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Review of methods for NO to NO_2 conversion in plumes at short ranges

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Steve Killeen

Steve Killeen
Head of Science

Executive Summary

This is the report of Task 2 in a larger study commissioned by the Environment Agency entitled 'Atmospheric chemistry and regional ozone'. The work was undertaken to investigate potentially important issues to the Environment Agency in its regulation of large emission sources of air pollutants. The most common regulatory approach to nitrogen dioxide (NO_2) is to assume a fixed ratio of NO_2 to total oxides of nitrogen (NO_x) as a rule of thumb, which seems to vary in value from 35% up to 100%. However the scientific literature shows and our modelling studies demonstrate (see Task 3 reports) a significant regulatory risk if a constant ratio for NO_2:NO_x is assumed. NO_2 is emitted by combustion sources and by some industrial processes, but once free in the atmosphere it participates in a variety of chemical reactions. The concentration of NO_2 downwind of a stack depends on the stack emissions and on the chemical reactions of species in the plume with species in the surrounding atmosphere. Consequently, the scientific evidence shows that a constant ratio is open to serious challenge and so poses a risk in regulation. This report examines the scientific literature on NO_2 as a precursor to model calculations. The Task 3 reports describe modelling work that provides the foundation for a more rigorous and more defensible regulatory approach to NO_2. NO_2 is regulated in terms of both hourly means and annual means; different methods may be needed for each averaging period.

The aim of the study as a whole is to examine the factors that may influence the concentrations of secondary pollutants produced by chemical reactions in the plumes from sources regulated by the Environment Agency and that may increase concentrations when they react with regional background levels of pollutants. The three tasks are interrelated:

1. plume chemistry on a regional scale;
2. NO_x to NO_2 conversion;
3. Large scale modelling of contributions to regional ozone.

This Task 2 report reviews published methods to estimate the NO_2:NO_x ratio in plumes. Unusual oxidation conditions are also mentioned in the Task 1 report. Other parts of the work that used modelling are described in the Task 3 reports, which also combine the modelling results with this literature review and make recommendations on a possible method to estimate NO_2:NO_x for the Environment Agency to use. Models that employ detailed chemical mechanisms are reviewed herein. One approach the Environment Agency could adopt to regulate NO_2 would be to use simulations of plume chemistry. This would need an efficient numerical solver together with a significantly reduced chemical mechanism; the computer costs and the complexities of assembling and inputting emissions data on hydrocarbon species will render this impractical for many permit applications. Simulations of plume rise, advection, turbulent dispersion, chemical reaction and wet or dry deposition processes require major computing resources. Only the largest stacks merit such effort. Rapid simplified methods are thus required for the majority of applications. Development of a consistent and workable regulatory protocol for NO_2 in large plumes thus represents a major challenge. This report is the first step in developing an approach for NO_2. The Task 3 reports (on the sensitivity modelling) present a simplified method for the Environment Agency to consider using as a regulatory tool.

Contents

1 Introduction

This report is part of a larger study for the Environment Agency. The work was undertaken to investigate issues of potential importance to the Environment Agency in the regulation of large emission sources of air pollutants. The aim of the study is to examine the factors that may influence the concentrations of secondary pollutants produced in regulated plumes and that may increase concentrations when combined with regional background levels of pollutants. The present report focuses on a review of literature relevant to computer modelling of the chemical processes found in regulated plumes. It draws on literature from the air-quality management community, chemical kinetics and reaction mechanisms, methods of numerical solution and readily available models that the Environment Agency may be using or be given results from. The practical goal is to identify empirical tools or numerical models that can be used by Environment Agency staff during the authorisation process. In this regard the Environment Agency emphasised the importance of assessing what methods might be available, how easy or complicated were their computational demands and what types of input data must be assembled in order to use the methods. This report explains the scientific basis of the available methods so that the philosophy of how they might be adapted, or not, for practical regulatory purposes may be understood. An important part of this report is therefore to explain the methods found in the literature. The contents of the reports for this project broadly follow the various topics set out in the three tasks of the Project Specification, but amended in the interests of clarity and to facilitate the presentation of a broad overview of widely differing ideas. Task 1 of the project on regional scale chemistry, such as for sulphur species, and Task 2 on nitrogen species are very closely related to Task 3, which involves plume-chemistry modelling, and encompasses Tasks 1 and 2 and more.

Task 2 requires a review of nitric oxide (NO) to nitrogen dioxide (NO_2) conversion in plumes at short ranges. In the past a number of approaches have been suggested to estimate the NO to NO_2 conversion rate for regulatory applications. These include:

1. assuming 100% conversion as a worst case;
2. assuming a constant ratio of NO to NO_2;
3. using different ratios for different seasons and/or distances based on measurements of NO and NO_2 in airborne industrial plumes (for example, Janssen *et al.* 1988);
4. using reactant-limited models, that is models with instantaneous conversion constrained only by the amount of oxidant(s) available;
5. using reactive plume models, that is models with full time-dependent chemistry;
6. applying a simplified atmospheric chemistry scheme, such as the Generic Reaction Set (GRS);
7. applying methods described in the recent UK Air Quality Expert Group (AQEG 2004) report to assess NO_2 conversion in urban areas.

In the report reference is made to a number of empirical studies of the long-term and short-term NO_2 concentrations in plumes from stationary sources. If any simple approach derived from urban monitoring data is to be adapted to regulate elevated large plumes, it is necessary first to establish whether the evidence supports their application to plumes. Such extrapolation cannot be safely made without careful testing of practical situations of interest to the Environment Agency. Therefore an important objective of this report is to review methods for estimating the ratios of NO_2 to nitrogen oxides (NO_x) in plumes, and to do this we must study the literature on various ways of assessing the oxidation of NO to NO_2.

In this report we first review the empirical results derived from urban monitoring and available aircraft studies before looking at more chemically based methods. A variety of chemical mechanisms are in use within different models. The Task 3 reports describe the modelling of secondary pollutants like NO_2 by addressing plume-chemistry sensitivities and the application of complex modelling.

NO_2 is much more toxic than NO. The WHO 1-hour Guideline for NO_2 is 200 μg m^{-3} [105 parts per billion (ppb); www.euro.who.int/document/aiq/7_1nitrogendioxide.pdf on page 24, Chapter 7.1 Nitrogen Dioxide].

The UK air-quality standards in terms of NO_2 are:

1. National UK Standard 1-hour mean, 287 μg m^{-3} (150 ppb);
2. UK Air Quality Strategy Objective 1-hour means, 200 μg m^{-3} (105 ppb) with a maximum of 18 exceedences per year;
3. UK Air Quality Strategy Objective annual mean, 40 μg m^{-3} (21 ppb);
4. UK Environmental Impact Assessment annual mean value for vegetation and ecosystems, 30 μg m^{-3} (16 ppb).

Air Quality Standards and Objectives for the U.K. are summarised at http://www.airquality.co.uk/archive/standards.php. Therefore in this work we examine empirical methods for hourly means and for annual means, as well as complex modelling schemes.

In simple plume-dispersion models ground-level concentrations of NO_x are calculated and other methods may be used to describe the fraction of the NO_x present as NO_2. Several ways have been developed to describe this fraction for hourly and annual average time periods. These historical approaches are reviewed, commencing with some of the earliest attempts, as these may serve as pointers to later ideas or even in developing new ideas. The alternative approach is to replace the simple dispersion model with a more complex one that models the dispersion and chemical reactions together. These models include the processes that control the formation of NO_2. Examples of these modelling approaches are summarised herein.

NO_2 episodes have occurred in both wintertime and summertime, with entirely different formation mechanisms. Wintertime episodes are far more important for urban, traffic-generated pollutants where NO to NO_2 conversion is accelerated under shallow, stagnant inversion layers. The role of direct oxidation of NO by O_2 in a trimolecular reaction may be significant in urban winter episodes and is discussed below. Large power stations usually make no contribution to wintertime NO_2 episodes because power-station NO_x emissions pass above the wintertime shallow stable layers into the free troposphere. Summertime NO_2 episodes are driven by the occurrence of ozone (O_3) formation on a regional scale. Elevated O_3 levels are advected into the UK from continental Europe and lead to short-term changes in the partitioning between NO_2 and NO_x. These short-term changes lead to NO_2 episodes and may involve both traffic and power-station emissions. AQEG (2004) has reviewed the current broad understanding of NO_2 and should therefore be consulted as the most authoritative UK position on NO_2.

In addition to urban monitoring by the Department of the Environment, Food and Rural Affairs (Defra), devolved administrations and local authorities, rural monitoring data for NO_2 have also been recorded at the monitoring stations operated by power-generating companies. However the analysis of such measurements is outside the scope of this project.

1.1 Review of monitoring results

Historical information from earlier work is reviewed in Cocks (1993) in the proceedings of a short symposium held in London on 19 February 1992. In Chapter 2 of these proceedings, Bower *et al.* (1993) discuss urban O_3 and NO_x using data from the Central London and Cromwell Road sites. Urban concentrations of NO_2, NO_x and O_3 were closely interrelated. The monitoring data also demonstrate the non-linear relationship between NO_2 and NO_x and show that primary vehicle emissions of NO_2 are not able to explain wholly the elevated NO_2 concentrations in urban areas. The authors invoke the fast reaction of NO with O_3 by way of explanation. Motor vehicles (~48%), and stationary sources (power stations and industry, ~40%) were described in 1991 as the major anthropogenic sources of the total NO_x. Primary emissions of NO_2 were ~5-10% of the total NO_x. In the late 1980s, vehicles accounted for ~70% of urban NO_2, rising to ~90% in episodes. However, since 1990 transport emissions of NO_x have decreased steadily according to the UK National Atmospheric Emissions Inventory (NAEI). In urban areas vehicle emissions dominate NO_x concentrations, in part because NO_x is emitted at low level.

This illustrates a very important consideration when examining the influence of source types: emission height and travel distance are important influences on ground-level concentrations attributable to a given source type.

Bower *et al*. (1993) summarise urban NO_x chemistry in eight reactions with NO_2, NO_x and O_3, light ($\lambda \leq 420$ nm), third body M, hydrocarbon RH, radical R*, peroxy radical RO_2, radical RO and, lastly, O_2 for the slow three-body reaction with NO. As the scheme was well known the authors do not quote the chemical kinetic rate data. The scheme is similar to the GRS (see Section 3.6) that is used in the Atmospheric Dispersion Modelling System (ADMS-Urban; see Section 3.5). Major chemical sinks for NO_2 include reactions with OH, forming HNO_3 by day, and with O_3 by night.

This section is a review of early work; for our current understanding see Section 2 of this report, as well as AQEG (2004). Bower *et al*. (1993) provide some of the earliest analyses of empirical NO_2:NO_x ratios. The authors discuss the topics described in Sections 1.1.1 to 1.1.5.

1.1.1 Short-term O_3:NO_x in urban areas

The main factors identified were:

(1) The diurnal emissions cycle (for example, from vehicles in morning and evening rush hour).
(2) The removal of O_3 by emitted NO_x, which is a dominant loss process for O_3 whenever local NO concentrations exceed 35 ppb, the typical 'background' O_3 level.
(3) The early summer-morning reaction of emitted NO with O_3 and peroxy radicals (the latter is a slower process).
(4) Vertical exchange processes (more active in summer) that disperse emissions upward and can bring residual layers that contain NO_2 downward, which suggests a later diurnal peak for summer NO_2 than for summer NO. Later in the day O_3 rises to a mid-afternoon maximum driven by the photolysis of NO_2. Then, during the evening rush hour, when more NO is emitted and the light levels decrease, O_3 declines. Overnight NO is depleted by O_3 scavenging, until the cycle restarts the next day.

In winter conditions urban air shows the NO and NO_2 peak together in the morning, as there is less vertical mixing, fast oxidation of NO into NO_2 by O_3 and possibly by heterogeneous processes (on surfaces or in droplets), and perhaps increased NO_2 emissions from idling engines. The total oxidant (NO_2 + O_3) is a useful marker, with lower oxidant levels at night, which decline with dry deposition of O_3 and chemical scavenging of both NO_2 and O_3 overnight. In the morning oxidant levels rise again as NO is emitted, with some NO_2 emissions, and as NO forms NO_2. In summer NO is oxidised by peroxy radicals to produce excess NO_2 (relative to the equilibrium or photostationary state) and corresponding increases in O_3 occur. The result is a rise in the summer of oxidant concentrations to a mid-afternoon maximum.

1.1.2 Long-term O_3:NO_x in remote and urban areas

For the long-term annual average, one can visualise a broadly constant annual average concentration over the UK, which is affected by loss mechanisms, particularly dry deposition at the surface, and reactions with NO. In urban air, the NO reaction is the dominant O_3 sink. Figure 2 from Bower *et al*. (1993) has the least-squares best fit:

annual average O_3 versus average NO_x
$O_3 = 0.24\ NO_x + 28$ (ppb)

1.1.3 Short-term NO_2:NO_x

Figure 3 from Bower *et al*. (1993) shows the frequency distribution of the yield of NO_2:NO_x (ratios of hourly means) at urban and rural sites. At the rural sites, NO_2 is frequently 60% or more of the NO_x (or $NO_2:NO_x \geq 0.6$) and the NO_2:NO_x ratio tends towards its daytime equilibrium value associated with the photostationary state of ~0.85. At urban background sites, such as Central London (1990-1991), NO_2:NO_x ratios average 0.47 in winter and 0.59 in summer, consistently exceeding the primary emissions ratio, which lies in the range 0.05-0.1 (and possibly 0.3 for warm idling engines in cold weather). At urban kerbside sites, such as Cromwell Road (1990-1991), local concentrations of NO are higher because of the proximity to the source, and NO_2:NO_x ratios are markedly lower, averaging 0.17 in winter and rising to 0.3-0.5 in summer. Such a rise in yield from winter to summer at the kerbside is associated with fast oxidation of NO, probably with O_3 or with aged air-masses transported in from afar and bearing elevated NO_2 concentrations. Overall, the yield NO_2:NO_x varies from ~0.17-0.5 at the kerbside through ~0.47-0.59 at urban background sites to ~0.85 at rural stations. This reflects the dilution of NO_x as travel distance increases and hence the greater availability of O_3. Figure 4 from Bower *et al*. (1993) shows scatter plots of NO_x versus NO_2 (hourly means) in winter and summer at an urban kerbside site. The data are typical of kerbside sites.

1.1.4 Annual average NO_2:NO_x

Figure 5 of Bower *et al*. (1993) shows NO_2 versus NO_x (annual means) and the characteristic bending of the curve as it enters the O_3-limited area (NO_2 > 30 ppb, say). At O_3-limited sites, where NO_x is large, annual average NO_2 is about ~40-50 ppb (ratio NO_2:NO_x ~0.4) over quite a wide range of NO_x. In the photostationary state this amounts to ~15 ppb O_3, while in rural sites where concentrations are lower (but the ratio NO_2:NO_x ~0.8) this amounts to ~30ppb O_3. [A similar averaged curve is used in the screening method described in the *Design Manual for Roads and Bridges* (DMRB) published by the Highways Agency, http://www.highways.gov.uk/contracts/index.htm.]

1.1.5 Spatial trends in NO_x, NO_2 and O_3 in the UK

However Bower *et al*. (1993) did not describe any empirical relationships to summarise their NO_2 and NO_x data, apart from annual average O_3 versus NO_x and annual average O_3 versus geostrophic drag coefficient (which relates to the wind field aloft). Their review chapter is, though, a useful marker to the state of knowledge at that time.

For the Photochemical Oxidants Review Group maps were generated that imply a dependence of O_3 upon height of topography (www.aeat.co.uk/netcen/airqual/reportshome.html). In terms of Environment Agency assessments, it may be useful to bear in mind that the UK National Emissions Inventory provides data from which NO_x emission trends may be estimated and also to take account of the processes that influence background or 'natural' O_3 concentrations at a given location.

1.2 Quality of Urban Air Review Group First Report

The Quality of Urban Air Review Group (QUARG) First Report (QUARG 1993) has chapters reviewing pollutants relevant to this project. Chapter 3 reviews nitrogen compounds, and Figure 3.17 (page 50) shows the frequency distribution of the NO_2:NO_x ratio at three types of site: kerb, urban and rural. A similar range of ratios may be expected for elevated, large point-source plumes (that is, the likelihood of a given value for the NO_2:NO_x ratio will be associated with plume concentrations). At lower NO_x concentrations, high ratios of NO_2:NO_x are more abundant. The QUARG First Report also plots scatter diagrams of the ratio NO_2:NO_x versus NO_x concentration, but this report does not develop any empirical functions. To attempt to extrapolate this kind of ground-level data to elevated plumes it is necessary to consider the role of low temperature, the abundance of O_3 and the concentration of NO_x. This should be borne in mind when using any of the empirical curves hitherto developed. Were the monitoring data on which the functions are based taken in conditions that are appropriate to plumes regulated by the Environment Agency?

1.3 Aircraft studies of plume chemistry

During the period 1980-1991 the electricity industry commissioned a series of aircraft and ground-based studies of atmospheric pollutants. This decade of atmospheric chemistry and dispersion research is described and summarised in Kallend (1995). The research studied the chemical evolution of power-plant pollutants, such as the oxides of nitrogen and sulphur over large distances, mainly in trajectories over the North Sea. The work also investigated factors leading to the production of ground-level oxidants and the generation of O_3 in the free troposphere. Plumes were labelled and tracked using tracers, so the chemical analyses could be related to plume identity. The chemical evolution of plumes up to 1000 km from the source was monitored. Techniques to collect and analyse cloud rainwater were also developed, providing samples for studies of acid rain chemistry.

The main conclusions reported by Kallend (1995) are:

1. It is valid for much of the time to think of a plume as being transported several hundred kilometres downwind from a source within a well-mixed boundary layer. The rate of dispersion is often significantly less over sea than over land and this is important for modelling deposition when appreciable chemical reaction occurs in the plume.
2. Sulphur dioxide (SO_2) in a plume is lost mainly by dry deposition at a rate of ~3% h^{-1}. Wet deposition via removal into cloud and rain is sensitive to other acidic or alkaline species.

3. In clear air the oxidation of SO_2 to sulphate aerosol is attributable to OH radicals and is fairly slow. In plumes, oxidants are deficient and other important reacting precursors, like O_3 and hydrocarbons, are also lacking. Hence SO_2 and NO_x can remain unoxidised for long travel times and distances when the dispersion is slow and the mixing of precursors into the plume is restricted.

The studies summarised by Kallend found no elevated levels of O_3 in plumes, though they were seen on the plume edges in two examples. This may arise where precursors mix with plume NO_x. Plumes exhibited an O_3 deficit associated with the reaction of plume NO with O_3 in the ambient air. Clear air in the free troposphere (above the more polluted boundary layer) has an O_3 minimum in winter and a maximum in summer. In the absence of other measurements, the Kallend review suggested that plumes probably contribute to tropospheric NO_x burdens in proportion to their total emissions and, ultimately, at sufficient distance or travel time, may contribute to increased global O_3. Models available to Kallend did not resolve plume chemistry across the plume, so could not, for instance, represent elevated O_3 at plume edges.

The Kallend report is a particularly useful review of plume chemistry as it was seen at the time. Since then there have been no such major airborne campaigns by the UK power industry to study detailed plume chemistry. It is clear that ground-based monitoring is insufficient to monitor properly the air pollution burdens from power-station plumes. Appendices to the Kallend report include dry and aqueous oxidation reactions, production of oxidants and notes on plume dispersion.

In the context of the present study, there is a need to examine more closely the availability of models that represent detailed species concentrations within plumes, so that production at plume edges can be handled, as well as the ultimate yield after long-range transport has occurred.

1.4 Aircraft data on NO_2 in power-station plumes

Janssen (1986) analysed aircraft data from power-station plumes, and also adapted the modelling approach of Carmichael and Peters (1981, quoted by Janssen 1986) to investigate the effect of inhomogeneity in plume–atmosphere mixing on the conversion of NO to NO_2. He concluded that it is necessary to take account of inhomogeneous mixing. Janssen (1986) presents a simulation model which is based upon equations for the rates of change of the volumes of exhaust gas, ambient air and their mixture. With this physical representation of the bringing together of exhaust and ambient gases, Janssen (1986) is able to include the chemical kinetics. The aircraft data are used to adjust some of the settings and constants in the model to bring it into line with observations. It can be viewed as a conceptual physical model that is matched or tuned to data.

Janssen *et al.* (1988) gave an empirical approach for the formation of NO_2 in a power-station plume. Their approach is based on empirical constants for different seasons, using data from aircraft measurements traversing plumes at different downwind distances. The ratio NO_2:NO_x was measured as a function of plume travel distance downwind. Using the rate of reaction for the oxidation of NO by O_3 to form NO_2, together with the wind speed at the plume height (calculated from a 10 m wind speed with a neutral profile), Janssen *et al.* (1988) expressed the rate of change of the ratio in terms of O_3 concentration, wind speed and downwind distance x. This expression contained O_3 concentration and the rate constant for the NO + O_3 reaction, together with the travel time. They derived a constant of proportionality based on assuming the photostationary state at a long distance downwind. At long distance, the mixing and dispersion processes are slower (long time scales) than the chemical reactions (short time scales).

The operational equation proposed by Janssen *et al.* (1988) is their equation (10):

$$\frac{[NO_2]}{[NO_x]} = \left(\frac{k_2}{k_1[O_3]} + 1 \right)^{-1} \left(1 - e^{-\alpha x}\right)$$

where square brackets indicate concentration, and the value of α is given by the wind speed and O_3 concentration as in their equation (5):

$$\alpha = \frac{k_1[O_3]}{u}$$

Here k_1 is the rate constant for NO + O_3 and k_2 is the rate of photolysis (photo-dissociation) of NO_2 by light (in daytime only). Note that the units for k_1 and k_2 are, respectively, ppm^{-1} min^{-1} and min^{-1}, which are not the usual units in chemical kinetics, so care is required to convert this equation into practical units (involving ppb). Here u is the wind speed at plume height.

Although their derivation assumes the plume is homogeneous and ignores variations in mixing and concentrations across the plume, Janssen *et al.* (1988) suggest the equation can be regarded as a first approximation to the NO_2:NO_x ratio in a plume. They give a range of values for the constants according to season and background O_3 concentration. In winter daytime, for instance, their calculations result in a higher yield of NO_2 than in summer, all else being equal, simply because the actinic flux is lower (lower solar elevation at midday in winter) and the photolysis reaction which removes NO_2 is slower. In a subsequent paper, Janssen *et al.* (1990) explain that the above equation can be considered to apply to a perfectly mixed gas under laboratory conditions. For use on real plumes however, the value of α should be derived from the aircraft observations, as a function of season and meteorological conditions.

We have rearranged the algebra of Janssen *et al.* (1988) to put their equation (10) into a more convenient form. Using *J* instead of k_2 for the usual symbol for the photolysis rate, and *k* instead of k_1 for the rate constant for the NO + O_3 reaction,

$$\frac{[NO_2]}{[NO_x]} = \left(1 - e^{-\alpha x}\right) \left(\frac{J}{k[O_3]} + 1 \right)^{-1}$$

If we define *A* = *J/k*, as in the box model BOXURB (Middleton 1998), the Janssen formula becomes:

$$\frac{[NO_2]}{[NO_x]} = \left(1 - e^{-\alpha x}\right) \left(\frac{[O_3]}{A + [O_3]} \right)$$

This can be written in the form:

$$\frac{[NO_2]}{[NO_x]} = \left(1 - e^{-\alpha x}\right) R_p$$

This formula is now easily understood from a practical perspective. The first term $\left(1-e^{-\alpha x}\right)$ is the near-source limiting term for O_3 diffusion, which rapidly approaches unity as O_3 increases or as the travel time increases. Here $\alpha x \equiv k[O_3]t$, where the reaction time available for reaction is the travel time $t = x/u$ for a downwind distance x and wind speed u . The second term $R_p = \left(\frac{[O_3]}{A+[O_3]} \right)$ is the limiting ratio for the photostationary state. This is achieved after around 200 seconds in the test calculations that we carried out for this study, with wind speeds of either 4 m s^{-1} or 10 m s^{-1}, and an O_3 concentration of 50 ppb. As discussed in Middleton (1998; see Section 2.7 below) once O_3 is above 30 ppb, for UK conditions the ratio R_p is not very sensitive to the exact magnitude of the O_3 concentration.

In the box model BOXURB, the value for the ratio R_p is calculated using the forecast O_3 together with $A = 8.7591$ ppb, which was derived empirically by analysing the monitoring data for Bexley, UK, during the summer of 1995, especially the May 1995 photochemical episode. In discussion at the time (circa 1995) Derwent (personal communication) had suggested that $A = 15$ ppb. Jenkin (2004a) Part 1 has representative annual values of $k = 3.7\times10^{-4}$ ppb^{-1} s^{-1} (temperature 283.15K) and $J = 2.2\times10^{-3}$ s^{-1} (latitude 51.5 N) which give $A = 5.9459$ ppb. With O_3 = 35 ppb, and $A = 5.9459$ for the Bexley data, we have $R_p = 0.855$. In other words, beyond around 200 seconds of travel time our calculations on the basis of Janssen's method suggest the ratio NO_2:NO_x converges towards 85.5% conversion in the limiting photostationary state.

In contrast, using the values of Janssen *et al.* (1988) of $J = 0.55$ min^{-1}, which is $J = 9.16667\times10^{-3}$ s^{-1}, and $k = 29$ ppm^{-1} min^{-1}, which is $k = 4.8333\times10^{-4}$ ppb^{-1} s^{-1}, we have $A = 18.9656$ ppb. With O_3 = 35 ppb, as before, we now find $R_p = 0.6486$. In Figure 1 the asymptotic value of the curve for 35 ppb O_3 and wind speed 10 m s^{-1} is 65% in full daylight. Only in the near-source region where diffusion limits the availability of O_3 does the model of Janssen *et al.* (1988) give a conversion that is smaller than that of the photostationary state. This reduction is seen close to the vertical axis in Figure 1.

The Janssen method is applied in the following fashion:

1. Use a dispersion calculation to obtain $[NO_x]$ at some distance x downwind. This should be a crosswind line-integrated concentration, to be consistent with the form of the aircraft data that Janssen (1986) used.
2. Then at *x* calculate the ratio or yield $[NO_2]$:$[NO_x]$ using the Janssen formula above.
3. Multiply $[NO_x]$ at *x* by the yield at *x* to derive the $[NO_2]$ concentration.

The resulting value of the NO_2 concentration assumes no change in the crosswind direction, because the original data of Janssen (1986) were in the form of line-integral measurements across the width of the plume. This is a potential limitation of the method. To measure the plume in this way also implies that Janssen's method is essentially a short-term one, not an annual mean. As we show in Section 2.8, deviations from the photostationary state can occur.

From these early studies we now turn to more recent empirical relationships, involving the fitting of functions or polynomials to data. These were developed in urban areas, largely for historical reasons. It is in cities that local air-quality management was introduced, necessitating rapid screening methods. It is also where the large monitoring data sets could support empirical approaches. These are examined in Section 2.

In this report a full list of all the aircraft studies is not provided, for the focus is to see what simplified procedures have been proposed that might be adapted for regulatory applications. Some aircraft studies are however discussed in the Task 1 report.

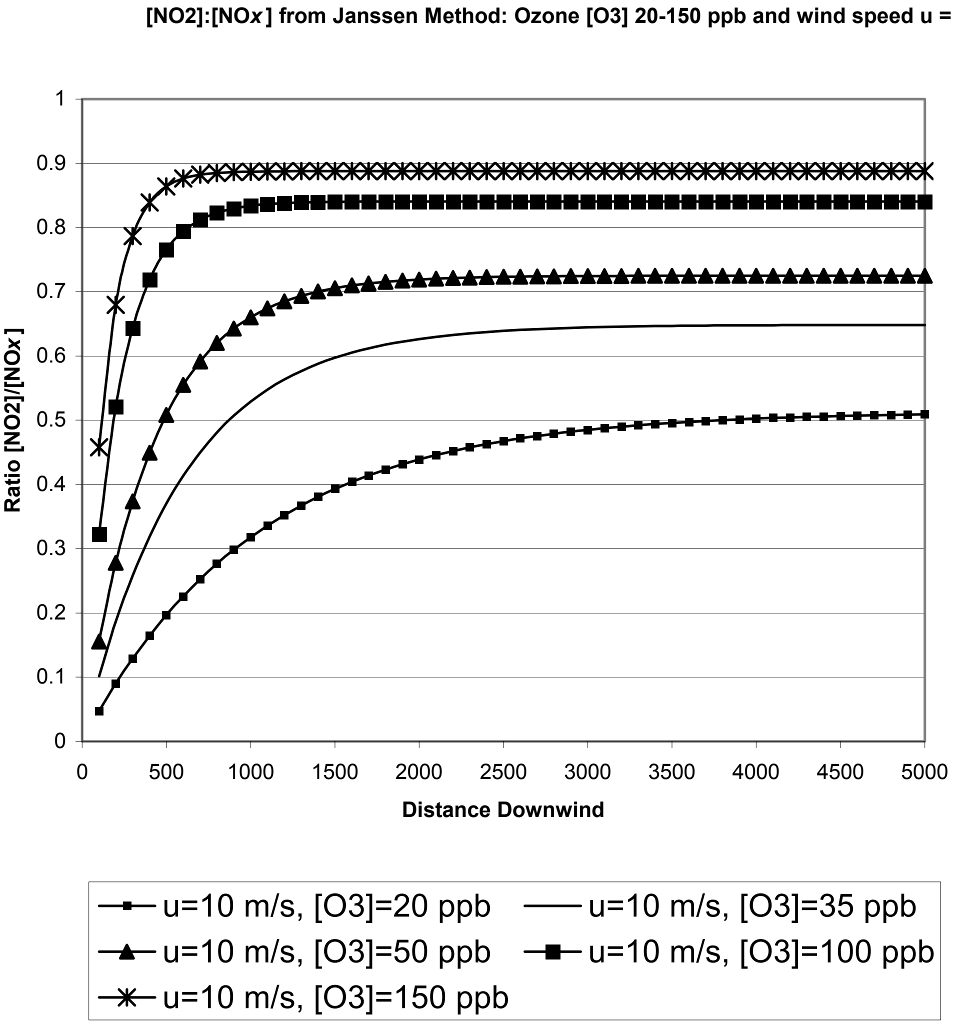

Figure 1
Plot of results for the yield or ratio [NO_2]:[NO_x] using the Janssen (Janssen 1986, Janssen *et al*. 1988) method of near-source diffusion-limited O_3, which soon becomes asymptotic to the photostationary state further from the source, after approximately 200 seconds of travel time (2 km downwind here). The effect of changes in O_3 concentration is shown. The wind speed alters the choice of curve according to travel time (distance/speed). (In these curves distance is plotted on the x-axis; empirical curves later in this report show NO_x on the x-axis.)

2 Empirical relationships for NO_2:NO_x

The challenge in looking at ways for the Environment Agency to assess NO_2 in plumes like those from large power stations, is to identify practical approaches. This section reviews empirical approaches to estimate NO_2 in a variety of situations, not necessarily in power station plumes. Most data appear to come from the urban monitoring networks. Reports from the power industry are available on monitoring around power stations, but now we turn to the urban empiricism as a pointer to what might be developed given suitable plume data; such data may only be obtainable by modelling however.

2.1 Derwent–Middleton curve

Derwent and Middleton (1996) took hourly concentrations in ppb for the NO_x species. To reduce the size of the data sets, concentrations of NO_x were sorted into 10 ppb bins along with their accompanying NO and NO_2 concentration values. All values of NO_2 belonging to a given NO_x bin were then averaged. The curve fitting was then applied to fit a function through the bin averages for NO_2 versus the upper bin limit of NO_x. The ensuing function was thus derived, see Figure 2.

Previous empirical relationships between hourly NO_2 and NO_x relied on a polynomial produced by Derwent and Middleton (1996) for a kerbside site at Exhibition Road, London, from May 1991 to June 1992, including a very high episode in December 1991,

$$[NO_2] = 2.166 - [NO_x](1.236 - 3.348\,A_{10} + 1.933\,A_{10}^2 - 0.326\,A_{10}^3)$$

where square brackets indicate the hourly mean concentration in ppb and $A_{10} = \log_{10}([NO_x])$. This function applied in the range 9.0 ppb < $[NO_x]$ < 1141.5 ppb, where:

1. Below 9.0 ppb NO_x, the yield or ratio $[NO_2]$:$[NO_x]$ was limited to 0.723.
2. Above 1141.5 ppb NO_x, the ratio $[NO_2]$:$[NO_x]$ was limited to 0.25.
3. The shape of the curve at higher concentrations was left open to debate, for there were few data here. For $[NO_x] \approx$ 10-1500 ppb, the ratio ranged from 0.73 to 0.25, respectively. The minimum of 0.13 occurred at $[NO_x] \approx$ 470-486 ppb.
4. The effect of these limits is included in Figure 2, and it appears as a discontinuity in the curve, which becomes a straight line above 1140 ppb NO_x.

The practical advantage of an empirical polynomial function to describe measurements of NO_2 versus NO_x is that values of urban NO_2 can be estimated very quickly, for example for projections of the impacts of future emission controls. The curve by Derwent and Middleton (1996) has been used by a number of local authorities, is part of the Aeolius street canyon model and has been used in the ADMS model. However we suggest that users should be advised to switch to using the newer West Midlands London Average (WMLA) polynomial by Dixon *et al.* (2001) described in Section 2.2.

2.2 Dixon–Middleton–Derwent polynomials

The second study was to determine whether some new relationship held true across different types of sites (background, kerbside and industrial) across the UK. It aimed to:

1. fit revised polynomials to a set of 12 study sites over 7 years of consecutive data;
2. calculate the yield, that is the ratio $[NO_2]:[NO_x]$, at differing concentrations of NO_x;
3. estimate the amount of NO_x reduction required for NO_2 to approach the hourly standard of 150 ppb at sites where NO_2 exceeded this. We also examine controls to meet the proposed 104.6 ppb limit;
4. generate a new empirical function for practical modelling.

The second study was published in an interim form as Dixon *et al*. (2000), and then in a complete form as Dixon *et al*. (2001). Their WMLA function (equation 13 in Dixon *et al*. 2001) is plotted in Figure 2. It uses a much larger data set in the curve fitting than that used by Derwent and Middleton (1996).

We now draw heavily on Dixon *et al*. (2001), but re-examine the approach taken in the context of the needs of the Environment Agency.

An important step in the second study was to modify the underlying form of the function that had been fitted, so that it could be regarded as a dimensionless yield of NO_2 for the corresponding NO_x concentration. By retaining parts per billion (ppb) as the units of concentration, the yield was in effect dimensionless, a mole ratio.

Since $[NO_x]=[NO_2]+[NO]$ we define the yield Y:

$$Y=\frac{[NO_2]}{[NO_x]}$$

where $0 \le Y \le 1$. Any points with Y outside this range represent artefacts or errors in the monitoring data set and were rejected. With $[NO_2]$, $[NO]$ and $[NO_x]$ all in ppb concentration units, the yield Y is a dimensionless mole ratio. The yield increases in summer when more oxidants are available.

The monitoring data were sorted on $[NO_x]$ into bins of constant width 10 ppb, and each bin captured a variable number of points. The $[NO_2]$ values for each bin were averaged to give the numerator in the equation as an average $[NO_2]$; the divisor was the bin upper $[NO_x]$ value. The divisor used the upper limit to avoid division by small values. The yield has one value for each bin. A curve-fitting program was used find the coefficients of function Y for the values of the bin yield versus bin upper limit on $[NO_x]$:

$$Y=f([NO_x])$$

which is a function of just one independent variable, the bin concentration $[NO_x]$.

Polynomials were fitted to the NO_2 and NO_x measurements assuming one independent variable, namely, concentration of NO_x. This is a great simplification of the dispersion and chemical processes that determine the yield of NO_2.

The analysis in the second study thus assumed [NO_x] is the sole independent variable. This assumption was adequate at the time for the needs of local air-quality management, especially for the simple screening models. However in conducting this review we must recognise that this assumption may break down in plumes of interest to the Environment Agency. It is not advisable here to assume that NO_x can be regarded as a sole independent variable.

The second study chose a more convenient function for the yield:

$$Y_2 = A + BA_{10} + CA_{10}^2 + DA_{10}^3 + EA_{10}^4$$

where *A, B, C, D* and *E* are published constants (*ibid.*, or via the Met Office web site).

Thus at urban sites the WMLA function 1991-1997 is:

$$Y_2 = -3.08308 + 7.472477.A_{10} - 5.11636.A_{10}^2 + 1.381938.A_{10}^3 - 0.12919.A_{10}^4$$

Square brackets indicate hourly mean concentration (ppb); $A_{10} = \log_{10}([NO_x])$. For $0 \leq [NO_x] \leq 15$ ppb one should use $Y_2\ (15.0) \approx 0.60$ (dimensionless).

According to Dixon *et al.* (2001) the root mean square error in NO_2 was calculated to be approximately 30-50% of the annual mean concentrations, relatively small compared with other errors in dispersion modelling (for example, uncertainties in emissions and dispersion calculations can give errors ≅ factor of 2). Dispersion modellers who use these polynomials in the absence of local monitoring data can be reassured that this empirical approach to NO_2 concentrations does not, on its own, cause excessive errors. Overall, the errors associated with the polynomial approach are smaller than those arising elsewhere in air quality modelling. The full set of coefficients was released on http://www.metoffice.com/environment/no2/index.html1.

The values of [NO_2], ppb, is given by calculating $[NO_x]Y_2$ and is shown in Figure 2. An important feature of the function is that it represents the upturn in NO_2 when total NO_x concentrations are very high. This is characteristic of urban winter episodes.

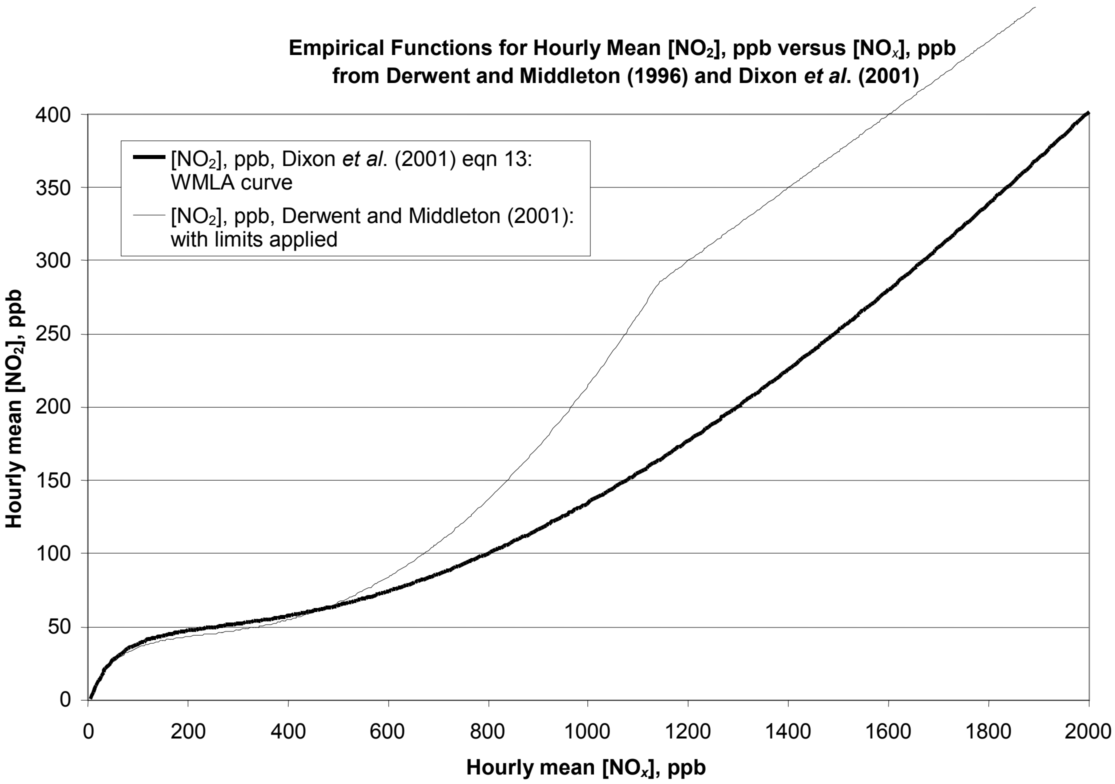

Figure 2: Empirical functions derived for urban monitoring data in the UK by Derwent and Middleton (1996), with limiting values applied as in their paper, and by Dixon *et al.* (2001) for WMLA combined data. The WMLA curve is initially a little above the Derwent–Middleton curve, but crosses it at around 450 ppb of NO_x (~60 ppb NO_2) and from then on to 2000 ppb NO_x (~400 ppb NO_2) the WMLA gives smaller estimates for NO_2.

2.3 Elevated NO_2 in winter episodes: a radical mechanism?

In December 1991 monitors across London recorded high concentrations of NO_2. Local primary emissions of NO and NO_2 from motor vehicles were trapped in a shallow layer by a strong inversion. At times conditions of freezing fog were reported. As mentioned above, Bower *et al.* (1993) discussed the role of possible elevated NO_2 emissions from warm but idling engines in cold weather. Bower *et al.* (1994) suggested that the causes of such elevated NO_2 concentrations were still not fully understood. Shi and Harrison (1997) suggested that the oxidation of NO by O_2 was too slow to explain the December 1991 results for elevated NO_2. They investigated whether diene-catalysed reactions could give rise to rapid oxidation of NO to NO_2. In diluted exhaust from a petrol generator they found the reaction rates for NO and NO_2 were almost invariant with time, so did not have the same kinetics as the three-body reaction between NO and O_2. Radical reactions may be involved in the fast oxidation of NO in petrol vapour, to give a mechanism that invokes an initiation reaction between conjugated dienes and NO_2. This is followed by the formation of RO_2, which oxidises NO and, through subsequent steps, also leads to OH formation. The OH may then lead to further peroxy radicals and further oxidisation of NO to NO_2. Shi and Harrison (1997) conclude that these reactions may cause enhanced free-radical oxidation of NO to NO_2 in the (urban) atmosphere in the absence of sunlight initiated reactions. We may conclude from this work that the latter point is significant; the reaction scheme could thus generate NO_2 at night or in wintertime foggy conditions in which light intensities are quite low. In winter anticyclones other pollutants from exhausts, such as hydrocarbons, are trapped in the air along with the emitted NO and NO_2. (Their quantity will depend on the efficiency of catalysts of vehicle exhausts in such conditions.)

From the Environment Agency's perspective this study is of interest as it draws attention to the existence of reaction schemes that invoke unsaturates (conjugated dienes) in the possibly fast oxidation of NO to NO_2. Other oxidation products (for example NO_z species, other nitrogen oxides apart from N_2O) may also be formed. It was also interesting that when benzaldehyde, a known radical inhibitor, was added the reaction rate slowed. However this is of low priority for this project, as such conditions seem unlikely in plumes regulated by the Environment Agency, being more associated with motor-vehicle exhausts in winter.

2.4 Transport Research Laboratory DMRB curve

The DMRB of the Transport Reseach Laboratory (TRL) is effectively an annual average data set designed for the kerbside, so it is of little relevance to plumes regulated by the Environment Agency. It is mentioned for completeness only. The *Highways Manual* has been used for many decades to specify the design of roads, including Volume 11, Part 3, which covers air quality assessments for new roads. It has an empirical curve used to read off the NO_2 for the estimated highway NO_x. For more details see http://www.official-documents.co.uk/document/deps/ha/dmrb/index.htm. Other annual mean curves are given in Sections 2.6.3 and 2.6.4.

2.5 Empirical Relationship for London

Carslaw *et al.* (2001) used London data to investigate further the concept of the Derwent–Middleton function, an empirical function for hourly mean NO_2 versus hourly mean NO_x (above). They note that the hourly NO_2 versus NO_x curves exhibit wide scatter, so for any value of NO_x there can be a wide range of values found for NO_2. This scatter is a source of uncertainty that should be taken into account when such curves are used in a regulatory procedure. By sorting the data into bins and averaging in each bin, the underlying shape of the curve is revealed to have three parts:

1. excess O_3 region (where NO_2 rises steeply with NO_x at low NO_x);
2. limited O_3 region (where NO_2 rises only slowly compared with NO_x);
3. winter episode peak where NO_2 rises again, perhaps because of the NO + O_2 three-body reaction, but for which we only have data from winter episodes when concentrations are sufficiently high to enter this region of the curve.

Carslaw *et al.* (2001) then derive an annual mean NO_2 concentration in either one of two ways:

1. average the hourly estimates of NO_2 derived from hourly NO_x using the empirical relationship that was fitted to the binned data;
2. sum the frequency-weighted bin averages of NO_2, that is by multiplying the bin-average NO_2 by the frequency of the bin (frequency being the number in the bin divided by total number of bins) and adding these weighted bin-averages together.

Carslaw *et al.* (2001) used the frequency weighted bin averages to investigate the implications for NO_2 if emissions of NO_x were successively reduced in steps (by a 5%

reduction each time). Here the NO_x was reduced by 5%, the data then sorted again back into bins to obtain a new frequency that is then used to obtain the new estimate of the annual mean NO_2. In this way they generated smooth curves for the likely (non-linear) fall in NO_2 as NO_x is reduced. These plots seem well behaved in that they bend down towards the origin as might be expected – zero NO_2 at zero NO_x.

We can remark that such a frequency weighted bin-average technique for the annual mean might be of value in a regulatory context if hourly estimates of NO_x are deduced by dispersion modelling, and must be used to estimate an annual mean for NO_2. For instance, likely compliance with an annual mean of, say, 21 ppb NO_2 may need assessment. Furthermore the extension of the method to demonstrate a non-linear reduction in annual mean NO_2 as NO_x is regulated may exhibit potential value as a regulatory aid. Although Carslaw *et al.* (2001) do not derive new empirical functions, they do present the statistically weighted use of bin averages for the annual mean NO_2 and its response to NO_x control (http://www.londonair.org.uk).

2.6 Allowance for total oxidant

Clapp and Jenkin (2001) have analysed the relationships between ambient *daylight* concentrations of O_3, NO and NO_2 as a function of NO_x from rural and urban stations across the UK. They introduce a variable 'OX', which represents the total concentration of oxidant, by adding the concentrations of O_3 and NO_2 together. With ppb units:

$$[OX] = [O_3] + [NO_2]$$

They investigate how this varies with NO_x. A graph of *daylight* OX versus NO_x was a straight line with a positive intercept. The intercept represents a steady background or regional value, while the upward slope of OX versus NO_x reflects local or primary emissions of NO_x. From their regression line, for six sites in November of 1998 and 1999,

$$[OX] = 0.104[NO_x] + 31.1 \text{ ppb}$$

They suggest that *daylight* OX may be regarded as comprising two parts:

1. a regional contribution (or background) that approximates to O_3 and is largely independent of NO_x;
2. a local contribution that correlates with the primary contribution of local NO_x emissions to local NO_2, plus local oxidation of NO into NO_2 by O_2 (which is more significant at high NO) and local emissions of some species, like HONO, that can contribute to the NO to NO_2 conversion.

Clapp and Jenkin (2001) investigated the variation of OX with NO_x, based on annual means, and derived functions for variation of annual mean NO_2 as a function of NO_x which take account of possible changes in the regional background of O_3.

This may provide a convenient way for a regulator to consider both O_3 and NO_2 together in *daylight* when looking at a permit application. However it is unclear what happens with this formula at night.

When they looked at other months of the year, a similar dependence was found, but for April to September scatter was significantly greater than that in winter. They suggest this reflects variations in regional or background contribution, with raised levels during photochemical episodes. From their regression lines in June 1998 and 1999, the episode days had the higher background:

$$[OX] = 0.112[NO_x] + 55.5 \text{ ppb}$$

The non-episode days had a lower background (but at 38.2 still a little larger than 31.1 seen in November):

$$[OX] = 0.097[NO_x] + 38.2 \text{ ppb}$$

By this method (and by excluding episode days) a seasonal variation in the intercept (regional or background contribution to OX) and slope (gradient of OX versus NO_x) was derived. The variability month by month is seen in the gradually changing intercept (background OX) and slope (dOX/dNO_x). They also produce an annual regression, which varies a little from site to site.

An implication of these results is that there is a potential mechanism here for regulators to impose tighter controls when episode days are forecast, as these would introduce a higher regional or background level of oxidant.

We now examine some of the chemistry of NO, NO_2 and O_3 that is covered by Clapp and Jenkin (2001) and then extended in Jenkin (2004a, 2004b).

2.6.1 Outline of Clapp and Jenkin (2001) methodology

Clapp and Jenkin (2001) analysed the relationship between O_3 and NO_x using monitoring data and reference to the photostationary state. Thermal oxidation by oxygen molecules is also mentioned. O_3, NO and NO_2 are chemically coupled, so O_3 and NO_2 are inextricably linked. The response of NO_2 to emissions reductions in NO_x is highly non-linear. Changes in global O_3, such as a rising background, influence local O_3 and NO_2 and affect the success of emission controls.

The behaviour of total oxidant OX is investigated. Most of the analysis uses 'daylight-hour averages', namely pollution data from those whole hours that fall between sunrise and sunset are averaged together for each day in turn. These are not daily averages, nor do they have the same averaging period through the year. They are used because photochemistry is closely linked to light intensity.

Chemical coupling by the normal two reactions of the photostationary state is discussed using the rate constant k for NO + O_3 and the NO_2 photolysis rate J. They derived an algebraic expression, which we show in Section 2.7, to be in part essentially equivalent to the usual one [such as R_p discussed by Middleton (1998) for the BOXURB model]. At 51.5°N in November they have the daylight-averaged photolysis rate $J = 2.9 \times 10^{-3}\ s^{-1}$. This daylight average is not strictly comparable to the rather smaller numerical values in the Nuclear Accident Model (NAME) and STOCHEM as quoted by Collins *et al.* (1997) for a solar zenith angle of 15°, clear sky and $z = 0.5$ km. Also, Clapp and Jenkin (2001) do not give either a value for k or the rate expression, so it is not possible to know the value of J/k that their Figure 1 was based upon. In this, O_3 is plotted against log NO_x, NO against log NO_x, NO_2 and log NO_x. From their paper alone the curves cannot be recalculated without knowing their value of k. The value they probably used may be inferred from other papers by them (discussed in Section 2.6.2) or from evaluated chemical databases for the NO + O_3 reaction, as in the paper they quote by Atkinson (1994).

Thus Clapp and Jenkin (2001) used the same photostationary state assumption as Middleton (1998) did in BOXURB, albeit in terms of NO, NO_2 and O_3 rather than NO_x, NO and O_3. The two forms are equivalent.

Clapp and Jenkin (2001) discuss the significance of the molecular reaction NO + NO + O_2 for oxidation of NO by O_2, which is second order in NO. This acts as a thermal source of NO_2, but it is strongly dependent on the reaction rate because it is much more rapid at high concentrations of NO, such as those found near to the emission source, or in winter episodes (see below). Note that this reaction is not present in either the STOCHEM chemistry scheme of Collins *et al.* (1997) or the NAME schemes by Redington *et al.* (2001), which closely followed the STOCHEM scheme. In such models the use of large grid cells lowers the effective concentrations presented to the chemistry scheme and this particular reaction, if in the reaction scheme, might well be very slow or even negligible with such grid cell sizes. Its absence from the list of reactions may represent a limitation of NAME under certain circumstances as the model will not show the upturn in NO_2 that is expected when NO is very large. This might cause some underprediction of NO_2 in the severest urban winter NO_2 episodes, as well as in plumes near to emission sources that have a large NO emission rate. To oxidise 1% of NO, the reaction takes about 20 seconds at 100 ppm NO compared with the much longer time of 1 hour for a much lower concentration of 0.5 ppm NO (500 ppb). For appreciable NO_2 production via this route the concentration of NO may need to be approaching ~1 ppm (1000 ppb). In London in December 1991 this NO_2 formation mechanism is thought to have been important [see Bower *et al.* (1993) and Bower (1994), who regarded this reaction as a factor in forming high NO_2 episodes]. Such levels are now rarely observed in the UK. Seinfeld (1986) also briefly mentions this reaction – it is important as it leads to small quantities of NO_2 found in exhaust gases from combustion sources where the $[NO]$ is high. Inclusion of the reaction in NAME merits attention.

Clapp and Jenkin (2001) briefly mention factors that influence NO_2 production, photolysis efficiency and radical chain length, but a fuller discussion, if desired, is given in Chapter 3 of Seinfeld (1986). They also suggest HONO may play a role as it is photolabile and so easily leads to more radical production in urban areas.

Much of Clapp and Jenkin (2001) covers their lengthy analyses of monitoring data from a range of UK sites, and is not reviewed here. In summary they suggest that a background oxidant level is the intercept in their plots (that is, constant, independent of the NO_x levels) and local oxidant is the variable. Following these site data analyses, they then consider the ability of idealised or theoretical curves to track the monitoring data. Their remarks have particular significance for the Environment Agency with reference to Task 2 in this project, where our goal is to find simple methods to predict NO_x conversion to NO_2.

Clapp and Jenkin (2001) suggest that idealised curves, which assume the photostationary state, are reasonable for daytime, but not at night. At sites with annual means around, say, 40 ppb NO_x, where $NO \approx O_3 \approx$ 10-15 ppb each, then neither is in excess and the reaction NO + O_3 is second order, with the rate of reaction given by $k[NO][O_3]$. The rate decreases as O_3 and NO are consumed. At night complete conversion of NO and O_3 to NO_2 and O_2, respectively, might be expected, but it is kinetics-limited – the reaction becomes too slow to reach completion within a reasonable time period. At night or in the dark the reaction does not reach completion and NO and O_3 may co-exist. The yield of NO_2 is less than unity. An idealised curve based on the photostationary state is liable to overpredict NO_2 yield, especially when NO_x at night ~40 ppb. It is difficult to give theoretical curves to describe NO_2 variation with NO_x, even though the broad qualitative behaviour can be explained. This is important, as it explains why Clapp and Jenkin (2001) conclude by arguing in favour of empirical relationships fitted to the monitoring data.

Summarising, from Clapp and Jenkin (2001) we identify two kinetics-limited situations:

1. At very high NO, as in an exhaust pipe or by the kerb in the cold winter smogs of the past, the oxidation of NO by molecular oxygen may be fast enough to cause an upturn in NO_2 yield when NO is above ~500 ppb (NAME presently omits this reaction). At anything other than the very highest NO concentrations the reaction is generally kinetics-limited and too slow to be very significant.
2. At night with modest NO_x ~40 ppb, oxidation of NO by O_3 becomes quite slow and gets slower as the reactants are consumed: it is unlikely to reach completion. Therefore at night some NO and O_3 may co-exist. The yield of NO_2 is kinetics-limited and will not reach 1.0.

Recently to examine policy controls on NO_x emissions, Jenkin (2004a) followed up this work with a paper that looks at NO, NO_2 and O_3 as a coupled system . This represents a potentially more general approach than the simplest empirical curves above, in which NO_x was assumed to be the primary and only independent variable. A variety of monitoring sites were used, from kerb to rural. He establishes:

1. how OX varies with NO_x;
2. the partitioning or fractional contributions NO_2:OX and O_3:OX.

He then uses these to formulate empirical expressions for different parts of the UK and to consider future NO_2 concentrations. His method decouples the chemical partitioning (NO_2 or O_3, as above) from sources of oxidant, so it is able to make predictions that distinguish regional oxidant changes (O_3 background) from local oxidant emissions (NO_2 from primary NO_x emissions). This approach appears to be very relevant to the requirements of Task 2 and is analysed in some detail in Sections 2.6.2 to 2.6.5.

2.6.2 Rearrangement and analysis of the Jenkin method

It is necessary for Task 2 of the current project to examine the Jenkin method in some detail because it has been of considerable interest to AQEG, the government's advisory body, and is discussed in their report *Nitrogen Dioxide in the United Kingdom* (AQEG 2004). However to explain the method, this review takes Jenkin's published ideas on NO_2 in a rearranged order, so that the key steps may be followed logically in as simple a way as possible. The Jenkin methodology can only be fully appreciated if three papers are studied together. These are Jenkin (2004a, 2004b) and the preceding paper by Clapp and Jenkin (2001). The methodology first explored in Clapp and Jenkin (2001) is used in Jenkin (2004a) to analyse annual mean data, and in Jenkin (2004b) to analyse hourly data.

All three papers contain the photostationary state equations, whereby the rate of reaction between NO and O_3 and the photolysis of NO_2 are assumed equal:

$$k[\mathrm{NO}][\mathrm{O_3}] = J[\mathrm{NO_2}]$$

By definition $[NO_x] = [NO] + [NO_2]$ and $[OX] = [NO_2] + [O_3]$. Jenkin (2004a) in the legend to his Figure 2 used the representative annual average values $J = 2.2 \times 10^{-3}\ s^{-1}$ at latitude 51.5°N, and $k = 3.7 \times 10^{-4}\ ppb^{-1}\ s^{-1}$ at $T = 283.15$ K, from which $J/k = 5.9459$ (ppb).

Note that Clapp and Jenkin (2001) use in their Figure 1 a November daylight averaged value for $J = 2.9 \times 10^{-3}\ s^{-1}$ at latitude 51.5°N, but no value for k is cited there [their likely source is Atkinson (1994), see Section 2.6.1]. However, in their Figure 13 Clapp and Jenkin (2001) use an estimated annual average value of $J = 2.9{\times}10^{-3}\ s^{-1}$ at latitude 51.5°N, but again no value for k is cited. These slightly obscure details are noted here to show the reader that care is needed when J and the temperature are selected to evaluate k.

The value for J/k of 5.9459 ppb compares favourably with the value of J/k = 8.7591 ppb which Middleton (1998) derived from a photochemical episode recorded in Bexley in May 1995. Middleton (1998) used it in the BOXURB model to calculate elevated NO_2 when similar conditions with expected high O_3 were forecast. The work showed that the yield or ratio NO_2:NO_x is not very sensitive to the exact value of $A = J/k$, once O_3 is above ~30 ppb. The yield curve versus O_3 as J/k was increased from 4 to 16 tended asymptotically towards a yield of 1 as O_3 increased.

In his Appendix A, Jenkin (2004a) rearranged and combined the above three equations. He then solved the resulting quadratic equation to obtain the following physically realistic solution by the use of the plus sign:

$$[NO_2] = \frac{-Z \pm \sqrt{Z^2 - 4[NO_x][OX]}}{2}$$

which has the units in ppb.

We define $Z = \left([NO_x] + [OX] + J/k\right)$ in ppb. This idealised photostationary state equation for NO_2 can be used to calculate NO_2 concentrations as a function of NO_x, provided a value for the total oxidant concentration of OX can be specified. In other words, the significance of Appendix A is that it gives us an idealised general function for NO_2 expressed as a function of NO_x.

Clapp and Jenkin (2001) plotted the monitoring data in the form of scatter plots. They plotted [OX] versus [NO_x] and obtained straight-line plots of the form:

$$[OX] = A[NO_x] + B$$

They called the slope A the '*local* oxidant concentration' because it represents the gradual rise in the local OX as the NO_x increases. They called their intercept B, which is a constant OX value, the '*regional* oxidant concentration' because it was independent of NO_x. The slopes A varied somewhat from one region or from one site location to another, but nevertheless most fell in the range 0-0.2 ppb ppb^{-1}, with many in the range 0.1-0.2 ppb ppb^{-1}. The intercepts were all very similar, so B falls in the range 33 ± 1 ppb.

Figure 13 in Clapp and Jenkin (2001) and Figure 2 (Part 1) in Jenkin (2004a) appear to be similar to the idealised curve calculated using the above solution, together with values of OX obtained from the best fit-lines in their scatter plots. Thus to use the idealised formula they use their empirical results from plots of the monitoring results. The empirical plots of annual means are used to estimate OX as a function of NO_x, and then the idealised formula is used to estimate NO_2 as a function of the NO_x.

The consequence of the above equations is that they can be used to plot the annual mean of NO_2 versus that of NO_x, taking account of the regional oxidant background (the intercept B) and the local oxidant (the slope A). Since the regional oxidant B is broadly constant (33 ± 1 ppb), site-to-site variations in annual mean NO_2 can be represented by the small changes in value of the fitted slope A (mostly ~0.1-0.2 ppb ppb^{-1}). The method allows for future increases in regional oxidant that may be envisaged under climate change.

2.6.3 Analysis of annual means by Jenkin (2004a)

The major part of Jenkin (2004a) is an analysis of annual mean data. He chose sites where NO, NO_2, NO_x and O_3 were all monitored, so that [OX] was immediately calculable. He plotted graphs for the annual means of OX versus NO_x, as discussed above, and arrived at his regional oxidant (intercept *B*) and local oxidant (slope *A*). He was able to sort the data from many stations into two broad groups. He describes the fraction of total oxidant that is attributable to NO_2 as $[NO_2]/[OX]$. He fitted polynomials $f([NO_x])$ to this ratio $[NO_2]/[OX]$ as a function of the total NO_x $x = [NO_x]$.

'Polynomial 1' is used to fit data from sites near to roads:

$$\frac{[NO_2]}{[OX]} = f_1(NO_x) = 8.962\times10^{-2} + 1.474\times10^{-2}x - 1.290\times10^{-4}x^2 + 5.527\times10^{-7}x^3 - 8.906\times10^{-10}x^4$$

'Polynomial 2' fits data for sites not near to roads:

$$\frac{[NO_2]}{[OX]} = f_2(NO_x) = 1.015\times10^{-1} + 1.367\times10^{-2}x - 6.127\times10^{-5}x^2 - 4.464\times10^{-8}x^3$$

Jenkin (2004a) uses the following steps to obtain empirical curves for annual means at a range of stations. By definition:

$$[NO_2] = [OX]\frac{[NO_2]}{[OX]}$$

where the first factor [OX] is from the scatter plot best-line fit $A[NO_x] + B$, and the second factor is the ratio $[NO_2]$:[OX] from the fitted polynomial using f and is either f_1 near to roads or f_2 not near to roads, as appropriate.

Hence the annual mean $[NO_2]$ is:

$$[NO_2] = (A[NO_x] + B)f([NO_x])C$$

Similarly, the annual mean $[O_3]$ is:

$$[O_3] = (A[NO_x] + B)(1-f)([NO_x])C$$

The factor *C* is an empirical multiplier usually near to unity that scales the method to fit the measurements.

The above method is for annual means at sites where O_3 was monitored; not all stations have this capability. To make estimates at other locations, Jenkin (2004a) combines data to obtain some generic expressions to represent his range of OX versus NO_x scatter-plot lines of fit, and f is either f_1 or f_2 as before:

1. in Central London, *A* = 0.140, *B* = 34.7 and *C* = 1.0;

2. outside Central London, *A* = 0.093, *B* is taken from the values in Table 1 of Jenkin (2004a) and *C* = 1.0.

The ‘national air quality model’ was developed in the UK by Stedman *et al.* (2001, 2003) and is another empirical formulation. Expressions of the following form were used to describe the annual mean $[NO_2]$ µg m^{-3} from monitoring data in relation to the monitored annual mean $[NO_x]$ µg m^{-3}:

$$[NO_2] = \chi\left([NO_x]\right)^{0.6887}$$

Here the factor χ is to adjust for site location and is 1.86 for Central London, 1.76 for Inner London, 1.67 for Outer London and 1.58 elsewhere. The AQEG report on NO_2 (AQEG 2004) makes use of the Stedman method, although slightly different values for the factor χ may be invoked. The exponent 0.6887 remains the same, however, so the general shape of the curve is not affected.

Jenkin (2004a) found his expression for ‘not near to road’ (using f_2) was in reasonable agreement with the ‘national’ annual average model of Stedman *et al*. (2003). Comparisons of annual methods are considered below.

2.6.4 Comparison of curves for annual mean NO_2 concentrations

Calculations were carried out as part of the present study to investigate the methods cited by Jenkin (2004a). Figure 3 contains results of our calculations of five different curves for the annual mean NO_2 concentration versus the annual mean NO_x concentration. The root of the quadratic in Appendix A of Jenkin (2004a) is plotted assuming an intercept for OX equal to 33 ppb. This generates a curve that rises steeply for the first 50 ppb of NO_x, and then rises at a steady but slower rate. The sensitivity of this curve to an increase in background total oxidant is also shown in Figure 3 by plotting the same curve but with an intercept for OX equal to 50 ppb. An increase in OX raises the annual mean NO_2 at all values of NO_x while following the same general shape.

For comparison, in Figure 3 the Stedman *et al*. (2003) ‘national’ model for annual mean NO_2 is plotted. Here we use the model for sites outside London:

$$[NO_2] = 1.58\left([NO_x]\right)^{0.6887}$$

Finally in Figure 3 we also plot the two empirical polynomials from Jenkin (2004a). These curves, as often happens when fitting polynomials to monitoring data for NO_2 and NO_x, quickly diverge to unrealistic values. In this case the curves rapidly decrease once outside their original range and then plunge to negative values. While we recognise that the larger annual mean concentrations of NO_x shown along the x-axis of Figure 3 are unlikely, the plot is useful. It reveals that the behaviour of these two polynomials is not consistent enough to be used for regulatory applications. Procedures to estimate annual mean NO_2 should explicitly exclude the use of these two polynomials, so that there is no possibility that they will inadvertently go out of range into decreasing or even negative results.

2.6.4.1 Key points

In this section we analysed the Jenkin (2004a) method to explain how he arrives at a scheme for estimating annual mean NO_2 and annual mean O_3 as a function of the local annual mean of total NO_x. While being in good agreement with the 'national' model it has the added advantage that it is able to take account of projected changes of regional oxidant that may arise through, say, climate change. The effect of a change in total oxidant from 33 to 50 ppb is shown in Figure 3.

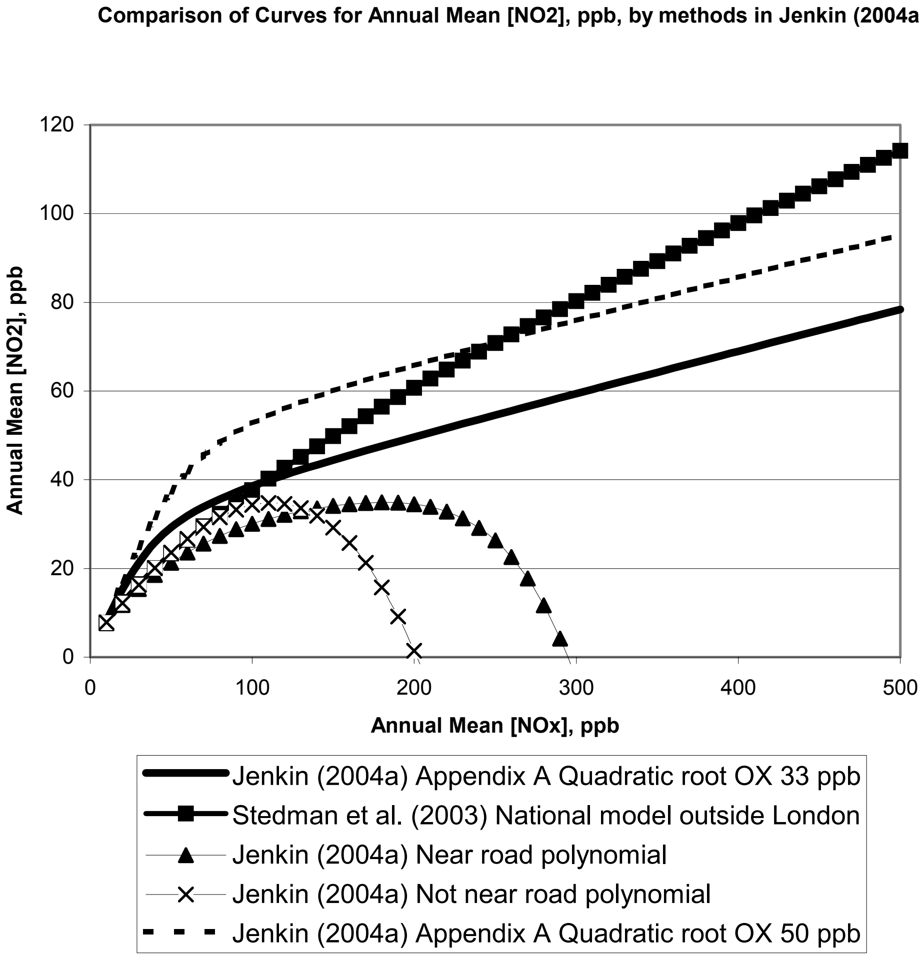

Figure 3: Comparison of methods for the curve of annual mean NO_2 versus annual mean NO_x, including the Jenkin (2004a) quadratic for total oxidant OX at 33 ppb and at 50 ppb, along with the 'national' model. Two empirical polynomials that appear unsuited for regulatory use are also shown.

2.6.5 Analysis of hourly means by Jenkin (2004b)

In Part 2 of Jenkin (2004b) he extends the above method to look at (short-term) hourly concentrations. Again he uses scatter plots of [OX] versus [NO_x] to isolate the regional contribution to total oxidant as an intercept. By treating the hourly data one month at a time he shows the seasonal variation in this regional oxidant. It reached a maximum concentration of ~43 ppb in the springtime (April). He also reveals a diurnal variation in the slope, which he considers to represent the local total oxidant, with the highest values by day (~0.11 ppb ppb^{-1}). Curiously, his analysis did not include summer photochemical episodes, when we know from the work of Middleton (1998) using Bexley data that NO_2 yield may be elevated. Jenkin (2004b) draws out some important observations that are relevant to regulating NO_2:

1. in 1999, hourly values for $[NO_x]$ spanned a wide range, 11-1145 ppb, with the annual mean of 204 ppb;
2. over the year, NO_2 was the dominant component of total oxidant, at 88% of OX;
3. when NO_x was low, typically summer night-time, NO_2 was only ~25% of OX;
4. when NO_x was high, typically winter daytime, NO_2 made up most of the OX.

This variation in the relative yield of NO_2 by time of day and season in the year should be considered when the amount of NO_x control needed to meet the hourly NO_2 standard is evaluated.

Finally, we note that although he analysed hourly data by the same method as for his annual data, Jenkin (2004b) appears to refrain from offering a generic expression that might be used to assess NO_2 in a regulatory context. This makes his short-term analysis less immediately applicable than his earlier (Clapp and Jenkin 2001; Jenkin 2004a) long-term analysis which did present a pair of generic expressions.

2.6.6 Key points

The Jenkin (2004b) analysis of hourly data seems less applicable for the Environment Agency than the apparently quite useful, and fairly simple to evaluate, annual mean generic expressions of Jenkin (2004a) and Clapp and Jenkin (2001). Work in this project using the Met Office's NAME model has looked at simple ways to evaluate short-term NO_2 concentrations, but not the annual means.

Since the Environment Agency has to consider both the annual mean and the hourly values, we suggest the Jenkin (2004a) and Clapp and Jenkin (2001) methodology be considered to regulate annual mean NO_2. Alternatively the 'national' model of Stedman *et al.* (2003) might be used. It is simpler, but will not allow for future changes in regional oxidant to be considered.

Our recommendations for a method to regulate short-term average NO_2 will therefore be considered in the modelling report using the NAME model under Task 3 (see Task 3 reports).

2.7 The photostationary state

This is an important simplification for the $NO–NO_2–O_3$ system in the presence of daylight. We encountered this in the preceding sections and it is discussed more fully here. The photostationary state assumes that the two reactions that photolyse NO_2 and oxidise NO by O_3 are rapid and soon achieve equilibrium. In the photostationary state, the ratio of NO_2:NO_x is given by the simple formula (Middleton 1998):

$$R_p = \frac{[NO_2]}{[NO_x]} = \frac{[O_3]}{A + [O_3]}$$

where $A = J/k$. Here J is the first-order rate constant for the photolysis of NO_2, and combines information on the light intensity (number of photons absorbed) and the quantum efficiency (number of molecules of NO_2 destroyed by photolysis per photon absorbed). The rate of photolysis is given by $J[NO_2]$. The oxidation of NO by O_3 has rate constant k so the rate is $k[NO][O_3]$. For a given value of A, the ratio R_p increases from zero when O_3 is zero to approach unity as O_3 increases. Above around 80 ppb of O_3, R_p approaches unity. When $[O_3] < 30$ ppb, the ratio R_p is strongly dependent upon the value of A, but for $[O_3] > 60$ ppb, the ratio R_p is much less sensitive to A. The chemistry routine in the dispersion model ADMS, especially the two-reaction scheme, is expected to reproduce this type of asymptotic behaviour, as it has the same two reaction steps. The photostationary state may be adapted for simple seasonal adjustments that can allow for the background concentration of O_3, and:

1. J can be calculated from solar elevation and the cloud cover. Solar elevation is well defined according to latitude, time of day and day of year. Cloud cover may be summarised climatologically for a given location [synoptic station data or numerical weather prediction (NWP) data for the nearest grid-point].
2. k can be calculated according to absolute temperature T using the activation energy. The temperature may be chosen at the effective plume height or at ground level, and can also be summarised climatologically for a given location (synoptic station data or NWP data for the nearest grid-point).
3. the semi-empirical variation in the value of A can be derived as a function of time of day and season.
4. R_p, the yield of NO_2 may then be estimated using two variables, the background O_3 concentration (from a seasonal climatological summary or from a predetermined threshold or modelling values), together with the value of A.

Once an algorithm, nomogram or climatology of R_p is determined, it can be multiplied by the expected plume concentration of NO_x (plus the background NO_x from area sources and roads if appropriate) to give the likely range of NO_2 concentrations. This has the potential to provide seasonal and diurnal variations in NO_2 for a given plume burden in the presence of a local background in NO_x and a general background O_3 concentration.

This should make it possible to make rapid assessments of likely NO_2 that can allow for the two important reaction steps according to seasonal sunlight and the concentrations of NO and O_3. It seems to have more flexibility than a fixed ratio, or the traditional empirical curve that has NO_x as the sole independent variable. It can be adapted to temperatures, either at plume height or the ground. Table 1 shows some values for $A = J/k$.

Table 1 Summary of values of $A = J/k$ for the ratio of the rate constant for NO_2 photolysis J to the rate constant k for the $NO+O_3$ reaction.

Source and application	Rate constant of NO_2 photolysis, J, (s^{-1})	Rate constant (O_3 + NO), k ($ppb^{-1}\ s^{-1}$)	Value of *A, J/k* (ppb)
Middleton (1998) Bexley hourly data	n/a	n/a	8.7591
Janssen *et al.* (1988) aircraft plume data	J ranges from 0.0 to 9.16667×10^{-3}	4.8333×10^{-4}	18.9656
Jenkin (2004a) Part 1, November daylight average annual mean data	2.2×10^{-3}	3.7×10^{-4}	5.9459

For a given O_3 concentration, the photostationary state ratio $[NO_2]:[NO_x]$ is given by $R_p = [O_3]/(A+[O_3])$. This, according to the plume data of Janssen *et al.* (1988), the Bexley data in Middleton (1998) and the root of the quadratic in Jenkin (2004a), represents a limiting downwind ratio for conversion of NO_x to NO_2 in daylight. The daytime conversion is thus sensitive to daylight (J) as well as to the temperature, which affects k, and to O_3 in the surrounding air, which appears in the ratio R_p.

2.8 Deviations from the photostationary state

The photostationary state is used in the Janssen *et al.* (1988) method as their downwind limiting case (see Section 1.4 above). Deviations arise near the stack because NO_2 formation is retarded by the mixing process (O_3 is limiting) and because the NO + NO + O_2 reaction may contribute where NO concentrations are very high. However the NO needs to be of the order of several ppm for this to be significant, as summarised in Sections 2.3 and 2.6.1 above. Janssen (1986) showed that inhomogeneous mixing in plumes should be taken into account. Finally, it is also necessary to remember that combustion gases typically contain a few per cent (~5% typically) of the total NO_x in the form of primary NO_2.

At night the photostationary state also cannot apply, for $J = 0$. Janssen *et al.* (1991) consider the formation of various products at night, NO_2, HNO_3 and NO_3, discussed in the Task 1 report. Different chemical pathways can be followed at night, as discussed in that report. Not only are the reaction mechanisms different, but the plume may be above the boundary layer, where more O_3 is available, or trapped below the inversion, where O_3 is limited in abundance. The availability of O_3 will affect the yield of NO_2. In the Task 3 reports we discuss the differences in results between daytime and night-time for the sensitivity runs carried out as part of Task 3 .

2.9 Summary of empirical schemes

Empirical schemes are valuable in situations where a very quick and approximate response is sufficient. In local air quality management, empirical forms allow decisions as to whether a particular area requires more detailed study. Similar considerations may apply to screening permit applications to the Environment Agency to establish which require detailed chemistry and plume modelling. Section 3 looks at such detailed approaches using numerical methods to solve the chemical kinetics. However such methods can demand large computer resources and require comprehensive data sets for chemical species, so are not necessarily appropriate in all regulatory scenarios.

3 Reactive plume models

The production of secondary pollutants, like NO_2, O_3 and particles, takes place by chemical reactions that occur while the plume travels with the wind. Thus a computer model of the chemical reactions that take place can be used to calculate the amount of pollutant generated and the rates of each reaction. This is the approach adopted in reactive plume modelling systems.

Such modelling systems are sensitive to a wide range of factors. Figure 4 summarises the many sensitivities or processes, both physical and chemical, that can influence the behaviour of chemical species in a large plume. Figure 4 shows that the principal factors are:

1. the national emissions background from the UK and Europe for hydrocarbons (anthropogenic and biogenic) and other precursors, such as NO_x;
2. the background concentrations of reactants, such as O_3 or hydrogen peroxide (H_2O_2);
3. the properties of the plume that influence plume rise and the entrainment of background air into the plume;
4. the atmospheric (meteorological) conditions that influence the path followed by the plume, its rate of mixing (dispersion) and whether it meets an inversion layer or approaches the ground;
5. the chemical mechanism contained within the system, as discussed elsewhere in the this report;
6. the deposition processes that influence removal from the plume.

As part of Task 3 some simple sensitivity studies were carried out to vary one component of the system at a time, and thereby reveal something of the range of high and low concentrations of secondary pollutants that a plume might generate. The new NAME III model has been used to explore the effects on a plume caused by changes in the background concentration of O_3. In such sensitivity studies Figure 4 reveals that, potentially, an enormous number of model runs may be tried. In practice, some degree of subjective judgement must be invoked to simulate variations in the most important independent variables only.

In the this section we focus on the modelling of plume chemistry. After looking briefly at the principles, we discuss a number of reactive plume models.

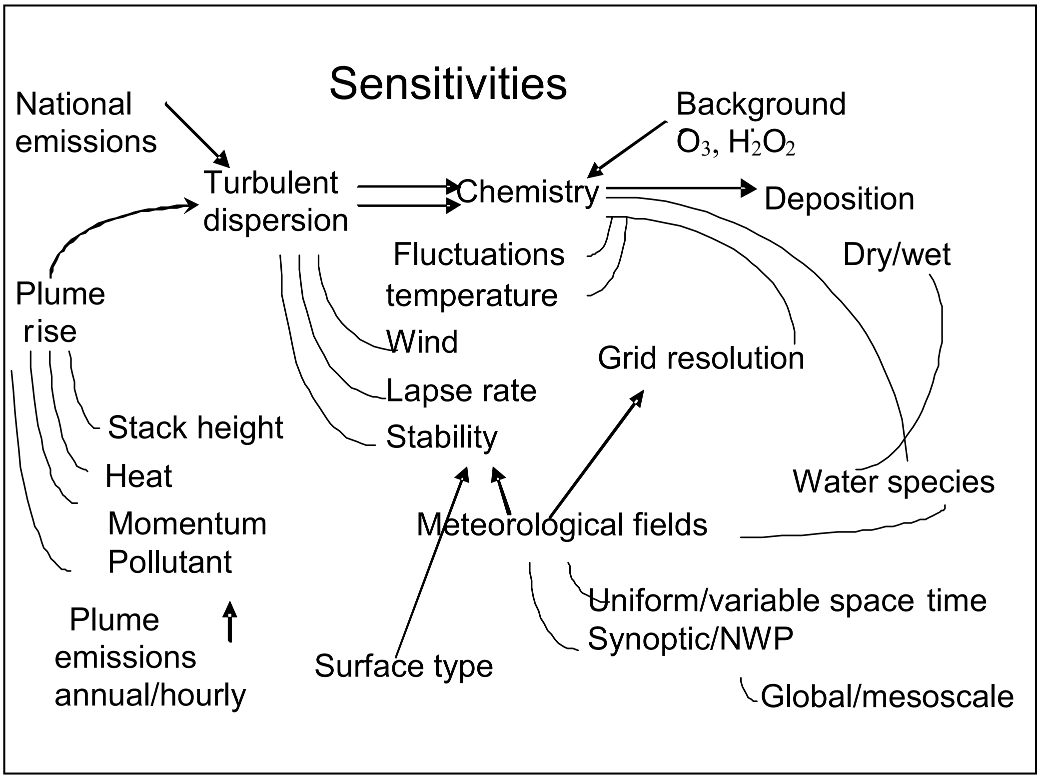

Figure 4 Schematic illustration of possible routes that may be investigated through model sensitivity analysis.

3.1 Numerical chemical kinetics equation solvers

The elementary steps in a chemical mechanism are typically ordinary differential equations (ODEs) in the form of one equation per chemical step. The equation is usually in the form: rate = rate constant times concentrations. While one or two ODEs can be simple to solve numerically (or even analytically), the large number of reaction steps in the atmosphere renders their integration to be a computationally very demanding task. The problem is exacerbated because such systems are often 'stiff', a mathematical concept meaning that some reactions are very fast, while others in the mechanism are much slower. Such disparity in rates makes solution more difficult. Well-established techniques exist to deal with this special type of problem.

In 1987, Byrne and Hindmarsh wrote a landmark review of the then 'state of the art' in solvers for ODE systems, which included those characteristic of chemical kinetics. Their review was written for the user seeking to learn how such systems of equations can be solved. They said that stiff ODEs could be solved 'more-or-less routinely'. They explain the concept of stiff ODEs, where they arise, and what the software needs to do. They included a number of numerical examples collected during the previous 15 years. Hindmarsh subsequently published the Livermore solver, LSODE (Radhakrishnan and Hindmarsh, 1993). Earlier Hindmarsh *et al.* (1984) had considered the conditions for stability when solving the advection dispersion equation, commonly used in air quality models, and strongly endorsed the von Neumann method for analysing stability.

A number of solvers are available as software packages, and for simpler chemical kinetics schemes the chemistry may be coded directly into the model. Users can select a solver package that suits the complexity of the reaction scheme they wish to model. The numerical problems experienced in the early days of solving the equations of chemical kinetics are no longer an issue and need not concern the model user. Here we have space only to consider codes most relevant to this particular study. We summarise the FACSIMILE scheme as used by Derwent and Nelson (2002) in the box modelling of their reactivity index. Atmospheric chemistry based on ASAD ('A Self-contained Atmospheric chemistry coDe') is currently being built into the Met Office's Unified Model, in a project called Air Quality in the Unified Model (AQUM). We also summarise the ADMS model chemistry and the NAME model chemistry (which derives from STOCHEM). The appendix to this report provides a short summary by Derwent of the very large literature which exists on tropospheric chemistry models.

3.2 FACSIMILE

FACSIMILE is the chemical kinetics solver developed at AEA Technology Ltd, Harwell. The FACSIMILE code is described in Curtis and Sweetenham (1987). FACSIMILE was used in the study of a chemical reactivity index by Derwent and Nelson (2002) to solve the chemical kinetics in the Master Chemical Mechanism (MCM), described in Section 3.3. The code is a variable-order Gear's method, able to handle some 2400 chemical species and the 7100 kinetics expressions in the mechanism.

3.3 Master chemical mechanism

As its name suggests, the MCM contains a very large set of chemical species and their reactions. It is designed to produce a comprehensive description of the photochemistry in the troposphere (that is, in the lowest part of the atmosphere where much of the shortest wavelengths of ultraviolet light from the sun have been filtered out by the stratosphere aloft). MCM was solved by FACSIMILE when used by Derwent and Nelson (2002) in a trajectory box model to calculate the yield of O_3 from different volatile organic compounds (VOCs) to derive a chemical reactivity index. The MCM is described by Saunders *et al.* (1997). At the time of writing, Version 3.1 of MCM is available at http://mcm.leeds.ac.uk/MCM. It has the chemistry for 135 emitted VOCs in a mechanism that contains 5900 chemical species and 13,500 chemical reactions.

3.4 UKCA, ASAD and the Met Office's Unified Model

The large modelling system to be covered here is unlikely to be used in typical regulatory applications. However to model plume chemistry requires some initial fields of concentrations for the background chemical species. It is therefore relevant to discuss in a brief manner the Met Office systems that might lead to background pollutant fields. It is also useful to point to future modelling developments that may be of interest to the Environment Agency, not least to assess possible implications for future policy.

The Met Office NWP model is called the Unified Model, because where possible it uses a common architecture for global and mesoscale weather forecasting and climate simulations. Traditionally, Met Office models for pollutant dispersion or atmospheric chemistry were coupled to the Unified Model in various ways. Briefly, these couplings comprise:

1. Storage of the arrays of numerical weather data (or 'fields-files') for use by the atmospheric dispersion model called NAME, developed for nuclear emergencies. It has been extended to include many dispersion applications ranging from volcanoes through fumigation events and the spread of foot-and-mouth virus to long-range transport and

chemical reaction of nitrogen and sulphur compounds to form aerosols and particles. The chemistry scheme in the NAME model is described in Section 3.7.

2. Use of these same fields-files as input to drive a global tropospheric chemistry model called STOCHEM. This has been used to examine problems such as future trends in O_3 concentrations as a function of future anthropogenic precursors (VOCs and NO_x). There are strong similarities in the NAME chemistry mechanism and STOCHEM, though they diverge in some aspects because the NAME scheme has been adapted to suit its own applications, such as aerosol chemistry. STOCHEM is described in Collins *et al.* (1997) and on the web site www.cgm.nerc.ac.uk listed with this reference..
3. Inclusion of stratospheric dissociation and chemical processes in the Unified Model to study interactions between stratospheric chemistry [including the possible effects of chlorofluorocarbons (CFCs)] and atmospheric dynamics. However as this focuses on the stratosphere where short-wavelength ultraviolet radiation is intense, it is not relevant to the current project.
4. Extraction of meteorological (analysis) fields and reformatting of the data to suit the well-known environmental impact models, such as ADMS or the American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD) that are used by the Environment Agency, local authorities and consultancies.

Recently the Met Office commenced the project AQUM as part of its research programme to incorporate UKCA (UK Chemistry and Aerosol Model) and ASAD chemistry into the code of the Unified Model. A joint team at the Met Office and the Universities of Leeds and Cambridge will carry this out. They will use the ASAD chemistry Fortran code from UKCA, which is described in Carver *et al*. (1997). See http://www.atm.ch.cam.ac.uk/acmsu/asad/ from where the following summary has been drawn. ASAD is designed to solve chemical kinetics without the users needing to develop their own numerical solver, but merely to list the species and their reactions. It includes a database for the chemical kinetics, which is drawn from International Union of Pure and Applied Chemistry (IUPAC) materials. The software is freely available subject to the terms of the licence.

Implementation of the code in the Unified Model requires modifications to the global and mesoscale codes, with testing for proper tracer diffusion and advection, in addition to verification of the chemical simulations that ensue. It should enable feedbacks between various processes, such as aerosol formation, radiation absorption and emission, and atmospheric dynamics. However it is expected to increase the computational burden of the combined model significantly. Initially it seems unlikely that runs will be available at grid sizes below 1 km, which may have implications for the proper modelling of individual point sources[1]. The influence of grid size depends upon the problem to be modelled and whether or not the grid size can be reduced or can be made of a variable resolution during the run. As presently envisaged, it is fair to assume the finest resolution will be at the 1 km scale.

The solver used with ASAD is not particularly fast, so for global application it proved necessary to consider ‘families’ of species. Work is in hand at the Met Office to experiment with faster solvers (though the initial trials with a faster ‘backward-Euler’ solver meant some loss of generality in being specific to a scheme tested in the trials). Work is also in hand at Leeds and Bristol to take the MCM and develop consistent sub-schemes at lower levels of complexity to enable faster solution of the chemistry. Global scales would not be used for plumes, other than as the first step to defining initial lateral boundary conditions for nested mesoscale model runs, which can go to much finer scales. These might be used for more local NAME runs, or AQUM could be run as a mesoscale system.

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[1] Other Eulerian grid models have a similar grid size limitation, and the NAME chemistry scheme in Section 3.7 has grid cells into which concentrations are calculated prior to the chemistry step, so grid cell volume is also an issue in NAME.

The ASAD code can be used as the kernel of an atmospheric chemical kinetics model, for the user has only to write input and output routines that transfer data to and from the kernel. It is also designed for the user to be able to code and add their own deposition modules and other processes, such as heterogeneous reactions or photolysis schemes. ASAD recognises ‘families’ or ‘non-families’ of chemical species, as used in lumped schemes, and also allows explicit use of individual species. The main reaction types are photolysis, bimolecular, trimolecular and heterogeneous. Branching reactions are also accepted (as two or more reactions). Species may be treated as separate species, as families or as tracers. The kinetic data can be user supplied or taken from IUPAC compilations in the public domain. The ASAD code can be adapted for use in pollution studies, the troposphere or the stratosphere.

3.5 Chemistry in ADMS and ADMS-Urban models

The ADMS and ADMS-Urban models are used to assess air quality at relatively short range, say 30 km. Hourly meteorological data are used to evaluate hourly mean concentrations; annual means may use hourly data or statistical summaries as frequency-weighted data. ADMS is often used for large point-source problems, such as impact assessment, while ADMS-Urban is used in local authority reviews and assessments of air quality. ADMS has a simple two-step photochemical scheme for NO_2. It also has the empirical curve from Derwent and Middleton (1996), as above.

The main chemistry options are:

1. ADMS and ADMS-Urban have the empirical curve from Derwent and Middleton (1996). To date, so far as we are aware, the later empirical curves from more recent studies, for example Dixon *et al*. (2001), have not been coded into either model.
2. ADMS has a simple two-reaction photochemical scheme for NO_2 reactions: photolysis of NO_2 and oxidation of NO by O_3.
3. ADMS-Urban was adapted for Reviews and Assessments in towns because it has additional features (ADMS-Urban 2.0 User Guide) such as multiple-source modelling capability, including line sources and a street canyon sub-model, and the GRS.

3.6 Generic Reaction Set

A pioneering study by Johnson (1991), Azzi and Johnson (1991) and Azzi *et al.* (1992) used smog-chamber data to develop the GRS. This contains seven generic reactions whose rates are modelled to represent much more complex chemistry that occurs in their experimental chamber. A number of papers have used the GRS, for example Venkatram *et al*. (1994, 1998) and Vukovich *et al*. (2001). Tonnesen and Jeffries (1994) have since examined some of its limitations, and developed the very useful concept of the O_3 isopleth diagram, which draws lines of constant predicted O_3 maximum as a function of VOCs and NO_x. Such a chart conveys output from many runs of their model at a glance, enabling different mechanisms to be compared. The ridge line in such a plot shows the maximum O_3 mixing ratio that can be achieved at a given VOC ratio and it could be of value if it were made applicable to plumes regulated by the Environment Agency. We discuss the O_3 isopleth diagram and other indicators for O_3 in the Task 3 reports.

As stated above, the GRS is a reduced chemical mechanism containing 7 symbolic reactions to describe the much more complicated photochemistry found in the Commonwealth Scientific and Industrial Research Organisation (CSIRO) smog-chamber experiments, which simulated the real atmosphere. The GRS does not, however, subtract out chamber-specific artefacts. GRS is symbolic in not necessarily using identifiable chemical species, but introduces aggregated species into four representative types: reactive organic compounds (ROCs), radical pool (RP), stable gaseous nitrogen products (SGNs) and stable non-gaseous nitrogen products (SNGNs). In the photolysis of ROCs it is assumed by the GRS that the reactivity is conserved. The GRS is an empirical fit to the laboratory measurements and does not directly model the real atmosphere. The seven equations in the GRS are:

1. $ROC + h\nu \rightarrow RO_2^{\bullet} + ROC$	Photolyse reactive organic compounds
2. $RO_2^{\bullet} + NO \rightarrow NO_2$	Oxidant is produced here
3. $NO_2 + h\nu \rightarrow NO + O_3$	Photostationary state
4. $NO + O_3 \rightarrow NO_2 + O_2$	Photostationary state
5. $RO_2^{\bullet} + RO_2^{\bullet} \rightarrow RO_2^{\bullet}$	Radical reaction
6. $RO_2^{\bullet} + NO_2 \rightarrow SGN$	Stable gaseous nitrogen
7. $RO_2^{\bullet} + NO_2 \rightarrow SNGN$	Stable non-gaseous nitrogen

3.7 Chemistry in Met Office NAME model

NAME is a Lagrangian model. It releases particles from each emission source and to each particle is assigned a small part of the mass emissions of pollutants released from the source. Large numbers of particles are needed for a good simulation. In NAME virtual particles are advected and dispersed after release into a model three-dimensional (3-D) atmosphere carrying emissions of background pollutants. Each particle also carries information to mark its release point and emission source identity, which allows pollution to be attributed back to its source.

Inputs to NAME include the Unified Model global or mesoscale meteorological data and pollutant emissions for the UK, using data for sources of area 1 km^2 and for large point sources from the NAEI. NAME also uses the European EMEP[2] 50 km emissions database, which is important for the UK when pollution is imported into the country.

Chemistry is solved by sorting the virtual particles into grid cells to obtain the concentrations and then solve the chemical kinetics: see Malcolm[3] *et al.* (2000), Malcolm and Manning (2001), Redington and Derwent (2002) and the PUMA Project Report by Redington *et al.* (2001), which is currently the best summary of NAME II chemistry. However recently new features have been developed by Alison Redington to give the NAME III model. These were used in this project, as is reported in the Task 3 reports. Pollutants calculated include sulphates, nitrates, particulates, carbon monoxide (CO), NO_x, O_3 and SO_2.

NAME chemistry uses seven types of organic compound – toluene ($C_6H_5CH_3$), ethene (C_2H_4, also known as ethylene), formaldehyde (HCHO), propene (C_3H_6, also known as propylene), *ortho*-xylene [$C_6H_4(CH_3)_2$], acetaldehyde (CH_3CHO) and butadiene (C_4H_6). Isoprene (C_5H_8) may be included if biogenics are to be added. NAME has the gas-phase photochemical reactions of these species (with intermediates) when reacted with O_3, NO_2, NO, SO_2 and water (all phases) to produce oxidation reactions and the formation of aerosols, such as ammonium nitrate and sulphate. Further information on NAME and how it is used is given in the Task 3 reports.

The main parameters in NAME are given in Sections 3.7.1 to 3.7.13.

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[2] Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) www.emep.int

[3] Malcolm is the maiden name of Alison Redington, so the lead author is the same.

3.7.1 Emission-source identity

1. Major point source (tall stacks).
2. Area source or grid square.

3.7.2 Species identities

Emissions in the UK use NAEI[4] (1 km or 10 km grids; large point sources) and in Europe EMEP (50 km grid) emissions inventories. NAME requires the following species:

1. SO_2.
2. NO_x comprising NO, NO_2 (plumes assume 90% and 10% of NO_x respectively).
3. CO.
4. VOCs – NAME explicitly models seven VOC emissions: formaldehyde (HCHO), ethene (C_2H_4), propene (C_3H_6), isoprene (C_5H_8), *ortho*-xylene $C_6H_4(CH_3)_2$, toluene ($C_6H_5CH_3$) and 1,3-butadiene (C_4H_6). The emissions of these species are scaled up to represent the full VOC emissions inventory.
5. Ammonia (NH_3) – mostly agricultural sources, some anthropogenic.
6. Fine particulate matter less than 10µm in diameter (PM_{10}) – primary emissions.

3.7.3 Species properties

1. Mass emission rate, units g s^{-1}.
2. Chemical properties – molecular weight (relative molar mass), dry and wet deposition velocities or 'resistances' (defined in a species file).

3.7.4 Plume properties

Stack exit data are the property of the source; other plume data are constants or derived:

1. stack height above ground (use effective plume height to include the plume-rise estimate when rise is not modelled);
2. stack exit velocity;
3. stack exit temperature;
4. stack exit diameter;
5. specific heat (assume air);
6. thermal capacity (assume air);
7. mass flux;
8. thermal flux;
9. momentum flux.

Plume rise is not usually calculated when chemistry is being run, because of the high computational cost over long runs (say over 2 years). A faster plume-rise algorithm, or runs with many fewer point sources, would be needed when modelling chemistry.

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[4] www.airquality.co.uk

3.7.5 Calculation of downwind concentrations

In the NAME model a Lagrangian approach is adopted. As particles are advected and dispersed in the atmosphere they become more spread out. NAME then calculates air concentrations for the chemistry scheme by imposing a 3-D grid over the model domain, counting virtual particles into predefined volumes and summing the masses of each chemical species associated with each virtual particle within the cell. Division by cell volume defines air concentration in mass per unit volume (for example, g m^{-3}).

3.7.6 Concentrations for chemical kinetics

Concentrations must then be converted into other units more suited to the rate expressions of chemical kinetics, molecules per unit volume (for example, molecules cm^{-3}). The units must also be suited to Henry's Law and adsorption calculations of the exchanges of gases between gaseous and aqueous phases.

3.7.7 Background species

As well as modelling chemical species released into the atmosphere, NAME must also represent those species already present in the atmosphere that react with the released species. These include oxidants, such as O_3 and H_2O_2, and very reactive radical species, such as hydroxyl (OH), hydroperoxy (HO_2) and alkylperoxy (RO_2) species. NAME currently represents 14 such species. Species with very short atmospheric lifetimes (OH, HO_2, etc.) are generated within the chemistry scheme on the static 3-D chemistry grid in every model time-step and are used in the chemical reactions.

For species such as O_3 and H_2O_2, which have much longer atmospheric lifetimes, the situation is more complex. At the start of each model run, NAME is initialised using regional background concentrations of O_3 and H_2O_2, which are obtained from the Met Office's global chemistry model, STOCHEM (Collins *et al.* 1997). Thereafter these fields are perturbed by the NAME chemistry scheme, that is depleted and replenished according to the chemical reactions that take place. It is important to note that these species are also stored in the static 3-D chemistry grid, and that in NAME II there is no mechanism for advecting these species within the model domain. NAME III has additional code to handle background species on virtual particles within a limited domain.

While it is reasonable to represent the very short-lived species on a static field, it is not suitable to represent species such as O_3 in this manner. Ideally the O_3 and H_2O_2 would also be carried on particles and advected around the model domain. Unlike primary pollutants, however, which have a specified source, these species are present throughout the atmosphere and therefore must be treated differently from those pollutants emitted from sources. One solution may be to represent the whole 3-D model domain with particles representing O_3 and H_2O_2. This problem is still under investigation.

At the time of writing the NAME model was undergoing further development to improve predictions of O_3.

3.7.8 Advection of reaction products

Products of the primary species (for example, ammonium sulphate, nitrate aerosol, etc.) are carried on the model particles from which the primary species came, and are therefore advected around the domain. Chemistry products not directly linked to a primary species are stored on the static chemistry grid, as described in the previous section.

3.7.9 Additional information for chemistry

Additional information is:

1. zenith angle for solar radiation in relevant wavelengths (light intensity or actinic flux);
2. water species (gas, liquid and solid), obtainable from the Unified Model data;
3. Henry's law or other coefficients to define the thermodynamics of gas–liquid–solid interactions.

Since the Unified Model cloud data were found to attenuate the light intensity so much that they effectively suppressed photolysis, the chemistry scheme assumes clear skies. Photochemistry is only modelled during daylight. Plume chemical reactions depend on concentrations within a plume, which are themselves affected by dispersion rates, concentration fluctuations, entrainment, etc. The reaction scheme is specified in a subroutine.

3.7.10 Concentrations for model outputs

After the chemistry has taken place, those species which were carried on model particles must be re-assigned back to the original particle from the grid box concentration, to avoid any artificial diffusion. Concentrations are output from the model as g m^{-3}.

3.7.11 Summary of species in the reaction scheme

1. Thirteen primary emitted species (SO_2, NO, NO_2, CO, seven VOCs, NH_3 and PM_{10}) and their products [HNO_3, NO_3, N_2O_5, NH_4NO_3, NO_3^-, H_2SO_4, $(NH_4)_2SO_4$, CH_3CHO and peroxyacetylnitrate (PAN)] are carried on model particles.
2. Nine highly reactive radical species or reaction intermediates (OH, HO_2 and RO_2 species) local to the cell are modelled on a static 3-D field.
3. Two species, O_3 and H_2O_2, which are photooxidants with longer lifetimes, are also modelled on the static 3-D field for the reasons detailed above.

3.7.12 Grid cells for concentration and reaction

Grid cells are flexible and easily defined by the user in 3-D. For a small model domain, small cells may be used. For a long 2 year run, using EMEP emissions on a 50 km grid, cells of 50 km may be used for the chemistry, but some discretion is needed: this is satisfactory for aerosol chemistry, but not for gaseous NO_x (NO plus NO_2) chemistry. If modelling a large stack, a 1 km cell might be used. A small model area allows more particles and the near-source scheme to be run, though this is costly in computation and best with few sources and without chemistry.

3.7.13 Developments with NAME III

NAME III is currently under development. There are plans to test NAME III against the Nottingham incident or other episode(s) alongside the Community Multiscale Air Quality (CMAQ) model. The new version III will have a combined puff-particle Lagrangian dispersion scheme. The latest chemistry subroutine will be put in the code. Tests in hand to evaluate the new version will be reported later, but the work is outside the scope of this project . It will include sensitivity studies that look at the effects of background polluted air into which the plume is dispersing. It will consider some runs with realistic meteorology.

3.8 Chemistry in CMAQ

The University of Hertfordshire is using this system for domains ranging from Europe down to London. Inputs include global meteorological data from the National Centre for Environmental Prediction (NCEP) in the USA with local emissions for the UK from the NAEI, which is maintained by the National Environmental Technology Centre (NETCEN, AEA Technology plc). It is at a 1 km grid resolution, and contains a list of major point sources. For European emissions, they input the EMEP data on a 50 km grid. The meteorology is based on Unifed Model data formatted and pre-processed via the MM5 model interface Meteorology-Chemistry Interface Processor (MCIP) to suit the chemistry model CMAQ. This in turn is being run using emissions processing software, with the Plume-in-Grid option to investigate point-source dispersion and plume chemistry. The work with CMAQ will be reported separately and will include a summary of its chemistry scheme.

3.9 Carbon bond mechanism IV

The Carbon Bond Mechanism IV (CBM-IV) scheme is a widely adopted chemical mechanism (see Gery *et al.* 1988). A resume appears in the Appendix. However later schemes may be preferred.

3.10 Chemistry in the Australian air quality forecasting system

This system was developed for the Sydney Olympics. It is described in three linked papers by Cope *et al.* (2004), Hess *et al.* (2004) and Tory *et al.* (2004). The system was trialled using the GRS (Azzi *et al.* 1992, Venkatram *et al*. 1994), and has the potential to run CBM-IV (Gery *et al*. 1989).

3.11 Current practice in the Environment Agency for reactive plumes

In the UK, regulatory responsibility for large industrial stacks and power stations rests with the Environment Agency. Procedures for assessing NO_2 contributions to rural and urban air sheds have been both simple to apply (to facilitate the regulatory workload) and conservative (so that a worst case situation is regulated for). The procedure has simple assumptions for the amount of emitted NO oxidised that are useful for evaluating annual mean concentrations. These range from 100% oxidation of NO to NO_2 (worst possible outcome – most conservative) through 75% oxidation (less conservative) and 50% oxidation (less conservative still) down to 35% oxidation to NO_2 (even less conservative). These fixed-ratio approaches have proved simple and clear to apply.

The philosophy has been acceptable historically within the Environment Agency, because in the UK the applicant must justify the protocol they have used to estimate their site's impact upon NO_2. For instance, if good monitoring data exist for location(s) downwind, these can be used in the estimating process. Some operators have used the method of Janssen (see Section 1.4 above), which was developed using aircraft data from plumes of *large* power-stations, but the Environment Agency have rejected this for use on *smaller* plumes. While unduly conservative, it is in practice the clarity of approach that supported such simple fixed ratios. The Environment Agency has applied the ADMS model, which contains a simplified reaction scheme (the 2-reaction photostationary state reactions, or the 7-reaction GRS). Currently the use of ADMS chemistry for planning applications that involve NO_2 plumes is difficult because of:

1. uncertainty in knowing what background concentrations of O_3 or VOC species to use (which determines ROCs for use in GRS);
2. uncertainty in representing photochemical episodes;
3. unusual primary NO_2 emissions, for example land-fill gas burners or engines up to ~20%, or industrial processes like steel acid-pickling, nitrate drying up to ~100%.

ADMS is an important tool for the Environment Agency, but discussions revealed that the Environment Agency also has to consider applications that invoke other models, including AERMOD.

4 Sensitivities

The yield of NO_2 is influenced in the short term by factors specific to the plume, such as its composition, temperature and the surrounding atmosphere. In addition there is a need to look at the pollution climate in the longer term, as this influences the composition of the urban or regional atmosphere with which the plumes react as they entrain air.

4.1 Sensitivity runs for idealised plumes

The sensitivity of NO to NO_2 conversion is studied using idealised modelling runs with NAME III. This model is being developed from the existing NAME II model and the work will be reported later, but is not within the scope of this project. Runs of the proposed set-up have proved encouraging (see Task 3 reports).

4.2 Significance of a changing environment

Climate change is outside the scope of this report. Air quality and climate change have been thoroughly reviewed in a report by AQEG (2007). In addition their report on NO_2 discusses future issues that may affect the NO_2:NO_x ratio, see AQEG (2004). There may be changes in the direct or primary emissions of NO_2, and in the growing background of O_3 in air across large regions. For example, relative primary NO_2 emissions may increase through unanticipated effects of particulate traps on heavy vehicles, or may decrease if power stations introduce NO_2 reduction measures. Urgent work to review primary NO_2 has been started by AQEG.

Climate change may lead to various effects including:

1. Rising temperatures may be accompanied by higher maximum temperatures in the summer; elevated temperatures are conducive to increased O_3 concentrations formed by photochemistry.
2. Changes in cloud cover may affect the intensity of light in photochemically active wavelengths, and alter the potential photochemical yield.
3. At the same time, changes in emissions of hydrocarbons and NO_x from sources distributed across the globe will stimulate changes in the O_3 background.

In discussion, Dr Paul Seakins (Leeds University) has remarked (personal communication) that any increases in the background concentrations of oxidising species, like O_3, are significant in terms of the ensuing increase of NO_2. One can envisage a scenario in which there are reduced emissions of total NO_x from, say, power stations, yet a rising O_3 background could increase the yield of NO_2 (by oxidation of the emitted NO). This could moderate the expected benefits of the control of NO_x emissions in terms of the expected NO_2 reductions. This is an important sensitivity that requires further research. Our review suggests that more than one approach uses the photostationary state, which is fairly insensitive to O_3 concentration. However care is needed to ascertain the situation in the dark when the photolysis rate is zero.

4.3 Changing oxidant in the empirical approaches

Not all the empirical functions to derive the NO_2 yield and reviewed here can be adjusted for changes in level of local oxidant and/or in O_3 background. In Sections 4.3.1 and 4.3.2 this aspect is considered for the hourly and annual mean functions.

4.3.1 Hourly mean functions

The empirical curves for urban data, such as Derwent and Middleton (1996) and Dixon *et al.* (2001), see Figure 2, are widely used in local air quality management. They have been found to be consistent and dependable screening tools, but are not sensitive to any change in O_3 background or local oxidant. They are able to suggest the increased conversion seen at the highest urban NO_x concentrations.

The method of Janssen *et al.* (1988) is applicable to hourly mean concentrations in very large plumes and does have an asymptotic value that is directly calculable using the O_3 concentration. As O_3 is increased, the limiting yield of NO_2 in daylight is increased (see Figure 1). However the Janssen plot we show is a function of travel distance (or more generally, it could have been plotted in terms of travel time to cover all wind speeds). Some work is needed to obtain the concentration of NO_x at each distance, and then to apply the Janssen curve as a transformation to NO_2 concentration. Furthermore, the method was based upon line-integrated concentrations measured through the plume in the crosswind direction. All the other methods give the independent variable as NO_x, rather than travel time (or distance). Overall however, our rearrangement of the Janssen *et al.* (1988) formula suggests a stronger resemblance, once past the near-source O_3 limiting region, to the photostationary state [and hence to the box model BOXURB of Middleton (1998)] than first supposed. In turn this hints that the Janssen methodology may be applicable to a wider range of situations than first expected (see Section 4.4), but this hypothesis needs further work to establish it.

4.3.2 Annual mean functions

The method of Jenkin (2004a) is applicable to annual mean concentrations in urban areas or in rural ones. The results can be recalculated assuming a change in the total oxidant or increase in the magnitude of the intercept for the best-line fit from the scatter plot, while the same slope of the line in the calculations is retained, as demonstrated by our calculations (Figure 3).

The two polynomials of Jenkin (2004a) for annual means near road and not near road are not well behaved once outside their range of data (Figure 3), are not sensitive to O_3 and are not suited to regulatory use.

The 'national model' of Stedman *et al.* (2003) also gives annual means (Figure 3), but it is not able to be adjusted for any future increase in local oxidant or regional O_3.

4.4 The effect of α in the Janssen method and smaller emission sources

The Janssen method was plotted (Figure 1) assuming that α takes the value given by the theory, that is it depends upon the travel time and the O_3 concentration and thus obeys equation (5) in Janssen *et al*. (1988). Uncertainties in the method were allowed for by Janssen *et al.* (1998); their measurements show that oxidation to NO_2 is delayed in the plume because of the slow mixing of the plume with background air containing O_3. Values of α from the measurements were much smaller than those calculated assuming a background O_3 level and the wind speed at plume height via a stability-dependent power law from the 10 m wind speed, and ignoring effects caused by inhomogeneous mixing. We suggest that the sensitivity of the near-source estimates for NO_2 production to the value of α needs to be investigated if the Janssen method is adopted for regulatory application. In particular, the Janssen method seems to be applicable to much smaller plumes than the power-plant plumes observed by Janssen and colleagues, because in the limit it is asymptotic to the photostationary state, provided values of α can be established for small plumes. These plumes will be at a lower height, so the wind speed at plume height is likely to be less, but the formula for α takes this into account. They will also tend to have smaller plume diameters, which will affect the degree of inhomogeneous mixing. However since we may speculate that the stack diameter is, perhaps, roughly in proportion to the square root of the emission-volume flow rate, assuming similar exit velocities, the inhomogeneous mixing effect may change less than expected in going to the smaller plumes.

Apart from some uncertainties regarding α therefore, it seems possible the Janssen method should be applicable to smaller plumes. To use this method with the theoretical value for α should be a conservative regulatory approach. This is preferable to an arbitrary choice of a smaller value for α, which moves the maximum $[NO_2]$:$[NO_x]$ ratio further downwind, and in turn may inadvertently mask or reduce the ground-level maximum concentration from an elevated plume. The Environment Agency has tended not to allow the use of the Janssen method for smaller plumes, but in the light of this review we suggest that further work may show this to have been a perhaps unduly cautious approach.

Table 1 at the end of Section 2 illustrates the range of values for A, which depends upon photolysis rate and the reaction rate constant. A range of values of the limiting photostationary ratio R_p exists and is another sensitivity to allow for. Also it is unclear what the Janssen method should do in the dark when $J = 0$ and $R_p = 1.0$.

5 Conclusions

This report summarises the literature that has been studied on ways of assessing or representing in simple functions the conversion of NO to NO_2 in large plumes[5]. The review includes information on empirical functions from urban studies, and one from aircraft studies of plumes. Monitoring data are much more abundant in urban areas, and that most empirical approaches for the rapid screening of NO_2:NO_x ratios were developed for local air quality management. The Environment Agency may be able to apply directly some of these approaches. Alternatively these ratios may be used as a methodology to be adopted to simplify the results of plume chemistry modelling. This may lead to some simple screening methods for NO_2 concentrations in plumes.

These urban schemes suggest that to assume 100% conversion, the first option available to the Environment Agency, is unrealistically conservative. Further the photostationary state does not indicate 100% conversion. We anticipate that 100% conversion would frequently give too high an estimate for the impact of NO_x. From a regulatory perspective a 100% conversion is the most conservative estimate that it is possible to make. Work by Janssen *et al.* (1988) suggests that for large plumes there is a near-source region with a low conversion, but this is rapidly asymptotic to the photostationary state after a modest travel time (of perhaps 200 seconds according to our calculation using their method). As such it bears an unexpected but welcome similarity to our understanding of urban NO_2 data. Hence we suggest the Janssen method may be more applicable to smaller plumes than has been recognised hitherto, provided care is taken to use appropriate, conservative values for α. This uses wind speed at plume height, O_3 background, NO + O_3 rate constant and NO_2 photolysis rate.

In Task 3 of this project we conducted sensitivity modelling studies of plumes that contain NO_x. Some runs use the newly developed NAME III model, which is being developed in parallel with this study, to represent the chemistry in a plume with a surrounding field of pollutants. These runs could represent a plume in an urban atmosphere. These sensitivity studies were conducted to vary concentrations of NO_x, hydrocarbons and O_3. They can also be used to analyse the model outputs for any day and night differences. The runs give insights into factors that influence the conversion of NO to NO_2. They also explore some aspects of the empirical functions reviewed here using NAME III results, leading to suggestions for simple approximations using enclosing curves. This work also explores sensitivities of the plume chemistry to the background fields.

Some episodes of high O_3 have been modelled using the NAME and the CMAQ models, and are described in the Task 3 reports. This enables direct comparison of the NAME chemistry and CMAQ chemistry when applied to plumes. It also gives insights into the effect of grid discretisation and its influence upon the chemistry modelling; both NAME and CMAQ have to employ grid based methods to solve the chemistry, even though NAME and CMAQ represent dispersion in different ways (Lagrangian and Eulerian respectively). For a discussion of grid discretisation see Chock *et al.* (2005).

This report summarises ways in which detailed chemical mechanisms have been modelled in the past, because one approach the Environment Agency could adopt is to run plume chemistry simulations as a matter of routine. However unless care is taken to select an efficient numerical solver together with a significantly reduced chemical mechanism, the

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[5] The project did not undertake analysis of monitoring data, such as hourly concentrations from urban monitoring stations, or the monitoring data from the Joint Environmental Programme (JEP) run by the power industry around large power stations. This review was designed to start with published work, and it was not to process raw data, nor was it to verify modelling against measured concentrations.

computer costs and complexities of input data on hydrocarbon species render this impractical for most scenarios. To conduct advanced photochemical modelling requires a comprehensive set of emissions data for a wide range of VOCs, as well as the appropriate meteorological data, which is a major constraint on any regulatory work.

To summarise, Task 2 examined studies of aircraft based plume data, ground-level urban empirical approaches and numerical models of the chemical kinetics. The former are simple and approximate; the latter need complex input data and significant computational power. The latter may thus not be appropriate for many scenarios submitted to the Environment Agency for approval. Task 1 on unusual oxidation in plumes (focused on S and N species with aerosol reactions) was undertaken in parallel with Task 2, and under Task 3 other material has been gathered on simple indices for regional O_3 concentrations.

Task 2 examined the scientific literature on NO_2 as a precursor to model runs. The Task 3 reports describe modelling work that provides the foundation for a more consistent and more defensible regulatory approach to NO_2. This report on Task 2 reviews published methods to estimate the NO_2:NO_x ratio in plumes in terms of diverse ways of assessing the oxidation of NO to NO_2.

The basic premise drawn from this study of the literature is that regulation of NO_2 in plumes requires a two-step process to estimate the NO_2:NO_x ratio:

1. a simple screening tool for the plume NO_2:NO_x ratio to be the first assessment criterion in many applications;
2. a more complex and sophisticated modelling procedure in the minority of large or sensitive applications.

A simple screening tool is described in the Task 3 reports on the subsequent modelling.

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Appendix:
Short survey of leading chemical mechanisms for the troposphere

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Introduction to the leading chemical mechanisms

Many chemical mechanisms have been proposed to account for ozone (O_3) formation in different air basins and over different spatial scales. For example, Derwent (1990) reviews 24 different chemical mechanisms that had been in common use up to that time. The five vastly differing chemical mechanisms considered here span the range from simple to complex and include:

1. Carbon Bond Mechanism, CBM (Gery *et al*. 1989);
2. Regional Atmospheric Chemistry Mechanism, RACM (Stockwell *et al*. 1997);
3. State-wide Air Pollution Research Center, SAPRC, mechanism (Carter 2000);
4. Master Chemical Mechanism, MCM (Jenkin *et al.* 1997);
5. Self-generating Explicit Mechanism (Aumont *et al*. 2005).

The CBM (Gery *et al*. 1989) is important because of its highly compact nature, which makes it well suited for application within complex three-dimensional (3-D) grid airshed models in which computer resources are at an absolute premium. The RACM is aimed at both regional acid deposition and O_3 formation, and addresses both polluted and remote atmospheres. In contrast to the CBM and RACM, the SAPRC mechanism and MCM are larger in size by orders of magnitude. The SAPRC mechanism (Carter 2000) addresses the urban scale with its associated conditions of high nitrogen oxides (NO_x), whereas the MCM (Jenkin *et al.* 1997) addresses the long-range transboundary transport scale of particular interest within Europe. The Self-generating Explicit Mechanism is highly detailed and sophisticated, and represents many millions of chemical processes.

Carbon Bond Mechanism

The CBM (Gery *et al*. 1989) is one of the most important mechanisms for modelling photochemical O_3 formation because of its widespread application in complex 3D urban airshed models, particularly in policy applications in North America. The CBM has been widely applied because it is the most compact and concise mechanism and because it is firmly and rigorously rooted in environmental chamber studies. It uses condensation methods to great advantage to produce highly compact mechanisms. In a lumped structure mechanism such as CBM, organic compounds are grouped according to their bond types, so the alkanes are represented as a onecarbon atom molecule surrogate called PAR (paraffin carbon bond). Most single-bonded carbon atoms, regardless of the compound in which they appear, are represented as PAR. Other surrogates are named ETH, TOL and XYL, representing ethylene, toluene, xylenes. An alkane such as *n*-pentane would thus be represented as 5 PAR on a molar basis. Also included is an additional non-reactive (NR) surrogate that takes no part in photochemical O_3 formation. As described in Gery *et al.* (1989), the CBM has been evaluated against about 200 different experiments performed in the University of North Carolina and in the University of California at Riverside smog chambers. Subsequently, CBM has been tested against experiments conducted in the smog chambers of the Tennessee Valley Authority and the Commonwealth Scientific and Industrial Research Organisation (CSIRO), as detailed by Dodge (2000).

The CBM has undergone a series of updates since the original version of Gery *et al.* (1989) to take into account new information obtained in kinetic and mechanistic studies. The latest version recommended for use in policy applications is that implemented in the Models-3 Community Multiscale Air Quality (CMAQ) modelling system (Gipson and Young 1999). This is sometimes called the Carbon Bond version 4 (CB4) and contains 93 chemical reactions and 36 chemical species.

Regional Atmospheric Chemistry Mechanism

The RACM was created to represent atmospheric chemistry from polluted urban atmospheres through to the most remote and clean regions of the lower atmosphere (Stockwell *et al.* 1997). The mechanism is based on that originally designed for regional acid-deposition modelling (RADM-2) by Stockwell *et al*. (1990), with revisions to take into account laboratory studies of chemical kinetics published in the interim. The full RACM contains 56 organic compounds and 237 reactions and so is somewhat more complex than the CBM, but several orders of magnitude less complex than the SAPRC mechanism or MCM. Stockwell *et al*. (1997) describe the testing of RACM against 20 smog-chamber runs with the Evacuable Chamber of the SAPRC (Carter *et al.* 1995). The mechanism performed well for the alkenes and aromatics, reproducing the concentrations of O_3, NO_2 and hydrocarbons measured in smog chambers to within about ±30%.

State-wide Air Pollution Research Center mechanism

The SAPRC mechanism is the most extensive and complete chemical mechanism employed anywhere in the world, and it is the most important for policy purposes because of its application in North America to underpin the maximum incremental reactivity (MIR) scale (Carter 1998). The SAPRC mechanism has been through several cycles of updating: SAPRC-90 (Carter 1990), SAPRC-93 (Carter *et al.* 1995), SAPRC-97 (Carter *et al.* 1997) and SAPRC-99 (Carter 2000). The following paragraphs have been based on the later version. The mechanism has five major components:

1. the base mechanism;
2. a set of estimation procedures for the initial reactions of the organic compounds with the main free radicals;
3. a mechanism-generation system;
4. a set of lumping procedures to condense the mechanism into product species and chemical operators representing NO to NO_2 conversions and organic nitrate formation,
5. lumping procedures that represent complex mixtures of emitted organic compounds.

The base mechanism represents the atmospheric chemical reactions of the inorganic species and radicals, the common organic reaction products and the intermediate organic radicals that lead to the organic reaction products. Many reactions are not in the base mechanism, but are added to the mechanism as explicit reactions. These explicit reactions are generated automatically using a sophisticated mechanism generator and estimation software system. Although many of the estimated rate coefficients and rate coefficient ratios are highly uncertain, this software system provides a consistent set of assumptions from which to develop best-estimate mechanisms. It enables rate coefficients and their ratios to be adjusted where laboratory and smog chamber data are available. The performance of the SAPRC mechanism in simulating O_3 formation, rates of NO oxidation and other measures of smog chamber reactivity have been evaluated by model simulations conducted for over 1600 smog chamber experiments.

Master Chemical Mechanism

The MCM is a large chemical mechanism which represents the chemistry of the radicals and intermediate reaction products formed in the photochemical oxidation of over 100 emitted organic compounds in the presence of NO_x. Few of the common simplification and condensation procedures adopted in many chemical mechanisms are applied and all the reactions are represented by elementary stoichiometric equations. Nevertheless, some simplifications still have to be made to generate a mechanism that is tractable. These involve, principally, disregarding sites of OH attack on alkanes that have low probability and the representation of the myriad of reactions between the many peroxy radicals. The complexity of the chemical mechanism produced means that its policy applications have necessarily been restricted to implementation within the Lagrangian trajectory and moving box models of the Empirical Kinetic Modeling Approach (EKMA) type. Few simplification and condensation procedures have been implemented so the MCM has been applied mostly in assessments of the role of individual organic compounds in the formation of photochemical O_3 on the regional and transboundary scales in Europe. These multi-day regional-scale episodes tend to occur under low NO_x conditions that are often far removed from the concentration regimes investigated in environmental chambers. Consequently, the reactivity estimates tend to be different from those appropriate to the intense single-day urban-scale O_3 episode conditions found in the cities of the USA. Such differences in reactivity appear strongly in the case of the alkanes.

The MCM has been through various cycles of updating and extension and is now at version 3.1 (MCM 2005), available from http://mcm.leeds.ac.uk/MCM.

Currently, MCM v3.1 compiles the atmospheric chemistry of 135 emitted organic compounds, and comprises 5900 organic species and 13,500 organic chemical reactions. The explicit reactions of each organic compound are generated using a sophisticated mechanism protocol (Jenkin *et al.* 1997). Although many of the estimated rate coefficients employed are highly uncertain, the protocol and estimation procedures provide a consistent basis on which to build explicit mechanisms for a wide range of organic compounds emitted into the ambient atmosphere in Europe.

The MCM construction protocol defines a series of generic reaction rules which apply to the OH-, O_3-, NO_3- and photolysis initiated reactions of organic compounds (Jenkin *et al.* 1997) and the organic radicals generated by them. The fate of the organic radicals produced initially is to react rapidly with oxygen under atmospheric conditions to form peroxy radicals and this is assumed in almost all cases in the MCM. A small number of exceptions are treated fully in the MCM. The MCM goes on to treat the full behaviours of the peroxy radical intermediates, the Criegee biradicals, the oxy radical intermediates and the subsequent reactions of the first and subsequent generations of degradation products. The initial MCM protocol has been updated for the 107 non-aromatic organic compounds in Saunders *et al.* (2003) and for the 18 aromatic organic compounds in Jenkin *et al.* (2003) and Bloss *et al.* (2005). In addition, an expert system has been developed for the automatic generation of tropospheric oxidation schemes (Saunders *et al.* 2003).

The MCM has been carefully evaluated against laboratory experimental and field campaign data. The mechanisms in the MCM have been compared against the SAPRC environmental chamber data, experimental data from the European Photoreactor (EUPHORE) and data from the CSIRO indoor environmental chamber. The MCM has been used to estimate OH, HO_2 and RO_2 concentrations during the Berlin Ozone Experiment (BERLIOZ) campaign and during the Eastern Atlantic Spring Experiment (EASE) in 1997 at Mace Head, Ireland.

Self-generating Explicit Mechanism

Major advances have been made towards the development of more explicit representations of the atmospheric chemistry of hydrocarbons, alkanes included, as replacements for the highly simplified and condensed mechanisms often used in urban and regional models. The National Center for Atmospheric Research Master Mechanism (Madronich and Calvert 1990, Aumont *et al.* 2000), with over 5000 reactions to represent the oxidation of 20 emitted hydrocarbons, is an important early example of such an explicit mechanism. However even this explicit mechanism neglects many reaction pathways as it assumes that individually they may make only a minor contribution. Aumont *et al.* (2005) have described a ‘self-generating’ approach to develop fully explicit atmospheric chemistry mechanisms for selected organic compounds in a level of detail that would be difficult, if not impossible, to write manually.

The ‘self-generating’ approach has two main elements (Aumont *et al.* 2005):

1. a generator – the computer program that produces the oxidation mechanism for a set of emitted organic compounds based on a predefined protocol;
2. a protocol – the set of rules that lays out the choice of reaction pathways and estimates the rate coefficients needed in the mechanism based on the molecular structure of the species.

The construction of the chemical scheme generator requires the identification of all of the reactions for each emitted organic compound and for each intermediate reaction product in the complete degradation of each emitted compound into CO and CO_2. These reactions generally include:

1. initiation of the atmospheric degradation by the attack of OH, NO_3, O_3 or photolysis, which leads to the formation of peroxy radicals;
2. reactions of peroxy radicals with NO, NO_2, NO_3, HO_2 and other RO_2 radicals, which lead to the formation of stable reaction intermediates or alkoxy radicals RO;
3. alkoxy radical reactions with O_2, unimolecular decomposition or isomerisation, which lead to the formation of stable reaction intermediates or new peroxy radicals.

The generator is therefore a computer program or expert system that mimics the steps by which chemists develop chemical mechanisms manually. First, the generator analyses the chemical structure of the emitted organic compound or stable reaction intermediate to identify reactive sites and determine all the reaction pathways. For each identified reaction the generator then searches a database of laboratory measurements to determine if they are already available. If not, an estimation is made of the reaction pathway and rate coefficient. Details of the reaction are then added to the mechanism and the generator moves on to the next emitted organic compound or reaction intermediate. The complete chemical mechanisms written by the generator are, in principle, no different from those written manually by chemists, given enough time. However, there are several important advantages to the automatic method, namely speed, accuracy and ease of updating.

The total number of species generated to describe the full oxidation grows exponentially with increasing carbon number. It is both possible and desirable to set a *de minimus* threshold to cut down the number of trivial reaction pathways. For propane, the number of chemical species in the generated mechanism is about 400, but this rises to about 460,000 with heptane. In each case, the number of chemical reactions identified is about 10 times the number of species, and reaches about 25 million for the oxidation of *n*-octane. The exponential growth of the number of generated species as a function of the carbon chain length can be explained by the exponential increase of the total number of species that can be produced by permuting all the possible functional groups produced during the oxidation of the parent compounds.

The vast majority of the reactions inferred by the generator have no direct laboratory measurements and hence reaction pathways and rate coefficients have to be inferred for them. This is the role of the protocol and the published structure activity relationships that underpin it. The main feature of the generator described above is to codify the various estimation methods to produce consistent and comprehensive oxidation schemes on a systematic basis. Structure activity relationships are used to describe the reactions of volatile organic compounds (VOCs) – VOC + OH, VOC + NO_3, VOC + O_3 and VOC photolysis, peroxyacylnitrate decomposition, and peroxy radical, alkoxy radical and Criegee radical reactions. In addition, the protocol describes how the steady-state approximation is used to decrease the number of reactive species in the mechanism, if they are highly reactive and possess a unique reaction pathway, by replacing them with their reaction products.

A predefined set of rules can also be provided to the generator as an additional ‘protocol’ devoted to reduce the size of the generated mechanism, namely rules to lump species and reactions according to their contribution to the budget of some target species. Various commonly used reduction methods were tested and implemented in the generator to simulate the gas-phase chemistry in various tropospheric situations, from polluted to remote conditions (Szopa *et al.* 2005), which ultimately leads to a mechanism small enough to be included in current 3-D models.

To evaluate the chemical mechanisms for the alkanes written by the generator, some comparisons were made with the SAPRC mechanism (Carter 2000) and MCM (Saunders *et al.* 2003) for the oxidation of *n*-heptane. Concentration–time profiles were compared for a simple box model that contained NO_x, O_3 and *n*-heptane undergoing atmospheric photolysis at the 10-40 ppb concentration level. The time profiles for certain tested O_3, NO_x and HO_x species simulated with the self-generating approach, SAPRC and MCM showed fairly good agreement, with mixing ratios matching to within ±20% between all three schemes. Secondary reaction products, such as formaldehyde, showed surprisingly good agreement between the three mechanisms, despite their huge difference in complexity. The representation of n-heptane in the self-generating approach required 460,000 species and 4,500,000 reactions compared with 269 species and 789 reactions with the MCM.

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