	Jul-00	Dec-02
Kensington and Chelsea 2	KC2	KC1	16.4	0.88	69	116	42	13.3	Jan-00	Dec-02
Kensington and Chelsea 3	KC3	KC1	17.1	0.90	92	125	44	15.3	Mar-00	Dec-02
Kensington and Chelsea 4	KC4	KC1	13.6	0.88	174	146	46	16.5	Sep-00	Dec-02
Lambeth 1	LB1	TD0	14.6	0.86	108	76	31	7.6	Sep-00	Dec-02
Lambeth 2	LB2	TD0	12.6	0.80	214	72	31	6.4	Dec-01	Dec-02
Marylebone Road	MY1	KC1	10.0	0.86	70	195	47	15.8	Jan-00	Dec-02
Redbridge 2	RB2	HG2	23.5	0.87	134	196	67	38.0	Jul-00	Dec-02
Redbridge 3	RB3	HG2	20.9	0.89	41	110	40	16.4	Jul-00	Dec-02
Redbridge 4	RB4	HG2	9.3	0.89	77	77	28	4.1	Jul-00	Dec-02
Richmond 1	RI1	TD0	12.2	0.90	122	50	23	3.3	Jul-00	Dec-02
Southwark 2	SK2	GR4	12.3	0.87	106	93	33	7.8	Jan-00	Dec-02
Sutton 1	ST1	TD0	7.5	0.89	42	64	24	3.0	Jan-00	Dec-02
Tower Hamlets 2	TH2	TH1 (Tower Hamlets 1)	10.6	0.88	25	109	35	7.6	Jan-00	Dec-02
Wandsworth 4	WA4	TD0	10.6	0.91	151	60	26	3.9	Jan-00	Dec-02
Wandsworth 2 (c)	WA2	TD0	10.1	0.89	190	68	28	4.4	Jan-00	Dec-02
Hackney 4 (c)	HK4	TD0	9.7	0.85	217	59	26	3.5	Jan-00	Dec-02
Lewisham 1 (c)	LW1	TD0	10.6	0.82	221	64	28	4.3	Jan-00	Dec-02
Mean	—	—	11.2	0.86	89	94	32	7.5	—	—

(a) The r^2 value relates to the relationship between measured and predicted hourly NO_2 concentrations when predictions are made using the primary NO_2 fractions listed in the table.

(b) The mean values are those calculated over the periods shown in the table for those hours where there is 100% data capture for roadside NO_X and NO_2 concentrations and background NO_X, NO_2 and O_3 concentrations.

(c) These sites are intermediate between roadside and background and have been included because it is believed they are strongly influenced by nearby roads.

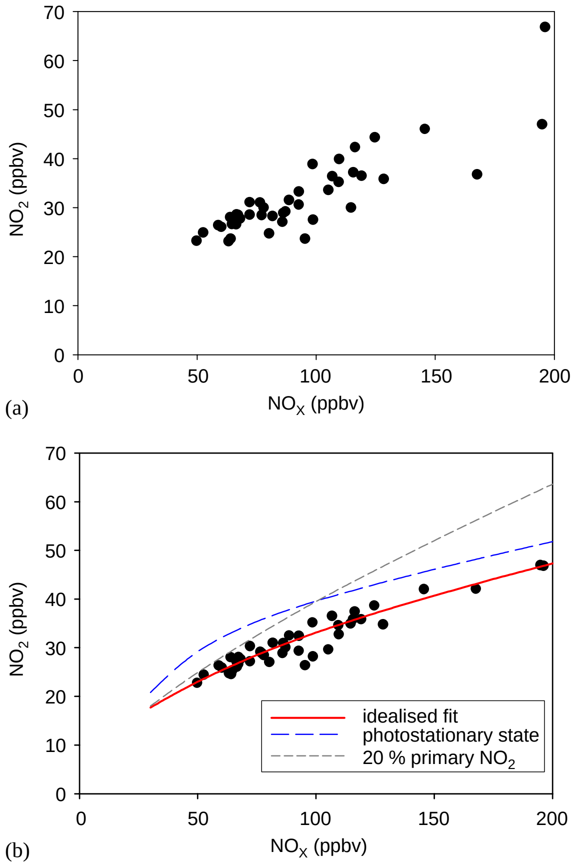

Fig. 6. (a) Mean measured NO_X vs. NO_2 for the 43 sites listed in Table 3. (b) Mean weekday NO_X vs. NO_2 for the same 43 sites assuming $NO_2(p) = 10.0\%$ and site-specific values of τ shown in Table 3.

a line assuming the photostationary state assumption, which clearly over predicts NO_2 concentrations and a line assuming $NO_2(p) = 20\%$. The RMS error of the measured NO_X and NO_2 concentrations against the best-fit line is 28.1 ppb. For the case where predictions have been made assuming a common primary NO_2 fraction of 10.0%, the RMS error is reduced to 13.1 ppbv. These results suggest that a significant amount of the variation observed between NO_2 concentrations at monitoring sites in London is the result of the influence of varying amounts of primary NO_2 being emitted by road vehicles. The remaining scatter shown in Fig. 6b is likely to be the result of the proximity of the site to the emission source therefore affecting the time available for the NO–O_3 reaction to take place, and the different background concentrations of NO_2 at each site. Some of the scatter might also be due to instrument error, since larger errors in NO_2 concentration might be expected at locations where concentrations of NO_X are high and are fluctuating. In terms of the contribution primary NO_2 emissions make towards total ambient concentrations of NO_2 close to roads, there is a large variation depending on the site considered. Calculations show that at the A3 site for example ($NO_2(p) = 3.9\%$), primary NO_2 accounts for approximately 3.5 ppbv of the observed 30.0 ppbv i.e. 11.7%. However, at locations where $NO_2(p)$ is higher, this proportion can be much greater e.g. at Marylebone Road the proportion is 33.7%, 34.5% at KC3 and 57.0% at RB2. The mean contribution that primary NO_2 emissions make towards ambient NO_2 concentrations at roadside locations was 21.2%.

3.2. *Comparison with previously reported estimates*

There are relatively few studies available with which to compare the estimates derived in the current study. Emissions studies of NO_2 measured from road vehicles report widely varying quantities of primary NO_2 that appear to depend upon fuel type, vehicle technology and vehicle operating conditions. Early emissions measurements from diesel vehicles highlight a wide range in $NO_2(p)$ from a few percent to 30% (Hilliard and Wheeler, 1979), with higher values reported at lower vehicle speeds. More recently, the Transport Research Laboratory (TRL) in the UK has conducted several experiments on the primary NO_2 emissions from different vehicle types (Latham et al., 2001). The TRL work also confirmed that diesel engines have higher $NO_2{:}NO_X$ ratios compared with petrol-engined vehicles and that higher $NO_2{:}NO_X$ mixing ratios were observed at low vehicle speeds for diesel vehicles. Tunnel experiments also report widely varying primary NO_2 emissions. For example, measurements from a tunnel in Germany indicated very low emissions from a petrol car (<0.2%) but 11.0% for a diesel truck (Kurtenbach et al., 2001).

Jenkin (2004a) applied the total oxidant approach to a large number of UK monitoring sites with co-located NO_X, NO_2 and O_3 monitors. Almost all the sites considered were background since only one site measures O_3 at a roadside location. For 15 sites in London based on 1998 and 1999 data, the calculated local oxidant gradient ranged from 3.9 to 16.8%. The four sites in central London showed higher values ranging from 12.6 to 16.8%. The mean value for all sites of 9.3% compares well with the 11.2% derived in the current study. The higher average value estimated in the current study might reflect the location of the roadside sites used i.e. many being located close to roads where vehicle flow is interrupted in some way and where it might be expected that primary NO_2 emissions are high. The Jenkin (2004a) results might also be expected to reflect typical values of primary NO_2 that include a contribution from non-road traffic sources such as emissions from natural-gas combustion because the sites are located at background locations.

4. Conclusions

Annual mean concentrations of NO_2 in excess of EU limit values in London will increasingly be limited to the direct vicinity of roads in London towards 2010. In this environment, the characteristics of the emission source can have a large influence on ambient concentrations. In particular, the level of primary NO_2 emissions is of importance since they can have a direct, significant effect on concentrations of NO_2 close to roads. The method developed in this paper and the results generated from it suggest that the mean primary NO_2 fraction from vehicle emissions varies widely from 3.2% to 23.5 vol% for different roads in London, with a median value of 10.6%. Primary NO_2 emission fractions of this magnitude are much higher than the frequently assumed 5.0 vol% used in the prediction of urban NO_2 concentrations. Consequently, around one-third of the measured NO_2 concentration at many roadside sites in London can be identified as comprising directly emitted NO_2 from road vehicles. These results have implications for studies of NO_2 concentrations in London and elsewhere that have assumed a constant 5.0 vol% primary NO_2 fraction since their accuracy will be limited by the current lack of information concerning directly emitted NO_2 levels. The limited data available on measured NO_2 emissions from single vehicles also confirm a wide range of primary NO_2 emission rates. It is clear, therefore, that primary NO_2 emissions from road vehicles in an urban area are likely to be highly variable depending on fuel type, vehicle technology and vehicle operating conditions. Further work is being undertaken to apportion the calculated primary NO_2 fractions to road traffic activity and composition and in particular vehicle speed and fuel type (Carslaw and Beevers, 2004a). In the UK and Europe, there is a sparsity of vehicle emissions data related to primary NO_2 since most emissions inventories only consider total emissions of NO_X. It is clear however, from the results obtained in this study that improved emissions data are required for primary NO_2 from road transport as well as other significant urban sources of NO_X.

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