

## Appendix A

### 1 Model Development

#### 1.1 Annual mean NO<sub>2</sub> vs. NO<sub>x</sub> relationships

The modelling approach adopted in this Stage 4 report builds on the approach described by Carslaw et al. (2001). In summary, the relationship between hourly NO<sub>x</sub> and NO<sub>2</sub> has previously been described by plotting NO<sub>2</sub> against NO<sub>x</sub> in different NO<sub>x</sub> 'bins', for example 0-10 ppb, 10-20 ppb etc, (Derwent and Middleton, 1996). The resulting NO<sub>x</sub> to NO<sub>2</sub> relationship describes the main features of NO<sub>x</sub> chemistry, first the NO<sub>x</sub>-limited regime where NO<sub>2</sub> concentrations increase rapidly with NO<sub>x</sub> and second the O<sub>3</sub>-limited regime where a change in NO<sub>x</sub> concentration has little effect on the concentration of NO<sub>2</sub>. A third and final regime also exists where, once again NO<sub>x</sub> and NO<sub>2</sub> increase pro-rata, related to extreme wintertime episodes. In all cases, the precise relationship is always both year and site dependent.

#### 1.2 NO<sub>x</sub> and NO<sub>2</sub> Relationships, the Adopted Method

##### 1.2.1 Background Concentrations

The ERG has adopted a revised approach to estimating background emissions to more fully describe the continued decrease of NO<sub>x</sub> (for example) away from a background site, for example in London's green areas where NO<sub>x</sub> concentrations are likely to reduce towards their centre.

This approach better describes the balance between the local road contribution and the background since it provides a good compromise between the most robust aspects of both modelling and measurements. Importantly it permits all background emission sources to be identified accurately within the modelling e.g. this means that if any emission source becomes less significant over time, it will feature less prominently in the final predictions and thus reflect the actuality of measurements.

The new approach uses a derived relationship, established by modelling all sources (apart from roads) in a 30x30km grid (to a depth of 10m). The areas close to roads (i.e. within 500m of their centre line) were removed from the dataset. These results were replaced with results from the separate modelling of road sources (see next section). The combined predictions for all NO<sub>x</sub> sites in London were then plotted against the measurements. Based on a multiple regression analysis of results the relationship can be described as:

$$\text{Concentration} = a.[\text{road cont}] + b.[\text{background cont}] + \text{const.}$$

This new approach provides improved predictions and produces a continuous and smooth fall-off in NO<sub>x</sub> away from roads. This permits monitoring sites to be better

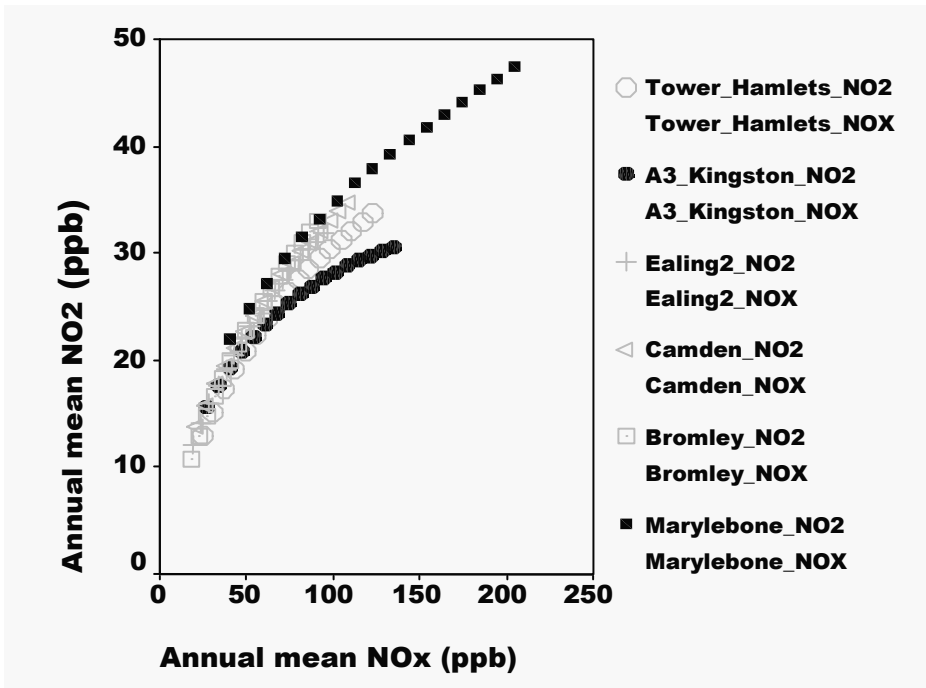
described in terms of background and roadside concentrations, further improving the understanding of the  $\text{NO}_x$  -  $\text{NO}_2$  relationship for the sites.

### 1.2.2 Roadside Concentrations

Of more use than the hourly relationship discussed earlier is the relationship between the annual mean  $\text{NO}_x$  and  $\text{NO}_2$  concentrations. The construction of these curves described in Carslaw et al. (2001) and is both site and year specific. The relationship for a site relates annual mean concentrations of  $\text{NO}_x$  to  $\text{NO}_2$  whilst implicitly including the full distribution of concentrations measured each hour of the year.

When using these relationships it is important to differentiate between those applicable to background locations and those applicable to roadside locations for any given predicted year.

The  $\text{NO}_x$  and  $\text{NO}_2$  relationships described above are year and site dependent. However, analysis of 1999, the year for which there are most sites shows that the roadside concentrations of  $\text{NO}_2$  for any  $\text{NO}_x$  concentration lies within a range of values that can be related to location. The range is from a central London, busy street canyon, at Marylebone Road to an outer London suburb with an open road location, i.e. the A3 dual carriageway. The contrast between the two locations relates specifically to the background concentration of  $\text{NO}_x$  and  $\text{NO}_2$ , with Marylebone Road (70,000 vehicles per day) in a region of very high background concentration and the A3 site (120,000 vehicles per day) in an area with a low background concentration of  $\text{NO}_x$  and  $\text{NO}_2$ , and thus it is similar to a rural motorway. For all years Marylebone Road provides the upper limit of  $\text{NO}_2$  concentrations and A3, the lower limit for any given concentration of  $\text{NO}_x$ . The hierarchy of  $\text{NO}_x$  and  $\text{NO}_2$  relationships, for 1999, is summarised in Figure 1, below.



**Figure 1** NO<sub>x</sub> and NO<sub>2</sub> Relationships at Roadside Sites across London (1999)

The range of NO<sub>2</sub> concentrations, for a given NO<sub>x</sub> concentration at the roadside are much larger than for background locations. This is because of a number of factors, including the relative contribution of the road to total NO<sub>x</sub> concentrations, the rapid fall-off in concentration away from a road and the rapid reaction between NO and O<sub>3</sub> to form NO<sub>2</sub>.

It is recognised that the approaches developed here are new and perhaps unfamiliar. However, confidence can be gained in their application through comprehensive validation, which is described in Appendix C.

### 1.3 The ERG PM10 Model

#### 1.3.1 Model Description

A new PM10 model has been developed specifically for the Stage 4 modelling study (Fuller et al., 2002). It uses the comprehensive PM10, PM2.5 and NO<sub>x</sub> measurements to derive a model to predict daily concentrations of PM10. The model splits PM10 into 4 component parts and relates each to the likely source/s of the particles. To achieve this, regression analysis of NO<sub>x</sub> with PM10 has been employed. Stedman (2000, 2001) and APEG (1999) used a similar analysis, however the ERG model has extended this to include PM2.5. The four component parts are summarised as:

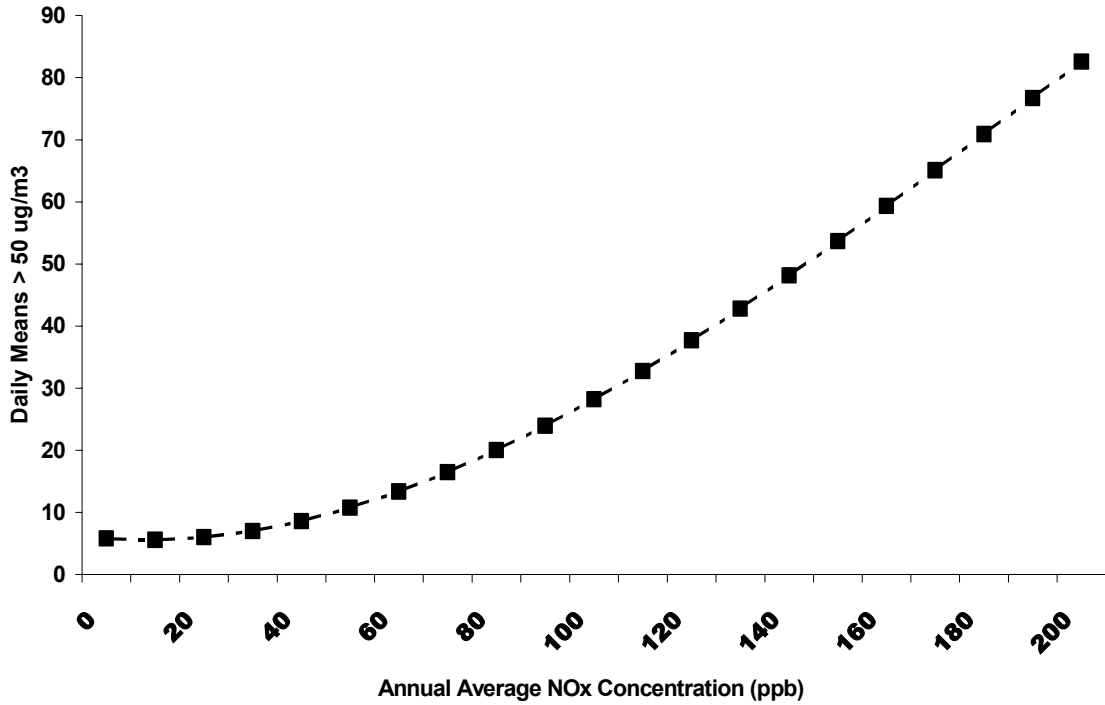
- PM2.5 that is related to NO<sub>x</sub>
- PM2.5 that is not related to NO<sub>x</sub>
- Coarse particles that are related to NO<sub>x</sub>
- Coarse particles that are not related to NO<sub>x</sub>.

### **1.3.2 Measurements used in the PM10 Model**

To determine the relationship between NO<sub>x</sub> and PM10, regression analysis has been undertaken for co-located rolling annual mean concentrations of NO<sub>x</sub>, PM10 and PM2.5 at monthly intervals. Rolling annual means have been chosen to test the stability of the derived relationships over time. A total of over 10 million, 15 minute mean measurements from November 1995 to March 2000 have been averaged to produce the rolling annual means at each site. Data have been used from all site types: kerbside, roadside, urban background, suburban and rural. A maximum of 22 sites have been used for PM10 and maximum of 5 sites for PM2.5. The sites used in each regression are not consistent and depend on the operational start date for each site and at least 75% annual data capture.

### **1.3.3 Modelling Daily Particle Concentrations**

Since the EU Limit values refer to daily mean concentration it is necessary to model and understand the particle concentrations with a daily time resolution. Time series of daily means for each of the components were calculated by applying the factors derived from regression analysis, to the daily mean NO<sub>x</sub>, PM10 and PM2.5 measured at each of the sites with co-located measurements. This allowed the calculation of the NO<sub>x</sub> dependent components. The non-NO<sub>x</sub> dependent components can be calculated by subtraction. Time series of each of the components has been calculated for the four years 1996 to 1999, inclusive. An example of the relationship between annual mean NO<sub>x</sub> and number of days greater than 50 µg/m<sup>3</sup> for 1999 (using the TEOM to gravimetric scaling factor of 1.3), is summarised in Figure 2 below.



**Figure 2** The relationship between annual mean NO<sub>x</sub> and days where PM10 > 50 µg/m<sup>3</sup>

**1.3.4 Background concentrations**

The predicted concentrations of PM10 at background locations are determined using the same method as for NO<sub>x</sub>, described earlier in section 1.2.1 of this Appendix.

For predictions in future years each part of the emissions information used can be changed independently. For example, in 2004 it has been assumed that the rural PM10 concentration reduces in line with national predictions for the primary and secondary components.

**1.3.5 Roadside concentrations**

The determination of concentrations of PM10 at the roadside is described in the next Appendix.