Analysis of the relationship between ambient levels of O₃, NO₂ and NO as a function of NOₓ in the UK

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Abstract

Monitoring data from the UK Automatic Urban and Rural Network are used to investigate the relationships between ambient levels of ozone (O₃), nitric oxide (NO) and nitrogen dioxide (NO₂) as a function of NOₓ, for levels ranging from those typical of UK rural sites to those observed at polluted urban kerbside sites. Particular emphasis is placed on establishing how the level of ‘oxidant’, OX (taken to be the sum of O₃ and NO₂) varies with the level of NOₓ, and therefore to gain some insight into the atmospheric sources of OX, particularly at polluted urban locations. The analyses indicate that the level of OX at a given location is made up of NOₓ-independent and NOₓ-dependent contributions. The latter is effectively a local contribution which correlates with the level of primary pollution. The local oxidant source has probable contributions from (i) direct NO₂ emissions, (ii) the thermal reaction of NO with O₂ at high NOₓ, and (iii) common-source emission of species which promote NO to NO₂ conversion. The final category may include nitrous acid (HONO), which appears to be emitted directly in vehicle exhaust, and is potentially photolysed to generate HOₓ radicals on a short timescale throughout the year at southern UK latitudes. The analyses also show that the local oxidant source has significant site-to-site variations, and possible reasons for these variations are discussed.

Relationships between OX and NOₓ, based on annual mean data, and fitted functions describing the relative contributions to OX made by NO₂ and O₃, are used to define expressions which describe the likely variation of annual mean NO₂ as a function of NOₓ at 14 urban and suburban sites, and which can take account of possible changes in the regional background of O₃.

Keywords: Ozone; Nitrogen dioxide; NOₓ; Oxidant; Regional pollution; Local pollution; Nitrous acid; Monitoring networks

1. Introduction

Ozone (O₃) and nitrogen dioxide (NO₂) are included in a series of eight air pollutants identified as part of the ‘Air Quality Strategy for England, Scotland, Wales and Northern Ireland’ (AQS, 2000), by virtue of their adverse impact on human health and the natural environment. The strategy sets air quality standards, based on scientific assessment of the potential impacts of the individual pollutants (e.g. EPAQS, 1994, 1996; WHO, 1994, 1995), and establishes objectives identifying the extent to which these standards should be achieved within a given timeframe. The ability to meet these objectives clearly depends on the influence of emission controls on future pollutant levels. Owing to the chemical coupling of O₃ and NOₓ (= NO + NO₂), the levels of O₃ and NO₂ are intrinsically linked. Consequently, the response to reductions in the emissions of NOₓ is highly non-linear (e.g. QUARG, 1993; PORG, 1997), and any resultant reduction in the level of NO₂ is invariably accompanied by an increase in the level of O₃. In addition, changes in the level of O₃ on a global scale lead to an increasing background which influences local...
O₃ and NO₂ levels and the effectiveness of local emission controls. It is therefore necessary to have a complete understanding of the relationships between O₃, NO and NO₂ under atmospheric conditions, if the success of the proposed control strategies is to be fully assessed.

In the present paper, monitoring data from a selection of southern UK sites are used to investigate the relationships between ambient levels of O₃, NO and NO₂ as a function of NOₓ, for levels of NOₓ ranging from those typical of UK rural sites to those observed at polluted urban kerbside sites. Particular emphasis is placed on establishing how the level of ‘oxidant’, OX (taken to be the sum of O₃ and NO₂) varies with the level of NOₓ, and therefore to gain some insight into the atmospheric sources of OX, particularly at polluted urban locations. The observed relationships between O₃, NO and NO₂ are also considered within the context of current understanding of their chemical coupling.

2. Analysis of monitoring data

2.1. Source of data

O₃ and NOₓ are simultaneously monitored at approximately 60 sites throughout the UK, as part of the Automatic Urban and Rural Network (AURN) set up by the ‘Department of the Environment, Transport and the Regions’, the ‘Scottish Executive’, the ‘National Assembly for Wales’ and the ‘Department of the Environment for Northern Ireland’. Measurements are made by well-established, conventional techniques (UV photometry for O₃ and chemiluminescence for NOₓ), using commercial instrumentation. Ambient mixing ratios are reported at hourly resolution, and may be obtained from the National Air Quality Information Archive at the AEA Technology National Environmental Technology Centre website (http://www.aeat.co.uk/netcen/airqual).

The analysis presented below has focused on selected locations in London and southern England, and has considered averaging intervals ranging between 1 h and 1 yr. Much of the analysis has concentrated on 1998 and 1999 data from four sites in central and west London, namely Marylebone Road (urban kerbside), Bloomsbury (urban centre), Hillingdon (suburban) and Teddington (urban background), and additional data from Reading, Berkshire (urban background) and Harwell, Oxfordshire (rural), allowing a wide range of NOₓ levels (typically ca. 2–500 ppbv) to be considered. Some information about the location and characteristics of these sites is given in Table 1. For the analysis of the annual mean data, additional London sites and additional years have also been considered, as discussed further in Section 2.6.

Much of the analysis has used ‘daylight-averaged’ data for the sites in Table 1. The hours of daylight for each day in 1998 and 1999 were defined on the basis of sunrise and sunset times obtained from the ‘astronomical applications’ facility on the US Naval Observatory website (http://aa.usno.navy.mil/AA/). Since monitoring data are available at hourly resolution, daylight hours were defined as complete hours falling between sunrise and sunset and, where available, the

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>Brief site description</th>
<th>Annual mean NOₓ (2000) a,b (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harwell</td>
<td>51.573°N 1.316°W</td>
<td>Rural site in field adjacent to Harwell Science Centre in Oxfordshire</td>
<td>9.4</td>
</tr>
<tr>
<td>Reading</td>
<td>51.453°N 0.954°W</td>
<td>Urban background site in technical college grounds, 20 m from A4 dual carriageway</td>
<td>37</td>
</tr>
<tr>
<td>London Teddington</td>
<td>51.422°N 0.339°W</td>
<td>Urban background site on rooftop in grounds of the National Physical Laboratory, about 500 m from the nearest road</td>
<td>23</td>
</tr>
<tr>
<td>London Hillingdon</td>
<td>51.496°N 0.461°W</td>
<td>Suburban site in residential area, 30 m from M4 motorway</td>
<td>73</td>
</tr>
<tr>
<td>London Bloomsbury</td>
<td>51.523°N 0.129°W</td>
<td>Urban centre site in garden area surrounded by an enclosed square of busy roads between 40 and 140 m from the site</td>
<td>59</td>
</tr>
<tr>
<td>London Marylebone Rd.</td>
<td>51.521°N 0.155°W</td>
<td>Kerbside site 1 m from busy street canyon (50,000 vehicles per day)</td>
<td>210 ppbv</td>
</tr>
</tbody>
</table>

a More detailed information is available from the National Air Quality Information Archive at http://www.aeat.co.uk/netcen/airqual.

b Although there is significant month-to-month variability, typical ranges in daily daylight-averaged NOₓ are as follows: Harwell, 2–20 ppbv; Reading, 15–150 ppbv; Teddington, 10–100 ppbv; Hillingdon, 15–300 ppbv; Bloomsbury, 40–250 ppbv; Marylebone Rd, 50–500 ppbv.
corresponding data were averaged to provide a single value for each of O₃, NO and NO₂ for each site for each day in 1998 and 1999. If more than 25% of data for a particular day/site/pollutant were unavailable, an average value was not defined.

2.2. The chemical coupling of O₃, NO and NO₂

It is well established that the interconversion of O₃, NO and NO₂ under atmospheric conditions is generally dominated by the following reactions (Leighton, 1961):

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2, \quad (1)
\]

\[
\text{NO}_2 + h\nu (+\text{O}_2) \rightarrow \text{NO} + \text{O}_3, \quad (2)
\]

which constitute a cycle with no net chemistry (i.e., the overall effect of reaction (2) is the reverse of reaction (1)). These reactions therefore represent a closed system which has the overall effect of partitioning NOₓ between its component forms of NO and NO₂, and oxidant (OX) between its component forms of O₃ and NO₂, but leaving the total mixing ratio of both NOₓ and OX unchanged. During daylight hours, NO, NO₂ and O₃ are typically equilibrated on the timescale of a few minutes, a condition usually referred to as ‘photostationary state’. The above cycle predicts that the photostationary state mixing ratios of the three species are related by the expression \([\text{NO}] \cdot \frac{[\text{O}_3]}{[\text{NO}_2]} = \frac{J_2}{k_1}\), where \(J_2\) is the rate of NO₂ photolysis, and \(k_1\) is the rate coefficient for the reaction of NO with O₃.

The observed variation of daylight average mixing ratios of O₃, NO and NO₂ with the total level of NOₓ is shown in Fig. 1 for November 1998 and 1999, using data from all six monitoring sites in Table 1. The lines in Fig. 1 were calculated using a November daytime average value of \(J_2 = 2.9 \times 10^{-3} \text{s}^{-1}\) (51.5°N latitude) with the assumption of photostationary state. Clearly, this provides an adequate description of the daylight-averaged observations, consistent with the chemical coupling of these species being dominated by reactions (1) and (2).

2.3. Local and regional contributions to oxidant

The data in Fig. 1 indicate that the NOₓ crossover point occurs at about 60 ppbv NOₓ. At lower levels, NO₂ is the major component of NOₓ, whereas NO dominates at higher mixing ratios. The OX crossover point occurs at about 25 ppbv NOₓ, with O₃ being the dominant form at lower levels, and NO₂ dominating at higher levels. This pattern is typical, although the precise crossover points vary with conditions (e.g., with the value of \(J_2\)).

Fig. 2a shows the same November 1998 and 1999 daylight data for O₃ and NO₂ on a linear NOₓ scale. This clearly shows the interconversion of O₃ and NO₂ as a function of NOₓ, but also indicates that NO₂ levels continue to increase with NOₓ when O₃ is almost completely removed (i.e. at > ca. 100 ppbv NOₓ). Indeed, Fig. 2b shows that the total OX appears to

![Figure 1](image-url)
increase linearly with NOx over the entire range considered, such that the level of OX at a given location has an NOx-independent contribution, and an NOx-dependent contribution. The former is effectively a regional contribution which equates to the regional background O3 level, whereas the latter is effectively a local contribution which correlates with the level of primary pollution.

Daylight average analyses were carried out for each month of the year, using the 1998 and 1999 data combined. A similar dependence of OX on NOx was observed for each month, although the data from the ‘photochemical season’ (April–September) showed significantly greater scatter than the winter months owing to a variation in the regional contribution resulting from periodically elevated levels of O3 during regional-scale photochemical events. The data for these months were therefore filtered to separate out ‘ozone episode’ days using the criterion that such days corresponded to a daylight average OX mixing ratio of > 50 ppbv at Teddington (the least polluted urban site considered). Fig. 3 shows the results of the analysis using the June data. This clearly shows that the level of OX at the complete range of sites was significantly elevated on episode days, as a result of the increased regional contribution, but that the local contribution (i.e. the slope) was not significantly influenced.
The seasonal variation of the regional and local contributions to OX are presented in Fig. 4, with the parameters for April–September obtained from an analysis of non-episode days only. As might be expected, the regional contribution (Fig. 4a) shows a seasonality with the characteristic springtime maximum observed for ‘background’ O3 in the Northern Hemisphere (e.g., see Monks, 2000). The local contribution (Fig. 4b) shows remarkably little variation with season, and amounts to about 10% of the NO\textsubscript{x} level throughout the year, based on an analysis of daylight-averaged data. Clearly, therefore, this can lead to a substantial ‘oxidant excess’ at polluted locations.

The local, NO\textsubscript{x}-dependent contribution could result from a number of sources, the most obvious being direct emission of a proportion of NO\textsubscript{x} in the form of NO\textsubscript{2}. The dominant NO\textsubscript{x} source in urban locations is road traffic exhaust. Available studies of combustion-related vehicular emissions indicate that the proportion of NO\textsubscript{x} emitted in the form of NO\textsubscript{2} depends on vehicle and fuel type, and on driving conditions (e.g., Heywood, 1988). For example, the output from diesel vehicles not only contains more NO\textsubscript{x} generically, but is also likely to have a higher proportion of NO\textsubscript{x} as NO\textsubscript{2}. In addition the NO\textsubscript{2}/NO\textsubscript{x} ratio is likely to decrease at higher speeds when the engine is under greater load. Although it is probable, therefore, that NO\textsubscript{2} input from direct emission varies from one location to another, or from one time to another, as a result of varying vehicle fleet composition and driving speeds, an average figure of approximately 5% (by volume) is often quoted (e.g., PORQ, 1997).

Direct emissions of NO\textsubscript{2} are therefore unlikely to account fully for the observed local oxidant contribution, suggesting that chemical sources are also likely to contribute. The termolecular reaction of NO with molecular oxygen,

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2, \]  

provides an additional thermal source of oxidant. The rate of this reaction is strongly dependent on the NO concentration, such that it is much more rapid at the elevated levels typical of those close to points of emission. For example, the time for 1% conversion of NO to NO\textsubscript{2} by this reaction is ca. 20 s at 100 ppbv NO in air, but increases dramatically as NO is diluted. At 500 ppbv NO (i.e. typical of the average at the high end of the range considered in the present analysis) the time for 1% conversion is ca. 1 h. It is probable, therefore, that some NO to NO\textsubscript{2} conversion by reaction (3) occurs immediately after emission before the reaction is effectively halted (or at least significantly reduced in rate) by dilution.

Reaction (3) has certainly been postulated to make a major contribution to NO\textsubscript{2} formation in wintertime pollution episodes when a shallow inversion layer can lead to a combination of high NO\textsubscript{x} levels and stagnant air for periods of a day or more (e.g., Bower et al., 1994). In addition, previous analyses of data obtained at Cromwell Road, London in 1991 and 1992 (e.g., QUARG, 1993) indicate a significant upward curvature in the NO\textsubscript{2} vs. NO\textsubscript{x} relationship (which would also be expected in the OX vs. NO\textsubscript{x} relationship) at NO\textsubscript{x} levels

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**Fig. 3.** Variation of daylight average mixing ratios of oxidant (OX) with the level of NO\textsubscript{x}. Data are presented for each day of June 1998 and 1999 at the six sites listed in Table 1. The lines were defined by regression analysis of ‘non-episode’ and ‘episode’ days (see discussion in text).
greater than about 1 ppmv, suggesting that such levels are generally required for reaction (3) to make a notable contribution to OX generation. It should be noted that the average NO\textsubscript{x} levels of this magnitude are now rarely observed in the UK, even at roadside sites, owing to the influence of NO\textsubscript{x} emission reductions from their peak value in 1991.

Other possible NO\textsubscript{x}-dependent sources of OX may derive from the concurrent emission of species which can lead to NO to NO\textsubscript{2} conversion. It is well-established that the sunlight-initiated, free radical catalysed degradation of VOC in the presence of NO\textsubscript{x} leads to the oxidation of NO to NO\textsubscript{2} (e.g. Atkinson, 1998; Jenkin and Clemitshaw, 2000). Consequently, the common-source emission of free radical precursors may provide additional sources of OX under polluted urban conditions. Two potential candidates are formaldehyde, HCHO (and possibly other carbonyls), and nitrous acid, HONO. HCHO is known to be emitted in road traffic exhaust (e.g., PORG, 1993), and there is some evidence for direct emissions of HONO (e.g., Kurtenbach et al., 2001; Martinez-Villa et al., 2000; Pitts et al., 1984). Each is comparatively photolabile, and may therefore lead to the generation of free radicals, and therefore NO to NO\textsubscript{2} conversion, in the sunlit atmosphere as shown schematically in Fig. 5. The presence of reactive VOC in general allows closure of the well-established free radical propagated cycle, and the possibility that each photolysis event may lead to several NO to NO\textsubscript{2} conversions before free radical loss by an alternative reaction (e.g., OH + NO\textsubscript{2}; OH + NO).

The potential importance of these species in leading to NO to NO\textsubscript{2} conversion depends on (i) their efficiency of photolysis to generate radicals, and (ii) on the ‘chain-length’ for NO\textsubscript{2} formation, i.e. essentially the number of free radical propagated cycles in Fig. 5 which occur under the prevailing ambient conditions. The photolysis lifetime of HCHO in the southern UK is ca. 6 h and 1 day under daylight-averaged midsummer and midwinter conditions, respectively. Consequently, it is unlikely that photolysis of emitted HCHO can have the major short-timescale impact required to contribute to the NO\textsubscript{x}-dependent oxidant source presented here, although it is recognised that HCHO (which is formed more significantly from VOC oxidation) does ultimately make an important contribution to boundary layer radical production. HONO is significantly more photolabile, its photolysis lifetime being typically 15 and 40 min under daylight-averaged midsummer and midwinter conditions, respectively (PORG, 1997). Consequently, emitted HONO may be photolysed comparatively rapidly throughout the year to generate free radicals, with the subsequent efficiency of the cycle in Fig. 5 depending mainly on the VOC/NO\textsubscript{x} ratio.

Fig. 4. Seasonal variation of (a) regional (i.e. NO\textsubscript{x}-independent) source of OX, and (b) local (i.e. NO\textsubscript{x}-dependent) source of OX. O\textsubscript{3} episode days (daylight average OX > 50 ppbv at Teddington) have been excluded from the analysis (see text). Error bars represent ±2σ.

Fig. 5. Schematic representation of the potential role of HONO and HCHO in initiating the free radical catalysed oxidation of VOC under polluted urban conditions, and the resultant oxidation of NO to NO\textsubscript{2}.
To test the potential importance of direct emissions of HONO, illustrative calculations were carried out using a photochemical trajectory model containing a detailed description of emissions of NO\textsubscript{X} and VOC, and boundary layer chemical processes (as described in detail by Derwent et al., 1998). A series of parallel linear trajectories travelling for 8h in an easterly direction to six arrival points in the London region at midday were considered to allow simulation of a range of NO\textsubscript{X} levels. Two sets of calculations were performed, one with NO\textsubscript{X} emitted as 95% NO and 5% NO\textsubscript{2}, and one with NO\textsubscript{X} emitted as 94% NO, 5% NO\textsubscript{2} and 1% HONO. This approximate proportion of HONO emission has been inferred from recent ambient measurements of HONO in roadside and tunnel studies (e.g., Kurtenbach et al., 2001; Martinez-Villa et al., 2000). Fig. 6 shows the simulated OX mixing ratios at the six trajectory endpoints as a function of NO\textsubscript{X} for midwinter conditions. These results demonstrate that direct emissions of HONO have a notable influence on the simulated level of OX, particularly at the more polluted locations. A regression analysis suggests an average increase of over 3% in the local contribution to OX (i.e., the slope), on the basis of the illustrative scenario considered. A similar set of calculations for midsummer conditions indicated a simulated average increase of ca. 4% in the local contribution to oxidant, suggesting that the influence of a 1% HONO emission may be significant and comparable throughout the year.

It should also be noted that the free radical-initiated oxidation chemistry oxidises emitted VOC into their first generation carbonyl products (see Fig. 5). Some carbonyl products, in particular the \(\alpha\)-dicarbonyls formed in significant yield from aromatic hydrocarbon oxidation (e.g. Atkinson, 1994) are themselves very photolabile, and can therefore lead to additional free radical generation (and NO to NO\textsubscript{2} conversion) on a comparatively short timescale.

2.4. Diurnal variations in OX–NO\textsubscript{X} relationship

The above analysis has so far considered daylight-averaged data. If photochemistry has an influence on OX levels at polluted locations, then a difference between daylight and nighttime might be expected. Further analysis of the dependence of OX on NO\textsubscript{X} for nighttime averaged data indicates that the local contribution to oxidant is consistently 2–3% lower at night throughout the year (e.g. see the comparison of November daylight- and nighttime-averaged data in Figs. 2 and 7). This analysis was further extended for selected months by investigating whether there is any hour-to-hour variation in the slope and/or intercept of the OX vs. NO\textsubscript{X} relationship. The corresponding data for January, March and August 1999 (shown in Fig. 8) confirm that there is a distinct diurnal dependence in the local contribution to oxidant, providing further evidence for the role of photochemistry on a local scale throughout the year. The diurnal variation of the regional contribution is typical of that observed for O\textsubscript{3} at unpolluted sites (e.g. see PORG, 1997), being almost absent in the winter, but showing an amplitude of about 20 ppbv in the summer.

Fig. 6. Simulated OX mixing ratios at six trajectory endpoints under midwinter conditions (see text). (1) NO\textsubscript{X} emitted as 95% NO and 5% NO\textsubscript{2}; (2) NO\textsubscript{X} emitted as 94% NO, 5% NO\textsubscript{2} and 1% HONO.
Fig. 7. Variation of nighttime average mixing ratios of oxidant (OX) with the level of NO\textsubscript{x}. Data are presented for each night of November 1998 and 1999 at the six sites listed in Table 1.

Fig. 8. Hour-by-hour variation of (a) regional (i.e. NO\textsubscript{x}-independent) source of OX, and (b) local (i.e. NO\textsubscript{x}-dependent) source of OX, for selected months in 1999 (data are for hour ending with the given time).
2.5. Site-to-site variations

The analyses presented above have made use of data from six monitoring sites with overlapping NO\textsubscript{x} ranges to cover a wide range of conditions, and it is apparent (e.g. from Fig. 1) that the data can largely be considered as a continuous data set. However, some of the more polluted sites cover a comparatively wide range of NO\textsubscript{x} (on a linear scale), and it is possible to perform similar analyses to those above for individual sites. The daylight-averaged data from Marylebone Rd (typically 50–500 ppbv), Bloomsbury (typically 40–250 ppbv) and Hillingdon (typically 15–300 ppbv) have therefore been analysed, with the particular aim of comparing the magnitudes of the local (i.e. NO\textsubscript{x}-dependent) oxidant sources at these sites.

Fig. 9 summarises the results for Marylebone Rd and Bloomsbury for each month of the year. Whereas the local oxidant contributions at the two sites are comparable for most of the year, the data provide clear evidence that the local source is substantially greater in mid-summer (July and August) than at Bloomsbury. A possible reason for this is the contribution of summertime biogenic hydrocarbon emissions very locally to the Bloomsbury monitoring site. This site is located in a central London ‘garden’ surrounded by an enclosed square of busy roads. The gardens are generally laid to grass with many mature trees, providing the possibility of elevated emissions of reactive biogenic hydrocarbons (e.g. isoprene) in the summer months. Such emissions would increase the local VOC/NO\textsubscript{x} ratio, and therefore the efficiency of the free radical catalysed cycles shown in Fig. 5. In contrast, the Marylebone Rd site has no significant biogenic sources in the vicinity of the site.

Hydrocarbon measurements are not made at the Bloomsbury site, so it is not possible to test this hypothesis directly. However, Fig. 10 shows a comparison of isoprene and 1,3-butadiene data measured at the London Eltham site and Marylebone Rd. Similar to Bloomsbury, the Eltham site has areas of grass and mature trees locally. Whereas 1,3-butadiene is believed to be solely of anthropogenic origin (primarily in vehicle exhaust), isoprene has contributions from both exhaust emissions and biogenic sources. Fig. 10 shows that the ratio isoprene/1,3-butadiene is consistently ca. 0.5 at both sites in the winter months (October–April). This figure is indicative of the relative emissions in vehicle exhaust, and is similar to previously reported values for locations in the UK, Canada and Switzerland (Burgess and Penkett, 1993; Derwent et al., 1995; McLaren et al., 1996; Reimann et al., 2000). During the summer months, the ratio at Marylebone Rd remains approximately constant, whereas the ratio at Eltham increases significantly, maximising in July and August when biogenic sources are most important. Local biogenic hydrocarbon sources therefore have a significant influence on the VOC/NO\textsubscript{x} ratio at Eltham, and the same may be true at Bloomsbury.

Fig. 9 also compares the magnitude of the local oxidant source at Hillingdon with those observed at the other sites. Owing to poor data capture for one or more of O\textsubscript{3}, NO and NO\textsubscript{2} during the months April–July, it is not possible to present OX vs. NO\textsubscript{x} data for this site in isolation during these months. However, for the months for which comparison is possible, the local source of oxidant is consistently lower than at Marylebone Rd, typically by ca. 3–4%. Despite being in a suburban area, the Hillingdon site is comparatively polluted because it is located adjacent to the M4 motorway, which provides the major local source of NO\textsubscript{x}.

Consequently, the characteristics of the site are somewhat different from those of Marylebone Rd and Bloomsbury, at least in terms of the driving conditions.
of the traffic providing the local NO\textsubscript{2} source. Whereas the traffic adjacent to the Marylebone Rd site, and in the vicinity of the Bloomsbury site, tends to be slow-moving or stationary, that adjacent to the Hillingdon site is generally moving significantly more rapidly. As discussed above in Section 4, it is probable that the proportion of NO\textsubscript{2} in the NO\textsubscript{x} emitted from the faster moving traffic is lower, and this may explain the consistently lower local oxidant contribution at Hillingdon.

2.6. Analysis of annual mean data

The analyses presented above have defined relationships between OX and NO\textsubscript{x} on the basis of linear regressions of data obtained at a number of sites (or selected individual sites) on a large number of days. In principal, a similar analysis can be performed using the annual mean data for sites where O\textsubscript{3}, NO and NO\textsubscript{2} are measured.

Fig. 11 shows how the annual mean levels of OX depend on NO\textsubscript{x} for the majority of London sites where the required measurements are available, and for Reading and Harwell. Clearly, the same general trend to the previous analyses is observed, but the data show a surprisingly large amount of scatter, given the level of averaging which has taken place. Closer inspection reveals that the scatter is primarily due to site-to-site variations with a given site showing a reasonably consistent pattern from one year to another. This is, perhaps, more apparent in Fig. 12, which shows only the data for the five urban and suburban sites considered in the previous analysis. In each case an associated regression line is presented, based on an intercept fixed at the value derived from analysis of the entire data set in Fig. 11 (although analysis of the comparably large Bloomsbury data set alone provided an almost identical intercept). Fig. 12 clearly shows a variation in magnitude of the local source of OX at Marylebone Rd, Bloomsbury and Hillingdon which is broadly consistent with the analysis presented in Section 2.5.

It has been recognised for some time that the annual average NO\textsubscript{2} levels show a distinct variation from one site to another, even for sites for which the annual average NO\textsubscript{x} is comparable (e.g. Stedman, 1999; Stedman et al., 1998, 2000). The above analysis suggests that this is partly due to variations in the local sources of OX from one site to another, resulting from a number of possible factors (e.g. local driving conditions; vehicle fleet composition; local sources of biogenic hydrocarbons), as discussed in previous sections. However, also of importance is the precise partitioning of OX between its component forms of NO\textsubscript{2} and O\textsubscript{3}. Fig. 13 shows the fraction of OX which is in the form of NO\textsubscript{2}, based on the annual average data for the sites in Fig. 10. As expected, the data generally show that a progressively greater proportion of OX is in the form of NO\textsubscript{2} as the level of NO\textsubscript{x} increases. However, the data appear to fall into two reasonably distinct groups, the first containing Hillingdon, Hackney, Wandsworth, Reading and Marylebone Rd, and the second containing the remaining sites, which generally show higher NO\textsubscript{2}/OX ratios. Although the reason for this distinction is not fully clear, such differences in the partitioning of NO\textsubscript{2} and O\textsubscript{3} presumably must relate (at least partially) to rates of, or the time available for, chemical processes. For example, a smaller proportion of OX might be expected to be in the form of NO\textsubscript{2} if either the photolysis rate (\(J_{\text{2}}\)) is notably higher at these sites (e.g. because they spend a greater proportion of the time out of the shade, or the local surfaces are of particularly high reflectivity), or there is significantly less time for the conversion of emitted NO to NO\textsubscript{2} to occur because the air flow is less stagnant at
these sites, or they are much closer to source. A short
time-lag between emission and measurement most likely
accounts for the low ratios in the first group identified
above: Marylebone Rd is a kerbsite site, Hackney and
Wandsworth are first-floor sites overlooking busy roads,
and the Hillingdon and Reading sites are in compara-
tive locations 30 and 20 m, respectively, from local traffic sources.

On the basis of the photostationary state relationship
discussed in Section 2.2 it is possible to infer an
expected variation of NO2/OX. The idealised variation
is also presented in Fig. 13, based on an estimated
annual average value of \( J_2 = 2.2 \times 10^{-3} \text{ s}^{-1} \), estimated from output of a two-stream isotropic scattering flux model (Hayman, 1997) for 51.5°N latitude. The
precise form shows a very weak dependence on the applied OX vs. NOx relationship which was taken to be the overall regression shown in Fig. 12. The other lines are fitted polynomial expressions based on data for groups of sites (see text).

![Fig. 13. Variation of annual mean [NO2]/[OX] as a function of NOx for London sites where O3, NO and NO2 are measured, Reading and Harwell. The black line is the calculated idealised variation based on the assumption of photostationary state and a value of \( J_2 = 2.2 \times 10^{-3} \text{ s}^{-1} \), estimated from output of a two-stream isotropic scattering flux model (Hayman, 1997) for 51.5°N latitude. The precise form shows a very weak dependence on the applied OX vs. NOx relationship which was taken to be the overall regression shown in Fig. 12. The other lines are fitted polynomial expressions based on data for groups of sites (see text).](image-url)
curveislikelytooverpredicttheproportionofOXinthe
formofNO\textsubscript{2},particularlyforsiteswhereNO\textsubscript{X}
levelsare
intheregionof40ppbvforasignificantproportionof
thetime.

Fromtheabovediscussion,itisclearthatitisdifficult
todefinetheoreticalexpressionswhichquantitatively
describethehowno\textsubscript{2}levelvarieswithNO\textsubscript{x},
eventhoughthequalitativebehaviourisadequatelyexplained
bycurrentunderstandingoftheprocessesinvolved.The
analysissuggeststhatitispermissibletoestablishreason-
ablyrobustexpressionswhichdescribethehowtheannual
meanOXlevelvarieswithNO\textsubscript{x},andwhichtakeaccount
ofsiteto-sitievaryingsitesaperfectsuchexpressionsis
providedinTable2foreachoftheurbanandsuburban
sitesinFig.11).However,thepreciserelationship
betweenannualmeanNO\textsubscript{2}andannualmeanOXis
subjecttoseveralvaryingfactors,andaappearnecessary
tousefittedfunctionsgroupsofsiteswith
particularlycharacteristics.The dataforthetwogroups
showninFig.13havethereforebeendesignedtoderive
the twopolynomialexpressionsgiveninTable2,anda
illustratedinthefigure.The datafortHarwellwereincluded
inbothsetstolowtheNO\textsubscript{x}rangeonetolow
levels.

TheexpressionsinTable2thereforeallow[NO\textsubscript{2}]vs.
[NO\textsubscript{x}]curvestobeinferredforall14urbanand
suburban sites. This is illustrated in Fig. 12 for the five
sites included in the more detailed analysis presented
inprevioussections. For the most part, the resultant curves
forNO\textsubscript{2}provideagooddescriptionofthedatatheach
site, eventhoughaslightbiasmayresultfromusing
expressionsforNO\textsubscript{2}/OXderivedfromfittingseveral
sites to describe individual sites. The inferred curves for
NO\textsubscript{2}allowtheannualmeanNO\textsubscript{X}mixingratioswhich
correspondtotheWHO21ppbvairquality guideline

<table>
<thead>
<tr>
<th>Site</th>
<th>[OX] = A [NO\textsubscript{x}] + B\textsuperscript{a}</th>
<th>[NO\textsubscript{2}]/[OX]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bexley</td>
<td>0.0771 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Bloomsbury</td>
<td>0.1272 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Brent</td>
<td>0.0616 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Bridge Place</td>
<td>0.1572 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Eltham</td>
<td>0.0477 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Hackney</td>
<td>0.1391 Fit 2</td>
<td></td>
</tr>
<tr>
<td>Hillingdon</td>
<td>0.0375 Fit 2</td>
<td></td>
</tr>
<tr>
<td>Lewisham</td>
<td>0.0332 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Marylebone Rd</td>
<td>0.0914 Fit 2</td>
<td></td>
</tr>
<tr>
<td>North Kensington</td>
<td>0.0873 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Reading</td>
<td>0.1121 Fit 2</td>
<td></td>
</tr>
<tr>
<td>Southwark</td>
<td>0.1129 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Teddington</td>
<td>0.0902 Fit 1</td>
<td></td>
</tr>
<tr>
<td>Wandsworth</td>
<td>0.0449 Fit 2</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Linear [OX] vs. [NO\textsubscript{x}] relationships derived from data for
each site presented in Fig. 11, with the assumption that the
regional OX contribution, B = 35.7 ppbv, is site-independent
and equivalent to that derived from the composite analysis of
all sites.

\textsuperscript{b}[NO\textsubscript{2}]/[OX] expressions are polynomial fits to
data presented in Fig. 13:

Fit 1: [NO\textsubscript{2}]/[OX]=(1.015 \times 10^{-1}) + (1.367 \times 10^{-2}) [NO\textsubscript{x}] -(6.127 \times 10^{-4} [NO\textsubscript{x}]^2) - (4.464 \times 10^{-8} [NO\textsubscript{x}]^3); applicable range, 10–90 ppbv NO\textsubscript{x}.

Fit 2: [NO\textsubscript{2}]/[OX]=(8.962 \times 10^{-2}) + (1.474 \times 10^{-2} [NO\textsubscript{x}] - (1.290 \times 10^{-4} [NO\textsubscript{x}]^2) + (5.527 \times 10^{-7} [NO\textsubscript{x}]^3)-(8.906 \times 10^{-10} [NO\textsubscript{x}]^4); applicable range, 10–210 ppbv NO\textsubscript{x}.

for annual mean NO\textsubscript{2} to be estimated for each site.

The resultant values (in ppbv) are: Teddington, 38.7; Reading, 42.1; Hillingdon, 48.6; Bloomsbury, 36.9;
Marylebone Rd, 43.5. Based on year 2000 annual mean NO\textsubscript{x}, the urban background sites (Teddington and Reading) are already below these thresholds, whereas the present analysis infers that NO\textsubscript{x} levels at Hillingdon (suburban), Bloomsbury (urban centre) and Marylebone Rd need to be reduced from 2000 levels by factors of ca. 33%, 37% and 79%, respectively, for the required ca.16%, 32% and 55% reductions in the annual mean NO\textsubscript{2} to be achieved.

It should be noted that this analysis is based on a single unchanging regional background oxidant level of 35.7 ppbv for the southern UK, which is reasonably consistent with the available measurements for the latter half of the 1990s. However, the results of recent global modelling studies suggest a gradual increasing ozone baseline above the UK from 34.3 ppbv in 1990 to 39.2 ppbv in 2030, based on the IPCC SRES (A2 variant) emission scenario (Collins et al., 2000; Stevenson et al., 2000). This corresponds to an average increase of ca. 0.12 ppbv annum\textsuperscript{-1}, which needs to be taken into account when assessing future success in achieving air quality standards. Within the methodology defined above, it is also possible to account for changes in regional oxidant contribution by varying the parameter ‘B’ from the value of 35.7 ppbv used in the present analysis. Fig.15 demonstrates how the NO\textsubscript{x} level corresponding to an annual mean NO\textsubscript{2} of 21 ppbv varies with regional oxidant background up to a value of 37 ppbv, for the same five sites discussed above. These calculations suggest that for every 0.1 ppbv increase in regional oxidant background, additional site-dependent decreases in annual mean NO\textsubscript{x} of between ca. 0.12 and 0.22 ppbv are required, for the NO\textsubscript{2} guideline of 21 ppbv to be achieved or maintained.

3. Conclusions

The analyses presented in the preceding subsections indicate that the level of OX at a given location is made up of NO\textsubscript{x}-independent and NO\textsubscript{x}-dependent contributions. The former is effectively a regional contribution which equates to the regional background O\textsubscript{3} level, whereas the latter is effectively a local contribution which correlates with the level of primary pollution. The local oxidant source has probable contributions from (i) direct NO\textsubscript{2} emissions, (ii) the thermal reaction of NO with O\textsubscript{2} (reaction (3)) at high NO\textsubscript{x}, and (iii) common-source emission of species which promote NO to NO\textsubscript{2} conversion. The final category particularly includes HONO, which appears to be emitted directly in vehicle exhaust, and is photolysed to generate HO\textsubscript{x} radicals on a short timescale throughout the year at southern UK latitudes.

Analysis of selected individual sites shows that the local oxidant source has significant site-to-site variations. These appear to relate to the characteristics of the site, e.g. variations in direct emissions of NO\textsubscript{2} owing to variations in local driving conditions or vehicle fleet composition; local sources of biogenic hydrocarbons which can amplify photochemically induced NO to NO\textsubscript{2} conversion under VOC-limited conditions.

Annual mean data for an extended number of sites demonstrate similar OX vs. NO\textsubscript{x} relationships, also
indicative of regional and local OX contributions, and distinct site-to-site variations. Some site-to-site variation is also apparent in the relative contributions to OX made by NO$_2$ and O$_3$ as a function of NO$_x$.

The presented analyses are either concerned with mean data, or with regressions of data obtained on a large number of days. Consequently, the analyses yield average relationships which may not be a good description of individual events or observations. For example, the daylight-averaged OX data in Fig. 2b show a scatter of ca. ±10 ppbv for a given level of NO$_x$, and observations on higher time resolution will show even greater deviations from the average. This scatter may reasonably be attributed to short-timescale variations in a number of factors discussed above (e.g., driving conditions; vehicle fleet composition; air mass stagnation; overnight accumulation of free-radical precursors).

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