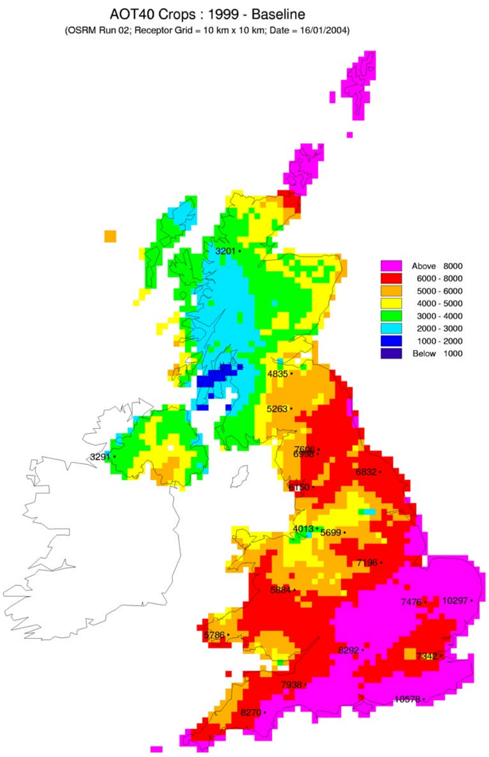
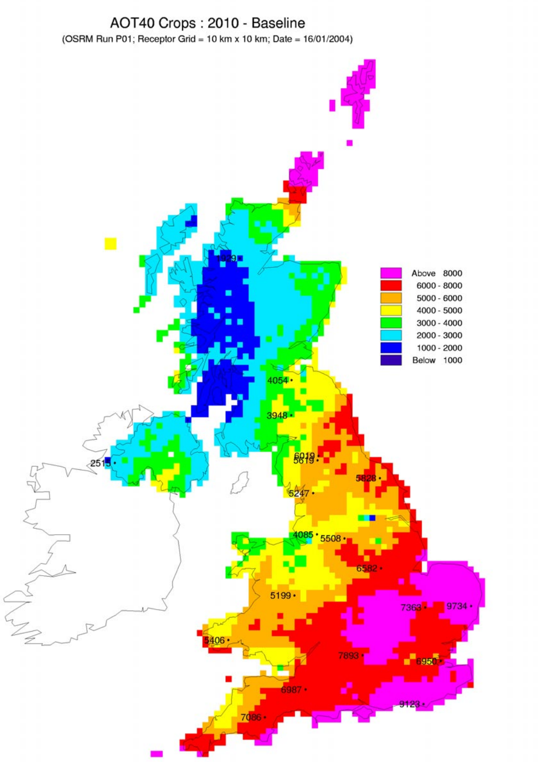
REPORT

Modelling of Tropospheric Ozone

A report produced for the Department for Environment, Food and Rural Affairs, the Scottish Executive, the National Assembly of Wales and the Northern Ireland Department of the Environment





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Executive Summary

The Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations (the Scottish Executive, the National Assembly of Wales and the Northern Ireland Department of the Environment) have awarded the contract **Modelling of Tropospheric Ozone** (EPG 1/3/200) to a consortium led by **netcen** (part of AEA Technology). The contract addresses ground-level ozone, its formation, impacts and control.

The non-linear nature of ground-level ozone production requires the use of sophisticated chemical transport models to understand its production and subsequent control. The Department and the Devolved Administrations (DAs) have funded the development of a number of models over the years. They seek to build on this work but now require a modelling capability to treat ozone formation (a) on all spatial scales from urban areas at high spatial resolution to the global scale so that ozone production on the regional and global scales is linked and (b) from timescales of hours to reproduce the diurnal behaviour of ozone to decades so that the influence of climate change can be assessed. The Ozone Source-receptor Model (OSRM) will be the main tool used to meet these requirements.

As part of their ozone research programme, DEFRA and the Devolved Administrations have supported the development of near explicit chemical mechanisms, especially that of the Master Chemical Mechanism. This was in recognition that a more targeted approach on ozone precursor emissions would bring greater environmental benefits than a simple percentage mass reduction. The Department and the DAs are continuing their support for this work.

The new project is not a simple continuation of earlier work. There is a stronger emphasis on model application to evaluate planned and proposed policies. In addition, new tasks have been identified: Technical assistance is required to fulfil commitments arising from the implementation of European Directives and in particular, the 3rd Daughter Directive on Ozone. Work is also in progress to move from the current AOT metrics for protection of ecosystems to a more realistic flux-based approach.

The principal aims of the project are thus:

- to maintain, develop and apply tools for modelling tropospheric ozone formation over a range of spatial scales
- to support and guide policy on emission reductions and objectives, and to verify compliance

To meet these aims and to address the intended applications, the programme of work has 5 main objectives or tasks:

- Objective 1 - **Development and Application of Ozone Models**
- Objective 2 - **Detailed Assessment of the Relationship between Ozone, NO and NO_2, and Factors Controlling Them**
- Objective 3 - **Policy Development and Scenario Analysis**
- Objective 4 - **Improvements to Photochemical Reaction Schemes**
- Objective 5 - **Development of Stomatal Flux Module for Crops and Semi-natural Vegetation**

This is the second annual report on the project and covers the period from 1st December 2003 to 30th November 2004. Overall, there has been a high level of project activity with significant contributions to the Review of the Air Quality Strategy. Very good progress has been maintained during the second year of the project on all of the 5 objectives. The key findings and policy implications of the work are:

- The realism and performance of the Ozone Source-receptor Model (OSRM) have been improved significantly through the introduction of a Surface Conversion algorithm (**Objective 1**). The performance of the OSRM has been compared to other models. These model developments and comparisons confirm that the OSRM is a robust model which can be used to assess the effectiveness of agreed or proposed actions and policies on ozone;

- Ambient levels of O_3 and NO_2 are strongly coupled (**Objective 2**). Thus, the response to reductions in the emissions of NO_x is highly non-linear. The success of proposed control strategies will depend on a complete understanding of the relationships between O_3, NO and NO_2 under atmospheric conditions. The extension of the previous analysis of O_3, NO and NO_2 measurements at relevant AURN sites to include 2002 and 2003 data has provided clear evidence that the fraction of NO_X emitted as NO_2 has increased significantly from the road vehicle fleets at a number of roadside and kerbside sites. At Marylebone Road, a number of factors may have contributed to the observed effect (such as an increase in the number of buses on routes running on Marylebone Road, and possibly by greater congestion resulting from Marylebone Road lying on the perimeter of the Congestion Charging zone), although further work is required to establish the exact cause. This will have implications for the attainment of the annual limit value for NO_2 (40 µg m^{-3}, 20.9 ppb).

  The analysis of hourly mean data for the site at Marylebone Road has provided insights into the seasonal and diurnal dependence of OX sources and their origins, and the conditions under which exceedences of the hourly mean NO_2 limit value (200 µg m^{-3}, 104.5 ppb) are more probable. The present analysis demonstrates that the ambient concentration of OX at Marylebone Rd is sensitive to a number of factors, such as primary NO_2 emissions and regional background O_3 concentrations, and that variation in the magnitudes of these factors leads to substantial diurnal and seasonal differences in the level of NO_X required for the hourly mean NO_2 limit value of 104.5 ppb to be exceeded.

- The OSRM and the UK Photochemical Trajectory Model (PTM) have been applied to evaluate a number of proposed ozone control measures and to the Review of the Air Quality Strategy (**Objective 3**):

  - Post Gothenburg Controls: Using its idealised episode trajectory, the UK PTM has shown that both VOC and NOx control are effective in improving ozone air quality. Model runs, in which NO_x and VOC emissions were separately reduced by 30% across-the-board, suggested that the worst-case trajectory to central Wales was still VOC limited (i.e., VOC control was more effective than NO_x control). Larger emission reductions indicated that the trajectory became NO_x limited.

  - The OSRM was used to assess a number of policy options relating to ozone:

    (a) Regulatory Impact Assessment of Directive on Decorative Paints

    (b) Proposed NO_x Emission Standards for Vehicles (EURO V Standards)

    (c) Regulatory Impact Assessment of Directive on Petrol Vapour Recovery

    (d) Post-Gothenburg Scenarios

    These were UK-scale model runs. As the surface-conversion algorithm was not available for use in these runs, the conclusions were therefore based on the unconverted outputs. There appeared to be two counteracting effects (a) photochemical production of ozone involving oxides of nitrogen and volatile organic compounds and (b) chemical titration by NO_x removing ozone. These two effects respond differently to emission control. VOC emission control always seemed to improve ozone air quality while NO_x emission control gave a more complex response, which was metric and region specific. Generally, NO_x emission control had an adverse effect on ozone air quality. Thus, either VOC emission control alone or combined VOC and NO_x emission controls are needed to improve ozone air quality.

    The OSRM outputs for the 2 Regulatory Impact Assessments were given to colleagues at netcen to undertake the cost-benefit analyses. A paper was prepared on all four series of model runs for the first phase of the review of the Air Quality Strategy.

  - The OSRM was used to investigate the impacts on ozone of a number of measures being considered in the first phase of the **Review of the Air Quality Strategy**. Model runs were undertaken to 41 UK receptors sites in urban and rural locations. These model runs have neglected the effects of the year-to-year variability in meteorology and the changing atmospheric composition arising from climate change and the global circulation. The output from the OSRM model runs was converted using the Surface Conversion algorithm. The model results were considered under the following headings:

(a) Effect of Additional Industrial NO_x Measures: Additional measures are being considered to reduce NO_x emissions from power stations, refineries, the iron and steel plants and cement kilns. The lower total NO_x emissions in these model runs improve nitrogen dioxide air quality but leads to varying increases in the ozone metrics, with the smallest relative increases between 2010 and 2020 seen in the metrics which are sensitive to peak ozone concentrations.

(b) Effect of EURO V/VI Emission Controls: Additional controls on vehicle exhaust emissions are being considered to reduce NO_x emissions (EURO V/VI Scenario G). The lower total NO_x emissions in these model runs improve nitrogen dioxide air quality but leads to an increase in the ozone metrics between 2010 and 2020. Although the overall level of emission reduction in 2020 is comparable between the two NO_x control scenarios (Additional NO_x Measures and EURO V/VI Emission Controls), there are differences in the spatial distribution of the emissions. The results suggest that there is a proportionately greater reduction in the NO_x emissions in London for the EURO V/VI scenarios, hence the larger changes seen in the ozone and nitrogen dioxide metrics for the London sites. There is however less difference, certainly for the metrics sensitive to peak ozone concentrations, for the UK-urban and UK-rural sites.

(c) Across-the-Board Reductions in VOC Emissions: The effect of 10% and 30% across-the-board reductions in VOC emissions in 2010, 2015 and 2020 were evaluated for both UK action and UK and European action. For a given year, the annual mean nitrogen dioxide concentration is virtually unaffected by the VOC emission reductions. There is a progressive improvement in all four ozone metrics as the VOC emissions are reduced from the base case (i.e., no reduction) to a 10% reduction in UK emissions through to a 30% reduction in UK and EMEP emissions (i.e., the largest emission reduction) for UK-rural, UK-urban and London sites. The response to a 10% reduction in UK VOC emissions is approximately half of that resulting from a 10% reduction in UK and EMEP emissions, implying that emission reductions in the UK or EMEP would be equally effective in improving ozone air quality. The responses to a 30% reduction in the UK or EMEP VOC emissions suggest that reductions in European emissions would be more effective in improving ozone air quality.

A paper was prepared on these model runs for the first phase of the review of the Air Quality Strategy.

The model runs undertaken for the Review of the Air Quality Strategy were largely based on specific emission control measures. Although desirable, the measures by themselves would not necessarily ensure attainment of ozone air quality targets or objectives. As a result, the Department was interested in the critical point where NO_x reductions would eventually result in less ozone, especially in urban areas. To answer this question, two series of OSRM model runs were undertaken in which the NOx emissions in (i) the UK and (ii) the UK and Europe were progressively reduced from 100% to 10% of their 2010 base case values in 10% increments. The model runs used the same 41 receptor sites as for the Review of the Air Quality Strategy.

The annual mean NO_2 concentration falls at all three sites as the overall NO_x emissions are reduced. However, the ozone metrics generally show an increase in value, reach a peak before then declining. The response is metric and site specific. The results indicate that large decreases in NO_x emissions (50-90%) would be required to overcome the ozone increase and to achieve compliance with air quality target and objectives. NO_x emission control in the UK and Europe was found to be more effective than control in the UK alone as a smaller percentage NO_x emission reduction is needed to reach the peak value in the ozone metrics. These model runs assumed no corresponding VOC emission reduction. As shown previously, any VOC emission reductions would improve ozone air quality. A lower level of NOx reduction would therefore be needed if VOC emissions were also controlled to achieve the same endpoint.

In previous OSRM scenario calculations, NO_x emission reductions alone gave a complex response. The response depended on the choice of ozone metric and could show regional differences for a given metric. Generally, there was a deterioration in ozone air quality if NO_x

emissions alone were controlled. Some insight into the NO_x emission response was also gained. The present model results suggest that there are potentially two counteracting factors (a) the reduction in photochemical ozone production as NO_x emissions are controlled, which is the situation classically simulated using the Photochemical Trajectory Model and (b) a NO_x titration effect. The relative importance of these effects varies during the year, the day and with site.

This explains the apparent inconsistency in the responses of the PTM and OSRM to NO_x control. Elevated concentrations of ozone over the UK are generally associated with photochemical production and easterly airflows. This is the situation modelled in the UK PTM with its idealised trajectory from central Europe to the UK. Reduction of NO_x (or VOC) emissions are effective in reducing ozone. In an OSRM model run, a calendar year is simulated and a wider range of trajectories is sampled, including those from other wind directions. These other trajectories may have little or no photochemical ozone production, especially if the trajectory has mainly passed over low emission areas (e.g., the sea). In this case, the NO_x titration effect controls the response to NO_x emission control.

- Work is in progress to assess the performance of the OSRM as a supplementary assessment technique. Model runs have been undertaken for a number of current years (1997 to 2003). This work will be included in the first report for the third Daughter Directive on ozone, which needs to be submitted to the European Commission in September 2005.
- The Chemical Mechanism development (**Objective 4**) has less immediate policy relevance but it does underpin the modelling tools used in the contract to assess ozone policy options. The reaction schemes for butane and isoprene in the MCM have been evaluated against chamber data. The evaluations have provided strong support for the MCM schemes for the most abundant components of emissions of anthropogenic and biogenic non-methane VOC, respectively. The study on multi-day reactivity has been completed using the MCM. The results demonstrate the need for a comprehensive chemical mechanism as simplified mechanisms could potentially lead to different ozone source-receptor relationships being used in integrated assessment models. The work on Objective 4 and the improvements to the MCM website contribute to the Department's desired outcome to maintain the leading position of the Master Chemical Mechanism;
- A module to calculate ozone stomatal fluxes (**Objective 5**) has been developed for use with the OSRM. This will provide the Department with a more realistic tool to evaluate the impact of ozone on crops and vegetation for the forthcoming reviews of the European Union's National Emission Ceilings Directive and the Gothenburg Protocol to the UN ECE Convention on Long-range Transboundary Air Pollution.

The work described above will make an important contribution to the development of UK actions and policies on ozone.

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Appendices

Appendix 1 – Brief Description of the Ozone Source-Receptor Model

Appendix 2 – Comparison of the Response of the OSRM and EMEP UNIOZONE Model

1 Introduction

The Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations (the Scottish Executive, the National Assembly of Wales and the Northern Ireland Department of the Environment) have awarded a contract **Modelling of Tropospheric Ozone** (EPG 1/3/200) to a consortium led by **netcen** (part of AEA Technology). The contract started on 2nd December 2002 and will end on 30th November 2005. The contract addresses ground-level ozone, its formation, impacts and control.

The concentrations of ground-level ozone, a pollutant that affects human health, ecosystems and materials, widely exceed environmental quality standards across the UK and Europe. Ozone is not emitted directly into the atmosphere, but is a secondary photochemical pollutant formed in the lower atmosphere from the sunlight-initiated oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO_x). Elevated concentrations of ozone over the UK are especially generated when slow-moving or stagnant high pressure (anticyclonic) weather systems occurring in the spring or summer bring in photochemically reacting air masses from mainland Europe.

Under conditions characteristic of photochemical pollution episodes, the formation and transport of ozone can occur over hundreds of kilometres, with concentrations at a given location influenced by the history of the airmass over a period of up to several days. In addition to this, the increasing levels of ozone in the free troposphere on a global scale also influence regional scale photochemical processes by providing an increasing background ozone level upon which the regional and national scale formation is superimposed. This effect now has to be considered when assessing whether proposed air quality standards for ozone are likely to be achieved.

The non-linear nature of ground-level ozone production requires the use of sophisticated chemical transport models to understand the factors affecting its production and subsequent control. The Department and the Devolved Administrations (DAs) have funded the development of a number of models over the years. They seek to build on this work but now require a modelling capability to treat ozone formation (a) on all spatial scales from urban areas at high spatial resolution to the global scale so that ozone production on the regional and global scales is linked and (b) from timescales of hours to reproduce the diurnal behaviour of ozone to decades so that the influence of climate change can be assessed. The Ozone Source-receptor Model (OSRM), developed during the previous project on Modelling of Tropospheric Ozone Formation (EPG 1/3/143), will be the main tool used to address these requirements.

As part of their ozone research programme, DEFRA and the Devolved Administrations have supported the development of near explicit chemical mechanisms, especially that of the Master Chemical Mechanism. This was in recognition that a more targeted approach on ozone precursor emissions would bring greater environmental benefits than a simple percentage mass reduction. The Department and the DAs wish to continue their support for this work.

The new project is not a simple continuation of earlier work. There is a stronger emphasis on model application to evaluate planned and proposed policies. In addition, new tasks have been identified: Technical assistance is required to fulfil commitments arising from the implementation of European Directives and in particular, the 3rd Daughter Directive on Ozone. Work is also in progress to move from the current AOT metrics for protection of ecosystems to a more realistic flux-based approach. The Department desires to gain added value from its own research programme and the work currently in progress within the EMEP research programme on this specific topic.

This is the second annual report on the project and covers the period from 1st December 2003 to 30th November 2004. The report is structured as follows:

Section	**Contents**
Section 2 - Overview and Progress	- Description of the project, its aims and structure. Summary of progress
Section 3 - Development and Application of Ozone Models (Objective 1)	- Development of the Ozone Source-Receptor Model and its performance compared to measurements
Section 4 - Detailed Assessment of the Relationship between Ozone, NO and NO_2, and Factors Controlling Them (Objective 2)	- Analysis of co-located O_3, NO and NO_2 measurements made at 65 UK monitoring sites. Relationship between these pollutants and comparison with those derived in the national empirical modelling.
Section 5 - Policy Development and Scenario Analysis (Objective 3a) and Ozone Daughter Directive (Objective 3b)	- Use of OSRM and the UK Photochemical Trajectory Model to evaluate a number of policy options and scenarios. - Preliminary Assessment report for the 3rd Daughter Directive on ozone.
Section 6 - Improvements to Photochemical Reaction Schemes (Objective 4)	- Oxidation schemes of 4 aromatic VOCs updated and compared to chamber data. Development of MCM website. Use of MCM to study multi-day reactivity.
Section 7 - Development of Stomatal Flux Module for Crops and Semi-natural Vegetation (Objective 5)	- Background and approach. Linkages between OSRM and Surface Ozone Flux model. Some initial calculations.
Section 8 - Other Project Activities	- Conferences and seminar attended and publications.
Section 9 - Acknowledgements	

2 Overview and Progress

2.1 PROJECT AIMS AND STRUCTURE

The principal aims of the project are:

- to maintain, develop and apply tools for modelling tropospheric ozone formation over a range of spatial scales
- to support and guide policy on emission reductions and objectives, and to verify compliance

To meet these aims and to address the intended applications, the programme of work has 5 main objectives or tasks:

- Objective 1 - **Development and Application of Ozone Models**
- Objective 2 - **Detailed Assessment of the Relationship between Ozone, NO and NO_2, and Factors Controlling Them**
- Objective 3 - **Policy Development and Scenario Analysis**
- Objective 4 - **Improvements to Photochemical Reaction Schemes**
- Objective 5 - **Development of Stomatal Flux Module for Crops and Semi-natural Vegetation**

There are strong linkages between the project objectives and with Defra's policy requirements, as shown in Figure 2-1.

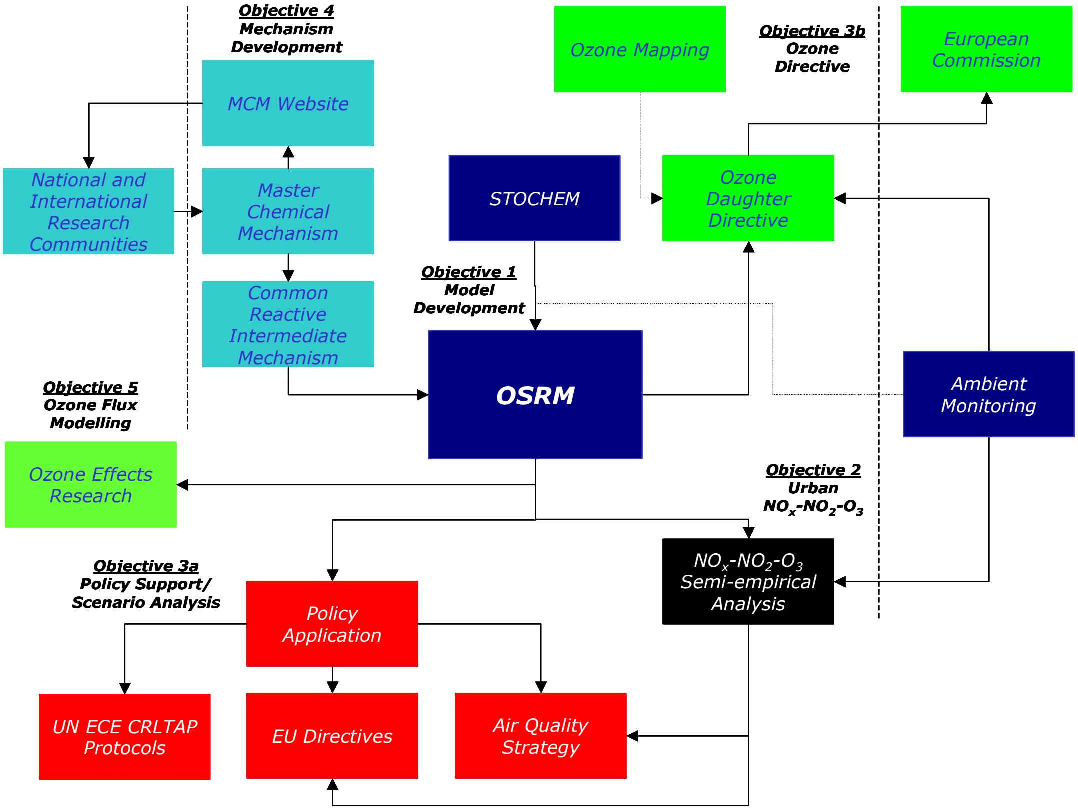

Figure 2-1: ***Schematic of the Linkages between the Project Objectives and with Defra's Policy Requirements.***

The key requirements for the project are:

- an ability to develop and apply numerical models for policy applications;

- an ability to develop tractable chemical mechanisms for policy applications;
- recognised expertise in the chemistry and physics of the lower atmosphere to understand the relationship between ozone and other pollutants of interest;
- detailed understanding of the key policy drivers; and
- networking to ensure timely uptake of the latest results from national and international research programmes.

2.2 PROJECT PARTNERS

The project team consists of a consortium of groups led by netcen. The consortium partners are Professor Dick Derwent, Dr Mike Jenkin (Imperial College), Professor Mike Pilling (University of Leeds) and Dr Peter Fitzgerald (SERCO Assurance)[1]. The consortium partners will be responsible for delivering specific tasks of the overall work programme, as shown in the schematic presented in Figure 2-2.

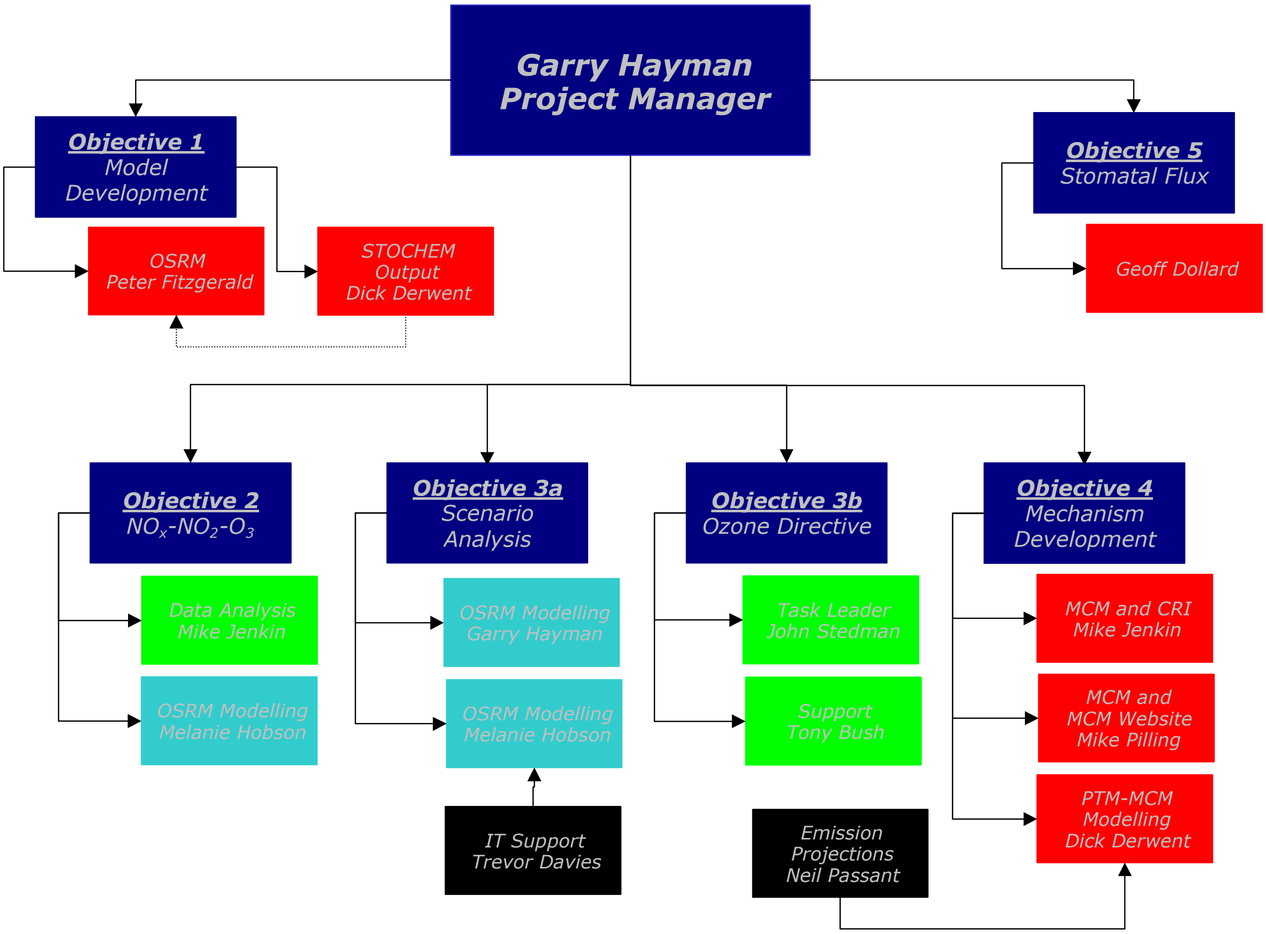

Figure 2-2: ***Allocation of the Objectives to the Consortium Partners.***

2.3 PROGRESS TO DATE

The project schedule proposed at the start of the project is shown in Figure 2-3.

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[1] Peter Fitzgerald completed the initial work on Objective 1. Following his departure from SERCO Assurance, he is no longer involved in the project. Future model development on the OSRM will be undertaken in house.

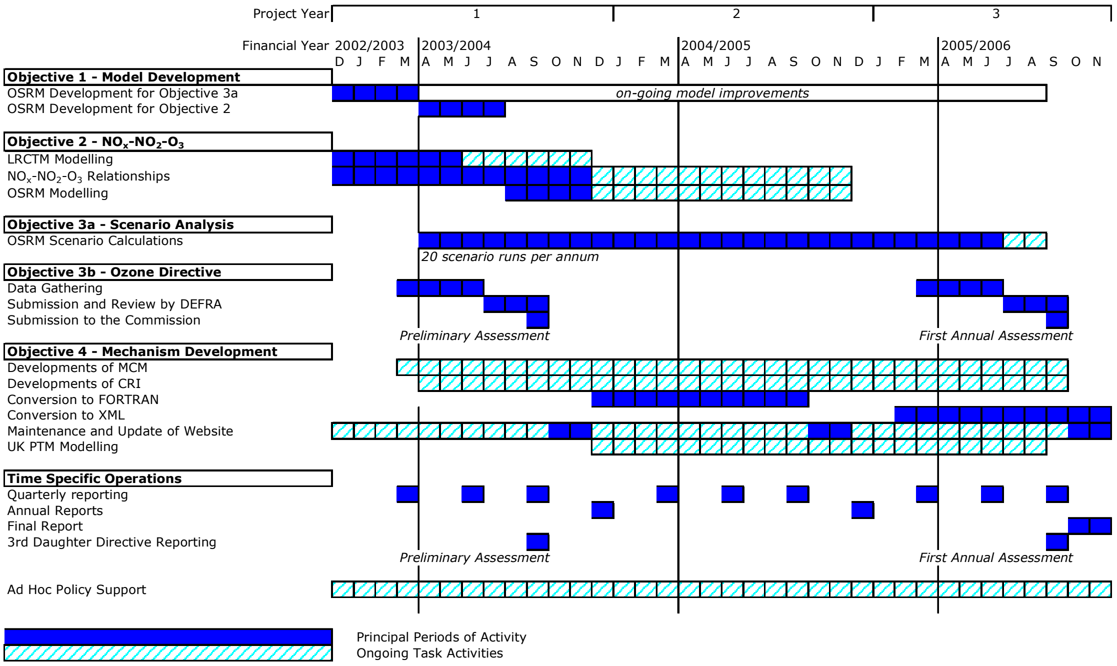


Figure 2-3: Project Schedule.

Overall, there has been a high level of project activity with significant contributions to the Review of the Air Quality Strategy. Very good progress has been maintained during the second year of the project on all of the 5 objectives. A review of progress by Objective is given below:

Objective 1: **Development and Application of Ozone Models**: The OSRM describes the boundary layer by a single box and assumes that this is well mixed. While this is a reasonable assumption for rural areas, it is less valid in urban areas with high NO_x emissions. In such areas, there will inevitably be a gradient in the NO_x concentration profile, with higher concentrations at the surface. This will lead to lower ozone concentrations at the surface through reaction with nitric oxide.

An algorithm has been developed and implemented in the OSRM post-processor to convert the mid-boundary layer concentrations to surface concentrations. This algorithm uses the meteorological parameters characterising the boundary layer, surface roughness appropriate for the surface types considered, resistance parameters for O_3 and NO_2, the local NO_x emission rates and a simple $NO\text{-}NO_2\text{-}O_3$ photostationary state chemistry. The performance of the Ozone Source-Receptor Model, especially in urban areas, has been significantly improved through the development and use of this Surface Conversion algorithm.

Further metrics have been added to the OSRM post-processor to address the impacts of ozone on human health and ecosystems:

- Annual mean of the difference between the maximum daily running 8-hour mean ozone concentration and 35 ppb (developed for the CAFÉ programme);
- Annual mean of the difference between the maximum daily running 8-hour mean ozone concentration and 50 ppb (used by COMEAP);
- AOT60 for the protection of human health (EMEP);
- AOT30 and AOT40 for the protection of fruit and of semi-natural vegetation (calculated using daylight hours (EMEP) and the fixed time periods of the EU).

The output of the OSRM has been compared with three established models – the UK Photochemical Trajectory Model, ADMS Urban and the EMEP UNIOZONE Model – which are widely used in the regulatory and policy context to assess different emission control options. On a like-for-like basis, the OSRM and UK Photochemical Trajectory Model were found to give identical output and responses. The comparison of the OSRM with the ADMS Urban and the EMEP UNIOZONE models gave similar overall responses, although there were differences, often significant, in the detail.

The model developments and comparisons confirm that the OSRM is a robust model that can be used to assist the development of policy.

Objective 2: **Detailed Assessment of the Relationship between Ozone, NO and NO_2, and Factors Controlling Them:** The ambient levels of O_3 and NO_2 are inextricably linked because of the chemical coupling of O_3 and NO_x. As a consequence, the response to reductions in the emissions of NO_x is highly non-linear and any resultant reduction in the level of NO_2 is invariably accompanied by an increase in the level of O_3. The success of proposed control strategies will depend on a complete understanding of the relationships between O_3, NO and NO_2 under atmospheric conditions.

A comprehensive analysis of 1998 and 1999 hourly mean data has been carried out for the site at Marylebone Road. This has provided insights into the seasonal and diurnal dependence of OX sources and their origins, and the conditions under which exceedences of the hourly mean NO_2 limit value (200 $\mu g\ m^{-3}$, 104.5 ppb) are more probable. The present analysis demonstrates that the ambient concentration of OX at Marylebone Rd is sensitive to a number of factors, such as primary NO_2 emissions and regional background O_3 concentrations, and that variation in the magnitudes of these factors leads to substantial diurnal and seasonal differences in the level of NO_X required for the hourly mean NO_2 limit value of 104.5 ppb to be exceeded. The factors that cause these differences at an individual site are also likely to contribute to the site-to-site variations in annual mean NO_X thresholds. However, the annual mean local OX contributions for a number of urban background and urban centre sites (i.e., up to ~20%) are significantly greater than the vehicular primary NO_2 fractions derived in the present work. This suggests that either the primary NO_2 fractions are elevated by factors such as traffic congestion, or that the local OX at these sites has additional contributions from local scale chemical processes. As discussed previously by AQEG and the project consortium, a number of thermal and photochemical sources may potentially contribute, through converting NO to NO_2, without associated removal of O_3.

In the first annual project report, an analysis of the annual mean concentrations (up to 2001) determined at 66 automatic sites where O_3 and NO_X are monitored was presented. That analysis showed that the description of annual mean concentrations of NO_2, and their dependence on $[NO_X]$, could be improved by the application of empirically-derived relationships between concentrations of O_3, NO_X and NO_2. In this way, it was possible to rationalise the variation of $[NO_2]$ with $[NO_X]$, and how it varies from one site to another, in terms of sources of OX and well-understood chemical processes. $[NO_2]$ vs. $[NO_X]$ relationships were recommended for 56 urban and suburban sites. In the present study, the previous analysis has been extended to include the annual mean data at selected sites in 2002 and 2003.

The measurements have provided clear evidence that the fraction of NO_X emitted as NO_2 has increased significantly from the road vehicle fleets at a number of roadside and kerbside sites. At Marylebone Rd, a number of factors may contribute to the observed effect, although further work is required to establish the exact cause. For example, the introduction of central London congestion charging in early 2003 was accompanied by an increase in the number of buses on routes running on Marylebone Rd, and possibly by greater congestion resulting from Marylebone Rd lying on the perimeter of the zone. Based on the diurnal dependence results, both effects would be expected to increase the local oxidant source. In addition, the buses are being fitted with oxidising particulate traps, which potentially result in substantially increased primary NO_2 emissions.

The relationships developed above have been incorporated into the empirically-based modelling work undertaken by netcen on other contracts for the Department.

Objective 3: **Policy Development and Scenario Analysis**: This objective comprises 2 main areas (a) Policy Development and Scenario Analysis and (b) Implementation of the Third Daughter Directive on Ozone.

(a.1) Policy Development and Scenario Analysis using the UK Photochemical Trajectory Model (PTM): The PTM was used to investigate the additional NO_x and VOC emission controls, which would be needed to achieve Ozone air quality standards and objectives beyond those agreed in the EU National Emission Ceilings Directive and the UN ECE Gothenburg Protocol. Three further stages of emission reductions were considered taking emissions below the 2010 levels by 30%, 60% and 90%. In all cases, these emission reductions were applied across-the-board on all source categories and on all countries. For the 30% emission reduction scenarios, the UK PTM is indicating that the arrival point in Wales is still VOC-limited in 2010, because the ozone benefit (74.2 down to 69.6 ppb) from reducing VOC emissions is larger than the ozone benefit (74.2 down to 69.9 ppb) from reducing NO_x emissions. However, looking at the 60% and 90% reductions, the situation reverses and the ozone benefits from NO_x reductions look substantially greater than those from VOC reductions.

(a.2) Policy Development and Scenario Analysis using the Ozone Source-receptor Model (OSRM): The OSRM was used to assess a number of policy options relating to ozone:

(i) **Regulatory Impact Assessment of Directive on Decorative Paints**: The European Commission has proposed a Directive to reduce the VOC content of decorative paints, varnishes and vehicle refinishing products. There is a requirement to calculate the benefits to the UK of reductions in VOCs arising from within UK, and in UK + rest of Europe. The Commission have calculated potential emission reductions that would arise from the proposed controls in 2010. UK-scale model runs were undertaken to a 10 km x 10 km grid.

(ii) **Proposed NO_x Emission Standards for Vehicles (EURO V Standards)**: The European Commission are expected to propose new emission standards for vehicles in 2004. The Department and the Department for Transport wish for information on the air quality implications of various scenarios to inform the UK position. Although the main focus to date has been on NO_2 and PM exposure, there is a need to assess the effects on ozone concentrations and hence human exposure. UK-scale model runs were undertaken to a 20 km x 20 km grid for computational reasons.

(iii) **Regulatory Impact Assessment of Directive on Petrol Vapour Recovery:** OSRM modelling calculations have been undertaken as part of the regulatory impact assessment on petrol vapour recovery (PVR) and possible derogations. UK-scale model runs were undertaken to a 10 km x 10 km grid.

(iv) **Post-Gothenburg Scenarios:** Assuming full compliance with the UN ECE Gothenburg Protocol and the EU National Emissions Ceilings Directive, the Department is interested the effectiveness of different controls on NO_x and/or VOC emissions to improve ozone air quality after 2010. Four OSRM model runs were undertaken with across-the-board reductions in the emissions of NO_x and/or VOC of 30%. UK-scale model runs were undertaken to a 10 km x 10 km grid.

The surface-conversion algorithm was not available for use in the above OSRM model runs. The discussion is therefore based on the unconverted outputs. There appeared to be two counteracting effects (a) photochemical production of ozone involving oxides of nitrogen and volatile organic compounds and (b) chemical titration by NO_x removing ozone. These two effects respond differently to emission control. Thus, either VOC emission control alone or combined VOC and NO_x emission controls are needed to improve ozone air quality. A paper was prepared on these model runs, from which the following are taken:

- **Trends in Base Case**: The reduction in NO_x emissions between 1999 and 2015 leads to a reduction in NO_2 concentrations by between 30-35% for England and Wales and ~40% for Scotland and Northern Ireland. There is a downward trend in the AOT40 for the protection of crops across the UK although there are still large parts of the country, which are above the threshold of 3,000 ppb hours (6,000 $\mu g\ m^{-3}$ hours). The annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day appears to fall at the extremities of the UK but rise in England where the emissions of nitrogen oxides are higher. However, the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day, which are greater than 35 ppb, on the other hand decreases between 1999 and 2005. Thereafter, there is a very slight increase.
- **Emission Reductions**: NO_x emission reductions alone (e.g., the EURO V Emission Standards) lead to lower NO_2 concentrations but to increases in the population-weighted annual mean of the maximum daily running 8-hour ozone concentrations. On the other hand, VOC emission reductions (Petrol Vapour Recovery and the proposed Directive on Decorative Paints) have little or no effect on the annual mean NO_2 concentration but do lead to lower values of all the ozone metrics considered.
- **Post-Gothenburg**: A 30% VOC emission reduction improves ozone air quality but a 30% reduction in NO_x emission reduction leads to poorer ozone air quality. Comparison of the scenario in which NO_x and VOC emissions are each reduced by 30% with separate 30% reduction in NO_x or VOC reductions indicates that the counteracting effects of photochemical production of ozone (by NO_x and VOC emissions) and the titration effect of NO_x emissions.
- **Regional Changes**: Compared to the 1999 model run, the base case runs show an improvement in ozone air quality, as measured by the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day, which are greater than 35 ppb, for each region (England, Wales, Scotland and Northern Ireland). On the other hand, there is a reduction in the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day for Northern Ireland, little change in this metric for Scotland and Wales and a deterioration for England. The annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day will be sensitive to all hours and trajectories, including those where the titration effect is dominant. The annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day will be more sensitive to the higher ozone concentrations, which are more likely to be of a photochemical origin.

(a.3) *Policy Development and Scenario Analysis using the Ozone Source-receptor Model (OSRM):* The OSRM was used to investigate the impacts on ozone of a number of measures being considered in the first phase of the **Review of the Air Quality Strategy**. Model runs were undertaken to 41 UK receptors sites in urban and rural locations. The output from the OSRM model runs was converted using the Surface Conversion algorithm. The model results were considered under the following headings:

- **Effect of Additional Industrial NO_x Measures**: In this set of model runs, additional measures have been implemented to reduce NO_x emissions from power stations, refineries, the iron and steel plants and cement kilns. The lower total NO_x emissions in these model runs leads to lower annual mean nitrogen dioxide concentrations compared to the corresponding base case run. Reducing NO_x emissions alone leads to varying increases in the ozone metrics, with the smallest relative increases between 2010 and 2020 seen in the metrics which are sensitive to peak ozone concentrations (such as the Annual Mean of the Daily Maximum of the 24 Daily Running 8-hour Mean

Ozone Concentrations or the Annual Mean of those Daily Maximum of the 24 Daily Running 8-hour Mean Ozone Concentrations > 70 $\mu g\ m^{-3}$).

- **Effect of EURO V/VI Emission Controls**: In this set of model runs, additional controls on vehicle exhaust emissions have been implemented to reduce NO_x emissions (EURO V/VI Scenario G). The lower total NO_x emissions in the scenario runs leads to lower annual mean nitrogen dioxide concentrations compared to the corresponding base case run. Again, as observed in the other model runs, reducing NO_x emissions alone leads to an increase in the ozone metrics between 2010 and 2020. Although the overall level of emission reduction in 2020 is comparable between the two NO_x control scenarios (Additional NO_x Measures and EURO V/VI Emission Controls), there are differences in the spatial distribution of the emissions. The results suggest that there is a proportionately greater reduction in the NO_x emissions in London for the EURO V/VI, hence the larger changes seen in the ozone and nitrogen dioxide metrics for the London sites. There is however less difference, certainly for the metrics sensitive to peak ozone concentrations, for the UK-urban and UK-rural sites.
- **Across-the-Board Reductions in VOC Emissions**: The effect of 10% and 30% across-the-board reductions in VOC emissions in (a) the UK and (b) the UK and EMEP region was investigated for the years 2010, 2015 and 2020. For a given year, the annual mean nitrogen dioxide concentration is virtually unaffected by the VOC emission reductions. There is a progressive improvement in all four ozone metrics as the VOC emissions are reduced from the base case (i.e., no reduction) to a 10% reduction in UK emissions through to a 30% reduction in UK and EMEP emissions (i.e., the largest emission reduction) for UK-rural, UK-urban and London sites.

  The response to a 10% reduction in UK VOC emissions is approximately half of that resulting from a 10% reduction in UK and EMEP emissions, implying that emission reductions in the UK or EMEP would be equally effective in improving ozone air quality. The responses to a 30% reduction in the UK or EMEP VOC emissions suggest that reductions in European emissions would be more effective in improving ozone air quality.

In summary, the OSRM model runs have shown that VOC emission reductions alone (e.g., the across-the-board reductions) lead to an improvement in ozone air quality for all the ozone metrics calculated by the OSRM post-processor. NO_x emission reduction scenarios alone generally lead to a deterioration in ozone air quality. This can largely be understood in terms of a reduced NO_x titration effect. The combination of lower NO_x and VOC emission reductions (e.g., change of base case year) gives a more complex response. Lower VOC emissions lead to lower values of the ozone metrics but this is offset by the reduced titration effect of the lower NO_x emissions, leading to higher ozone concentrations and values of the ozone metrics.

These OSRM scenario model runs neglected the effects of the year-to-year variability in meteorology and the changing atmospheric composition arising from climate change and the global circulation. Some indication of the sensitivity to the year-to-year variability in meteorology can be found in the OSRM model runs undertaken for 2 current years (1999 and 2001), although the emissions were also changed in these runs.

(a.4) *Policy Development and Scenario Analysis using the Ozone Source-receptor Model (OSRM):* The model runs described in (a.3) above were largely based on specific emission control measures. The emission reductions implied by the measures were used to prepare the emission inventories for the model runs. Although desirable, the measures by themselves would not necessarily ensure attainment of ozone air quality targets or objectives. As a result, the Department was interested in the critical point where NO_x reductions would eventually result in less ozone, especially in urban areas. To answer this question, two series of

OSRM model runs were undertaken in which the NOx emissions in (i) the UK and (ii) the UK and Europe were progressively reduced from 100% to 10% of their 2010 base case values in 10% increments. The model runs used the same 41 receptor sites as for the Review of the Air Quality Strategy.

Three sites (Strathvaich Dam, Harwell and London Bloomsbury) were selected for further investigation. The annual mean NO_2 concentration falls at all three sites as the overall NO_x emissions are reduced. However, the ozone metrics generally show an increase in value, reach a peak before then declining. The response is metric and site specific, with the greatest decline observed in the AOT40 – crops and, to a lesser extent, the number of days when the maximum daily running 8-hourly average ozone concentration exceeded 100 $\mu g\ m^{-3}$. The results indicate that large decreases in NO_x emissions (50-90%) would be required to overcome the ozone increase and to achieve compliance with air quality target and objectives.

As expected, NO_x emission control in the UK and Europe was found to be more effective than control in the UK alone. A smaller NO_x emission reduction is needed to reach the peak value in the ozone metrics. These model runs assumed no corresponding VOC emission reduction. As shown previously, any VOC emission reductions would improve ozone air quality. A lower level of NOx reduction would therefore be needed if VOC emissions were also controlled to achieve the same endpoint.

To understand the above further, the effect of the emission reductions on the hourly ozone concentrations was investigated. Comparison of the base case and 90% emission reduction runs showed that the absolute magnitude and the periods of elevated ozone concentrations are much reduced during the middle part of the year, indicating that there has been a significant reduction in photochemical ozone production. There is evidence, certainly at Harwell and London Bloomsbury, that the modelled ozone concentrations are higher at the beginning and end of the year. Also, the minimum ozone concentrations are generally higher in the emission reduction case. In the absence of photochemical ozone production, it is expected that the NO_x emissions would have a titration effect on ozone and its concentrations. As the NOx emissions are reduced, the titration effect would be diminished and the ozone concentrations would rise.

In previous OSRM scenario calculations, NO_x emission reductions alone gave a complex response. The response depended on the choice of ozone metric and could show regional differences for a given metric. Generally, there was a deterioration in ozone air quality if NO_x emissions alone were controlled. These model results suggest that there are potentially two counteracting factors (a) the reduction in photochemical ozone production as NOx emissions are controlled. This is the situation classically simulated using the Photochemical Trajectory Model and (ii) a NO_x titration effect. The relative importance of these effects varies during the year, the day and with site.

(b) *Implementation of the Third Daughter Directive on Ozone:* As required by the Directive, a preliminary assessment report was prepared and submitted to Defra in August 2003. This assessment, largely based on monitoring data, reviewed the current position and the likelihood of achieving the proposed target values and long-term objectives for ozone. The target values for 2010 do not appear particularly stringent but long-term objectives are likely to be more difficult to achieve.

The Directive allows the use of supplementary assessment techniques. Work is in progress to confirm the suitability of the OSRM as a possible supplementary assessment technique. Model runs have been undertaken for a number of current years (1997 to 2003) using year-specific meteorology and emission inventories. The model outputs will be compared with empirical maps based on measurements. This work will be included in the first report for the third Daughter Directive on ozone, which needs to be submitted to the European Commission in September 2005.

Objective 4: **Improvements to Photochemical Reaction Schemes**: Work has been undertaken on the following topics:

(a) *Updating of the Master Chemical Mechanism:* The MCM v3 degradation schemes for butane and isoprene have been evaluated using the large environmental chamber dataset of the Statewide Air Pollution Research Center (SAPRC) at the University of California. The MCM v3 mechanisms for both butane and isoprene were found to provide an acceptable reaction framework for describing the NO_X-photo-oxidation experiments, and generally performed well. A number of parameter refinements were identified which resulted in an improved performance. While the recommended updates are certainly necessary to maintain the MCM fully, it is emphasised that they have only a minor influence on the performance of the butane and isoprene schemes in atmospheric models. Consequently, these evaluation activities provide strong support for the MCM schemes for butane and isoprene, which are the most abundant components of emissions of anthropogenic and biogenic non-methane VOC, respectively.

(b) *MCM Website:* The Master Chemical Mechanism (MCM) has been updated to MCM version 3.1. MCM v3.1 now contains 135 primary emitted VOCs which lead to a mechanism containing *ca.* 5,900 species and 13,500 reactions. As part of the ongoing improvements to the MCM a new version of the website has been developed with the primary objectives of making the website clearer and easier to navigate and of improving access to the MCM itself. The site can be found at the address: **http://mcm.leeds.ac.uk/MCM/**.

(c) *Code Conversion*: The MCM is now available in several output formats (a) the standard FACSIMILE output, which has been improved, (b) FORTRAN and (c) XML, although work is in progress to develop the most appropriate and useful design for the XML schema and the properties of Chemical Markup Language (CML) are being examined to understand the ways in which XML is currently used to represent chemistry. The FORTRAN and XML formats are more robust than that of FACSIMILE and are more future proof. This should further improve the uptake of the Master Chemical Mechanism.

(d) *The Common Rective Intermediate (CRI) Mechanism:* Using the knowledge and understanding gained from developing the MCM, a reduced mechanism - the Common Reactive Intermediate (CRI) mechanism - was derived from the Master Chemical Mechanism. The CRI mechanism treats the degradation of methane and 120 VOC using approximately. 570 reactions of 270 species (*i.e.* about 2 species per VOC). It thus contains < 5% of the number of reactions and < 7% of the number of chemical species in MCM v3.1, providing a computationally attractive mechanism. The CRI mechanism has been benchmarked against the MCM and was shown to produce almost identical concentrations for key species to those calculated using the full Master Chemical Mechanism. Whilst it is recognised that CRI v1 correctly represents ozone formation from the VOC mixture, it may not fully recreate the relative contributions of component VOC or VOC classes within the emitted mixture. A new version of the mechanism is being developed which will treat the degradation of individual classes of VOC (e.g., alkanes, alkenes, aromatics) separately. The work to date has demonstrated that the mechanism is improved by defining separate series of representative intermediates for some VOC classes. This will result in an ultimate increase the size of the mechanism over that of CRI v1, but will allow a more rigorous description of the impact of the different VOC emission sectors, and an improved foundation for the expansion of the mechanism to the treatment of the several hundred minor VOC not currently represented in MCM or CRI.

(e) *Multi-day Reactivity:* The UK Photochemical Trajectory Model incorporating the Master Chemical Mechanism has been used to investigate how the reactivity of different classes of volatile organic compounds changes with time. An air parcel was followed as it travelled on an easterly wind from its trajectory release point in Austria across Europe to its arrival point at the England-Wales border. The work has now been completed and three mechanisms have been found to account for ozone formation on subsequent days following their emissions. These are (a) the carry over of unreacted VOCs, (b) the formation of peroxyacetylnitrates and (c) the consecutive reactions of aldehyde formation and degradation. From a study of the chemical mechanisms used in most policy models, EMEP included, it is likely that the multi-day formation of ozone from alkenes and carbonyl compounds is underestimated because of the simplifications and approximations made in the compression of the chemical mechanisms.

The use of the MCM v3.1 has resolved some previous anomalies in the behaviour of certain aromatic compounds (p-xylene, ethylbenzene, propylbenzene and i-propylbenzene). As suspected, there were problems in the detailed mechanisms for these four aromatic species in the previous version of the MCM (v3.0).

(f) *PTM Modelling of the TORCH Measurements*: The UK Photochemical Trajectory Model (PTM), containing speciated emissions of 124 non-methane VOC and a comprehensive description of the chemistry of VOC degradation (provided by MCM v3.1 and the CRI mechanism), has been used to simulate the measurements made at a site in the southern UK during the NERC Tropospheric Organic Chemistry Experiment (TORCH). The measurement campaign coincided with the August 2003 photochemical pollution episode. The comparison of the simulated and observed distributions of 34 emitted hydrocarbons provides strong support for the VOC speciation used in the NAEI, but is indicative of an under representation of the input of biogenic hydrocarbons, particularly at elevated temperatures. The model calculations also provided detailed distributions of ca. 1250 carbonyl compounds, formed primarily from the degradation of 124 emitted VOC. Although the simulated distributions of four aldehydes and three ketones correlated well with observations for each class of compound, the simulated concentrations of the aldehydes were systematically lower than those observed, whereas those of the higher ketones were systematically higher. The MCM is one of the few chemical mechanisms available to predict the patterns and structures of oxidised products, such as simple and multifunctional carbonyls, thereby allowing a much more detailed examination of atmospheric chemical mechanisms. These model calculations will allow further refinement of the formation routes of these compounds in the MCM.

Objective 5: **Development of Stomatal Flux Module for Crops and Semi-natural Vegetation**: The objective is to provide a link between the ozone assessment capability of OSRM and the Surface Ozone Flux Model (SOFM). This will provide the Department with a robust assessment tool that will allow the preparation of UK maps of accumulated stomatal flux for wheat, potatoes and beech trees for use with damage/loss response functions for impact assessment.

Working closely with the Department's contractors on Ozone Effects (Lisa Emberson and Mike Ashmore), a module has been developed to calculate the effects of ozone deposition on crops in the United Kingdom based on predictions of ozone concentrations made using the Ozone Source Receptor Model (OSRM). The capability of the module to produce UK-scale maps has been demonstrated.

The model predicted that the growth of beech trees in 2001 was affected by ozone deposition, with greater than 5% loss in biomass throughout the country. Ozone deposition to beech trees in much of the southern part of the UK was limited by the availability of soil moisture for plant uptake during the latter path of the growing season. The model predicted that the growth of winter wheat throughout much of England and Wales in 2001 was affected by ozone deposition. Ozone deposition was associated with more than 5% loss in yield in central England. The loss in yield was smaller in cooler areas in Scotland and in coastal areas of England with lower maximum temperatures. The model also predicted that the growth of potatoes was not substantially affected by ozone deposition. Ozone deposition was associated with less than 5% loss in yield throughout the country.

Model predictions of stomatal flux based on ozone concentrations calculated using the OSRM were compared with stomatal flux estimates based on measured ozone concentrations in 2001. The comparison suggested that the OSRM can provide an effective means of predicting accumulated flux over threshold to vegetation types.

Overall, very good progress has been maintained during the second year of the project on all of the 5 objectives. The development of a module to calculate ozone stomatal fluxes is now complete, although it is planned to review the current outputs with key stakeholders in the Ozone Efffects community. Sections 3 to 7 provide more detailed information on the work undertaken under each Objective.

2.4 POLICY RELEVANCE

The work reported here assists the development of UK actions and policies on ozone as follows:

- The realism and performance of the Ozone Source-receptor Model (OSRM) have been improved significantly through the introduction of a Surface Conversion algorithm (**Objective 1**). The performance of the OSRM has been compared to other models. These model developments and comparisons confirm that the OSRM is a robust model which can be used to assess the effectiveness of agreed or proposed actions and policies on ozone;
- Ambient levels of O_3 and NO_2 are strongly coupled (**Objective 2**). Thus, the response to reductions in the emissions of NO_x is highly non-linear. The success of proposed control strategies will depend on a complete understanding of the relationships between O_3, NO and NO_2 under atmospheric conditions. The extension of the previous analysis of O_3, NO and NO_2 measurements at relevant AURN sites to include 2002 and 2003 data has provided clear evidence that the fraction of NO_X emitted as NO_2 has increased significantly from the road vehicle fleets at a number of roadside and kerbside sites. At Marylebone Road, a number of factors may have contributed to the observed effect (such as an increase in the number of buses on routes running on Marylebone Road, and possibly by greater congestion resulting from Marylebone Road lying on the perimeter of the Congestion Charging zone), although further work is required to establish the exact cause. This will have implications for the attainment of the annual limit value for NO_2 (40 $\mu g\ m^{-3}$, 20.9 ppb).

  The analysis of hourly mean data for the site at Marylebone Road has provided insights into the seasonal and diurnal dependence of OX sources and their origins, and the conditions under which exceedences of the hourly mean NO_2 limit value (200 $\mu g\ m^{-3}$, 104.5 ppb) are more probable. The present analysis demonstrates that the ambient concentration of OX at Marylebone Rd is sensitive to a number of factors, such as primary NO_2 emissions and regional background O_3 concentrations, and that variation in the magnitudes of these factors leads to substantial diurnal and seasonal differences in the level of NO_X required for the hourly mean NO_2 limit value of 104.5 ppb to be exceeded.
- The OSRM and the UK Photochemical Trajectory Model (PTM) have been applied to evaluate a number of proposed ozone control measures and to the Review of the Air Quality Strategy (**Objective 3**):
  - Post Gothenburg Controls: Using its idealised episode trajectory, the UK PTM has shown that both VOC and NOx control are effective in improving ozone air quality. Model runs, in which NO_x and VOC emissions were separately reduced by 30% across-the-board, suggested that the worst-case trajectory to central Wales was still VOC limited (i.e., VOC control was more effective than NO_x control). Larger emission reductions indicated that the trajectory became NO_x limited.
  - The OSRM was used to assess a number of policy options relating to ozone:
    (a) Regulatory Impact Assessment of Directive on Decorative Paints
    (b) Proposed NO_x Emission Standards for Vehicles (EURO V Standards)
    (c) Regulatory Impact Assessment of Directive on Petrol Vapour Recovery

(d) Post-Gothenburg Scenarios

These were UK-scale model runs. As the surface-conversion algorithm was not available for use in these runs, the conclusions were therefore based on the unconverted outputs. There appeared to be two counteracting effects (a) photochemical production of ozone involving oxides of nitrogen and volatile organic compounds and (b) chemical titration by NO_x removing ozone. These two effects respond differently to emission control. VOC emission control always seemed to improve ozone air quality while NO_x emission control gave a more complex response, which was metric and region specific. Generally, NO_x emission control had an adverse effect on ozone air quality. Thus, either VOC emission control alone or combined VOC and NO_x emission controls are needed to improve ozone air quality.

The OSRM outputs for the 2 Regulatory Impact Assessments were given to colleagues at netcen to undertake the cost-benefit analyses. A paper was prepared on all four series of model runs for the first phase of the review of the Air Quality Strategy.

- The OSRM was used to investigate the impacts on ozone of a number of measures being considered in the first phase of the **Review of the Air Quality Strategy**. Model runs were undertaken to 41 UK receptors sites in urban and rural locations. These model runs have neglected the effects of the year-to-year variability in meteorology and the changing atmospheric composition arising from climate change and the global circulation. The output from the OSRM model runs was converted using the Surface Conversion algorithm. The model results were considered under the following headings:

(a) Effect of Additional Industrial NO_x Measures: Additional measures are being considered to reduce NO_x emissions from power stations, refineries, the iron and steel plants and cement kilns. The lower total NO_x emissions in these model runs improve nitrogen dioxide air quality but leads to varying increases in the ozone metrics, with the smallest relative increases between 2010 and 2020 seen in the metrics which are sensitive to peak ozone concentrations.

(b) Effect of EURO V/VI Emission Controls: Additional controls on vehicle exhaust emissions are being considered to reduce NO_x emissions (EURO V/VI Scenario G). The lower total NO_x emissions in these model runs improve nitrogen dioxide air quality but leads to an increase in the ozone metrics between 2010 and 2020. Although the overall level of emission reduction in 2020 is comparable between the two NO_x control scenarios (Additional NO_x Measures and EURO V/VI Emission Controls), there are differences in the spatial distribution of the emissions. The results suggest that there is a proportionately greater reduction in the NO_x emissions in London for the EURO V/VI scenarios, hence the larger changes seen in the ozone and nitrogen dioxide metrics for the London sites. There is however less difference, certainly for the metrics sensitive to peak ozone concentrations, for the UK-urban and UK-rural sites.

(c) Across-the-Board Reductions in VOC Emissions: The effect of 10% and 30% across-the-board reductions in VOC emissions in 2010, 2015 and 2020 were evaluated for both UK action and UK and European action. For a given year, the annual mean nitrogen dioxide concentration is virtually unaffected by the VOC emission reductions. There is a progressive improvement in all four ozone metrics as the VOC emissions are reduced from the base case (i.e., no reduction) to a 10% reduction in UK emissions through to a 30% reduction in UK and EMEP emissions (i.e., the largest emission reduction) for UK-rural, UK-urban and London sites. The response to a 10% reduction in UK VOC emissions is approximately half of that resulting from a 10% reduction in UK and EMEP emissions, implying that emission reductions in the UK or EMEP would be equally effective in improving ozone air quality. The responses to a 30% reduction in the UK or EMEP VOC emissions suggest that reductions in European emissions would be more effective in improving ozone air quality.

A paper was prepared on these model runs for the first phase of the review of the Air Quality Strategy.

The model runs undertaken for the Review of the Air Quality Strategy were largely based on specific emission control measures. Although desirable, the measures by themselves would not necessarily ensure attainment of ozone air quality targets or objectives. As a result, the

Department was interested in the critical point where NO_x reductions would eventually result in less ozone, especially in urban areas. To answer this question, two series of OSRM model runs were undertaken in which the NOx emissions in (i) the UK and (ii) the UK and Europe were progressively reduced from 100% to 10% of their 2010 base case values in 10% increments. The model runs used the same 41 receptor sites as for the Review of the Air Quality Strategy.

The annual mean NO_2 concentration falls at all three sites as the overall NO_x emissions are reduced. However, the ozone metrics generally show an increase in value, reach a peak before then declining. The response is metric and site specific. The results indicate that large decreases in NO_x emissions (50-90%) would be required to overcome the ozone increase and to achieve compliance with air quality target and objectives. NO_x emission control in the UK and Europe was found to be more effective than control in the UK alone as a smaller percentage NO_x emission reduction is needed to reach the peak value in the ozone metrics. These model runs assumed no corresponding VOC emission reduction. As shown previously, any VOC emission reductions would improve ozone air quality. A lower level of NOx reduction would therefore be needed if VOC emissions were also controlled to achieve the same endpoint.

In previous OSRM scenario calculations, NO_x emission reductions alone gave a complex response. The response depended on the choice of ozone metric and could show regional differences for a given metric. Generally, there was a deterioration in ozone air quality if NO_x emissions alone were controlled. Some insight into the NO_x emission response was also gained. The present model results suggest that there are potentially two counteracting factors (a) the reduction in photochemical ozone production as NO_x emissions are controlled, which is the situation classically simulated using the Photochemical Trajectory Model and (b) a NO_x titration effect. The relative importance of these effects varies during the year, the day and with site.

This explains the apparent inconsistency in the responses of the PTM and OSRM to NO_x control. Elevated concentrations of ozone over the UK are generally associated with photochemical production and easterly airflows. This is the situation modelled in the UK PTM with its idealised trajectory from central Europe to the UK. Reduction of NO_x (or VOC) emissions are effective in reducing ozone. In an OSRM model run, a calendar year is simulated and a wider range of trajectories is sampled, including those from other wind directions. These other trajectories may have little or no photochemical ozone production, especially if the trajectory has mainly passed over low emission areas (e.g., the sea). In this case, the NO_x titration effect controls the response to NO_x emission control.

- Work is in progress to assess the performance of the OSRM as a supplementary assessment technique. Model runs have been undertaken for a number of current years (1997 to 2003). This work will be included in the first report for the third Daughter Directive on ozone, which needs to be submitted to the European Commission in September 2005.
- The Chemical Mechanism development (**Objective 4**) has less immediate policy relevance but it does underpin the modelling tools used in the contract to assess ozone policy options. The reaction schemes for butane and isoprene in the MCM have been evaluated against chamber data. The evaluations have provided strong support for the MCM schemes for the most abundant components of emissions of anthropogenic and biogenic non-methane VOC, respectively. The study on multi-day reactivity has been completed using the MCM. The results demonstrate the need for a comprehensive chemical mechanism as simplified mechanisms could potentially lead to different ozone source-receptor relationships being used in integrated assessment models. The work on Objective 4 and the improvements to the MCM website contribute to the Department's desired outcome to maintain the leading position of the Master Chemical Mechanism;
- A module to calculate ozone stomatal fluxes (**Objective 5**) has been developed for use with the OSRM. This will provide the Department with a more realistic tool to evaluate the impact of ozone on crops and vegetation for the forthcoming reviews of the European Union's National Emission Ceilings Directive and the Gothenburg Protocol to the UN ECE Convention on Long-range Transboundary Air Pollution.

3 Development and Application of Ozone Models (Objective 1)

3.1 INTRODUCTION

The current project has a strong UK focus with national (Objective 3a) and local (Objective 2) scale interests. This is further emphasised by the work needed to provide the preliminary and interim assessments of the 3rd Daughter Directive (Objective 3b). For these reasons, the Ozone Source-Receptor Model (OSRM) was proposed as the primary modelling tool to meet these objectives. The Ozone Source-Receptor Model was developed during the previous DEFRA project on Modelling of Tropospheric Ozone Formation (EPG 1/3/143) [Hayman *et al.*, 2002].

The OSRM covers the EMEP model domain and uses global meteorological datasets provided by the Met Office to derive 96-hour back trajectories to specified receptor sites (UK/EMEP monitoring sites or a 10km x 10km grid covering the UK). The chemical scheme is almost the same as that used in the STOCHEM model. The mechanism has ~70 chemical species involved in ~154 thermal and photochemical reactions. The mechanism represents ozone formation using 10 VOCs, which provides an adequate description of ozone formation on the regional scale. The emission inventories are taken from EMEP for Europe with the option to use NAEI emission inventories for the UK, which have been aggregated to 10 km x 10 km and into 8 key sectors. Further details are provided in Appendix 1.

Using a backwards-iterative EULER solver with a 240s timestep, a single trajectory calculation on a Dell Precision Workstation 650 MiniTowers (containing dual Intel® Xeon 3.06GHz processors) takes 0.016 s per trajectory (*i.e.*, ~60 trajectories per second). Making use of the two available processors on the workstation gives a runtime of ~2.6-2.8 days for a calendar-year UK-scale model run to ~3,000 receptor sites.

3.2 SURFACE CONVERSION ALGORITHM

The OSRM describes the boundary layer by a single box and assumes that this is well mixed. While this is a reasonable assumption for rural areas, it is less valid in urban areas with high NO_x emissions. In such areas, there will inevitably be a gradient in the NO_x concentration profile, with higher concentrations at the surface. This will lead to lower ozone concentrations at the surface through reaction with nitric oxide.

An algorithm has been developed and implemented in the OSRM post-processor to convert the mid-boundary layer concentrations to surface concentrations. This algorithm uses the meteorological parameters characterising the boundary layer, surface roughness appropriate for the surface types considered, resistance parameters for O_3 and NO_2, the local NO_x emission rates and a simple NO-NO_2-O_3 photostationary state chemistry.

The algorithm solves the following set of coupled differential equations, which presumes mass balance for each species:

NO $$\frac{\partial}{\partial z}\left(\frac{ku^* z}{\phi}\frac{\partial[NO]}{\partial z}\right)-k_1[NO][O_3]+J[NO_2]=0 \qquad (1)$$

O_3 $$\frac{\partial}{\partial z}\left(\frac{ku^* z}{\phi}\frac{\partial[O_3]}{\partial z}\right)-k_1[NO][O_3]+J[NO_2]=0 \qquad (2)$$

NO$_2$ $$\frac{\partial}{\partial z}\left(\frac{ku^{*}z}{\phi}\frac{\partial[NO_2]}{\partial z}\right)+k_1[NO][O_3]-J[NO_2]=0 \tag{3}$$

The assumption is then made that the stability parameter (*ku*/*ϕ), defined by Equation (4), is constant throughout surface boundary layer.

$$\frac{ku^{*}}{\phi}=\frac{1}{R_A}\ln\left(\frac{H/10}{z_0}\right) \tag{4}$$

where u* is the friction velocity and *k* is the von Karman constant. The differential equations (1) to (3) are transformed from a height-based co-ordinate system (z) to a resistance-based co-ordinate system (r) using the substitution:

$$r=\frac{\phi}{ku^{*}}\ln\left(\frac{z}{z_0}\right) \tag{5}$$

The differential equations (1) to (3) can be rewritten as:

$$\frac{\phi}{ku^{*}}\frac{\partial^2[NO]}{\partial r^2}-k_1[NO][O_3]z+J[NO_2]z=0 \tag{6}$$

with corresponding expressions for O_3 and NO_2.

The upper boundary conditions at $r=R_A$ are $[NO] = [NO]_{mbl}$, $[NO_2] = [NO_2]_{mbl}$ and $[O_3] = [O_3]_{mbl}$. The lower boundary conditions at r=0 is:

$$\frac{\partial[NO]}{\partial r}=-E_{NO}+v_d[NO] \tag{7}$$

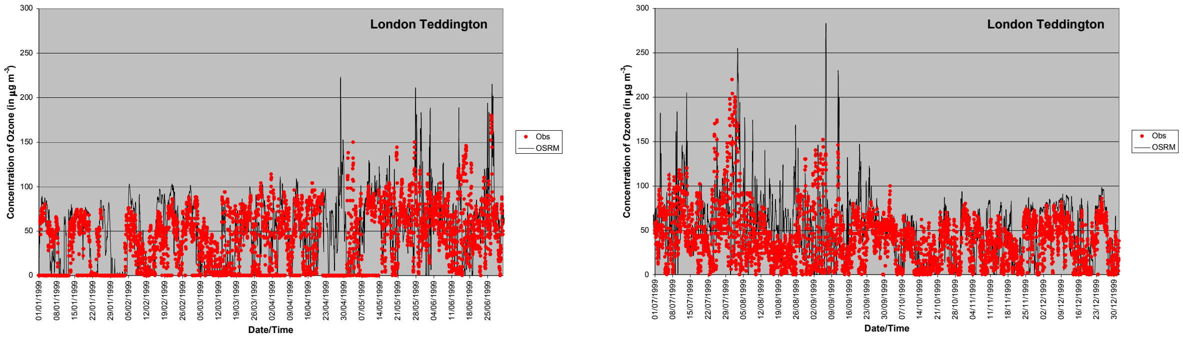
where E_{NO} is the emission rate of nitric oxide;
v_d is the non-aerodynamic deposition velocity ($=1/(r_b+r_{sur})$)

with similar expressions for O_3 and NO_2.

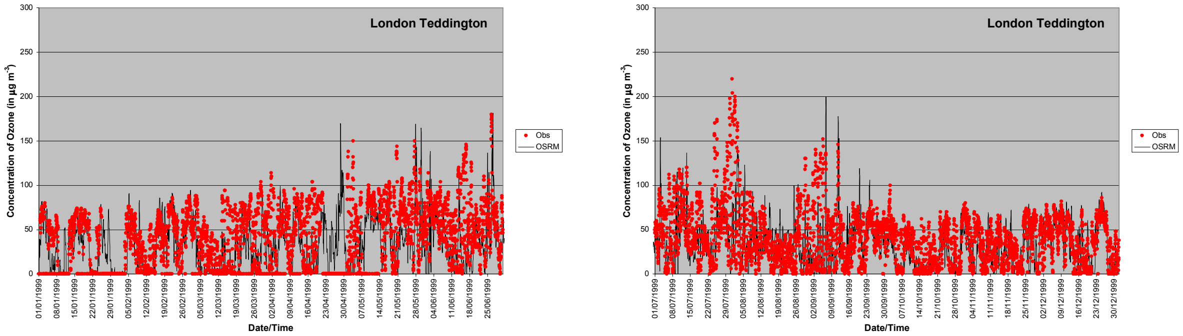
The differential terms in each of the equations are replaced by finite difference approximations and the resulting simultaneous linear equations solved by Gaussian elimination along the tridiagonal. As the chemical reaction term introduces some non-linearity, it is necessary to repeat the calculations a few times to obtain convergence with successive approximations to the non-linear terms. The parameters needed for the conversion are taken from a combination of additional output generated during the OSRM model run and databases calculated using the Surface Ozone Flux Model (see Section 7).

The effect of the surface correction algorithm can be seen in Figure 3-1 and Figure 3-2. These figures compare the observed hourly concentrations of ozone and of oxides of nitrogen (= Nitric Oxide + Nitrogen Dioxide) observed at the London sites of Teddington and Bloomsbury in 1999 with those calculated using the OSRM. Bloomsbury is a site in central London while Teddington is a suburban site to the west of London. Panels (a) and (c) of Figure 3-1 and Figure 3-2 compare the OSRM mid-boundary-layer output against the measurements while Panels (b) and (d) show the surface-corrected results. There is a marked improvement in the comparison against the measurements at both sites, most noticeably for the London Bloomsbury site.

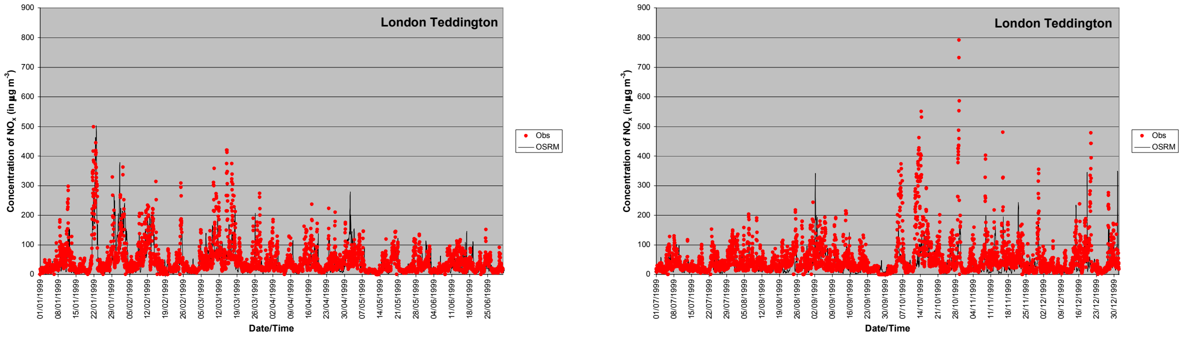
(a) Ozone – No OSRM Post-processor Surface Conversion



(b) Ozone – OSRM Post-processor Surface Conversion



(c) Nitrogen Oxides – No OSRM Post-processor Surface Conversion



(d) Nitrogen Oxides – OSRM Post-processor Surface Conversion

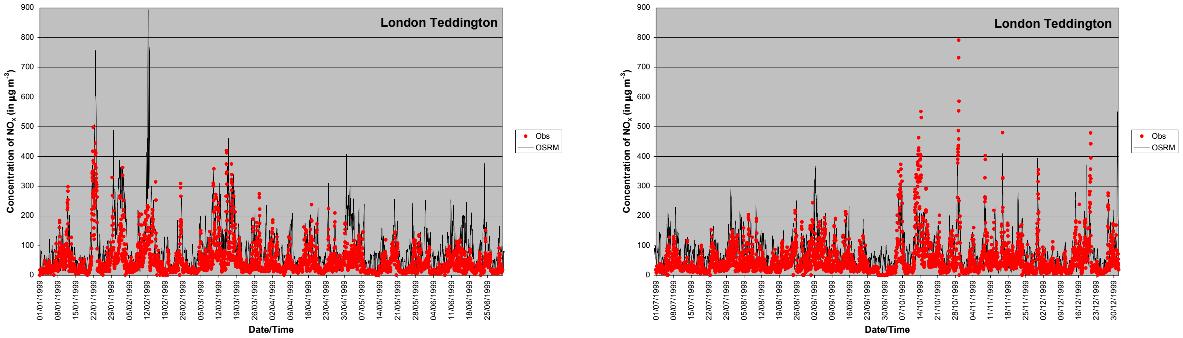
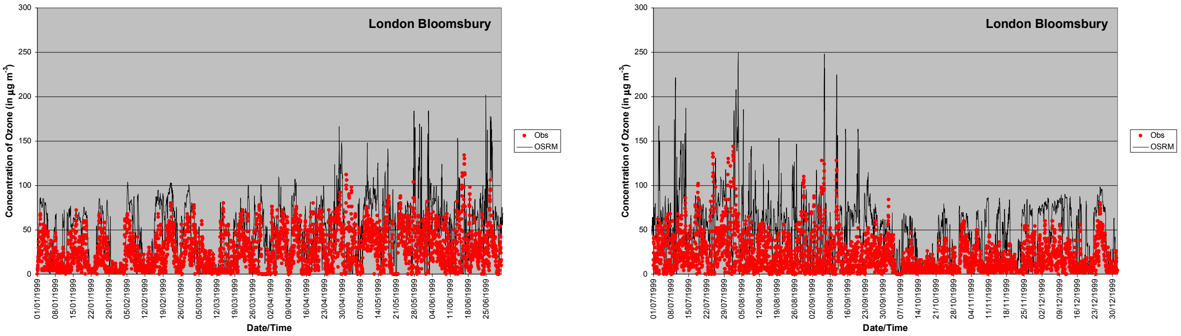
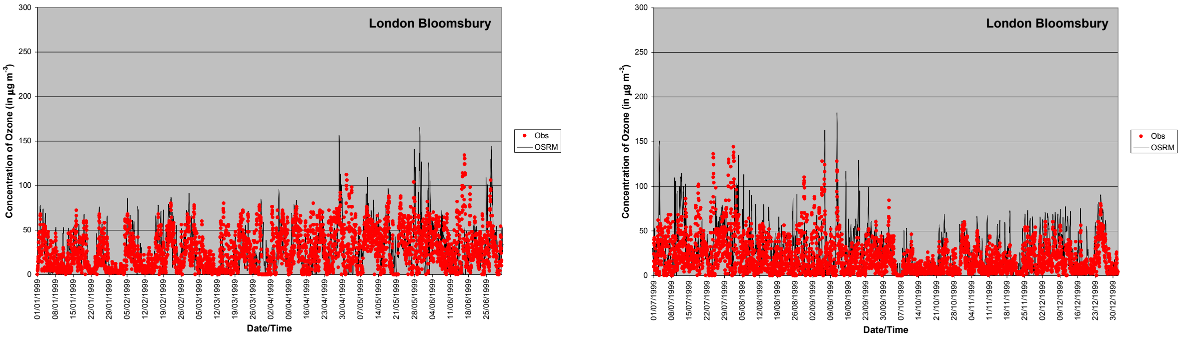


Figure 3-1: Comparison of the Observed and Modelled Hourly Concentrations (in µg m^{-3}) of Ozone (Panel a) and Oxides of Nitrogen (= Nitric Oxide + Nitrogen Dioxide, Panel b) for the London Teddington Site in 1999.

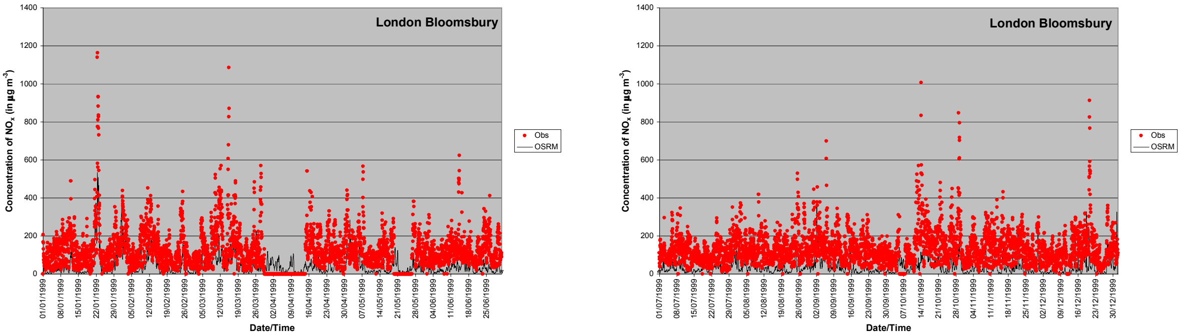
(a) Ozone – No OSRM Post-processor Surface Conversion



(b) Ozone – OSRM Post-processor Surface Conversion



(c) Nitrogen Oxides – No OSRM Post-processor Surface Conversion



(d) Nitrogen Oxides – OSRM Post-processor Surface Conversion

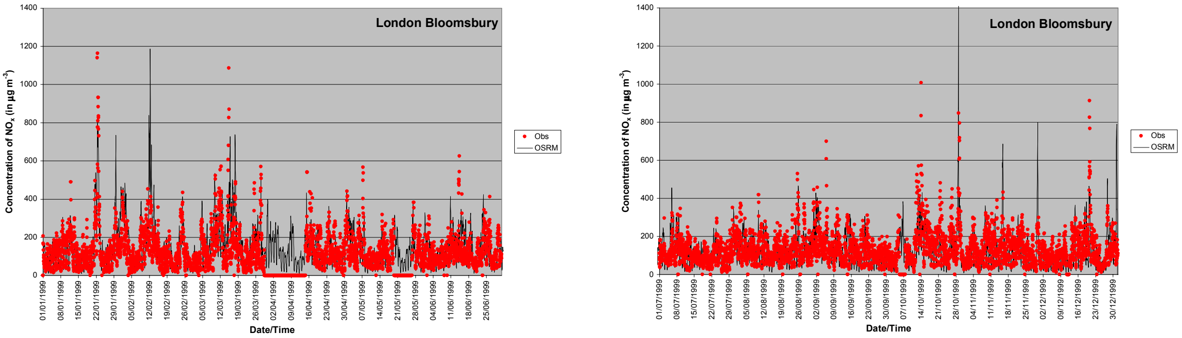


Figure 3-2: Comparison of the Observed and Modelled Hourly Concentrations (in $\mu g\ m^{-3}$) of Ozone and Oxides of Nitrogen (= Nitric Oxide + Nitrogen Dioxide) for the London Bloomsbury Site in 1999.

Table 3-1 compares the performance of the OSRM against observations made at 41 UK ozone monitoring sites in 1999 for the annual mean of the maximum daily running 8-hour mean ozone concentration ($\mu g\ m^{-3}$) and the number of days when the running 8-hour mean ozone concentration exceeds 100 $\mu g\ m^{-3}$. The table presents the OSRM results for the uncorrected and surface-corrected output. There is a significant improvement in the performance of the OSRM, particularly for the London and other urban sites, when the surface correction is applied. The surface-correction algorithm was used in the processing of all the subsequent OSRM output.

Table 3-1: Comparison of the Uncorrected and Surface-Corrected OSRM Output for the Annual Mean of Maximum Daily Running 8-Hour Mean Ozone Concentration ($\mu g\ m^{-3}$) and the Number of Days when the Running 8-hour Mean Ozone Concentrations exceeds 100 $\mu g\ m^{-3}$ for 1999 against the Values derived from the Measured Ozone Concentrations.

Site	Annual Mean of Maximum Daily Running 8-Hour Mean Ozone Concentration ($\mu g\ m^{-3}$)			Number of days when the Running 8-hour Mean Ozone Concentrations exceeds 100 $\mu g\ m^{-3}$		
	Observed	OSRM (Uncorr)	OSRM (Corr)	Observed	OSRM (Uncorr)	OSRM (Corr)
Strathvaich Dam	82.9	83.0	72.2	26	63	31
Aston Hill	76.7	79.9	70.9	22	53	32
Bush	70.3	78.5	67.0	8	49	27
Eskdalemuir	69.3	82.8	74.1	16	68	33
Great Dun Fell	-	82.4	74.1	-	60	32
Harwell	71.0	76.2	62.9	31	66	26
High Muffles	75.4	81.0	71.0	31	66	36
Ladybower	72.0	74.2	62.7	21	42	27
Lullington Heath	79.0	82.0	66.9	53	88	38
Narberth	77.4	85.2	67.0	26	89	15
Rochester	71.0	73.5	53.1	36	59	23
Sibton	68.2	79.1	64.0	23	79	33
Somerton	77.8	79.7	69.4	35	69	34
Wharley Croft	-	82.1	73.8	-	59	35
Wicken Fen	67.2	75.4	63.5	31	56	36
Wray	-	81.0	71.5	-	61	33
Yarner Wood	76.0	85.6	73.2	34	83	38
Bottesford	68.7	72.3	59.3	19	50	27
Glazebury	59.8	74.4	57.6	13	43	22
Lough Navar	65.6	81.7	71.4	6	52	24
London Bexley	61.4	74.1	56.5	23	57	22
London Bloomsbury	38.8	71.9	42.9	3	52	13
London Brent	61.0	74.6	61.6	27	60	29
London Eltham	61.9	74.0	61.4	26	54	27
London Hackney	48.5	72.7	55.4	8	55	23
London Haringey	56.9	74.4	59.8	25	58	26
London Hillingdon	43.1	74.4	52.1	9	59	18
London N Kensington	57.0	73.2	43.7	25	56	13
London Teddington	-	73.9	49.6	31	62	17
London Westminster	-	73.0	47.2	-	56	16
Birmingham Centre	57.1	72.3	52.5	8	46	18
Birmingham East	55.7	71.9	50.3	14	44	15
Manchester Pic.	44.0	73.8	56.4	5	44	19
Leeds Centre	56.2	71.8	53.5	13	43	15
Newcastle Centre	59.5	82.0	70.7	10	61	29
Bristol	60.7	76.1	61.8	14	56	25
Southampton Centre	54.3	78.5	57.3	9	66	21
Glasgow	47.4	79.6	65.0	-	53	22
Edinburgh	50.3	77.7	63.4	2	49	24
Belfast Centre	62.2	80.9	65.4	8	58	15
Cardiff	58.0	77.1	56.8	19	61	9

A similar trend is seen when the OSRM model output is compared to 2001 measurements. The improved performance of the OSRM provides further confirmation of its suitability as a robust tool to assess current and planned policy options.

3.3 NEW METRICS FOR OZONE AND NO_X

As reported last year [Hayman *et al.*, 2004], a postprocessor code has been developed to process the output of the OSRM. The code can handle the output from ~3,000 receptor sites needed for the production of 10 km x 10 km maps. The post-processor code currently calculates the following metrics for ozone and nitrogen dioxide and produces output datafiles for generating maps of these metrics.

Ozone:
(1) annual mean concentration
(2) AOT30 for the protection of crops (EU and UN ECE)
(3) AOT30 for the protection of forests (EU and UN ECE)

(4) AOT40 for the protection of crops (EU and UN ECE)
(5) AOT40 for the protection of forests (EU and UN ECE)
(6) AOT60 for the protection of human health (EU and UN ECE)
(7) maximum hourly concentration in the year
(8) maximum 8-hour running mean concentration in the year
(9) annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day
(10) number of days when the maximum of the 24 possible 8-hour running mean concentrations in each day exceeds 100 $\mu g\ m^{-3}$ (metric in the UK Air Quality Strategy)
(11) number of days when the maximum of the 24 possible 8-hour running mean concentrations in each day exceeds 120 $\mu g\ m^{-3}$ (metric in the EU 3rd Daughter Directive)
(12) AOT30 for the protection of horticulture (EU and UN ECE)
(13) AOT30 for the protection of semi-natural vegetation (EU and UN ECE)
(14) AOT40 for the protection of horticulture (EU and UN ECE)
(15) AOT40 for the protection of semi-natural vegetation (EU and UN ECE)
(16) annual mean of those maxima of the 24 possible 8-hour running mean concentrations in each day > 35 ppb
(17) maximum hourly concentration in the summer
(18) AOT35 for the protection of human health[2]
(19) AOT50 for the protection of human health[2]
Nitric Oxide: **(20) annual mean concentration**
Nitrogen Dioxide: (21) annual mean concentration
(22) maximum hourly concentration in the year
(23) number of hours in the year when the hourly concentration exceeds 200 $\mu g\ m^{-3}$

The metrics highlighted in bold have been added during the present reporting period to address the impacts on specific ecosystems or on human health.

3.4 COMPARISON WITH OTHER MODELS

3.4.1 UK Photochemical Trajectory Model

The UK-Photochemical Trajectory Model (PTM) has been used extensively to assist the evaluation of ozone policy options. The responses of the Ozone Source Receptor and UK Photochemical Trajectory Models to a 30% across-the-board reduction in VOC and NO_X emissions have been compared. The UK PTM used the idealised episode trajectory from Central Europe to mid-Wales. For the OSRM, the date of the maximum hourly ozone concentration calculated for 1999 at the receptor site corresponding to the end point of the PTM trajectory was identified and this trajectory was used in the emission reduction calculations. The trajectory came from an easterly direction and the latter part of the trajectory followed a broadly similar path to that of the PTM trajectory. In all other respect, the standard features of the OSRM were used.

The peak ozone concentrations calculated at the end of the PTM trajectory were taken from Dick Derwent's modelling work on Post-Gothenburg emission reduction scenarios (see Section 5.2.1 later) and are presented in Table 3-2. The corresponding OSRM values are also shown in the same table. Although the OSRM concentrations are about 35 ppb higher, the changes to emission reductions are remarkably consistent. This gives some confidence in the use of the OSRM for policy applications.

To provide further confirmation of the responses and to identify why the OSRM calculated higher ozone concentrations, a more direct comparison has been made. The OSRM was configured to calculate ozone concentrations along the idealised linear trajectory of the PTM. As far as was possible, the two models used (a) the same emission inventories (EMEP and the previous biogenic

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[2] This is an effective AOT metric using the maximum of the 24 possible 8-hour running mean concentrations in each day instead of the hourly ozone concentration. Using a 35 ppb or 50 ppb cutoff, the AOTxx is the annual mean of the difference between the maximum daily 8-hour running mean concentration and the cutoff of xx ppb.

emission inventory with no temporal emission factors), (b) the same VOC speciation and (c) the same treatment and parameter values for the photolysis and dry deposition processes. The remaining differences were the chemical mechanisms and solvers used in the two models (PTM: CRI Mechanism with a variable order Gear solver; OSRM: the modified STOCHEM mechanism with a backward Euler solver). The modified STOCHEM mechanism was used in the OSRM and the CRI mechanism in the PTM.

Table 3-2: Comparison of the PTM and OSRM

Scenario	PTM Peak Ozone (in ppb)	OSRM Peak Ozone (in ppb)
1999 Current Case	85.5	119.2
2010 Base Case	74.2 (-11.3)	110.0 (-9.2)
2010 Base Case + 30% NOx Reduction	69.9 (-15.6)	104.3 (-14.9)
2010 Base Case + 30% VOC Reduction	69.6 (-15.9)	103.7 (-15.5)

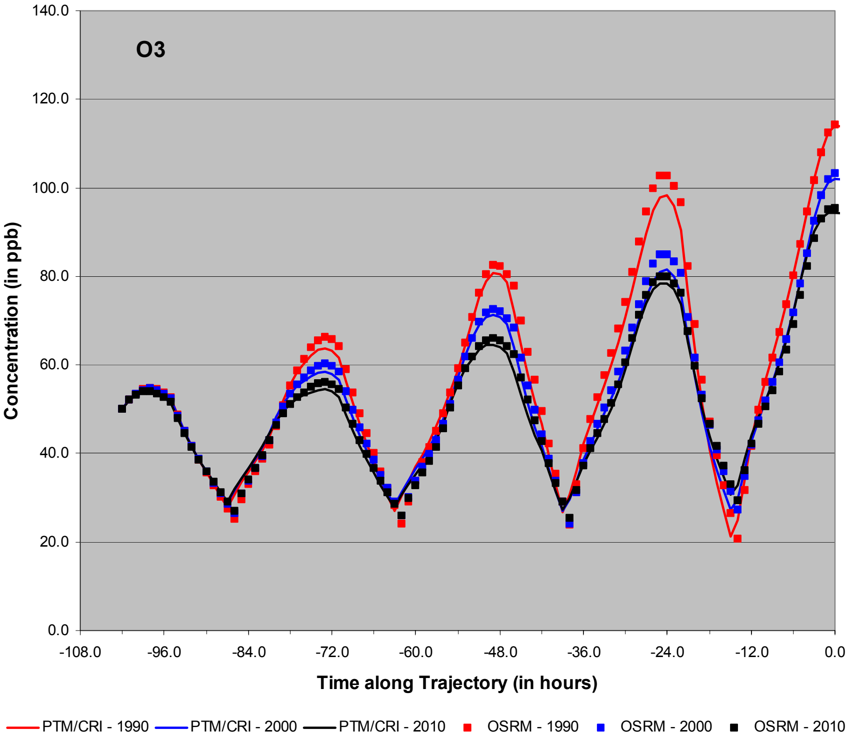

Figure 3-3: Comparison of the Ozone Concentrations Calculated by the OSRM and PTM for Three Different Emission Years along the Idealised Episode Trajectory of the PTM.

Figure 3-3 shows a comparison of the ozone concentrations calculated along the idealised episode trajectory by the two models for three different emission years. The peak ozone concentrations in these model runs, together with additional runs in which the VOC and NO_X emissions were reduced by 30% across-the-board, are presented in Table 3-3. The agreement between the two models is excellent.

Table 3-3: Comparison of the Peak Ozone Concentrations Calculated by the PTM and OSRM for Different Emission Scenarios along the Idealised Episode Trajectory of the PTM.

Model Run	PTM Peak Ozone (in ppb)	OSRM Peak Ozone (in ppb)
1990 Base Case	114.9	115.1
2000 Base Case	102.6	103.9
2010 Base Case	95.1	96.2
2010 Base Case + 30% NOx Reduction	92.0	95.2
2010 Base Case + 30% VOC Reduction	86.5	85.2

A series of OSRM runs were undertaken for the 2000 base case in which the changes made to the current version of the model were reversed. The peak ozone concentrations calculated are shown in Table 3-4.

Table 3-4: Effect of Changes to the OSRM Formulation on the Peak Ozone Concentrations Calculated along the Idealised Episode Trajectory of the PTM.

Model Run	OSRM Peak Ozone (in ppb)
2000: OSRM in Normal Configuration	132.1
2000: OSRM with PTM dry deposition scheme	117.8
2000: OSRM with *l,m,n* photolysis rate scheme	132.6
2000: OSRM with no temporal emission variation	132.3
2000: OSRM with old biogenic VOC emission inventory	116.4
2000: OSRM configured as PTM	103.9

Table 3-4 shows that the major differences between the OSRM in its normal configuration and as the PTM arise from (a) the different biogenic VOC emission inventories and (b) the dry deposition schemes and parameter used. The PTM uses a higher dry deposition velocity for ozone. Although this difference is to a certain extent addressed by the surface conversion algorithm used in the OSRM post-processor, the dry deposition scheme used in the OSRM is more realistic taking into account the aerodynamic component of the resistance and the seasonal variation in the ozone stomatal resistance.

3.4.2 ADMS Urban

The OSRM has been used to generate maps of ozone and nitrogen dioxide metrics for London for 2010 and a number of current years (1997-2002). Model runs were undertaken to calculate the hourly ozone and nitrogen dioxide concentrations for a model domain covering Greater London using meteorological data and UK and EMEP emission inventories for the relevant years. The model domain used a 1 km x 1 km grid of 1,639 receptor sites. From the hourly concentrations, maps were derived of the annual mean NO_2 concentration, the annual mean of the maximum daily running 8-hour mean ozone concentration and the annual mean of the maximum daily running 8-hour mean ozone concentrations which are greater than 35 ppb. Both surface-converted and unconverted maps were prepared.

Under a separate contract let by Defra and the Devolved Administrations, CERC have used ADMS-Urban to generate concentrations maps of the annual mean ozone and nitrogen dioxide concentrations for Greater London for 1999 and 2010 [CERC, 2003]. These are compared with the corresponding surface-corrected OSRM maps in Figure 3-4. While the OSRM maps do not have the detailed structure of the CERC maps, the OSRM maps do show the high concentrations of NO_2 (and low concentrations of O_3) in central London and in the vicinity of Heathrow airport, which reflect the areas of high NO_x emissions in London. There is also evidence of the major London roads (*e.g.*, the M3, M4 and A40 to the west and the North Circular Road). The OSRM NO_2 concentrations are generally lower than those in the ADMS-Urban maps and as a result the OSRM maps show higher O_3 concentrations.

Both models show a reduction in the annual mean NO_2 concentration between 1999 and 2010 as the NO_x emissions are lower. There is a corresponding increase in the annual mean ozone concentration as a result of the reduced NO_x titration effect.

3.4.3 The EMEP UNIOZONE Model

The UK Ozone Source-receptor and the EMEP UNIOZONE models were compared, as part of a review on UK and EMEP modelling tools commissioned by the Department. The Ozone Source-receptor and the EMEP UNIOZONE models both simulate photochemical ozone production on the regional scale. Although the models use the EMEP model domain, the OSRM is a lagrangian model while the EMEP model is Eulerian in character. In this section, a comparison is made of the general performance of the models and their response to a notional 25% reduction in UK anthropogenic emissions of (a) sulphur and nitrogen oxides, and (b) carbon monoxide and non-methane volatile organic compounds. The reference year used was 2000.

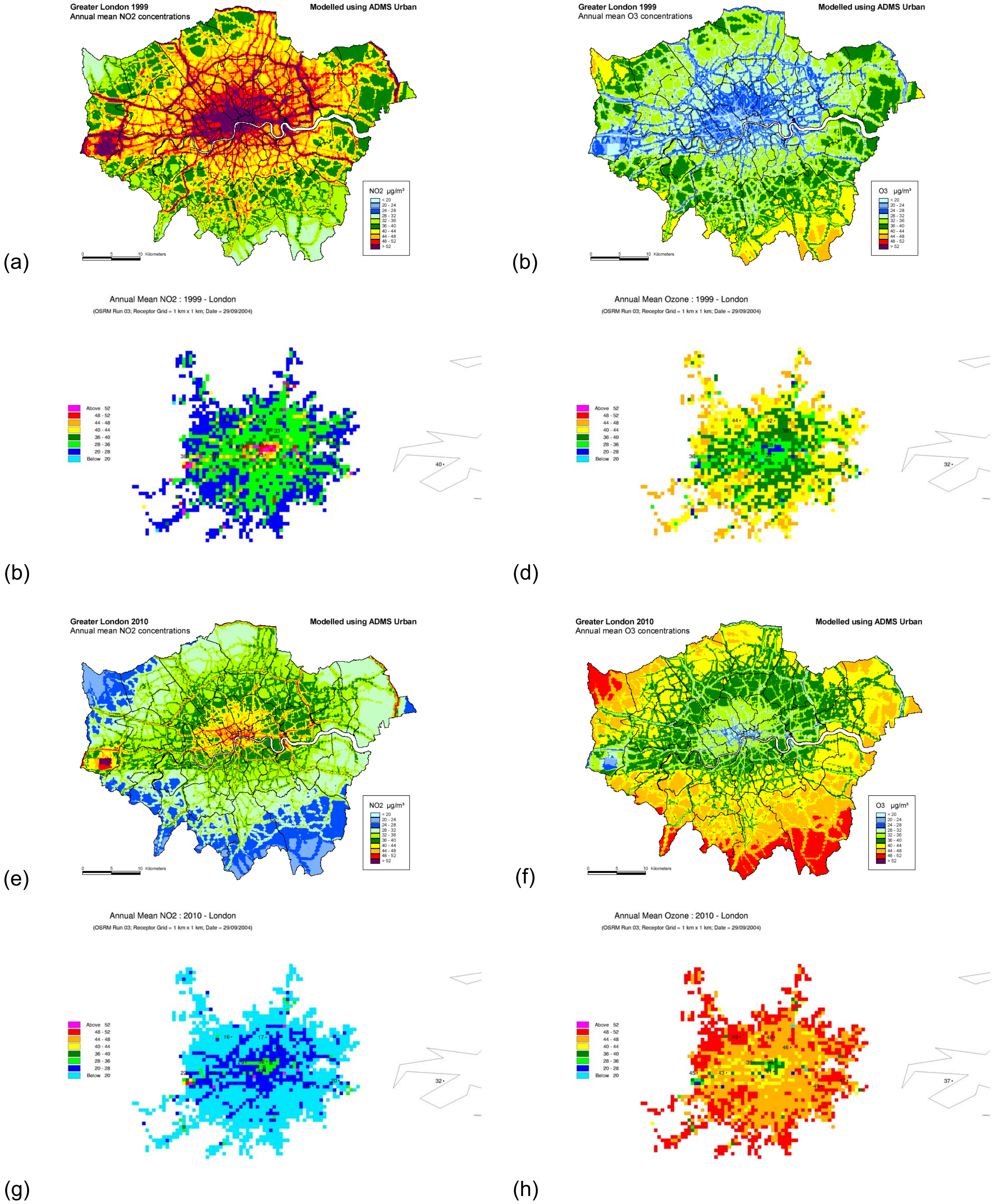

Figure 3-4: Comparison of Maps for Greater London of Annual Mean Concentrations of NO_2 (left-hand panels) and O_3 (right-hand panels) calculated by CERC's ADMS-Urban (panels a, b, e and f) and the Ozone Source-receptor (panels c, d, g and h) Models for 1999 and 2010.

General Performance

The upper panels of Figure 3-5, taken from the EMEP report on the performance of the Unified EMEP Model (EMEP, 2003), compares the calculated maximum of the daily ozone concentrations with those observed at two UK monitoring sites – Yarner Wood and Aston Hill. The EMEP model is generally able to give a good description of the observations. The modelled mean concentrations agree with the observations and the correlation coefficient is high. For many of the observed high ozone events, the EMEP model tends to underestimate both the maximum and minimum ozone concentration.

The corresponding comparisons of the OSRM modelled maximum of the daily hourly ozone concentrations with those observed at Yarner Wood and Aston Hill are shown the lower panels of Figure 3-5. The OSRM mid-boundary-layer concentrations have been converted into surface ozone concentrations. While the OSRM is generally able to reproduce the observed concentrations and the occurrence of elevated ozone concentrations, the model has a tendency to overpredict the peak ozone concentrations. This will have implications for the calculations of the exceedence metrics such as AOT40 or AOT60.

Table 3-5 compares the observed and modelled values for the 12-monthly mean of the maximum daily ozone concentration. The table also presents regression coefficients between the observed and modelled concentrations. Both models are able to reproduce the observed 12-monthly mean of the maximum daily ozone concentration. The EMEP model however appears to have the higher correlation coefficient (R).

Table 3-5: Comparison of the Observed and Modelled 12-monthly Mean of Maximum Daily Ozone Concentration (in ppb) and the Correlation between the Observed and Modelled Maximum Daily Ozone Concentration for Aston Hill and Yarner Wood in 2000.

Ozone Metric	Aston Hill	Yarner Wood
12-monthly Mean of Maximum Daily Ozone Concentration (in ppb)		
- Observed	38.04	37.17
- EMEP	37.46	36.28
- OSRM	36.88	38.34
Correlation Coefficient (R)		
- EMEP vs. Observed	0.72	0.75
- OSRM vs. Observed	0.41	0.53

A comparison of the observed and OSRM-derived values for a number of ozone metrics – annual mean concentration, AOT40 Crops, AOT40 Forests and AOT60 is presented in Table 3-6 for Aston Hill and Yarner Wood in 2000. While the agreement for the annual mean concentration and the AOT40 (Forest) metrics is good, the AOT40 (Crops) metric is underestimated while the overestimation of the peaks by the OSRM leads to significantly larger values for the AOT60 metric than those observed.

Table 3-6: Comparison of the Observed and OSRM-derived AOT40 Crops , AOT40 Forests and AOT60 for Aston Hill and Yarner Wood in 2000.

Ozone Metric	Aston Hill	Yarner Wood
Annual Mean (in ppb)		
- Observed	31.5	28.6
- OSRM	27.6	29.0
AOT40 Crops (in ppb hours)		
- Observed	4328	4554
- OSRM	3443	2428
AOT40 Forests (in ppb hours)		
- Observed	6544	7166
- OSRM	5696	7814
AOT60 (in ppb hours)		
- Observed	352	514
- OSRM	2088	5875

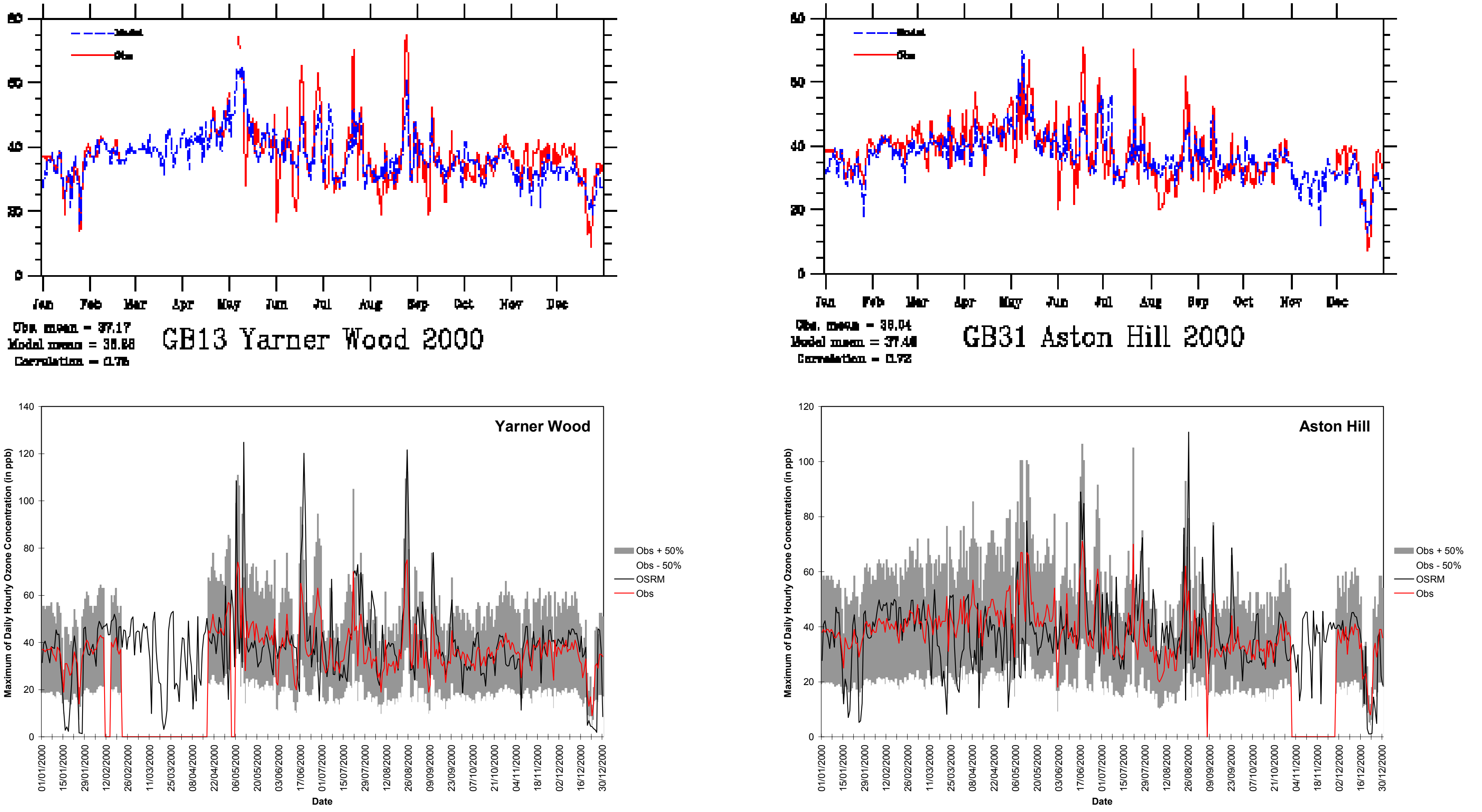

Figure 3-5: Comparison of the Observed Maximum Daily Ozone Concentration (in parts per billion) with those calculated by the EMEP Unified Model (upper panels) and by the Ozone Source-receptor Model (lower panel).

Model Responses to Emission Reductions

The responses of three ozone metrics - AOT40 Forests, AOT60 and the maximum ozone concentration between June and August - to a 25% reduction in UK anthropogenic emissions of (a) sulphur and nitrogen oxides (and particulate matter), and (b) carbon monoxide and non-methane volatile organic compounds (and ammonia) have been calculated using the EMEP UNIOZONE model (see Appendix B of the status report on the unified EMEP model [EMEP, 2003]). The reference year used for the meteorology and emission inventories was 2000. The response is taken to be Ozone Metric (base case) - Ozone Metric (emission scenario). Thus, negative values indicate an increase in the metric.

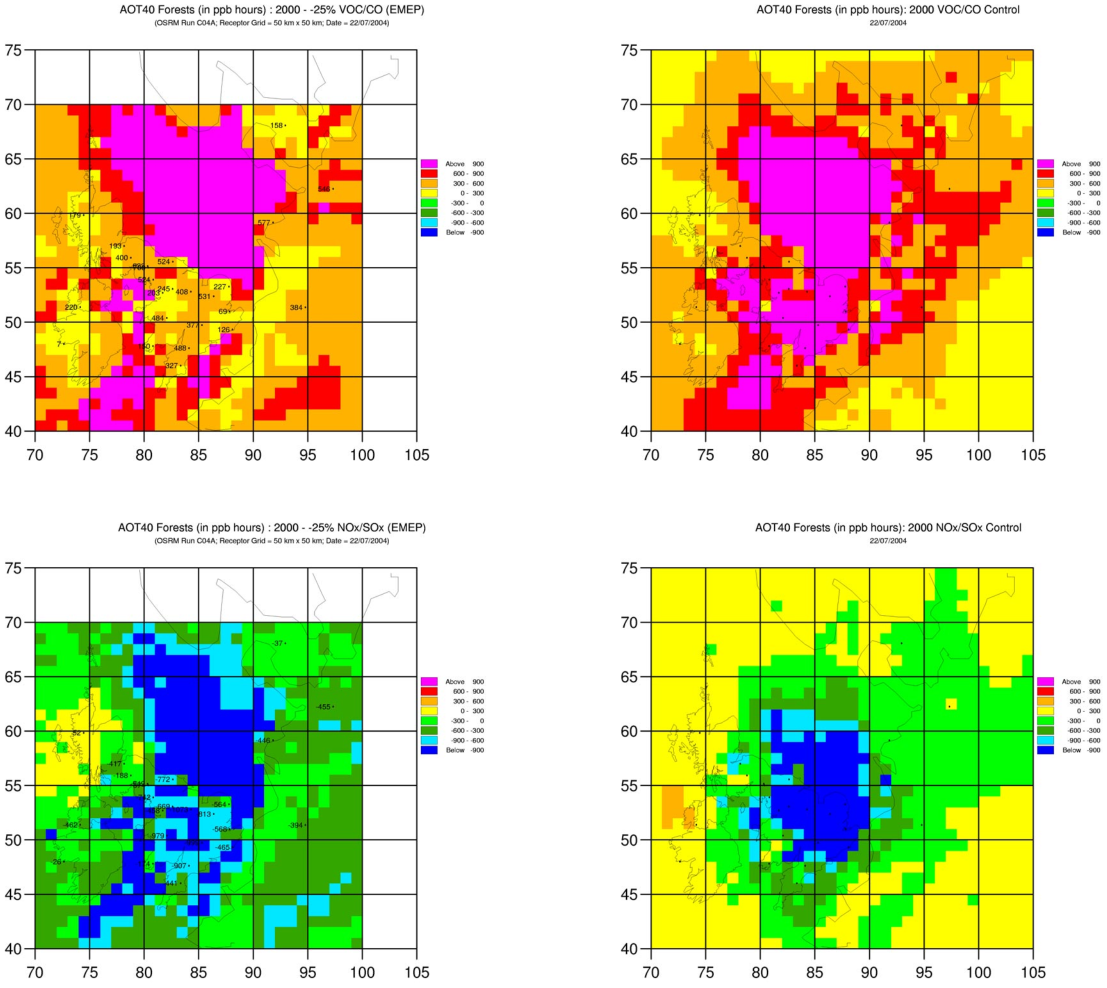

Figure 3-6: Maps of the Response of the Ozone Metric - AOT40 Forests - as calculated by the Ozone Source-receptor (left-hand panels) and the EMEP UNIOZONE (right-hand panels) Models to Emission Control. The maps show, as differences, the Impact of a 25% Reduction in UK Anthropogenic Emissions of (a) Sulphur and Nitrogen oxides (upper panels), and (b) Carbon monoxide and Non-methane Volatile Organic Compounds (lower panels). The Reference Year used is 2000. Note: Negative Values indicate an Increase in the Metric.

The same emission reduction scenarios were also modelled using the OSRM. For computational reasons, a receptor grid covering a limited area of the EMEP model domain (EMEP-x = 70-100, EMEP-y = 40-70[3]) was selected. This domain included the British Isles and part of North West Europe and Scandinavia. Figure 3-6 compares the responses of the AOT40 - Forests using the OSRM and EMEP UNIOZONE model to a 25% reduction in UK anthropogenic emissions of (a)

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[3] The OSRM was developed on the former EMEP extended 50 km x 50 km model domain. The grid square (35,12) on the extended domain corresponds to (1,1) on the current domain.

sulphur and nitrogen oxides (and particulate matter), and (b) carbon monoxide and non-methane volatile organic compounds (and ammonia). The equivalent responses for the other two metrics - AOT60 and the maximum ozone concentration between June and August - can be found in Appendix 1. The same reference year (2000) was used for the meteorology and emission inventories. The OSRM mid-boundary layer concentrations have been converted to surface values.

There are some similarities and some notable differences in the maps:

- **Response to Emission Control**: The OSRM model output gives the same general response to (a) NO_x/SO_x and (b) VOC/CO emission control. The NO_x/SO_x emission control leads to an increase in the three metrics while VOC/CO emission control reduces the values of the three metrics. There appears to be two counteracting effects (a) photochemical production of ozone involving oxides of nitrogen and volatile organic compounds and (b) chemical titration by NO_x removing ozone. These two effects respond differently to emission control. VOC and CO emission reductions lead to an improvement in ozone air quality for all three ozone metrics. NO_x and SO_x emission reductions generally lead to a deterioration in ozone air quality. This can largely be understood in terms of a reduced NO_x titration effect.
- **Strength of Response**: As shown earlier in Figure 3-5, the OSRM tends to overpredict peak ozone concentrations and hence metrics which are more sensitive to elevated concentrations, such as AOT60 and the maximum ozone concentration. The absolute magnitude of the response of AOT40 (Forests) to emission control is very similar in the two models but is significantly larger in the OSRM for the other two metrics.

  In other work undertaken for the Department (Jones and Pye, 2004), the OSRM was used to calculate AOT40 (Crops) to a 10 km x 10 km receptor grid covering the United Kingdom. The map, based on mid-boundary layer ozone concentrations, was combined with UK crop distributions and the response function of the different crops to the AOT40 (Crops) metric to give crop yields. The reductions in crop yields were calculated for a base case and three VOC emission reduction scenarios. A similar set of maps was produced using the interactive IIASA RAINS model[4]. The OSRM response was typically about 60%-80% of the IIASA RAINS model for the VOC emission reduction scenarios considered. The IIASA RAINS model uses ozone source-receptor relationships generated using the earlier EMEP Lagrangian photochemical ozone model. Thus the OSRM response seems to lie between the responses of the EMEP Eulerian and Lagrangian photochemical ozone models.
- **Spatial Patterns**: There are some similarities in the spatial pattern of the response of the two models to emission control (see Figure 3-6 and Figures A2.1 and A2.2 of Appendix 2) and, especially the response of AOT40 (Forests) or the Maximum Ozone concentration to VOC/CO emission control. There appear to be significantly different spatial patterns in the response of the AOT60 metric differences. The AOT40 (Forests) is more sensitive to ozone concentrations slightly above the mean while the maximum ozone concentration will be sensitive to a particular ozone event (and meteorology). The two models appear to show similar behaviour for these two situations. In contrast, the response of the AOT60 metric is very different. For this metric, which is sensitive to ozone concentrations above 60 ppb, the OSRM significantly overpredicts this metric compared to measured values (even allowing for data capture). This could either arise from overestimating the ozone concentrations on those trajectories contributing to the observed AOT60 or a larger number of OSRM trajectories contribute to the modelled AOT60. If the latter is true, it is not surprising that the responses of the two models appear different.

Both models have similar levels of performance and are able to reproduce observed ozone concentrations and metrics. The UNIOZONE modelled mean concentrations agree with the observations and the correlation coefficient is high. For many of the observed high ozone events, the EMEP model tends to underestimate both the maximum and minimum ozone concentration. While the OSRM is generally able to reproduce the observed concentrations and the occurrence of elevated ozone concentrations, the model has a tendency to overpredict the peak ozone concentrations. This will have implications for the calculations of the exceedence metrics such as AOT60.

In the EMEP model, control of VOC and CO emissions leads to a decrease in the values of the three ozone metrics shown. On the other hand, control of SO_x and NO_x emissions, generally, leads to an

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[4] http://www.iiasa.ac.at/web-apps/tap/RainsWeb/

increase in the value of the metrics. The OSRM model output gives the same general response as the EMEP model to (a) NO_x/SO_x and (b) VOC/CO emission control. NO_x/SO_x emission control leads to an increase in the three metrics while VOC/CO emission control reduces the values of the three metrics. As the OSRM tends to overpredict peak ozone concentrations and hence metrics which are more sensitive to elevated concentrations, the OSRM response was generally larger than that of the EMEP Eulerian model. There were some similarities in the spatial pattern of the response of the two models to emission control, for example, the response of AOT40 (Forests) or the Maximum Ozone concentration to VOC/CO emission control. There appeared to be significantly different spatial patterns in the response of the AOT60 metric.

3.4.4 Summary

The output of the OSRM has been compared with three established models – the UK Photochemical Trajectory Model, ADMS Urban and the EMEP UNIOZONE Model. The models are widely used in the regulatory and policy context to assess different emission control options. On a like-for-like basis, the OSRM and UK Photochemical Trajectory Model were found to give identical output and responses. The comparison of the OSRM with the ADMS Urban and the EMEP UNIOZONE models gave similar overall responses, although there were differences, often large, in detail. These comparison demonstrate that the OSRM is a robust model which can be used to assist the development of policy.

3.5 REFERENCES

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4 Detailed Assessment of the Relationship between Ozone, NO and NO_2, and Factors Controlling Them (Objective 2)

4.1 INTRODUCTION

Owing to the chemical coupling of O_3 and NO_X, ambient levels of O_3 and NO_2 are inextricably linked. Consequently, the response to reductions in the emissions of NO_X is highly non-linear [e.g. AQEG, 2003], and any resultant reduction in the level of NO_2 is invariably accompanied by an increase in the level of O_3. It is therefore necessary to have a complete understanding of the relationships between O_3, NO and NO_2 under atmospheric conditions, if the success of proposed control strategies is to be fully assessed.

Data from 66 automatic sites where O_3 and NO_X are monitored in 13 UK zones have previously been analysed to determine whether the description of annual mean concentrations of NO_2, and their dependence on $[NO_X]$, can be improved by the application of empirically-derived relationships between concentrations of O_3, NO_X and NO_2 [Clapp and Jenkin, 2001; Jenkin, 2004]. That analysis made use of annual mean data up to 2001. It was demonstrated that additional insights could be gained by establishing, first, how the concentration of 'oxidant', [OX] (taken to be the sum of $[O_3]$ and $[NO_2]$), varies with the concentration of NO_X and, secondly, how the fractional contribution of NO_2 to OX (i.e., $[NO_2]/[OX]$) varies with $[NO_X]$. In this way, it was possible to rationalise the variation of $[NO_2]$ with $[NO_X]$, and how it varies from one site to another, in terms of sources of OX and well-understood chemical processes. $[NO_2]$ vs. $[NO_X]$ relationships were recommended for 56 urban and suburban sites.

In the present study, the analysis has been extended to the consideration of annual mean data at selected sites in 2002 and 2003. In addition, a comprehensive analysis of 1998 and 1999 hourly mean data has been carried out for Marylebone Rd. This has allowed insights into the seasonal and diurnal dependence of OX sources and their origins, and the conditions under which exceedences of the hourly mean NO_2 limit value (200 $\mu g\ m^{-3}$, 104.5 ppb) are more probable. In conjunction with NO_X emissions estimates, based on traffic flow statistics, the data are used to draw conclusions about the likely fractional contribution of primary NO_2 to NO_X emissions from diesel and petrol-fuelled vehicles.

4.2 THE CHEMICAL COUPLING OF O_3, NO AND NO_2

The interconversion of NO, NO_2 and O_3 under atmospheric conditions is generally dominated by the following reactions:

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

$$NO_2 + h\upsilon\ (+O_2) \rightarrow NO + O_3 \qquad (2)$$

As a result, the behaviour of NO and NO_2 is highly coupled, and it is convenient to refer to them collectively as NO_X. Because this coupling also involves O_3, however, NO_2 and O_3 are also often collectively defined as 'oxidant (OX)' [e.g. Kley et al., 1994]. Reactions (1) and (2) are thus a cycle with no net chemistry, which has the overall effect of partitioning NO_X between its component forms of NO and NO_2, and OX between its component forms of O_3 and NO_2, but leaving the total concentration of both NO_X and OX unchanged. At low levels of NO_X, O_3 is the major component of OX, whereas NO_2 dominates at high levels.

The previous studies [Clapp and Jenkin, 2001; Jenkin, 2004] were able to show that the concentration of OX ($[OX] = [O_3]+[NO_2]$) tends to increase linearly with $[NO_X]$, such that it is made up of two identifiable contributions: a NO_X-independent (or regional) contribution and a NO_X-dependent (or local) contribution. The former equates to the regional background O_3 level, whereas the latter correlates with the level of primary pollution. A significant (sometimes dominant) fraction of this local contribution is likely to result from emission of a fraction of NO_X directly in the form of NO_2. A number of thermal and photochemical sources also potentially contribute, as also discussed by Clapp and Jenkin [2001]. These are all processes which convert NO to NO_2 without associated removal of O_3, and are therefore net sources of OX.

4.3 ANALYSIS OF HOURLY MEAN DATA AT MARYLEBONE RD

4.3.1 Site Characteristics and Methodology

Marylebone Rd is a kerbside site in inner London, located next to a busy (80,000 vehicles per day) six-lane road in a street canyon. The site is characterized by generally high levels of NO_X (e.g., annual mean = 204 ppb in 1999), with NO_2 being by far the dominant form of OX on an annual mean basis, e.g. accounting for 88% in 1999 [Jenkin, 2004]. However, hourly mean concentrations of NO_X throughout the course of a year typically cover a wide range of values. In 1999, this range was 11-1145 ppb, with values at the low end of the range typically occurring overnight in the summer months, and the highest values occurring during daytime in the winter. Accordingly, the partitioning of the OX components also varies substantially. At the low end of the 1999 NO_X range, NO_2 accounted for only ca. 25% of OX whereas, at the high end, OX was essentially exclusively in the form of NO_2. Owing to the influence of NO_2 photolysis by reaction (2), the partitioning also depends on time of day and time of year. Hourly mean NO_X concentrations > ca. 200 ppb are typically required for OX to be >95% in the form of NO_2 during the night, whereas this threshold increases to ca. 350 ppb in the middle of the day, on average. These variations further emphasise the usefulness of the methodology applied here, which quantifies OX sources without the need to consider the chemical partitioning of the component species.

The present study considers hourly mean OX and NO_X data for 1998 and 1999, and focuses on weekdays (excluding national holidays). Data for photochemical episode days, when the regional background OX level is elevated, were also excluded from the analysis. These were defined as days between April and September when the daylight mean concentration of OX exceeded 50 ppb at the comparatively unpolluted urban background AURN site at London Teddington [the method also employed by Clapp and Jenkin, 2001]. The data were subdivided by hour of day and month of year, to allow investigation of diurnal and seasonal effects. Because of local one hour changes between Greenwich Mean Time (GMT) and British Summer Time (BST) on the final weekends in March and October, the small amount of data for relevant weekdays at the ends of these months were analysed as part of the April and November data, respectively. As a result of data inavailability in July 1998, and a significant number of photochemical episode days in July 1999, there are insufficient data for meaningful analysis, and July was therefore not considered.

4.3.2 Diurnal and Seasonal Dependence of Local and Regional OX Contributions

The NO_X-dependence of hourly mean OX concentrations was analysed on a month-by-month basis for data recorded in each hour of the day. Example plots of data for the hours ending at 0600 and 1200 in the months of March and October are shown in Figure 4-1. For each of these months, regression analysis indicates that the slope of the [OX] vs. [NO_X] plot (i.e. the local OX contribution) is significantly greater for the 1200 hr data than for the 0600 hr data, although the intercept (i.e. the regional OX contribution) in each case is comparable. The corresponding full diurnal variations of the local and regional OX contributions are presented for March and October in Figure 4-2, along with the data for August. Although there is some scatter (particularly for the August data), a strong diurnal dependence in the local OX contribution is apparent for all three months, with significantly greater values observed during the daytime. This pattern was clearly observable in the data for every month analysed.

In contrast, the regional contributions show only weak diurnal variations, with slightly higher values generally observed during the daytime in each month. It is also clear that the regional OX varies from month to month, with the October values being notably lower than those in March or August. Accordingly, Figure 4-3 shows the full seasonal dependence of the diurnally-averaged regional OX concentration, which is believed to provide an estimate of the regional O_3 background. Also shown in the figure are data presented by Scheel et al. (1997) for two sites in the EUROTRAC TOR (Tropospheric Ozone Research) network, namely Mace Head (Ireland) and Kollumerwaard (Netherlands). These sites are low altitude sites in northwest Europe, and therefore the most appropriate for comparison with the present data. The seasonally-varying concentrations derived from the present analysis are clearly in good agreement with those reported from the TOR network. The fact that the regional O_3 background concentrations can be retrieved from analysis of data from one of the most polluted UK sites provides strong support for

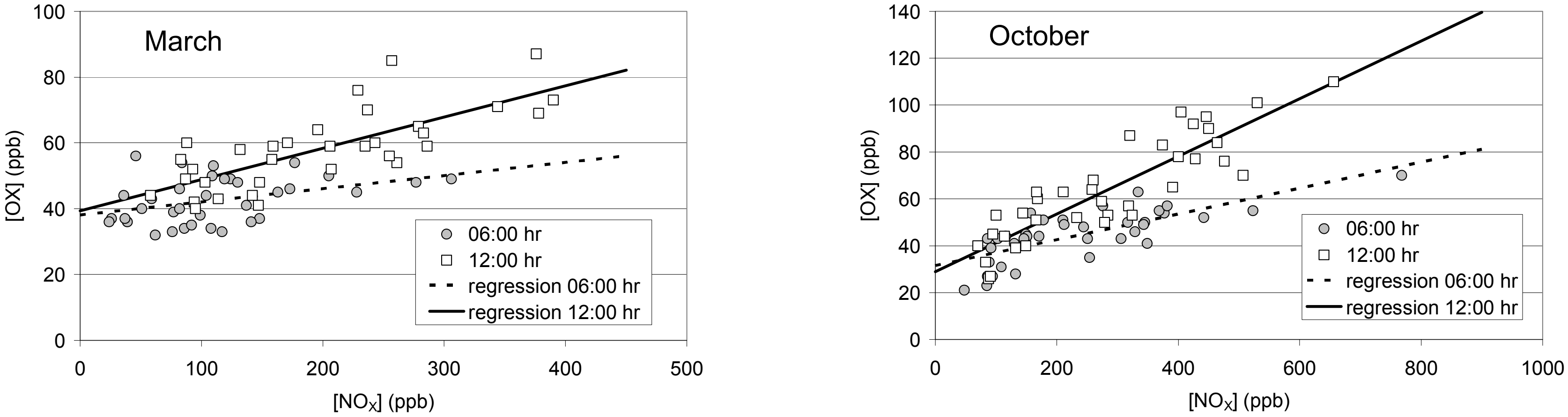

Figure 4-1: The Variation of Hourly Mean [OX] with $[NO_X]$, using Data recorded for the Hours ending 0600 hr and 1200 hr on Weekdays in March and October. Regression Analysis of the March Data yields $[OX] = (0.040 \pm 0.017).[NO_X] + (38.1 \pm 2.2)$, for 0600 hr, and $[OX] = (0.095 \pm 0.015).[NO_X] + (39.3 \pm 3.3)$ for 1200 hr. Regression analysis of the October Data yields $[OX] = (0.055 \pm 0.008).[NO_X] + (31.6 \pm 2.2)$, for 0600 hr, and $[OX] = (0.123 \pm 0.011).[NO_X] + (28.9 \pm 3.7)$ for 1200 hr.

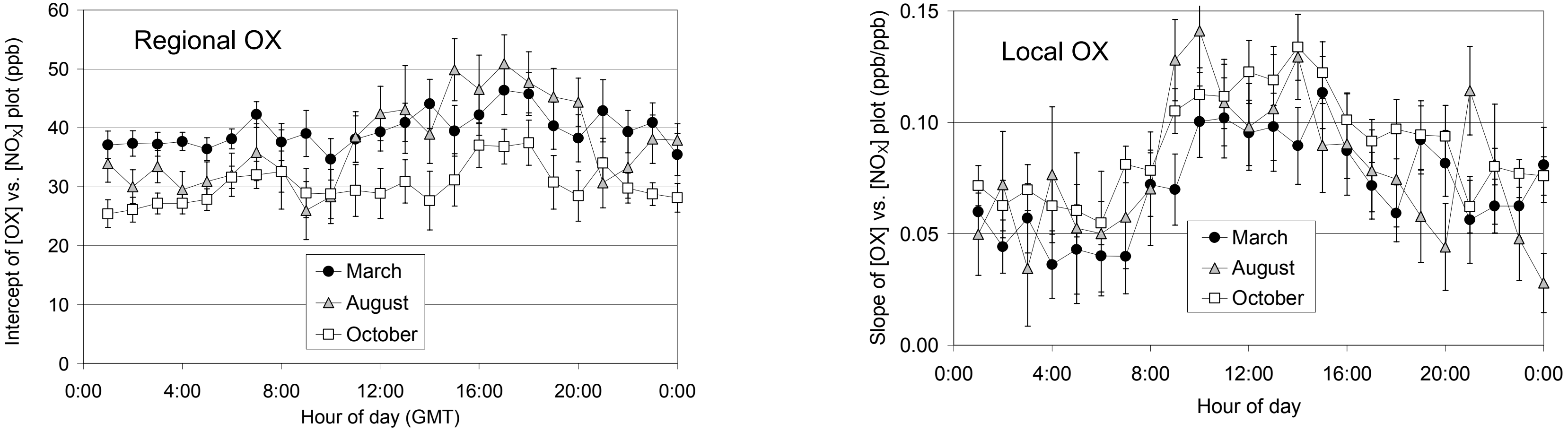

Figure 4-2: The Diurnal Variation of Regional and Local Oxidant Sources in Selected Months, based on Weekday Hourly Mean Data in 1998 and 1999.

employed method of data interpretation, i.e. in terms of regional (NO_X-independent) and local (NO_X-dependent) OX contributions.

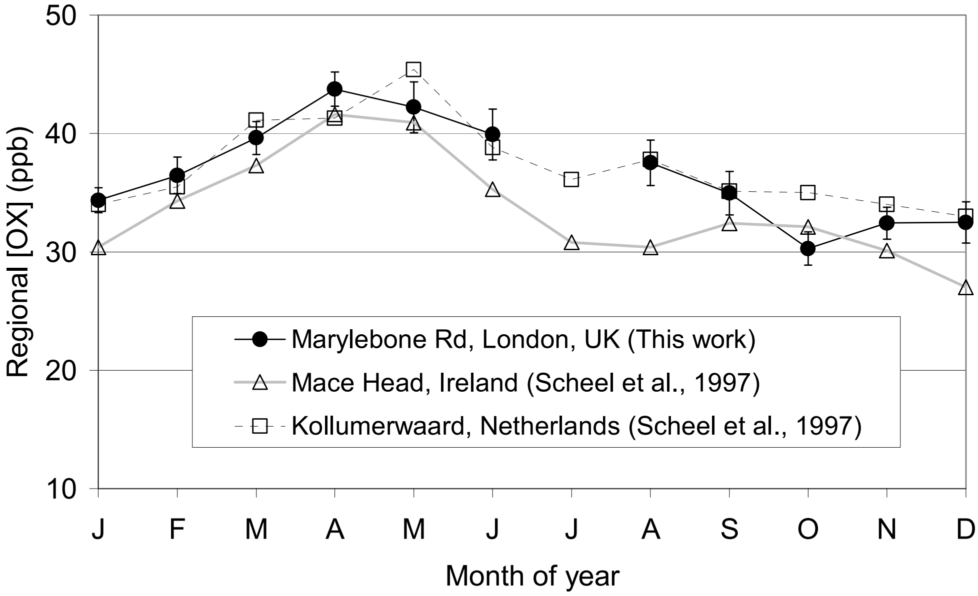

Figure 4-3: Seasonal Variation of Regional [OX] at Marylebone Rd. Also Shown are Data presented by Scheel et al. (1997) for Mace Head, Ireland (based on O_3 in Unpolluted Air Masses), and for Kollumerwaard, Netherlands (based on OX in Unpolluted Air Masses).

The diurnal dependences of the local OX contribution were averaged over the months of the year when GMT and BST operate. The corresponding results, shown in Figure 4-4, are denoted 'winter' and 'summer', respectively. A temporal shift between the winter and summer data is clearly apparent, giving a strong indication that the origin of the diurnal variation is related to road transport emissions, specifically an hour-to-hour variation in the fractional contribution of NO_2 to NO_X emissions. The form of the two profiles is very similar, although there is also some evidence that the winter night-time values are slightly higher than those observed in the summertime. The data were further averaged to give the annual mean diurnal profile in Figure 4-5. This was achieved by applying a shift of one hour to the data for the summer months prior to averaging. The resultant profile is therefore believed to represent the annual mean diurnal variation in the primary NO_2 emissions fraction, based on local hour.

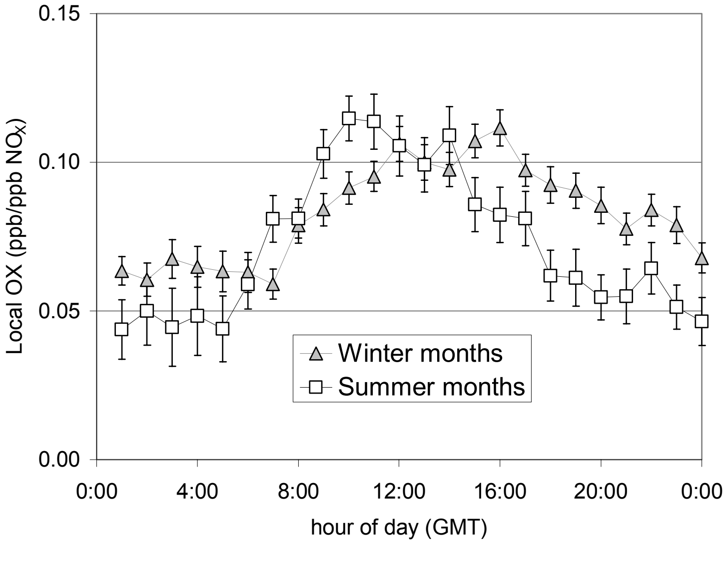

Figure 4-4: The Diurnal Variation of the Local OX, Averaged over Winter and Summer Months. Summer Months are defined as the Period when British Summer Time, BST (i.e. one hour ahead of GMT), operates (see text).

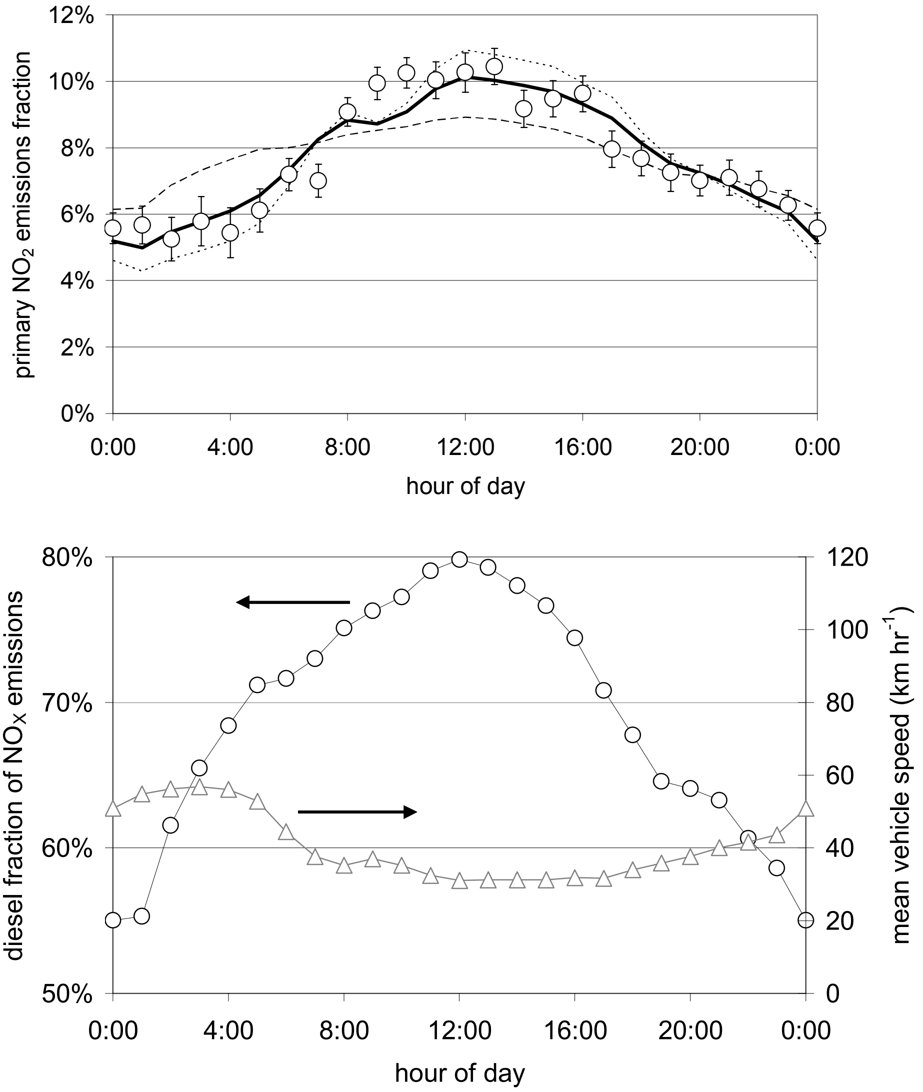

Figure 4-5: Upper Panel - Annual Mean Diurnal Variation of Primary NO_2 emissions, as a Volumetric Fraction of NO_X. Circles are values inferred from the Observed Local OX Contributions: Solid line is the Calculated Variation, based on Equation (i) for Diesel Vehicles. Broken and Dotted Lines are the Calculated Variation, using Speed Exponents of v^0 and v^{-1}, respectively. Lower panel: Annual Mean Diurnal Variation of Hourly Mean Vehicle Speed and Diesel Fractional Contribution to NO_X Emissions, based on Vehicle Flow Data and Emissions Estimates for 1999 reported by Carslaw and Beevers (2004).

4.3.3 Estimation of Primary NO_2 Emissions from Diesel and Petrol Vehicles

The diurnal variation in the primary NO_2 emissions fraction, inferred from the local OX data, is likely to originate from a variation in the vehicle fleet composition and/or driving conditions. Carslaw and Beevers [2004] have recently estimated hourly emissions of NO_X from diesel and petrol vehicles from July 1998 to December 2002, based on automatic and manual traffic flow statistics at Marylebone Rd, and vehicle, fuel and speed-dependent NO_X emission factors recommended by the UK National Atmospheric Emissions Inventory [Goodwin *et al.*, 2001]. On the basis of their data for 1999 [D. Carslaw, personal communication], Figure 4-5 shows the annual mean diurnal dependence of the NO_X emissions fraction which derives from diesel vehicles. The diesel contribution varies over the approximate range 55-80%, maximizing in the middle of the day, with the balance being due to petrol vehicles. Also shown is the diurnal variation of mean vehicle speed, estimated from the automatic traffic flow data. This shows that the mean speed falls from almost 60 km hr^{-1} overnight to around 30 km hr^{-1} during the middle part of the day.

These data give a clear indication that diesel emissions must make an important contribution to the observed primary NO_2, as inferred from the local OX measurements in the present study. The emissions and vehicle speed data were used to calculate diurnal variations in the primary NO_2 emissions fraction, as presented in Figure 4-5 (upper panel). By optimizing the calculated profile to the observed primary NO_2 profile (using residual least squares methodology), it was possible to estimate primary NO_2 emissions fractions for diesel and petrol vehicles. In order to recreate the shape of the diurnal profile, however, it was also necessary to take account of the vehicle speed such that the primary NO_2 fraction decreases at higher speeds, using an assumed function. The best fit to the data was obtained with the assumption that primary NO_2 derives wholly from diesel vehicle emissions, with the NO_2 emissions, as a volumetric fraction of NO_X emissions, being well described by the following equation:

$$\text{Diesel primary } NO_2 \text{ fraction} = 0.996\, v^{-0.6} \qquad \text{(i)}$$

where v is the mean vehicle speed in km hr^{-1}. This indicates that NO_2 accounts for 8.5% of NO_X emissions (by volume) from diesel vehicles travelling at a mean speed of 60 km hr^{-1}, increasing to 12.9% at 30 km hr^{-1}. Although this is a comparatively weak dependence, the profile is sensitive to quite small variations in the vehicle speed exponent, as illustrated in Figure 4-5. Because the representation of the speed dependence employed here has no fundamental basis (and is clearly invalid for stationary traffic), this equation can only be regarded as valid over the mean speed range of the data used to derive it, i.e., 30-60 km hr^{-1}. Allowing for the diurnal variation in the absolute magnitude of the NO_X emissions, the present analysis leads to an integrated diurnal primary NO_2 emission of (11.8 ± 1.2) % of NO_X from diesel-fuelled vehicles at Marylebone Rd, where the uncertainty reflects only the scatter and error in the observed local OX contribution data.

Although the data were best described with the assumption that petrol vehicles emit no primary NO_2, it was possible to get reasonable fits to the observations with primary NO_2 emissions up to about 3% of NO_X, and this upper limit value is therefore suggested on the basis of the present data. At this upper limit value for petrol vehicles, the diesel primary NO_2 fractions optimized simultaneously were about 1% lower than those quoted above.

Table 4-1: Summary of Reported Contributions of NO_2 to NO_X Emissions

Study	NO_X Emission Source	NO_2/NO_X (Volume %)	Comment
Jimenez et al., 2000	Diesel truck	5.6 – 10.9	a
Kurtenbach et al., 2001	Vehicle mix MAN diesel truck Petrol car Diesel car	5.0 11.0 < 0.2 5.9	b,c b,d b,d b,d
Carslaw and Beevers, 2004	Diesel vehicles Petrol vehicles	(12.7 ± 0.1) (0.6 ± 0.2)	e e
This work	Diesel vehicles Petrol vehicles	$99.6\, v^{-0.6}$ (11.8 ± 1.2) < 3	f,g f,h f

a: Operating at ca. 30 km hr^{-1} during mild acceleration. Measurements by TILDAS; b: Kiesbergtunnel, Wuppertal, Germany. Measurements by DOAS; c: traffic mix with ≤ 6% heavy duty trucks, 6% commercial vans, 12.3% diesel cars, 74.7% petrol cars; d: single vehicle experiment, 0-40 km hr^{-1}; e: Marylebone Rd, London, UK. Derived from differential measurements of [OX] compared to local background site and detailed traffic statistics over period 1998-2002; f: Marylebone Rd., London, UK. Derived from [OX] vs [NO_X] dependence using 1998-1999 weekday data, and detailed traffic statistics for 1999; g: for $30 < v/\text{km hr}^{-1} < 60$; h: integrated diurnal contribution.

The present results can be compared with a number of other published estimates of primary NO_2 from diesel and petrol vehicles, as summarized in Table 4-1. These studies all indicate that diesel vehicles have a greater propensity to emit NO_X in the form of NO_2, and reasonably consistent fractional contributions have been reported. In particular, the present results are fully consistent with the diesel and petrol primary emissions fractions reported for Marylebone Rd in the recent study of Carslaw and Beevers [2004]. In addition to the studies summarized in Table 4-1, recent work at the UK Transport Research Laboratory (TRL) has evaluated NO_2 emissions from a small sample of vehicles over a series of legislative and real-world driving cycles, on a chassis dynamometer [Latham *et al.*, 2001; AQEG, 2003]. The results of that study also suggest that diesel engines emit a higher proportion of NO_X as NO_2 than petrol vehicles, and that this proportion tends to increase at lower vehicle speeds.

As a result of the strong diurnal variation in the local OX contribution, it is clear that the level of NO_X required for OX in the form of NO_2 to exceed the hourly mean limit value of 104.5 ppb is likely to vary dramatically with time of day, under typical conditions. In addition to this, the seasonal dependence of the regional background OX concentration will have a less dramatic, but nonetheless important, influence. Figure 4-6 shows estimated hourly mean NO_X thresholds which correspond to 104.5 ppb OX as a function of season and hour of day, based on the results of the present study. At the NO_X concentrations concerned (≥ ca. 600 ppb), OX is almost exclusively in the form of NO_2 such that the displayed thresholds effectively correspond to the level of NO_X required for exceedence of the hourly mean NO_2 limit value. This illustration demonstrates that the lowest NO_X threshold concentrations are likely to occur in the middle of day, with the lowest calculated values of ca. 600 ppb in the spring. The highest values are calculated to occur in the early hours, maximising at over 1400 ppb in October-December. It should be noted, however, that these illustrative figures are based on average driving conditions for the given hour and month. The actual conditions clearly show some variation about the mean, as demonstrated by the scatter in Figure 4-1.

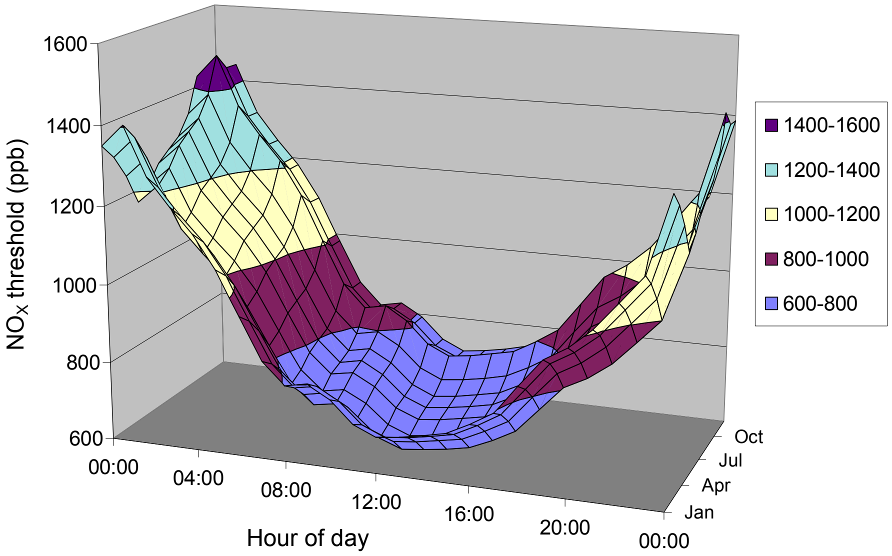

Figure 4-6: Estimated Hourly Mean NO_X Thresholds which correspond to 104.5 ppb OX, based on the Diurnal Local OX contributions in Figure 4-5, and the Seasonal Regional OX concentrations in Figure 4-3 (with the July Value assumed to be the Average of the June and August Values). At these NO_X Concentrations, the Thresholds are an approximation to those required for Exceedence of the Hourly Mean NO_2 Limit Value (104.5 ppb, 200 $\mu g\ m^{-3}$) to occur (see text).

In addition to this, the analysis presented here specifically does not consider summertime photochemical pollution episode conditions. Under these circumstances, elevated regional OX concentrations would lead to an additional lowering of the NO_X levels required for the hourly mean NO_2 limit value to be exceeded.

4.3.4 Conclusions

The present analysis demonstrates that the ambient concentration of OX at Marylebone Rd is sensitive to a number of factors, such as primary NO_2 emissions and regional background O_3 concentrations, and that variation in the magnitudes of these factors leads to substantial diurnal and seasonal differences in the level of NO_X required for the hourly mean NO_2 limit value of 104.5 ppb to be exceeded. The factors which cause these differences at an individual site are also likely to contribute to the site-to-site variations in annual mean NO_X thresholds, discussed in detail in the previously (Jenkin, 2004). However, it is noted that annual mean local OX contributions for a number of urban background and urban centre sites in the companion study (i.e., up to ca. 20%) are significant greater than the vehicular primary NO_2 fractions derived in the present work. This suggests that either the primary NO_2 fractions are elevated by virtue of factors such as traffic congestion, or that the local OX at these sites has additional contributions from local scale chemical processes. As discussed previously by Clapp and Jenkin [2001] and AQEG [2003], a number of thermal and photochemical sources may potentially contribute, through converting NO to NO_2, without associated removal of O_3.

4.4 ANALYSIS OF 2002 AND 2003 ANNUAL MEAN DATA

The previous detailed analysis of the relationships between ambient concentrations of O_3, NO and NO_2, using AURN data up to 2001 (Jenkin, 2004), has been extended to consideration of 2002 and 2003 annual mean data at a series of sites.

Data from a series of urban centre sites (Belfast, Birmingham, Bristol, Cardiff, Edinburgh, Leeds and Southampton) demonstrate that the more recent data are generally well described by the semi-empirical NO_2 vs NO_X expressions derived previously from the data up to 2001 (see examples in Figure 4-7). At many of these sites, the observed annual mean OX concentration in 2003 is slightly elevated (1-2 ppb), this being fully explained by the inter-annual variation in the regional ozone background (e.g. the annual mean ozone concentrations at Strath Vaich in 2002 and 2003 were 34 ppb and 36 ppb, respectively, compared with a mean value of 34.3 ppb over the period 1992-2003).

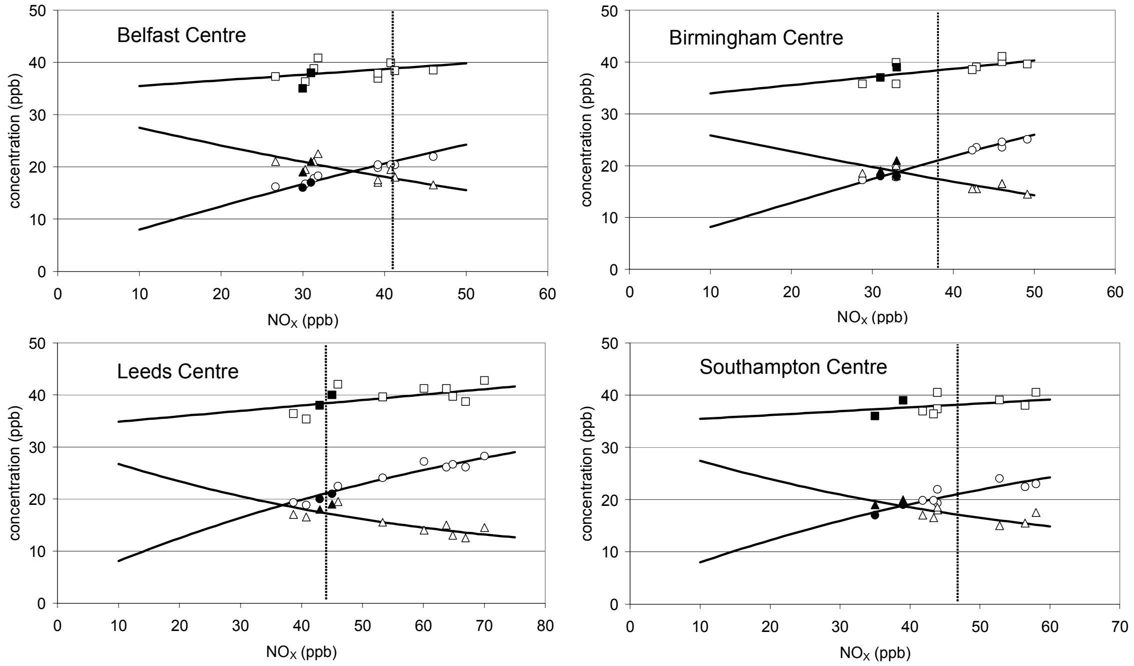

Figure 4-7: Annual Mean Concentration Data for NO_2 (circles) O_3 (triangles) and Oxidant (squares) at Selected Urban Centre Sites. Open Symbols are Data up to 2001: Filled Symbols are Data for 2002 and 2003. Lines are the Predicted Concentration Variations with [NO_X], based on the Semi-empirical Method described by Jenkin (2004), derived from data up to 2001. Vertical lines show the NO_X Concentration which corresponds to 20.9 (40 μg m-3) NO_2.

It is noted that the annual mean concentrations of NO_2 at the above sites are close to or below the limit value (40 μg m^{-3}, 20.9 ppb). Data for the kerbside and roadside sites, Marylebone Rd and Bury Roadside were therefore considered. As shown in Figure 4-8, The 2002 data at these sites are also consistent with the previous expressions. In contrast data from 2003 (and most of 2004) demonstrate a significant discontinuity at both sites, consistent with an abrupt increase in the local oxidant source (i.e. primary NO_2). At Marylebone Rd, the increase is indicative of a change in the primary NO_2 emissions fraction from ca. 10% of emitted NO_X prior to 2003, to ca. 18% in 2003, with the excess oxidant manifested almost entirely in the form of NO_2. Revised estimates of how annual mean [NO_2], [O_3] and [OX] vary with [NO_X], taking account of the inferred increase in primary NO_2, are also shown in Figure 4-8. As a result of this change, the projected NO_X annual mean concentration threshold corresponding to the annual mean limit value for NO_2 has decreased by nearly 20%, from ca. 44 ppb to ca. 36 ppb. The 2004 data suggest that the local oxidant contribution may be slightly higher again (ca. 20%), possibly indicative of a trend of increasing primary NO_2 emissions.

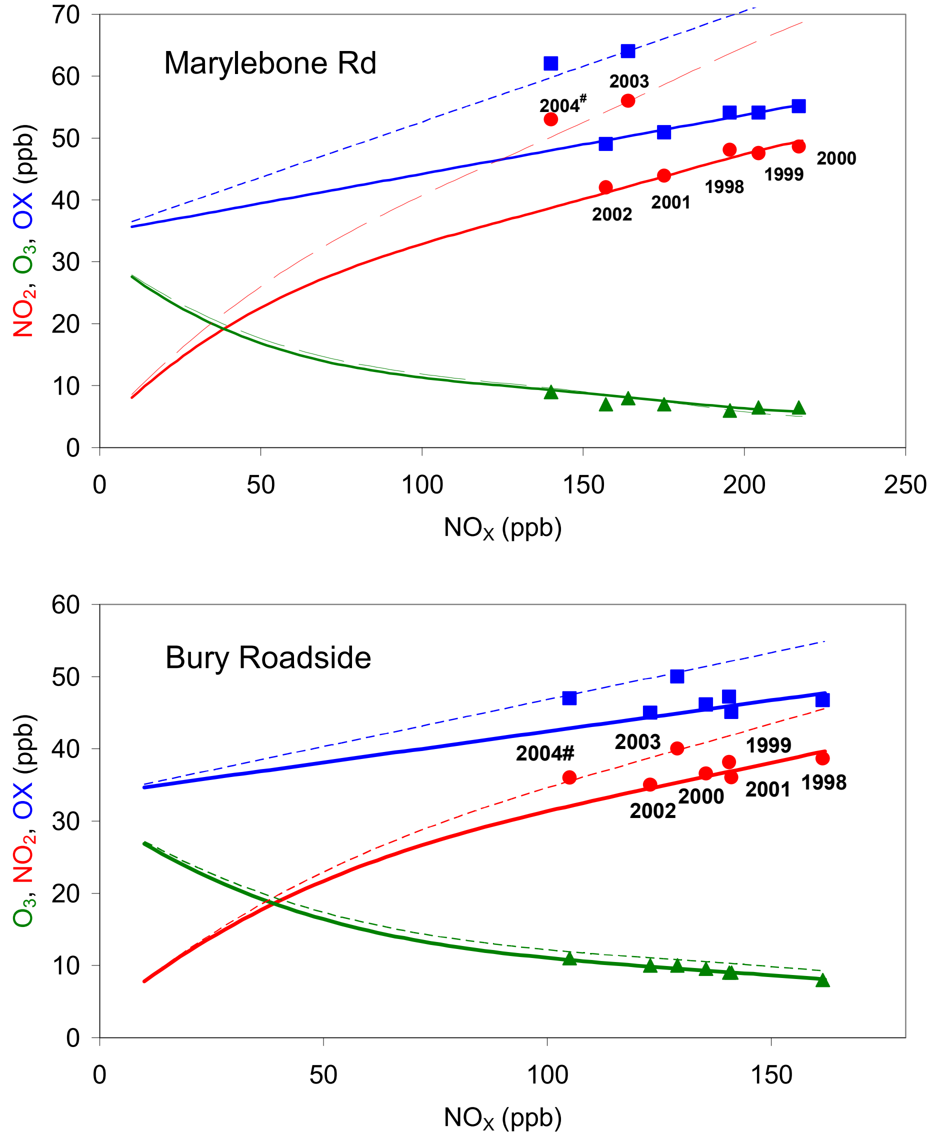

Figure 4-8: Annual Mean Concentration Data for NO_2, O_3 and Oxidant at Marylebone Rd and Bury Roadside (2004# represents mean of data up to 23 November 2004). Full lines are the Predicted Concentration Variations with [NO_X], based on the Semi-empirical Method described by Jenkin (2004). Broken lines are Revised Dependences allowing for Increased Primary NO_2 Emissions (see text).

At Bury Roadside, the data indicate a change in the primary NO_2 emissions fraction from ca. 9% of emitted NO_X prior to 2003, to ca. 13% in 2003 and 2004, with the excess oxidant once again manifested in the form of NO_2. As a result of this change, the projected NO_X annual mean concentration threshold corresponding to the annual mean limit value for NO_2 has decreased by about 7%, from ca. 47 ppb to ca. 44 ppb.

The data thus provide clear evidence that the fraction of NO_X emitted as NO_2 has increased significantly from the road vehicle fleets at these locations. At Marylebone Rd, a number of factors may contribute to the observed effect, although further work is required to establish the exact cause. For example, the introduction of central London congestion charging in early 2003 was accompanied by an increase in the number of buses on routes running on Marylebone Rd (D. Carslaw, personal communication), and possibly by greater congestion resulting from Marylebone Rd lying on the perimeter of the zone. Based on the diurnal dependence results presented above in section 1.3, both effects would be expected to increase the local oxidant source. In addition, the buses are being fitted with oxidising particulate traps [D. Carslaw, personal communication], which potentially result in substantially increased primary NO_2 emissions [AQEG, 2003].

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5 Policy Development and Scenario Analysis (Objective 3a) and Ozone Daughter Directive (Objective 3b)

5.1 INTRODUCTION

In this section of the report, the available modelling tools – the UK Photochemical Trajectory Model (UK PTM) and Ozone Source-receptor Model (OSRM) – have been used to assess a number of policy options relating to ozone (Section 5.2). In Section 5.3, initial results are presented on the use of the OSRM as a supplementary assessment technique for the 3rd Daughter Directive on Ozone.

5.2 POLICY DEVELOPMENT AND SCENARIO ANALYSIS

During the reporting period, the UK PTM was used to investigate the additional NO_x and VOC emission control which would be needed to achieve Ozone air quality standards and objectives beyond that agreed in the EU National Emission Ceilings Directive and the UN ECE Gothenburg Protocol. The Ozone Source-receptor Model (OSRM) was used to assess a number of policy options relating to ozone.

(v) **Regulatory Impact Assessment of Directive on Decorative Paints**: The European Commission has proposed a Directive to reduce the VOC content of decorative paints, varnishes and vehicle refinishing products. There is a requirement to calculate the benefits to the UK of reductions in VOCs arising from within UK, and in UK + rest of Europe. The Commission have calculated potential emission reductions that would arise from the proposed controls in 2010.

(vi) **Proposed NO_x Emission Standards for Vehicles (EURO V Standards)**: The European Commission are expected to propose new emission standards for vehicles in 2004. The Department and the Department for Transport wish for information on the air quality implications of various scenarios to inform the UK position. Although the main focus to date has been on NO_2 and PM exposure, there is a need to assess the effects on ozone concentrations and hence human exposure.

(vii) **Regulatory Impact Assessment of Directive on Petrol Vapour Recovery:** OSRM modelling calculations have been undertaken as part of the regulatory impact assessment on petrol vapour recovery (PVR) and possible derogations.

(viii) **Post-Gothenburg Scenarios:** Assuming full compliance with the UN ECE Gothenburg Protocol and the EU National Emissions Ceilings Directive, the Department is interested the effectiveness of different controls on NO_x and/or VOC emissions to improve ozone air quality after 2010. Four model runs were undertaken with across-the-board reductions in the emissions of NO_x and/or VOC of 30%.

(ix) **Review of the Air Quality Strategy:** The OSRM was used to investigate the impacts on ozone of a number of measures being considered as part of the Review of the Air Quality Strategy. Model runs were undertaken to 41 UK receptors sites in urban and rural locations.

The initial results of the first two policy options were reported in the First Annual project report. Further analysis was undertaken which is included in this report.

The UK PTM calculations are reported in Section 5.2.1 and the OSRM runs outlined above are described in Sections 5.2.2 and 5.2.3.

5.2.1 UK PTM Modelling

Post Gothenburg Emission Control

The UK PTM was set up with the standard trajectory case that starts in Austria and finishes in Wales. This case is meant to represent the worst-case peak episodic conditions of long-range transport into the British Isles. When running using 1999 precursor emissions for the UK and the rest of Europe, the air parcel arrived in Wales with a peak ozone concentration of 85.5 ppb.

The emission conditions were then changed to represent the full implementation of the UN ECE Gothenburg Protocol and the EU National Emissions Ceilings Directive in the year 2010. The peak ozone concentration dropped to 74.2 ppb and these results are shown as ‘GP’ in Figure 5-1. The reduction in ozone exposures is clearly dramatic following the control measures expected through to the year 2010.

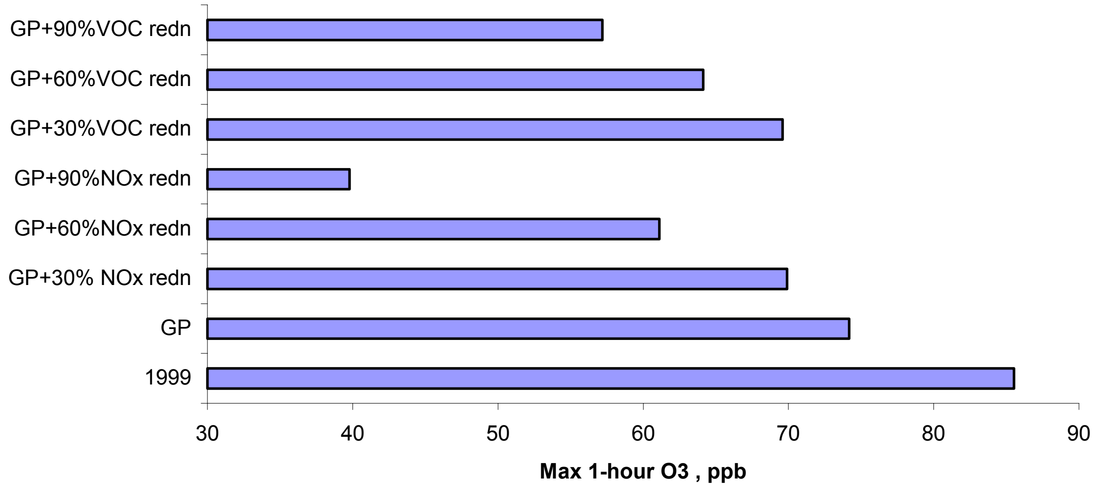


Figure 5-1: The Impact of Various Emission Scenarios on the Peak Ozone Concentrations predicted with the UK PTM for an Arrival Point in Wales.

In a series of model experiments, the impact of further emission controls beyond those envisaged in the UN ECE Gothenburg Protocol and the EU National Emissions Ceilings Directive were examined. Three further stages of emission reductions were considered taking emissions below the 2010 levels by 30%, 60% and 90%. In all cases, these additional percentage reductions were applied across-the-board on all source categories and on all countries. When these further stages were applied to NO_x emissions, peak ozone fell from 74.2 ppb in 2010 to 69.9, 61.1 and 39.8 ppb, respectively. These results are presented in Figure 5-1 as ‘GP+30%NO_x redn’ and so on. When applied to VOC emissions, peak ozone fell to 69.6, 64.1 and 57.2 ppb, respectively, shown as ‘GP+30%VOC redn’ in Figure 5-1.

Looking at the 30% reductions beyond the Gothenburg Protocol, the UK PTM is indicating that the arrival point in Wales is still VOC-limited in 2010, because the ozone benefit (74.2 down to 69.6 ppb) from reducing VOC emissions is larger than the ozone benefit (74.2 down to 69.9 ppb) from reducing NO_x emissions. However, looking at the 60% and 90% reductions, the situation reverses and the ozone benefits from NO_x reductions look substantially greater than those from VOC reductions.

5.2.2 UK-scale Modelling using the OSRM

The OSRM was used to investigate the policy measures or scenario analyses listed below. Details of the OSRM runs are given in Table 5-1. Maps of (a) the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day, (b) the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day which are greater than 35 ppb, (c) the AOT40 for the protection of crops and (d) the annual mean concentration of nitrogen dioxide were generated for each OSRM run.

- **Current Ozone**: Three OSRM model runs were undertaken (see Table 5-1) to simulate the current ozone climatology (1998, 1999 and 2001). The model runs used meteorology and emission inventories for the relevant year.

Table 5-1: Summary of the Meteorology, Emission Inventories and Emission Reductions used in the OSRM Model Runs.

Policy Option/Model Runs	Meteorology	Base UK Inventories	Base EMEP Inventories	Emission Control
Current Year				
- 1998 Base Case	1998	NAEI 1998 (2001)	EMEP 1997	
- 1999 Base Case	1999	NAEI 1999 (2001)	EMEP 1999	
- 2001 Base Case	2001	NAEI 2001 (2001)	EMEP 2001	
RIA: VOC from Paints				VOC Emission Control
- 2010 Base Case	1999	NAEI 2010 (2001)	EMEP 2010	- 2001 NAEI Projections
- 2010 Base Case – UK (30 kt pa)	1999			- NAEI 2001 spatial maps scaled to 2015 by OSRM sector totals; EMEP 2001 spatial map scaled
- 2010 Base Case – EU (278 kt pa)	1999			
- 2010 Base Case – UK (2 kt pa)	1999			
- 2010 Base Case – EU-14 (250 kt pa)	1999			
EURO V NO_x Scenarios				NO_x Emission Control
- 2015 Base Case (Road transport =	1999	NAEI 2015 (2001*)	EMEP 2010	- NAEI Projections revised
- 2015 Best (Road transport =	1999			- NAEI 2001 spatial maps scaled to 2015 by OSRM sector totals; EMEP 2001 spatial map scaled
- 2015 Most Probable (Road transport =	1999			
- 2015 Worse (Road transport =	1999			
RIA: PVR				VOC Emission Control
- 2005 Base Case	1999	NAEI 2005 (2001*)	EMEP 2010	- Point and Area sources for SNAP 5 revised
- 2005 Base Case – PVR1	1999	NAEI 2005 (2001*)		- NAEI 2001 spatial maps scaled to 2015 by OSRM sector totals; EMEP 2001 spatial map scaled
- 2010 Base Case	1999	NAEI 2010 (2001*)		
- 2010 Base Case – PVR2a	1999	NAEI 2010 (2001*)		- Control on petrol stations with throughput > 3000 m^3
- 2010 Base Case – PVR2b	1999	NAEI 2010 (2001*)		- Control on petrol stations with throughput > 3500 m^3
Post-Gothenburg Scenarios				NO_x or VOC Control
- 2010 Base Case – 30% VOC (including natural)	1999	NAEI 2010 (2001*)	EMEP 2010	- 30% across the board reduction (including natural)
- 2010 Base Case – 30% NO_x	1999	NAEI 2010 (2001*)		- 30% across the board reduction
- 2010 Base Case – 30% VOC (excluding natural)	1999	NAEI 2010 (2001*)		- 30% across the board reduction
- 2010 Base Case – 30% VOC and 30% NO_x	1999	NAEI 2010 (2001*)		- 30% across the board reduction

Note: NAEI 1998 (2001) indicates that the spatial distributions used in the model run were based on the 2001 NAEI inventory year and scaled to the 1998 emission totals.

- **Regulatory Impact Assessment of Directive on Decorative Paints**: Work undertaken at netcen for the Regulatory Impact Assessment (RIA) concluded that the effect of the proposed legislation on the VOC content of paints and the emissions from the car-refinishing sector will lead to a further reduction of approximately 2 ktonnes per annum over the current NAEI base case projection for 2010. These are significantly smaller than those proposed by the European Commission [], as much of the reduction identified by the Commission is now included in the base case projection.

  Five OSRM model runs were undertaken (see Table 5-1). The outputs were provided to colleagues at netcen to undertake the Regulatory Impact Assessment. The effects of the emissions reductions on human health (evaluated using the annual mean ozone concentration) and on crops (evaluated using AOT40 for crops) were determined.

  Proposed EURO V Road Transport Emission Standards: The European Commission is expected to propose new emission standards for vehicles in 2004. The Department and the Department for Transport wish for information on the air quality implications of various scenarios to inform the UK position. Although the main focus to date has been on NO_2 and PM exposure, there is a need to assess the effects on ozone concentrations and hence human exposure.

  As the new standards would not take effect until 2010, 2015 was selected for this work as the NO_2 and PM assessments have already been undertaken for this year [Stedman, 2003]. Estimates of the NO_x emissions in 2015 have been developed for a number of possible road transport scenarios [Murrells, 2003]. The base case road transport emissions were projected to be 280.3 ktonne per annum reducing to 248.9, 220.8 and 205.4 ktonne per annum in the worse, most probable and best scenarios, respectively (see Figure 5-2). No assessment has been made to date of the effect of these measures on the emissions of other pollutants. The emissions for CO, SO_2 and VOCs for 2015 were taken from the latest NAEI projections (see NAEI emission projections (December 2003) in Table 5-5). Four OSRM model runs were undertaken (see Table 5-1).

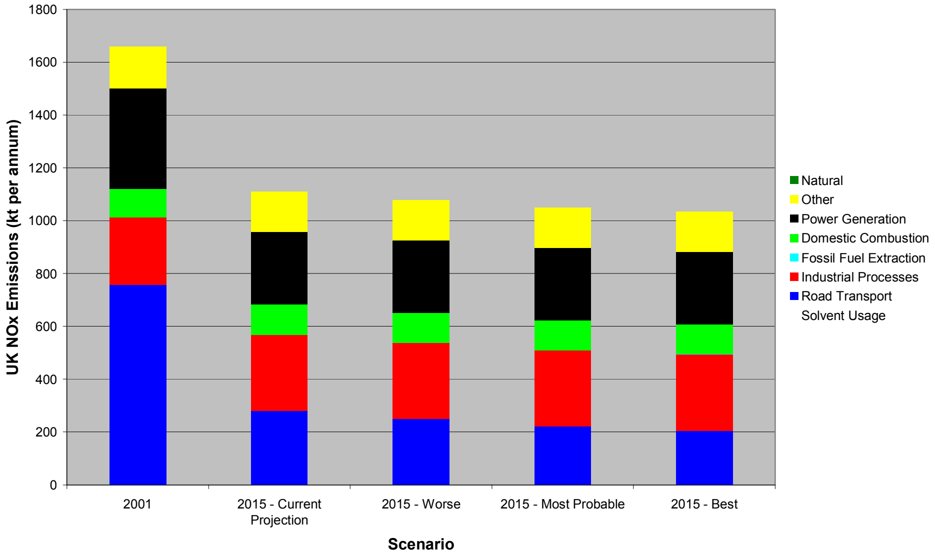


Figure 5-2: Total UK NO_x Emissions and Breakdown by OSRM Source Sector for 2001, 2015 and Possible EURO V Emission Reduction Scenarios.

- **Regulatory Impact Assessment of Directive on Petrol Vapour Recovery:** OSRM modelling calculations were undertaken as part of the regulatory impact assessment on petrol vapour recovery (PVR) and possible derogations:

  1. **PVR I Derogation**: Assessment of the unabated emissions and benefits relating to derogation for service stations with thresholds of >100 m^3 - <500 m^3 petrol throughput per annum in 2005.

2. **PVR II Controls**: Assessment of the costs and benefits of Petrol Vapour Recovery Stage II controls in 2010, using 100% compliance for service stations with thresholds of >3000 m^3 and >3500 m^3 petrol throughput per annum (PVR II).

Information was provided on the location of UK service stations and their throughputs as part of the regulatory impact assessment. The information was used to refine the VOC emissions for the CORINAIR SNAP 5 emission sector on fossil fuel extraction and distribution. The revised 2001 NAEI projections were used for the other pollutants and emission source sectors. The VOC emissions used in the model runs are shown in Table 5-2.

Table 5-2: VOC and NO$_x$ Emissions Used in the Petrol Vapour Recovery Model Runs.

Scenario	VOC Emission From SNAP 5 (kt per annum)	Total UK VOC Emission (kt per annum)	Total UK NOx Emission (kt per annum)
Run 1: 2005 Base Case	273.3	1,282.9	1,452.3
Run 2: with no PVR I derogation	273.1	1,282.8	1,452.3
Run 3: 2010 Base Case	281.3	1,214.1	1,221.5
Run 4: with PVR II control on throughputs > 3,000 m^3	256.9	1,189.8	1,221.5
Run 5: with PVR II control on throughputs > 3,500 m^3	259.0	1,191.9	1,221.5

The outputs were provided to colleagues at netcen to undertake the Regulatory Impact Assessment (RIA 2004). The effects of the emissions reductions on human health (evaluated using the annual mean ozone concentration) and on crops (evaluated using AOT40 for crops) were determined. Work is in progress to repeat the PVR II scenarios using new emission data.

- **Post-Gothenburg Scenarios:** Assuming full compliance with the UN ECE Gothenburg Protocol and the EU National Emissions Ceilings Directive, the Department is interested the effectiveness of different controls on NO$_x$ and/or VOC emissions to improve ozone air quality after 2010. Four model runs were undertaken with across-the-board reductions in the emissions of NO$_x$ and/or VOC of 30%.

The OSRM calculations described above used the meteorology for 1999, as a typical ozone year, to calculate the hourly ozone concentrations at 2,946 10 km x 10 km (or 836 20 km x 20 km) receptor sites covering the UK. Further details (base case emission inventories, emission control scenarios) about the OSRM model runs can be found in the report prepared by Hayman *et al.* [2004b].

Maps of (a) the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day, (b) the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day which are greater than 35 ppb, (c) the AOT40 for the protection of crops and (d) the annual mean concentration of nitrogen dioxide for the base case runs (1999 as a current year, 2005, 2010 and 2015) are shown in Figure 5-3 and Figure 5-4. Apart from the Post-Gothenburg emission scenarios, the other model runs generally show relatively small changes from the related base case run.

To aid the comparison of the different OSRM scenario runs, the population-weighted values have been derived for the

- annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day,
- annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day which are greater than 70 μg m^{-3} (i.e., 35 ppb)
- annual mean concentration of nitrogen dioxide

These population-weighted metrics were calculated for the UK and separately for England, Wales, Scotland and Northern Ireland. As an example, Table 5-3 shows how the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day which are greater than 70 μg m^{-3} responds to the different emission control scenarios.

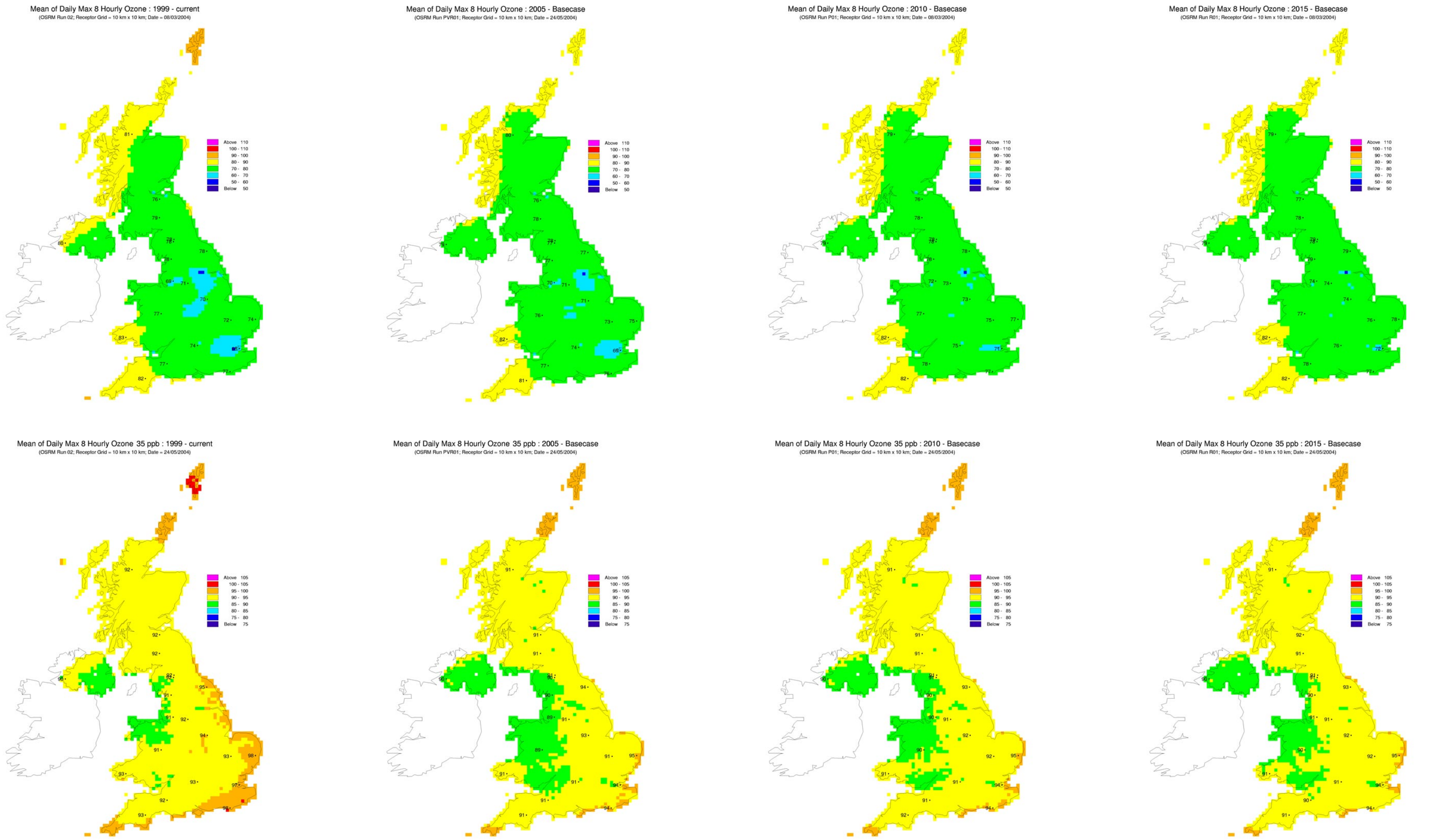


Figure 5-3: Maps of the Annual Mean of the Maximum Daily Running 8-hour Mean Ozone Concentration (upper panels) and the Annual Mean of the Maximum Daily Running 8-hour Mean Ozone Concentrations which are greater then 35 ppb (lower panels) calculated using the Ozone Source-Receptor Model for 1999, 2005, 2010 and 2015.

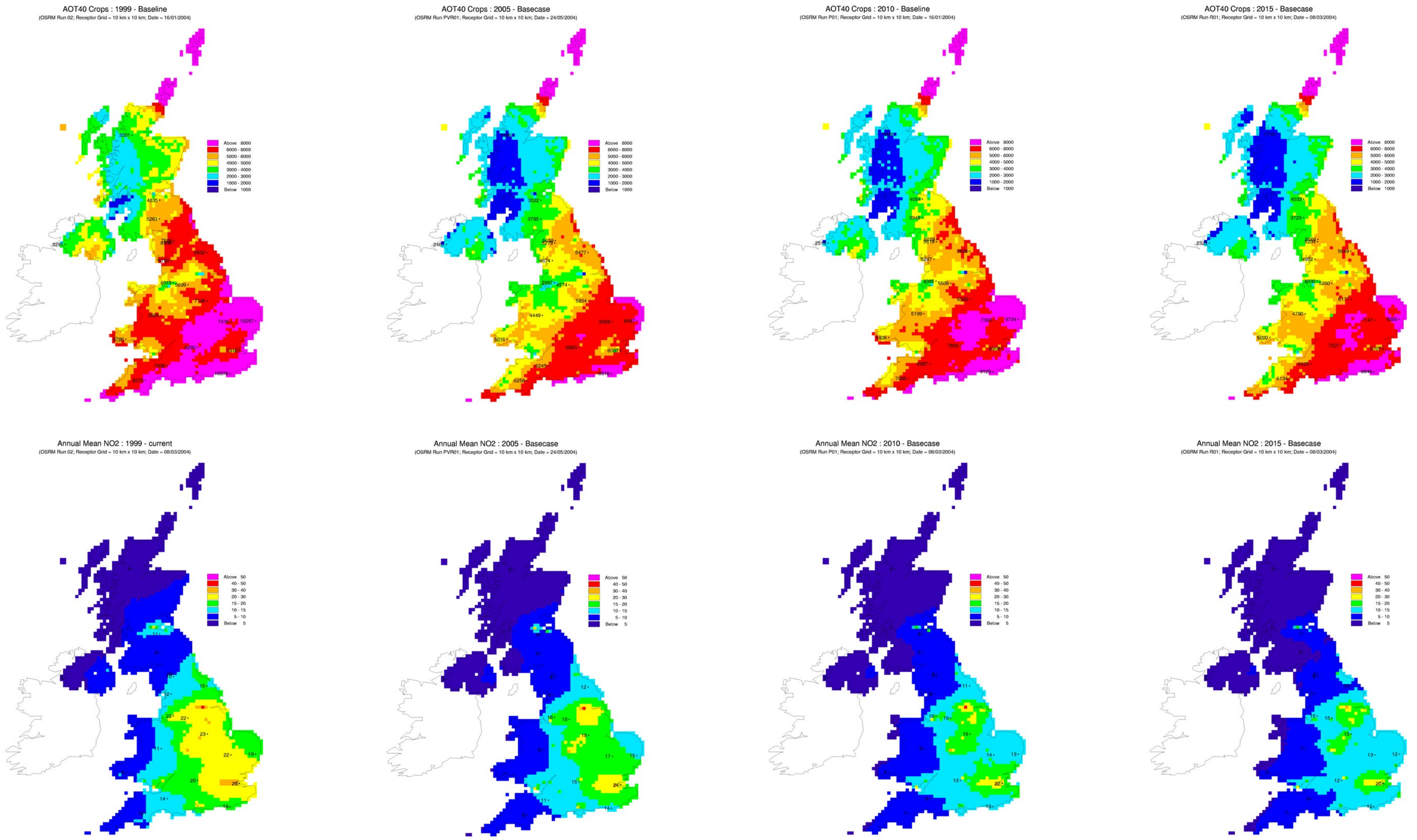


Figure 5-4: Maps of the AOT40 for the Protection of Crops (Upper Panels) and the Annual Mean Nitrogen Dioxide Concentration (Lower Panels) calculated using the Ozone Source-Receptor Model for 1999, 2005, 2010 and 2015.

Table 5-3: Summary of the Population-weighted Annual Mean of the Maximum Daily Running 8-hour Mean Ozone Concentration (in $\mu g\ m^{-3}$ and as Percentage of the 1999 Values) Calculated in the Various OSRM Scenario Runs for the UK, England, Wales, Scotland and Northern Ireland.

Scenario Run	Year	Annual Mean of the Maximum Daily Running 8-hour Mean Ozone Concentrations > 70 $\mu g\ m^{-3}$ (in $\mu g\ m^{-3}$)					Annual Mean of the Maximum Daily Running 8-hour Mean Ozone Concentrations > 70 $\mu g\ m^{-3}$ (as % of 1999 Value)				
		UK	England	Scotland	Wales	Northern Ireland	UK	England	Scotland	Wales	Northern Ireland
Current											
Current	1998	88.1	88.4	86.2	87.5	87.9	94.9%	94.9%	93.7%	96.7%	98.0%
Current	1999	92.8	93.2	92.1	90.4	89.7	100.0%	100.0%	100.0%	100.0%	100.0%
Current	2001	90.2	90.7	86.9	90.5	86.1	97.2%	97.3%	94.3%	100.1%	96.0%
Petrol Vapour Recovery RIA											
Base Case	2005	91.0	91.1	91.1	89.2	89.0	98.0%	97.8%	98.9%	98.6%	99.2%
PVR I - No Derogation	2005	91.0	91.1	91.1	89.2	89.0	98.0%	97.8%	98.9%	98.6%	99.2%
Base Case	2010	91.3	91.5	91.2	89.5	89.1	98.3%	98.2%	99.0%	98.9%	99.3%
PVR IIa (> 3000 m3)	2010	91.2	91.4	91.1	89.5	89.1	98.3%	98.1%	99.0%	98.9%	99.3%
PVR IIb (> 3500 m3)	2010	91.2	91.4	91.1	89.5	89.1	98.3%	98.2%	99.0%	98.9%	99.3%
Decorative Paints RIA											
Base Case	2010	91.2	91.4	91.1	89.5	89.1	98.3%	98.1%	99.0%	98.9%	99.3%
UK VOC Reduction of 30 ktonne pa	2010	91.0	91.2	91.0	89.3	89.0	98.1%	97.9%	98.8%	98.8%	99.1%
EU + UK VOC Reduction of 278 ktonne pa	2010	91.2	91.4	91.1	89.4	89.0	98.2%	98.1%	98.9%	98.9%	99.2%
EU + UK VOC Reduction of 252 ktonne pa	2010	91.1	91.2	91.0	89.4	89.0	98.1%	97.9%	98.8%	98.8%	99.2%
EU VOC Reduction of 250 ktonne pa	2010	91.1	91.2	91.0	89.4	89.0	98.1%	97.9%	98.8%	98.8%	99.2%
Post-Gothenburg Scenarios											
30% VOC Reduction (including natural)	2010	87.7	87.6	88.9	87.6	87.8	94.5%	94.0%	96.6%	96.9%	97.9%
30% NOx Reduction	2010	92.1	92.3	91.7	90.4	89.3	99.2%	99.1%	99.6%	100.0%	99.5%
30% VOC Reduction	2010	89.7	89.8	90.1	88.6	88.4	96.6%	96.4%	97.9%	97.9%	98.5%
30% VOC/ 30% NOx Reduction	2010	90.4	90.5	90.6	89.0	88.5	97.3%	97.1%	98.4%	98.4%	98.6%
EURO V Emission Standards											
Base Case	2015	91.4	91.6	91.3	89.4	89.1	98.5%	98.3%	99.2%	98.9%	99.2%
EURO V – Worse	2015	91.6	91.8	91.4	89.8	89.1	98.7%	98.6%	99.2%	99.3%	99.3%
EURO V – Most Probable	2015	91.7	91.9	91.5	89.9	89.2	98.8%	98.7%	99.4%	99.4%	99.4%
EURO V – Best	2015	91.8	92.0	91.5	90.0	89.2	98.8%	98.7%	99.4%	99.5%	99.4%

A visual comparison of the maps presented in Figure 5-3 and Figure 5-4 indicates that:

- there is a downward trend in the AOT40 for the protection of crops across the UK although there are still large parts of the country which are above the threshold of 3,000 ppb hours (6,000 µg m^{-3} hours);
- annual mean concentrations of nitrogen dioxide fall with the decrease in nitrogen oxide emissions, most noticeably in the Midlands and South-East of England;
- the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day appears to fall at the extremities of the UK but rise in England where the emissions of nitrogen oxides were higher;
- the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day, which are greater than 35 ppb, on the other hand decreases between 1999 and 2005. Thereafter, there is a slight increase.

Discussion

Elevated concentrations of ozone over the UK are generally associated with photochemical production and easterly airflows. This is the situation modelled in the UK PTM with its idealised trajectory from central Europe to the UK. It is expected that reduction of NO_x and/or VOC emissions would be effective in reducing ozone. In an OSRM model run, a calendar year is simulated and a wider range of trajectories is sampled, including those from other wind directions. These other trajectories may have little or no photochemical ozone production, especially if the trajectory has mainly passed over low emission areas (e.g., the sea). One can envisage that there will be a chemical titration of the ozone in such air masses when these air masses pass over NO_x emission sources. This seems to be apparent in the maps of annual mean ozone concentrations where the ozone concentrations are suppressed in regions of high NOx emissions (central and South-East England). As the NO_x emissions are reduced, there will be less titration and hence higher ozone concentrations. This is clearly seen in the increase in the annual mean ozone concentrations.

The total NOx and VOC emissions for the UK and the EMEP model domain used in the OSRM model run for 1999 and the base case runs for 2005, 2010 and 2015 are shown in Table 5-4. The UK emissions are taken from the latest NAEI projections and include the changes to the NO_x road transport emission projections. The EMEP totals assume full compliance with the UN ECE Gothenburg Protocol and EU National Emission Ceilings Directive. For other part of the EMEP model domain, the time series trends are used to estimate these emissions. The totals shown for the EMEP model domain will not necessarily match emission totals contained in EMEP reports.

Table 5-4: The Total NOx and VOC Emissions for the UK and the EMEP Model Domain used in the OSRM for 1999 and the Base Case Runs for 2005, 2010 and 2015.

	1999	2005	2010	2015
UK NO_x Emissions (ktonne pa) % Change on 1999 emissions	1,794.0	1,453.8 -19.0%	1,221.5 -31.9%	1,108.9 -38.2%
UK VOC Emissions (ktonne pa) % Change on 1999 emissions	1,670.9	1,276.5 -23.6%	1,196.6 -28.4%	1,191.3 -28.7%
EMEP NOx Emissions % Change on 1999 emissions	21,559		17,375 -19.4%	
EMEP VOC Emissions % Change on 1999 emissions	18,548		13,998 -24.5%	

Using these emission estimates, the results from the different OSRM model runs, which were presented in Figure 5-3, Figure 5-4 of the base case runs and Table 5-3, suggest that:

- **Trends in Base Case**: The reduction in NO_x emissions between 1999 and 2015 leads to a reduction in NO_2 concentrations by between 30-35% for England and Wales and ~40% for Scotland and Northern Ireland.

  There is a downward trend in the AOT40 for the protection of crops across the UK although there are still large parts of the country, which are above the threshold of 3,000 ppb hours (6,000 mg m-3 hours). The annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day appears to fall at the extremities of the UK but rise in England where the emissions of nitrogen oxides are higher. However, the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day, which are greater than 35 ppb, on the other hand decreases between 1999 and 2005. Thereafter, there is a very slight increase.

- **Emission Reductions**: NO_x emission reductions alone (e.g., the EURO V Emission Standards) lead to lower NO_2 concentrations but to increases in the population-weighted annual mean of the maximum daily running 8-hour ozone concentrations. On the other hand, VOC emission reductions have little or no effect on the annual mean NO_2 concentration but do lead to lower values of the ozone metrics.
- **Post-Gothenburg**: Again, a 30% VOC emission reduction improves ozone air quality but a 30% reduction in NO_x emission reduction leads to poorer ozone air quality. Comparison of the scenario in which NO_x and VOC emissions are each reduced by 30% with separate 30% reduction in NO_x or VOC reductions indicates that the counteracting effects of photochemical production of ozone (by NO_x and VOC emissions) and the titration effect of NO_x emissions.
- **Regional Changes**: Compared to the 1999 model run, the base case runs show an improvement in ozone air quality, as measured by the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day, which are greater than 35 ppb, for each region (England, Wales, Scotland and Northern Ireland). On the other hand, there is a reduction in the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day for Northern Ireland, little change in this metric for Scotland and Wales and a deterioration for England. The annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day will be sensitive to all hours and trajectories, including those where the titration effect is dominant. The annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day will be more sensitive to the higher ozone concentrations, which are more likely to be of a photochemical origin.

Thus, there appears to be two counteracting effects (a) photochemical production of ozone involving oxides of nitrogen and volatile organic compounds and (b) chemical titration by NO_x removing ozone. These two effects respond differently to emission control. Thus, either VOC emission control alone or combined VOC and NO_x emission controls are needed to improve ozone air quality.

5.2.3 OSRM Modelling for the Review of the Air Quality Strategy

The Ozone Source-receptor Model has been used to investigate the impact on ozone and nitrogen dioxide concentrations of various policy measures being considered as part of the Review of the Air Quality Strategy.

Emission Projections

The emission projections of sulphur dioxide, oxides of nitrogen, volatile organic compounds and carbon monoxide for the UK for 2010, 2015 and 2020 were taken from the National Atmospheric Emission Inventory program. Two base case emission projections were used, as shown in Table 5-5:

- **Modified 2001 NAEI Emission Projections** (December 2003): The forecast energy demand was based on energy paper EP68. The main difference with the 2001 NAEI Emission Projections is for the NO_x emissions from road transport, which were updated to include the introduction of variable rates of catalyst failure for EURO I-IV vehicles, lower initial emission factors and reduced emissions from the bus fleet in London.
- **Intermediate NAEI Emission Projections** (June 2004): The forecast energy demand is based on energy paper UEP1, which has led to changes in the emission projections for sulphur dioxide (more coal combustion, assumptions about the compliance of marine vessels), nitrogen oxides (attainment of large combustion plant directive) and volatile organic compounds (new data used in UEP1). The road transport emissions have been changed to reflect the increased penetration of diesel vehicles. VOC emissions from industrial adhesives and gas pipeline leakages have also been modified.

The Intermediate Emissions Projections were used to produce two variant projections to assess the effect of (a) additional measures to reduce NO_x emissions from power stations, refineries, the iron and steel plants and cement kilns (Measures 12, 18, 19 combined) and (b) additional controls on NO_x

Table 5-5: Summary and Breakdown of the NAEI Emission Projections (in ktonne per annum) Used in the OSRM Scenario Runs.

Pollutant OSRM Sector	**NAEI Emission Projection (December 2003)**				**Intermediate NAEI Emission Projection (June 2004)**				**Intermediate Projection + Additional NO$_x$ Measures (June 2004)**			**Intermediate Projection + EURO V/VI Measures (June 2004)**		
Sulphur Dioxide	**2001**	**2010**	**2015**	**2020**	**2001**	**2010**	**2015**	**2020**	**2010**	**2015**	**2020**	**2010**	**2015**	**2020**
Solvent Usage	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Road Transport	3.41	0.79	0.82	0.85	3.41	0.77	0.80	0.83	0.77	0.80	0.83	0.77	0.80	0.83
Industrial Processes	282.83	278.17	276.54	274.10	282.83	243.66	247.47	251.69	243.66	247.47	251.69	243.66	247.47	251.69
Fossil Fuel Extraction and Delivery	0.55	0.61	0.64	0.69	0.55	0.61	0.64	0.69	0.61	0.64	0.69	0.61	0.64	0.69
Domestic Combustion	65.17	33.84	28.80	23.81	65.17	24.29	21.23	19.14	24.29	21.23	19.14	24.29	21.23	19.14
Power Generation	742.89	237.47	175.43	97.46	742.89	280.18	138.14	87.12	280.18	138.14	87.12	280.18	138.14	87.12
Other	31.86	18.95	18.76	19.02	32.40	34.79	32.63	34.09	34.79	32.63	34.09	34.79	32.63	34.09
Natural	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	**1126.72**	**569.82**	**500.99**	**415.93**	**1127.25**	**584.30**	**440.91**	**393.56**	**584.30**	**440.91**	**393.56**	**584.30**	**440.91**	**393.56**
Oxides of Nitrogen	**2001**	**2010**	**2015**	**2020**	**2001**	**2010**	**2015**	**2020**	**2010**	**2015**	**2020**	**2010**	**2015**	**2020**
Solvent Usage	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Road Transport	757.72	376.84	280.33	267.40	760.44	384.37	291.43	279.95	384.37	291.43	279.95	370.40	196.52	119.17
Industrial Processes	255.54	284.27	288.29	292.51	255.54	224.65	229.39	234.66	171.83	174.87	178.76	224.65	229.39	234.66
Fossil Fuel Extraction and Delivery	0.71	0.94	1.00	1.07	0.71	0.94	1.00	1.07	0.94	1.00	1.07	0.94	1.00	1.07
Domestic Combustion	106.71	108.92	113.24	116.25	106.71	106.96	111.84	116.01	106.96	111.84	116.01	106.96	111.84	116.01
Power Generation	379.38	297.66	274.16	223.03	379.38	276.17	257.47	194.92	125.57	116.97	92.82	276.17	257.47	194.92
Other	157.62	152.90	151.82	152.34	170.02	160.02	157.25	163.40	160.02	157.25	163.40	160.02	157.25	163.40
Natural	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	**1657.68**	**1221.53**	**1108.85**	**1052.60**	**1672.80**	**1153.11**	**1048.38**	**990.01**	**949.69**	**853.36**	**832.01**	**1139.14**	**953.47**	**829.23**
VOC	**2001**	**2010**	**2015**	**2020**	**2001**	**2010**	**2015**	**2020**	**2010**	**2015**	**2020**	**2010**	**2015**	**2020**
Solvent Usage	425.31	369.92	370.67	371.40	425.31	341.93	250.03	264.19	341.93	250.03	264.19	341.93	250.03	264.19
Road Transport	251.09	70.87	59.33	60.34	245.18	67.97	55.26	55.33	67.97	55.26	55.33	67.97	55.26	55.33
Industrial Processes	194.60	192.40	192.77	193.10	194.60	179.48	177.19	174.32	179.48	177.19	174.32	179.48	177.19	174.32
Fossil Fuel Extraction and Delivery	284.21	263.67	269.42	278.31	284.00	255.77	269.29	287.59	255.77	269.29	287.59	255.77	269.29	287.59
Domestic Combustion	41.96	25.19	25.07	25.45	41.96	25.17	24.93	25.23	25.17	24.93	25.23	25.17	24.93	25.23
Power Generation	8.50	8.87	10.04	11.24	8.50	9.88	10.49	12.05	9.88	10.49	12.05	9.88	10.49	12.05
Other	83.85	87.62	85.94	87.81	83.85	84.85	86.31	88.39	84.85	86.31	88.39	84.85	86.31	88.39
Natural	178.00	178.00	178.00	178.00	178.00	178.00	178.00	178.00	178.00	178.00	178.00	178.00	178.00	178.00
Total	**1467.53**	**1196.55**	**1191.25**	**1205.66**	**1461.40**	**1143.05**	**1051.50**	**1085.10**	**1143.05**	**1051.50**	**1085.10**	**1143.05**	**1051.50**	**1085.10**
CO	**2001**	**2010**	**2015**	**2020**	**2001**	**2010**	**2015**	**2020**	**2010**	**2015**	**2020**	**2010**	**2015**	**2020**
Solvent Usage	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Road Transport	2182.21	640.49	475.33	471.92	2183.00	628.20	466.50	462.90	628.20	466.50	462.90	628.20	466.50	462.90
Industrial Processes	665.54	579.70	591.34	602.88	659.98	631.34	628.82	627.10	631.34	628.82	627.10	631.34	628.82	627.10
Fossil Fuel Extraction and Delivery	0.51	1.38	1.47	1.57	0.51	1.38	1.47	1.57	1.38	1.47	1.57	1.38	1.47	1.57
Domestic Combustion	255.94	192.46	200.35	213.10	246.52	181.16	187.91	199.28	181.16	187.91	199.28	181.16	187.91	199.28
Power Generation	71.78	57.30	54.86	46.54	71.65	62.78	59.64	48.74	62.78	59.64	48.74	62.78	59.64	48.74
Other	439.75	450.71	452.15	454.12	503.09	483.50	478.43	485.04	483.50	478.43	485.04	483.50	478.43	485.04
Natural	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	**3615.74**	**1922.05**	**1775.51**	**1790.14**	**3664.75**	**1988.36**	**1822.77**	**1824.63**	**1988.36**	**1822.77**	**1824.63**	**1988.36**	**1822.77**	**1824.63**

emissions from motor vehicles (EURO V/VI standards, Scenario G). Emission inventories were also produced for these two variant projections for the years 2010, 2015 and 2020. These variant emission projections are also included in Table 5-5.

Emission inventories for other countries and sources on the EMEP model domain were taken from EMEP for the relevant current year. Following previous discussions with the Department, the model runs for 2010, 2015 and 2020 used the same 2010 emission inventories for the European domain. The inventories for 2010 have been prepared by scaling the current country spatial distribution by the ratio of the 2010 country emission total to the current country emission total. The emission totals assume full compliance with the EU National Emission Ceilings Directive or the UN ECE Gothenburg Protocol.

OSRM Model Runs

OSRM model runs were undertaken to 41 receptor sites, comprising UK ozone monitoring sites in rural and urban locations, using the meteorology for 1999, as a typical ozone year.

Although the OSRM post-processor derives a range of metrics from the calculated hourly ozone and nitrogen dioxide concentrations, the subsequent discussion will focus on (a) the new health-based ozone metric – the annual mean of the maximum of the 24 possible 8-hour running mean concentrations in each day with and without a cut off of 35 ppb (or 70 mg m^{-3}), (b) the number of days when the maximum of the 24 possible 8-hour running mean concentrations in each day exceeds 100 µg m^{-3} (metric used in the UK Air Quality Strategy), (c) AOT40 (Crops) and (d) the annual mean NO_2 concentration.

Further details about the model runs and the results obtained can be found in the report submitted to Defra [Hayman, Abbott and Thomson, 2004].

OSRM Model Results

For ease, the OSRM model runs were considered under the following headings:

- **Comparison of the Modified 2001 NAEI and the Intermediate Emission Projections**: There are significant differences between the emissions in these projections, resulting from different assumptions made on energy demand and on transport. The modified 2001 NAEI emission projections have higher NO_x and VOC emissions for 2010, 2015 and 2002 compared to the intermediate projections (see Table 5-5). Previous scenario analysis using the OSRM [see previous Section 5.2.2) would suggest that the higher VOC emissions would lead to higher values of the ozone metrics but that this would be offset by the greater titration effect of the higher NO_x emissions.

  For both projections, there is a decline in the nitrogen oxide emissions and this results in a reduction in the annual mean nitrogen dioxide concentration, as shown in Table 5-6. The annual mean nitrogen dioxide concentrations show the expected pattern with the highest concentrations observed for the London sites and the lowest concentrations in rural areas. The picture is more complex for the ozone metrics, which show an initial decline between 1999 and 2010 and an increase between 2010/2015 and 2020 for both projections. The strength of the response is different at the UK-rural, UK-urban and London sites. While the pattern of the ozone metrics generally follows expectations (i.e., rural values are higher than urban values), there are some apparent inconsistencies (e.g., the AOT40 Crops for London). This may be a result of the model performance, in which the London values are overestimated, or because the London sites are tightly clustered in the South East whereas the UK-rural and UK-urban sites cover a wider spatial range of ozone climatologies (i.e., the sites are distributed across England, Scotland, Northern Ireland and Wales).

- **Effect of Additional NO_x Measures (Measures 12, 18 and 19)**: In this set of model runs, additional measures (Measures 12, 18, 19 combined) have been implemented to reduce NO_x emissions from power stations, refineries, the iron and steel plants and cement kilns. The lower total NO_x emissions in these model runs (using the Intermediate emission projections with additional NO_x measures) leads to lower annual mean nitrogen dioxide concentrations compared to the corresponding Intermediate emission projection base case (see Table 5-6). As observed in the other model runs, reducing NO_x emissions alone leads to varying increases in the ozone

Table 5-6: The Effect of Different UK NO_x and VOC Emissions on Selected Ozone and Nitrogen Dioxide Metrics, as Calculated by the Ozone Source Receptor Model.

Annual Mean of the Daily Maximum of the 24 Daily Running 8-hour Mean Ozone Concentrations (in µg m^{-3})

Scenario	UK-Rural Current	UK-Rural 2010	UK-Rural 2015	UK-Rural 2020	UK-Urban Current	UK-Urban 2010	UK-Urban 2015	UK-Urban 2020	London Current	London 2010	London 2015	London 2020
1999 (Modified 2001 Projections)	67.3	-	-	-	59.4	-	-	-	53.0	-	-	-
2001 (Modified 2001 Projections)	61.2	-	-	-	53.5	-	-	-	50.1	-	-	-
2001 (Intermediate Projections)	61.1	-	-	-	53.3	-	-	-	50.0	-	-	-
Base case (Modified 2001 Projections)	-	68.6	69.3	69.7	-	62.7	63.9	64.5	-	60.8	63.2	63.7
Base case (Intermediate Projections)	-	68.9	69.4	69.8	-	63.4	64.3	65.0	-	60.9	62.9	63.4
Base case (Int + Add. NOx Measures)	-	70.3	70.7	70.9	-	65.7	66.6	66.9	-	62.0	64.0	64.3
Base case (Int + EURO V/VI Scenario G)	-	69.0	70.1	71.0	-	63.5	65.4	66.8	-	61.3	65.5	67.9

Annual Mean (in µg m^{-3}) of those Daily Maximum of the 24 Daily Running 8-hour Mean Ozone Concentrations > 70 ug m-3 (i.e. 35 ppb)

Scenario	UK-Rural Current	UK-Rural 2010	UK-Rural 2015	UK-Rural 2020	UK-Urban Current	UK-Urban 2010	UK-Urban 2015	UK-Urban 2020	London Current	London 2010	London 2015	London 2020
1999 (Modified 2001 Projections)	91.0	-	-	-	89.3	-	-	-	91.9	-	-	-
2001 (Modified 2001 Projections)	88.2	-	-	-	87.6	-	-	-	96.7	-	-	-
2001 (Intermediate Projections)	88.2	-	-	-	87.5	-	-	-	96.6	-	-	-
Base case (Modified 2001 Projections)	-	88.8	88.9	88.9	-	87.4	87.4	87.6	-	88.8	89.3	89.3
Base case (Intermediate Projections)	-	88.8	88.8	88.9	-	87.4	87.3	87.5	-	88.9	89.1	89.2
Base case (Int + Add. NOx Measures)	-	89.1	89.0	89.1	-	88.0	88.0	88.2	-	89.0	89.2	89.2
Base case (Int + EURO V/VI Scenario G)	-	88.8	88.8	89.0	-	87.4	87.5	87.9	-	89.1	89.5	89.6

AOT40 Crops (in µg m^{-3} hours)

Scenario	UK-Rural Current	UK-Rural 2010	UK-Rural 2015	UK-Rural 2020	UK-Urban Current	UK-Urban 2010	UK-Urban 2015	UK-Urban 2020	London Current	London 2010	London 2015	London 2020
1999 (Modified 2001 Projections)	3051.2	-	-	-	1968.1	-	-	-	2359.0	-	-	-
2001 (Modified 2001 Projections)	3380.8	-	-	-	2612.8	-	-	-	2876.3	-	-	-
2001 (Intermediate Projections)	3349.6	-	-	-	2575.2	-	-	-	2837.2	-	-	-
Base case (Modified 2001 Projections)	-	2522.1	2649.7	2734.6	-	1822.7	1992.3	2091.2	-	2800.7	3292.5	3429.5
Base case (Intermediate Projections)	-	2548.6	2582.7	2681.1	-	1880.6	1960.5	2076.5	-	2796.5	3103.4	3243.3
Base case (Int + Add. NOx Measures)	-	2796.8	2816.4	2881.8	-	2206.9	2274.2	2344.1	-	3049.7	3342.2	3448.8
Base case (Int + EURO V/VI Scenario G)	-	2569.0	2704.4	2890.1	-	1906.7	2121.9	2352.5	-	2869.2	3649.6	4225.6

Annual Mean NO_2 Concentration (in µg m^{-3} hours)

Scenario	UK-Rural Current	UK-Rural 2010	UK-Rural 2015	UK-Rural 2020	UK-Urban Current	UK-Urban 2010	UK-Urban 2015	UK-Urban 2020	London Current	London 2010	London 2015	London 2020
1999 (Modified 2001 Projections)	17.0	-	-	-	26.7	-	-	-	36.5	-	-	-
2001 (Modified 2001 Projections)	17.1	-	-	-	26.4	-	-	-	32.9	-	-	-
2001 (Intermediate Projections)	17.2	-	-	-	26.5	-	-	-	33.1	-	-	-
Base case (Modified 2001 Projections)	-	12.0	11.1	10.6	-	19.5	18.1	17.4	-	22.3	19.5	19.0
Base case (Intermediate Projections)	-	11.5	10.7	10.2	-	18.5	17.2	16.4	-	22.0	19.4	18.9
Base case (Int + Add. NOx Measures)	-	9.8	9.1	8.9	-	15.6	14.4	14.1	-	21.0	18.3	18.0
Base case (Int + EURO V/VI Scenario G)	-	11.4	10.0	8.9	-	18.3	16.0	14.3	-	21.6	16.6	14.0

metrics, with the smallest relative increases between 2010 and 2020 seen in the metrics which are sensitive to peak ozone concentrations (such as the Annual Mean of the Daily Maximum of the 24 Daily Running 8-hour Mean Ozone Concentrations or the Annual Mean of those Daily Maximum of the 24 Daily Running 8-hour Mean Ozone Concentrations > 70 $\mu g\ m^{-3}$).

- **Effect of EURO V/VI Emission Controls**: In this set of model runs, additional controls on vehicle exhaust emissions have been implemented to reduce NO_x emissions (EURO V/VI Scenario G). The lower total NO_x emissions in the model runs using the Intermediate emission projections with additional NO_x controls on road transport emissions leads to lower annual mean nitrogen dioxide concentrations compared to the corresponding Intermediate emission projection base case (see Table 5-6). Again, as observed in the other model runs, reducing NO_x emissions alone leads to an increase in the ozone metrics between 2010 and 2020. Although the overall level of emission reduction in 2020 is comparable between the two NO_x control scenarios (Additional NO_x Measures and EURO V/VI Emission Controls), there are differences in the spatial distribution of the emissions. The results suggest that there is a proportionately greater reduction in the NO_x emissions in London for the EURO V/VI, hence the larger changes seen in the ozone and nitrogen dioxide metrics for the London sites. There is however less difference, certainly for the metrics sensitive to peak ozone concentrations, for the UK-urban and UK-rural sites.
- **Effect of Measure 21 (Across-the-Board reductions in VOC Emissions)**: The effect of 10% and 30% across-the-board reductions in VOC emissions in (a) the UK and (b) the UK and EMEP region was investigated for the years 2010, 2015 and 2020. Figure 5-5 shows the impact of these four different across-the-board reductions in UK and European VOC Emissions in 2015 for the 5 ozone and nitrogen dioxide metrics of interest for the Intermediate emission projections. The same general trend is observed for the other emission projections and years considered.

  The annual mean nitrogen dioxide concentration is virtually unaffected by the VOC emission reductions. There is a progressive improvement in all four ozone metrics as the VOC emissions are reduced from the base case (i.e., no reduction) to a 10% reduction in UK emissions through to a 30% reduction in UK and EMEP emissions (i.e., the largest emission reduction) for UK-rural, UK-urban and London sites. For a given year, the annual mean nitrogen dioxide concentration is virtually unaffected by the VOC emission reductions. There is a progressive improvement in all four ozone metrics as the VOC emissions are reduced from the base case (i.e., no reduction) to a 10% reduction in UK emissions through to a 30% reduction in UK and EMEP emissions (i.e., the largest emission reduction) for UK-rural, UK-urban and London sites.

  The response to a 10% reduction in UK VOC emissions is approximately half of that resulting from a 10% reduction in UK and EMEP emissions, implying that emission reductions in the UK or EMEP would be equally effective in improving ozone air quality. The responses to a 30% reduction in the UK or EMEP VOC emissions suggest that reductions in European emissions would be more effective in improving ozone air quality.

In summary, the OSRM model runs have shown that VOC emission reductions alone (e.g., the across-the-board reductions in Measure 21) lead to an improvement in ozone air quality for all the ozone metrics calculated by the OSRM post-processor. NO_x emission reduction scenarios alone (e.g., comparison of the Intermediate projection against the Intermediate projection and Additional NO_x Measures or EURO V/VI Controls) generally lead to a deterioration in ozone air quality. This can largely be understood in terms of a reduced NO_x titration effect. The combination of lower NO_x and VOC emission reductions (e.g., change of base case year) gives a more complex response. Lower VOC emissions lead to lower values of the ozone metrics but this is offset by the reduced titration effect of the lower NO_x emissions, leading to higher ozone concentrations and values of the ozone metrics.

The OSRM scenario model runs described above have neglected the effects of the year-to-year variability in meteorology and the changing atmospheric composition arising from climate change and the global circulation. Some indication of the sensitivity to the year-to-year variability in meteorology can be found in the OSRM model runs undertaken for 2 current years (1999 and 2001), although the emissions were also changed in these runs.

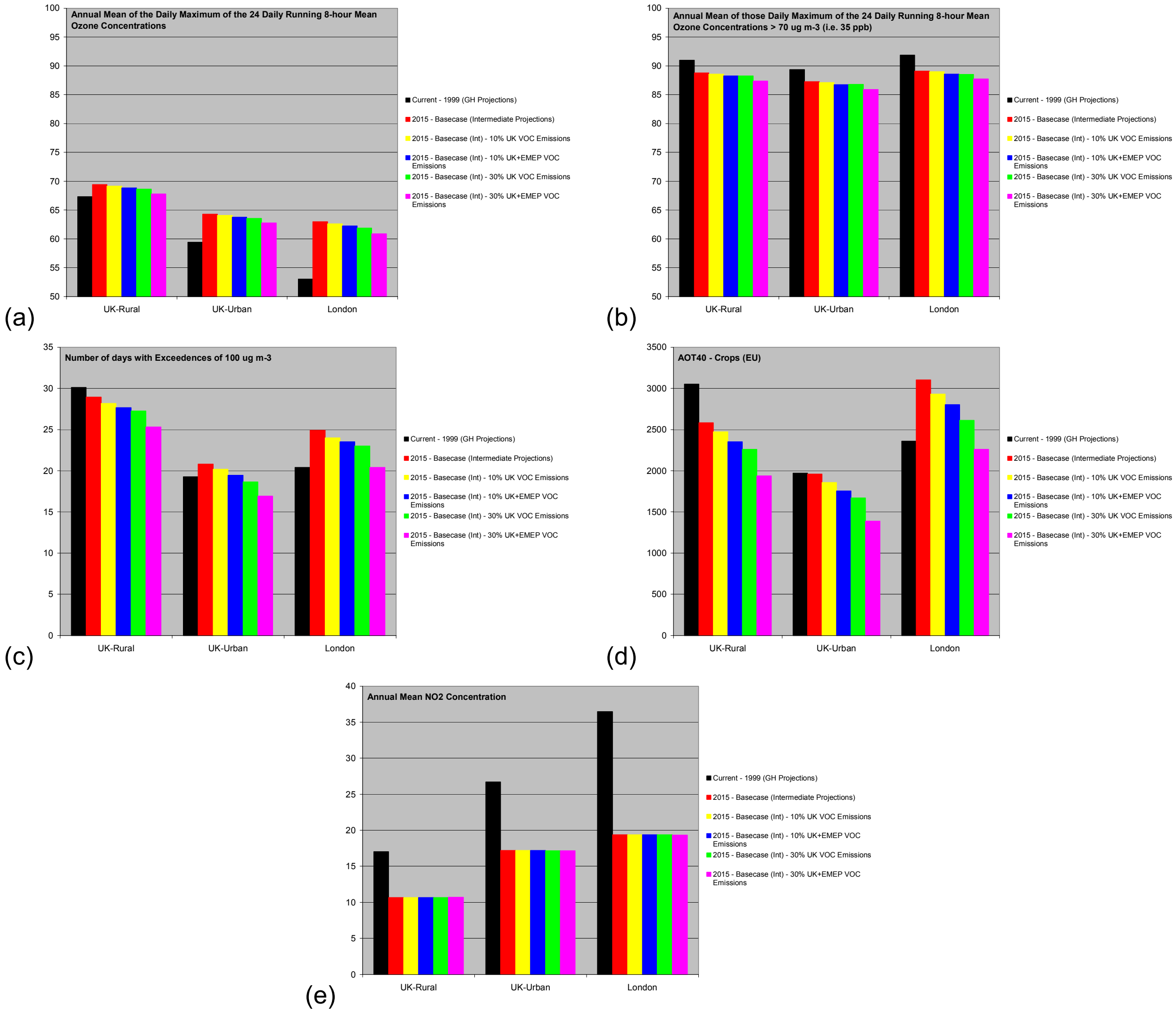


Figure 5-5: Effect of Across-the-Board Reductions in UK and European VOC Emissions for Selected Ozone and Nitrogen Dioxide Metrics in 2015 [Panel a - Annual Mean (µg m^{-3}) of Maximum Daily Running 8-Hour Mean Ozone Concentration; b - Annual Mean (µg m^{-3}) of those Maximum Daily Running 8-Hour Mean Ozone Concentration which are greater than 70 µg m^{-3}; c – Number of Days when the Daily Running 8-Hour Mean Ozone Concentration exceeds 100 µg m^{-3}; d - AOT40 Crops (in µg m^{-3} hours); e – Annual Mean Nitrogen Dioxide Concentration (in µg m^{-3})] Calculated by the Ozone Source Receptor Model.

5.2.4 Attainment of Ozone Air Quality Targets and Objectives

The OSRM model runs undertaken for the Review of the Air Quality Strategy were largely based on specific emission control measures (see the previous Section 5.2.3). The emission reductions implied by the measures were used to prepare the emission inventories for the model runs. Although desirable, the measures by themselves would not necessarily ensure attainment of ozone air quality targets or objectives. As a result, the Department were interested in the critical point where NO_x reductions would eventually result in less ozone, especially in urban areas. To answer this question, two series of OSRM model runs were undertaken in which the NOx emissions in (i) the UK and (ii) the UK and Europe were progressively reduced from 100% to 10% of their 2010 base case values in 10% increments. The model runs used the same 41 receptor sites as for the Review of the Air Quality Strategy (see the previous Section 5.2.3).

Figure 5-6 shows the response of selected ozone and nitrogen dioxide metrics to the progressive reduction in NO_x emissions Control in (a) the UK and (b) the UK and Europe for 2010 at three ozone monitoring sites: Strathvaich Dam, Harwell and London Bloomsbury.

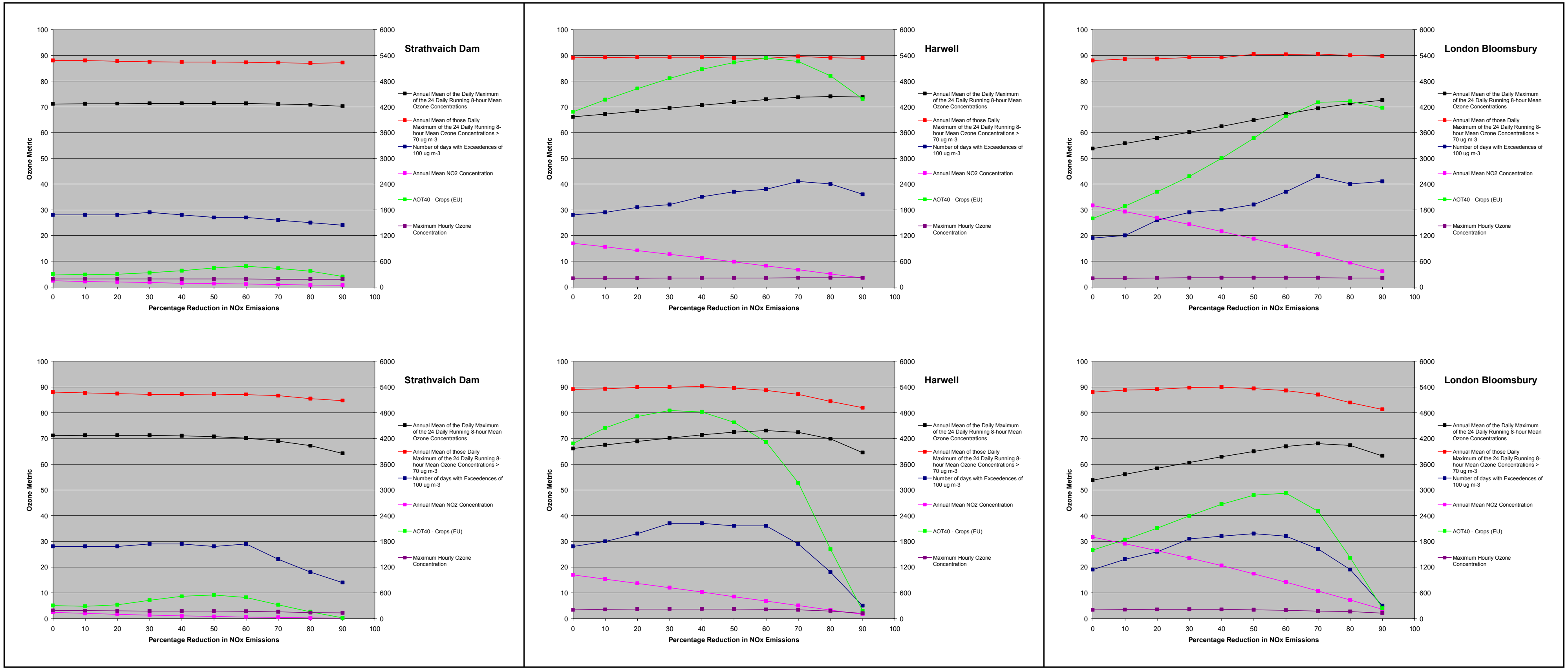


Figure 5-6: Response of Selected Ozone and Nitrogen Dioxide Metrics for 2010 to Progressive NO_x Emission Control in the UK (Upper Panels) and in the UK and Europe (Lower Panels) Calculated using the OSRM for Strathvaich Dam (Left-hand Pair of Panels), Harwell (Central Pair of Panels) and London Blommsbury (Right-hand Pair of Panels).

The annual mean NO_2 concentration at all three sites falls as the overall NO_x emissions are reduced. However, the ozone metrics generally show an increase in value, reach a peak before then declining. The response is metric and site specific, with the greatest decline observed in the AOT40 – crops and, to a lesser extent, the number of days when the maximum daily running 8-hourly average ozone concentration exceeded 100 $\mu g\ m^{-3}$. Figure 5-6 shows that large decreases in NO_x emissions would be required to overcome the ozone increase and to achieve compliance with air quality target and objectives. Comparing the upper and lower panels in Figure 5-6, NO_x emission control in the UK and Europe is seen to be more effective than control in the UK alone. A smaller NO_x emission reduction is needed to reach the peak value in the ozone metrics. These model runs assumed no corresponding VOC emission reduction. As shown previously, any VOC emission reductions would improve ozone air quality. A lower level of NOx reduction would therefore be needed if VOC emissions were also controlled to achieve the same endpoint.

To understand the above further, Figure 5-7 shows the hourly ozone concentrations calculated at the same three sites for the 2010 base case model run and for two of the NO_x emission reduction cases: (i) a 50% Reduction in UK NO_x emissions and (ii) a 90% Reduction in UK and European NO_x emissions. Comparing the base case and 90% emission reduction runs (black and blue traces in Figure 5-7), the absolute magnitude and the periods of elevated ozone concentrations are much reduced during the middle part of the year, indicating that there has been a significant reduction in photochemical ozone production. It is not surprising therefore that the AOT40 – Crops metric shows the greatest response of the ozone metrics considered to NO_x emission control. The AOT40 – Crops metric is calculated for daylight hours between May to July. There is evidence, certainly at Harwell and London Bloomsbury, that the modelled ozone concentrations are higher at the beginning and end of the year. Also, the minimum ozone concentrations are generally higher in the emission reduction case. In the absence of photochemical ozone production, it is expected that the NO_x emissions would have a titration effect on ozone and its concentrations. As the NOx emissions are reduced, the titration effect would be diminished and the ozone concentrations would rise.

For the intermediate NOx reduction run shown (50% UK emission reduction), the minimum ozone concentrations are higher in the emission reduction case. There is generally little change in the peak ozone concentrations from the base case. While there are examples of lower ozone concentrations in the peaks, there are also periods when the emission reduction has increased ozone concentrations. The increase in the low ozone concentrations presumably accounts for the increases observed in the ozone metrics shown previously in Figure 5-6.

In previous OSRM scenario calculations, NO_x emission reductions alone gave a complex response. The response depended on the choice of ozone metric and could show regional differences for a given metric. Generally, there was a deterioration in ozone air quality if NO_x emissions alone were controlled. Figure 5-6 and Figure 5-7 suggest that there are potentially two counteracting factors (a) the reduction in photochemical ozone production as NOx emissions are controlled. This is the situation classically simulated using the Photochemical Trajectory Model and (ii) a NO_x titration effect. The relative importance of these effects varies during the year, the day and with site. It is not surprising that the response of the different ozone metrics vary and could vary across the country.

5.3 OSRM MODELLING FOR THE THIRD DAUGHTER DIRECTIVE

A series of UK-scale model runs has been undertaken for a number of current years (1997 to 2002) to evaluate the performance of the OSRM as a supplementary assessment technique for the third Daughter Directive on Ozone. The model runs made use of meteorological data and UK and EMEP emission inventories for the relevant years. The OSRM post-processor calculated ozone and nitrogen dioxide metrics from the hourly ozone, NO and NO_2 concentrations. The OSRM output was processed with and without the surface-conversion algorithm activated.

Figure 5-8 presents examples of the effect of the surface-conversion algorithm on the annual mean concentrations of ozone and nitrogen dioxide calculated for 1999. As expected, there is a strong inverse relationship between the annual mean concentrations of these two pollutants. The areas with highest NO_2 concentrations have the lowest ozone concentrations and *vice versa*.

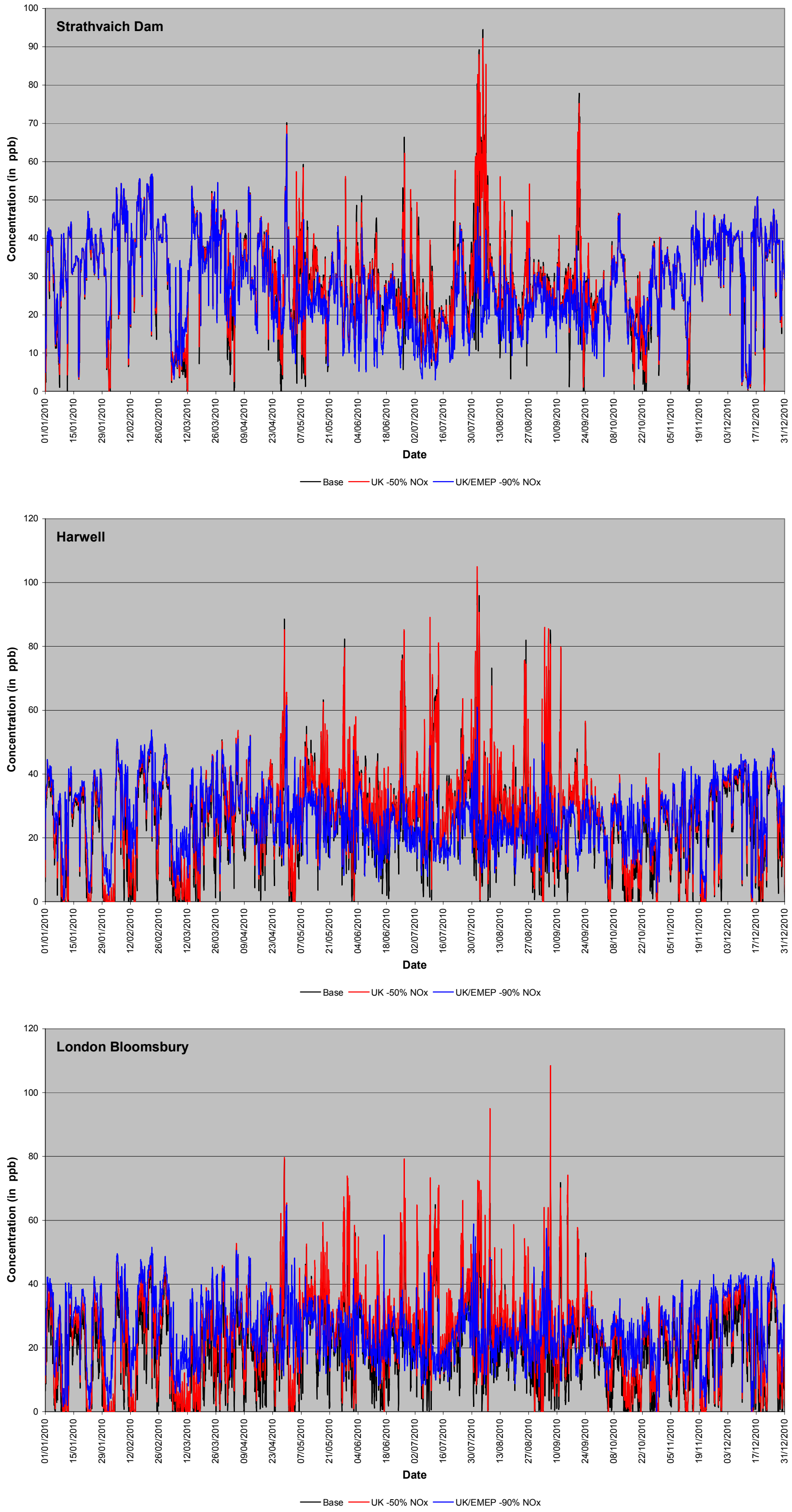
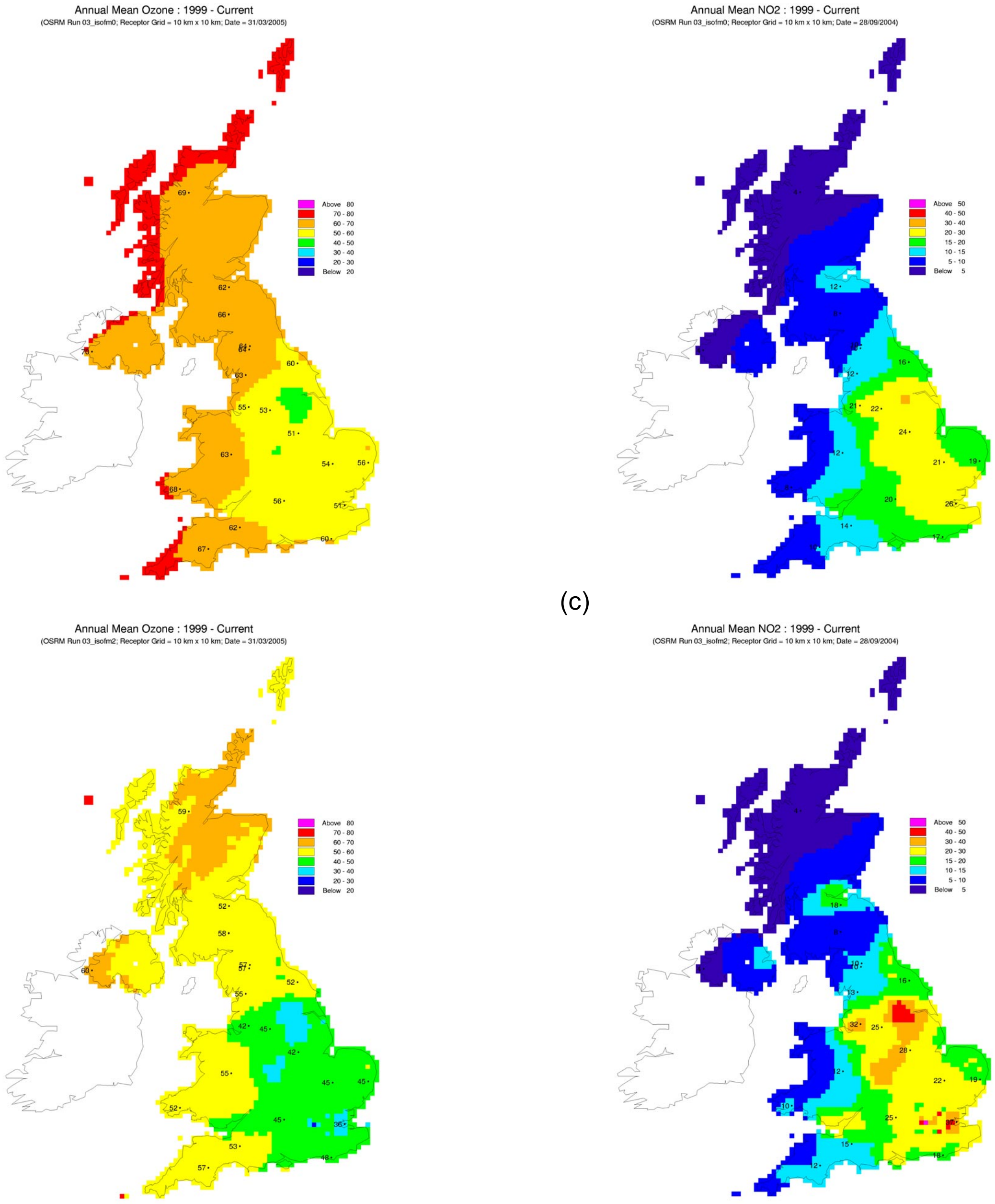


Figure 5-7: Response of the Hourly Ozone Concentrations Calculated using the OSRM for (a) a 2010 Base Case (black trace), (b) 50% Reduction in UK NO_x Emissions (red trace) and (c) 90% Reduction in UK and European NO_x Emissions (blue trace) at 3 Receptor Sites: Strathvaich Dam (Upper Panel), Harwell (Middle Panel) and London Blommsbury (Bottom Panel).



(a) (c)

(b) (d)

Figure 5-8: Maps of the Annual Mean Concentrations of O_3 (in µg m^{-3}, Panels a and b) and NO_2 (in µg m^{-3}, Panels c and d) Calculated for 1999 with (Lower Panels) and without (Upper Panels) Surface Conversion.

UK maps of a number of relevant ozone and nitrogen dioxide metrics have been generated for the years 1997 to 2002 with and without the surface algorithm activated. The OSRM maps (unconverted and converted) are compared in Figure 5-9 to Figure 5-12 with the corresponding maps produced from measurements using semi-empirical techniques:

- **AOT40 for Crops for 2001**: The empirical map was derived from measurements by CEH Edinburgh and was presented in the Preliminary Assessment for the Third Daughter Directive on Ozone (see First Annual Report on the project);
- **The Number of Days in 2001 for which the Maximum of the 24 Possible Daily Running 8-hour Mean Concentrations exceeded 120 µg m^{-3}**: The empirical map was derived from measurements and was presented in the Preliminary Assessment for the Third Daughter Directive on Ozone (see First Annual Report on the project);

- **Annual Mean Ozone Concentration**: The map was derived by Stedman[5] from the UK NO_x Map for 2002 and the O_3-NO-NO_x relationships of Jenkin (2004).
- **Annual Mean of the Maximum of the 24 Possible Daily Running 8-hour Mean Concentrations**: The map of this metric was derived by Stedman[5] from the annual mean ozone map and the relationship between the annual mean ozone concentration and this metric derived from measurements.

Apart from the exceedence map (note the scale on the OSRM maps), the other empirical maps generally lie between the OSRM unconverted and surface-converted maps. While the conversion algorithm has improved the agreement between the maps of the exceedence metric, it has generally made the ozone concentrations in the surface-converted maps of the annual mean concentrations and AOT40 for Crops too low. This is because the surface conversion algorithm reduces the mid-boundary layer ozone concentration on all the hourly values and not just peak values.

Some simplifying assumptions were made in this initial comparison (the UK land cover was assumed to be grass[6] and no altitude correction was made). A more rigorous comparison is planned. The comparison will identify areas where the OSRM could be modified to improve its performance. For example, it is evident from the nitrogen dioxide map that the treatment of the emissions from high level sources should be modified. As part of this exercise, a review of the surface-conversion algorithm will be undertaken to identify additional improvements that could be made to the OSRM post-processor.

5.4 REFERENCES

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[5] J R Stedman (2004) Note to Defra.

[6] A land cover dataset has been prepared for use in the OSRM post-processor. Some modification to the OSRM post-processor code will be needed to enable its use.

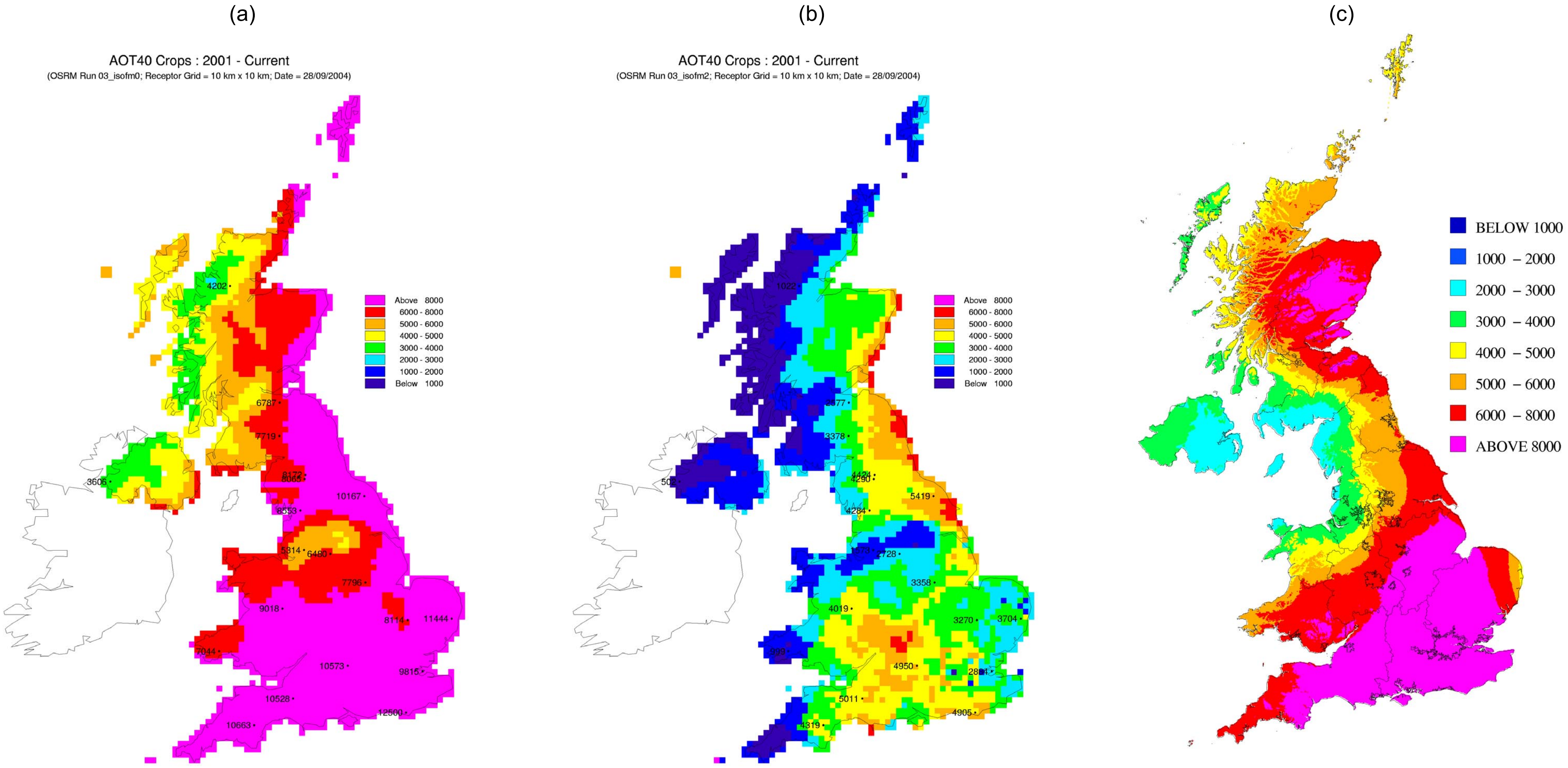


Figure 5-9: Comparison of the Maps of the AOT40 for Crops (in µg m^{-3} hours): Panel (a) the Unconverted Map for 2001, (b) the Surface-converted Map for 2001 and (c) the Map derived from Measurements Reported in the Preliminary Assessment for the Third Daughter Directive on Ozone (see First Annual Project Report).

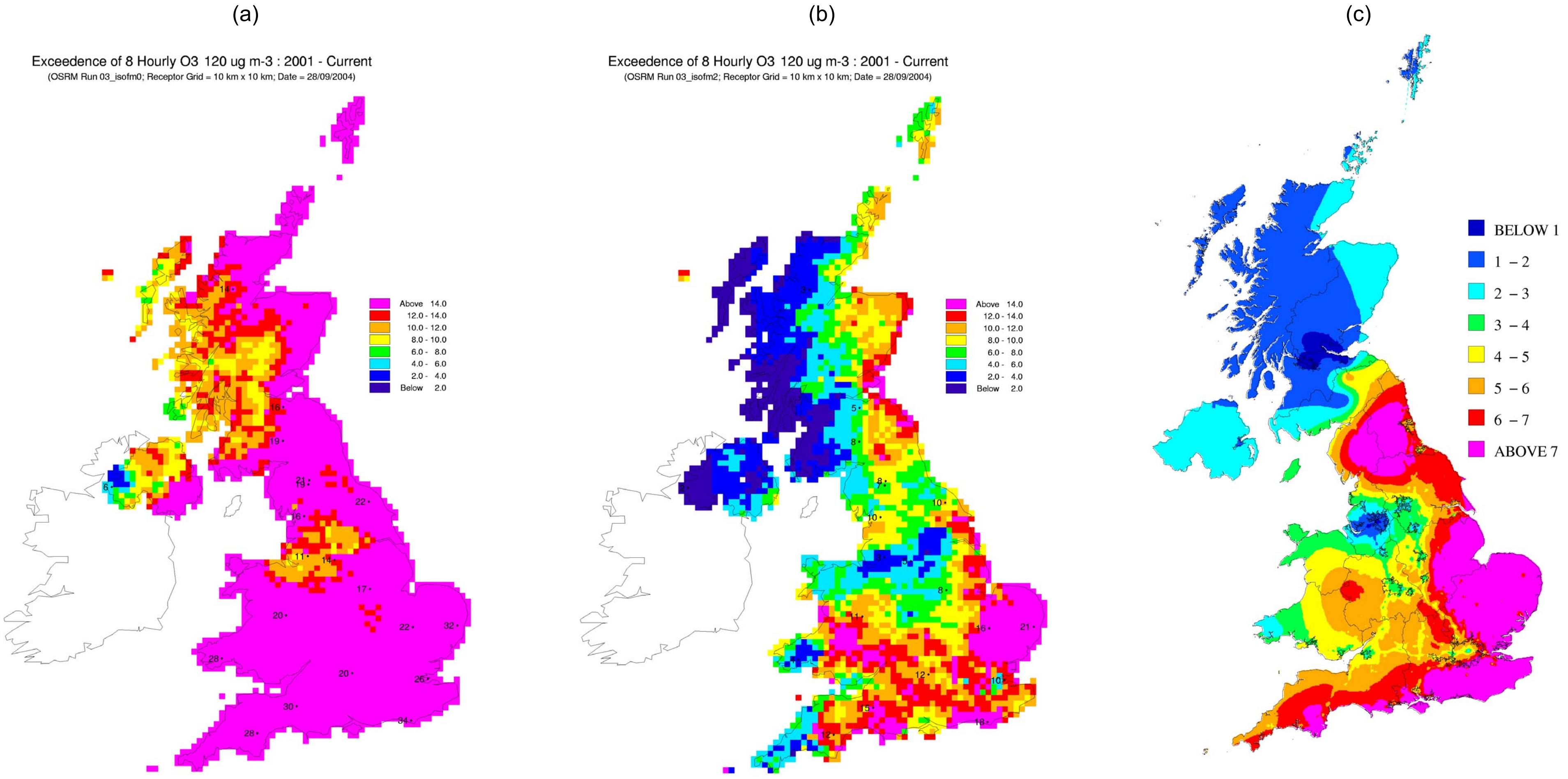


Figure 5-10: Comparison of the Maps of the Number of Days on which a Running 8-hour Mean Ozone Concentration exceeded 120 μg m^{-3}: Panel (a) the Unconverted Map for 2001, (b) the Surface-converted Map for 2001 and (c) the Map derived from Measurements Reported in the Preliminary Assessment for the Third Daughter Directive on Ozone (see First Annual Project Report).

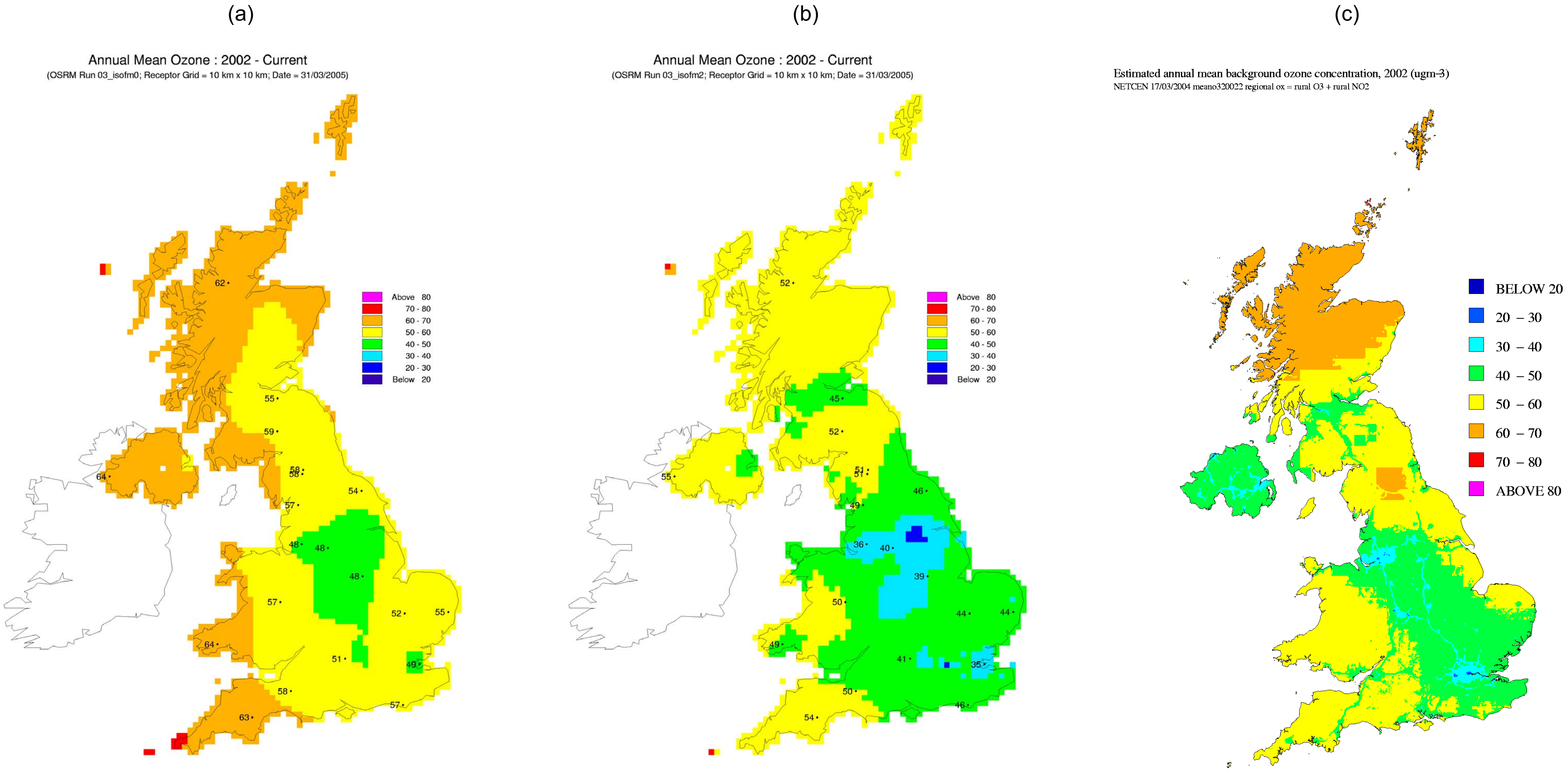


Figure 5-11: Comparison of the Maps of the Annual Mean Ozone Concentration (in $\mu g\ m^{-3}$): Panel (a) the Unconverted Map for 2002, (b) the Surface-converted Map for 2002 and (c) the Map derived by Stedman from a NO_x Map and the O_3-NO-NO_x Relationships of Jenkin.

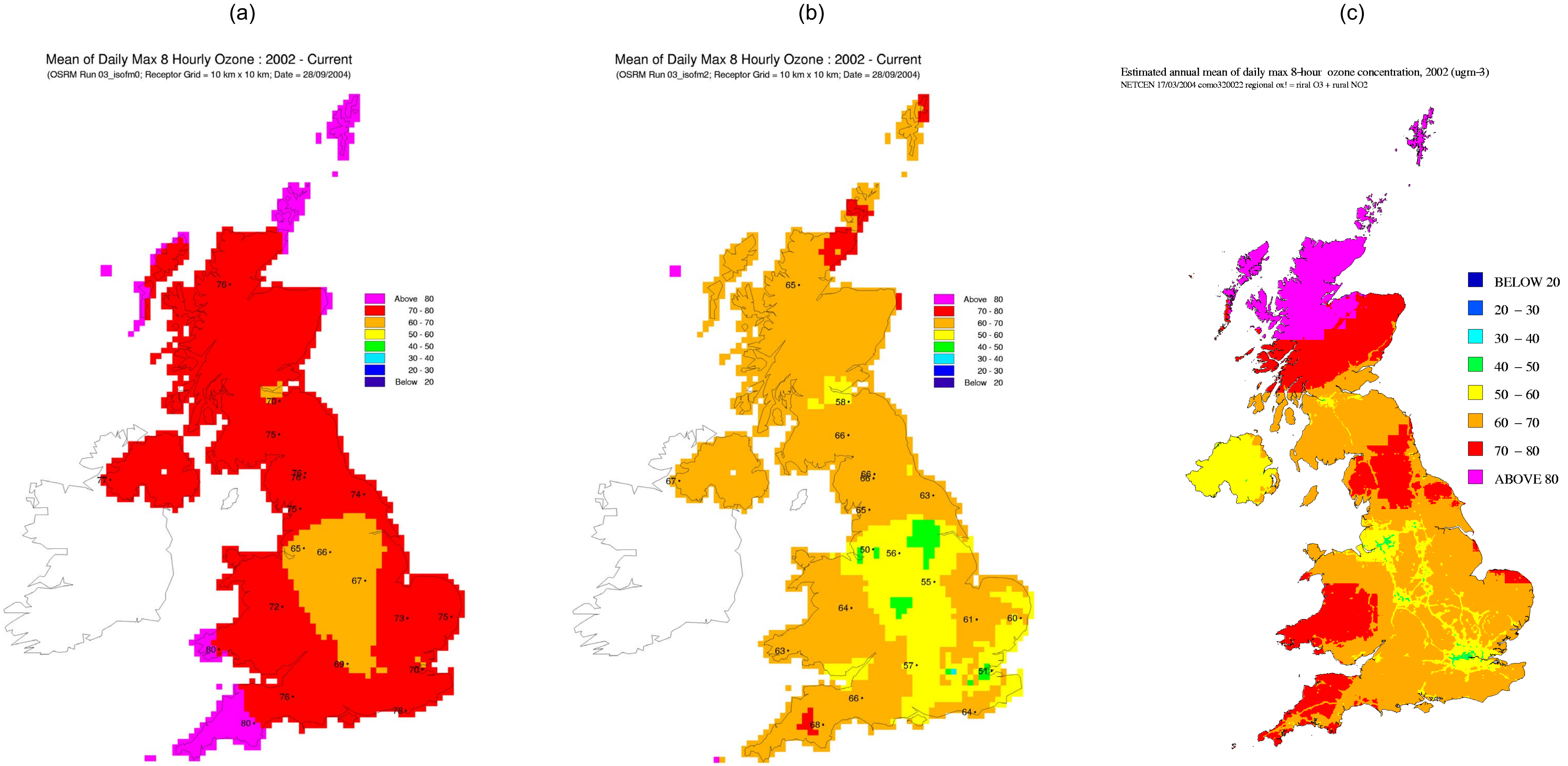


Figure 5-12: Comparison of the Maps of the Annual Mean of the Maximum Daily Running 8-hour Mean Ozone Concentration (in µg m^{-3}): Panel (a) the Unconverted Map for 2002, (b) the Surface-converted Map for 2002 and (c) the Map derived by Stedman from a NO$_x$ Map and the O$_3$-NO-NO$_x$ Relationships of Jenkin.

6 Improvements to Photochemical Reaction Schemes (Objective 4)

6.1 MECHANISM DEVELOPMENT

6.1.1 Evaluation of Master Chemical Mechanism (MCM v3) using Environmental Chamber Data

Introduction and Methodology

In collaboration with Paulo de Pinho and Casimiro Pio, University of Aveiro, Portugal [Pinho *et al.*, 2004], the MCM v3 degradation schemes for butane and isoprene have been evaluated using the large environmental chamber dataset of the Statewide Air Pollution Research Center (SAPRC) at the University of California [Carter *et al.*, 1995]. In addition to evaluation using butane-NO_X and isoprene-NO_X photo-oxidation experiments, this work has made use of experiments involving the major degradation products of butane (methylethyl ketone, MEK, acetaldehyde, CH_3CHO, and formaldehyde, HCHO), and of isoprene (methylvinyl ketone, MVK, methacrolein, MACR, and formaldehyde, HCHO). The formation of MEK, CH_3CHO and HCHO from the degradation of butane is shown schematically in Figure 6-1, illustrating the participation of the carbonyl products in the degradation of butane to CO_2. In cases of both butane and isoprene, a procedure was adopted in which the experiments for the carbonyl products were used to test the corresponding subsets of the parent hydrocarbon mechanism, prior to evaluation of the full scheme. This step-by-step approach is advantageous, because it allows any compensating errors in the sub-mechanisms to be identified.

The full evaluation considered 46 butane-NO_X-air, 6 MEK-NO_X-air, 11 CH_3CHO-NO_X-air, 24 HCHO-NO_X-air, 9 isoprene-NO_X-air, 8 MACR-NO_X-air and 5 MVK-NO_X-air experiments (i.e. 109 experiments in total). The ranges of reagent concentrations are presented in Table 6-1. Throughout the study, the performance of the MCM v3 chemistry was simultaneously compared with that of the corresponding chemistry in the SAPRC-99 mechanism, which was developed and optimized in conjunction with the chamber datasets [Carter, 2000].

Results and Conclusions

The MCM v3 mechanisms for both butane and isoprene were found to provide an acceptable reaction framework for describing the NO_X-photo-oxidation experiments, and generally performed well (e.g., Figure 6-2 shows results for selected butane experiments). A number of parameter refinements were identified which resulted in an improved performance, the refined mechanism being denoted MCM v3a. The refinements all relate to the magnitude of sources of free radicals from organic chemical process, such as carbonyl photolysis rates and the yields of radicals from the reactions of O_3 with unsaturated oxygenates, which are under review in MCM development activities. Specifically, recommendations have been made [Pinho *et al.*, 2004] to update the photolysis parameters for HCHO, MEK, MACR and MVK, and the OH yields from the reactions of O_3 with MACR and MVK, either in line with data reported since the MCM mechanism development protocol [Jenkin et al., 1997], or on the basis of optimization in the current study.

While the recommended updates are certainly necessary to maintain the MCM fully, it is emphasised that they have only a minor influence on the performance of the butane and isoprene schemes in atmospheric models. Consequently, these evaluation activities provide strong support for the MCM schemes for butane and isoprene, which are the most abundant components of emissions of anthropogenic and biogenic non-methane VOC, respectively.

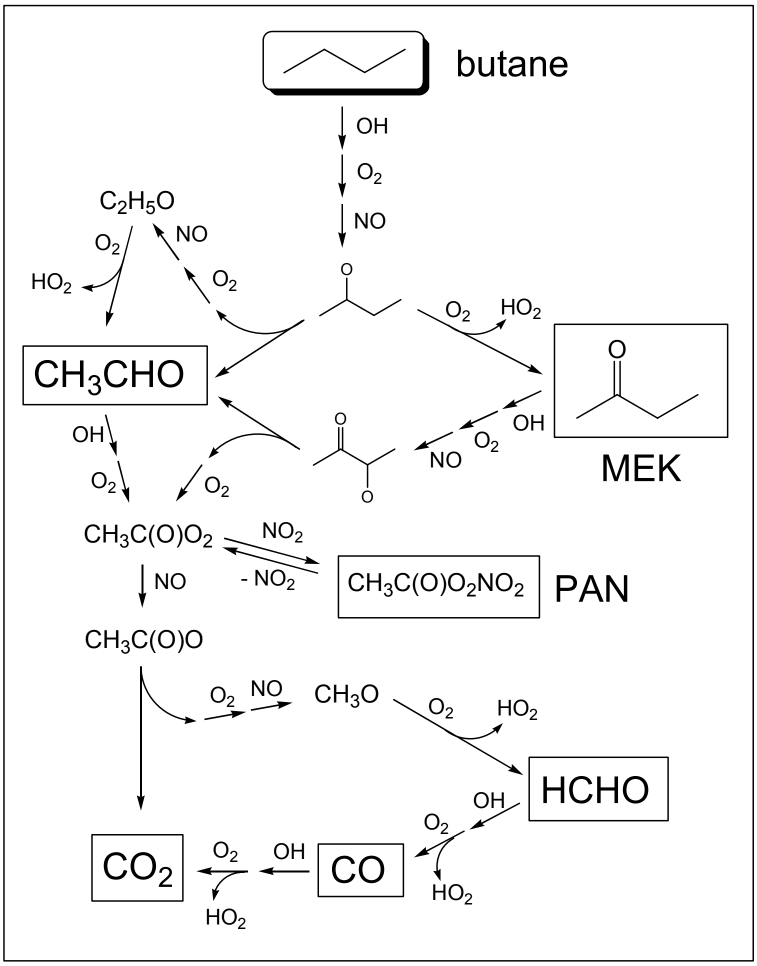


Figure 6-1: Schematic Representation of the Major Radical Propagation Pathways of the OH-initiated Degradation of butane, also illustrating the Sequential Formation of the Intermediate Products MEK, CH_3CHO, HCHO and CO. Reaction Steps involving NO are Reactions with Organic Peroxy Radical Intermediates, which lead to NO-to-NO_2 Conversion and O_3 Production. The Reactions of OH with butane and MEK possess Additional Channels which are fully represented in the Mechanism, but not shown in the Diagram.

Table 6-1: Ranges of Reagent Concentrations for the Considered Experiments

	Butane-NOx	MEK-NOx	CH_3CHO-NOx	HCHO-NOx	Isoprene-NOx	MACR-NOx	MVK-NOx
[VOC] (ppm)	1.47–4.95	7.83–9.49	0.44–1.67	0.29–1.01	0.27–1.00	1.53–4.41	0.87–2.00
[NOx] (ppm)	0.09-0.66	0.09–0.29	0.14–0.28	0.16-0.54	0.15–0.60	0.24–0.57	0.51–0.60
[VOC]/[NOx]	5.22-39.89	26.61–99.44	1.71–11.73	1.00–3.40	0.62-2.08	3.57–9.19	1.73–3.72

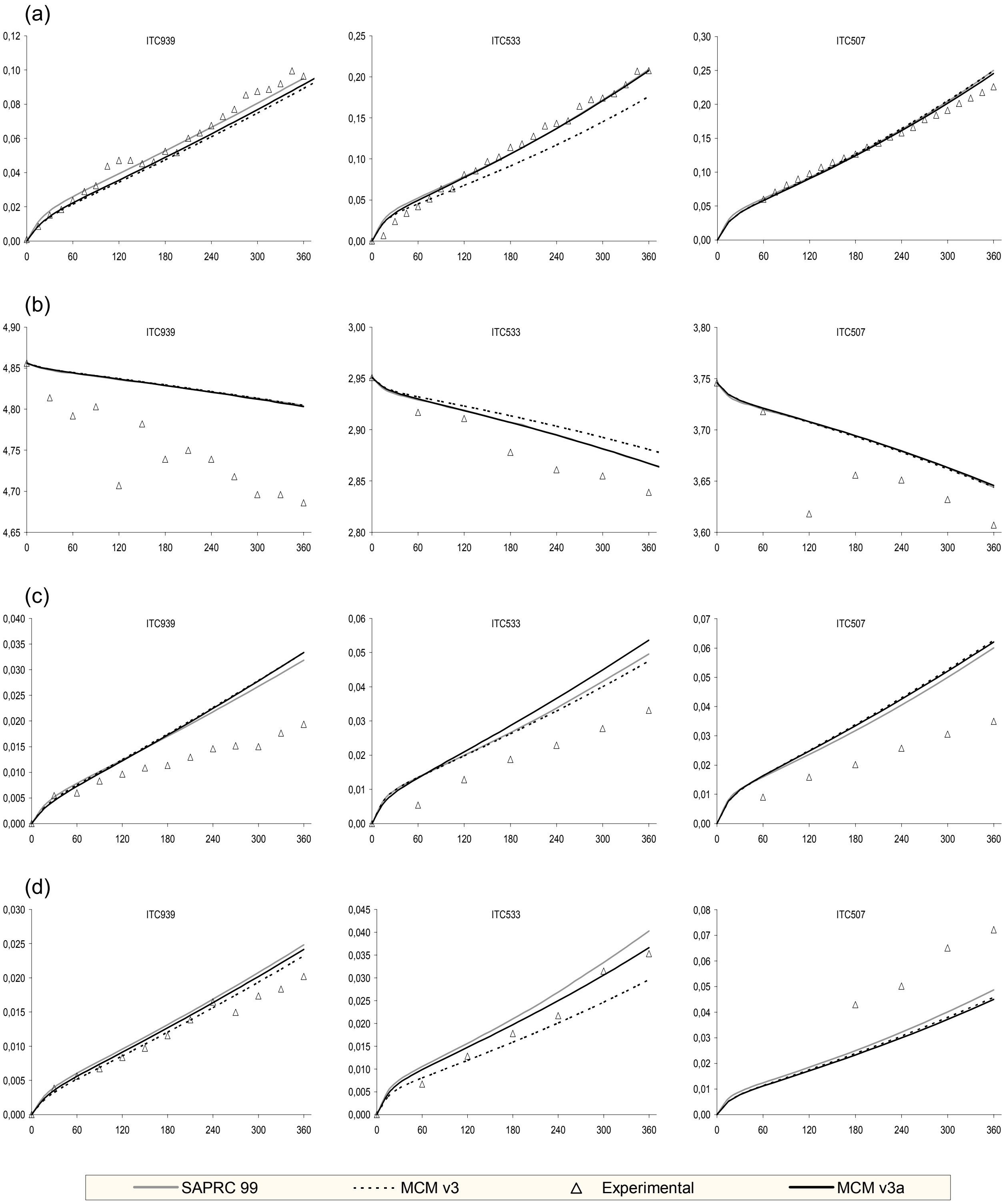


Figure 6-2: Observed and Calculated Δ(O_3-NO) (ppm) vs. Time (min) (Top Row of Panels), Butane vs. Time (min) (Second Row of Panels), CH_3CHO (ppm) vs. Time (min) (Third Row of Panels) and MEK (ppm) vs. Time (min) (Third Row of Panels) for the Same Selected butane/NO_X/Air Experiments.

6.1.2 The Common Representative Intermediates (CRI) Mechanism

Introduction

The complete oxidation of a given VOC though to CO_2 and H_2O normally proceeds via a series of intermediate oxidised products. At each stage, the chemistry is propagated by reactions of free radicals leading to the oxidation of NO to NO_2 and resultant formation of O_3 as a by-product, following the photolysis of NO_2:

$$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O(^3P) \quad (1)$$

$$O(^3P) + O_2\ (+M) \rightarrow O_3\ (+M) \quad (2)$$

The total quantity of O_3 potentially generated is therefore dependent on the number of NO to NO_2 conversions which can occur during the degradation, but is restricted by the time available for the chemistry to occur. Consequently, the O_3 forming ability of VOC has sometimes been expressed in terms of 'kinetic' and 'mechanistic' or 'structure-based' components [*e.g.*, Carter, 1994; Derwent *et al.*, 1998].

On the basis of understanding of the detailed chemistry for simple hydrocarbons such as methane, ethane and ethene, the total quantity of O_3 potentially formed as a by-product of the complete OH-initiated and NO_X-catalysed oxidation to CO_2 and H_2O can be represented by the following overall equations:

$$CH_4 + 8O_2 \rightarrow CO_2 + 2H_2O + 4O_3 \quad (3)$$

$$C_2H_6 + 14O_2 \rightarrow 2CO_2 + 3H_2O + 7O_3 \quad (4)$$

$$C_2H_4 + 12O_2 \rightarrow 2CO_2 + 2H_2O + 6O_3 \quad (5)$$

In the case of ethane, for example, this is based on the oxidation via CH_3CHO, HCHO and CO as intermediate oxidised products, as shown in Figure 6-3. According to equations (3) - (5), therefore, the complete oxidation of one molecule of each of these compounds leads to the production of 4, 7 and 6 molecules of O_3 respectively. Logically, the number of O_3 molecules produced in each case (i.e. the number of NO to NO_2 conversions) is equivalent to the number of reactive bonds in the parent molecule, that is the number of C-H and C-C bonds which are eventually broken during the complete oxidation to CO_2 and H_2O.

Construction of the CRI Mechanism

In the CRI mechanism, this simple rule is used to define a series of generic intermediate radicals and products, which mediate the breakdown of larger VOC into smaller fragments (e.g., HCHO), the chemistry of which is treated explicitly [Jenkin *et al.*, 2002]. Version 1 of the CRI mechanism treats the degradation of methane and 120 emitted VOC using about 570 reactions of 250 species (i.e. an average of about 2 species per VOC). It thus contains < 5% of the number of reactions and < 7% of the number of chemical species in MCM v3.1, providing a computationally economical alternative. The mechanism was previously optimised through comparison with the MCM, by adjusting the reactivity of representative intermediate carbonyl products, such that it was able to generate concentrations of ozone, OH, peroxy radicals, NO and NO_2 which were in excellent agreement with those calculated using the MCM, in simulations using the PTM on a standard trajectory (Jenkin *et al.*, 2002).

Whilst it is recognised that CRI v1 correctly represents ozone formation from the VOC mixture, it may not fully recreate the relative contributions of component VOC or VOC classes within the emitted mixture. CRI v2 development activities are therefore focussing on the treatment of the degradation of individual classes of VOC (e.g., alkanes, alkenes, aromatics). Each class is being considered separately, and validated using the representation in MCM v3.1. This has demonstrated that the mechanism is improved by defining separate series of representative intermediates for some VOC classes. This will result in an ultimate increase the size of the mechanism over that of CRI v1, but will allow a more rigorous description of the impact of the different VOC emission sectors, and an improved foundation for the expansion of the mechanism to the treatment of the several hundred minor VOC not currently represented in MCM or CRI.

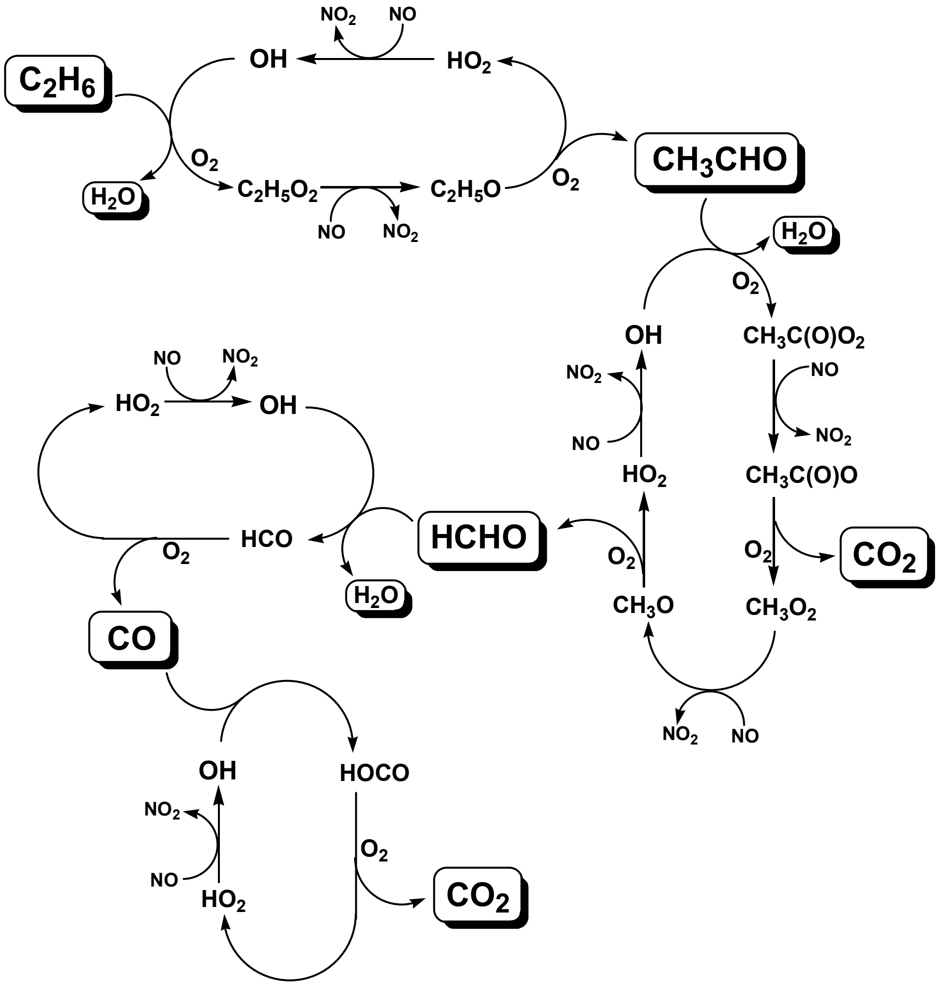


Figure 6-3: Schematic Representation of the Reactions involved in the OH initiated, NO_X catalysed Oxidation of Ethane to CO_2. The Reaction Sequence shows the Formation of Acetaldehyde (CH_3CHO), Formaldehyde (HCHO) and CO as Intermediate Oxidised Products. The Complete Sequence results in 7 NO to NO_2 conversions. Subsequent photolysis of NO_2 regenerates NO and leads to Ozone Formation (Reactions (1) and (2)), with the Net Overall Chemistry as shown in Reaction (4). (N.B. The Oxidation of CO to CO_2 partially proceeds via OH + CO $\rightarrow$ H + CO_2, followed by H + O_2 + M $\rightarrow$ HO_2 + M, which has the Same Overall Chemistry as that displayed above, i.e. OH + CO + M $\rightarrow$ HOCO + M, followed by HOCO + O_2 $\rightarrow$ HO_2 + CO_2).

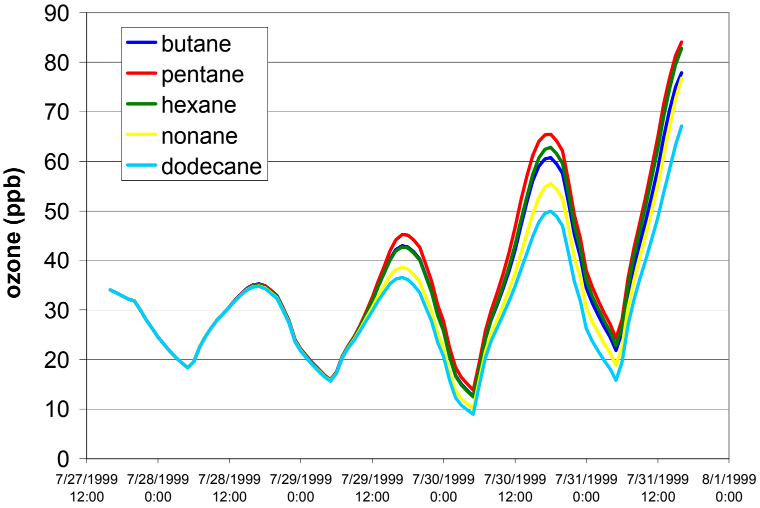


Figure 6-4: Reference Concentrations of Ozone along 31 July 1999 Trajectory to Aston Hill, simulated with PTM-MCM v3.1 with VOC emitted entirely as each of a Series of Alkanes.

The construction and optimisation procedure makes use of reference simulations of ozone concentrations, using PTM-MCM v3.1 operating on archived trajectories for an ozone episode on 31 July 1999. The model is run with VOC emissions entirely in the form of an individual VOC. The results for a series of alkanes (Figure 6-4) demonstrate that different amounts of ozone are generated with each different VOC. Starting with the smallest alkane, simulations are performed with the CRI mechanism, and the reactivity of appropriate intermediate products is varied to optimise ozone formation in comparison with MCM v3.1, and the procedure is repeated in turn for the larger alkanes. To illustrate this, Figure 6-5 shown a portion of the mechanism in which pentane is degraded until an intermediate also formed from the degradation of butane is generated.

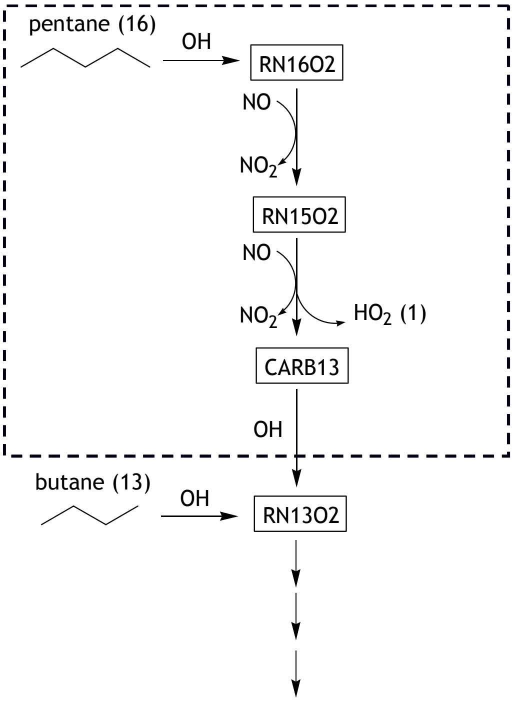


Figure 6-5: Schematic Representation of a Portion of the Degradation Chemistry in CRI v2, showing the Degradation of Pentane and how it feeds into the Butane Degradation Mechanism. The Index assigned (in brackets) to each Alkane is the Total Number of C-H and C-C bonds it contains. The Indices within the Generic Radicals and Carbonyls (e.g. ‘16’ in $RN16O_2$ and ‘13’ in CARB13), thus represent the Number of NO to NO_2 Conversions which can result from the Subsequent Complete Degradation.

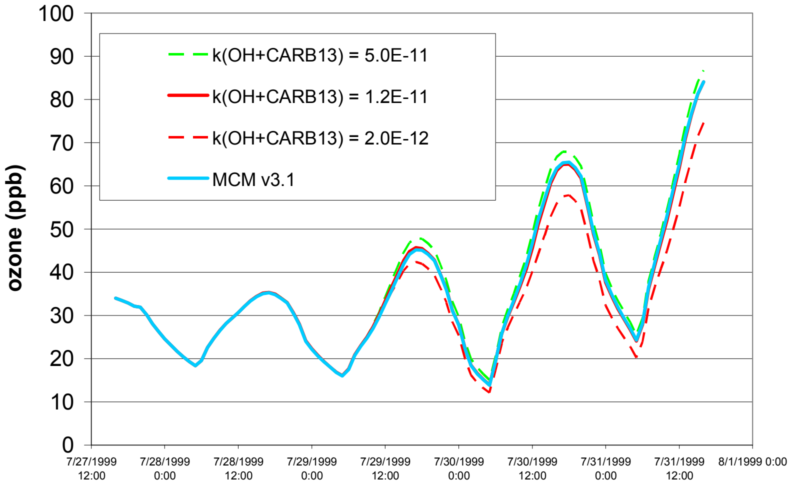


Figure 6-6: Concentrations of Ozone along 31 July 1999 Trajectory to Aston Hill, simulated with the PTM with VOC emitted entirely as Pentane. Simulations are shown for MCM v3.1 Chemistry, and CRI v2 Chemistry with varying OH Reactivity for the Intermediate CARB13.

Given that the representation of butane degradation is already optimised, optimisation of the pentane scheme can be achieved through variation of the reactivity of the intermediate 'CARB13' (Figure 6-5), as illustrated in Figure 6-6. In this way, the mechanism for complete classes of VOC is built up and optimised.

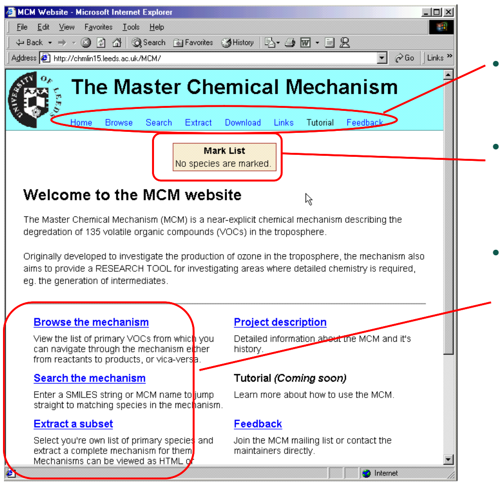
6.2 THE NEW MCM WEBSITE

As reported in the first year, the Master Chemical Mechanism (MCM) has been updated to MCM version 3.1. Major updates in MCMv3.1 include an extensive revision of the aromatic mechanisms, which are important in the photochemistry of the polluted boundary layer, and also the addition of a number of new degradation schemes including MBO (2-methyl-3-buten-2-ol) which is an important biogenic species. MCMv3.1 now contains 135 primary emitted VOCs which lead to a mechanism containing *ca.* 5,900 species and 13,500 reactions.

As part of the ongoing improvements to the MCM a new version of the website has been developed with the primary objectives of making the website clearer and easier to navigate and of improving access to the MCM itself. The new site can be linked to through the published address, along with the older version of the site which is currently being hosted by the University of Western Australia: **http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html** or at the new address: **http://mcm.leeds.ac.uk/MCM/**.

6.2.1 New Layout and Web Tools

The new site has three main self-explanatory functions; ***Browse***, ***Search*** and ***Extract*** as shown in Figure 6-7.



The Master Chemical Mechanism

Mark List
No species are marked.

Welcome to the MCM website

The Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism describing the degradation of 135 volatile organic compounds (VOCs) in the troposphere.

Originally developed to investigate the production of ozone in the troposphere, the mechanism also aims to provide a RESEARCH TOOL for investigating areas where detailed chemistry is required, eg. the generation of intermediates.

Browse the mechanism
View the list of primary VOCs from which you can navigate through the mechanism either from reactants to products, or vica-versa.

Search the mechanism
Enter a SMILES string or MCM name to jump straight to matching species in the mechanism.

Extract a subset
Select you're own list of primary species and extract a complete mechanism for them. Mechanisms can be viewed as HTML or

Project description
Detailed information about the MCM and it's history.

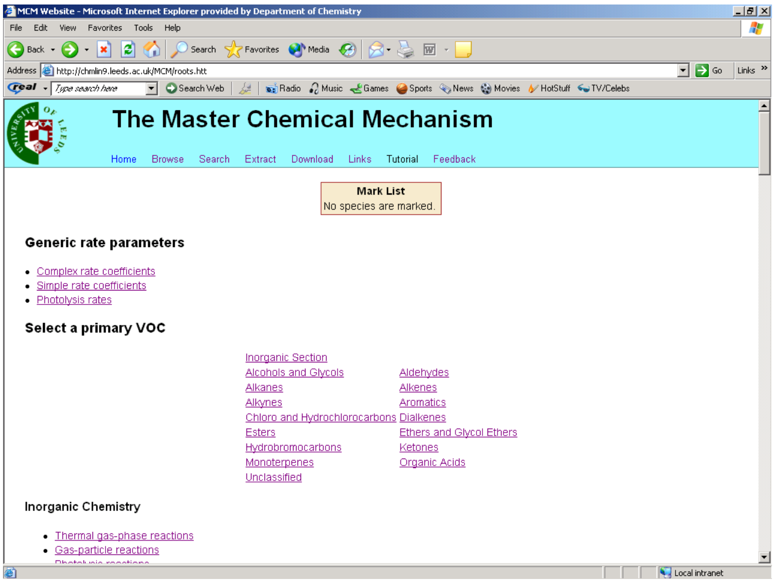
Tutorial *(Coming soon)*
Learn more about how to use the MCM.

Feedback
Join the MCM mailing list or contact the maintainers directly.

- Menu Bar
- Mark species for later processing
- Three main functions
  - *Browse*
  - *Search*
  - *Extract*

Figure 6-7: The New MCMv3.1 Homepage

Also illustrated in Figure 6-7 is the permanently displayed ***Mark List*** which is effectively a "shopping basket" for collecting species of interest as you browse around the MCMv3.1 ready for mechanism extraction. The ***Browse*** facility enables the user to look through the MCMv3.1 by category in a similar way to the old site except the species now have structures associated with them. Figure 6-8 shows the *Browse* web page. All 135 primary VOCs are listed by category along with the inorganic chemistry (gas and particle reactions and photolysis rates) as well as listings for the generic rate coefficients used throughout MCMv3.1 including the photolysis rate parameterisations.



The Master Chemical Mechanism

Home Browse Search Extract Download Links Tutorial Feedback

Mark List
No species are marked.

Generic rate parameters

- Complex rate coefficients
- Simple rate coefficients
- Photolysis rates

Select a primary VOC

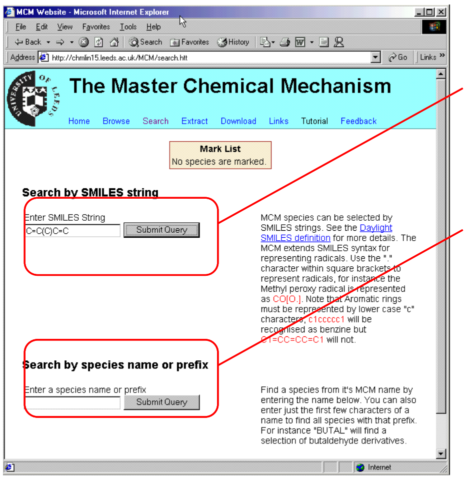
Inorganic Section	
Alcohols and Glycols	Aldehydes
Alkanes	Alkenes
Alkynes	Aromatics
Chloro and Hydrochlorocarbons	Dialkenes
Esters	Ethers and Glycol Ethers
Hydrobromocarbons	Ketones
Monoterpenes	Organic Acids
Unclassified	

Inorganic Chemistry

- Thermal gas-phase reactions
- Gas-particle reactions

Figure 6-8: MCMv3.1 *Browse* Facility.

Alternatively the *Search* function allows the user to search the MCMv3.1 either by SMILES string (tutorial on SMILES linked to website) or by MCM species name as shown in Figure 6-9. For example, in the case of isoprene (2-methyl-1,3-butadiene) if either the SMILES string (C=C(C)C=C) or MCM species name (C_5H_8) is entered as a query then the search results should return the structure of the species and the MCM name as seen in Figure 6-10.



The Master Chemical Mechanism

Home Browse Search Extract Download Links Tutorial Feedback

Mark List
No species are marked.

Search by SMILES string

Enter SMILES String: C=C(C)C=C

MCM species can be selected by SMILES strings. See the Daylight SMILES definition for more details. The MCM extends SMILES syntax for representing radicals. Use the "." character within square brackets to represent radicals, for instance the Methyl peroxy radical is represented as CO[O.]. Note that Aromatic rings must be represented by lower case "c" characters, c1ccccc1 will be recognised as benzine but C1=CC=CC=C1 will not.

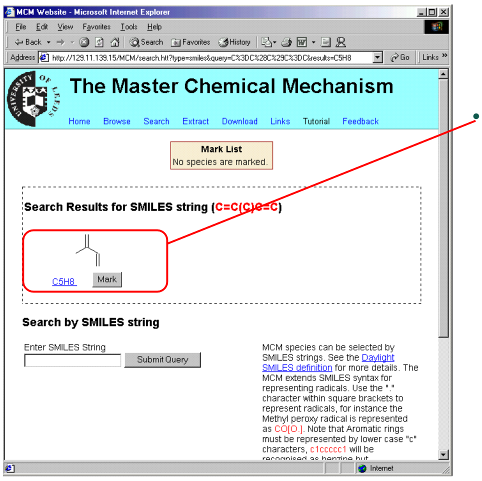
Search by species name or prefix

Enter a species name or prefix

Find a species from it's MCM name by entering the name below. You can also enter just the first few characters of a name to find all species with that prefix. For instance "BUTAL" will find a selection of butaldehyde derivatives.

- **Enter SMILES string**
  - *e.g. isoprene:* C=C(C)C=C
- **Enter a MCM species name**
  - *e.g. n-butane:* NC4H10

Figure 6-9: MCMv3.1 *Search* Facility



The Master Chemical Mechanism

Home Browse Search Extract Download Links Tutorial Feedback

Mark List
No species are marked.

Search Results for SMILES string (C=C(C)C=C)

Search by SMILES string

Enter SMILES String

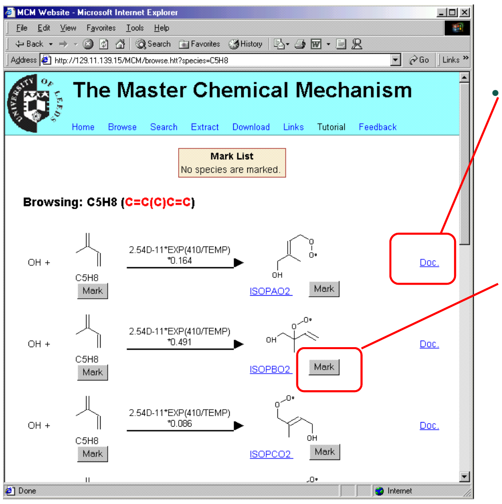
MCM species can be selected by SMILES strings. See the Daylight SMILES definition for more details. The MCM extends SMILES syntax for representing radicals. Use the "." character within square brackets to represent radicals, for instance the Methyl peroxy radical is represented as CO[O.]. Note that Aromatic rings must be represented by lower case "c" characters, c1ccccc1 will be

- Structure image linked to reaction listing.

Figure 6-10: MCMv3.1 *Search* Results.

If the MCM species name is then clicked upon then the user will be lead to its degradation scheme (with reactant and product structural information) as illustrated in Figure 6-11, again for isoprene.

Each individual reaction within the reaction listing displays its rate constant and branching ratio. Any generic rate constants and photolysis rates are directly linked to an appropriate table which list the equations and parameters used to calculate their value. Each reaction product's degradation scheme can be accessed in a similar fashion by clicking on its MCM species name. Also individual reactants and products have an associated "mark" button so that they can be added to (and displayed in) the *Mark List* for complete mechanism extraction later.



Mark List
No species are marked.

Browsing: C5H8 (C=C(C)C=C)

OH + C5H8 2.54D-11*EXP(410/TEMP)*0.164 → ISOPAO2

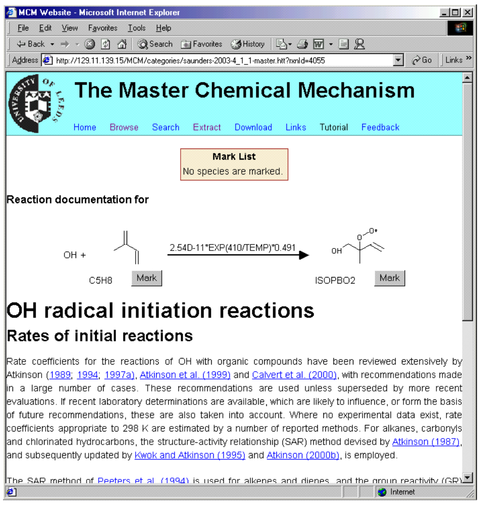
OH + C5H8 2.54D-11*EXP(410/TEMP)*0.491 → ISOPBO2

OH + C5H8 2.54D-11*EXP(410/TEMP)*0.086 → ISOPCO2

- Reaction source information
- Add species to Mark List

Figure 6-11: MCMv3.1 Degradation Scheme for Isoprene

To the right of each equation is the "doc" link (see Figure 6-11). This leads to a webpage containing contextual information from the MCM protocols (Jenkin *et al*. 1997a, Saunders *et al*. 2003) on where the rate constants and branching ratios come from or how they were calculated (from a suitable structure activity relationship) as shown in Figure 6-12.



Mark List
No species are marked.

Reaction documentation for

OH + C5H8 2.54D-11*EXP(410/TEMP)*0.491 → ISOPBO2

OH radical initiation reactions

Rates of initial reactions

Rate coefficients for the reactions of OH with organic compounds have been reviewed extensively by Atkinson (1989; 1994; 1997a), Atkinson et al. (1999) and Calvert et al. (2000), with recommendations made in a large number of cases. These recommendations are used unless superseded by more recent evaluations. If recent laboratory determinations are available, which are likely to influence, or form the basis of future recommendations, these are also taken into account. Where no experimental data exist, rate coefficients appropriate to 298 K are estimated by a number of reported methods. For alkanes, carbonyls and chlorinated hydrocarbons, the structure-activity relationship (SAR) method devised by Atkinson (1987), and subsequently updated by Kwok and Atkinson (1995) and Atkinson (2000b), is employed.

The SAR method of Peeters et al. (1994) is used for alkenes and dienes, and the group reactivity (GR)

- Information based on Protocol papers
- Hyperlinked citations

Figure 6-12: Contextual Information on Reaction of Interest.

The protocol web pages are linked to a central citations database which contains a list of references complete with abstract (where available). Figure 6-13 shows a flow diagram breakdown of the MCM by reaction category along with the protocol section references used to construct the contextual web pages.

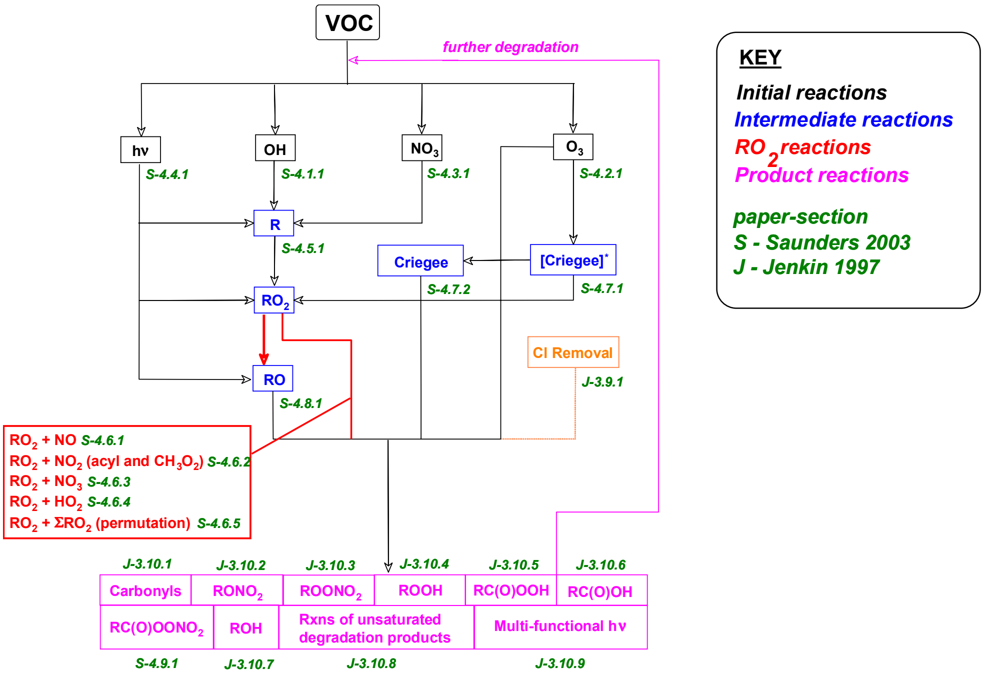
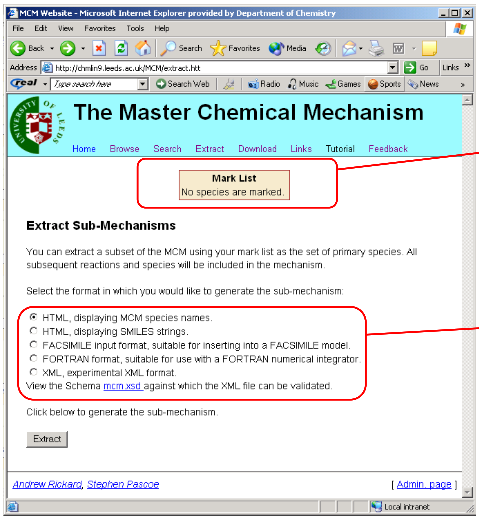


Figure 6-13: Flow Chart showing the Major MCM reaction Categories considered in the MCM Protocols



Address: http://chmlin9.leeds.ac.uk/MCM/extract.htt

The Master Chemical Mechanism

Mark List
No species are marked.

Extract Sub-Mechanisms

You can extract a subset of the MCM using your mark list as the set of primary species. All subsequent reactions and species will be included in the mechanism.

Select the format in which you would like to generate the sub-mechanism:

● HTML, displaying MCM species names.
○ HTML, displaying SMILES strings.
○ FACSIMILE input format, suitable for inserting into a FACSIMILE model.
○ FORTRAN format, suitable for use with a FORTRAN numerical integrator.
○ XML, experimental XML format.
View the Schema mcm.xsd against which the XML file can be validated.

Click below to generate the sub-mechanism.

Andrew Rickard, Stephen Pascoe [Admin. page]

- Use Mark List as primary species
- Choose output format
  - *HTML*
  - *FACSIMILE*
  - *FORTRAN*
  - *XML*

Figure 6-14: The MCMv3.1 *Extract* Tool and Output Options.

As already mentioned the new *Extract* web-tool can extract complete subset mechanisms of the MCMv3.1 for the species listed in the *Mark list*. The MCM is primarily set up for use with the FACSIMILE integrator. In order to encourage the MCM's wider use within the modelling community several extraction output formats and options are now available as shown in Figure 6-14 and listed below:

(i) The FACSIMILE output has been improved by additionally including a list of species variables and a peroxy radical summation list so that the mechanism can be more easily integrated into a FACSIMILE box model.

(ii) A FORTRAN subset extractor option is available which directly interprets the material retrieved from the database by the subset extractor and produces the files needed to run the subset with a FORTRAN solver. The reactions are produced in a numerical format which can be easily read into the user's own numerical integrator. Details of rate coefficients for each reaction are also output in a FORTRAN subroutine which includes all the expressions for the calculation of the complex rate coefficients and photolysis rates. A further FORTRAN subroutine is output which can be used to calculate the right hand side of the rate equations of the subset.

A converter which will allow users to convert their own mechanisms from a standard FACSIMILE format to FORTRAN format is in the final developmental stages and will shortly be available on the website. This will allow the user to generate all the data files described above for any existing FACSIMILE file. This code only extracts the reaction structure from the file, it is then up to the user to adapt the output files to allow simulation of the required conditions.

(iii) XML version of the subsets can also be extracted. This extractor has been updated so that subsets are accurately produced in full in a developmental XML format. Work is continuing to develop the most appropriate and useful design for the XML schema and the properties of Chemical Markup Language (CML) are being examined to understand the ways in which XML is currently used to represent chemistry. This on-going research will lead to the production of a simple but flexible method by which extracted subsets can be displayed and analysed.

Both FORTRAN and XML formats are more robust than FACSIMILE and are more future proof. Complete FACSIMILE MCMv3.1 box models are available in the “Download” section of the website in both PC and UNIX versions. A new mailing list option has been added to the site in order that users can give feedback on the MCMv3.1 and the site, report errors and receive regular updates.

6.2.2 Mechanism Reduction using the CRI mechanism

There is also on-going work developing techniques which can be used to generate mechanisms of reduced dimension in a more automatic fashion (Whitehouse *et al.* 2004a, 2004b). In particular work is in progress using the CRI mechanism (“CRIMECH”, see Section 6.1.2 earlier) to create a lower dimension mechanism using the automatic lumping of species with similar lifetimes. Groups of species which have the potential to be successful lumps can be identified using an algorithm based on the type of reaction rates. CRIMECH is an ideal candidate for the application of this due to the large numbers of identical reaction rates. A preliminary investigation using a subset of CRIMECH has led to a 70 % reduction in the number of species in the mechanism. This work will be continued using the full mechanism.

6.2.3 Under the Hood: New Design and Interactive Database

Fundamentally important to the new website design/operation was the conversion of the central MCM database (where the basic reaction and species information is stored) to just one MySQL integrated and interactive database on the web server. The online MySQL database essentially consists of three tables containing information on the species, reactions and generic rate parameters, from which the website representation of the MCMv3.1 is constructed. The updating and maintenance of the MySQL database is facilitated *via* ODBC (open database connectivity) through the usual Access/Accord front end. A simple flow chart illustrating the connectivity between the online and offline central MCM databases is shown in Figure 6-15.

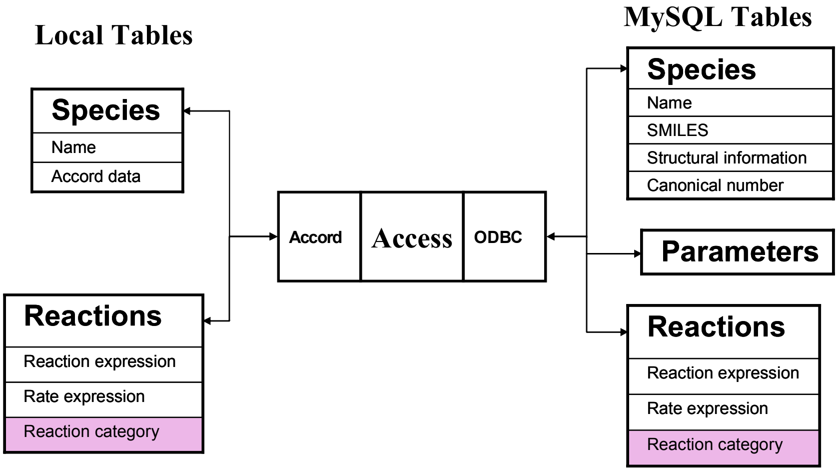


Figure 6-15: Flow Chart for the Central MCM Database.

Accord structural information stored in the local species table is converted and stored as Cartesian coordinates in the online MySQL table. Programs embedded within the MCM website then use this information to construct the reactant and product structures when called upon and these images are then stored in a cache file for future use. The unique conical numbers (derived from the structural information) and SMILES string information in the MySQL species table are used by the website for efficient searching of the MCM database. The reaction category in the local and MySQL reactions tables store the web links to pages containing contextual information on each reaction (*e.g.* Figure 6). The inner workings of the new website are summarised in Figure 6-16.

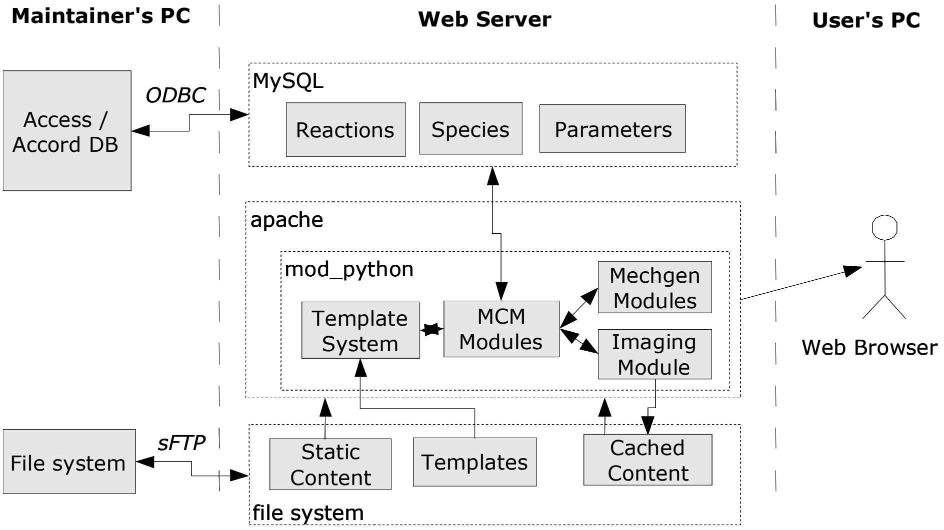


Figure 6-16: Design Layout of the new MCM Website

For future mechanism development new reactions and updated rate data will be added to an offline development version of the database in order to test self-consistency prior to addition to an offline "master" database. This master database will be an identical mirror of the online MySQL version and would serve as a back up facility. The new mechanisms and updated data will be transferred to the online database approximately every 6 months and information regarding the changes documented and made available on the website.

6.2.4 Future and Ongoing Work

The MCM and its website will continue to be developed, tested and validated. Highlighted below are two directions of work that are currently underway:

- A substantial review of literature cross-section and quantum yield data is currently underway in order to update the calculation of the various photo-dissociation coefficients for inorganic and organic species in the MCM. This will be carried out using the discrete ordinate radiative transfer models *TUV* (Madronich *et al.* 1998) and *PHOTOL* (Jenkin *et al.* 1997b), which is used in the OSRM. New calculations will be compared and contrasted to the old calculations and parameterisations. It is hoped that links to the latest versions of TUV and PHOTOL can be added to the MCM website (along with instructions for use if necessary) enabling the user to calculate their own photolysis rates under a variety of atmospheric conditions.

- It is also proposed to take the addition of contextual information a step further by developing the MCM into a more comprehensive kinetic database. This database would comprise literature based channel branching ratios and rate constant citations for all the reactions incorporated in the MCM, along with estimations of their uncertainties. This large database will be linked directly to the MCM website. This new facility would give the MCM an extra dimension by providing an extremely useful reference tool for the user and subject the MCM to a wider user group. It is an essential element for the assessment of model uncertainty. The research proposed fits well within the auspices of the Process Informatics Model (PrIMe) initiative (www.me.berkeley.edu/prime/) in the United States whose objectives focus more on combustion chemistry. PrIMe is a cooperative activity aimed at the development of predictive reaction models for the combustion community. This work will require a significant amount of effort and is not covered in the DEFRA remit for the MCM development and will be funded from other sources.

An MCM workshop has been organised for December 2004 in order for users of the MCM to present and discuss the results of their research and for expert group discussion of future developments and directions of the MCM and website.

6.3 MULTI-DAY REACTIVITY SCALES ESTIMATED WITH THE MASTER CHEMICAL MECHANISM

6.3.1 Model Set-up

In this study, an air parcel was followed as it travelled on an easterly wind from its trajectory release point in Austria across Europe to its arrival point at the England-Wales border. The air parcel picked up emissions of NO_x, SO_2, CO, methane, isoprene and 120 man-made organic compounds en route. The chemical reactions occurring in the air parcel were represented using the Master Chemical Mechanism v3.0. In the base case model experiment, ozone concentrations steadily built up from 50 ppb at the trajectory release point to 90 ppb at the arrival point.

After the air parcel had been travelling for 69 hours, whilst the air parcel was over Northern France, a spike or pulse of a single organic compound was injected into the air parcel by increasing the emission rate of that organic compound over a one-hour period. The spike was exactly the same magnitude for each organic compound, namely 2.3 ppb. The chosen size of the spike was quite arbitrary, being small enough not to disturb significantly the photochemistry in the air parcel but large enough to produce detectable changes in the chemistry over and above the noise in the model. All of the experimental results were generated by subtracting the species concentrations from each of the spiked experiments from those in the base case experiment.

6.3.2 Mechanism for Second-day Ozone Formation for Alkenes and Carbonyl Compounds

From work carried out during the first year of this project, two mechanisms have been established for VOCs to produce ozone during subsequent days following their emission. The first mechanism involved the carry over into subsequent days of any unreacted VOC. This is clearly the most important mechanism for ketones, such as acetone, that are of low reactivity. The second mechanism involved the formation of peroxyacylnitrates during the first day. Such species may be an important source of ozone formation on the second day because they can survive the first night and decompose to NO_x and peroxy radicals during the second day thereby stimulating additional ozone formation. This appears to be an important route for second day ozone formation with many of the alkenes, aldehydes and ketones.

From plots of second day ozone production vs. night-time PAN concentrations, it is apparent that the above mechanisms are not the only mechanisms that drive second day ozone production. A further mechanism has been investigated involving the formation of aldehydes and ketones during the first day and their survival through the first night to stimulate second day ozone production. To this end, Table 6-2 presents the night-time concentrations of a selection of aldehyde and ketone products following the emission pulses of a selection of highly reactive olefins.

Table 6-2: The Concentrations (in ppb) of a Selection of Aldehydes and Ketones during the First Night following the Emission of a Pulse of a Selection of Different Olefins.

Olefins	HCHO	CH_3CHO	C_2H_5CHO	i-C_3H_7CHO	Acetone	MEK
Ethylene	0.41	-0.01	0.00	0.00	0.01	0.00
Propylene	0.25	0.04	0.00	0.00	0.00	0.00
but-1-ene	0.18	0.15	0.01	0.00	0.00	0.00
cis but-2-ene	0.22	0.02	0.00	0.00	0.01	0.00
trans but-2-ene	0.21	0.01	0.00	0.00	0.01	0.01
cis pent-2-ene	0.20	0.09	0.00	0.00	0.01	0.00
trans pent-2-ene	0.20	0.09	0.00	0.00	0.01	0.00
pent-1-ene	0.14	0.14	0.07	0.00	-0.01	0.00
2-methylbut-1-ene	0.11	0.03	0.00	0.00	0.01	0.69
3-methylbut-1-ene	0.04	0.00	0.00	0.00	0.81	0.00
2-methylbut-2-ene	0.08	-0.01	0.00	0.00	0.74	0.01
Butylene	0.04	-0.01	0.00	0.00	1.19	0.00

Following the emission of a pulse of ethylene, 0.41 ppb of formaldehyde survives during the first night to stimulate ozone formation on the second day. Because of the chemical structure of ethylene, no production of the other aldehydes and ketones is to be expected and, indeed, none is seen in Table 6-2.

Propylene is more reactive than ethylene and so its oxidation products, formaldehyde and acetaldehyde are produced earlier in the day and hence they have less chance to survive into the first night. But-1-ene is yet more reactive than propylene and virtually none of its C_2H_5CHO product survives into the first night. The major oxidation product of C_2H_5CHO is acetaldehyde and significantly more of the acetaldehyde from but-1-ene oxidation survives into the first night than from propylene. This apparently contradictory results is a consequence of the consecutive nature of the kinetic system which is operating here:

but-1-ene $\Rightarrow C_2H_5CHO \Rightarrow CH_3CHO \Rightarrow HCHO$

The consecutive nature of the kinetic system, delays the production of the subsequent oxidation products and thus enables their survival into the first night.

The influence of the delay mechanism that results from the consecutive nature of the kinetic system is apparent with 1-pentene, see Table 6-2, where it is an important source of night-time formaldehyde, acetaldehyde and propionaldehyde, despite its exceptionally short lifetime.

pent-1-ene $\Rightarrow C_3H_7CHO \Rightarrow C_2H_5CHO \Rightarrow CH_3CHO \Rightarrow HCHO$

For a series of consecutive reactions where, for the sake of simplicity, each species has the same first order removal coefficient, k:

$A \Rightarrow B \Rightarrow C \Rightarrow D \Rightarrow E \Rightarrow F \Rightarrow$

Then it can be shown that the time of the concentration maximum of B following the emission pulse of A, occurs after 1/k. The concentration maximum of C occurs after 2/k, that of D after 3/k and so on. So the maximum concentrations are delayed by the consecutive reaction system, despite each member being highly reactive.

The rapid reactions of olefins and their aldehydehyde oxidation products in a consecutive kinetic system, provides an important mechanism for short-chain aldehydes to survive through to the second day to stimulate ozone production. This second day ozone production mechanism is thus an important feature of the Master Chemical Mechanism and is a consequence of its explicit representation of the degradation pathways for olefins, aldehydes and ketones.

In all, three mechanisms have been found to account for ozone formation on subsequent days, following their emissions. These are:

a. the carry over of unreacted VOCs,
b. the formation of peroxyacetylnitrates
c. the consecutive reactions of aldehyde formation and degradation.

From a study of the chemical mechanisms used in most policy models, EMEP included, it is likely that the multi-day formation of ozone from alkenes and carbonyl compounds is underestimated because of the simplifications and approximations made in the compression of the chemical mechanisms.

A write-up describing the work has been accepted for publication in Atmospheric Environment.

6.3.3 Multi-day Ozone Formation from Alkanes and Aromatic VOCs

To complete the analysis of multi-day ozone formation, the experimental setup was changed and the MCM v3.1 was implemented with all other aspects remaining unchanged.

The left-hand panel of Figure 6-17 shows how, in response to the spike, each alkane stimulated additional ozone production on the first and second day. Ozone productivities for the short chain alkanes, ethane and propane, are low because of their slow reactions with OH radicals and hence they are positioned close to the origin of the plot in Figure 6-17. Neopentane is found close to them appearing to be unreactive because it contains only primary C-H bonds. With increasing carbon chain length and hence increasing numbers of secondary C-H bonds, OH reactivity increases steadily through n-butane and n-pentane and together with it, both first and second day's ozone productivities.

A change in behaviour sets in for n-hexane, n-heptane, n-octane and upwards of n-octane, with decreasing first day ozone productivities and constant second day ozone productivities. The mechanistic interpretation of this behaviour is the subject of further work.

The right-hand panel of Figure 6-17 shows how, in response to the spike, each aromatic compound stimulated additional ozone production on the first and second day using MCMv3.1. For the large part, this figure shows monotonically increasing trends in first and second day ozone productivities. This behaviour is markedly different to the corresponding plot found with the MCMv3.0 in which anomalous behaviour was found for p-xylene, ethylbenzene, propylbenzene and i-propylbenzene. All four compounds now lie in the same region of the plot as the remaining aromatic compounds (see Figure 6-17). This confirms what had been suspected, that there were problems in the detailed mechanisms for these four aromatic species in MCMv3.0. Further work is now planned to understand the mechanisms that control first and second day ozone production following the emission of a spike in each aromatic compound.

6.4 MODELLING THE AMBIENT DISTRIBUTION OF ORGANIC COMPOUNDS USING THE PTM

6.4.1 Introduction

Modelling studies using detailed emitted VOC speciation and comprehensive descriptions of the chemistry of VOC degradation are able to quantify the roles played by individual VOC in atmospheric chemistry generally, and in ozone formation in particular. Furthermore, they allow the prediction of the patterns and structures of oxidised products, such as simple and multifunctional carbonyls, thereby allowing a much more detailed examination of atmospheric chemical mechanisms.

In the present section, the results of detailed simulations of the ambient distributions of organic compounds are described. The photochemical trajectory (PTM) containing speciated emissions of 124 non-methane VOC (based on the NAEI), and a comprehensive description of the chemistry of VOC degradation (provide by MCM v3.1 and the CRI mechanism), has been used to simulate the chemical evolution of boundary layer air masses arriving at a field campaign site in the southern UK, during the August 2003 photochemical pollution episode. The simulated concentrations and distributions of organic compounds at the arrival location (Writtle College, near Chelmsford) are compared with observations of a series of hydrocarbons and selected carbonyl compounds, which were measured as part of the first campaign of the Tropospheric Organic Chemistry Experiment (TORCH). The organic compounds were measured using GC-FID and multidimensional GC methods by the University of York, as reported by Utembe *et al.* [2004]. The results of the model-measurement comparison are discussed in terms of the magnitude and speciation of emitted VOC, the distribution of simple and multifunctional carbonyls formed as degradation products, and the impacts of these carbonyls on free radical formation.

6.4.2 Speciation and Temporal Variation of non-methane VOC Emissions

The speciation of the emitted anthropogenic VOC was based on the NAEI, which identifies ca. 650 individual species. To allow coupling with the chemical mechanisms, the speciation was represented by the 124 species identified in Figure 6-18, which collectively account for *ca.* 70 % of the NAEI emissions, by mass. The outstanding > 500 species, which each makes a small contribution to the remaining 30 %, were emitted in the form of appropriate surrogates, which were assigned on the basis of chemical class and reactivity. For example, the longer chain n-alkanes $\geq C_8$ were generally used to represent alkanes isomers of the same carbon number, dodecane was used to represent all alkanes $\geq C_{12}$, and cyclohexane was used to represent all cycloalkanes. Biogenic VOC were emitted as isoprene (50 %) and the monoterpenes α-pinene (30 %) and β-pinene (20 %).

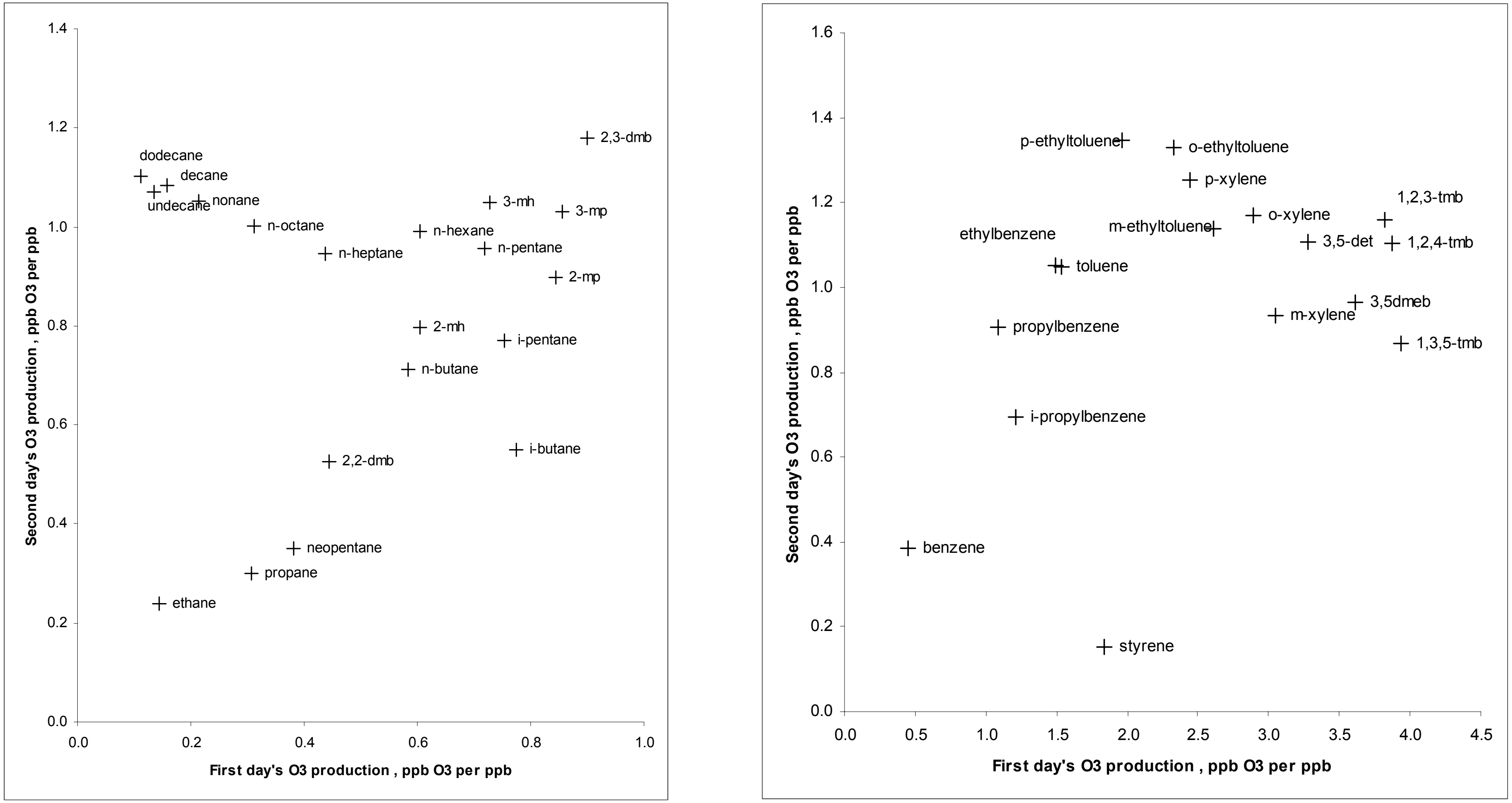


Figure 6-17: The First and Second Day's Additional Ozone Production following the Emission of a Spike of each Alkane (Left-hand Panel) and of each Aromatic (Right-hand Panel).

The temporal variations applied to the emissions of VOC and NO_X were based on those estimated for the UK by Jenkin *et al.* [2000]. In that study, single representative profiles describing the seasonal, day-of-week and hour-of-day variations in emissions were assigned to each of over 180 source categories included in the NAEI. Where possible, the profiles were based on available temporally resolved data (*e.g.*, fuel consumption, electricity generation, traffic volume statistics), which can be related to emissions. The temporal variation of biogenic VOCs takes account of typical seasonal and diurnal variations in photosynthetically active radiation (PAR) and temperature, and were determined using the methodology of Guenther *et al.* [1994] as also discussed for Europe by Simpson *et al.* [1995].

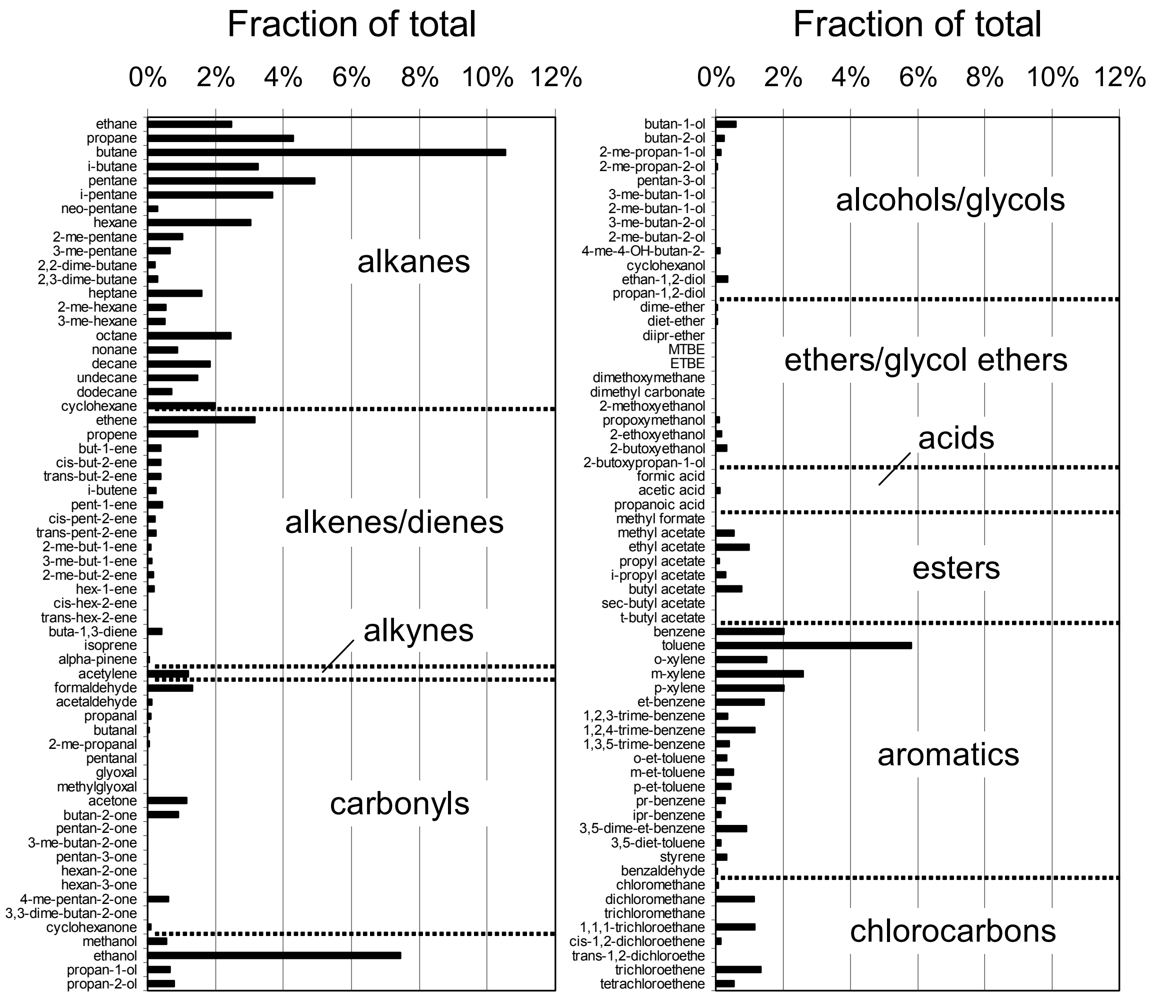


Figure 6-18: Speciation of Anthropogenic non-methane VOC Emissions used in PTM (see text).

6.4.3 Simulations of Emitted Hydrocarbons using the CRI Mechanism

The PTM-CRI was used to simulate the chemical development of air parcels arriving at the Writtle site at six-hourly resolution for the entire TORCH-1 campaign. Comparisons of the simulated and observed concentrations of a series of 34 emitted hydrocarbons are presented in Figures 3-5. This provides a test of a combination of aspects of the model, i.e. the emissions speciation of the hydrocarbons, their lifetimes under the prevailing conditions and the quantity collected along the applied trajectory paths. The simulated concentrations generally recreate the overall features of the campaign (Figure 6-19 and Figure 6-20). The correlation of the campaign mean concentrations (Figure 6-20) also demonstrates that the simulated concentrations of the majority of hydrocarbons were within a factor of *ca.* 2 of those observed. The model generally provides a good description of the observed concentrations of anthropogenic hydrocarbons. As shown in Figure 6-19 and Figure 6-21, the concentration variation and mean concentrations of aromatic hydrocarbons, buta-1,3-diene and acetylene are in very good agreement with observations. The concentrations of C_4 alkanes (butane and methylpropane) are also reasonably well described, although the smaller alkanes (ethane and propane) tend to be slightly underestimated by the model. The comparison for C_5-C_7 aliphatic alkanes tends to show scatter around the 1:1 line, although the simulated and observed total

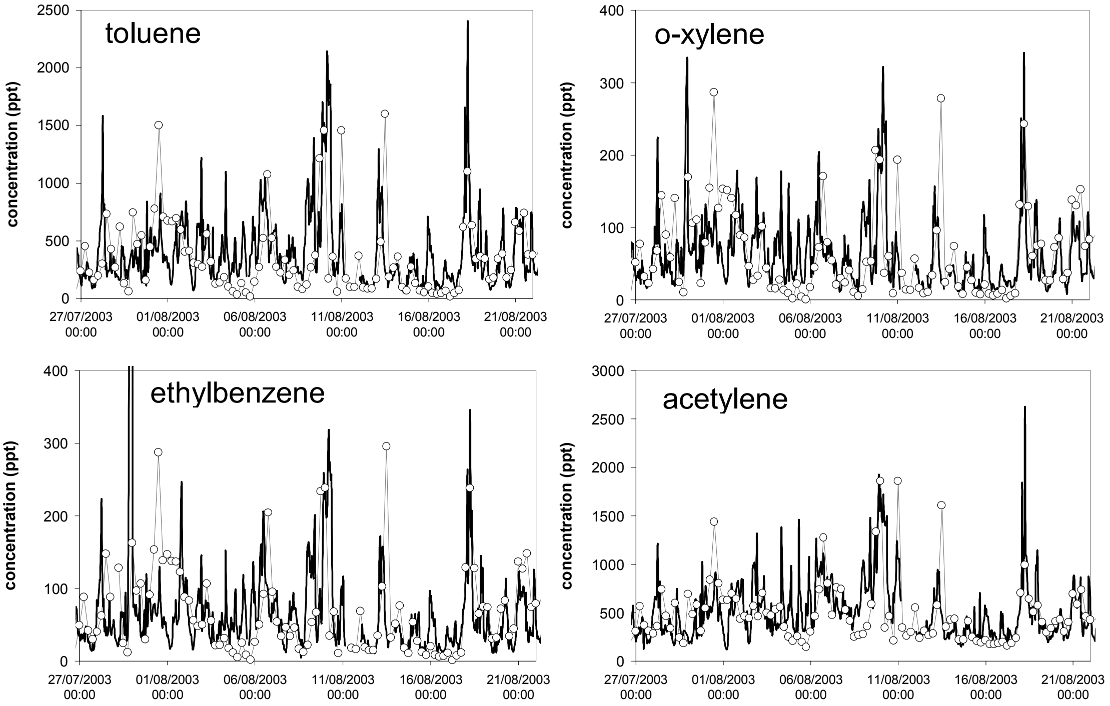


Figure 6-19: Comparison of Observed and Simulated Concentrations of Selected Aromatic Hydrocarbons and Acetylene. The Heavy Black Lines represent the Observed Concentrations. The Points are the Simulated Concentrations at Six-hourly Intervals.

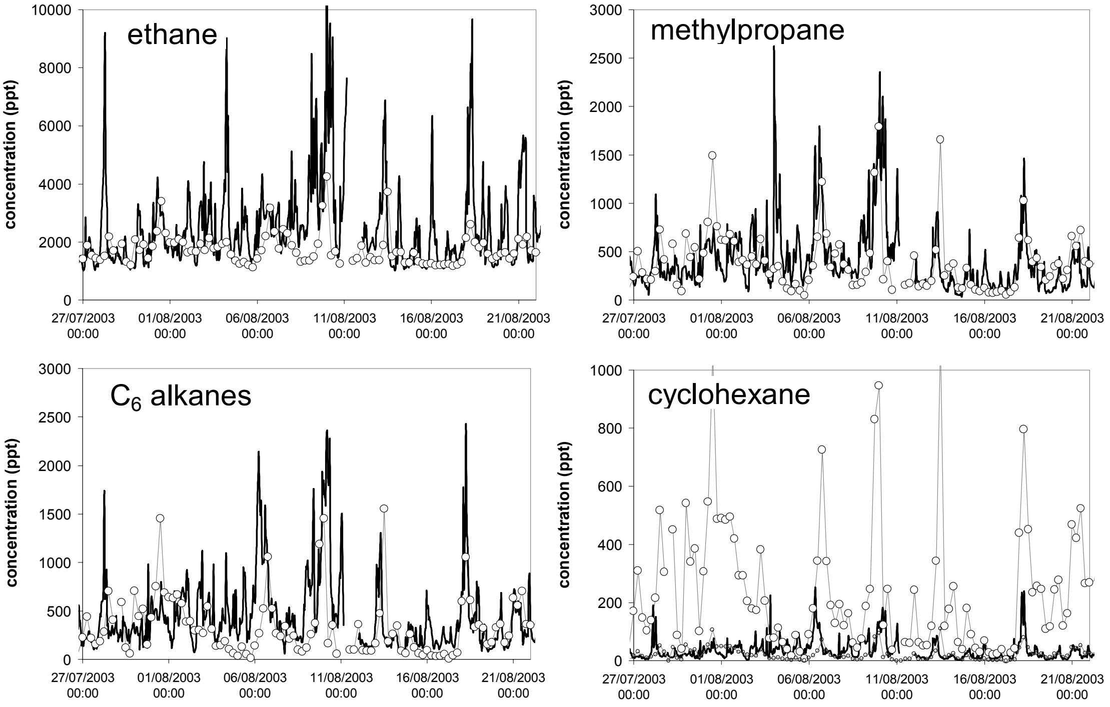


Figure 6-20: Comparison of Observed and Simulated Concentrations of Selected Alkanes. C_6-Alkanes are Hexane, Methylpentane Isomers and Dimethylbutane Isomers. The Heavy Black Lines represent the Observed Concentrations. The Points are the Simulated Concentrations at Six-hourly Intervals. The Smaller Points on the Cyclohexane plot are 10% of the Simulated Concentrations (see text).

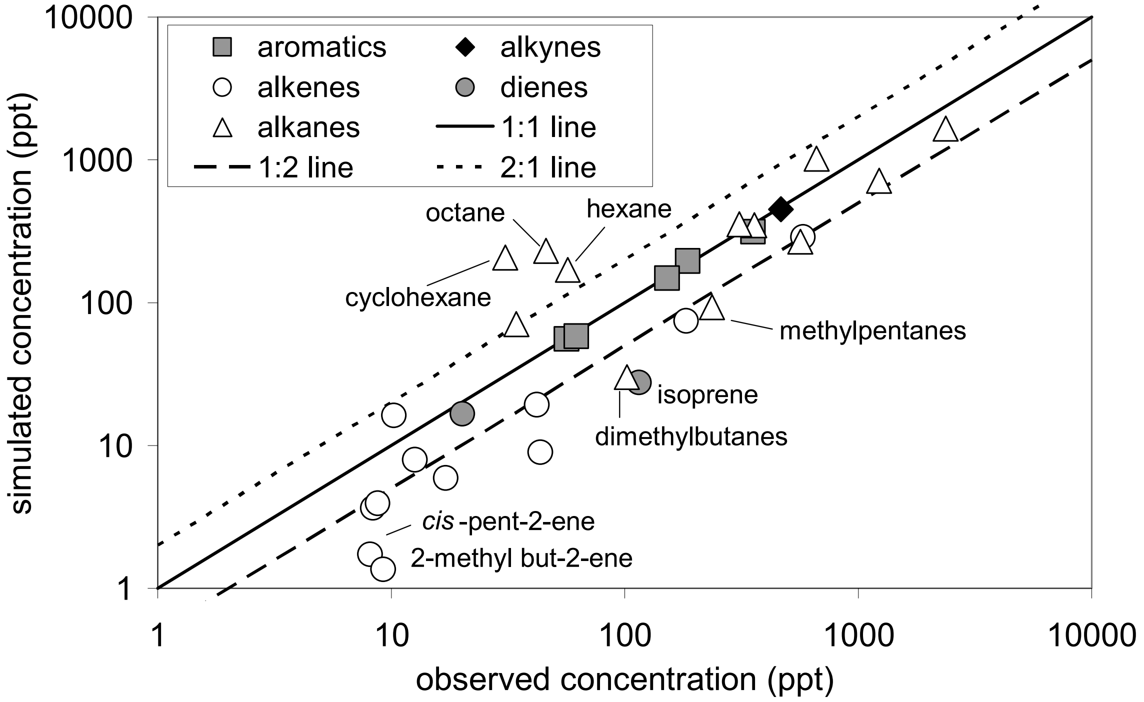


Figure 6-21: Comparison of Observed and Simulated Campaign Mean Concentrations of 34 Emitted Hydrocarbons.

concentrations for a given carbon number are generally in reasonable agreement. For example, Figure 6-21 shows that the mean concentration of hexane is overestimated by the model, whereas the concentrations of the methylpentane and dimethylbutane isomers are underestimated. As shown in Figure 6-20, however, the concentration sum of these C_6 alkanes agrees reasonably well with the observations. It is likely that the inventory speciation within a given carbon number tends to overestimate the contribution of the n-alkanes, since information supplied to inventory compilers often includes nominal components such as 'hexane', when it is probable that a mixture of hexane isomers is actually emitted.

The simulated concentrations of longer-chain alkanes (*e.g.*, octane) and cyclohexane are typically overestimated by the model, mainly due to these species being used as surrogates for other long-chain alkanes which are not included in the chemical mechanisms. This is demonstrated for cyclohexane (see Figure 6-20), which, as indicated above, is used as a surrogate for all cycloalkanes in the NAEI inventory, even though it only accounts for *ca.* 10 % of cycloalkane emissions. Consequently, the simulated concentrations are about an order of magnitude greater than those observed.

The simulated concentrations of the alkenes are typically lower than those observed, particularly for some of the larger species (*e.g.*, *cis*-2-pentene and 2-methy-but-2-ene), with a similar effect also observed for isoprene (see Figure 6-21). This may be indicative of under representation in the emissions speciation. However, the larger alkenes and isoprene are generally the most reactive hydrocarbons, and are therefore most prone to underestimation if there are sources comparatively local to the measurement site. The local representation of emissions in the model is based on the average over the 10 km square containing the measurement site, and the simulated concentrations also assume rapid vertical mixing within the boundary layer. Because the lifetimes of the larger alkenes and isoprene are typically of the order of 10-30 minutes under the prevailing daytime conditions, the ambient concentrations would be expected to show horizontal and vertical variations which may not be captured by the model. This would lead to a bias towards underestimation by the model if local sources are greater than the 10 x 10 km average, and a bias toward overestimation if local sources are below the average.

The extent of under simulation for isoprene was found to be greatest (*i.e.*, typically a factor of ca. 10) during the most severe period of the photochemical episode (6th-11th August), when the highest temperatures (> 30 °C) were also observed. This suggests that the representation of biogenic emissions, based on mean monthly and diurnal temperatures, may be inadequate, and work is currently in progress to implement biogenic emissions based on trajectory-specific meteorological conditions. The discrepancies between simulated and observed concentrations of the larger alkenes also tend to be greater during the high temperature period, suggesting that there could be a biogenic input of these hydrocarbons. Support for this is provided by the measurements of Klemp *et al.* [1997] at Schauinsland, Germany. They observed evidence for biogenic sources of larger alkenes (specifically the butene isomers in their study), which displayed a clear dependence of temperature.

6.4.4 Simulations of Carbonyl Distributions with the MCM

The PTM-MCM v3.1 was used to simulate the detailed chemical composition of the air parcels travelling along five case study trajectories, allowing calculated concentration distributions of organic species which are produced by chemical processing of the emitted VOC. The resultant information for carbonyl compounds at the arrival point is shown in Table 6-3.

Simulated concentration data for ca. 1250 compounds containing the carbonyl functionality were obtained. This includes both simple carbonyls (i.e. aldehydes and ketones), and carbonyls containing one or more additional functional groups (*e.g.*, carbonyl; hydroxyl). The simulated concentrations of 61 selected aldehydes, ketones and bifunctional carbonyls for each of the five case study trajectories are given in Table 6-3. These species collectively account for between 88 and 91 % of the simulated total molecular concentrations of carbonyl species. Additional small contributions were made by species such methacrolein, methylvinyl ketone, pinonaldehyde and nopinone, which are derived from the biogenic precursors isoprene, α̃-pinene and β̃-pinene. The balance was made up of almost 1200 carbonyl species individually making very small contributions, but collectively accounting for up to ca. 10 % of the total carbonyl concentration.

The simulated concentrations of the carbonyl compounds are dominated by their secondary formation from the degradation of emitted VOC, with primary emissions of the limited number of carbonyls (Figure 6-18) making only very small contributions to their concentrations at the arrival point. Accordingly, the total carbonyl concentrations given in Table 6-3 broadly correlate with the integrated VOC emissions along the corresponding trajectory. The simulated distributions for each class of carbonyl compound shows a general decrease in concentration as carbon number increases, consistent with a progressively smaller number of precursor VOC being available: and also because larger carbonyls are generally degraded to form smaller ones, as illustrated for aldehydes by Derwent *et al.* (2004).

The results of the simulations are therefore in broad agreement with reported trends in ambient distributions of carbonyl compounds with size [*e.g.*, Andreini *et al.*, 2000; Christensen *et al.*, 2000; Possanzini *et al.*, 2000; Grosjean *et al.*, 2002; Bakeas *et al.*, 2003]. Figure 6-22 shows a comparison of the simulated concentrations for seven aldehyde and ketone species with observed concentrations measured using the GCxGC technique, for the arrival hour of four of the case study trajectories. It is apparent that the relative concentration variation for aldehydes and ketones shows a good degree of consistency, although there are systematic discrepancies in the absolute concentrations.

6.4.5 Conclusions

The comparison of the simulated and observed distributions of 34 emitted hydrocarbons provides support for the magnitude and applied emissions speciation of anthropogenic hydrocarbons (based primarily on the NAEI), but is indicative of an under representation of the input of biogenic hydrocarbons, particularly at elevated temperatures. Simulations of the detailed distribution of ca. 1250 carbonyl compounds, formed primarily from the degradation of 124 emitted VOC, focus on 61 aldehydes, ketones, and bifunctional carbonyls which collectively account for ca. 90 % of the simulated total molar concentration of carbonyls. The simulated distributions of four aldehydes and three ketones correlated well with observations for each class of compound. However, the simulated concentrations of the aldehydes were systematically lower than those observed, whereas those of the higher ketones were systematically higher.

Table 6-3: Simulated Concentrations (in ppt by volume)[a] of Selected Carbonyls at Arrival Point for 5 Case Study Trajectories (2nd, 4th, 6th, 7th and 31st August 2003, respectively).

	Trajectory number				
	1	2	3	4	5
Total carbonyl species[b]	**11,321**	**3,788**	**13,127**	**9,432**	**6,573**
Simple aldehydes ($\leq C_6$)	**4,072 (36.0 %)**	**1,540 (40.7 %)**	**6,150 (46.9 %)**	**3,347 (33.9 %)**	**3,116 (47.4 %)**
formaldehyde	2,988 (26.4 %)	1,283 (33.9 %)	3,852 (29.3 %)	2,480 (26.3 %)	2,205 (34.6 %)
acetaldehyde	901 (7.96 %)	216 (5.71 %)	1,773 (13.5 %)	737 (7.81 %)	729 (11.1 %)
propanal	138 (1.22 %)	28 (0.74 %)	413 (3.15 %)	90 (0.95 %)	143 (2.18 %)
butanal	20 (0.17 %)	6 (0.15 %)	50 (0.38 %)	17 (0.18 %)	17 (0.27 %)
2-methylpropanal	9 (0.08 %)	2 (0.06 %)	21 (0.16 %)	7 (0.08 %)	8 (0.12 %)
pentanal	4 (0.03 %)	2 (0.05 %)	5 (0.04 %)	5 (0.05 %)	2 (0.03 %)
2-methylbutanal	1 (0.01 %)	-	4 (0.03 %)	2 (0.02 %)	2 (0.03 %)
hexanal	6 (0.05 %)	2 (0.05 %)	7 (0.06 %)	6 (0.06 %)	3 (0.05 %)
acrolein	5 (0.05 %)	1 (0.03 %)	25 (0.19 %)	3 (0.04 %)	7 (0.11 %)
Simple ketones ($\leq C_6$)	**5,139 (45.4 %)**	**1,728 (45.6 %)**	**4,467 (34.0 %)**	**4,544 (48.2 %)**	**2,211 (33.6 %)**
acetone	4,371 (38.6 %)	1,340 (35.4 %)	3,118 (23.8 %)	3,374 (35.8 %)	1717 (26.2 %)
butanone	436 (3.85 %)	278 (7.35 %)	793 (6.04 %)	745 (7.89 %)	273 (4.16 %)
pentan-2-one	21 (0.19 %)	11 (0.28 %)	33 (0.25 %)	30 (0.32 %)	13 (0.20 %)
pentan-3-one	54 (0.48 %)	28 (0.73 %)	89 (0.68 %)	84 (0.89 %)	33 (0.50 %)
3-methyl-butan-2-one	44 (0.39 %)	19 (0.51 %)	71 (0.54 %)	65 (0.69 %)	26 (0.40 %)
hexan-2-one	4 (0.03 %)	2 (0.06 %)	7 (0.05 %)	6 (0.07 %)	2 (0.04 %)
hexan-3-one	12 (0.10 %)	5 (0.13 %)	18 (0.14 %)	15 (0.16 %)	7 (0.11 %)
4-methyl-pentan-2-one	8 (0.07 %)	3 (0.08 %)	35 (0.27 %)	65 (0.69 %)	11 (0.17 %)
3-methyl-pentan-2-one	3 (0.02 %)	1 (0.03 %)	4 (0.03 %)	3 (0.03 %)	2 (0.03 %)
2-methyl-pentan-3-one	6 (0.05 %)	2 (0.06 %)	9 (0.07 %)	7 (0.08 %)	4 (0.06 %)
cyclohexanone [c]	180 (1.59 %)	39 (1.03 %)	290 (2.21 %)	150 (1.58 %)	123 (1.88 %)
Dicarbonyls ($\leq C_6$)	**394 (3.48 %)**	**87 (2.30 %)**	**599 (4.56 %)**	**277 (2.94 %)**	**246 (3.74 %)**
glyoxal	183 (1.62 %)	31 (0.82 %)	219 (1.66 %)	110 (1.17 %)	99 (1.51 %)
methylglyoxal	76 (0.67 %)	14 (0.38 %)	197 (1.50 %)	44 (0.46 %)	65 (0.99 %)
malonaldehyde	34 (0.30 %)	3 (0.08 %)	10 (0.08 %)	11 (0.12 %)	17 (0.26 %)
ethylglyoxal	14 (0.12 %)	5 (0.12 %)	36 (0.27 %)	11 (0.12 %)	11 (0.16 %)
3-oxo-butanal	14 (0.13 %)	4 (0.10 %)	22 (0.16 %)	14 (0.15 %)	9 (0.14 %)
propylglyoxal	1 (0.01 %)	-	1 (0.01 %)	1 (0.01 %)	-
i-propylglyoxal	-	-	1 (0.01 %)	-	-
3-oxo-pentanal	18 (0.16 %)	3 (0.07 %)	27 (0.21 %)	12 (0.12 %)	13 (0.19 %)
4-oxo-pentanal	10 (0.09 %)	2 (0.06 %)	13 (0.10 %)	9 (0.10 %)	6 (0.09 %)
4-oxo-hexanal	7 (0.06 %)	1 (0.04 %)	9 (0.07 %)	6 (0.06 %)	5 (0.07 %)
buta-2,3-dione	4 (0.04 %)	2 (0.05 %)	13 (0.10 %)	4 (0.04 %)	4 (0.05 %)
penta-2,3-dione	-	-	1 (0.01 %)	-	-
penta-2,4-dione	14 (0.12 %)	13 (0.35 %)	23 (0.18 %)	31 (0.33 %)	7 (0.11 %)
hexa-2,4-dione	-	3 (0.07 %)	1 (0.01 %)	-	-
hexa-2,5-dione	19 (0.17 %)	6 (0.16 %)	26 (0.20 %)	24 (0.26 %)	10 (0.16 %)
Hydroxycarbonyls ($\leq C_6$)	**305 (2.69 %)**	**77 (2.03 %)**	**483 (3.68 %)**	**254 (2.69 %)**	**209 (3.18 %)**
glycolaldehyde	92 (0.81 %)	24 (0.64 %)	133 (1.01 %)	78 (0.82 %)	61 (0.93 %)
2-hydroxypropanal	-	-	1 (0.01 %)	1 (0.01 %)	-
3-hydroxypropanal	21 (0.18 %)	5 (0.13 %)	31 (0.24 %)	18 (0.19 %)	15 (0.23 %)
2-hydroxybutanal	1 (0.01 %)	1 (0.02 %)	1 (0.01 %)	2 (0.02 %)	-
3-hydroxybutanal	2 (0.02 %)	1 (0.02 %)	3 (0.03 %)	3 (0.03 %)	1 (0.02 %)
4-hydroxybutanal [d]	14 (0.13 %)	3 (0.09 %)	25 (0.19 %)	13 (0.14 %)	10 (0.16 %)
2-hydroxypentanal	1 (0.01 %)	1 (0.02 %)	1 (0.01 %)	2 (0.02 %)	-
3-hydroxypentanal	1 (0.01 %)	-	1 (0.01 %)	1 (0.01 %)	-
4-hydroxypentanal [d]	10 (0.08 %)	2 (0.06 %)	15 (0.11 %)	8 (0.08 %)	7 (0.11 %)
4-hydroxyhexanal [d]	7 (0.06 %)	1 (0.04 %)	10 (0.07 %)	5 (0.05 %)	5 (0.08 %)
4-hydroxy-4-methylpentanal [d]	3 (0.03 %)	1 (0.01 %)	7 (0.05 %)	2 (0.02 %)	3 (0.04 %)
hydroxyacetone	11 (0.10 %)	7 (0.19 %)	18 (0.13 %)	13 (0.14 %)	8 (0.12 %)
1-hydroxybutan-2-one	4 (0.04 %)	2 (0.06 %)	8 (0.06 %)	7 (0.07 %)	3 (0.05 %)
3-hydroxybutan-2-one	2 (0.02 %)	1 (0.03 %)	4 (0.03 %)	3 (0.03 %)	1 (0.02 %)
4-hydroxybutan-2-one	13 (0.11 %)	5 (0.12 %)	20 (0.15 %)	9 (0.10 %)	9 (0.14 %)
1-hydroxypentan-2-one	1 (0.01 %)	-	1 (0.01 %)	1 (0.01 %)	-
3-hydroxypentan-2-one	-	-	1 (0.01 %)	-	-
5-hydroxypentan-2-one [d]	62 (0.55 %)	12 (0.32 %)	99 (0.76 %)	52 (0.55 %)	42 (0.65 %)
5-hydroxyhexan-2-one [d]	22 (0.19 %)	3 (0.08 %)	37 (0.28 %)	14 (0.14 %)	16 (0.25 %)
6-hydroxyhexan-3-one [d]	27 (0.24 %)	5 (0.12 %)	44 (0.34 %)	19 (0.20 %)	19 (0.29 %)
4-hydroxy-4-methylpentan-2-one [d]	7 (0.06 %)	2 (0.05 %)	16 (0.12 %)	-	6 (0.09 %)
5-hydroxy-3-methylpentan-2-one	4 (0.04 %)	1 (0.02 %)	7 (0.06 %)	3 (0.03 %)	3 (0.05 %)
Aromatic aldehydes ($\leq C_8$)	**21 (0.19 %)**	**26 (0.68 %)**	**53 (0.40 %)**	**12 (0.13 %)**	**20 (0.30 %)**
benzaldehyde	14 (0.12 %)	26 (0.68 %)	36 (0.28 %)	8 (0.09 %)	13 (0.20 %)
2-methylbenzaldehyde	1 (0.01 %)	-	3 (0.02 %)	1 (0.01 %)	1 (0.02 %)
3-methylbenzaldehyde	2 (0.02 %)	-	5 (0.04 %)	1 (0.01 %)	2 (0.03 %)
4-methylbenzaldehyde	4 (0.04 %)	-	9 (0.07 %)	2 (0.02 %)	4 (0.05 %)

Notes: (a) Concentrations are rounded to the nearest ppt. A missing entry indicates a sub-ppt concentration. Percentage contribution to total (rounded to nearest 0.01% for less abundant species), is given in brackets. (b) Concentration sum of species containing one or more carbonyl groups. (c) Concentrations for cyclohexanone should be regarded as indicative of total anthropogenically-derived cycloalkanone concentrations. (d) Concentrations for 1,4-hydroxycarbonyls notionally include contributions from isomeric cyclic hemiacetals (see text)

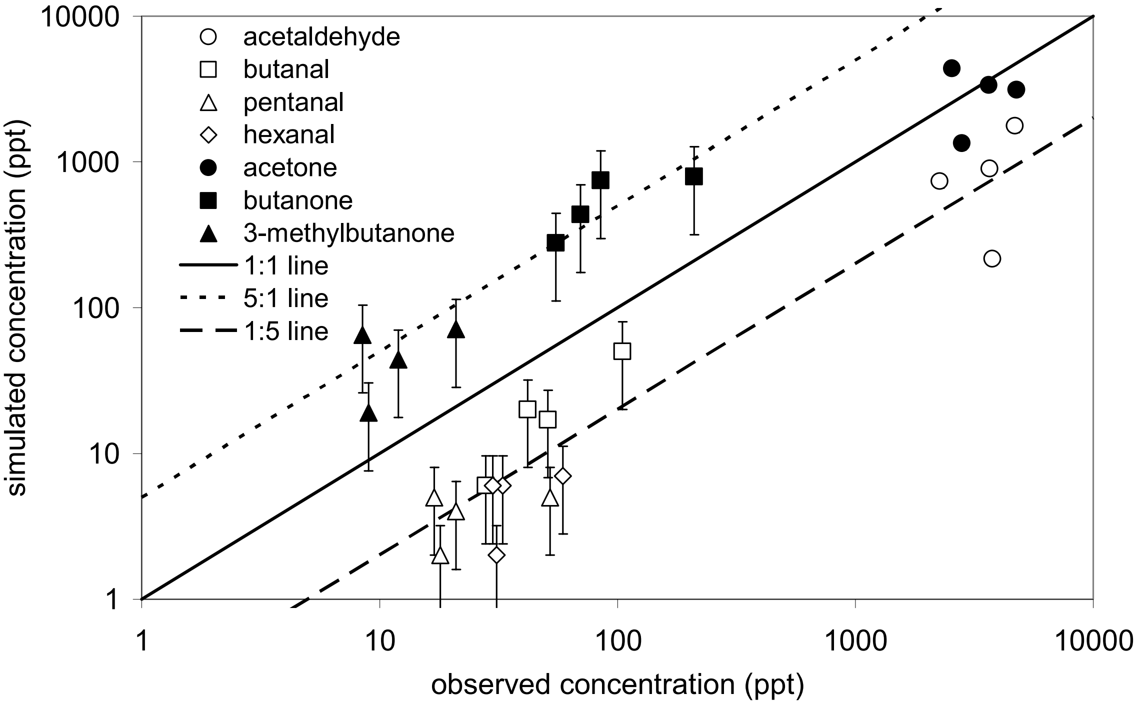


Figure 6-22: Comparison of Observed and Simulated Concentrations of 7 Carbonyls for the Arrival Hour of Trajectories 1-4. Open symbols are Aldehydes; Filled Symbols are Ketones.

6.5 IMPLEMENTATION OF THE DEPARTMENT'S VOC PROJECTIONS

6.5.1 Updating the UK PTM to 2004 Version

The UK PTM model equipped with the Master Chemical Mechanism v3.1 has been downloaded from the MCM website. Some halocarbon species have been removed and some additional emitted VOC species have been created. Altogether this 2004 version of the UK PTM model has 135 emitted non-methane VOC species in the following groups:

- 23 alcohols and glycols
- 11 aldehydes, dicarbonyls and unsaturated carbonyls
- 21 alkanes and cycloalkanes
- 18 alkenes and dialkenes
- 1 alkyne
- 18 aromatics
- 8 chlorinated hydrocarbons
- 8 esters
- 10 ethers and glycol ethers
- 10 ketones
- 2 monoterpenes
- 3 organic acids
- 2 oxygenated compounds.

The NAEI speciated VOC inventories for the years 2000 through to 2020 have been provided by Neil Passant of netcen. These inventories provide emissions for 589 individual species, arising from 235 separate emission source categories. The 2004 version of the UK PTM treats 112 VOC species out of the 589 species in the NAEI inventory, responsible for 1,126 thousand tonnes per year out of the total man-made VOC emission of 1,420 thousand tonnes per year, that is 79.3 % of the total mass emission.

The 2004 version of the UK PTM therefore is unable to account for 20.6 % of the total mass emission in the NAEI inventory. Of this unaccounted for material, there are 430 uniquely identified compounds, responsible for 114 thousand tonnes per year, 8% of the total mass emission. In addition, there are 48 species that are described as unresolved mixtures of compounds, responsible for 180 thousand tonnes per year, 12% of the total mass emission. Those unresolved mixtures responsible for more than 0.01 thousand tonnes per year are listed in Table 6-4.

Up until now, the approach adopted within the UK PTM has been to use the Master Chemical Mechanism to treat fully the chemistry of as many individual VOC species as has been practical. In this way, the majority of the important VOC species have been accurately represented. If this approach was continued, a significant amount of work would have to be undertaken for relatively small returns in terms of unaccounted for ozone production.

It would seem more sensible to tackle the unresolved mixtures in Table 3 because there are many times fewer of them and they are responsible for more then twice the unaccounted for emissions. The proposed strategy is to represent these mixtures using the CRI mechanism approach which has the dual advantage of being a more compact mechanism and one that does not need to resolve the detail of the mixtures, compared with the MCM mechanism.

Using the 2005 version of the UK PTM and the standard trajectory from Austria to mid-Wales, the following base case results have been obtained to benchmark its performance:

- 2000 emissions, 2000 VOC speciation, peak ozone 82.1 ppb
- 2000 emissions, 2010 VOC speciation, peak ozone 79.9 ppb
- 2010 emissions, 2010 VOC speciation, peak ozone 67.4 ppb.

Table 6-4: Details of the Unresolved Mixtures in the NAEI Inventory.

Unspeciated mixture	Annual Emission (ktonnes per annum)
unspeciated	49.17
C_{13+} aromatic hydrocarbons	23.10
unspeciated alkanes	21.23
C_{13+} alkanes	15.81
C_9 aromatic hydrocarbons	10.39
C_7 alkanes	9.85
C_8 alkanes	8.55
C_{10} alkanes	5.57
C_{11} alkanes	4.48
C_{13} alkanes	3.92
C_9 alkenes	3.81
unspeciated aromatic hydrocarbons	3.31
unspeciated cycloalkanes	2.91
C_{12} alkanes	2.85
unspeciated alkenes	2.63
C_{10} aromatic hydrocarbons	2.51
C_{10} cycloalkanes	1.80
unspeciated hydrocarbons	1.72
C_6 alkenes	1.36
C_7 cycloalkanes	0.67
C_7 alkenes	0.61
C_{11} aromatic hydrocarbons	0.57
pine oil	0.49
C_8 alkenes	0.46
C_8 cycloalkanes	0.25
Unspeciated ketones	0.23
C_{12} alkenes	0.22
unspeciated alcohols	0.18
unspeciated aliphatic hydrocarbons	0.17
Terpenes	0.14
C_{11} cycloalkanes	0.12
C_{10} alkenes	0.11
C_9 cycloalkanes	0.10
C_{12} aromatic hydrocarbons	0.07
C_9 alkenes	0.05
C_{12} cycloalkanes	0.05
C_{11} alkenes	0.04
C_5 alkenes	0.02
C_{14} alkanes	0.01
unspeciated amines	0.01
C_{15} alkanes	0.01
C_{16} alkanes	0.01

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7 Development of Stomatal Flux Module for Crops and Semi-natural Vegetation (Objective 5)

7.1 BACKGROUND

The impact of ozone on vegetation are assessed by comparison with critical levels above which direct adverse effects may occur according to present knowledge. To date, the main method to assess the impact of ozone on vegetation has been the concentration-based (AOTx) approach. Separate concentration–based critical levels have been set for agricultural crops, horticultural crops, semi-natural vegetation and forest trees. A short-term critical concentration level has also been set for visible injury to plants.

It is now widely believed that the plant response to ozone is more closely related to the flux of ozone to the plant. Flux-based critical levels based on accumulated stomatal flux of ozone have been set for wheat, potato and provisionally for sensitive deciduous tree species. The Department has funded work through its research programme at the University of Bradford, Stockholm Environment Institute (SEI, University of York) and CEH Edinburgh in support of the development of the EMEP Surface Ozone Flux model.

Objective 5 of the current project requires the integration of the ozone assessment capability of OSRM, *i.e.*, scenarios for precursor reduction and subsequent impact on surface ozone concentrations, to allow the production of critical levels maps of ozone for the UK using the flux-based approach. An initial workshop was held in York in May 2003, which was attended by personnel from Defra and the Devolved Administrations as well as contractors working on the Department and DAs' ozone research programme. A number of specific actions were identified and netcen was tasked to develop a programme of work. Following meetings with SEI and discussions at a subsequent workshop in November 2003, the preferred approach was to develop a postprocessor code to derive ozone fluxes from the ozone concentrations calculated by the OSRM and the resistance components provided by a Surface Ozone Flux model (SOFM). A schematic of this modelling framework is shown in Figure 7-1.

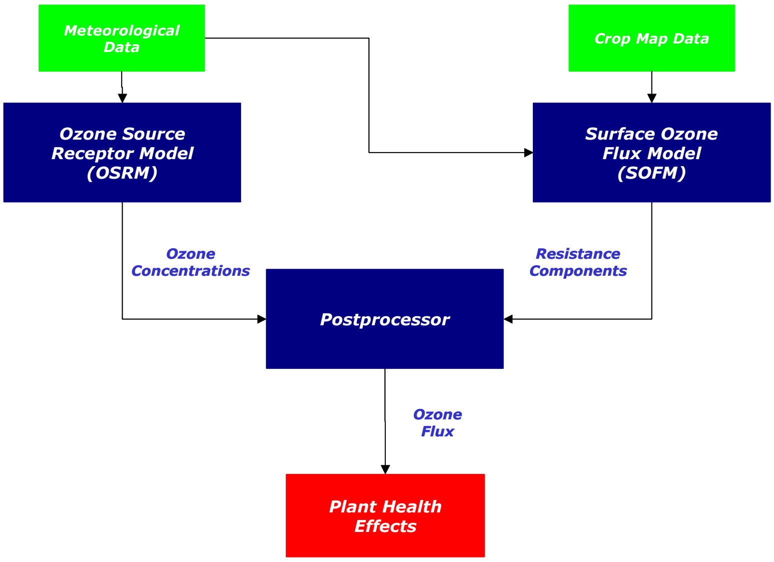


Figure 7-1: Modelling Framework to Calculate Stomatal Ozone Fluxes.

During the second year of the project, a Surface Ozone Flux Model (SOFM) has been developed at netcen, which incorporates the algorithms for the calculation of stomatal flux developed by Emberson *et al*. (2000) and those included in the UNECE mapping manual UN ECE, 2003). The Surface Ozone Flux Model was then used to calculate stomatal ozone fluxes for beech, winter wheat and potatoes at four UK locations. This was subsequently extended to the UK scale.

7.2 MODEL COMPONENTS

7.2.1 Surface Ozone-Flux Model

The Surface Ozone Flux Model has primarily been developed to use output generated by the Ozone Source-Receptor Model, although it can also use ambient ozone monitoring data.

The algorithms used in the Surface Ozone Flux Model are based the resistance analogue model, which is shown schematically in Figure 7-2. The purpose of the Surface Ozone Flux Model is to calculate the values of component resistances to the ozone flux between a reference height and the bulk canopy, the upper canopy leaves or flag leaves and the ground. For beech and potatoes, the critical leaves are the uppermost canopy leaf whereas the flag leaf is the most relevant leaf for wheat. The surface area of the individual upper canopy leaf or flag leaf is very small so that it has little effect on the ozone concentrations. The ozone concentrations in the canopy are dominated by the fluxes to the canopy and to the ground. However, the yield loss in crops or the loss of biomass in woodlands is related to the ozone flux to the upper canopy leaf or the flag leaf. It is therefore necessary to calculate the ozone flux to the whole canopy in order to determine the flux to the most sensitive leaves.

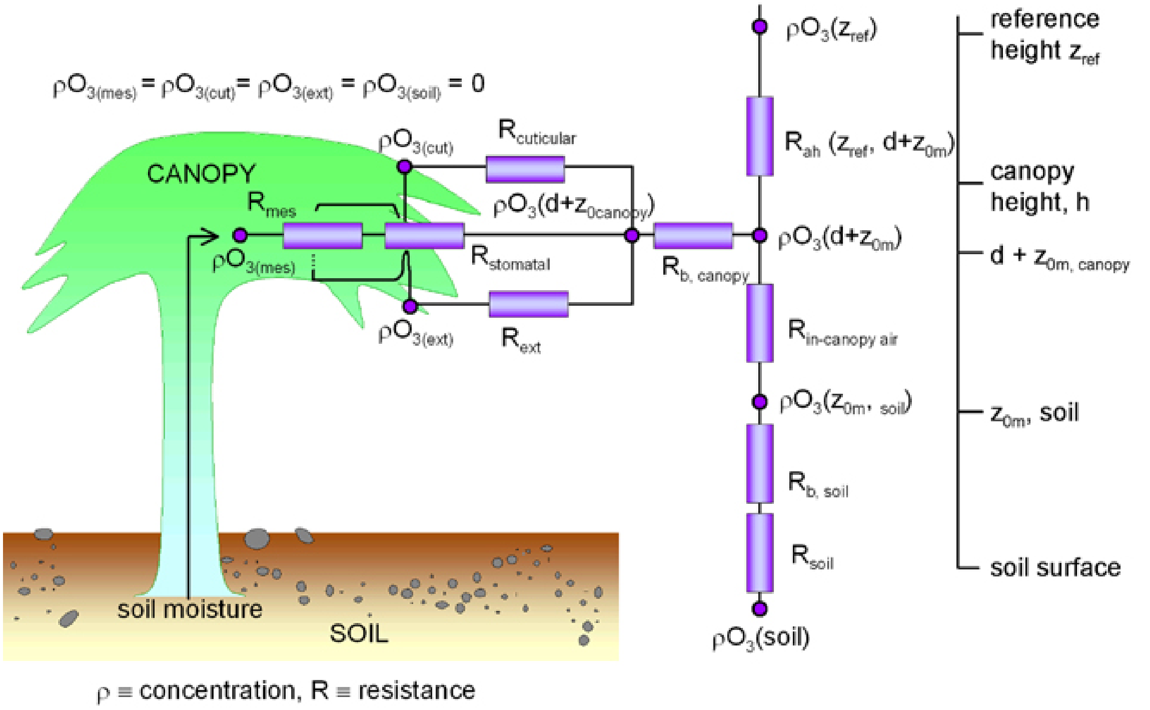


Figure 7-2: Resistance Analogue of Ozone Transfer between the Atmospheric Surface Layer and Terrestrial Ecosystems [taken from NEGTAP, 2001].

The component resistances are:

- aerodynamic resistance from a specified reference height to the canopy displacement height
- stomatal resistance of the bulk canopy
- the external resistance to external plant tissue in the canopy
- the quasi-laminar resistance to the canopy
- the in-canopy air resistance below the displacement height
- the ground surface resistance
- stomatal resistance to the upper canopy/flag leaf
- the external resistance to external plant tissue of the leaf
- the quasi-laminar resistance to the leaf

The UNECE mapping manual describes the methods to calculate the stomatal resistance, external resistance and quasi-laminar resistance to the upper canopy leaf: these methods have been implemented within the surface ozone flux model for winter wheat, potatoes and beech trees.

Methods to calculate the bulk canopy resistances are not specified in the mapping manual. The methods used in the Surface Ozone Flux Model have been developed from those reported by Emberson *et al*. [2000] and presented in the EMEP Unified Model description [Simpson *et al.,* 2003]. The model developments at netcen have involved extensive detailed discussions with Dr Emberson and have included the intercomparison of model outputs.

The stomatal conductances are calculated using a multiplicative algorithm with the following formulation:

$$g_{sto} = g_{max} \times [\min (f_{phen}, f_{03})] \times f_{light} \times [\max (f_{min}, (f_{temp} \times f_{VPD} \times f_{SWP})]$$

where g_{sto} is the actual stomatal conductance and g_{max} is the species specific maximum stomatal conductance. The parameters f_{phen}, f_{O3}, f_{light}, f_{temp}, f_{VPD} and f_{SWP} are factors in the range 0-1 that take account of the effect of plant phenology, ozone-induced senescence, light levels, temperature, water vapour pressure deficit and soil water pressure.

The vapour pressure deficit is calculated in the Surface Ozone Flux Model using an analogous bulk canopy stomatal flux model adapted for water vapour. The soil water pressure is estimated using a simple box model taking account of precipitation, evaporation from leaf surfaces and evapotranspiration through the plant stomata. As the actual soil water pressure will depend to a great extent on the type of soil and the soil structure, it is not possible to make general predictions about the soil water pressure without detailed data on soil types. However, model predictions for a characteristic soil type (loam) are made in order to assess the potential effect of water stress on ozone fluxes.

The Surface Ozone Flux Model calculates the resistances of each of the components. Details of the calculation methods are provided in Abbott [2004]. A combined surface resistance, R_{sur}, is calculated that includes the contributions from each of the bulk canopy component resistances. Key model outputs include:

- the aerodynamic resistance, R_{aero},
- the laminar canopy resistance
- the surface resistance, R_{sur}
- the upper leaf/flag leaf stomatal surface deposition velocity, F_{st}/c_i where F_{st} is the stomatal flux and c_i is the ozone concentration at the interface node.

7.2.2 Meteorological Pre-processor

The Ozone Source Receptor Model and the Surface Ozone Flux Model make use of the same Numerical Weather Prediction data provided by the Meteorological Office. Use of the same meteorological data set for both models takes account of possible correlations between weather conditions and ozone concentrations and between weather conditions and stomatal resistances. However, the data are provided at 1° latitude and 1° longitude intervals every 6 hours throughout the year. The Ozone Source Receptor Model requires data at the nodes of the EMEP grid at one hour intervals. The meteorological preprocessor interpolates the data both in time and space. It scales and formats the data. It also derives a grid-square average estimate of the aerodynamic resistance from the meteorological data. Details of the meteorological pre-processor can be found in Appendix 1 of the report by Abbott [2004].

7.2.3 Ozone Flux Post-processor

The purpose of the ozone flux post-processor is to calculate the flux of ozone to the stomata of the upper canopy leaf for beech and potatoes and the flag leaf for winter wheat from the outputs of the OSRM and SOFM models. It calculates the ozone concentration at the interface node from the mid-boundary layer height concentration calculated by OSRM. It then multiplies this value by the upper leaf/flag leaf stomatal surface deposition velocity, F_{st}/c_i to give the calculated stomatal flux. The accumulated stomatal flux are calculated using the algorithms specified in the UNECE mapping manual. Details of the program can be found in the report by Abbott [2004].

7.3 OZONE FLUX CALCULATIONS

Selected model outputs are presented in this section. Upper leaf surface conductances were predicted for winter wheat, potatoes and beech at four selected sites in the UK throughout the growing season (day 90-270) for 2001:

- 55.5°N, 3.5°W (near Edinburgh);
- 52.5°N, 2.5°W (in the border area between Wales and England);
- 52.5°N, 1.5°W (in the Midlands);
- 52.5°N, 1.5°E (in East Anglia, near Lowestoft).

Accumulated ozone fluxes to the three vegetation types were derived at UK monitoring sites using ozone concentrations calculated by the OSRM and the fluxes were compared with those based on measured ozone concentrations. Finally, maps of accumulated ozone flux over threshold and crop yields are presented based on OSRM model runs at 10 km resolution.

7.3.1 Upper-leaf Surface Conductance

The upper leaf surface conductance is calculated as the ratio of the ozone flux to the upper leaf or flag leaf per unit projected leaf area to the ozone concentration at the displacement height, F_{st}/c.

- Winter Wheat: The maximum daily stomatal conductances for winter wheat were calculated at the four sites for the accumulation period specified in the UNECE mapping manual. The upper panel of Figure 7-3 shows the stomatal fluxes calculated for winter wheat at a location in the Midlands (52.0°N, 1.5°W) in 2001. The accumulation period for winter wheat is based on phenological models and so the accumulation occurs much earlier in the year in southern England than it does further north.

  The maximum daily stomatal conductance approached 8 mm s^{-1}. This may be compared with the species specific maximum conductance, g_{max} for wheat of 450 mmol m^{-2} PLA s^{-1} or 11 mm s^{-1}. The predicted maximum daily conductance in East Anglia (at 52.5°N, 1.5°E) was rather less than that predicted in more northerly and westerly locations. This occurred because the temperatures at this near coastal location were influenced by the presence of the sea. Relatively mild temperatures in the early part of the year brought forward the growing season but maximum daily temperatures were rather less than those inland.

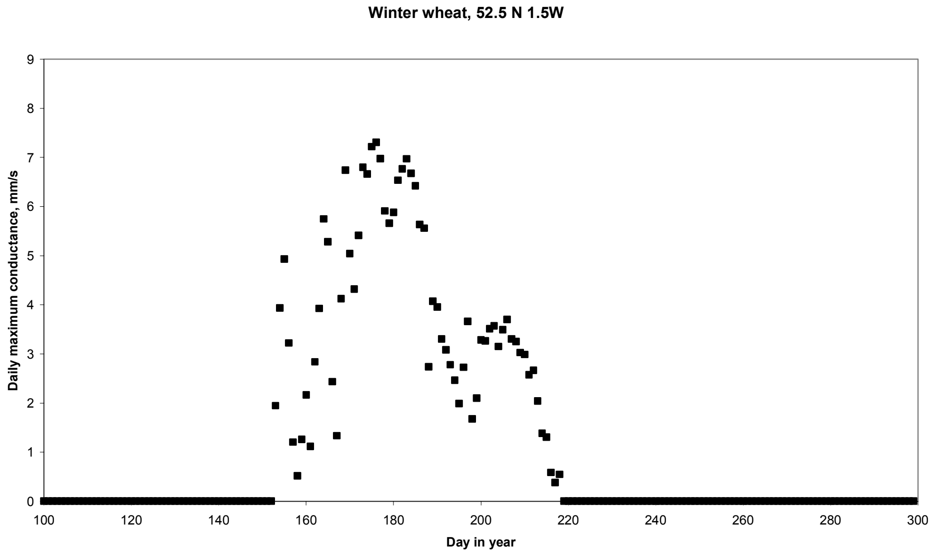
- Potatoes: The maximum daily predicted stomatal conductance for potatoes were calculated at the same sites for the accumulation period specified in the UNECE mapping manual, based on a fixed emergence data of day 146. The accumulation period for potatoes is based on phenological models and the accumulation period is rather shorter in southern England than it is further north.

  The maximum daily stomatal conductance approached 10 mm s^{-1}. This may be compared with the species specific maximum conductance, g_{max} for potatoes of 750 mmol m^{-2} PLA s^{-1} or 18.3 mm s^{-1}. The predicted maximum daily conductance at the site in East Anglia was rather less than that predicted in more northerly and westerly locations because the maximum daily temperatures are affected by the sea at this near coastal location.

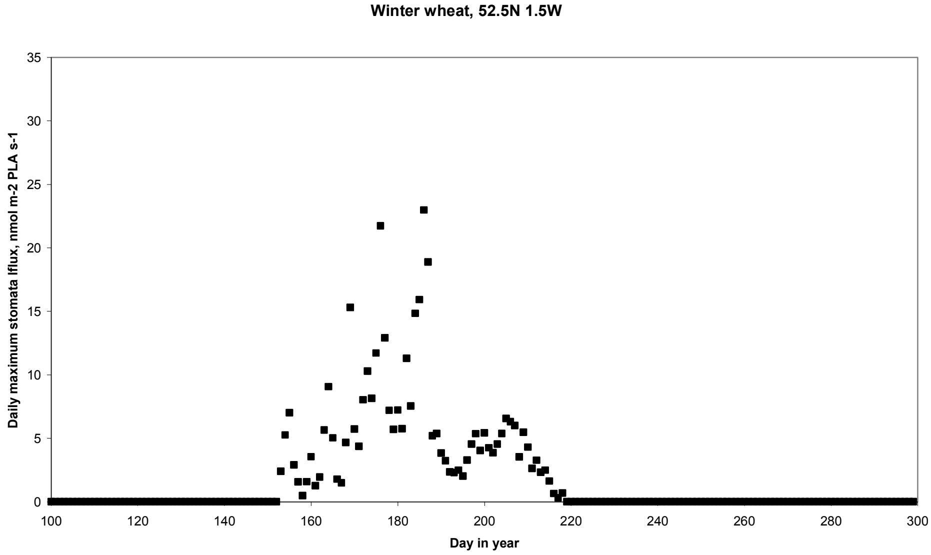
- Beech: The maximum daily stomatal conductance approached 3 mm s^{-1}. This may be compared with the species-specific maximum conductance, g_{max} for beech of 134 mmol m^{-2} PLA s^{-1} or 3.3 mm s^{-1}. The modelled maximum daily conductance for the site in the Midlands and to a lesser extent in East Anglia decreased sharply in the latter part of the growing season. This occurred because of the lower predicted soil water pressure in inland areas in the south eastern part of the UK.

7.3.2 Upper Leaf Stomatal Fluxes

The upper leaf surface conductance is calculated as the ratio of the ozone flux to the upper leaf or flag leaf per unit projected leaf area to the ozone concentration at the displacement height, F_{st}/c. The upper leaf stomatal flux is then the product of the upper leaf surface conductance (F_{st}/c) and the ozone concentration at displacement height. The ozone concentration at displacement height was calculated from the OSRM mid-boundary layer height using a height correction factor calculated for each hour and crop type by the Surface Ozone Flux Model.



(a)



(b)

Figure 7-3: Maximum Daily Stomatal Conductance (Left-hand Panel) and Maximum Daily Stomatal Ozone Flux (Right-hand Panel) Calculated for Winter Wheat for 2001 at a Location in the Midlands using the Ozone Source-receptor and Surface Ozone Flux Models.

- Winter Wheat: The lower panel of Figure 7-3 shows the stomatal fluxes calculated for winter wheat at a location in the Midlands (52.0°N, 1.5°W) in 2001. The maximum daily stomatal flux in 2001 was calculated to exceed the threshold value of 6 nmol m^{-2} PLA s^{-1} specified in the UNECE mapping manual on relatively few days throughout the accumulation period.

- Potatoes: The maximum daily stomatal flux in 2001 was calculated to exceed the threshold value of 6 nmol m^{-2} PLA s^{-1} specified in the UNECE mapping manual for on relatively few days throughout the accumulation period.

- Beech: The maximum daily stomatal flux in 2001 was calculated to exceed the threshold value of 1.6 nmol m^{-2} PLA s^{-1} specified in the UNECE mapping manual for much of the accumulation period. However, predicted stomatal flux during the latter part of the accumulation period at the two more south-easterly sites was restricted by the limited soil moisture content.

7.3.3 Accumulated Ozone fluxes at UK Monitoring sites

The accumulated ozone stomatal flux over threshold was calculated as the sum of the calculated hourly ozone stomatal flux above threshold values, over an accumulation period specified in the UNECE mapping manual. Table 7-1 shows the calculated stomatal fluxes over threshold for beech, winter wheat and potatoes using OSRM-derived hourly ozone concentrations at rural ozone monitoring sites in the UK Automatic Urban and Rural Network.

Table 7-1: Accumulated Ozone Stomatal Fluxes over Threshold at UK Rural Monitoring Sites: Comparison of Predictions based on OSRM Ozone Concentrations with Predictions based on Measured Ozone Concentrations

	Accumulated Ozone Stomatal Flux over Threshold (mmol m^{-2} PLA)					
Site	Using OSRM O_3 concentrations			Using Measured O_3 Concentrations		
	Beech	Winter Wheat	Potatoes	Beech	Winter Wheat	Potatoes
Aston Hill	6.14	2.04	2.61	*	*	*
Bush Estate	5.97	0.86	0.95	5.83	0.32	0.41
Eskdalemuir	6.12	1.07	0.97	5.19	0.64	0.62
Great Dun Fell	5.89	2.48	2.31	7.92	2.96	2.80
Harwell	3.39	2.45	3.61	4.38	3.37	4.93
High Muffles	5.28	3.13	2.90	*	*	*
Ladybower	3.05	2.31	3.02	*	*	*
Lullington Heath	5.89	0.20	2.05	7.55	0.21	1.53
Narbeth	9.53	0.02	0.62	10.23	0.01	0.41
Rochester	2.43	1.05	3.33	4.72	1.74	3.44
Sibton	6.65	0.38	1.69	6.92	0.08	0.90
Somerton	5.22	2.35	3.54	6.32	2.74	4.06
Wicken Fen	2.96	2.06	3.71	4.13	3.61	5.66
Yarner Wood	4.41	1.82	3.16	5.92	2.64	3.27
Bottesford	4.16	2.13	2.82	5.75	3.25	4.41

Note * less than 90% data capture

The OSRM-derived accumulated ozone stomatal fluxes were then compared with stomatal flux estimates based on measured ozone concentrations. These estimates are also shown in Table 7-1. As shown in Figure 7-4, there appears to be a good correlation between the two sets of ozone fluxes: to some extent this is inevitable because the same meteorological data were used in both cases. Nevertheless, the comparison suggests that OSRM can provide an effective means of predicting accumulated flux over threshold to vegetation types.

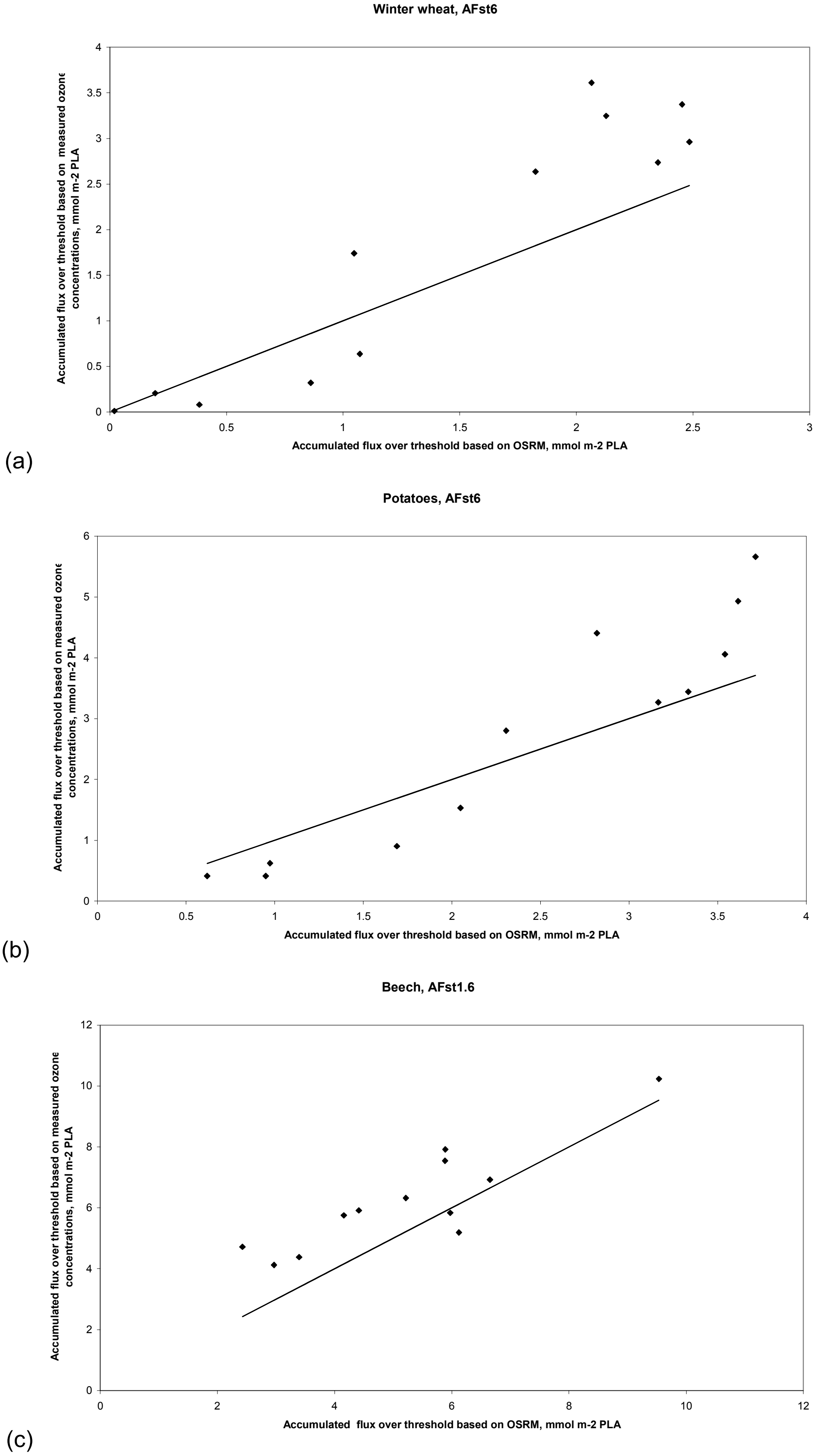


Figure 7-4: Predicted Accumulated Ozone Fluxes over Threshold for Winter Wheat (Panel a), Potatoes (Panel b) and Beech Trees (Panel c) at UK Rural Ozone Monitoring Sites for 2001: Comparison of Predicted Fluxes based on OSRM-derived and Measured Ozone Concentrations.

7.3.4 UK MAPs of Accumulated Fluxes

The Surface Ozone Flux Model was used to calculate UK maps of the accumulated ozone stomatal fluxes in 2001 to beech, winter wheat and potatoes. Panels (a) and (b) of Figure 7-5 show maps of these fluxes to winter wheat and potatoes at a 10 km resolution throughout the UK. The maps of winter wheat, potatoes and also beech show that

- the accumulated flux over threshold, $AF_{st}6$ for winter wheat exceeded the critical value of 1 mmol m^{-2} PLA (projected sunlit leaf area) over much of England and Wales. The critical value corresponds to a 5% loss of yield. The accumulated flux was below the critical value over most of Scotland and Northern Ireland and in coastal areas in England and Wales. The accumulated flux in these areas was limited to some extent by lower maximum temperatures.
- the accumulated flux over threshold, $AF_{st}6$ for potatoes did not exceed the critical value of 5 mmol m^{-2} PLA (projected sunlit leaf area) in the UK in 2001. The critical value corresponds to a 5% loss of yield. The accumulated flux was smallest in Scotland and Northern Ireland and in coastal areas in England and Wales. The accumulated flux in these areas is limited to some extent by lower maximum temperatures.
- the accumulated flux over threshold, $AF_{st}1.6$ for beech exceeded the critical value of 4 mmol m^{-2} PLA (projected sunlit leaf area) over much of the UK. The critical value corresponds to a 5% loss of biomass. The accumulated flux was below the critical value in an area extending north-west from London and covering much of the Midlands. However, the stomatal conductance was limited in this area by soil moisture potential during the latter part of the accumulation period. Trees on soil with better water retention in this area than the loam used in the assessment would have been affected by ozone to a greater extent.

The UNECE mapping manual provides simple statistical relationships between the crop yield for wheat and potatoes affected by ozone uptake as a fraction of the unaffected yield and the accumulated ozone flux over threshold, $AF_{st}6$. For wheat, the relationship is Yield = 1.0 – 0.048 $AF_{st}6$ and for potatoes, the corresponding relationship is Yield = 1.01 – 0.013 $AF_{st}6$.

Panels (c) and (d) of Figure 7-5 show the percentage yield for wheat and potatoes calculated for 2001 at locations throughout the UK. Panel (c) indicates that there was more than 15% loss in wheat yield in a small area in the north-east of England, and more than 10% loss in yield over much of central England. Panel (d) suggests that there was less than 5% loss in the yield of potatoes throughout the UK.

The UN ECE mapping manual recommends that similar maps should not be prepared for forest trees.

7.4 SUMMARY

The feasibility of preparing maps that show the effects of ozone deposition on crops in the United Kingdom based on predictions of ozone concentrations made using the Ozone Source Receptor Model (OSRM) has been demonstrated. Computer programs have been prepared that implement the algorithms for the calculation of stomatal flux, developed by Emberson *et al.* (2000) and those included in the UNECE mapping manual.

Model predictions of stomatal flux based on ozone concentrations calculated using the OSRM were compared with stomatal flux estimates based on measured ozone concentrations. The comparison suggested that the OSRM can provide an effective means of predicting accumulated flux over threshold to vegetation types.

The model predicted that the growth of beech trees in 2001 was affected by ozone deposition, with greater than 5% loss in biomass throughout the country. Ozone deposition to beech trees in much of the southern part of the UK was limited by the availability of soil moisture for plant uptake during the latter path of the growing season.

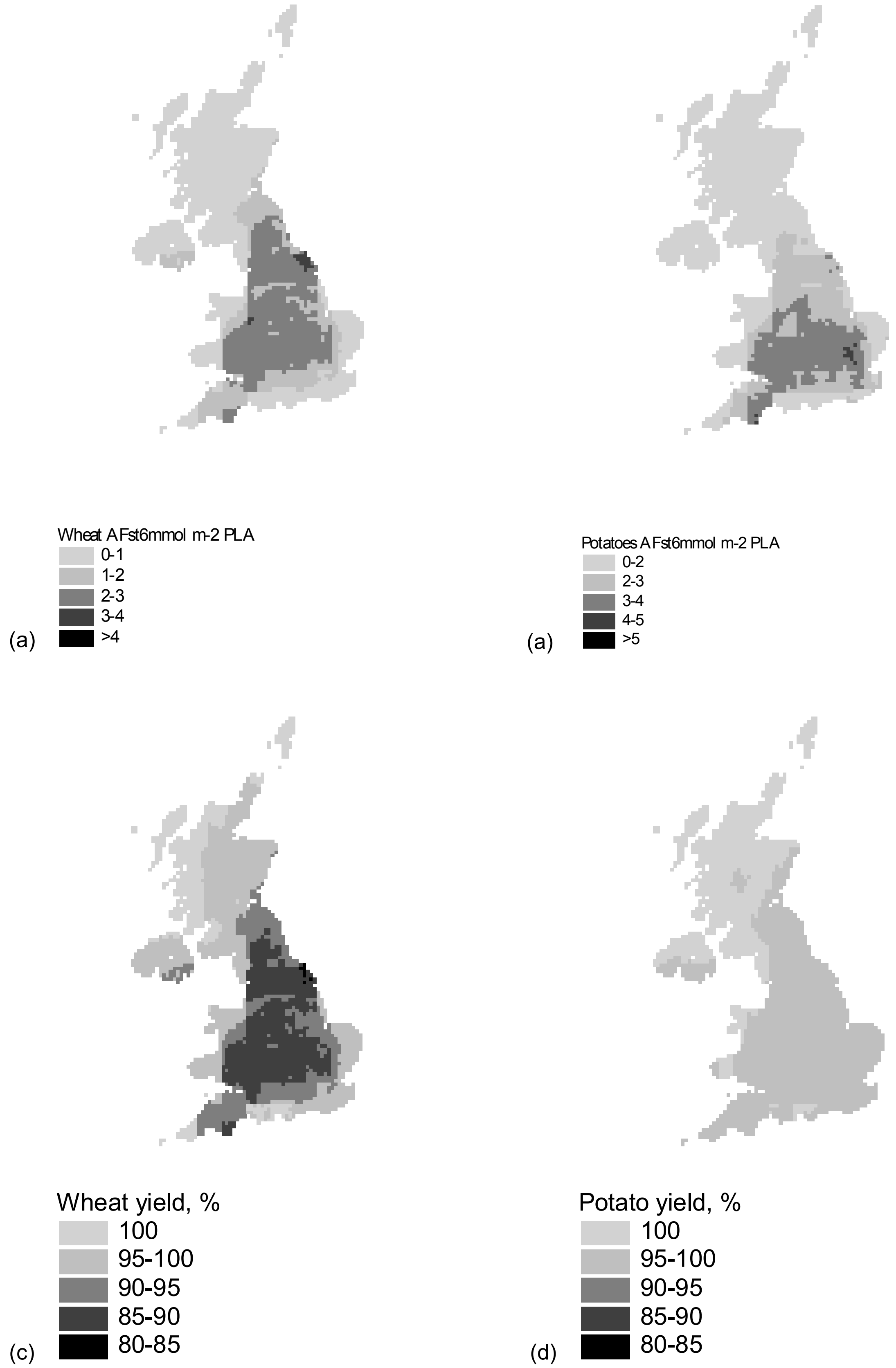


Figure 7-5: Predicted Accumulated Stomatal Fluxes over Threshold (Upper Panels) and Yields (Lower Panels) for Winter Wheat and Potatoes for 2001.

The model predicted that the growth of winter wheat throughout much of England and Wales in 2001 was affected by ozone deposition. Ozone deposition was associated with more than 5% loss in yield in central England. The loss in yield was smaller in cooler areas in Scotland and in coastal areas of England with lower maximum temperatures. The model also predicted that the growth of potatoes was not substantially affected by ozone deposition. Ozone deposition was associated with less than 5% loss in yield throughout the country.

7.5 REFERENCES

Abbott, J.A. (2004) **Development of an Ozone Surface Flux Model**. Report in preparation.

Emberson, L. D., D. Simpson, J.-P. Tuovinen, M. R. Ashmore and H. M. Cambridge (2000) **Towards a Model of Ozone Deposition and Stomatal Uptake over Europe**. Research Note No. 42. EMEP/MSC-W 2000.

NEGTAP (2001) **Transboundary Air Pollution: Acidification, Eutrophication and Ground-level ozone in the UK** (ISBN 1 870393 61 9). Prepared by the National Expert Group on Transboundary Air Pollution (NEGTAP) on behalf of the Department for Environment, Food and Rural Affairs, the Scottish Executive, Welsh Assembly Government and the Department of the Environment in Northern Ireland.

Simpson, D., H. Fagerli, H. E. Jonson, S. Tsyro, P. Wind and J.-P. Tuovinen (2003) **Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe. Part 1. Unified EMEP Model Description**. EMEP Status report 2003.

UN ECE (2003) see http://www.oekodata.com/pub/mapping/manual/mapman3.pdf.

8 Other Project Activities

8.1 PROJECT MEETINGS AND REPORTS

The third and fourth six-monthly progress meetings were held in London on the 20th January and the 16th September 2004, respectively, with attendance from Defra and the project consortium members. Apologies were received from the members of the Devolved Administrations. A series of presentation were given on (a) the key policy issues, (b) an overview of the project and (c) work undertaken on the project objectives by members of the project consortium.

Other project meetings of the project partners have been held during the current reporting period on specific project objectives:

- An **Ozone Science-Policy Meeting** was held in London on the 9th March 2004 with attendance from Defra, the Devolved Administrations and the project consortium members. A series of presentations were given on recent issues and the policy relevance of ozone and nitrogen dioxide on (a) the urban, (b) the national and (c) regional and global scales.
- A second **Ozone Science-Policy Meeting** was held in London on the 11th June 2004 with attendance from Defra and members of the project consortium. A series of presentations were given on recent issues and the policy relevance of ozone and nitrogen dioxide on (a) the urban, (b) the national and (c) regional and global scales.
- The project manager attended a meeting at Defra on 17th June 2004 related to **Preliminary Scenario Modelling of Non-transport Measures for the Review of the Air Quality Strategy**. At the meeting, the non-transport measures were reviewed and the programme of ozone model runs was defined.
- A workshop on **Ozone Flux Modelling (Objective 5)** was held at York in April 2004. The workshop was attended by Defra and DA personnel, as well as contractors working on the Department and DAs' ozone research programme. The agenda comprised presentations on the different contracts followed by discussion on the approach which should be adopted to calculate exposure using ozone fluxes and their response to emission controls.
- A presentation on the Modelling of Tropospheric Ozone was given at the **Department's Air Quality Research Seminar**, which was held in London on the 7th January 2004, with attendance from Defra and the Devolved Administrations.
- A presentation on the Modelling of Tropospheric Ozone project and related activities was given at the **Joint Defra-NERC TORCH Meeting**, which was held in London on the 12th February 2004.

In addition to progress and annual reports, the following reports have also been produced:

G. D. Hayman (April 2004) **Observed and Modelled Trends in Ground-level Ozone**.

G. D. Hayman, C. Thomson and R. G. Derwent (May 2004) **Summary and Interpretation of Recent Ozone Modelling Runs.**

G. D. Hayman and J. Abbott (June 2004) **OSRM Modelling of Ozone in London**.

G. D. Hayman, J. Abbott and C. Thomson (July 2004) **OSRM Modelling of Ozone for the Review of the Air Quality Strategy**.

8.2 PUBLICATIONS

The following papers have been produced by the project consortium for publication in the scientific literature:

R.G. Derwent, M.E. Jenkin, S.M. Saunders, M.J. Pilling, and N.R. Passant (2004) **Multi-day Ozone Formation for Alkenes and Carbonyls investigated with a Master Chemical Mechanism under European Conditions**. Submitted to Atmospheric Environment.

M. E. Jenkin (2004) **Analysis of the Sources and Partitioning of Oxidant in the UK. Part 1: The NO_x-dependence of Annual Mean Concentrations of Nitrogen Dioxide and Ozone**. Atmospheric Environment, **38**, 5117-5129.

M. E. Jenkin (2004) **Analysis of the Sources and Partitioning of Oxidant in the UK. Part 2: Contributions of Nitrogen Dioxide Emissions and Background Ozone at Kerbside Locations in London**. Atmospheric Environment, **38**, 5131-5138.

P.G. Pinho, C.A. Pio and M.E. Jenkin (2004) **Evaluation of the Detailed Tropospheric Chemical Mechanism, MCM v3, using Environmental Chamber Data. Part 1: Butane and its Degradation Products**. Submitted to Atmospheric Environment.

P.G. Pinho, C.A. Pio and M.E. Jenkin (2004) **Evaluation of the Detailed Tropospheric Chemical Mechanism, MCM v3, using Environmental Chamber Data. Part 2: Isoprene and its Degradation Products**. Submitted to Atmospheric Environment.

L. Whitehouse, Tomlin, A.S. and Pilling, M.J. (2004) **Systematic Reduction of Complex Tropospheric Chemical Mechanisms, Part 1: Sensitivity and Time-Scale Analysis**. Atmospheric Chemistry and Physics, **4**, 2025-2056.

L. Whitehouse, Tomlin, A.S. and Pilling, M.J. (2004) **Systematic Reduction of Complex Tropospheric Chemical Mechanisms, Part 2: Lumping using a Time-Scale Based Approach**, Atmospheric Chemistry and Physics, **4**, 2057-2081.

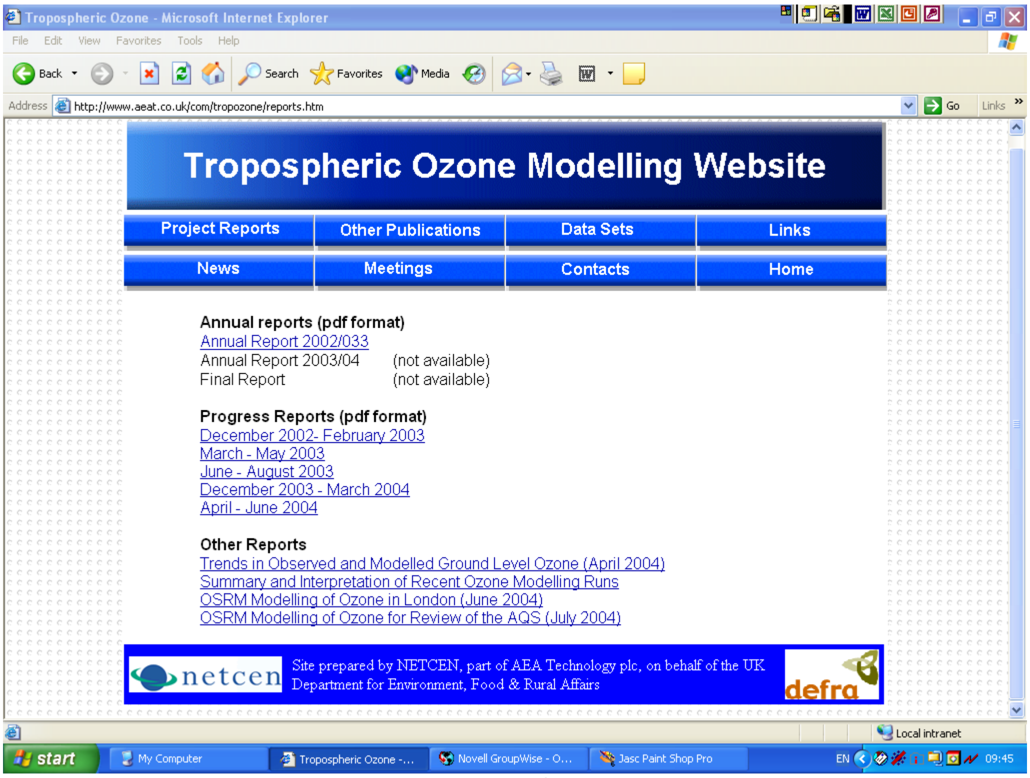
8.3 CONFERENCES ATTENDED

Presentations were given at the following conferences describing work carried out under this contract:

- M.J. Pilling; **Developing and Using Mechanisms for the Oxidation of Organic Compounds in the Atmosphere**, *ACS, Molecular Modeling and Reaction Chemistry,* Anaheim, March, 2004
- M.J. Pilling and M.E. Jenkin; **Chemical Mechanisms and Timescales for the Oxidation of Biogenic Compounds**, *Gordon Conference*, Barga, Italy, May 2004
- S.M. Saunders, M.E. Jenkin, C. Bloss, V. Wagner, A.R. Rickard, L. Whitehouse, S. Pascoe and M.J Pilling; **The Master Chemical Mechanism – Latest Improvements (MCMv3.1)**, *Poster Presentation, 18th International Symposium on Gas Kinetics,* Bristol, August 2004.
- M.J. Pilling; Aromatic Hydrocarbon Oxidation: **The Contribution of Chamber Photo-oxidation Studies**, *NATO Meeting*, Zakopane, Poland, October 2004
- M.J. Pilling; **A Master Chemical Mechanism (MCM): Approaches to its Use in CTMs**, *German Chemical Societies*, Frankfurt, November 2004
- C. Bloss, A.R. Rickard, L. Whitehouse, S. Pascoe, M. E. Jenkin, S.M. Saunders, V. Wagner, R.G. Derwent and M.J. Pilling**; Gas-phase MCM Development Activities at Leeds**, *MCM Developer and User Workshop*, Leeds, December 2004.
- S. Pascoe, A.R. Rickard, L. Whitehouse, C. Bloss, S.M. Saunders, M. E. Jenkin, and M.J. Pilling; **MCM Website Developments**, *MCM Developer and User Workshop*, Leeds, December 2004.

8.4 PROJECT WEBSITE

A simple, password-protected project website has been set-up to be an archive of project outputs (reports, datasets, etc) and to facilitate the dissemination of these outputs to stakeholders. The address is www.aeat.co.uk/com/tropozone and the home page is shown in Figure 8-1.



Tropospheric Ozone Modelling Website

Annual reports (pdf format)
Annual Report 2002/033
Annual Report 2003/04 (not available)
Final Report (not available)

Progress Reports (pdf format)
December 2002- February 2003
March - May 2003
June - August 2003
December 2003 - March 2004
April - June 2004

Other Reports
Trends in Observed and Modelled Ground Level Ozone (April 2004)
Summary and Interpretation of Recent Ozone Modelling Runs
OSRM Modelling of Ozone in London (June 2004)
OSRM Modelling of Ozone for Review of the AQS (July 2004)

Site prepared by NETCEN, part of AEA Technology plc, on behalf of the UK Department for Environment, Food & Rural Affairs

Figure 8-1: Home Page of the Project Website.

9 Acknowledgements

The consortium partners acknowledge the support provided by the Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations (the Scottish Executive, the National Assembly of Wales and the Northern Ireland Department of the Environment) under contract EPG 1/3/200.

Appendices

CONTENTS

Appendix 1

Brief Description of the Ozone Source-Receptor Model

CONTENTS

The Ozone Source-receptor Model

The Ozone Source-Receptor Model (OSRM) is a recently-developed model to describe photochemical ozone production in the UK [Hayman *et al.*, 2002; 2004]. The OSRM is similar in concept to the UK Photochemical Trajectory Model (UK PTM) in that it simulates the chemical development of species in an air parcel moving along a trajectory and the ELMO source-receptor model in that calculations can be undertaken to a 10 km x 10 km grid covering the UK. The OSRM has a number of notable differences and advantages to these models:

- **Air Mass Trajectories**: Realistic air mass trajectories are derived from wind fields extracted from meteorological datasets. The UK PTM and ELMO model use linear trajectories. Meteorological datasets are available for use with the OSRM for the years 1995 to 2003;
- **Meteorology**: The boundary layer depth and other meteorological parameters characterising the boundary layer are interpolated in space and time from the input meteorological datasets;
- **Chemical Mechanisms**: Three chemical mechanisms have been developed for use in the OSRM (a) the chemical mechanism used in the ELMO or STOCHEM models, (b) a modified and extended version of chemical mechanism used in the ELMO or STOCHEM models. The chemical mechanism has been modified to include the formation of HONO and organic nitrates and a more extensive chemistry of NO_3, and (c) a reduced version of the Common Reactive Intermediate mechanism where the CRI concept has been used for the VOCs used in the mechanism. The modified STOCHEM mechanism is currently used in the OSRM. Table x provides a comparison of these three chemical mechanisms;

Table x – A Comparison of Mechanisms used in the OSRM

	STOCHEM	**Modified STOCHEM**	**Mini-CRI**
# of Species	70	70	70
# of Reactions	154	180	198
# of VOCs	10	12	12
Emitted VOCs	ethane propane *n*-butane ethane propene toluene *o*-xylene methanol acetone methyl ethyl ketone	ethane propane *n*-butane ethane propene toluene *o*-xylene methanol acetone methyl ethyl ketone formaldehyde acetaldehyde	ethane propane *n*-butane ethane propene toluene *o*-xylene methanol acetone methyl ethyl ketone formaldehyde acetaldehyde
Biogenic VOCs	isoprene	isoprene	isoprene
VOC speciation	NAEI 1998	NAEI 1998	NAEI 1998

- **Photolysis Rates**: Photolysis rates have been calculated off line using a modified version of the PHOTOL code. The input database contains the dependence of photolysis rates for 17 species on zenith angle, cloud cover, land surface type and column ozone;
- **Emissions:** The model uses up-to-date emission inventories for nitrogen oxides, volatile organic compounds, carbon monoxide and sulphur dioxide taken from UK (National Atmospheric Emission Inventory) and European (EMEP) sources. The emissions of each pollutant have been divided into to 8 broad source categories (solvent usage, road transport, industrial processes, power generation, fossil fuel extraction and delivery, domestic combustion, natural and other). The assignment of the ~600 VOCs in the UK speciated VOC emission inventory to the 13 model VOCs was based on reactivity and structural considerations.
- **Temporal Emission Factors**: The OSRM converts the annual emission estimates to instantaneous emission rates using temporal profiles for the emissions of NO_x,

VOCs, SO_2 and CO generated by Jenkin *et al*. (2000). These profiles were derived either from real activity data or by using one of small set of default profiles.

- **Biogenic VOC Emissions:** An additional emission term is added to the emission rate of isoprene to represent the natural biogenic emissions from European forests and agricultural crops. The emission estimates can either be the same as those used in the UK PTM and taken from Simpson *et al.* [1995] or the new biogenic inventory produced using the PELCOM land cover dataset and the TNO tree species inventory. The later emission inventory gives emission potentials aggregated to the EMEP 50 km x 50 km grid for isoprene (from deciduous and evergreen trees: temperature and PAR sensitive), monoterpenes (from deciduous and evergreen trees: temperature or temperature and PAR sensitive) and OVOCs (from deciduous and evergreen trees: temperature sensitive);
- **Dry Deposition**: Dry deposition processes are represented using a conventional resistance approach, in which the rate of dry deposition is characterised by a deposition velocity. Different deposition velocities are used over land and sea. The ozone deposition velocity over land has an imposed diurnal and seasonal cycle.
- **Initialisation**: The concentrations of O_3, CO, CH_4, C_2H_6, HNO_3 and PAN are initialised on each OSRM trajectory using output from the global tropospheric STOCHEM model. This improves the realism of the model as the seasonal cycle in ozone is now represented. It also allows for coupling between regional scale ozone production and the hemispheric circulation. A full set of daily concentration fields are currently available for 2 calendar years, one representing the climatology of the late 1990's (actually 1998) and the second a future atmosphere (IPCC SRES scenarios for 2030). This will allow model runs to be undertaken to assess the effect of climate change on regional ozone concentrations.

The model was originally designed to use the variable-order GEAR solver that is employed in the FACSIMILE numerical integration programme. To speed up the OSRM model, a backwards-iterative EULER solver has been incorporated into the model and this has led to a factor of 6 improvement in runtime with no loss of accuracy. Following the purchase of two Dell Precision Workstation 650 MiniTowers (containing dual Intel® Xeon 3.06GHz processors), a single trajectory calculation the using the backwards-iterative EULER solver with a longer timestep of 240s now takes ~0.015 s. Making use of the two available processors on the workstation gives a runtime of ~3 days for a calendar-year UK-scale model run to ~3,000 receptor sites.

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Hayman, G. D., Jenkin, M. E., Pilling, M. J. and Derwent, R. G. (2002) **Modelling of Tropospheric Ozone Formation.** A Final Project Report produced for the Department for Environment, Food and Rural Affairs and Devolved Administrations on Contract EPG 1/3/143.

Hayman, G. D., Bush, A., Kent, A., Derwent, R. G., Jenkin, M. E., Pilling, M. J. and Abbott, J. (2004) **Modelling of Tropospheric Ozone.** The First Annual Report produced for the Department for Environment, Food and Rural Affairs and Devolved Administrations on Contract EPG 1/3/200.

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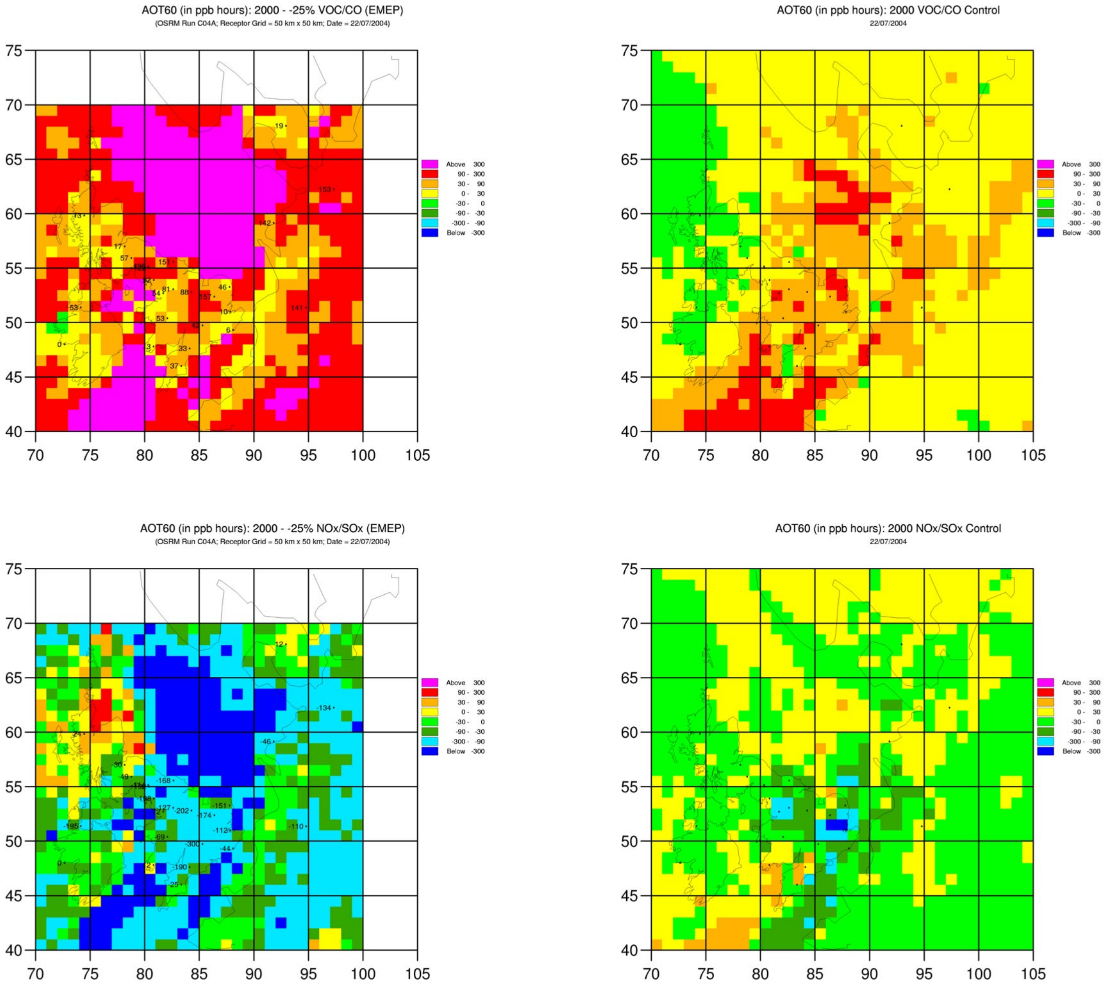
Simpson, D., Guenther, A., Hewitt, C.N., Steinbrecher, R. (1995) **Biogenic Emissions in Europe 1. Estimates and Uncertainties**. J. Geophys. Res, 100, 22875-22890.

Appendix 2

Comparison of the Response of the OSRM and EMEP UNIOZONE Model

CONTENTS



AOT60 (in ppb hours): 2000 - -25% VOC/CO (EMEP)
(OSRM Run C04A; Receptor Grid = 50 km x 50 km; Date = 22/07/2004)

AOT60 (in ppb hours): 2000 VOC/CO Control
22/07/2004

AOT60 (in ppb hours): 2000 - -25% NOx/SOx (EMEP)
(OSRM Run C04A; Receptor Grid = 50 km x 50 km; Date = 22/07/2004)

AOT60 (in ppb hours): 2000 NOx/SOx Control
22/07/2004

Figure A2.1: Maps of the Response of the Ozone Metric – AOT60 - as calculated by the Ozone Source-receptor (left-hand panels) and the EMEP UNIOZONE (right-hand panels) Models to Emission Control. The maps show, as differences, the Impact of a 25% Reduction in UK Anthropogenic Emissions of (a) Sulphur and Nitrogen oxides (upper panels), and (b) Carbon monoxide and Non-methane Volatile Organic Compounds (lower panels). The Reference Year used is 2000. Note: Negative Values indicate an Increase in the Metric.

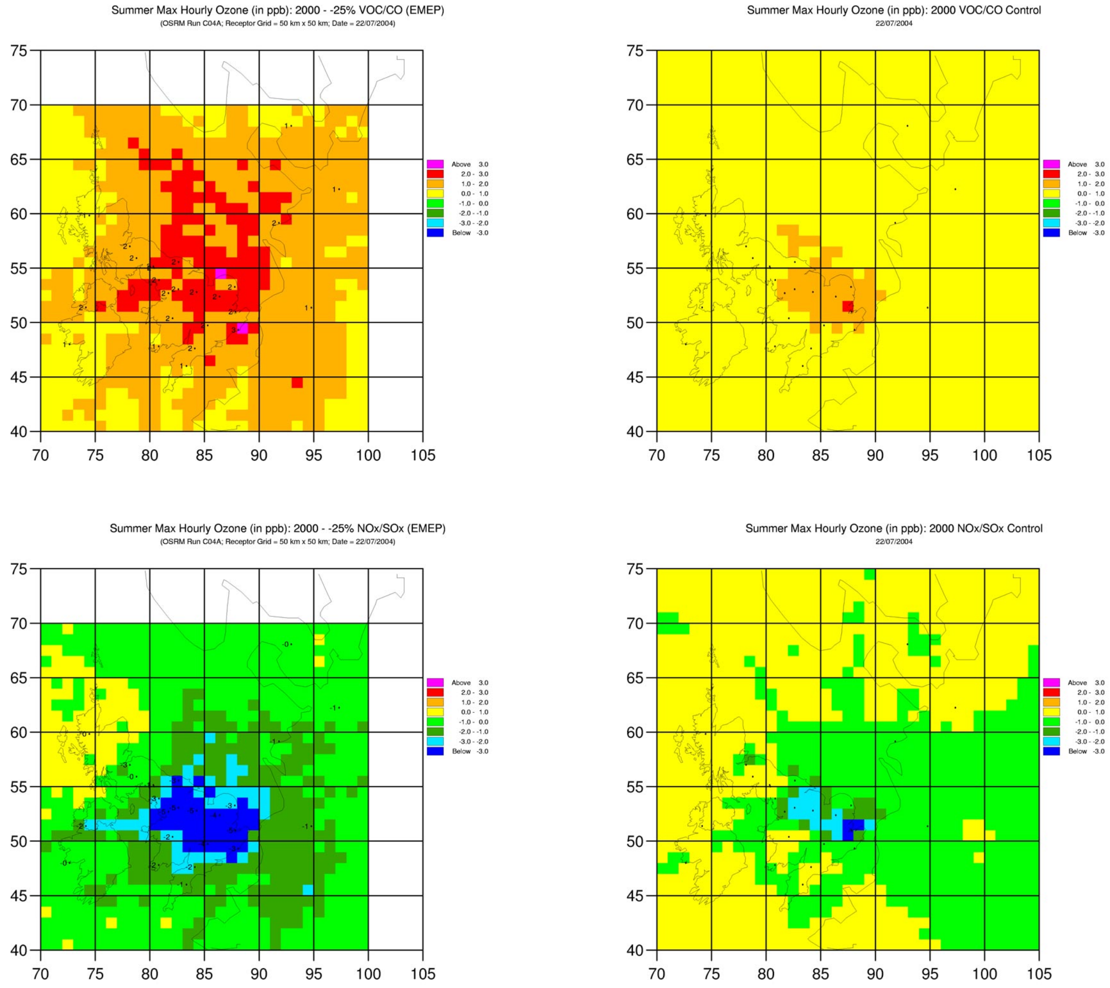


Figure A2.2: Maps of the Response of the Ozone Metric – Maximum Ozone Concentration between June and August - as calculated by the Ozone Source-receptor (left-hand panels) and the EMEP UNIOZONE (right-hand panels) Models to Emission Control. The maps show, as differences, the Impact of a 25% Reduction in UK Anthropogenic Emissions of (a) Sulphur and Nitrogen oxides (upper panels), and (b) Carbon monoxide and Non-methane Volatile Organic Compounds (lower panels). The Reference Year used is 2000. Note: Negative Values indicate an Increase in the Metric.