Analysis of the relationship between ambient levels of O_3, NO_2 and NO as a function of NO_x 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 (O_3), nitric oxide (NO) and nitrogen dioxide (NO_2) as a function of NO_x, 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 O_3 and NO_2) varies with the level of NO_x, 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 NO_x-independent and NO_x-dependent contributions. The former is effectively a regional contribution which equates to the regional background O_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_2 emissions, (ii) the thermal reaction of NO with O_2 at high NO_x, and (iii) common-source emission of species which promote NO to NO_2 conversion. The final category may include nitrous acid (HONO), which appears to be emitted directly in vehicle exhaust, and is potentially photolysed to generate HO_x 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 NO_x, based on annual mean data, and fitted functions describing the relative contributions to OX made by NO_2 and O_3, are used to define expressions which describe the likely variation of annual mean NO_2 as a function of NO_x at 14 urban and suburban sites, and which can take account of possible changes in the regional background of O_3. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ozone (O_3) and nitrogen dioxide (NO_2) 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 O_3 and NO_x ($= NO + NO_2$), the levels of O_3 and NO_2 are inextricably linked. Consequently, the response to reductions in the emissions of NO_x is highly non-linear (e.g. QUARG, 1993; PORG, 1997), and any resultant reduction in the level of NO_2 is invariably accompanied by an increase in the level of O_3. In addition, changes in the level of O_3 on a global scale lead to an increasing background which influences local

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O_3 and NO_2 levels and the effectiveness of local emission controls. It is therefore necessary to have a complete understanding of the relationships between O_3, NO and NO_2 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 O_3, NO and NO_2 as a function of NO_x, for levels of NO_x 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 O_3 and NO_2) varies with the level of NO_x, and therefore to gain some insight into the atmospheric sources of OX, particularly at polluted urban locations. The observed relationships between O_3, NO and NO_2 are also considered within the context of current understanding of their chemical coupling.

2. Analysis of monitoring data

2.1. Source of data

O_3 and NO_x 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 O_3 and chemiluminescence for NO_x), 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 focussed 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), Blooms- bury (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 NO_x 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 addi- tional 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 1
Information on selected sites used for detailed analysis of O_3, NO, NO_2 relationships

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

[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 NO_x 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 O_3, NO and NO_2 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 O_3, NO and NO_2

It is well established that the interconversion of O_3, NO and NO_2 under atmospheric conditions is generally dominated by the following reactions (Leighton, 1961):

$$NO + O_3 \rightarrow NO_2 + O_2, \qquad (1)$$

$$NO_2 + hv(+O_2) \rightarrow NO + O_3, \qquad (2)$$
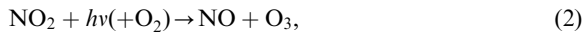
which constitute a cycle with no net chemistry (i.e., the overall effect of reaction (2) is the reverse of reaction (1)). These reactions therefore represent a closed system which has the overall effect of partitioning NO_x between its component forms of NO and NO_2, and oxidant (OX) between its component forms of O_3 and NO_2, but leaving the total mixing ratio of both NO_x and OX unchanged. During daylight hours, NO, NO_2 and O_3 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 $[NO] \cdot [O_3]/[NO_2] = J_2/k_1$, where J_2 is the rate of NO_2 photolysis, and k_1 is the rate coefficient for the reaction of NO with O_3.

The observed variation of daylight average mixing ratios of O_3, NO and NO_2 with the total level of NO_x 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 $J_2 = 2.9 \times 10^{-3}\,s^{-1}$ (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 NO_x crossover point occurs at about 60 ppbv NO_x. At lower levels, NO_2 is the major component of NO_x, whereas NO dominates at higher mixing ratios. The OX crossover point occurs at about 25 ppbv NO_x, with O_3 being the dominant form at lower levels, and NO_2 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 O_3 and NO_2 on a linear NO_x scale. This clearly shows the interconversion of O_3 and NO_2 as a function of NO_x, but also indicates that NO_2 levels continue to increase with NO_x when O_3 is almost completely removed (i.e. at > ca. 100 ppbv NO_x). Indeed, Fig. 2b shows that the total OX appears to
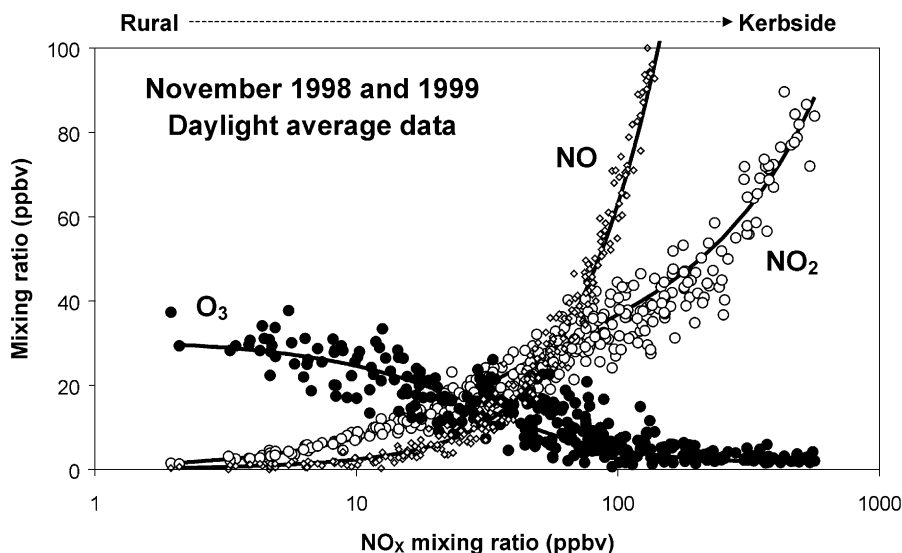

Fig. 1. Variation of daylight average mixing ratios of O_3, NO and NO_2 with the level of NO_x. Data are presented for each day of November 1998 and 1999 at the six sites listed in Table 1 (NB the NO_x axis is logarithmic). The lines were calculated with the assumption of photostationary state, using a daylight-averaged value of $J_2 = 2.9 \times 10^{-3}\,s^{-1}$ (51.5° latitude) which was based on calculations using a two-stream isoptropic scattering model (Hayman, 1997).
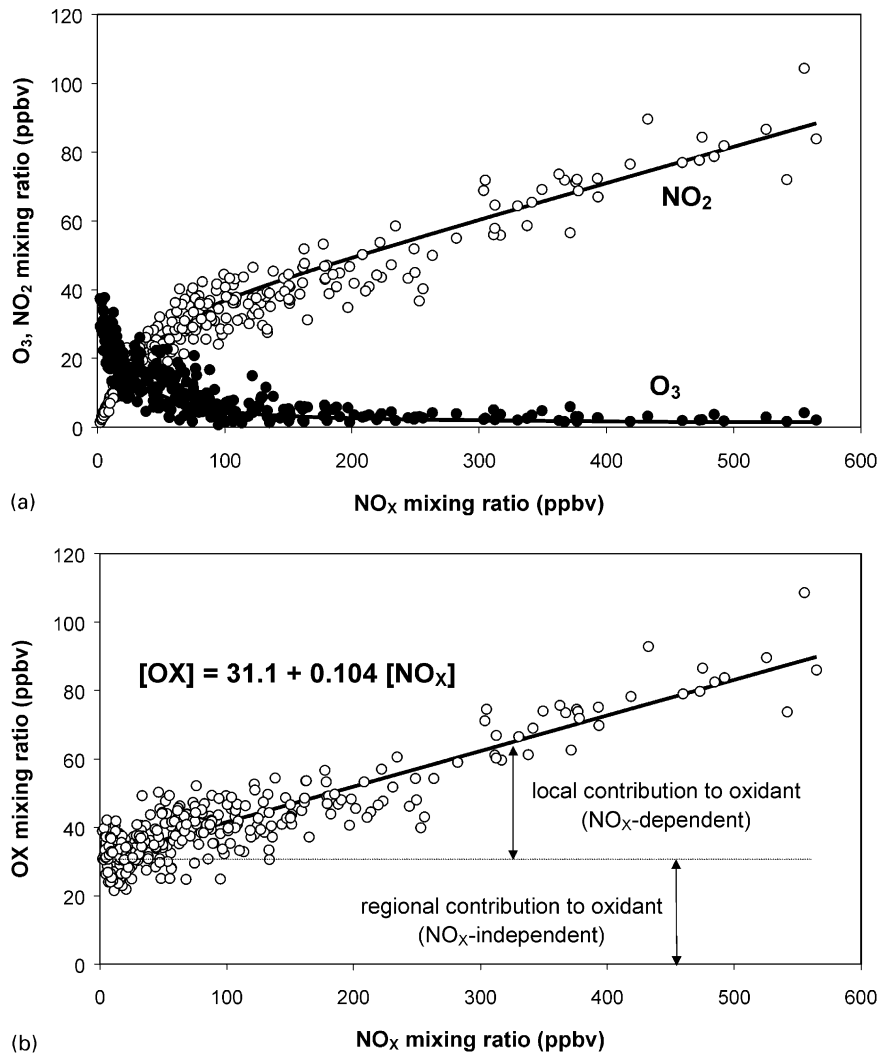
Fig. 2. Variation of daylight average mixing ratios of (a) O_3 and NO_2, and (b) oxidant (OX) with the level of NO_x. Data are presented for each day of November 1998 and 1999 at the six sites listed in Table 1. The lines in Fig. 2(a) were calculated with the assumption of photostationary state (see Fig. 1 caption). The line in Fig. 2(b) was defined by regression analysis.

increase linearly with NO_x over the entire range considered, such that the level of OX at a given location has an NO_x-independent contribution, and an NO_x-dependent contribution. The former is effectively a *regional* contribution which equates to the regional background O_3 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 NO_x 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 O_3 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.
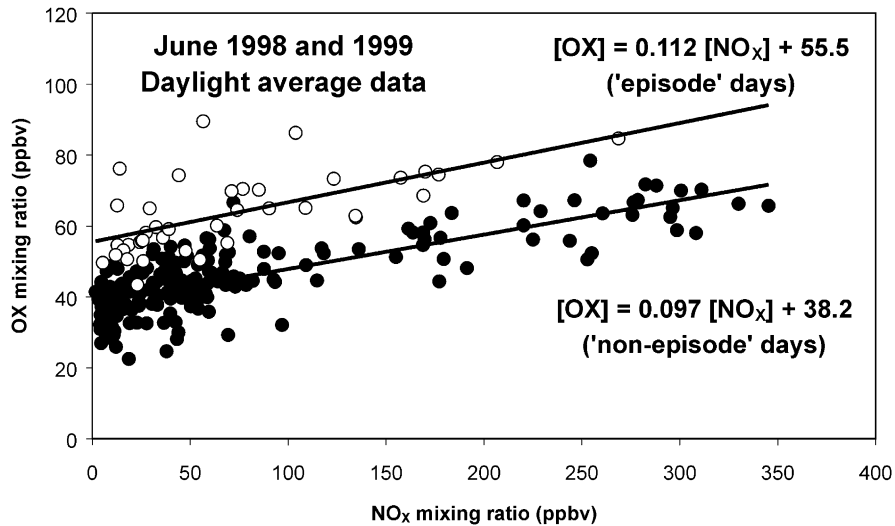
Fig. 3. Variation of daylight average mixing ratios of oxidant (OX) with the level of NO_x. Data are presented for each day of June 1998 and 1999 at the six sites listed in Table 1. The lines were defined by regression analysis of 'non-episode' and 'episode' days (see discussion in text).

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' O_3 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_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_x-dependent contribution could result from a number of sources, the most obvious being direct emission of a proportion of NO_x in the form of NO_2. The dominant NO_x source in urban locations is road traffic exhaust. Available studies of combustion-related vehicular emissions indicate that the proportion of NO_x emitted in the form of NO_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_x generically, but is also likely to have a higher proportion of NO_x as NO_2. In addition the NO_2/NO_x ratio is likely to decrease at higher speeds when the engine is under greater load. Although it is probable, therefore, that NO_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. PORG, 1997).

Direct emissions of NO_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,

$$2NO + O_2 \rightarrow 2NO_2, \tag{3}$$

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_2 by this reaction is ca. 20 s at 100 ppmv 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_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_2 formation in wintertime pollution episodes when a shallow inversion layer can lead to a combination of high NO_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_2 vs. NO_x relationship (which would also be expected in the OX vs. NO_x relationship) at NO_x levels
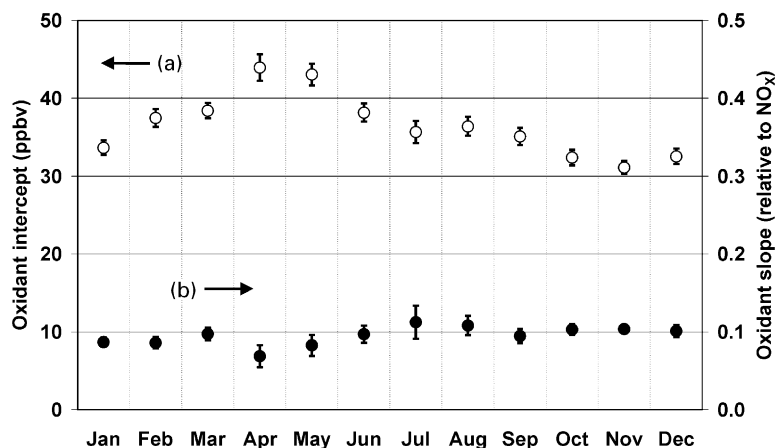
Fig. 4. Seasonal variation of (a) regional (i.e. NO_x-independent) source of OX, and (b) local (i.e. NO_x-dependent) source of OX. O_3 episode days (daylight average OX > 50 ppbv at Teddington) have been excluded from the analysis (see text). Error bars represent $\pm 2\sigma$.

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_x levels of this magnitude are now rarely observed in the UK, even at roadside sites, owing to the influence of NO_x emission reductions from their peak value in 1991.

Other possible NO_x-dependent sources of OX may derive from the concurrent emission of species which can lead to NO to NO_2 conversion. It is well-established that the sunlight-initiated, free radical catalysed degradation of VOC in the presence of NO_x leads to the oxidation of NO to NO_2 (e.g. Atkinson, 1998; Jenkin and Clemit-shaw, 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_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_2 conversions before free radical loss by an alternative reaction (e.g., $OH + NO_2$; $OH + NO$).

The potential importance of these species in leading to NO to NO_2 conversion depends on (i) their efficiency of photolysis to generate radicals, and (ii) on the 'chain-length' for NO_2 formation, i.e. essentially the number of
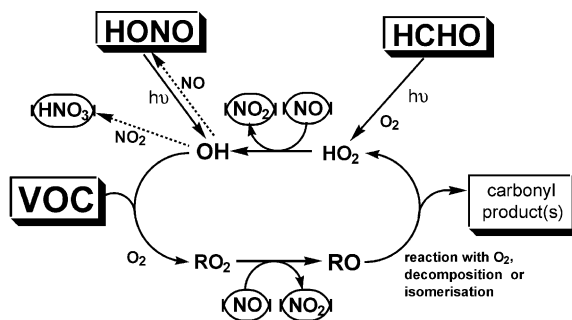

Fig. 5. Schematic representation of the potential role of HONO and HCHO in initiating the free radical catalysed oxidation of VOC under polluted urban conditions, and the resultant oxidation of NO to NO_2.

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_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_x ratio.

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_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 8 h in an easterly direction to six arrival points in the London region at midday were considered to allow simulation of a range of NO_x levels. Two sets of calculations were performed, one with NO_x emitted as 95% NO and 5% NO_2, and one with NO_x emitted as 94% NO, 5% NO_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_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 OX, 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 α-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_2 conversion) on a comparatively short timescale.

2.4. Diurnal variations in OX–NO_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_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_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_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.
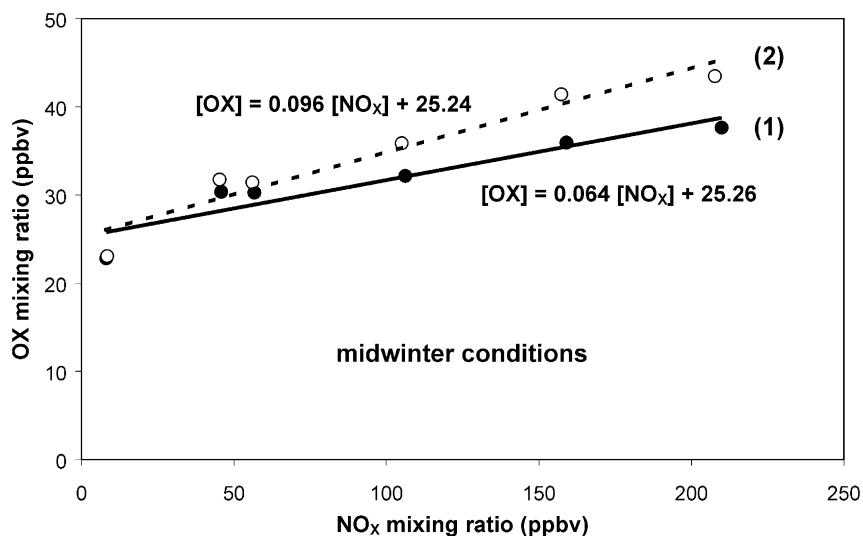

Fig. 6. Simulated OX mixing ratios at six trajectory endpoints under midwinter conditions (see text). (1) NO_x emitted as 95% NO and 5% NO_2; (2) NO_x emitted as 94% NO, 5% NO_2 and 1% HONO.
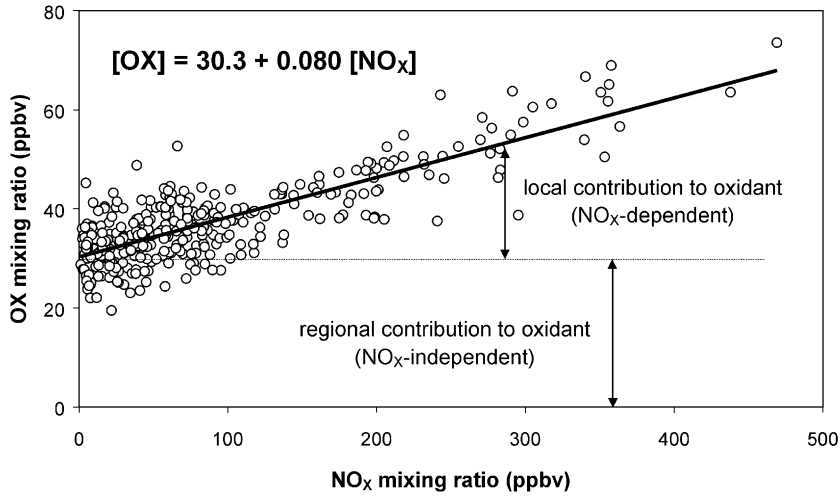
Fig. 7. Variation of nighttime average mixing ratios of oxidant (OX) with the level of NO_x. Data are presented for each night of November 1998 and 1999 at the six sites listed in Table 1.
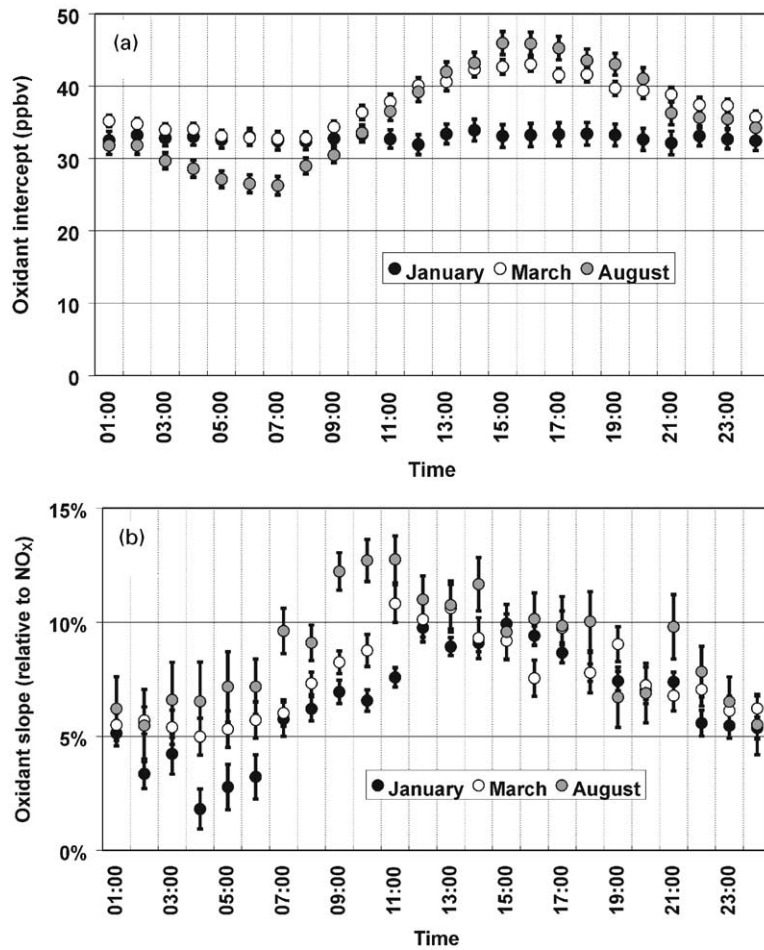

Fig. 8. Hour-by-hour variation of (a) regional (i.e. NO_x-independent) source of OX, and (b) local (i.e. NO_x-dependent) source of OX, for selected months in 1999 (data are for hour ending with the given time).

2.5. Site-to-site variations

The analyses presented above have made use of data from six monitoring sites with overlapping NO_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_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_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) 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_x ratio, and therefore the efficiency of the free radical catalysed cycle 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_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_3, NO and NO_2 during the months April–July, it is not possible to present OX vs. NO_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_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

Fig. 10. Comparison of monthly mean isoprene/1,3-butadiene ratios measured at Eltham and Marylebone Rd, as part of the DETR Automatic Hydrocarbon Network in 1998 and 1999. Based on data taken from AEA Technology website (http://www. aeat. co. uk/netcen/airqual).
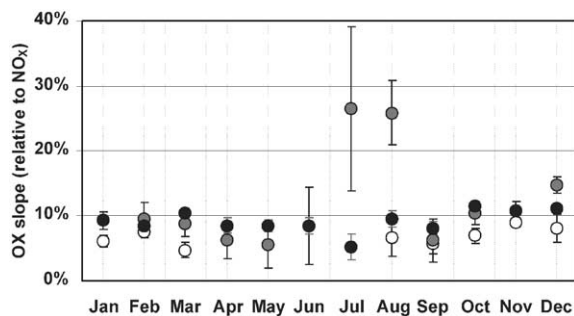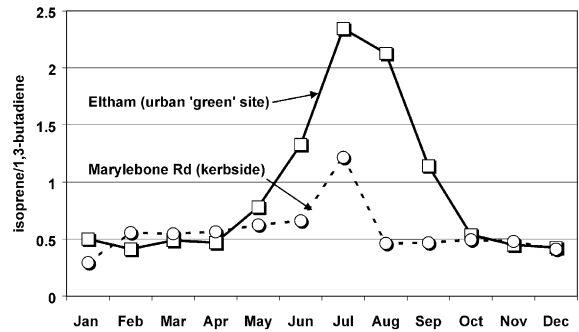
Fig. 9. Comparison of local sources of oxidant at Marylebone Rd. (black), Bloomsbury (grey) and Hillingdon (white), based on daylight-averaged data in 1998 and 1999. April–July data for Hillingdon unavailable due to low data capture for one of O_3, NO or NO_2 (see text).

of the traffic providing the local NO_x 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_2 in the NO_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_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_3, NO and NO_2 are measured.

Fig. 11 shows how the annual mean levels of OX depend on NO_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
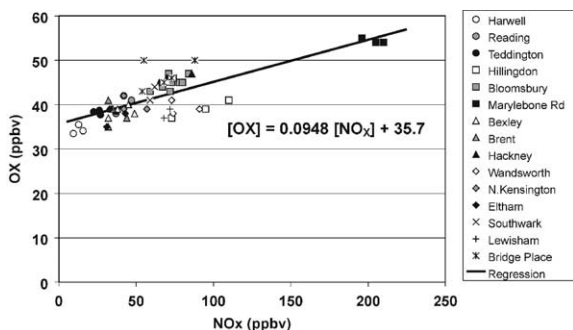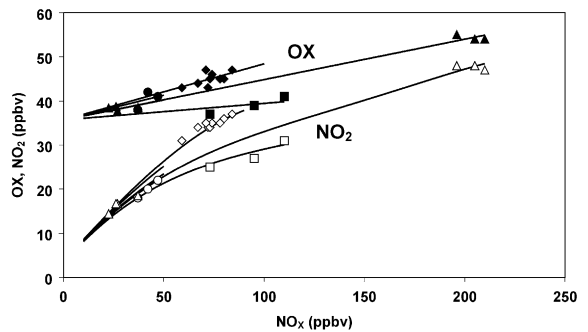

Fig. 12. Annual mean OX (closed symbols) and NO_2 (open symbols) as a function of NO_x at Reading (circles), Teddington (triangles at low end of NO_x range), Hillingdon (squares), Bloomsbury (diamonds) and Marylebone Rd (triangles at high end of NO_x range). Lines are calculated from the expressions in Table 2.

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_2 levels show a distinct variation from one site to another, even for sites for which the annual average NO_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_2 and O_3. Fig. 13 shows the fraction of OX which is in the form of NO_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_2 as the level of NO_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_2/OX ratios. Although the reason for this distinction is not fully clear, such differences in the partitioning of NO_2 and O_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_2 if either the photolysis rate (J_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_2 to occur because the air flow is less stagnant at

Fig. 11. Variation of annual mean OX mixing ratio with NO_x for London sites where O_3, NO and NO_2 are measured, Reading and Harwell. The number of years of available data vary from one site to another, but all displayed data were obtained during 1992–2000.
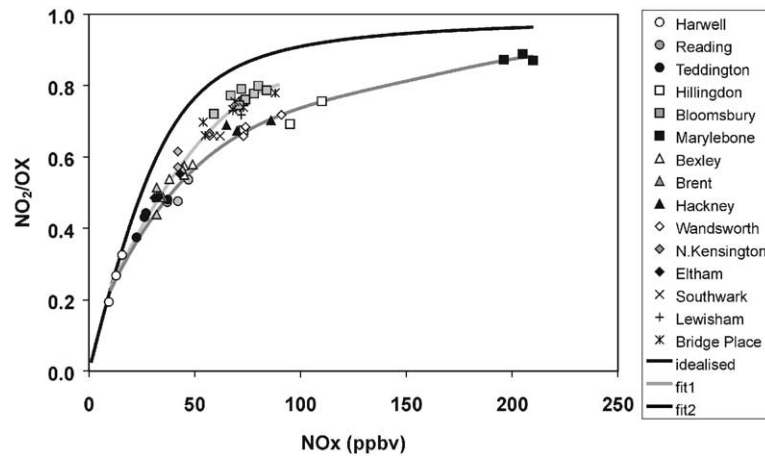
$[OX] = 0.0948 [NO_x] + 35.7$

Fig. 13. Variation of annual mean [NO$_2$]/[OX] as a function of NO$_x$ for London sites where O$_3$, NO and NO$_2$ 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. NO$_x$ 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).

these sites, or they are much closer to source. A short time-lag between emission and measurement most likely accounts for the lower 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 comparatively open 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 NO$_2$/OX. The idealised variation is also presented in Fig. 13, based on an estimated annual average value of $J_2 = 2.2 \times 10^{-3} \, \text{s}^{-1}$. This shows the same general trend as the observed points, but lies consistently higher over the entire NO$_x$ range. The normalised difference between the observed and calculated idealised values is shown in Fig. 14, for the data from both groups of sites identified in Fig. 13. This shows that the deviation between the observed and idealised is lower at the ends of the NO$_x$ range, maximising at approximately 40 ppbv NO$_x$. There are a number of reasons why this is the case. First, the idealised dependence describes how the partitioning of the oxidant components varies for a range of unique levels of NO$_x$, whereas each observed data point represents the mean of a large number of measurements at many NO$_x$ levels. If a number of discrete measurements describes a curve of the form shown in Fig. 13, then the mean of the measurements must lie below the curve. The deviation from the curve will be greater if the degree of curvature is greater. Therefore, the deviation would be expected to be lower at the ends of the NO$_x$

range (as observed), where the degree of curvature is lower. In addition to this, the deviation for a given site would be expected to be greater if the observed range of NO$_x$ levels is greater. This will clearly contribute to variations from one site to another, and may be of particular relevance to Hillingdon for which the observed NO$_x$ range is notably high.

It is also probable that chemical factors contribute to the observed deviation, as discussed above. The idealised curve assumes that the photostationary state relationship applies. Whereas this may be a reasonable assumption for daylight hours (e.g. as shown in Fig. 1), it is almost certainly not a good assumption for nighttime (which accounts for 50% of the year). It is therefore unlikely that an idealised curve based on an annual average value of J_2 can give a fully quantitative indication of the expected partitioning in annual average NO, NO$_2$ and O$_3$. A particular problem arises at sites where intermediate levels of NO$_x$ occur for a significant proportion of the time. At ca. 40 ppbv NO$_x$, the levels of NO and O$_3$ are predicted to be comparable, in the region of 10–15 ppbv. Consequently, neither species is in significant excess, and their reaction to form NO$_2$ (reaction (1)) approximates to second order kinetics. Under these circumstances, the reaction rate decreases significantly as the reaction proceeds. At night, therefore, the complete conversion of NO and O$_3$ to NO$_2$ at these intermediate NO$_x$ levels has a very long time constant, even though the simple photostationary state relationship with $J_2 = 0$ (Section 2.3) would predict that O$_3$ and NO cannot co-exist at night, i.e., conversion to NO$_2$ occurs instantaneously. As a result, the idealised
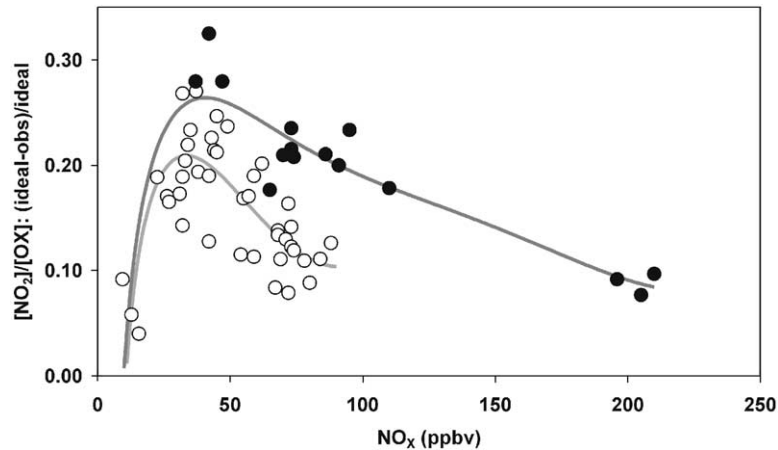
Fig. 14. Normalised difference between the observed and idealised $[NO_2]/[OX]$ data presented in Fig. 13 as a function of NO_x. Closed circles: data from Hillingdon, Hackney, Reading, Wandsworth and Marylebone Rd. Open circles: data from the remaining sites identified in Fig. 13. Lines correspond to Fit 1 (light grey) and Fit 2 (dark grey) in Fig. 14 (see text).

curve is likely to overpredict the proportion of OX in the form of NO_2, particularly for sites where NO_x levels are in the region of 40 ppbv for a significant proportion of the time.

From the above discussion, it is clear that it is difficult to define theoretical expressions which quantitatively describe how the level of NO_2 varies with NO_x, even though the qualitative behaviour is adequately explained by current understanding of the processes involved. The analysis suggests that it is possible to establish reasonably robust expressions which describe how the annual mean OX level varies with NO_x, and which take account of site-to-site variations (a series of such expressions is provided in Table 2 for each of the urban and suburban sites in Fig. 11). However, the precise relationship between annual mean NO_2 and annual mean OX is subject to several varying factors, and it appears necessary to use fitted functions for groups of sites with particular characteristics. The data for the two groups shown in Fig. 13 have therefore been used to derive the two polynomial expressions given in Table 2, and illustrated in the figure. The data for Harwell were included in both sets to allow the NO_x range to be extended to low levels.

The expressions in Table 2 therefore allow $[NO_2]$ vs. $[NO_x]$ curves to be inferred for all 14 urban and suburban sites. This is illustrated in Fig. 12 for the five sites included in the more detailed analysis presented in previous sections. For the most part, the resultant curves for NO_2 provide a good description of the data at each site, even though a slight bias may result from using expressions for NO_2/OX derived from fitting several sites to describe individual sites. The inferred curves for NO_2 allow the annual mean NO_x mixing ratios which correspond to the WHO 21 ppbv air quality guideline

Table 2
Summary of $[OX]$ vs. $[NO_x]$ and $[NO_2]/[OX]$ vs. $[NO_x]$ relationships derived from the analysis of annual mean data presented in Figs. 12 and 14 (see discussion in text)

Site	$[OX] = A\,[NO_x] + B$[a]	$[NO_2]/[OX]$
	A	Expression [b]
Bexley	0.0771	Fit 1
Bloomsbury	0.1272	Fit 1
Brent	0.0616	Fit 1
Bridge Place	0.1572	Fit 1
Eltham	0.0477	Fit 1
Hackney	0.1391	Fit 2
Hillingdon	0.0375	Fit 2
Lewisham	0.0332	Fit 1
Marylebone Rd	0.0914	Fit 2
North Kensington	0.0873	Fit 1
Reading	0.1121	Fit 2
Southwark	0.1129	Fit 1
Teddington	0.0902	Fit 1
Wandsworth	0.0449	Fit 2

[a] Linear $[OX]$ vs. $[NO_x]$ 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.

[b] $[NO_2]/[OX]$ vs. $[NO_x]$ expressions are polynomial fits to data presented in Fig. 13: *Fit 1*: $[NO_2]/[OX] = (1.015 \times 10^{-1}) + (1.367 \times 10^{-2})\,[NO_x] - (6.127 \times 10^{-5}\,[NO_x]^2) - (4.464 \times 10^{-8}\,[NO_x]^3)$: applicable range, 10–90 ppbv NO_x.

Fit 2: $[NO_2]/[OX] = (8.962 \times 10^{-2}) + (1.474 \times 10^{-2}\,[NO_x]) - (1.290 \times 10^{-4}\,[NO_x]^2) + (5.527 \times 10^{-7}\,[NO_x]^3) - (8.906 \times 10^{-10}\,[NO_x]^4)$: applicable range, 10–210 ppbv NO_x.

for annual mean NO_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;
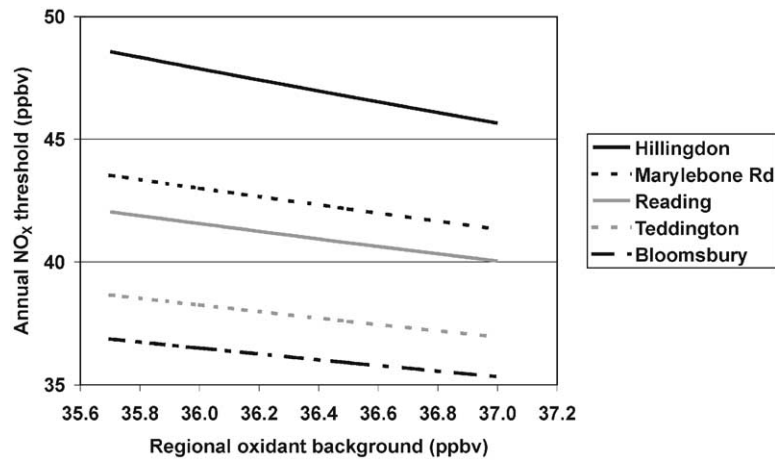
Fig. 15. Calculated annual mean NO_x thresholds corresponding to annual mean NO_2 of 21 ppbv, as a function of regional oxidant background (B). Calculations are based on the expressions in Table 2, with the value of B varied between 35.7 and 37.0. Over this range, the observed variation is almost linear, and well described by the following expressions: Reading, NO_x threshold = 97.2−1.647 B; Teddington, NO_x threshold = 85.9−1.324 B; Hillingdon, NO_x threshold = 128.7−2.245 B; Bloomsbury, NO_x threshold = 78.8−1.176 B; Marylebone Rd., NO_x threshold = 103.8−1.689 B.

Marylebone Rd, 43.5. Based on year 2000 annual mean NO_x, the urban background sites (Teddington and Reading) are already below these thresholds, whereas the present analysis infers that NO_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_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^{-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_x level corresponding to an annual mean NO_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_x of between ca. 0.12 and

0.22 ppbv are required, for the NO_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_x-independent and NO_x-dependent contributions. The former is effectively a regional contribution which equates to the regional background O_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_2 emissions, (ii) the thermal reaction of NO with O_2 (reaction (3)) at high NO_x, and (iii) common-source emission of species which promote NO to NO_2 conversion. The final category particularly includes HONO, which appears to be emitted directly in vehicle exhaust, and is photolysed to generate HO_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_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_2 conversion under VOC-limited conditions.

Annual mean data for an extended number of sites demonstrate similar OX vs. NO_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).

Acknowledgements

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