![AEA Energy & Environment - From the AEA group]

Ozone 2006
Number of days exceeding
120 µg m^{-3}
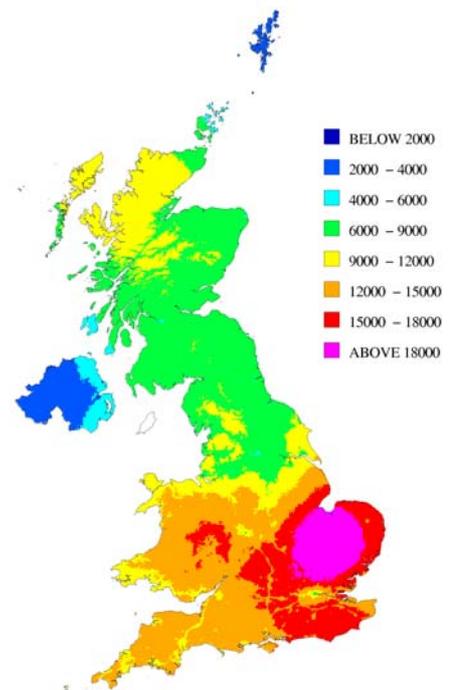
Ozone 2006
AOT40 (µg m^{-3}.hours)

Modelling of Tropospheric Ozone
First Annual Report

Report to The Department for Environment, Food and Rural Affairs, Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland

ED48749001

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	Date	2nd February 2008

Executive summary

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).

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 for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations (DAs, the Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland) have funded the development of ozone modelling tools 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 and changes in emissions can be assessed.

The overall purpose of the project is to maintain, develop, and apply tools for modelling tropospheric ozone formation and distribution over a range of spatial scales (global, regional and national). The modelling will be used to support and guide Defra's policy on emission reductions and objectives for pollutants that influence ozone, and to verify compliance with UK policy and with European directives on ground-level ozone.

To meet these aims and to address the intended applications, the current project has a programme of work comprised of four main objectives:

Objective 1:   **Policy development and scenario analysis**

Objective 2:   **Detailed assessment of relationship between ozone, nitrogen oxide and nitrogen dioxide levels, and factors controlling them**

Objective 3:   **Improvements to photochemical reaction schemes**

Objective 4:   **Development of multi-trajectory modelling capacity using forward track trajectories**

This is the first annual report on the project and covers the period from 1st January 2007 to 31st December 2007. Significant progress and activity has been carried out on the first three objectives, with the precise detail of work on Objective 4 to be agreed with Defra in the next year of the project.

The work to date can be broadly categorised as **application** of existing models of tropospheric ozone formation for policy purposes and further **research and development** of the models and the underpinning science. The main conclusions from the work and the policy relevance are as follows:

Application of Tropospheric Ozone Models and Policy Support

UK Ozone Climate in 2006:
The UK ground-level ozone climate for 2006 has been characterised by the Pollution Climate Mapping (PCM) empirical modelling approach and the Ozone Source Receptor Model (OSRM). Both models indicated 2006 was a relatively high ozone year, with elevated concentrations measured in the summer when peak episodic conditions prevailed.

Results from the PCM, that are based on 2006 ozone monitoring data, are summarised for the EU Target Value for ozone concentration metrics for human health and vegetation in 2010 (an average over the past 3 years) and the Long-term Objectives for ozone in the following tables, respectively.

UK summary results of air quality assessment relative to the Target Values for ozone for 2010

Target Value	Number of zones exceeding
Max Daily 8-hour mean Target Value	none
AOT40 Target Value	none

UK summary results of air quality assessment relative to the Long-term Objectives for ozone

Long-term Objective	Number of zones exceeding
Max Daily 8-hour mean Long-term Objective	43 zones (41 measured + 2 modelled)
AOT40 Long-term Objective	41 zones (32 measured + 9 modelled)

There were particularly high numbers of exceedences of the 120 µg m^{-3} Long-term Objective value in East Anglia and the South-East.

The OSRM is a process model calculating the formation of ozone in the UK based on a chemical transport modelling approach using emissions inventory and real meteorological data for 2006. It shows broadly similar patterns compared with the empirical maps in terms of these ozone metrics for 2006, identifying significantly higher concentrations in the south and east of the UK, however there are some specific spatial differences and overall, as has been shown previously, the OSRM in 2006 has generally under estimated ozone concentration metrics compared with measured data. Furthermore, the difference between the concentrations predicted by OSRM and the measured concentrations were larger for the high ozone year (2006) than in previous (low ozone) years (2004 and 2005). This had been observed for a previous high ozone year (2003).

Modelling Impacts of Emission Scenarios on Future UK Ozone:
The process modelling capability of the OSRM has been used to model a number of future emission scenarios relevant to policy.

- The impact on UK ozone concentrations of four additional transport emission reduction measures were modelled for the Air Quality Strategy Review (AQSR). For the road transport measures that involved reductions in NO_x emissions due to tighter Euro 5/6(VI) standards on vehicle emissions, the results tended to show a worsening in the health-based ozone metrics. A slight improvement in ozone was observed when measures reducing NO_x emissions from shipping were included.

- A separate study looked at the impact of reducing shipping emissions alone, using assumptions used in the Air Quality Strategy Review. All metrics show that reducing NO_x emissions from shipping by 9% leads to a reduction in ozone concentrations. Reducing SO_2 emissions by 33% also leads to a small beneficial effect on ozone, but the impact is considerably smaller than the effect of reducing NO_x emissions. It was recommended that the effect of shipping emissions on ozone concentrations be given a more detailed analysis.

- The OSRM was used to model the impacts of changing VOC emissions from road transport across Europe arising from the EU Fuel Quality Directive and the uptake of bioethanol-petrol blends. The focus was on the impacts of potential increases in acetaldehyde emissions from engine exhausts and an increase in evaporative emissions from cars as a consequence of the relaxation of volatility limits of summer blends of petrol to enable the market penetration of bioethanol blends across Europe. The overall conclusion from the modelling study was that the effect of introducing up to 10% bioethanol petrol blends in Europe is unlikely to show any effect on UK ozone levels in the UK up to 2020.

Climate Change Consequences of VOC Emission Controls:
A report entitled "*Climate Change Consequences of VOC Emission Controls*" was prepared for Defra to be used as a guide for industry, providing a simple approach, with worked examples, for quantitatively assessing the climate change consequences of VOC emission control by incineration. Defra expect the report to be used as supplementary background technical information for a wider set of guidelines for industry operators and regulators covering the issue of VOC abatement and its environmental consequences.

Research and Development of Ozone Models

Chemical Mechanisms in Ozone Models:
A substantial and in-depth review of the **Master Chemical Mechanism** was carried out by members of the project consortium. The review report was independently peer-reviewed and in response to this, the review's authors prepared a set of revised recommendations for future development of the MCM. The direct policy relevance of the MCM as a crucial tool and source of chemical reactivity information in models for assessing the affect of VOC control options on ozone and other transboundary air pollutant formation in Europe was demonstrated in the review and this demonstration is now being extended.

NO_x-NO_2-O_3 Relationships:
A number of analyses of monitoring data have been undertaken to provide more information on local, regional and global contributions to oxidant at UK locations, and to improve the description of the partitioning of oxidant into its component species (i.e., O_3 and NO_2). The work undertaken so far will help to improve the treatment of NO_x-NO_2-O_3 relationships in the PCM empirical model and the surface conversion algorithm of the OSRM, helping to improve predictions of ozone concentrations in urban environments. Such analysis includes further insight into the contribution made by direct emissions of NO_2 principally from traffic sources in urban areas providing a direct additional source of oxidant. Work is currently underway in the Pollution Climate Mapping Programme on incorporating these findings to date into the PCM models.

Modelling Secondary Particulate Matter:
Whilst this project is primarily focused on modelling of tropospheric ozone, there is considerable overlap with approaches used to model secondary particulate matter (PM). Process models for forecasting the response of secondary PM formation to changes in precursor emissions (NO_x, SO_2, NH_3, NMVOCs) require similar chemical transport models to the types used for predicting ozone concentrations and there is overlap in terms of evaluating policies affecting the formation of both pollutants. Work was undertaken in this project using the Photochemical Trajectory Model (PTM) and the Met Office NAME model to examine the sensitivity of secondary PM component concentrations to changes in the emissions of PM precursors. The aim was to develop scaling factors that could be used in the PCM to gauge the importance of these non-linearities for policy-making in relation to changes in precursor emissions.

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Appendix 1 - Model Information Sheet for the Ozone Source Receptor Model Completed for Defra's External Review of Tools for Modelling Tropospheric Ozone

Appendix 2 - Worked Example (E) for Method for Assessing the Climate Change Consequences of VOC Emission Control and tables of GWPs and fuel CO_2 conversion factors

1   Introduction

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 influences regional scale photochemical processes by providing an increasing background ozone level upon which the regional and national scale formation is superimposed. This effect 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 for Environment, Food and Rural Affairs (DEFRA) and the Devolved Administrations (DAs, the Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland) have funded the development of ozone modelling tools 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 and changes in emissions can be assessed.

The previous contract funded by DEFRA and the DAs (Modelling of Tropospheric Ozone, EPG 1/3/200) had a strong emphasis on model application to evaluate planned and proposed policies, such as the Review of the Air Quality Strategy. Technical assistance was also provided to fulfill commitments arising from the implementation of the European Directives, in particular the 3rd Daughter Directive on Ozone. Model development work focused on the complex relationships between ozone and nitrogen oxides in order to improve the predictive capability of models in urban areas where local sources influence the balance between nitric oxide (NO), nitrogen dioxide (NO_2) and ozone. This new project aims to continue with the development and application of ozone modelling tools in these areas.

As part of their ozone research programme, DEFRA and the Devolved Administrations have over the years supported the development of near explicit chemical mechanisms, especially that of the Master Chemical Mechanism based on fundamental knowledge of the detailed photochemical reaction pathways involved in the formation of tropospheric ozone from the wide range of individual types of volatile organic compounds emitted into the atmosphere from anthropogenic and natural sources. 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 further development of the Master Chemical Mechanism and its application in ozone models continues to be of interest to the Department and the DAs and will be contingent on the outcome of a review of the Master Chemical Mechanism to be carried out in this project.

The importance of the treatment of meteorological and chemical transport processes in ozone models is widely recognised. This is reflected in the current project with a shift in emphasis on model development from chemistry to meteorology, with inclusion of a new objective on developing and using multiple trajectories and understanding the influence of meteorology on ground-level ozone concentrations. The exact approach will be considered following an independent review of current ozone models commissioned by the Department in the first year of this project. The outcomes of this review will influence the direction of the work carried out later in this project.

This is the first annual report on the current project covering the period from 1st January 2007 to 31st December 2007. The report is structured as follows:

Section	Contents
Section 2 - Overview and Progress	Description of the project, its aims and structure and summary of progress and activities
Section 3 - Overview of the Ozone Source Receptor Model	A brief description of the OSRM model is given
Section 4 - Modelling for National and International Policy Development (Objective 1a)	Use of OSRM to evaluate a number of policy options affecting ozone precursor emissions
Section 5 - Support for Policy Implementation (Objective 1b)	Description of additional policy support using available tools and knowledge to guide policy implementation
Section 6 - Ozone in the UK: 2006 - Modelling Support for the Third Daughter Directive (Objective 1c)	Description of modelling and results from PCM and OSRM to characterise the UK ozone climate of 2006
Section 7 - Detailed Assessment of Relationship Between Ozone, Nitrogen Oxide and Nitrogen Dioxide Levels, and Factors Controlling Them (Objective 2)	Analysis of NO_x, NO_2 and O_3 monitoring data from co-located sites to understand the relationship between these pollutants to improve treatment in models
Section 8 - Improvements to Photochemical Reaction Schemes (Objective 3)	Review of Master Chemical Mechanism and maintenance of website
Section 9 - Other Project Activities	Description of other project activities, report, *ad-hoc* requests and publications
Section 10 - Conclusions and Policy Relevance	Summary of key conclusions of work to date and their policy relevance
Section 11 – Acknowledgements	

2 Overview and Progress

2.1 Project Aims and Structure

The overall aim of this project is to maintain, develop, and apply tools for modelling tropospheric ozone formation and distribution over a range of spatial scales (global, regional and national). The modelling will be used to support and guide policy on emission reductions and objectives, and to verify policy compliance.

The programme of work consists of 4 main objectives to meet the overall aims of the project.

Objective 1:   **Policy development and scenario analysis**

Objective 2:   **Detailed assessment of relationship between ozone, nitrogen oxide and nitrogen dioxide levels, and factors controlling them**

Objective 3:   **Improvements to photochemical reaction schemes**

Objective 4:   **Development of multi-trajectory modelling capacity using forward track trajectories**

There are strong linkages between these core objectives as shown in Figure 2.1.

Figure 2.1: Schematic showing linkages between different objectives
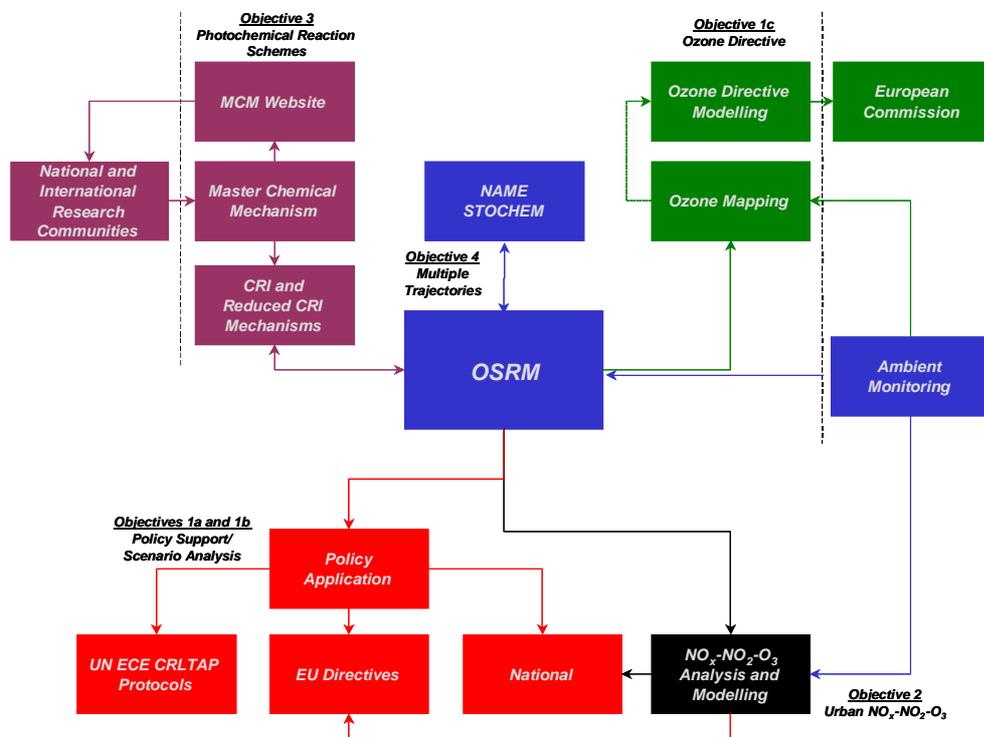
At the heart of this is the **Ozone Source Receptor Model (OSRM)**, developed in previous DEFRA tropospheric ozone modelling contracts and the now the main provider of health-and non-health-based ozone concentration metrics on a national scale used for DEFRA ozone policy development.

The OSRM simulates the chemical development of species in an air parcel moving along a trajectory to receptor points on a 10 x 10 km grid covering the UK. It uses real 6-hourly meteorological data for a calendar year to define 96-hour back trajectories to different receptor points, each trajectory picking up emissions within the EMEP domain and using a simplified chemistry scheme to simulate the photochemical production of ozone as the air parcel reaches each receptor point. The model provides national scale ozone concentration metrics and can demonstrate how these change in response to changes in emissions and meteorology. An overview of the OSRM is provided in Section 3 and more detail is given in Hayman et al. (2006a). Much of the model development and application work in this project is on and with the OSRM, but there are links between the OSRM and other models and tools used for ozone policy.

The **UK Photochemical Trajectory Model (UK PTM)** uses a linear trajectory under idealised anticyclonic, ozone episode conditions, to simulate photochemical ozone production as the air arrives at specific receptor sites over the UK. With its simplified description of meteorology, the UK PTM can accommodate large chemical schemes such as the Master Chemical Mechanism and therefore can examine policies aimed at targetting emissions of individual volatile organic compounds (VOCs). The UK PTM has been used to derive Photochemical Ozone Creation Potentials (POCPs) of over 100 different VOCs. More details of the UK PTM can be found in Derwent et al. (1998, 2004).

AEA's **empirical modeling approach** uses monitoring data from AURN network sites and empirical mapping techniques to develop maps of UK ozone concentration metrics reported under the 3rd Air Quality Daughter Directive. Bush and Targa (2005) have shown that the empirical modelling approach provides better agreement with monitoring data across the UK for the four concentration metrics reported annually to the Commission compared with output from the OSRM and thus it was decided in the last contract to use the empirical modelling approach to supplement measurement data reported to the Commission. This better agreement reflects the fact that monitoring data are used in both creating the rural field of the empirical maps and in calibrating the metrics in urban areas. However, while the empirical modelling approach does have some physical understanding of the processes occurring that influence ozone concentrations, the OSRM provides a better understanding of the fundamental photochemical processes occurring in ozone production in the UK. This means that in terms of ozone policy making, the OSRM is better suited than the empirical modelling approach at forecasting future ozone concentrations and how these might respond to changes in precursor emissions.

Thus the three modelling methods described are complementary:

> ➢ The **empirical modeling approach** provides the best means of quantifying and spatially representing the current UK ozone concentration climate;

> ➢ The **UK Photochemical Trajectory Model** provides the best means of quantifying how UK peak ozone concentrations at specific receptor sites will respond to changes in individual VOC emissions and demonstrating the relative reactivity of different VOC species;

> ➢ The **Ozone Source Receptor Model** provides the best means of forecasting ozone and associated health- and non-health-based metrics in a policy context on a UK-wide scale and the effect of changes in meteorology and changes in emissions caused by policy decisions.

While Objectives 2-4 are generally of a research nature and aimed at improving the understanding and treatment of chemical amd meteorological processes in ozone models, Objective 1 applies the existing models and knowledge to assisting with ozone policy. Thus Objective 1 is divided into three sub-tasks:

Objective 1a: Modelling for national and international policy development – using the OSRM and PTM to run scenarios relating to ozone policy

Objective 1b: Support for policy implementation – using available tools to guide policy implementation and provide general advice as required by DEFRA

Objective 1c: Modelling support for the Third Daughter Directive – using the empirical modelling approach and the OSRM to provide the modelling outputs (ozone metrics) to meet the Supplementary Assessment Modelling requirements of the Third Air Quality Daughter Directive reporting each year.

The requirements of Objectives 1a and 1b are of an *ad-hoc* nature, as and when required by DEFRA and the DAs. Objective 1c represents an annual data delivery requirement.

The linkages between Objectives 1-4 shown in Figure 2.1 will bring the following benefits to the work:

✓   Linkage of scales. The work under Objective 2 on urban scale ozone production and ozone-NO_x-NO_2 relationships will have implications for ozone concentrations both in urban environments and downwind of urban centres. This could potentially have significant implications for policy modelling on the national scale using the OSRM and in improving the techniques for empirical mapping of ozone concentrations for reporting to the Commission (Objective 1).

✓   Improvements to the main ozone modelling tool, the OSRM, will be made under Objectives 3 (Chemistry) and 4 (Meteorology). These improvements will be introduced into the version of the OSRM used for policy applications (Objective 1).

✓   Linking the Master Chemical Mechanism (MCM, Objective 3) to ozone modelling (Objective 1). The historic focus has been on increasing the number of VOCs in the MCM. One version of the MCM now treats the atmospheric oxidation of over 175 VOCs, representing 90% of the UK anthropogenic emissions. The insight gained from this work will be beneficial to the UK PTM applied in Objective 1and will be used to derive reduced mechanisms which can be used in the available ozone modelling tools (OSRM).

✓   The greater emphasis on meteorology in the proposed work programme (Objective 4) will be used to benchmark and ultimately improve the meteorological treatment in the OSRM by comparison against a model with a state-of-the-art meteorological treatment.

✓   Consistency in input datasets or treatment of processes. Currently, the input concentration fields and the meteorological data are derived from different sources and these datasets may not be fully consistent. The work under Objective 4 will allow these to be derived from the same source.

A further objective was added by DEFRA after the start of the project, aimed at development of methods for assessing the costs and benefits of solvent reduction and substitution policies:

Objective 7:   Costs, Benefits and Trade-offs: Volatile Organic Solvents

This task will involve a demonstration of the Master Chemical Mechanism and the underlying knowledge gained from its development in a more direct link to policy making and the task will in itself feed into the current review of the MCM in Objective 3.

2.2   Project Partners

The project team for the main project encompassing Objectives 1-4 consists of a consortium of groups led by **AEA Energy & Environment**. The other consortium partners are **Professor Dick Derwent (rdscientific), Dr Mike Jenkin (Atmospheric Chemistry Services), Professor Mike Pilling (University of Leeds) and the Met Office**. Each of these partners will be undertaking specific tasks as shown in the schematic presented in Figure 2.2.

Figure 2.2 Schematic showing the involvement of consortium partners to the main project objectives
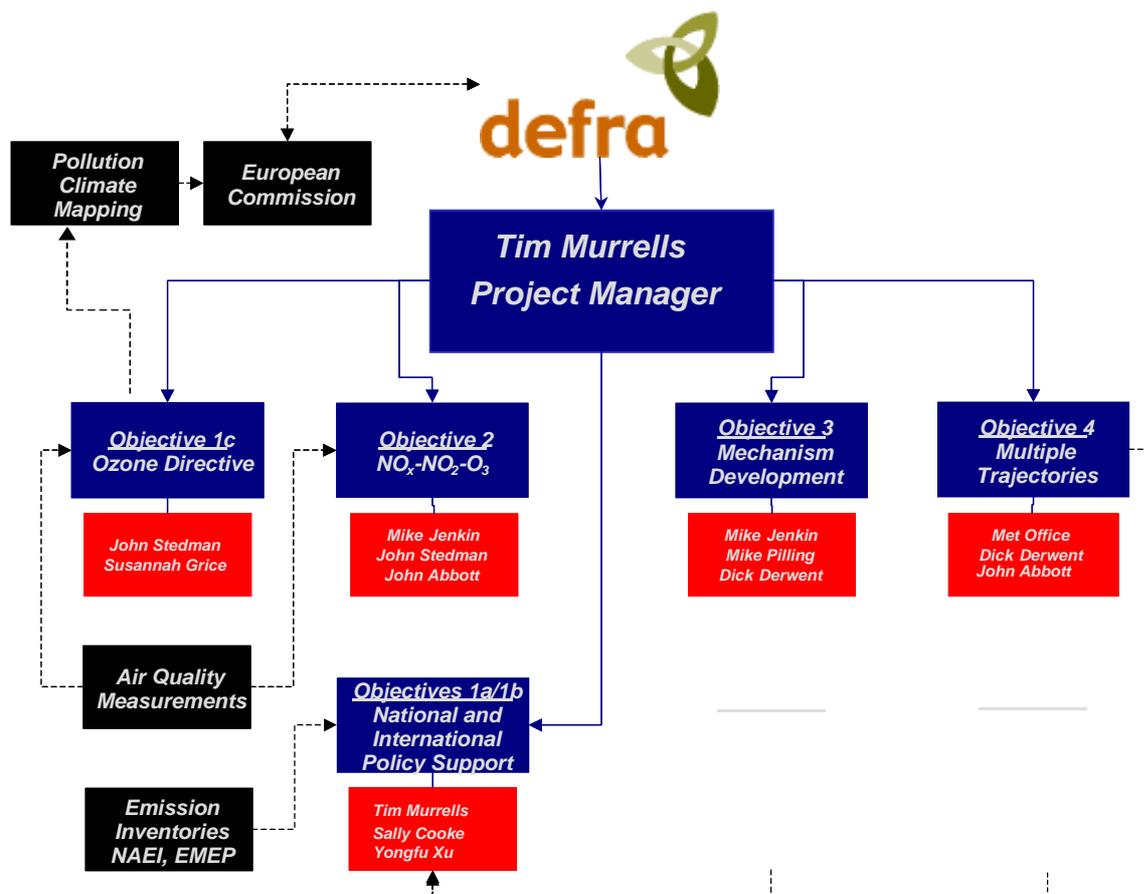
2.3   Progress to Date

The project schedule proposed at the start of the project is shown in Figure 2.3.

Overall, there has been a high level of project activity and progress made on Objectives 1-3. Work on Objective 4 is due to be concentrated in the second year of the project. The precise details of the work plan are still to be agreed with Defra in light of the recommendations of the recent independent review of Defra's ozone modelling requirements. This is likely to help define the best way forward for improving the treatment of meteorological processes in the OSRM.

The progress and activities on Objective 1-3 can be summarised as follows:

Objective 1a: Modelling for national and international policy development:
OSRM was used to run ozone scenarios in relation to:
   a)   emission reduction measures being explored in the 2007 Air Quality Strategy Review
   b)   the effect of changes in VOC emissions from uptake of bioethanol road fuels across Europe
   c)   the effect of changes in shipping emissions on UK ozone concentrations

Objective 1b: Support for policy implementation:
Using available tools and knowledge to guide policy implementation and providing advice on:
   a)   The development of a method for assessing the climate change consequences of VOC
        emission control;

b) Secondary particulate matter (PM) modelling using the Photochemical Trajectory Model
(PTM) and the Met Office NAME model.

Figure 2.3: Project schedule
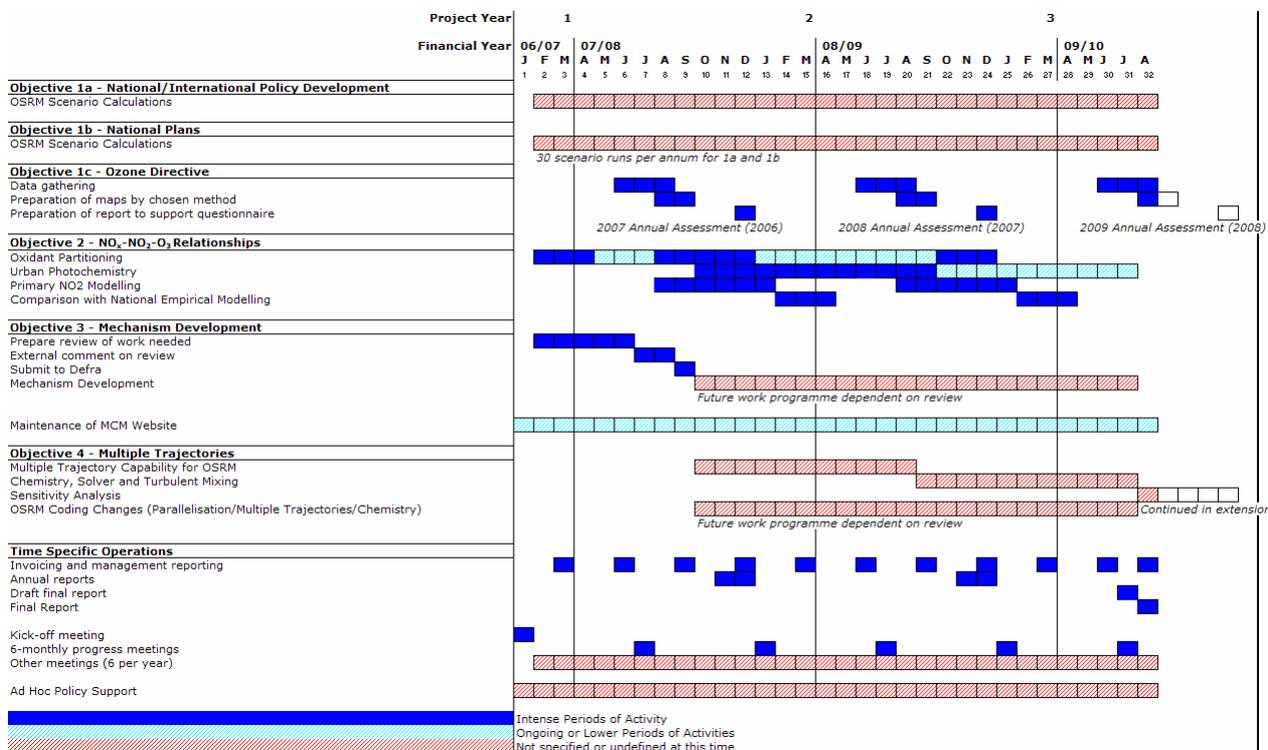
Objective 1c: Modelling support for the Third Daughter Directive:
The UK ground-level ozone climate for 2006 has been characterised by the Pollution Climate Mapping
(PCM) empirical modelling approach and the Ozone Source Receptor Model (OSRM). The
Supplementary Assessment Modelling for the 3rd Daughter Directive on Ozone Reporting for 2006
used outputs from the empirical modelling approach, but comparisons have been made with results
from the OSRM

**Objective 2:   Detailed assessment of relationship between ozone, nitrogen oxide and
nitrogen dioxide levels, and factors controlling them**
Monitoring data have been analysed to provide more information on local, regional and global
contributions to oxidant at UK locations, and to improve the description of the partitioning of oxidant
into its component species (i.e., O_3 and NO_2).

Objective 3:   Improvements to photochemical reaction schemes
A substantial and in-depth review of the **Master Chemical Mechanism** was carried out by members
of the project consortium. The review report was independently peer-reviewed and in response to
this, the review's authors prepared a set of revised recommendations for future development of the
MCM.

3   Overview of 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, 2005; 2006a). 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 based on that used in the STOCHEM model. The mechanism has ~70 chemical species involved in ~180 thermal and photochemical reactions. The mechanism represents ozone formation using 12 VOCs, which provides an appropriate description of ozone formation on the regional scale. The emission inventories are taken from EMEP for Europe with the option to use National Atmospheric Emissions Inventory (NAEI) data for the UK, which have been aggregated to 10 km x 10 km and into 8 key sectors. A slightly fuller description of the model is given in Box 3.1.

The OSRM describes the boundary layer by a single box and assumes that this is well mixed. When the model is required to handle and generate concentrations of species near to the surface, account must be taken of surface removal processes (dry deposition and chemical reactions) and emissions that will generate gradients in the concentrations of ozone and oxides of nitrogen. This will result in lower and higher concentrations, respectively, of these species compared to their corresponding mid-boundary layer concentrations. These effects are of particular significance in urban areas. An algorithm has been developed and implemented in an OSRM post-processor to convert the hourly mid-boundary layer concentrations to surface concentrations. The 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.

From the hourly concentrations, the post-processor calculates a large number of different metrics for ozone and nitrogen dioxide and produces output datafiles for generating maps of these metrics.

The OSRM has been tested by comparison with results from monitoring data. More details of the model performance are given in Hayman et al (2006a). Overall, the OSRM is a model which now has a robust and flexible construction that makes it ideal for the demands of assisting in the development of policy. The improvements made to the OSRM during the previous modelling contract produced a model that is able to reproduce boundary-layer concentrations of ozone and oxides of nitrogen, representative of the UK.

In the context of ozone formation, the OSRM and UK Photochemical Trajectory Model were found to give identical output and responses, on a like-for-like basis. For the determination of surface concentrations of ozone and oxides of nitrogen, the OSRM has post-processor options, which take account of local emissions and removal processes. The comparison of the OSRM with the ADMS Urban model gave similar responses and showed similar spatial patterns. These comparisons demonstrate that, through the successful development to the current version, the OSRM now provides a consistent and robust modelling tool, able to support the Department in the development of policy based upon strong science.

During the first year of the current project, Defra commissioned an independent review on tropospheric ozone modelling and the review summarised and compared key features of all the available modelling tools including the OSRM and the PTM. The Model Information Sheet completed for the OSRM as part of the model information gathering stage of the review process is given in Appendix 1.

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Box 3.1: Description of the Ozone Source Receptor Model

The OSRM is similar in concept to the UK Photochemical Trajectory Model (UK PTM) [Derwent *et al.*, 1998, 2004] in that it simulates the chemical development of species in an air parcel moving along a trajectory and to the ELMO source-receptor model [Metcalfe *et al.*, 2002] in that calculations can be undertaken to a 10 km x 10 km grid covering the UK. The OSRM (version 2.2a) has a number of notable enhancements and advantages to these models:

➢ **Air Mass Trajectories**: Realistic two-dimensional air mass trajectories are derived from wind fields extracted from meteorological datasets. The UK PTM and ELMO model use linear trajectories (although the UK PTM has since been adapted to use two- or three-dimensional air mass trajectories). Meteorological datasets are available for use with the OSRM for the years 1995 to 2005;

➢ **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, (c) version 1 of the Common Reactive Intermediate mechanism and (d) 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. The table below provides details of these chemical mechanisms;

Table: *Details of the Chemical Mechanisms used in the OSRM.*

	STOCHEM	Modified STOCHEM	Mini-CRI	Mini-CRI
# of Species	70	70	70	280
# of Reactions	154	180	198	
# of VOCs	12	12	12	125
Emitted VOCs	➢ **alkanes** (ethane, propane, *n*-butane) ➢ **alkenes** (ethene, propene) ➢ **aromatics** (toluene, *o*-xylene) ➢ **oxygenated VOCs** (methanol, acetone, methyl ethyl ketone, formaldehyde, acetaldehyde)	➢ **alkanes** (ethane, propane, *n*-butane) ➢ **alkenes** (ethene, propene) ➢ **aromatics** (toluene, *o*-xylene) ➢ **oxygenated VOCs** (methanol, acetone, methyl ethyl ketone, formaldehyde, acetaldehyde)	➢ **alkanes** (ethane, propane, *n*-butane) ➢ **alkenes** (ethene, propene) ➢ **aromatics** (toluene, *o*-xylene) ➢ **oxygenated VOCs** (methanol, acetone, methyl ethyl ketone, formaldehyde, acetaldehyde)	➢ **alkanes** ➢ **alkenes** ➢ **dienes** ➢ **alkynes** ➢ **aromatics** ➢ **oxygenated VOCs** ➢ **chlorinated VOCs** ➢ **biogenic VOCs**
Biogenic VOCs	Isoprene	isoprene	isoprene	isoprene, pinene
VOC speciation	NAEI 1998	NAEI 1998	NAEI 1998	NAEI 1998, 2000

➢ **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.

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> ➢ **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;

> ➢ **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.

A single trajectory calculation using the backwards-iterative EULER solver with a chemical timestep of 240s takes ~0.025 s (i.e., ~40 trajectories per second) using a Dell Precision Workstation 650 MiniTower (containing dual Intel® Xeon 3.06GHz processors). Making use of the two available processors on the workstation gives a runtime of ~4.5 days for a UK-scale model run to ~3,000 receptor sites for a calendar year.

4 Modelling for National and International Policy Development (Objective 1a)

Work carried out for this objective is of an *ad-hoc* nature involving using available tools to show impacts of planned and proposed policies on ozone levels, as required by Defra. During the first year of the project, the Ozone Sourse Receptor Model was used to simulate ozone concentrations and provide health- and non-health based metrics for various emission scenarios relating to two main policy areas. One set of scenarios was in relation to emission reduction measures being explored in the 2007 Air Quality Strategy Review (Section 4.1). The second set of scenarios examined the effect of changes in VOC emissions from uptake of bioethanol road fuels across Europe (Section 4.2). The OSRM was also used to examine the effect of changes in shipping emissions on UK ozone concentrations (Section 4.3).

4.1 Ozone Modelling of Additional Measures for the Review of the Air Quality Strategy

The Ozone Sourse Receptor Model has previously been used to determine UK ozone air quality in future years to assess the impact of a range of emission control measures examined for the Review of the Air Quality Strategy (Hayman et al, 2006b). Modelled changes in ozone concentrations and metrics are one of the inputs to the cost-benefit analysis that has been undertaken for the Review of the Air Quality Strategy (Defra, 2006a, 2006b). Many of the measures considered for the Review are measures affecting road transport emissions of NO_x and particulate matter (PM), but other measures considered refer to controls of NO_x, VOC and SO_2 emissions from stationary combustion, industrial and other transport sources and combinations of these and road transport measures.

During the first year of this current project the Ozone Source Receptor Model (OSRM) was used to model the impacts of four additional transport emission reduction measures on projected ozone concentrations in the next phase in the Air Quality Strategy Review (AQSR). The measures were defined by Defra and involve two new measures that affect road transport emissions of NO_x, CO and hydrocarbons and two that combine these measures with measures modelled previously: a Low Emission Vehicle (LEV) measure and a measure affecting emissions of NO_x and SO_2 from shipping.

The measures are summarised as:

Measure A2 - Revised Euro V/VI Scenario A affecting road transport emissions of NO_x, CO and HCs

Measure C2 - Revised Early Euro V/VI Scenario C affecting road transport emissions of NO_x, CO and HCs

Measure R - Combination of Measures C2, E (LEV Measure for road transport) and N (shipping emission reduction measure affecting NO_x and SO_2)

Measure S - Combination of Measures A2, E (LEV Measure for road transport) and N (shipping emission reduction measure affecting NO_x and SO_2)

4.1.1 Assumptions used for transport measures

Measures A2 and C2 involved using emission reductions for light duty vehicles that were believed to be more representative of the Commission's proposed limit values for Euro 5 and 6(VI) vehicles introduced in 2010 and 2015 at the time the emissions modelling work was undertaken. Details of the emission reductions assumed for Measures A2 and C2 are shown in Table 4.1. NO_x standards for all new diesel cars and LGVs are introduced in two stages: 2010/2011 for Euro 5 standards followed by tighter limits for Euro 6 from 2015/2016. Euro VI standards for HDVs are introduced from 2013. The

Table 4.1: Emission reductions assumed for road vehicles in Measures A2

			% reduction rel. to Euro 4/IV	Introduction	Note
NO_x	Petrol cars/small vans	Euro 5	12.5%	1st Jan 2010	160,000 durability, deterioration factor 1.4, but no change in degradation rate
	Med/large petrol vans	Euro 5	15%	1st Jan 2011	
	Diesel cars/small vans	Euro 5	28%	1st Jan 2010	160,000 durability, but no change in degradation rate
	Med/large diesel vans	Euro 5	28%	1st Jan 2011	
	Diesel cars/small vans	Euro 6	72%	1st Jan 2015	160,000 durability, but no change in degradation rate. Includes 5% catalyst failure and higher cold start emissions for Euro VI, with SCR or LNT
	Med/large diesel vans	Euro 6	75%	1st Jan 2016	
	HGVs and buses	Euro VI	50% reduction relative to Euro V occurring from 1st Jan 2013		
VOCs	Petrol cars/small vans	Euro 5	32%	1st Jan 2010	160,000 durability, deterioration factor 1.4, but no change in degradation rate
	Med/large petrol vans	Euro 5	32%	1st Jan 2011	
	Diesel cars and vans	Euro 5	No change		
		Euro 6	No change		
	HGVs and buses	Euro VI	No change		
CO	Petrol cars/small vans	Euro 5	0%	1st Jan 2010	160,000 durability, deterioration factor 1.4, but no change in degradation rate
	Med/large petrol vans	Euro 5	0%	1st Jan 2011	
	Diesel cars and vans	Euro 5	No change		
		Euro 6	No change		
	HGVs and buses	Euro VI	No change		

standards for NO_x emissions for light duty vehicles involve changes to emission limits and durability standards. For VOCs, the standards only involve changes to the emission limits and durability standards for petrol cars and LGVs; there are no changes assumed for diesel vehicles. For CO, the standards only involve changes to the durability standards for petrol cars and LGVs; again, there are no changes assumed for diesel vehicles.

For Measure C2, the emission changes for the various emission standards are the same as for A2, but the dates of introduction are assumed to be brought forward by 2 years for cars and vans and by 3 years for HGVs and buses due to a programme of incentives.

Measure R is a combination of Measures C2, E and N. Measure E is a Low Emission Vehicle (LEV) measure that affects only NO_x emissions from petrol and diesel cars. For a petrol LEV, NO_x emissions are reduced by 37.5% relative to Euro 4 and sales reach 10% of petrol car sales by 2010

and 25% by 2020; for a diesel LEV, NO_x emissions are reduced by 80% relative to Euro 4 and sales reach 5% of diesel car sales by 2010 and 20% by 2020. Measure N is a shipping emission reduction measure affecting NO_x and SO_2 emissions on the global fleet of ships above 100 tonnes. The requirement is for all existing ships to use fuels with a sulphur limit of 1% from 2010 (current requirement is 1.5%) and for NO_x emissions from all new ships to be reduced by 25%.

Measure S is a combination of Measures A2, E and N.

Further details of Measures E and N are given in the report of Stedman et al (2006) prepared as a supplementary report for Defra to the Air Quality Strategy Review Consultation report.

4.1.2   Emission reduction results for transport measures

The road transport emissions model of the National Atmospheric Emissions Inventory (NAEI) was used to calculate the changes in UK road transport emissions for each measure relative to the basecase. The results are shown in Table 4.2.

Table 4.2: Reduction in UK road transport emissions for each AQSR Measure

	Measure	2010	2015	2020
NO_x	A2	1%	16%	37%
	C2	3%	22%	40%
	R	4%	23%	42%
	S	1%	17%	39%
CO	A2	5%	40%	63%
	C2	10%	44%	66%
	R	10%	44%	66%
	S	5%	40%	63%
VOCs	A2	1%	9%	12%
	C2	3%	10%	13%
	R	3%	10%	13%
	S	1%	9%	12%

The assumptions for Measure A2 are the ones mainly responsible for most of the emission reductions in the variant Measure C2 and the combined measures R and S.

The reduction in UK shipping emissions as a result of Measure N is shown in Table 4.3.

Table 4.3: Reduction in UK shipping emissions for Measure N

	2010	2015	2020
NO_x	0.8%	5%	9%
SO_2	33%	33%	33%

4.1.3   Effect of AQSR Measures on Different Ozone Concentration Metrics Modelled Using the OSRM

The effect of each of the four AQSR Measures on 7 different ozone concentration metrics was modelled using the OSRM for 2010, 2015 and 2020. The basecase condition assumed 2003 meteorology (a year characterised by high summer ozone episodes) and base NAEI emission

projections associated with the BERR's UEP12 energy projections. These conditions were used in all the previous model runs undertaken for the Air Quality Strategy Review during 2005-2006.

Full UK-scale model runs were undertaken to obtain hourly concentrations on a 10x10 km grid of the UK for each day of the year and the data processed to obtain results for the following 7 ozone metrics:

Health impacts:
- Population-weighted annual mean of the maximum daily running 8-hr means
- Population-weighted annual mean of the difference between daily maximum running 8-hr mean and 70 µg/m^3
- Population-weighted annual mean of the difference between daily maximum running 8-hr mean and 100 µg/m^3
- Population weighted number of days when maximum daily running 8-hr mean exceeds 100 µg/m^3

Non-health impacts:
- Area weighted annual mean O_3
- Area weighted AOT40 - crops
- Area-weighted AOT40 - forests

These are the ozone concentration metrics used in the original modelling work for the Air Quality Strategy Review carried out by Hayman et al (2006b).

Each Measure was modelled by changing the UK road transport emissions of NO_x, CO and VOCs by the relative amounts shown in Table 4.2. Different considerations were given to the impact of these measures from road transport emissions in the rest of Europe:

- Measures A2 and C2 will apply to all other EU countries, so it was assumed for these measures that the same percentage reductions occurred for emissions in the road transport sector for all other countries.

- The LEV Measure E was assumed to apply only to the UK, so in the combined Measures R and S, European road transport emissions were scaled according to the changes in Measures C2 and A2 for the UK, respectively.

- The same relative changes in shipping emissions for Measure N were assumed for all European sea territories in the EMEP emission region: the North Sea, Mediterranean, Baltic Sea, Black Sea and remaining North-East Atlantic.

The effects of each Measure on the 7 ozone metrics for the UK, Scotland, Wales, Northern Ireland, Inner London, Outer London and the rest of England in 2010, 2015 and 2020 are shown in Tables 4.4 to 4.10. The results tend to show a worsening in the health-based ozone metrics for Measures A2 and C2, most likely because of the reductions in NO_x emissions and the impact that has on the chemical titration effect of ozone in urban areas. The combined measures lead to an improvement in the situations for ozone relative to the respective Euro 5/6(VI) measure, e.g. comparing S versus A2 and R versus C2. This is in spite of further reductions in NO_x emissions brought about by the LEZ Measure E and appears to be due to the impact of the reductions in regional shipping emissions. Independent modelling of the shipping scenarios suggest this is primarily due to reductions in shipping NO_x emissions, but reductions in SO_2 shipping emissions also have a beneficial effect on ozone (Section 4.3).

The OSRM results for these AQSR Measures were provided to Defra and included in the latest document on the Review of the Air Quality Strategy (Defra, 2007).

Table 4.4: Population-weighted annual mean of the maximum daily running 8-hr mean ozone concentrations (µg/m³)

µg/m³	Scotland	Wales	Northern Ireland	Inner London	Outer London	Rest of England	All UK
2010 - Base Case	73.03	76.73	76.42	65.30	65.51	69.65	69.96
2010 - Measure A2	73.04	76.75	76.43	65.34	65.56	69.68	69.99
2010 - Measure C2	73.08	76.80	76.45	65.49	65.71	69.78	70.09
2010 - Measure R	73.07	76.78	76.43	65.49	65.71	69.78	70.08
2010 - Measure S	73.02	76.73	76.41	65.34	65.56	69.67	69.98
2015 - Base Case	74.85	79.01	77.96	68.40	68.62	72.34	72.58
2015 - Measure A2	75.05	79.28	78.02	69.18	69.40	72.86	73.07
2015 - Measure C2	75.13	79.40	78.05	69.47	69.70	73.06	73.27
2015 - Measure R	75.07	79.33	77.97	69.47	69.70	73.04	73.25
2015 - Measure S	74.99	79.21	77.94	69.18	69.41	72.84	73.05
2020 - Base Case	76.46	81.16	79.39	70.62	70.88	74.57	74.72
2020 - Measure A2	76.79	81.66	79.44	72.37	72.63	75.67	75.78
2020 - Measure C2	76.81	81.69	79.43	72.50	72.75	75.74	75.85
2020 - Measure R	76.66	81.52	79.24	72.49	72.74	75.68	75.78
2020 - Measure S	76.64	81.50	79.25	72.36	72.62	75.61	75.71

Table 4.5: Population-weighted annual mean of the difference between daily maximum running 8-hr mean and 70 µg/m^3 ozone (µg/m^3)

µg/m^3	Scotland	Wales	Northern Ireland	Inner London	Outer London	Rest of England	All UK
2010 - Base Case	11.10	15.07	12.73	9.26	9.31	11.08	11.10
2010 - Measure A2	11.10	15.07	12.72	9.27	9.32	11.08	11.11
2010 - Measure C2	11.11	15.08	12.72	9.32	9.37	11.12	11.14
2010 - Measure R	11.10	15.06	12.71	9.30	9.36	11.10	11.12
2010 - Measure S	11.08	15.04	12.71	9.26	9.31	11.07	11.09
2015 - Base Case	12.21	16.51	13.73	10.70	10.80	12.52	12.51
2015 - Measure A2	12.25	16.55	13.67	10.95	11.06	12.68	12.66
2015 - Measure C2	12.27	16.58	13.66	11.04	11.17	12.75	12.72
2015 - Measure R	12.21	16.48	13.58	10.98	11.12	12.69	12.66
2015 - Measure S	12.19	16.46	13.59	10.88	11.00	12.62	12.60
2020 - Base Case	13.29	18.02	14.73	11.87	12.03	13.88	13.82
2020 - Measure A2	13.28	18.02	14.53	12.47	12.69	14.20	14.12
2020 - Measure C2	13.27	18.01	14.50	12.51	12.73	14.21	14.13
2020 - Measure R	13.12	17.80	14.33	12.40	12.63	14.09	14.01
2020 - Measure S	13.13	17.82	14.35	12.36	12.58	14.08	13.99

Table 4.6: Population-weighted annual mean of the difference between daily maximum running 8-hr mean and 100 µg/m³ ozone (µg/m³)

µg/m³	Scotland	Wales	Northern Ireland	Inner London	Outer London	Rest of England	All UK
2010 - Base Case	1.80	2.89	2.01	1.92	1.86	2.18	2.14
2010 - Measure A2	1.79	2.89	2.00	1.92	1.87	2.18	2.14
2010 - Measure C2	1.79	2.89	2.00	1.93	1.88	2.19	2.15
2010 - Measure R	1.79	2.88	2.00	1.93	1.87	2.18	2.14
2010 - Measure S	1.79	2.88	2.00	1.91	1.86	2.18	2.14
2015 - Base Case	2.06	3.34	2.29	2.28	2.23	2.55	2.50
2015 - Measure A2	2.05	3.33	2.26	2.32	2.27	2.57	2.52
2015 - Measure C2	2.06	3.34	2.26	2.35	2.29	2.59	2.53
2015 - Measure R	2.04	3.31	2.25	2.32	2.26	2.57	2.51
2015 - Measure S	2.04	3.30	2.25	2.30	2.24	2.55	2.50
2020 - Base Case	2.43	3.96	2.63	2.66	2.61	3.01	2.95
2020 - Measure A2	2.40	3.91	2.53	2.77	2.74	3.05	2.98
2020 - Measure C2	2.39	3.90	2.52	2.77	2.75	3.05	2.98
2020 - Measure R	2.34	3.82	2.47	2.72	2.71	3.00	2.93
2020 - Measure S	2.35	3.83	2.48	2.71	2.70	3.00	2.94

Table 4.7: Population weighted number of days when maximum daily running 8-hr mean exceeds 100 μg/m^3 ozone

No. days	Scotland	Wales	Northern Ireland	Inner London	Outer London	Rest of England	All UK
2010 - Base Case	34.11	57.89	42.98	33.71	34.28	38.96	38.99
2010 - Measure A2	34.03	57.85	42.90	33.71	34.29	38.95	38.97
2010 - Measure C2	34.16	57.85	42.64	33.87	34.41	39.09	39.09
2010 - Measure R	34.07	57.70	42.44	33.59	34.19	38.92	38.92
2010 - Measure S	34.00	57.64	42.69	33.71	34.14	38.79	38.83
2015 - Base Case	41.27	66.84	49.00	44.09	43.20	47.17	47.23
2015 - Measure A2	41.23	67.09	47.25	45.39	43.81	47.64	47.63
2015 - Measure C2	41.38	67.05	46.79	45.64	43.94	47.82	47.78
2015 - Measure R	41.07	66.05	45.70	44.36	43.73	47.08	47.07
2015 - Measure S	40.79	66.11	46.18	44.36	43.22	46.96	46.94
2020 - Base Case	49.47	76.92	55.18	51.04	49.78	55.17	55.14
2020 - Measure A2	49.22	75.05	51.18	50.30	51.26	56.17	55.71
2020 - Measure C2	49.01	74.80	50.86	50.52	51.58	56.22	55.75
2020 - Measure R	48.00	73.04	48.50	48.71	50.22	55.06	54.49
2020 - Measure S	48.04	73.19	48.72	48.79	50.19	55.00	54.47

Table 4.8: Area weighted annual mean O$_3$ (µg/m^3)

µg/m^3	Scotland	Wales	Northern Ireland	Inner London	Outer London	Rest of England	All UK
2010 - Base Case	65.34	65.13	65.98	50.19	50.01	58.27	61.48
2010 - Measure A2	65.35	65.15	65.99	50.25	50.07	58.30	61.51
2010 - Measure C2	65.37	65.20	66.02	50.42	50.23	58.40	61.57
2010 - Measure R	65.37	65.19	66.01	50.43	50.24	58.40	61.57
2010 - Measure S	65.34	65.14	65.98	50.26	50.08	58.30	61.50
2015 - Base Case	66.76	67.11	67.47	53.30	53.11	60.70	63.50
2015 - Measure A2	66.86	67.39	67.60	54.20	54.00	61.19	63.83
2015 - Measure C2	66.90	67.50	67.65	54.54	54.33	61.38	63.96
2015 - Measure R	66.86	67.46	67.60	54.59	54.38	61.40	63.95
2015 - Measure S	66.82	67.36	67.55	54.25	54.05	61.21	63.82
2020 - Base Case	68.14	68.94	68.84	55.47	55.30	62.86	65.34
2020 - Measure A2	68.31	69.50	69.08	57.50	57.30	63.92	66.03
2020 - Measure C2	68.32	69.53	69.09	57.64	57.45	64.00	66.08
2020 - Measure R	68.22	69.45	68.98	57.70	57.51	63.99	66.03
2020 - Measure S	68.21	69.41	68.97	57.56	57.37	63.92	65.99

Table 4.9: Area weighted AOT40 – crops (µg/m³ hours)

µg/m³ hours	Scotland	Wales	Northern Ireland	Inner London	Outer London	Rest of England	All UK
2010 - Base Case	7249	8451	6706	6094	5836	7544	7456
2010 - Measure A2	7234	8434	6695	6102	5842	7533	7444
2010 - Measure C2	7209	8412	6682	6144	5880	7527	7430
2010 - Measure R	7185	8376	6660	6122	5858	7496	7402
2010 - Measure S	7210	8397	6674	6080	5820	7502	7415
2015 - Base Case	8003	9626	7593	7705	7407	8799	8525
2015 - Measure A2	7828	9449	7456	7892	7576	8702	8396
2015 - Measure C2	7775	9396	7413	7965	7642	8676	8359
2015 - Measure R	7685	9243	7326	7857	7538	8554	8247
2015 - Measure S	7738	9293	7370	7786	7473	8578	8283
2020 - Base Case	8944	11028	8557	9027	8750	10231	9769
2020 - Measure A2	8474	10530	8130	9402	9076	9932	9397
2020 - Measure C2	8434	10486	8091	9415	9086	9902	9362
2020 - Measure R	8251	10194	7902	9182	8864	9667	9141
2020 - Measure S	8291	10236	7942	9170	8854	9696	9175

Table 4.10: Area weighted AOT40 – forests (µg/m^3 hours)

µg/m^3 hours	Scotland	Wales	Northern Ireland	Inner London	Outer London	Rest of England	All UK
2010 - Base Case	12198	15772	12462	11837	11559	14329	13634
2010 - Measure A2	12183	15759	12443	11853	11574	14326	13625
2010 - Measure C2	12169	15762	12422	11938	11653	14354	13635
2010 - Measure R	12140	15720	12388	11912	11627	14321	13602
2010 - Measure S	12153	15717	12409	11827	11548	14293	13592
2015 - Base Case	13674	17997	13794	14297	14017	16628	15608
2015 - Measure A2	13550	17926	13583	14743	14463	16722	15603
2015 - Measure C2	13527	17931	13523	14944	14661	16789	15629
2015 - Measure R	13420	17767	13388	14847	14573	16684	15517
2015 - Measure S	13445	17762	13449	14643	14371	16617	15491
2020 - Base Case	15438	20566	15371	16359	16137	19190	17855
2020 - Measure A2	14990	20214	14789	17585	17320	19340	17736
2020 - Measure C2	14945	20172	14734	17671	17400	19339	17715
2020 - Measure R	14698	19820	14450	17514	17243	19114	17469
2020 - Measure S	14745	19864	14506	17425	17163	19117	17492

4.2 Ozone Modelling of the Effect of Changes in VOC Emissions from Uptake of Bioethanol Road Fuels

The Ozone Source Receptor Model (OSRM) was used to model the impacts of changing VOC emissions from road transport arising from the EU Fuel Quality Directive and the uptake of bioethanol-petrol blends. The work was based on earlier work of AEA carried out for Defra and the Department for Transport (DfT) which suggested a) an increase in acetaldehyde emissions from engine exhausts (Murrells and Norris, 2007) and b) an increase in evaporative emissions from cars as a consequence of the relaxation of volatility limits of summer blends of petrol to enable the market penetration of bioethanol blends across Europe (Li et al., 2007). In this project, the objective was to model the extent by which the increased exhaust emissions of acetaldehyde (one of the VOC species among the cocktail emitted from vehicle exhausts) and evaporative emissions of VOCs from vehicles across Europe would effect UK ozone concentrations in 2010, 2015 and 2020.

4.2.1 Assumptions and modelling approach

The work involved (a) changing the VOC speciation profile for exhaust emissions used in the OSRM to reflect changes in acetaldehyde emissions and (b) changing the total VOC emissions from transport due to evaporative losses in each European country reflecting the uptake rates of bioethanol in each country from 2010 to 2020. The key input assumptions in the OSRM were the impact of the bioethanol on emissions from each vehicle using the fuel and the fuel uptake rates in each country. The bioethanol uptake rates were defined by Defra for different EU countries as follows (Table 4.11):

Table 4.11: Biethanol uptake rates assumed in OSRM modelling

Countries	Fuel blend	2010	2015	2020
Czech Rep., Estonia, Lithuania, Poland, Spain, UK	5% bioethanol	100%	0%	0%
	10% bioethanol	0%	100%	100%
Other EU countries	5% bioethanol	0%	100%	0%
	10% bioethanol	0%	0%	100%

Based on these uptake rates, three core scenarios were required to be modelled.

Scenario 1 involved modelling the effect of changes in acetaldehyde exhaust emissions on ozone concentrations in the UK. Based on the AEA work for Defra carried out in the NAEI programme, it was assumed that a vehicle switching to 5% bioethanol (E5) blends led to a factor of 2.5 increase in acetaldehyde emissions relative to base petrol; a vehicle switching to 10% bioethanol (E10) blends led to a factor of 5 increase in acetaldehyde emissions relative to base petrol.

Scenario 2 involved modelling the effect of just changes in evaporative emissions on ozone concentrations in the UK as a result of changing the fuel volatility (expressed as Reid Vapour Pressure, RVP) from 60 to 70 kPa. For this scenario, it had to be considered that the increase in evaporative emissions occurs only in the summer months because it is only then that the increase in volatility from 60 to 70 kPa occurs due to the relaxation of the volatility limits for bioethanol blends. Moreover, some northern European countries (including the UK) are designated for the purpose of the Fuels Directive as "arctic countries" in terms of summer climate conditions meaning that the volatility limits of summer fuel blends are already relaxed to 70 kPa, so in these countries the uptake of bioethanol blends was assumed not to effect fuel volatility and hence evaporative emissions during the summer months.

The work of AEA for DfT (Li et al, 2007) showed that the increase in fuel volatility from 60 to 70 kPa would increase the annual rate of evaporative emissions from vehicles in Europe by 8-9% over the period from 2010 to 2020; over the summer months, when the higher volatility fuels are sold, the increase in evaporative emissions from vehicles in Europe would be around 18% in 2010 falling to 16% in 2020.

Taking into account the defined uptake rates for bioethanol and the VOC emissions from all other sources, Scenario 2 was calculated to lead to the following increases in VOC emissions from evaporation only and from all sources over (i) a whole period of a year and (ii) during the summer months only (Table 4.12):

Table 4.12: Relative increases in VOC emissions from evaporative losses and from all sources in Europe as a consequence of increasing RVP of summer blends of petrol from 60 to 70 kPa (based on Li et al., 2007)

		2010	2015	2020
Annual rate of emissions	Vehicle evaporative emissions only	0%	1%	8%
	All VOC sources	0.00%	0.02%	0.06%
Summer emissions	Vehicle evaporative emissions only	0%	2%	16%
	All VOC sources	0.00%	0.04%	0.13%

Because evaporative emissions from road vehicles have declined so much by 2010, due to the fitting of carbon canister devices for evaporative emission control, the contribution of evaporative losses to total VOC emissions in Europe is small such that although emissions are increased significantly in relative terms for the individual vehicle switching to bioethanol blends, the overall changes in total VOC emissions across Europe are very small. The changes averaged over the whole year are smaller than the changes occurring during the summer months.

In addition to the individual Scenario 1 (increase in exhaust acetaldehyde emissions) and Scenario 2 (increase in evaporative emissions), Defra also requested ozone modelling for a combined Scenario 3 (= Scenario 1 + Scenario 2).

The OSRM is not currently structured to allow variations in the VOC speciation profile for emissions for a specific source in different countries which Scenario 1 requires. At present, for a given source sector, the same speciation profile (i.e. the fraction of individual VOCs that make up the total mass emitted) is assumed for all European countries. However, the OSRM source code was modified to allow for the profile (principally the acetaldehyde fraction) to be varied for each model year.

The OSRM also cannot allow different temporal profiles in emissions (e.g. the pattern representing changes in emissions by time of day, day of week, month of year) for different EU countries to reflect a situation where the volatility of summer fuels (and hence evaporative emissions) during the summer changes in some countries, but not others (e.g. in the UK and other "arctic" countries).

As a compromise, it was agreed with Defra to model two limiting sub-scenarios for each main Scenario 1 and 2 reflecting a "weakest" and "strongest" effect situation:

Scenario 1a: Acetaldehyde increase, strongest effect situation
A situation where the VOC speciation profile (increased acetaldehyde) for the whole of Europe reflects the UK uptake rate situation (higher uptake rate than most countries in Europe, so strongest effect situation)

Scenario 1b: Acetaldehyde increase, weakest effect situation
A situation where the VOC speciation profile (increased acetaldehyde) for the UK reflects the European uptake rate situation (generally lower uptake rate, weighted by petrol consumption in each country). So this would reflect a weakest effect situation.

Scenario 2a: Evaporative increase, weakest effect situation
A situation where the increase in summer emissions in Europe (but no change in UK or "arctic" countries) is smeared out over the whole year. This would reflect a smallest impact situation because the increase in summer emissions based on the current temporal profile would be less than will actually occur, thus having a smaller effect on summer ozone levels.

Scenario 2b: Evaporative increase, strongest effect situation

A situation where the relative increase in summer emissions in Europe is applied across the whole year (but no change in UK or "arctic" countries). This would reflect a biggest impact situation because while the summer ozone will be reflected correctly, using the current temporal profile would lead to higher winter VOC emissions.

Scenario 3a: Combined scenario 1a+ 2b, combined strongest effect situation

Scenario 3b: Combined scenario 1b+ 2a, combined weakest effect situation

Because the effects on ozone concentrations were expected to be small for these scenarios, to save computational time, the OSRM was run to provide output for three ozone metrics at 41 UK receptor sites, rather than carry out full UK scale modelling. The ozone metrics were:

- Annual Mean of the Daily Maximum of the 24 Daily Running 8-hour Mean Ozone Concentrations (μgm^{-3})
- Number of days when the maximum of the 24 possible running 8-hour Mean Ozone Concentrations in each day exceeds 100 μgm^{-3}
- AOT40-crops

2003 meteorology was assumed for all model years and output was provided for 2010, 2015 and 2020.

4.2.2   OSRM Results for Bioethanol Scenarios

The results for the basecase and Scenarios 1a, 2a and 2b are shown for each of the three ozone metrics in Tables 4.13-4.15. Because there is no uptake of E10 anywhere in Europe in 2010 affecting evaporative losses, Scenarios for 2a and 2b are not relevant to this year, but 2010 did involve the introduction of E5 in certain countries impacting on acetaldehyde emissions in Scenario 1a.

The effects of all the scenarios are almost imperceptibly small, in fact it is only AOT40 which shows any differences at all from the basecase.

Because the effects for Scenario 1a were so small, the weakest effect Scenario 1b was not run as the effects would be even smaller than for Scenario 1a. The minute effects that were seen were generally negative, indicating a slight improvement in ozone. In this scenario, the overall VOC exhaust emissions are not changed, only the speciation profile, i.e. the mix of different VOCs in the exhaust emissions, and although the fractional increase in acetaldehyde emissions is high on an individual vehicle (x5 for E10), the changes are from a very small base emissions of this VOC species. The slight improvement in ozone is due to the fact that the POCP for acetaldehyde is slightly lower than the weighted average POCP for total vehicle exhausts and as the total VOC exhaust emissions are not being changed, only the speciation profile (so by definition the fraction of other VOCs are decreased proportionately to accommodate the increase in acetaldehyde), this has an overall slightly beneficial effect.

Scenarios 2a and 2b also had a very small effect on ozone concentrations, Scenario 2b having a slightly larger effect than Scenario 2a, as expected. Only Scenario 2b showed any change (a tiny increase) in the Annual Mean of the Daily Maximum of the 24 Daily Running 8-hour Mean Ozone Concentrations at some sites. This may not be surprising given that even the strongest effect Scenario 2b involves a maximum increase in total VOC emissions from all countries in the EMEP domain of just 0.13%.

The combined Scenarios 3a and 3b were not run given how small the effects of the individual scenarios are, especially as it would be expected that the small ozone decreasing effect of Scenario 1 would counteract the small ozone increasing effects of Scenario 2.

The overall conclusion from this modelling study is that the effect of introducing up to 10% bioethanol petrol blends in Europe, with increased acetaldehyde exhaust emissions from vehicles running on them and increased evaporative emissions due to relaxation of volatility limits of summer fuel blends,

is unlikely to show any effect on UK ozone levels in the UK up to 2020. This is mainly because of the small contribution made by vehicle evaporative emissions to overall VOC emissions in Europe beyond 2010 and because of the relatively low baseline contribution of acetaldehyde to exhaust emissions of VOCs from vehicles. However, other environmental consequences of higher acetaldehyde emissions (e.g. toxicity effects) have not been considered.

4.3 Ozone Modelling on the Effect of Changes in Shipping Emissions of NO_x and SO_2

Section 3.1 described OSRM modelling carried out for several emission reduction measures considered for the Air Quality Strategy Review (AQSR). Among these were Measures R and S which combined measures to reduce NO_x and SO_2 emissions from shipping with measures to reduce road transport emissions of NO_x and NMVOCs. It had been noted that adding a shipping emission reduction measure to measures reducing road transport emissions led to a very slight improvement in ozone concentrations expressed as population or area-weighted means of the various ozone concentration metrics modelled on a UK scale. However, a shipping emission reduction-only scenario had never before been modelled using the OSRM and the interest was whether relative to the basecase, reducing shipping emissions alone would reduce UK ozone concentrations and whether the reductions were due to the reductions in NO_x or SO_2 emissions. Although locally emitted NO_x consumes ozone in urban areas (the NO_x titration effect), on a regional scale it is involved in ozone production. SO_2 also has a minor role in ozone loss and production through its interaction with free radicals involved in generating ozone. However, its involvement is complex and has a small POCP that varies with the number of trajectory days.

The AQSR shipping measure (N) involves a 33% reduction in SO_2 emissions from the global shipping fleet above 100 tonnes relative to current baseline levels as a results of a requirement to use fuels with a sulphur limit of 1% by 2010. The measure also requires NO_x emissions from all new ships to be reduced by 25% from 2010. Taking account of the turnover in the shipping fleet, leads to an estimated change in NO_x emissions from shipping of between 0.8% in 2010 to 9% by 2020 compared with baseline predicted levels (Stedman et al., 2006). The OSRM covers shipping emissions over the EMEP sea territories and this includes the north-east Atlantic to the west of the British Isles.

Using these assumptions, two OSRM runs were made for 2020 using 2003 meteorology to observe the effect of changing shipping emissions in the EMEP sea territories on UK ozone: in one case, NO_x emissions in these sea territories were reduced by 9%; in the other case, SO_2 emissions in these sea territories were reduced by 33%.

The results for 4 different ozone metrics averaged over the whole of the UK are shown in Table 4.16 comparing the NO_x shipping emission reduction scenario and the SO_2 shipping emission reduction scenario with the basecase for 2020.

Table 4.16: Effect of changes in shipping emissions on UK ozone concentrations in 2020 for different ozone concentration metrics

	Metric 1	Metric 2	Metric 3	Metric 4
2020 - Base	74.72	55.14	65.34	9769
2020 - Shipping NO_x reduction	74.64	53.80	65.30	9547
2020 - Shipping SO_2 reduction	74.70	55.03	65.33	9754

Metrics are:
Metric 1: Population-Weighted Annual Mean of Daily Maximum Running 8 Hourly Ozone Concentration (μgm^{-3}).
Metric 2: Population-Weighted Number of Days when the Daily Maximum Running 8 Hourly Ozone Concentration exceeds 100 μgm^{-3}
Metric 3: Area-Weighted Annual Mean Ozone Concentration (μgm^{-3}).
Metric 4: Area-Weighted AOT40 - Crops (μgm^{-3}.hours)

All metrics show that the reduction in NO_x emissions from shipping leads to a reduction in ozone concentrations. Reducing SO_2 emissions also leads to a small beneficial effect on ozone, but the impact is considerably smaller than the effect of reducing NO_x emissions from shipping.

The effect of shipping emissions on ozone concentrations may benefit from a more detailed analysis, for example to see the influence of shipping in different sea regions on UK ozone levels and using more up-to-date basecase shipping emission projections in the OSRM.

Table 4.13: Annual Mean of the Daily Maximum of the 24 Daily Running 8-hour Mean Ozone Concentrations (μgm^{-3}) at the 41 receptor sites for the basecase and Bioethanol Scenarios 1a, 2a and 2b

	Sites	2010					2015					2020			
		Base	1a	2a	2b		Base	1a	2a	2b		Base	1a	2a	2b
1	Strathvaich Dam	78.12	78.12	N/A	N/A		79.24	79.24	79.24	79.24		80.47	80.47	80.47	80.47
2	Aston Hill	75.76	75.76	N/A	N/A		77.74	77.74	77.74	77.74		79.75	79.75	79.76	79.76
3	Bush	73.36	73.36	N/A	N/A		75.20	75.20	75.20	75.20		76.92	76.92	76.92	76.92
4	Eskdalemuir	76.95	76.95	N/A	N/A		78.47	78.46	78.47	78.47		80.08	80.08	80.08	80.08
5	Great Dun Fell	75.33	75.33	N/A	N/A		76.94	76.94	76.94	76.94		78.55	78.55	78.55	78.55
6	Harwell	70.22	70.22	N/A	N/A		72.88	72.88	72.88	72.88		75.04	75.04	75.04	75.04
7	High Muffles	76.31	76.31	N/A	N/A		78.35	78.35	78.35	78.35		80.51	80.51	80.51	80.51
8	Ladybower	70.06	70.06	N/A	N/A		72.27	72.27	72.27	72.27		74.34	74.34	74.34	74.35
9	Lullington Heath	79.95	79.95	N/A	N/A		82.34	82.34	82.34	82.34		84.66	84.66	84.66	84.66
10	Narberth	83.60	83.60	N/A	N/A		85.49	85.49	85.49	85.49		87.36	87.36	87.36	87.36
11	Rochester	71.44	71.44	N/A	N/A		74.50	74.50	74.50	74.50		78.02	78.02	78.02	78.02
12	Sibton	76.27	76.27	N/A	N/A		79.31	79.31	79.31	79.31		81.98	81.98	81.98	81.98
13	Somerton	77.99	77.99	N/A	N/A		80.40	80.40	80.40	80.40		82.52	82.52	82.52	82.53
14	Wharley Croft	75.86	75.86	N/A	N/A		77.65	77.65	77.65	77.65		79.34	79.34	79.34	79.34
15	Wicken Fen	71.70	71.70	N/A	N/A		74.33	74.33	74.33	74.33		76.56	76.56	76.56	76.56
16	Wray	75.52	75.52	N/A	N/A		77.37	77.37	77.37	77.37		79.19	79.19	79.20	79.20
17	Yarner Wood	81.33	81.33	N/A	N/A		83.48	83.48	83.48	83.48		85.55	85.55	85.55	85.56
18	Bottesford	68.02	68.02	N/A	N/A		70.54	70.54	70.54	70.54		73.06	73.06	73.06	73.06
19	Glazebury	72.09	72.09	N/A	N/A		74.83	74.83	74.83	74.83		77.24	77.24	77.24	77.24
20	Lough Navar	81.55	81.55	N/A	N/A		82.77	82.77	82.77	82.77		84.01	84.01	84.01	84.01
21	London Bexley	67.15	67.15	N/A	N/A		70.27	70.27	70.28	70.28		72.73	72.73	72.73	72.74
22	London Bloomsbury	55.72	55.71	N/A	N/A		58.62	58.62	58.62	58.62		60.40	60.40	60.40	60.40
23	London Brent	67.42	67.42	N/A	N/A		70.39	70.39	70.39	70.39		72.67	72.67	72.68	72.68
24	London Eltham	69.31	69.31	N/A	N/A		72.48	72.48	72.48	72.48		74.86	74.86	74.86	74.86
25	London Hackney	63.35	63.35	N/A	N/A		66.49	66.49	66.49	66.49		68.73	68.73	68.73	68.73
26	London Haringey	66.18	66.18	N/A	N/A		69.29	69.29	69.29	69.29		71.60	71.60	71.60	71.60

27	**London Hillingdon**	63.32	63.32	N/A	N/A		66.56	66.56	66.56	66.56		68.83	68.83	68.83	68.83
28	**London N Kensington**	62.38	62.38	N/A	N/A		65.79	65.79	65.79	65.79		68.01	68.01	68.01	68.01
29	**London Teddington**	68.63	68.63	N/A	N/A		72.04	72.04	72.04	72.04		74.45	74.45	74.45	74.45
30	**London Westminster**	61.87	61.87	N/A	N/A		65.11	65.11	65.11	65.11		67.25	67.25	67.25	67.26
31	**Birmingham Centre**	60.86	60.86	N/A	N/A		63.88	63.88	63.88	63.88		65.87	65.87	65.87	65.87
32	**Birmingham East**	67.00	67.00	N/A	N/A		70.09	70.09	70.10	70.10		72.41	72.41	72.41	72.41
33	**Manchester Pic.**	60.82	60.82	N/A	N/A		63.67	63.67	63.67	63.67		65.65	65.65	65.66	65.66
34	**Leeds Centre**	61.75	61.75	N/A	N/A		64.97	64.97	64.97	64.97		67.25	67.25	67.25	67.25
35	**Newcastle Centre**	68.86	68.86	N/A	N/A		71.45	71.45	71.45	71.45		73.19	73.19	73.19	73.19
36	**Bristol**	69.33	69.33	N/A	N/A		72.59	72.59	72.59	72.59		74.81	74.81	74.82	74.82
37	**Southampton Centre**	77.18	77.18	N/A	N/A		80.06	80.06	80.06	80.06		82.31	82.31	82.31	82.31
38	**Glasgow**	65.28	65.28	N/A	N/A		67.92	67.92	67.92	67.92		69.54	69.54	69.54	69.55
39	**Edinburgh**	68.55	68.55	N/A	N/A		70.73	70.73	70.73	70.73		72.39	72.39	72.39	72.39
40	**Belfast Centre**	73.84	73.84	N/A	N/A		76.26	76.26	76.26	76.26		77.91	77.91	77.91	77.91
41	**Cardiff**	69.50	69.50	N/A	N/A		72.24	72.24	72.24	72.24		74.68	74.68	74.68	74.68

Table 4.14: Number of days when the maximum of the 24 possible running 8-hour Mean Ozone Concentrations in each day exceeds 100 µgm^{-3} at the 41 receptor sites for the basecase and Bioethanol Scenarios 1a, 2a and 2b

	Sites	2010					2015					2020			
		Base	1a	2a	2b		Base	1a	2a	2b		Base	1a	2a	2b
1	Strathvaich Dam	46	46	N/A	N/A		50	50	50	50		60	60	60	60
2	Aston Hill	50	50	N/A	N/A		59	59	59	59		67	67	67	67
3	Bush	32	32	N/A	N/A		42	42	42	42		54	54	54	54
4	Eskdalemuir	43	43	N/A	N/A		51	51	51	51		63	63	63	63
5	Great Dun Fell	39	39	N/A	N/A		48	48	48	48		56	56	56	56
6	Harwell	42	42	N/A	N/A		50	50	50	50		58	58	58	58
7	High Muffles	49	49	N/A	N/A		58	58	58	58		67	67	67	67
8	Ladybower	35	35	N/A	N/A		46	46	46	46		51	51	51	51
9	Lullington Heath	84	84	N/A	N/A		96	96	96	96		108	108	108	108
10	Narberth	79	79	N/A	N/A		92	92	92	92		98	98	98	98
11	Rochester	55	55	N/A	N/A		67	67	67	67		74	74	74	74
12	Sibton	70	70	N/A	N/A		82	82	82	82		93	93	93	93
13	Somerton	63	63	N/A	N/A		73	73	73	73		85	85	85	85
14	Wharley Croft	40	40	N/A	N/A		49	49	49	49		57	57	57	57
15	Wicken Fen	44	44	N/A	N/A		53	53	53	53		57	57	57	57
16	Wray	42	42	N/A	N/A		53	53	53	53		60	60	60	60
17	Yarner Wood	69	69	N/A	N/A		78	78	78	78		90	90	90	90
18	Bottesford	33	33	N/A	N/A		37	37	37	37		45	45	45	45
19	Glazebury	37	37	N/A	N/A		53	53	53	53		57	57	57	57
20	Lough Navar	54	54	N/A	N/A		61	61	61	61		69	69	69	69
21	London Bexley	42	42	N/A	N/A		51	51	51	51		56	56	56	56
22	London Bloomsbury	16	16	N/A	N/A		22	22	22	22		25	25	25	25
23	London Brent	41	41	N/A	N/A		48	48	48	48		56	56	56	56
24	London Eltham	44	44	N/A	N/A		53	53	53	53		63	63	63	63
25	London Hackney	29	29	N/A	N/A		37	37	37	37		44	44	44	44
26	London Haringey	37	37	N/A	N/A		44	44	44	44		51	51	51	51
27	London Hillingdon	27	27	N/A	N/A		36	36	36	36		41	41	41	41
28	London N Kensington	27	27	N/A	N/A		36	36	36	36		40	40	40	40

29	**London Teddington**	44	44	N/A	N/A			53	53	53	53		64	64	64	64
30	**London Westminster**	29	29	N/A	N/A			35	35	35	35		41	41	41	41
31	**Birmingham Centre**	18	18	N/A	N/A			23	23	23	23		29	29	29	29
32	**Birmingham East**	32	32	N/A	N/A			39	39	39	39		48	48	48	48
33	**Manchester Pic.**	19	19	N/A	N/A			24	24	24	24		30	30	30	30
34	**Leeds Centre**	19	19	N/A	N/A			23	23	23	23		32	32	32	32
35	**Newcastle Centre**	31	31	N/A	N/A			35	35	35	35		42	42	42	42
36	**Bristol**	36	36	N/A	N/A			45	45	45	45		53	53	53	53
37	**Southampton Centre**	63	63	N/A	N/A			72	72	72	72		84	84	84	84
38	**Glasgow**	18	18	N/A	N/A			22	22	22	22		29	29	29	29
39	**Edinburgh**	22	22	N/A	N/A			25	25	25	25		34	34	34	34
40	**Belfast Centre**	38	38	N/A	N/A			48	48	48	48		53	53	53	53
41	**Cardiff**	34	34	N/A	N/A			43	43	43	43		47	47	47	47

Table 4.15: AOT40-crops (µgm⁻³.hrs) at the 41 receptor sites for the basecase and Bioethanol Scenarios 1a, 2a and 2b

	Sites	2010					2015					2020			
		Base	1a	2a	2b		Base	1a	2a	2b		Base	1a	2a	2b
1	Strathvaich Dam	5988.50	5988.44	N/A	N/A		6575.24	6575.13	6575.30	6575.36		7366.89	7366.77	7367.29	7367.68
2	Aston Hill	7781.61	7781.55	N/A	N/A		8771.96	8771.78	8772.06	8772.15		10032.66	10032.41	10033.31	10033.96
3	Bush	7076.92	7076.84	N/A	N/A		8030.93	8030.69	8031.04	8031.14		9155.02	9154.75	9155.80	9156.56
4	Eskdalemuir	7857.56	7857.49	N/A	N/A		8699.28	8699.03	8699.41	8699.51		9783.95	9783.67	9784.70	9785.43
5	Great Dun Fell	6639.74	6639.63	N/A	N/A		7493.92	7493.57	7493.97	7494.03		8508.45	8508.03	8508.82	8509.20
6	Harwell	6588.45	6588.27	N/A	N/A		7702.05	7701.68	7702.13	7702.21		8881.83	8881.41	8882.42	8882.99
7	High Muffles	8362.59	8362.35	N/A	N/A		9551.39	9550.70	9551.47	9551.54		11104.61	11103.79	11105.06	11105.50
8	Ladybower	5998.45	5998.27	N/A	N/A		7034.81	7034.34	7034.90	7034.98		8240.23	8239.70	8240.87	8241.49
9	Lullington Heath	12318.14	12318.01	N/A	N/A		13993.11	13992.72	13993.32	13993.51		15856.30	15855.84	15857.61	15858.89
10	Narberth	9988.05	9988.09	N/A	N/A		11408.16	11408.19	11408.31	11408.44		12990.91	12990.88	12991.73	12992.58
11	Rochester	7488.80	7488.67	N/A	N/A		9355.92	9355.45	9356.09	9356.25		12112.91	12112.19	12113.93	12114.93
12	Sibton	7394.83	7394.76	N/A	N/A		9659.05	9658.64	9659.28	9659.49		11957.15	11956.54	11958.57	11959.97
13	Somerton	10161.81	10161.72	N/A	N/A		11334.54	11334.23	11334.66	11334.77		12782.80	12782.39	12783.46	12784.12
14	Wharley Croft	7113.83	7113.70	N/A	N/A		8010.96	8010.61	8011.03	8011.09		9093.12	9092.70	9093.51	9093.89
15	Wicken Fen	5630.94	5630.73	N/A	N/A		7057.33	7056.74	7057.46	7057.57		8654.23	8653.50	8655.05	8655.86
16	Wray	7593.32	7593.16	N/A	N/A		8592.47	8592.02	8592.55	8592.62		9787.41	9786.87	9787.83	9788.25
17	Yarner Wood	9718.34	9718.27	N/A	N/A		10999.64	10999.51	10999.77	10999.90		12557.82	12557.65	12558.60	12559.39
18	Bottesford	6102.08	6101.90	N/A	N/A		7534.81	7534.31	7534.94	7535.05		9255.34	9254.68	9256.08	9256.81
19	Glazebury	7841.27	7841.07	N/A	N/A		9298.93	9298.37	9299.04	9299.14		10809.79	10809.11	10810.44	10811.07
20	Lough Navar	6920.32	6920.33	N/A	N/A		7678.52	7678.48	7678.59	7678.66		8528.82	8528.76	8529.20	8529.58
21	London Bexley	6263.93	6263.68	N/A	N/A		7933.75	7932.98	7933.85	7933.95		9320.45	9319.55	9321.00	9321.56
22	London Bloomsbury	2470.68	2470.52	N/A	N/A		3368.81	3368.39	3368.88	3368.95		4030.97	4030.47	4031.42	4031.88
23	London Brent	7073.24	7072.97	N/A	N/A		8752.88	8752.05	8752.99	8753.09		10237.08	10236.14	10237.77	10238.45
24	London Eltham	7349.84	7349.57	N/A	N/A		9157.21	9156.38	9157.33	9157.45		10696.04	10695.08	10696.80	10697.55
25	London Hackney	4869.99	4869.76	N/A	N/A		6410.81	6410.12	6410.91	6411.02		7665.88	7665.08	7666.60	7667.29
26	London Haringey	6210.98	6210.69	N/A	N/A		7894.77	7893.93	7894.88	7894.99		9348.37	9347.37	9349.09	9349.79
27	London Hillingdon	5190.65	5190.43	N/A	N/A		6660.62	6660.02	6660.69	6660.76		7788.79	7788.11	7789.23	7789.66

28	**London N Kensington**	4648.80	4648.56	N/A	N/A		6251.27	6250.57	6251.35	6251.44		7428.79	7428.02	7429.34	7429.88
29	**London Teddington**	7825.28	7825.02	N/A	N/A		9717.93	9717.18	9718.05	9718.15		11265.27	11264.37	11265.97	11266.65
30	**London Westminster**	4530.28	4530.06	N/A	N/A		5994.83	5994.22	5994.93	5995.02		7013.13	7012.44	7013.70	7014.27
31	**Birmingham Centre**	4003.54	4003.46	N/A	N/A		5182.40	5182.14	5182.51	5182.60		6174.58	6174.23	6175.24	6175.87
32	**Birmingham East**	6735.06	6734.91	N/A	N/A		8384.03	8383.64	8384.18	8384.31		9817.50	9816.99	9818.31	9819.08
33	**Manchester Pic.**	3425.40	3425.28	N/A	N/A		4520.16	4519.79	4520.25	4520.33		5475.83	5475.36	5476.34	5476.84
34	**Leeds Centre**	3796.95	3796.77	N/A	N/A		5225.46	5224.90	5225.52	5225.59		6631.38	6630.71	6631.89	6632.39
35	**Newcastle Centre**	6111.48	6111.40	N/A	N/A		7291.06	7290.72	7291.16	7291.25		8301.44	8301.01	8301.95	8302.46
36	**Bristol**	6679.61	6679.53	N/A	N/A		8425.39	8425.06	8425.49	8425.58		9835.96	9835.56	9836.60	9837.23
37	**Southampton Centre**	10738.15	10737.98	N/A	N/A		12342.20	12341.77	12342.36	12342.51		13888.07	13887.65	13889.10	13890.12
38	**Glasgow**	2920.81	2920.77	N/A	N/A		3881.73	3881.63	3881.82	3881.91		4649.63	4649.53	4650.26	4650.88
39	**Edinburgh**	5599.92	5599.86	N/A	N/A		6578.63	6578.46	6578.75	6578.84		7504.58	7504.36	7505.23	7505.87
40	**Belfast Centre**	5764.19	5764.21	N/A	N/A		7355.44	7355.47	7355.57	7355.70		8620.75	8620.70	8621.48	8622.18
41	**Cardiff**	6150.49	6150.46	N/A	N/A		7626.95	7626.79	7627.07	7627.16		9256.06	9255.78	9256.66	9257.25

5 Support for Policy Implementation (Objective 1b)

Work carried out for this objective is of an *ad-hoc* nature using available tools to guide policy implementation and providing technical advice as required by Defra. During the first year of the project, Defra requested work in two main policy areas directly and indirectly related to ozone policy:

- The development of a method for assessing the climate change consequences of VOC emission control;

- Secondary particulate matter (PM) modelling using the Photochemical Trajectory Model (PTM) and the Met Office NAME model.

5.1 A Method for Assessing the Climate Change Consequences of VOC Emission Control

Professor Derwent (rdscientific) and AEA Energy & Environment were specifically asked to prepare an authoritative report on the climate change consequences of VOC emission control by incineration. Incineration is one potential control measure for industry to reduce its emissions of VOCs to comply with the European Commission's Solvent Emissions Directive (SED). Industry has questioned the wisdom of incineration because of the apparent conflict between the climate change consequences of increased fuel usage by the incineration equipment and the requirements of the SED to reduce photochemical ozone formation. However, there may be climate change consequences of the uncontrolled emission of the solvent. The question is whether the climate change penalty of incineration outweighs the climate change benefit from controlling the solvent emission. The ground-level ozone benefits of VOC emission controls are taken for granted within the SED.

A report entitled "*Climate Change Consequences of VOC Emission Controls*" was prepared for Defra to be used as a guide for industry, providing a simple approach for quantitatively assessing the climate change consequences of VOC emission control by incineration (Murrells and Derwent, 2007). A method was presented for quantitatively assessing the CO_2 equivalent emissions of incineration *versus* direct release of the VOC taking into account the VOC's direct global warming potential and the use of any supplementary fuel from fossil fuel feedstocks required to aid incineration. The approach is provided with worked examples and the report includes a table of Global Warming Potentials (GWPs) of some common VOCs and a table of fuel CO_2 conversion factors for different fuel types that might be used to aid incineration.

One of the Worked Examples and tables of GWPs and fuel CO_2 conversion factors are provided in Appendix 2, but more details can be found on this work in the report of Murrells and Derwent (2007). Defra expect the report to be used as supplementary background technical information for a wider set of guidelines for industry operators and regulators covering the issue of VOC abatement and its environmental consequences.

5.2 Modelling of Secondary Particulate Matter Using the Photochemical Trajectory Model and the NAME Model

Whilst this project is primarily focused on modelling of tropospheric ozone, there is considerable overlap with modelling approaches and methods used to model secondary particulate matter (PM), namely sulphate, nitrate and ammonium aerosol formed from precursor NO_x, SO_2 and NH_3 emissions. Like ozone, secondary PM is a transboundary air pollutant and affects local concentrations of PM_{10} made up of primary emitted PM_{10}, secondary organic and inorganic aerosol and coarse PM. Process models for forecasting the response of secondary PM formation to changes in precursor emissions

(NO_x, SO_2, NH_3, NMVOCs) require similar chemical transport models to the types used for predicting ozone concentrations and there is overlap in terms of evaluating policies affecting the formation of both pollutants. Modelling of both secondary PM and ozone benefit from good description of the chemical mechanisms and meteorological processes, much of which are common to both pollutants.

Empirically-based mapping models have played a significant role in policy development for $PM_{2.5}$ and PM_{10} in the United Kingdom (AQEG, 2005). Stedman et al. (2007) have used these models to prepare UK maps for $PM_{2.5}$ and PM_{10} for a base year 2004 and for 2010 and 2020, on the basis of current policies. These predicted maps for 2010 and 2020 have been used to check future compliance with air quality regulations. Whilst forecasting the future primary PM component in empirical models is relatively straightforward if accurate primary PM emission inventories are available for the present and future years, dealing with secondary PM is more difficult. Currently, empirical models use outputs from the EMEP model, which explicitly models the formation of secondary inorganic aerosols, to provide single UK wide scaling factors for use in the empirical Pollution Climate Mapping (PCM) model. However, there is currently some uncertainty in how robust this method was.

Work was undertaken in this project using the Photochemical Trajectory Model (PTM) and the Met Office NAME model to assist in understanding the behaviour of secondary particulates as the emissions of their primary precursors decline and to examine the sensitivity of secondary PM component concentrations to changes in the emissions of PM precursors. The PTM was used to develop sensitivity coefficients for each secondary PM component, showing the likely importance of non-linearities in the atmospheric chemistry of secondary PM formation, that could be used in the PCM to gauge the importance of these non-linearities for policy-making in realtion to changes in precursor emissions. The NAME model was used to see whether the model could capture the observed changes in sulphate and nitrate aerosol resulting from the changing emissions over the period 2000 to 2006 and to establish whether the NAME results were robust enough to be of use to provide the PCM model with suitable scaling factors to assist in providing baseline projections of inorganic aerosols.

5.2.1   Secondary PM Modelling Using the UK Photochemical Trajectory Model

The United Kingdom Photochemical Trajectory Model (UK PTM) was used by rdscientific to describe the day-to-day variations throughout 2006 in the concentrations of ozone and a range of PM components at the Harwell site, a rural location in Oxfordshire. Details of the model are given in Derwent et al. (1996) and Abdulmogith et al. (2006). The model employs emissions for 1999 from the NAEI and EMEP and utilises the Carbon Bond Mechanism. It has been further refined by inclusion of a scheme for gas phase and particulate ammonia, 96-hour 3-dimensional back track air mass trajectories from the NAME atmospheric dispersion model of the Met Office and initial and background concentrations from the EMEP site at the Valentia Observatory, Ireland and the atmospheric baseline station at Mace Head, Ireland. Model performance was evaluated against the hourly ozone observations and the daily PM component concentrations available for the Harwell site from the DEFRA networks.

5.2.1.1 Estimation of Emission Sensitivity Coefficients for Across-the-board Emission changes

The UK PTM model was run for mid-afternoon (15:00z) conditions for each day of 2006 using 30 equal probability 96-hour 3-dimensional back-track trajectories from the NAME dispersion model of the Met Office. The mean and standard deviation of the results from the 30 model runs were then estimated for each day of the year, together with an estimate of the daily 84-percentile value. This was taken to be a representative value of the distribution of model values for each day.

The annual mean PM component concentrations for 2006 were then calculated from the daily representative values and are presented in Table 5.1 as the base case values 'with initial' and background concentrations set for PM components and their precursors. PM fine sulphate characterises the model mass of PM sulphate present as sulphuric acid, ammonium bisulphate and ammonium sulphate. PM fine nitrate characterises the model mass of PM nitrate present as ammonium nitrate only. PM fine ammonium characterises the model mass of PM ammonium present as ammonium bisulphate, ammonium sulphate and ammonium nitrate. PM coarse nitrate characterises the model mass of sodium nitrate only, formed by sea-salt displacement reactions.

Table 5.1. Annual mean PM component concentrations calculated with the UK PTM for Harwell, Oxfordshire for 2006 with base case PM precursor emissions for 1999 and for various across-the-board emission reduction cases.

Scenario case	PM fine sulphate mass, $\mu g\ SO_4\ m^{-3}$	PM fine nitrate mass, $\mu g\ NO_3\ m^{-3}$	PM fine ammonium, $\mu g\ NH_4\ m^{-3}$	PM coarse nitrate, $\mu g\ NaNO_3\ m^{-3}$
Base case				
With initial	3.00	0.73	2.55	1.13
Without initial	1.66	0.64	1.24	0.60
30% VOC case	2.99	0.71	2.53	1.12
30% NO_x case	3.08	0.63	2.50	1.01
30% NH_3 case	3.00	0.54	2.31	1.16
30% CO case	3.00	0.73	2.55	1.13
30% SO_2 case	2.51	0.77	2.41	1.12

All initial and boundary concentrations of the secondary PM components and their precursors were then set to zero and the model calculations were repeated to simulate PM formation within Europe from European PM precursors alone. The corresponding annual mean PM component concentrations are also shown in Table 5.1 as 'base case without initial and boundary concentrations' set.

A series of sensitivity experiments were then run with PM precursor emissions: namely VOC, NO_x, NH_3, CO and SO_2, reduced by 30% across-the-board, relative to the base case 1999 emissions. The annual mean PM component concentrations are also shown in Table 5.1 for these sensitivity cases.

Sensitivity coefficients, E_{ij}, were then calculated for PM component, i, for changes in the emissions of precursor pollutant, j, as follows:

$$E_{ij} = \frac{\dfrac{\text{Change in PM component, i, concentration}}{\text{Base case PM component, i, concentration}}}{\dfrac{\text{Change in emissions of pollutant, j}}{\text{Base case emission of pollutant, j}}}$$

The sensitivity coefficients, Eij, are presented in Table 5.2 in two ways: the first, by making allowance for initial and background PM and PM precursor concentrations and in the second by making no allowance for them. The first set of coefficients therefore looks at the sensitivity of the PM formed within Europe to European emission changes, whereas the second set looks at the sensitivity of the total PM to European emission changes, irrespective of the origins of the PM components and their precursors.

5.2.1.2 Discussion of the Results for 30% Across-the-board Emissions Reductions

The PM fine sulphate mass formed within Europe appears to be accurately linear with respect to European SO_2 emission reductions, see Table 5.2. In addition, it exhibits a moderate but significant negative sensitivity to NO_x emissions. That is to say, PM fine sulphate mass increases as NO_x emissions decrease. This arises because OH radical number densities rise as NO_x levels are reduced, increasing the oxidation rate of SO_2 to particulate sulphate. There appears to be a small but significant positive sensitivity to VOC emissions. That is to say, PM fine sulphate mass decreases as VOC emissions decrease. This arises because increasing VOC emissions stimulate the production of photochemical oxidants, thereby stimulating the conversion of SO_2 to particulate sulphate, and the converse for decreasing VOC emissions. The sensitivities of PM fine sulphate mass to the emissions of CO and NH_3 are insignificant.

The PM fine nitrate mass formed within Europe appears to be significantly less than linear in NO_x emissions, showing a moderate sensitivity coefficient in Table 5.2. This less than linear relationship

Table 5.2. Emission sensitivity coefficients for the different PM components calculated with the UK PTM model for 30% across-the-board emission reductions.

Scenario case	PM fine sulphate mass, $\mu g\ SO_4\ m^{-3}$	PM fine nitrate mass, $\mu g\ NO_3\ m^{-3}$	PM fine ammonium, $\mu g\ NH_4\ m^{-3}$	PM coarse nitrate, $\mu g\ NaNO_3\ m^{-3}$
Without initial and boundary concentrations of PM components and their precursors				
VOC emission	0.02	0.09	0.04	0.08
NO_x emission	-0.17	0.51	0.13	0.67
NH_3 emission	0	0.97	0.65	-0.14
CO emission	0	0	0	0
SO_2 emission	1.0	-0.21	0.37	0.04
With initial and boundary concentrations of PM components and their precursors				
VOC emission	0.01	0.08	0.02	0.05
NO_x emission	-0.09	0.45	0.06	0.36
NH_3 emission	0	0.86	0.31	-0.07
CO emission	0	0	0	0
SO_2 emission	0.55	-0.19	0.18	0.02

between PM fine nitrate mass and NO_x emissions arises because as NO_x emissions decrease, OH radical number densities increase somewhat, increasing the conversion rate of NO_x to gaseous nitric acid and counteracting the decrease in NO_x concentrations. In contrast, the PM fine nitrate mass is almost accurately linear in NH_3 emissions. This means that, on average, the formation of ammonium nitrate is controlled more strongly by the availability of gaseous ammonia rather than the availability of the strong acid, gaseous nitric acid. On average, conditions appear to be ammonia-limiting, rather than strong acid-limiting. There appears to be a small but significant negative sensitivity to SO_2 emissions. That is to say, as SO_2 emissions decrease, fine PM nitrate mass increases, reflecting the shift between ammonium sulphate and ammonium nitrate under the ammonia-limiting conditions. There is a small sensitivity to VOC emissions, reflecting their influence on photochemical oxidant production. The sensitivity to CO emissions is insignificant.

The PM fine ammonium formed within Europe appears to be significantly less than linearly related to ammonia emissions, showing a moderate positive coefficient, reflecting that as ammonia emissions decrease, the fractional decrease in PM ammonium is smaller than the fractional decrease in emissions. Effectively, this means that the fraction of the total ammonia plus ammonium present as ammonium increases as total ammonia plus ammonium decreases. This is plausible if there is another important fate for gaseous ammonia, namely dry deposition, and if conditions are ammonia-limiting, with an excess of strong acids. PM fine ammonium mass shows small, positive sensitivities to NO_x and SO_2 emissions, consistent with PM formation on average ammonia-limited and where strong acids are in excess.

The PM coarse nitrate mass formed in Europe shows a moderate, positive sensitivity to NO_x emissions that is considerably less than linear because of the coupling between NO_x emissions and strong acid formation through OH radical densities. A small negative sensitivity is observed to ammonia emissions, reflecting the competition between the reactions of gaseous nitric acid and ammonia and sea-salts. Small but significant sensitivities were observed with VOC and SO_2 emissions, consistent with the sensitivities reported for the fine PM components.

5.2.1.3 Results for National and Foreign Emission Reductions Cases

A second and third series of sensitivity experiments were then run with PM precursor emissions reduced by 30% relative to 1999 base case emissions on a national, UK-only, and foreign, UK-excepted, basis. The annual mean PM component concentrations are shown in Table 5.3 for these sensitivity cases.

Table 5.3. Annual mean PM component concentrations calculated with the UK PTM for Harwell, Oxfordshire for 2006 with base case PM precursor emissions for 1999 and for various emission reduction cases carried out in the UK only (national cases) and in the rest of Europe (foreign cases).

Scenario case	PM fine sulphate mass, $\mu g\ SO_4\ m^{-3}$	PM fine nitrate mass, $\mu g\ NO_3\ m^{-3}$	PM fine ammonium, $\mu g\ NH_4\ m^{-3}$	PM coarse nitrate, $\mu g\ NaNO_3\ m^{-3}$
Base case				
With initial	3.00	0.73	2.55	1.13
Without initial	1.66	0.64	1.24	0.60
UK-only reduction cases				
30% VOC case	2.99	0.72	2.54	1.12
30% NO_x case	3.08	0.69	2.53	1.10
30% NH_3 case	3.00	0.66	2.43	1.14
30% CO case	3.00	0.73	2.55	1.13
30% SO_2 case	2.69	0.75	2.51	1.13
Rest-of-Europe reduction cases				
30% VOC case	2.99	0.72	2.54	1.13
30% NO_x case	3.01	0.67	2.51	1.05
30% NH_3 case	3.00	0.62	2.43	1.15
30% CO case	3.00	0.73	2.55	1.13
30% SO_2 case	2.81	0.75	2.45	1.13

The fractional changes in PM component concentrations, i, ΔPM, for changes in the emissions of precursor, j, were calculated as follows:

$$\Delta PM_{i,j} = \frac{\text{Change in PM component, i, concentration}}{\text{Base case PM component, i, concentration}}$$

These fractional changes are presented in Table 5.4 by making allowance for initial and background PM and PM precursor concentrations. In this way, attention is directed only to the sensitivity of the PM formed within Europe to national or foreign emission reductions.

Considering first PM fine sulphate, Table 5.4 shows that its fractional response to 30% SO_2 emission reductions applied within the UK, national case, is -0.185. The corresponding fractional response to 30% SO_2 emission reductions carried out in the rest of Europe, foreign case, is -0.112. Taken together, the sum of these fractional changes is -0.297, which when divided by the fractional change in emissions of -0.3, gives the emission sensitivity coefficient 0.99 as recorded in Table 5.2. So, of the total response to the 30% across-the-board reduction in SO_2 emissions found for PM fine sulphate, two-thirds comes from the response within the UK and one-third from the responses elsewhere across Europe.

There is an increase in the PM fine sulphate in response to a decrease of 30% in NO_x emissions. The fractional increase in PM fine sulphate amounts to 0.047 for national NO_x reductions and 0.004 for foreign reductions. This non-linear term is therefore highly spatially variable. PM fine sulphate decreases in response to a 30% decrease in VOC emissions. The fractional decreases are considerably higher for VOC reductions in the UK compared with those carried out in the rest of Europe. Again, this non-linear term is highly spatially variable.

Table 5.4. Fractional changes in the concentrations of the different PM components calculated with the UK PTM model for 30% emission reductions cases carried out in the UK only (national cases) and in the rest of Europe (foreign cases), without initial and boundary concentrations of PM and PM precursors.

Scenario case	PM fine sulphate mass, $\mu g\ SO_4\ m^{-3}$	PM fine nitrate mass, $\mu g\ NO_3\ m^{-3}$	PM fine ammonium, $\mu g\ NH_4\ m^{-3}$	PM coarse nitrate, $\mu g\ NaNO_3\ m^{-3}$
UK-only cases				
30% VOC case	-0.006	-0.012	-0.004	-0.018
30% NO_x case	0.047	-0.060	-0.012	-0.060
30% NH_3 case	0	-0.111	-0.093	0.010
30% CO case	0	0	0	0
30% SO_2 case	-0.185	0.027	-0.032	-0.004
Rest-of-Europe				
30% VOC case	-0.001	-0.015	-0.006	-0.008
30% NO_x case	0.004	-0.089	-0.026	-0.140
30% NH_3 case	0	-0.174	-0.095	0.030
30% CO case	0	0	0	0
30% SO_2 case	-0.112	0.036	-0.077	-0.009

PM fine nitrate shows a fractional decrease of -0.060 for a 30% decrease in national NO_x emission reductions but -0.089 for foreign NO_x emission reductions. So, of the total response to the 30% across-the-board reduction in NO_x emissions found for PM fine nitrate, two-fifths comes from the national response and three-fifths from the foreign response. This pattern of responses for PM fine nitrate is characteristically different to that seen for PM fine sulphate and is due to the larger spatial scale of nitrogen compared with sulphur. This larger spatial scale arises because NO_x is not as efficiently dry deposited as SO_2.

PM fine nitrate shows a fractional decrease of -0.111 for a 30% decrease in national NH_3 emissions but -0.174 for foreign emission reductions. So, of the total response to the 30% across-the-board reduction in NH_3 emissions found for PM fine nitrate, two-fifths comes form the national response and three-fifths from the foreign response, following the pattern revealed for the NO_x emission responses. PM fine nitrate increases in response to decreasing SO_2 emissions. These non-linear responses are greatest for foreign emission changes compared with national changes. This same pattern of behaviour is also found for the small positive non-linearities found in response to VOC emission reductions.

PM fine ammonium shows almost identical fractional changes in response to 30% NH_3 emission reductions carried out in the UK or in the rest of Europe. This follows as a consequence of the ammonia limitation found for the across-the-board NH_3 emission reductions. The small positive sensitivities found for PM fine ammonium to across-the-board NO_x and SO_2 emission reductions appear to have resulted predominantly from responses to foreign reductions rather than national ones.

A 30% across-the-board reduction in NO_x emissions produces a fractional change in PM coarse nitrate of -0.202. This is composed of a fractional change of -0.060 due to the national emission reduction and -0.140 from the foreign reduction. That is to say, there is a one-third to two-thirds split in favour of the foreign reduction. This is because of the large spatial scale associated with the night-time NO_2 + O_3 reaction that acts as a major source of the N_2O_5 precursor to PM coarse nitrate. The 30% across-the-board reduction in NH_3 emissions produces a fractional increase of +0.041 in PM coarse nitrate, of which one quarter arises from the national emission reduction and three quarters from the foreign. Ammonia competes for nitric acid in competition with sea-salts to form fine and coarse nitrate, respectively. As ammonia emissions are reduced, more nitric acid becomes available to form PM coarse nitrate. Because these are relatively slow and minor processes, they operate over a relatively large spatial scale, hence the greater foreign responses compared with national responses. Small but significant decreases in PM coarse nitrate were also observed in response to 30% reductions in SO_2 and VOC emissions. The former response arises from the greater availability of ammonia following the

decreased strong acid production from SO_2 oxidation, leading to increased competition for nitric acid and hence decreased PM coarse nitrate formation. The response of national VOC emission reductions was much greater than foreign reductions, reflecting the more NO_x-limited nature of photochemical ozone formation over the rest of Europe compared with the more VOC-limited situation over the UK.

5.2.2   Secondary PM Modelling Using the Met Office NAME Model

The NAME model is able to explicitly model the formation of sulphate and nitrate aerosol over the UK given emission estimates of the primary precursors. A preliminary study by the Met Office indicated that the response of sulphate and nitrate aerosol to SO_2 and NO_x emission reductions was non-linear. In this project, further full year runs of NAME were carried out to see whether the model could capture the observed changes in sulphate and nitrate aerosol resulting from the changing emissions over the period 2000 to 2006 and to establish whether the NAME results were robust enough to be of use to provide the PCM model with suitable scaling factors to assist in providing baseline projections of inorganic aerosols.

5.2.2.1 Validation of NAME in 2000, 2003 and 2006

The NAME model calculations of secondary PM were validated against monitoring data for 2000, 2003 and 2006. An emissions file comprising 2003 NAEI data over the UK and 2003 EMEP data for the rest of Europe was scaled according to the emissions details to provide emissions fields for 2000 and 2006.

The following model runs were then performed:
- Year 2000 with 2000 emissions and meteorology
- Year 2003 with 2003 emissions and meteorology
- Year 2006 with 2006 emissions and meteorology

The model domain was 46N to 65N and 15W to 16.5E and the chemistry grid was defined to be 20 km x 20 km horizontally, with 100m layers vertically up to 2500m and then larger layer thickness up to 20000m.

Modelled daily sulphate aerosol was compared with measured daily aerosol at five rural network sites (AEA Air Quality Archive), Barcombe Mills, Yarner Wood, Lough Navar, Eskdalemuir and High Muffles, for 2000, 2003 and 2006. Average statistics of correlation (r), bias, normalised mean square error (nmse) and factor within a percentage of two (fac2) are presented in Table 5.5 as an average over the 5 sites for each year. Figure 5.1 shows the model data plotted against the observations at each of the sites for 2003. Further comparisons for 2000 and 2006 are given in a report by Redington (2007).

Table 5.5 Yearly average statistics for model versus measured daily sulphate aerosol. (r – correlation, bias – positive amount is over-prediction, negative is under-prediction, unit is µg/m³, nmse – normalised mean square error, fac2 – factor within a percentage of two of the measured data.)

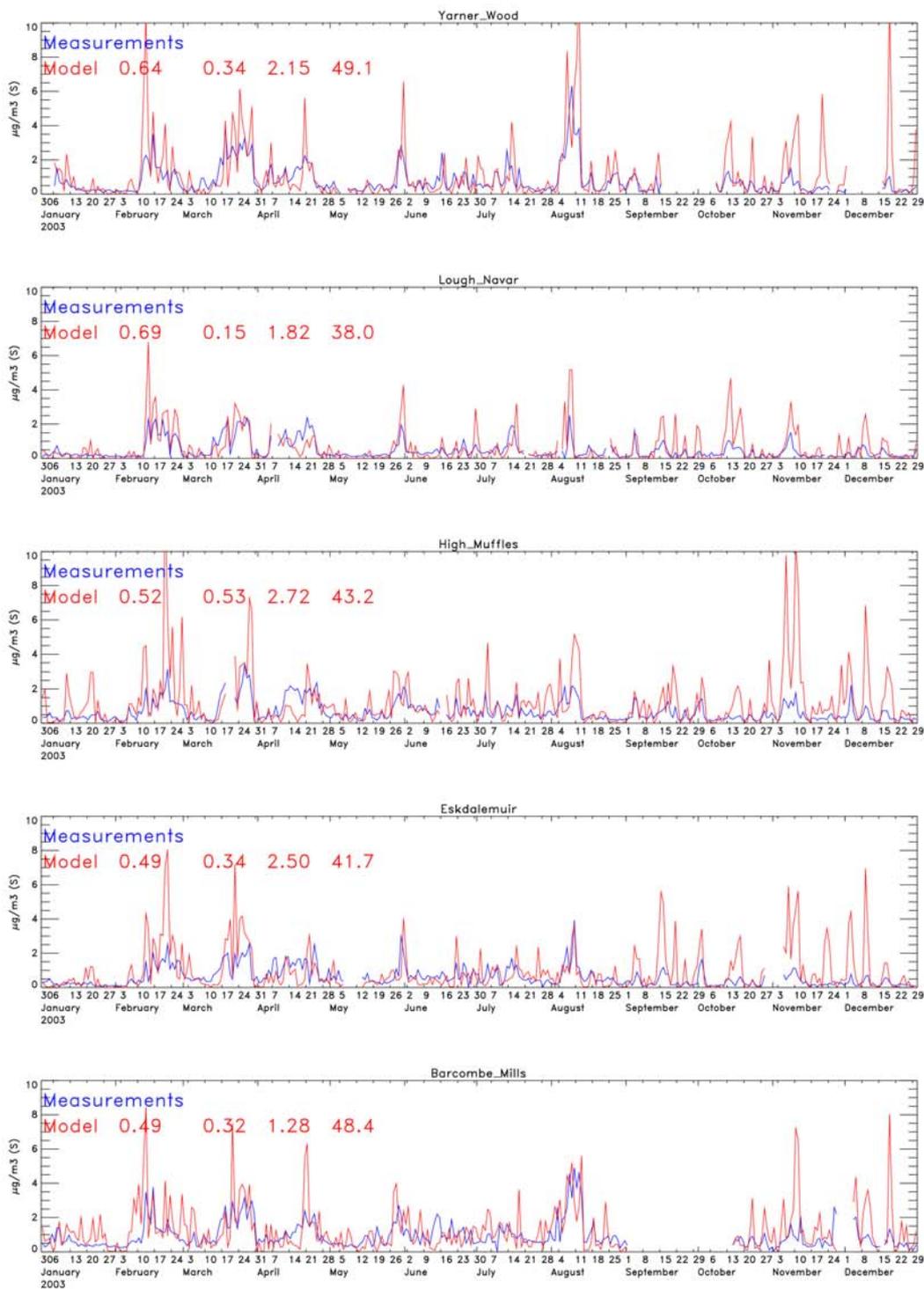| year	r	Bias (µg/m³)	nmse	fac2 (%)
2000	0.5	0.14	1.91	44.4
2003	0.57	0.34	2.09	44.1
2006	0.54	0.18	1.64	43.8

Figure 5.1 Daily sulphate aerosol at the five rural measurement sites, Yarner Wood, Lough Navar, High Muffles, Eskdalemuir and Barcombe Mills for 2003. The data are shown as µg/m^3 (S). The measurements are shown in blue and the model data in red. On each plot are shown the same set of four statistics (r, bias, nmse, fac2) as presented above in Table 1 but for each individual site.

The statistics show that reasonable correlations are achieved but with a positive bias at all sites, most notably in 2003. The normalised mean square error is quite high, but over 40% of the modelled data are within a factor of 2 of the measured data over all three years. Looking at the results in Figures 5.1 enables an understanding of the statistics. It is clear that the model is capturing the broad pattern of the observations which is reflected in the correlation, however the model at times greatly over-estimates the measured sulphate aerosol, most noticeably in the winter months, for example at Eskdalemuir in 2003. The cause of these large model over-predictions is currently being studied (under DEFRA contract AQ0902) and initial results indicate that it is a problem with the aqueous phase production of sulphate within the model.

Table 5.6 presents the same set of statistics as shown in Table 5.5 for modelled versus observed data at Harwell for sulphate and nitrate aerosol. The Harwell data were provided by NPL through the DEFRA Particle Number and Composition Network contract. The correlations obtained are comparable with those seen in Table 5.5 however for both sulphate aerosol (which we would expect to be similar to the results for the five rural sites) and nitrate aerosol the model shows a negative bias (under-prediction) and much greater normalised mean square errors and lower percentages within a factor of two.

Table 5.6: Yearly average statistics are presented for 2006 for Harwell for both sulphate and nitrate aerosol.

Harwell	year	r	Bias ($\mu g/m^3$)	nmse	fac2 (%)
Sulphate aerosol	2006	0.51	-0.74	3.71	13.5
Nitrate aerosol	2006	0.43	-0.46	3.30	16.0

A detailed comparison between modelled and observed data for Harwell in 2006 showed the model is not capturing the lowest measured sulphate aerosol values very well and is under-predicting measured values of around $0.5\mu g/m^3$ and it is these values that are causing the negative bias seen in Table 5.6. For nitrate aerosol the NAME model falls down in its ability to capture winter-time concentrations. The summer is reasonably well predicted but the winter is greatly under-predicted and further work is required to fully understand this. This is also the subject of research under DEFRA contract AQ0902.

Figures 5.2 and 5.3 show NAME modelled annual averages for sulphate and nitrate respectively for 2000, 2003 and 2006. The data were derived by extracting model results at the twelve monthly measurement sites (Strathvaich, Glensaugh, Eskdalemuir, Lough Navar, Sutton Bonnington, Cumystwth, Stoke Ferry, Rothamsted, Barcombe Mills, Yarner Wood, Bush and High Muffles) and are plotted against the measurement data from these sites and results from the PCM model.

The daily sulphate aerosol statistics for the five rural sites in Table 5.5 (Yarner Wood, Eskdalemuir, Barcombe Mills, High Muffles and Lough Navar) gave positive biases consistent with the biases seen in Figure 5.2 for sulphate aerosol and the model is reproducing the overall shape of the measurement data though the over-prediction seen in the daily data (e.g. Figure 5.1) is dominating the results and it is hoped that resolving the aqueous phase production issues could give a big improvement in this.

The nitrate aerosol picture is harder to understand (Figure 5.3) as there is only daily data in 2006 with which to compare. It would be useful to compare with the monthly data for each year to look at the seasonal biases. This data will be obtained and compared with model data as part of the work carried out under DEFRA contract AQ0902. In 2006 there was a big under-prediction in January, February and March at Harwell indicating we should expect approximately $2\mu g$ NO_3 under prediction in 2006 from the Harwell data. The 12 monthly sites are however only under-predicted by $1.1\mu g/m^3$ NO_3 in 2006. The 2003 nitrate appears to agree well with the network mean though monthly data or daily data may reveal under and over predictions during the year that are having a cancelling effect. The model under-predicts the 2000 data by 0.45 $\mu g/m^3$ NO_3. Study of additional measurement data is necessary to understand further the nitrate aerosol and it should be noted that differences could be due to the different measurement techniques employed for the monthly and daily observations.

Figure 5.2 NAME yearly average sulphate aerosol for 2000, 2003 and 2006 plotted against measurement data and estimates from the PCM model µg/m³(SO₄). NAME modelled data and measurement data are derived by averaging data at the 12 monthly sites.

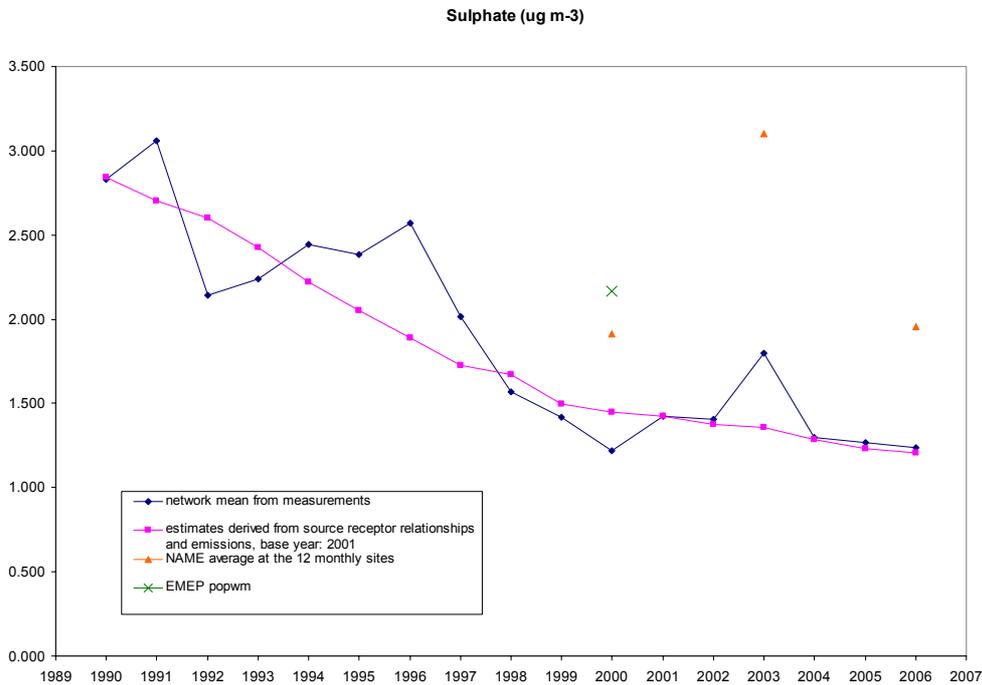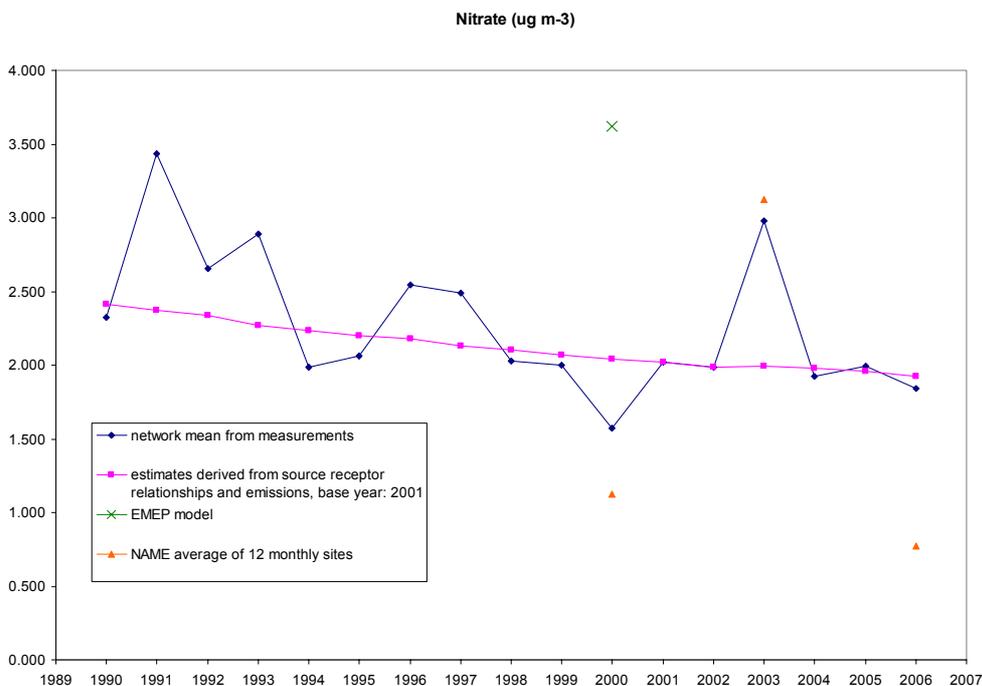**Figure 5.3 NAME yearly average nitrate aerosol for 2000, 2003 and 2006 plotted against measurement data and estimates from the PCM model µg/m³(NO₃). NAME modelled data and measurement data are derived by averaging data at the 12 monthly sites**.

5.2.2.2 Results from preliminary emission reduction scenario runs

The NAME model has been run to simulate the effect of reducing SO_2 and NO_X emissions on the annual average sulphate and nitrate aerosol concentrations. 2006 meteorology has been used and 2003 emissions data which used the NAEI over the UK and EMEP elsewhere.

In order to produce some results quickly a winter month (February) and a summer month (August) have been modelled and the results have been averaged. More robust results would be obtained by modelling the full year for each of the scenarios as February and August alone are clearly not representative of the full spectrum of meteorology that would be seen over a year.

The idea was to reduce all emissions except for shipping which would stay at 2003 levels. This was possible with the EMEP emissions data but not for the NAEI data as it was not clear how to separate out the shipping.

Three scenarios were run on 2006 meteorology:
1) base case - 2003 NAEI and EMEP emissions
2) reduced SO_2 by 15% for NAEI and EMEP (except shipping)
3) reduced SO_2 and NO_X by 15 % for NAEI and EMEP (except shipping)

Figures 5.4 and 5.5 show the annual averages for sulphate aerosol and nitrate aerosol for 2006 from the base case run. The maxima in sulphate aerosol over the UK is in the range 4.0-6.0 µg/m^3 SO_4 over southern and central England. The maxima in nitrate aerosol is in the range 1.0-2.0 µg/m^3 NO_3 and is over the south eastern area of England.

Figure 5.4 *Base case*: average NAME sulphate aerosol for 2006 based on 2003 emissions.
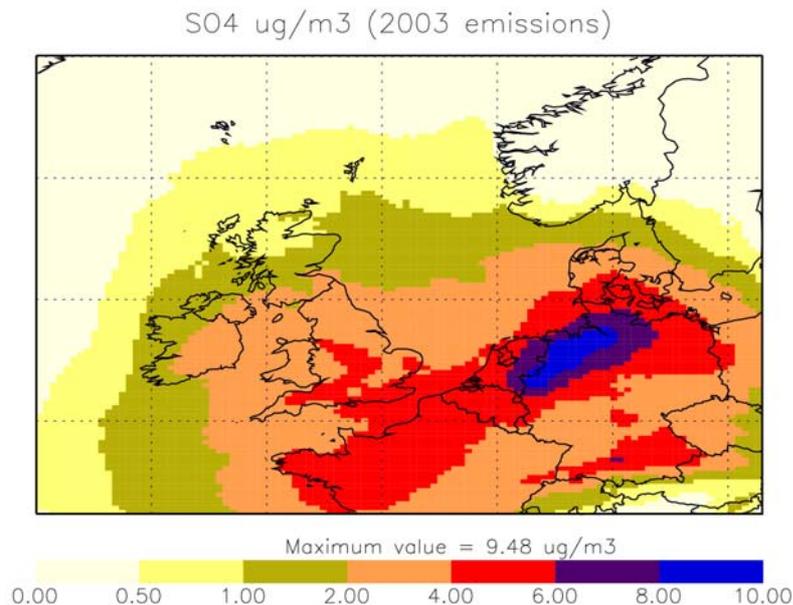
Figure 5.5 *Base case*: average NAME nitrate aerosol for 2006 based on 2003 emissions.
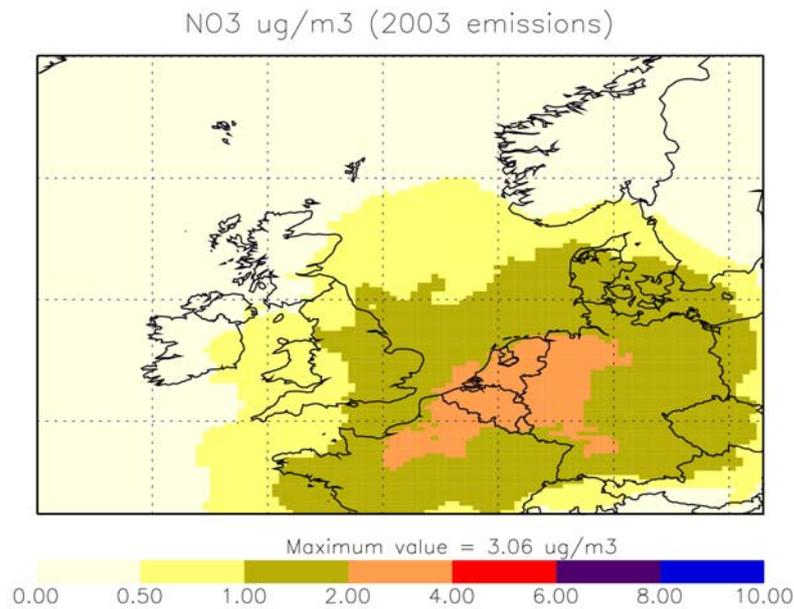
Figures 5.6 and 5.7 show the annual average sulphate and nitrate aerosol for scenario 2, a 15% reduction in SO_2 except for EMEP shipping emissions. There is a clear reduction in sulphate aerosol over the UK with greatly reduced areas in the 4.0-6.0 µg/m^3 SO_4 range. The nitrate aerosol is largely unchanged.

Figure 5.6 *Reduced SO$_2$*: average NAME sulphate aerosol for 2006. 2003 emissions minus15% SO$_2$.
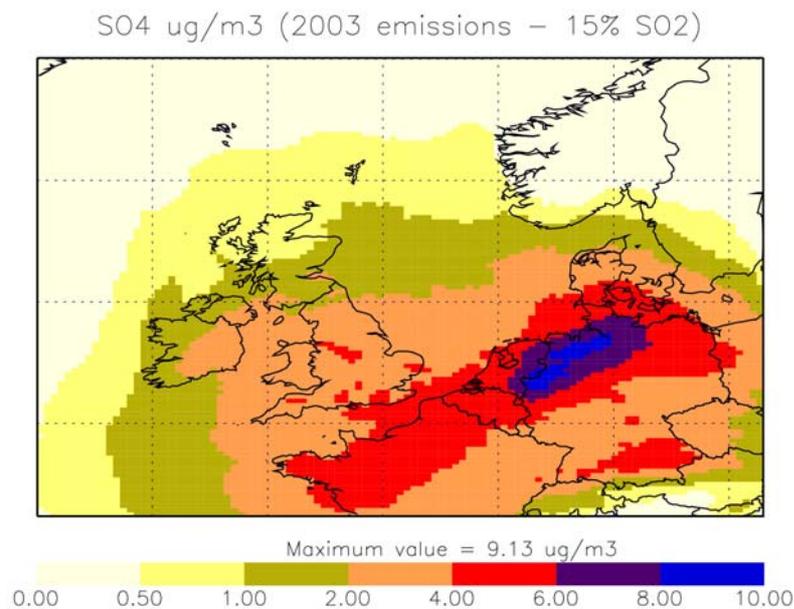
Figure 5.7 *Reduced SO$_2$*: **average NAME nitrate aerosol for 2006. 2003 emissions minus 15% SO$_2$.**
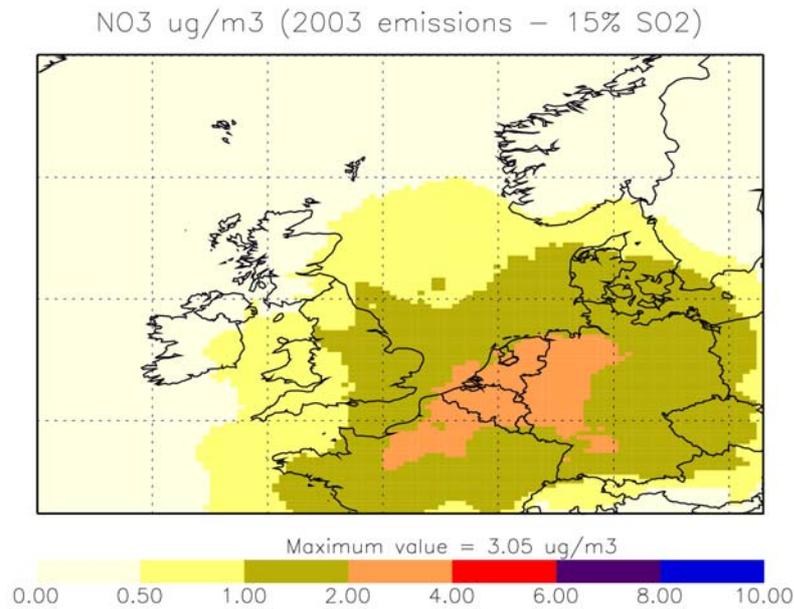
Figures 5.8 and 5.9 show annual average sulphate and nitrate aerosol for scenario 3 which is a 15% reduction in SO$_2$ and NO$_X$ except for EMEP shipping emissions. Figure 15 shows that as NO$_x$ is reduced as well as SO$_2$ the reduction in SO$_4$ seen in figure 13 is lost, and the SO$_4$ levels are very similar to those seen in figure11 the base case. The annual average nitrate is slightly reduced over the

Figure 5.8 *Reduced SO$_2$ and NO$_X$*: **average NAME sulphate aerosol for 2006. 2003 emissions minus 15% SO$_2$ and NO$_X$.**

Figure 5.9 *Reduced SO$_2$ and NO$_X$*: **average NAME nitrate aerosol for 2006. 2003 emissions minus 15% SO$_2$ and NO$_X$.**
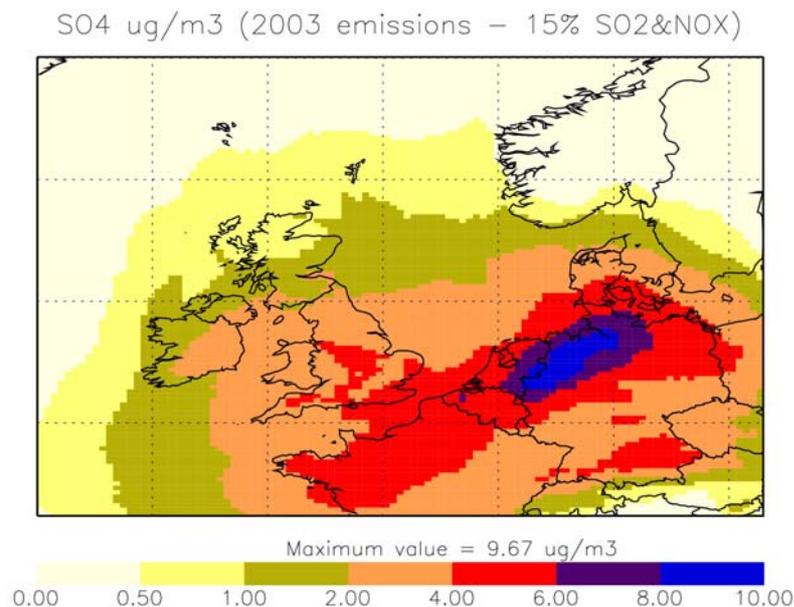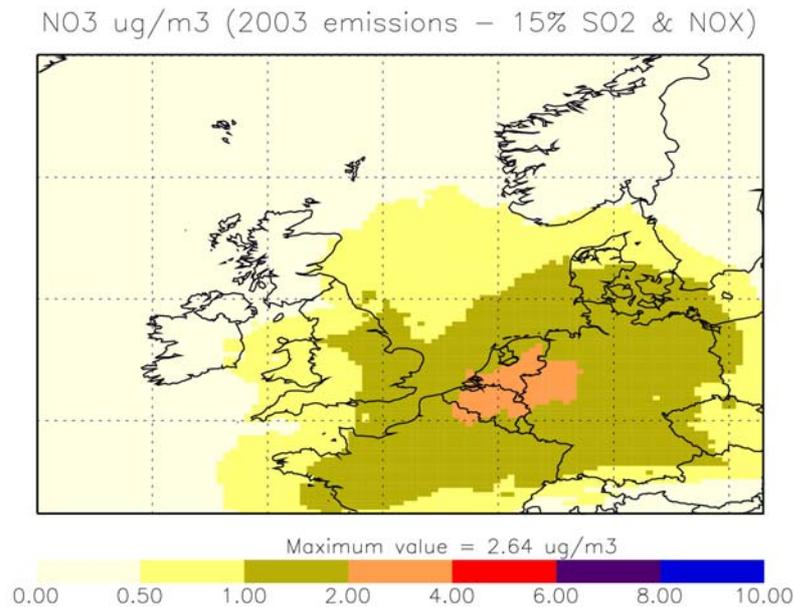

UK but more noticeably over Europe. It should be noted that the results are based on modelling only 2 months of 2006 and more robust results would be obtained from a year run of each scenario. Additional scenarios might also be useful such as reduced NO$_X$ emissions only or reduced NH$_3$ emissions alone and in combination with reducing other species.

5.2.2.3   Summary of NAME Modelling of Secondary PM

This work has shown that NAME can predict the changing levels in sulphate and nitrate aerosol between 2000 and 2006 but there are significant biases that need to be understood. Further research in understanding the modelling of sulphate and nitrate aerosol is being carried out under DEFRA contract AQ0902. The dominant factor affecting the modelled annual average appears to be the meteorology rather than the change in emissions of precursor species. To investigate the effect of purely changes in emissions it would be instructive to run 2006 emissions on 2000 meteorology.

Changing meteorological patterns in the future could prove to be one of the biggest uncertainties affecting the robustness of future predictions. It would certainly be advisable to run with worst case 2003 type met data as well as worst case emission scenarios.

This work has provided extensive validation of NAME modelled sulphate and nitrate aerosol and it would be useful to extend the preliminary reduction scenarios described in Section 5.2.2.2. NAME could be run to produce UK wide emission sensitivity coefficients to reductions in SO$_2$, NO$_x$ and NH$_3$. These could then be used in the PCM to allow a comparison with predictions made using NAME results as well as EMEP and PTM results.

6 Ozone in the UK: 2006 - Modelling Support for the Third Daughter Directive (Objective 1c)

Directive 96/62/EC on Ambient Air Quality Assessment and Management (the Framework Directive) establishes a framework under which the EU sets limit values or target values for the concentrations of specified air pollutants. Directive 2002/3/EC (the third Daughter Directive) sets Target Values (TVs) and Long-term Objectives (LTOs) to be achieved for ozone.

2006 is the third year for which an annual air quality assessment for the third Daughter Directive pollutants is required. A questionnaire has been completed for submission to the EU containing the results of this air quality assessment along with those required for the first and second Daughter Directives. The assessment takes the form of comparisons of measured and modelled air pollutant concentrations with the Target Values and Long-term Objectives set out in the Directives.

Air quality modelling of ozone is necessary to supplement the information available from the UK national air quality monitoring networks. In the previous tropospheric ozone modelling contract, AEA submitted a report evaluating the suitability of the OSRM and an empirical model calibrated to ozone data from network monitoring sites for providing the supplementary modelling data. It was proposed then and confirmed for this contract that the empirical modelling approach should continue to be used to provide the supplementary modelling data for the Commission as this provides better agreement with monitoring data for the key ozone metrics, but that each year the performance of the OSRM would be re-evaluated against the outputs from the empirical model.

The empirical modelling is based on assessments of ozone monitoring data for the relevant calendar year. The OSRM calculates ozone concentrations from relevant emissions data and real meteorological data for the relevant calendar year. Completion of the air quality questionnaire specified by the Commission and based on the monitoring data and empirical model results is carried out under AEA's Pollution Climate Mapping contract with Defra. The questionnaire submitted each year is accompanied by a report on the Supplementary Assessment Modelling for the 3rd Daughter Directive on Ozone Reporting. The Third Daughter Directive report that relates to ozone is written separately from, but in parallel with, the report covering the other Daughter Directive pollutants. The Third Daughter Directive report details the modelling methodology used to derive 1x1 km resolution maps of ambient air quality for ozone over the UK and presents modelled and measured data to illustrate instances where the European objectives have been exceeded.

The Supplementary Report for 2006 based on the empirical modelling has been being prepared (Kent and Stedman, 2008). The metrics covered by the report include:

- Days greater than 120 μg m^{-3} (2006) (Long Term Objective for Human Health)
- Days greater than 120 μg m^{-3} (2004-2006) (Target Value for Human Health)
- AOT40 (2006) (Long Term Objective for Vegetation)
- AOT40 (2002-2006) (Target Value for Vegetation)

This is the second year for which data from Gibraltar has been included in this report. Although no modelling is performed for Gibraltar, measured data from the continuous automatic air monitoring campaign is used in the assessment.

Section 6.1 summarises the empirical modelling approach and the results submitted to the Commission for 2006. Section 6.2 provides model results from the OSRM for 2006 and compares results with those from the empirical modelling method.

6.1 Empirical Modelling of Ozone in the UK in 2006

6.1.1 Methodology

The modelling and mapping for 2006 used a slightly different methodology than in previous years. Now measured ozone concentrations from rural monitoring sites in the UK's national networks are used to interpolate a rural background map of ozone concentrations for each metric. This map will overestimate concentrations in urban and roadside locations where titration with NO_x will lower ozone concentrations. The scavenging influence of NO_x concentrations is accounted for by calculating a percentage decrement that represents the changing ozone concentrations with changing NO_x concentrations. This decrement is subtracted from the interpolated rural map.

While this method has not resulted in an obvious improvement in the model performance (it remains similar to previous years), it more easily facilitates alterations to the different model components, making the model more flexible and tailored for future scenario based work.

6.1.2 Results from Empirical Modelling

The summary of the report results is presented in Tables 6.1 to 6.4 below that show the number of zones exceeding the Directive objectives using both the monitoring data and the model results. Further details are given in Kent and Stedman (2008).

Table 6.1: UK summary results of air quality assessment relative to the Target Values for ozone for 2010

Target Value	Number of zones exceeding
Max Daily 8-hour mean Target Value	none
AOT40 Target Value	none

Table 6.1 is a summary of the number of UK zones and agglomerations exceeding the Target Value for ozone. The Target Values are based on multi-year metrics for both health (averaged over 3 years) and vegetation (averaged over 5 years). Due to the averaging involved in the calculation of these metrics, even comparatively high ozone years can be averaged down by historic (often lower) data so these metrics tend to be less stringent than the corresponding single-year Long-Term Objectives. 2006 was no exception in this regard – despite the early heatwave and associated elevations in ozone concentrations, neither of the Target Values were exceeded across any zone in the UK. This assessment also incorporated monitoring data from the UK national networks.

Table 6.2: UK summary results of air quality assessment relative to the Long-term Objectives for ozone

Long-term Objective	Number of zones exceeding
Max Daily 8-hour mean Long-term Objective	43 zones (41 measured + 2 modelled)
AOT40 Long-term Objective	41 zones (32 measured + 9 modelled)

Table 6.2 is the corresponding summary table for the Long-Term Objective metrics for health and vegetation. These metrics are far more sensitive to high ozone years because they are based on only a single year of data and therefore there is no averaging out of high values. The elevated concentrations measured in 2006 are therefore reflected in these metrics. Again, the use of measured data was a large part of this assessment and many of the exceedences listed in Table 6.2 were identified from the measured data (although modelling also identified them). However there were a few zones and agglomerations that were identified by modelled data but not by the measured data (2 zones for the health metric and 9 zones for the vegetation metric).

Maps showing the Long Term Objective and Target Value ozone metrics for human health (days greater than 120 μgm^{-3}) and vegetation (AOT40) are shown in Figures 6.1 and 6.2. One can see in these maps, the areas in the South-East of England and East Anglia shown in orange and red in Figure 6.1 where the number of days with the maximum daily 8-hour mean exceeding 120 μg m^{-3} (the human health metric) was greater than the 2010 target threshold of 25 days in 2006. The area of East

Anglia generally exceeds the AOT40 target threshold of 18,000 μg m^{-3} .hours in 2006 (Figure 6.2). When averaged over the last 3 years (health-based metric) and 5 years (vegetation), though, there are no exceedences of the 2010 target value

The corresponding summary results for Gibraltar are shown in Tables 6.3 and 6.4.

Table 6.3: Gibraltar summary results of air quality assessment relative to the Target Values for ozone for 2010

Target Value	Number of zones exceeding
Max Daily 8-hour mean Target Value	none
AOT40 Target Value	none

Table 6.4: Gibraltar summary results of air quality assessment relative to the Long-term Objectives for ozone

Long-term Objective	Number of zones exceeding
Max Daily 8-hour mean Long-term Objective	1 zone (measured)
AOT40 Long-term Objective	1 zone (measured)

6.1.3   Empirical Model verification

Tables 6.5 and 6.6 show the average measured and modelling concentrations at sites in the AURN (used to calibrate the model) and at verification sites (completely independent of the model).

Table 6.5: Summary statistics for comparison between modelled and measured number of days exceeding 120 μg m^{-3} as a maximum daily 8-hour mean

		Mean of measurements (days)	Mean of model estimates (days)	r^2	% outside data quality objectives	No. sites
National Network	2006	13.1	12.8	0.68	6	72
Verification Sites	2006	13.2	14.5	0.17	28	18
National Network	2004-6	7.3	7.0	0.79	3	72
Verification Sites	2004-6	7.8	8.0	0.33	21	19

Table 6.6: Summary statistics for comparison between modelled and measured AOT40 vegetation metric

		Mean of measurements (µg.hours)	Mean of model estimates (µg.hours)	r^2	% outside data quality objectives	No. sites
National Network	2006	10497	10252	0.80	4	69
Verification Sites	2006	10887	12528	0.11	24	17
National Network	2002-6	5346	5137	0.86	3	65

These statistics are standard Pollution Climate Mapping empirical model summary outputs that are also used for other pollutants modelled for the Daughter Directives. They show averages of the measured metric, corresponding averages of the modelled metric, the correlation coefficient of plotted measured *vs*. modelled concentrations (R^2, presented in verification plots in the main report), the number of sites used in the assessment and the percentage of these sites that fall outside the +/- 50% data quality objective (DQO) range. The table shows these for National Network sites (AURN sites used in the model) and for Verification sites (independent sites that are suitable for assessing model performance). Comparisons have been made for single years (corresponding to the Long Term Objectives (LTOs)) and for multiple years (corresponding to the Target Values).

Figure 6.1: Long-term Objective (2006) and Target Value (2004-2006) for Human Health

Days greater than 120 μg m^{-3} (2006)

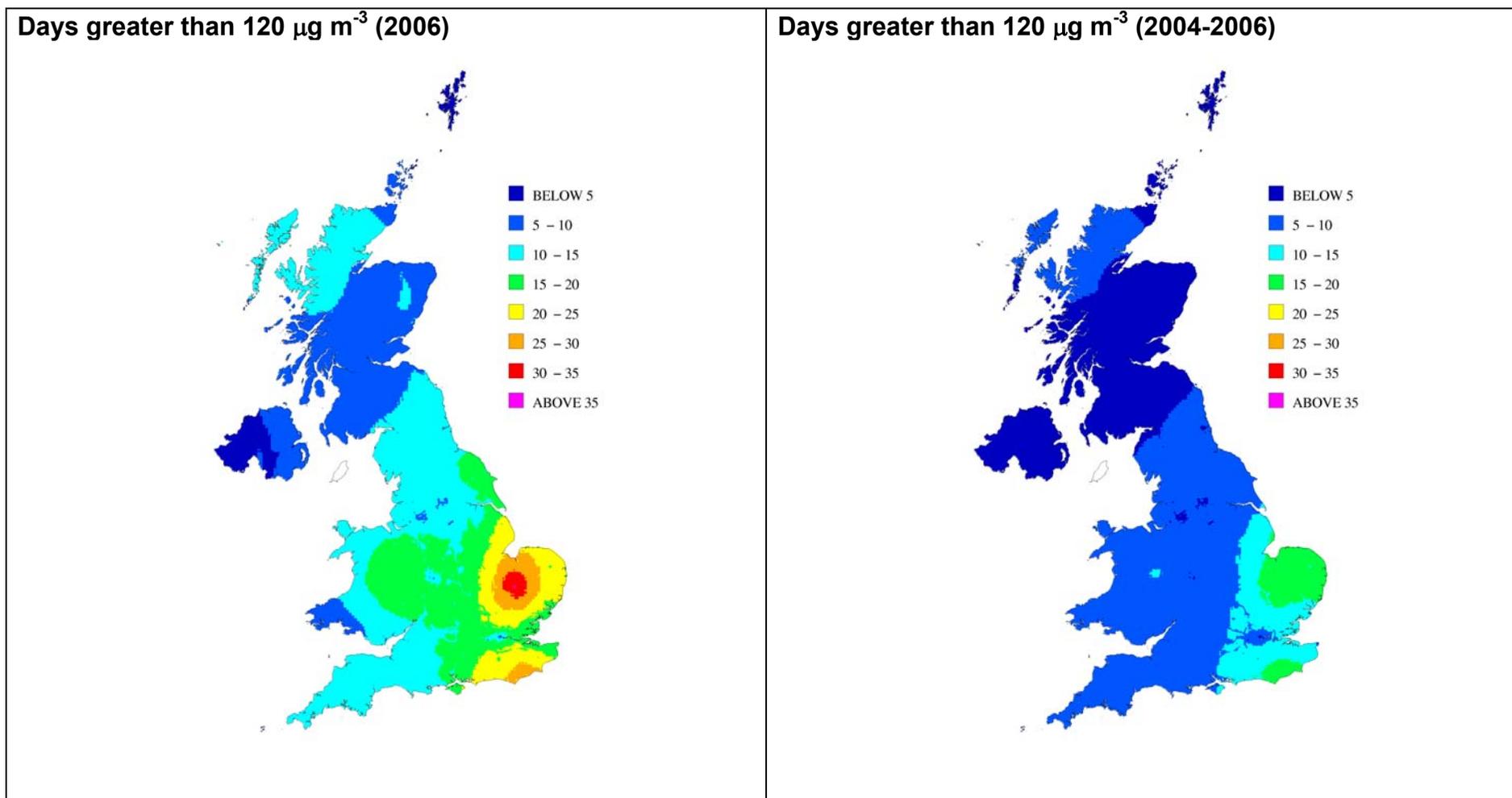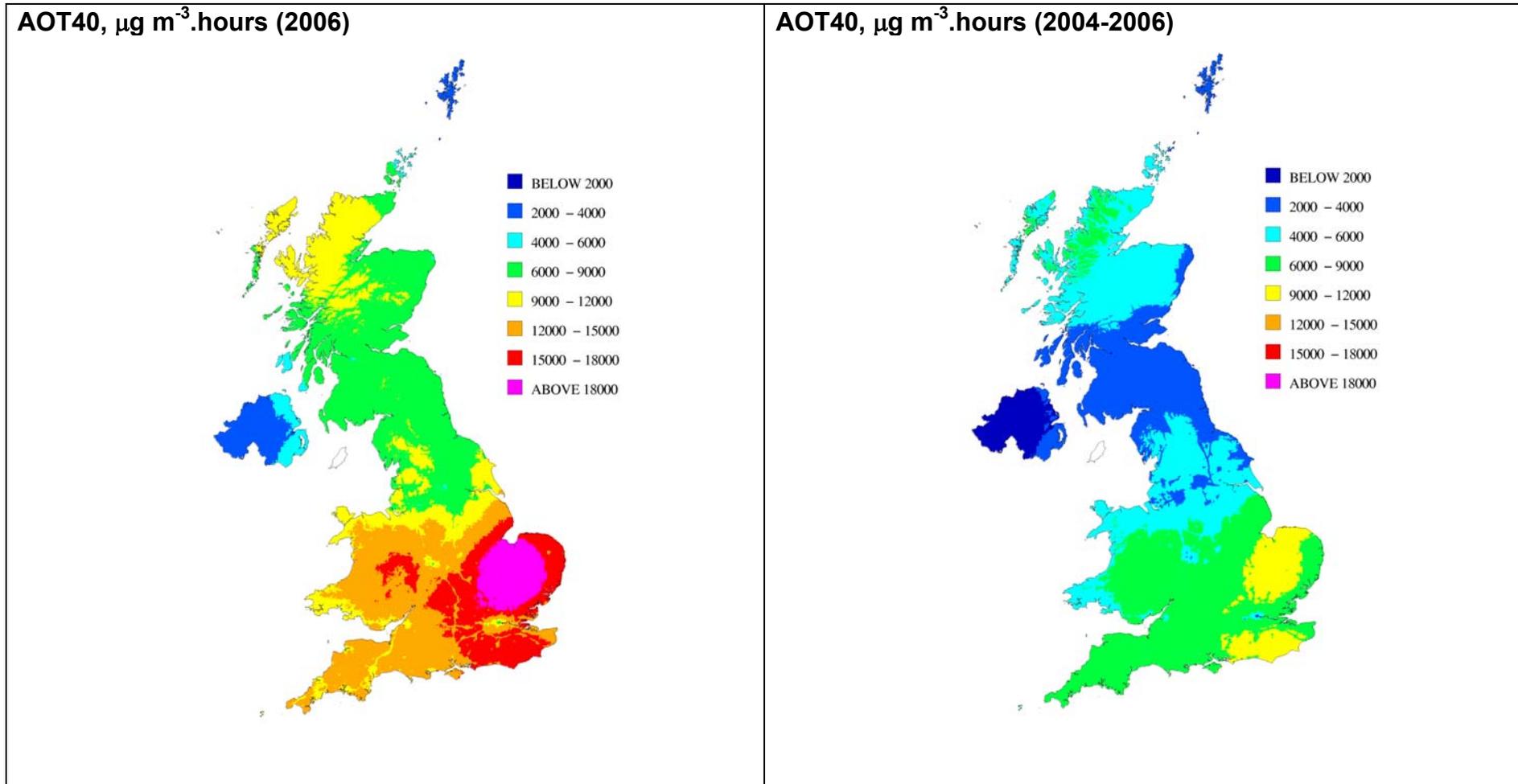Days greater than 120 μg m^{-3} (2004-2006)

Figure 6.2: Long-term Objective (2006) and Target Value (2002-2006) for Vegetation

The measured and modelled averages are generally very similar and slightly more favourable for the National Network sites. This is quite understandable given that theses sites have been used in the model (calibration and interpolation etc). This is also why the R^2 is significantly higher for the National Network sites than for the Verification Sites and why a higher percentage of Verification sites fall outside the DQO range. The multi-year metrics exhibit an even closer agreement between measured and modelled data than the LTOs. This is due to the averaging out of peaks in the calculation of the metric.

6.2   OSRM Modelling of Ozone in the UK in 2006 and Comparisons with the Empirical Model

The previous tropospheric ozone modelling contract had shown that the empirical modelling approach used in the Pollution Climate Mapping (PCM) model traditionally gives results for ozone concentration metrics that are more representative of the measured concentrations in model verification than corresponding outputs provided by the OSRM. Hence, the PCM empirical model is used to provide outputs submitted to the European Commission on behalf of Defra, as described in Section 6.1. The OSRM, on the other hand, has a stronger role to play in scenario analysis and policy development.

The OSRM is a process-based Lagrangian model with a surface conversion post-processor using emissions and realistic meteorological data to calculate ozone concentrations so has the capability to be used for future year scenario modelling using alternative emissions and meteorological data fields.

The PCM is mainly an empirical model based on actual measurements data incorporating some process-based components, but is not so well suited for future sceanrio modelling.

Each year both models are verified against measured data to provide confidence in their performance. It is also useful to check the model results against each other in order to make clear and informed decisions about how best to use each model for their respective strengths. The two models have been compared in previous years, most recently for 2004 and 2005 which were noted as relatively "low ozone" years (Hayman et al, 2006a). By contrast, 2006 was a high ozone year and so a comparison for this year will illustrate the OSRM model performance during a particularly high ozone year with significant photochemical episodes. Ozone concentrations measured across the AURN's 92 ozone monitoring sites in 2006 reached concentrations of up to 260 µg m^{-3} at Wicken Fen in East Anglia. All except one site (London Marylebone Road) exceeded the unregulated Air Quality Strategy objective of 100 µg m^{-3} as a daily maximum running 8-hour mean.

The performance of the OSRM for 2006 was demonstrated using the two Long-Term Objective (LTO) metrics used in the Third Daughter Directive reporting that correspond to the specific calendar year 2006:

- Days greater than 120 μg m^{-3} as a maximum daily running mean (Long Term Objective for Human Health)
- AOT40 (Long Term Objective for Vegetation)

The multi-year Target Value metrics will not be as good an indicator of model performance during a high ozone year as the Long-Term Objective metrics because averaging over several years will remove from the metric the peak concentrations associated with a particular year. For this reason, the single year LTO metrics for human health and vegetation were compared for 2006.

OSRM runs for 2006 were made by implementing 6-hourly meteorological data provided by the Met Office and using UK emissions inventory data for 2006 based on projected figures from the the 2005 version of the NAEI.

6.2.1 Comparison of Maps of OSRM and PCM Outputs for Ozone Metrics in 2006

The maps that have been generated from the outputs of the OSRM and empirical PCM model for both the health and vegetation Long-Term Objective metrics are presented in Figures 6.3 to 6. 6. Figure 6.3 presents the map of the number of days exceeding 120 µg m^{-3} in 2006 from the OSRM and Figure 6.4 shows the same metric output from the PCM empirical model. Figure 6.5 shows the OSRM map for the AOT40 metric in 2006 and Figure 6.6 shows the corresponding map from the PCM empirical model. Figures 6.4 and 6.6 are the same as the PCM Long-term Objective (2006) maps shown in Figures 6.1 and 6.2, respectively.

As noted in previous comparisons (Hayman, 2006c), both maps successfully identify areas of ozone depletion due to NO$_X$ titration (large city areas and major roads). These are better represented by the PCM empirical map than the OSRM because the spatial resolution of this model is finer (1km). The empirical model utilises a modelled NO$_X$ map (described in Kent *et al*., 2008) with a coefficient to describe the decrement in ozone concentrations with NO$_X$. The OSRM uses the surface conversion algorithm in conjunction with NAEI NO$_X$ emissions maps to account for the effects of NO$_X$ titration on ozone concentrations.

The north/south gradient in ozone concentrations that has been seen in previous years is apparent in 2006 in the empirical model output. This is a natural feature of the increase frequency and magnitude of photochemical events in the more southerly and easterly areas of the UK. It has been noted (Hayman, 2006c) that the marginally increasing concentrations in the north west of Scotland may be the result of higher hemispheric background ozone concentrations here being represented in the monitoring data being fed into the model.

The OSRM shows broadly similar patterns compared with the empirical maps, however there are some specific spatial differences. The coarser resolution (10km) prevents the map from picking out smaller towns, cities and road links so the NO$_X$ titration effect is not as spatially pronounced as the empirical maps. The OSRM output is consistent with the empirical maps in correctly identifying significantly higher concentrations in the south and east of the UK. However, the OSRM map estimates notably higher concentrations of ozone in the south west of the country over Cornwall that have not been captured in the corresponding empirical map output. The high ozone concentrations that OSRM estimates in East Anglia are limited to the coastal fringe whereas the empirical map places it further inland as a result of measured concentrations from the Wicken Fen site which measured the highest ozone concentrations in the national network in 2006. The majority of high ozone concentration areas identified by OSRM in 2006 are in coastal fringe areas. This is consistent with OSRM outputs from previous years. Some unusual features are that coastal regions of the north eastern Scotland together with the Orkney and Shetland Islands are estimated to have high concentrations according to OSRM. This is unlikely given the latitude of these regions, but is a feature of the OSRM observed previously for other years. It has been suggested by Hayman (2006c) that this coastal 'edge effect' might be the result of the lack of ozone deposition over the sea surface or limitations of meteorological datasets.

The highest modelled concentration of the AOT40 metric in the empirical map was located in East Anglia and resulted from the high measured concentrations from the Wicken Fen monitoring site. The modelled map of the metric from OSRM closely follows the spatial pattern of the OSRM map for the days greater than 120 µg m^{-3} metric: some coastal locations display higher concentrations than inland (Scottish coast and Orkneys and Shetlands), and the highest concentrations are on the southern and south eastern coasts.

Figure 6.3. Number of days exceeding 120 µg m^{-3} (2006) (OSRM map)
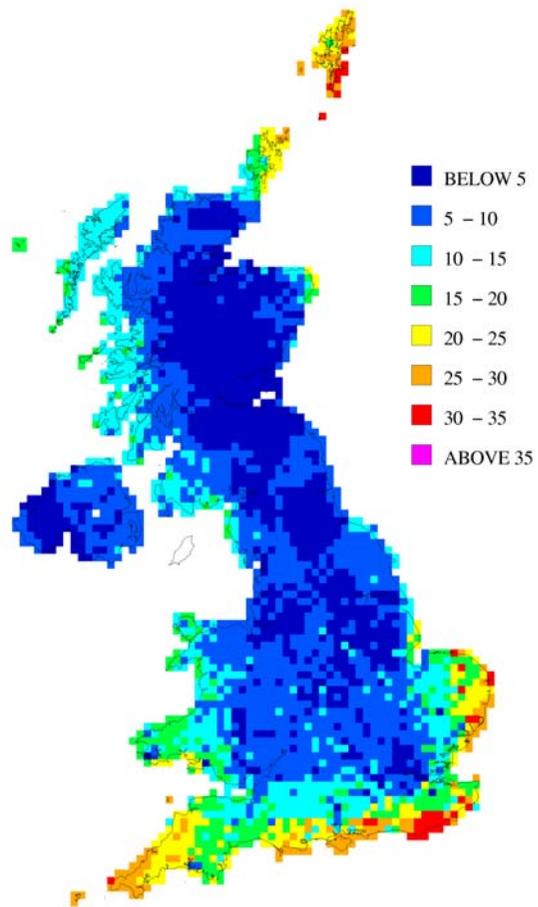
Figure 6.4. Number of days exceeding 120 µg m^{-3} (2006) (PCM empirical map)

Figure 6.5. AOT40 (μg m^{-3}.hours) (2006) (OSRM map)

BELOW 2000
2000 – 4000
4000 – 6000
6000 – 9000
9000 – 12000
12000 – 15000
15000 – 18000
ABOVE 18000
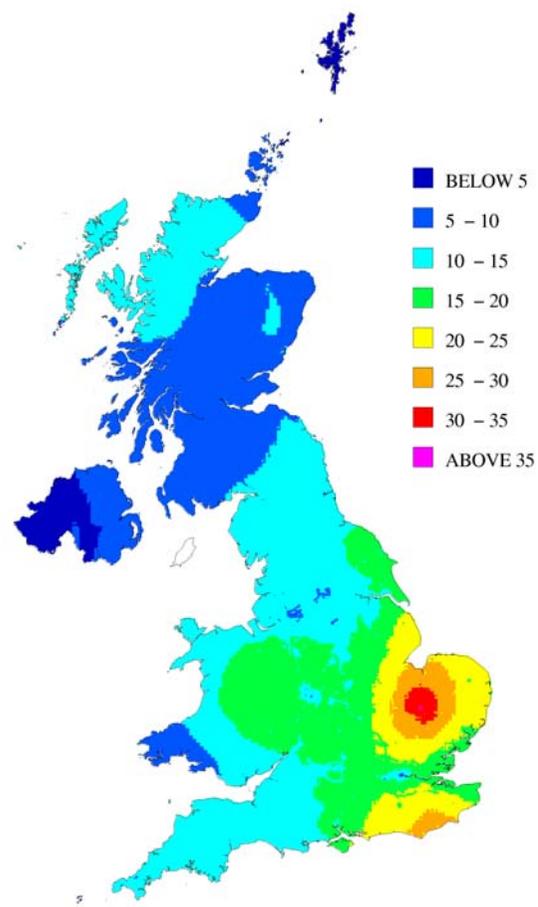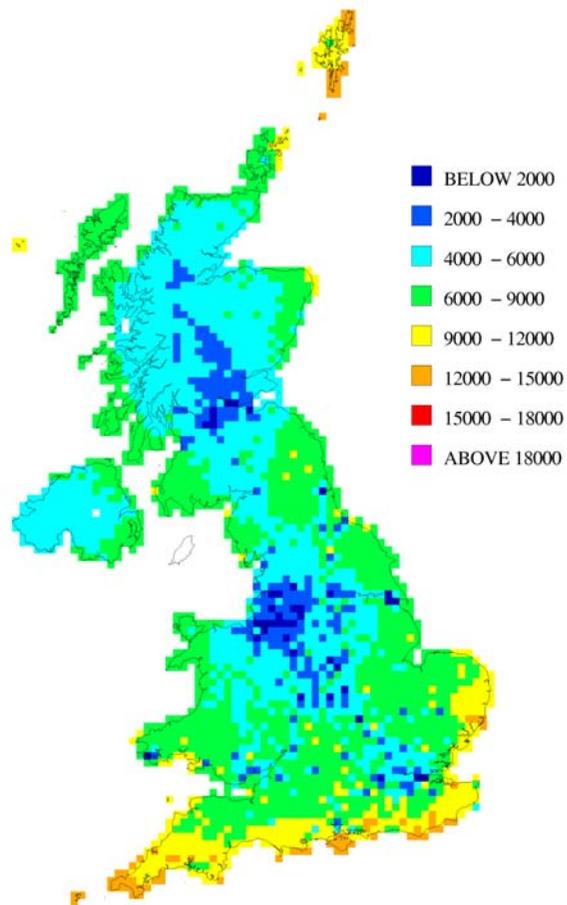
Figure 6.6. AOT40 (2006) (μg m^{-3}.hours) (PCM empirical map)

BELOW 2000
2000 – 4000
4000 – 6000
6000 – 9000
9000 – 12000
12000 – 15000
15000 – 18000
ABOVE 18000
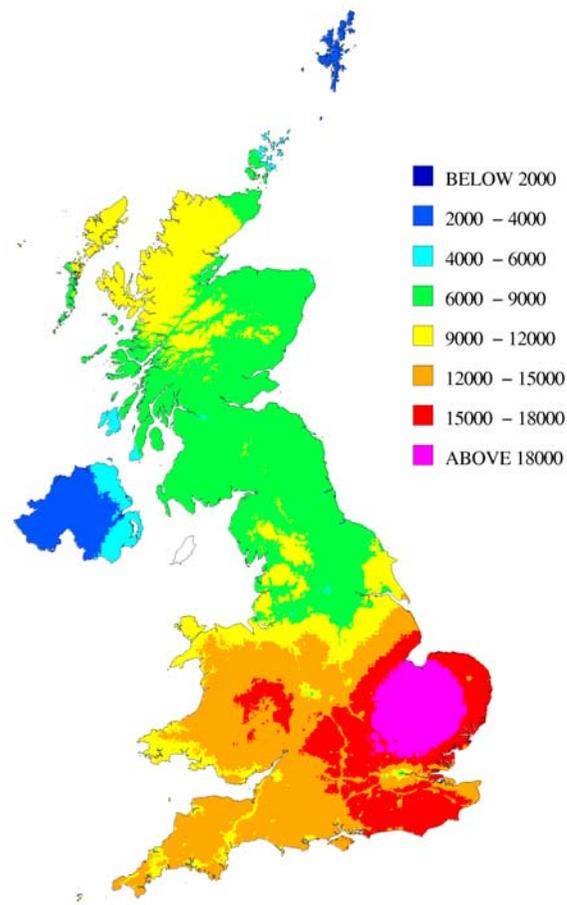
6.2.2   Verification of OSRM and PCM Outputs for Ozone Metrics in 2006

An evaluation of OSRM and PCM model performance has been undertaken, comparing model results for 2006 with measured concentrations from monitoring campaigns around the UK and against each other.

The model verification is represented in scatter plots comparing the model outputs with the corresponding measured metrics at ozone monitoring sites around the UK (Figures 6.7-6.10) for OSRM and the PCM empirical model for the same health- and vegetation-based Long-Term Objective metrics as compared in the maps. Two groups of sites are presented in the verification charts and summary tables:

- national network (AURN) monitoring sites
- verification sites

The AURN sites were used as a direct input to the PCM empirical model and therefore provide a useful check during the verification process, but are not able to provide a completely independent representation of model performance. For this reason there are a separate group of sites labelled 'verification sites' that are completely independent from the model. These typically come from local authorities, research institutions and *ad-hoc* monitoring campaigns for which AEA holds and ratifies the data. These monitoring data are ratified to the same standard as the AURN. Both groups of sites provide an independent verification of the OSRM because this is a process model which does not use monitoring data as an input or a calibration method. A data capture threshold of 75% has been applied to the monitoring data prior to analysis.

The verification charts also present a 1:1 line and lines representing the data quality objectives (DQO) defined in the third Daughter Directive (+/- 50%).

Corresponding summary tables (Tables 6.7 to 6.10) are also provided which display the average of measured concentrations, the average of the modelled estimates, the R^2 of the fit line, the number of monitoring sites used and the percentage of these monitoring sites that fall outside the DQO.

The OSRM days greater than 120 µg m^{-3} verification presented in Figure 6.7 and Table 6.7, show that there is a high degree of scatter across all sites in 2006. **In general the OSRM under predicted the measured metric**. Table 6.7 suggests that the model performance was similar for the national network sites and the verification sites. The percentage of sites outside the DQO range in both national network and verification sites was high (57-58%).

By contrast, the PCM empirical map better represented the measured number of days exceeding 120 µg m^{-3} in 2006 – largely as a result of the measured data feeding into the model. Figure 6.8 and Table 6.8 confirm this – average modelled and measured results are very similar for both the national network sites and more encouragingly, for the independent verification sites that provide a more meaningful indicator of model performance. There was a smaller percentage of sites outside the DQO range (18-28%) than the OSRM model output. These were the result of small over predictions by the model at the lower end of the concentration range and the sites involved were generally urban sites for which the model does not perform optimally.

The AOT40 metric displayed similar features to the days greater than 120 µg m^{-3} metric, with OSRM (Figure 6.9 and Table 6.9) **generally under predicting concentrations**, and the PCM empirical map (Figure 6.10 and Table 6.10) performing better, but over predicting lower concentrations at some urban sites.

Figure 6.7. OSRM verification (Days greater than 120 μg m⁻³)

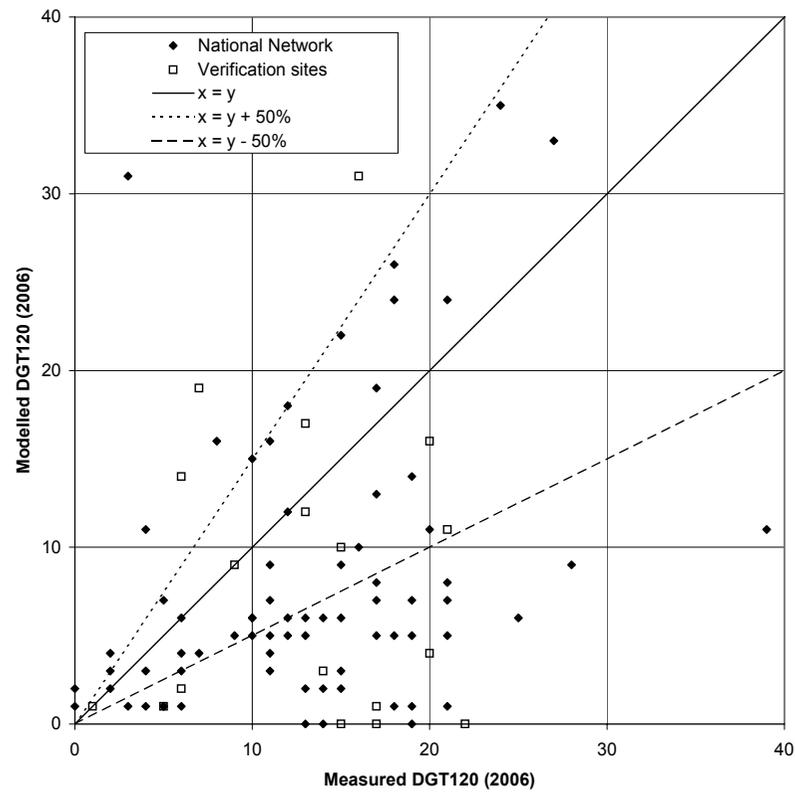**Figure 6.8. PCM empirical model verification (Days greater than 120 μg m⁻³)**
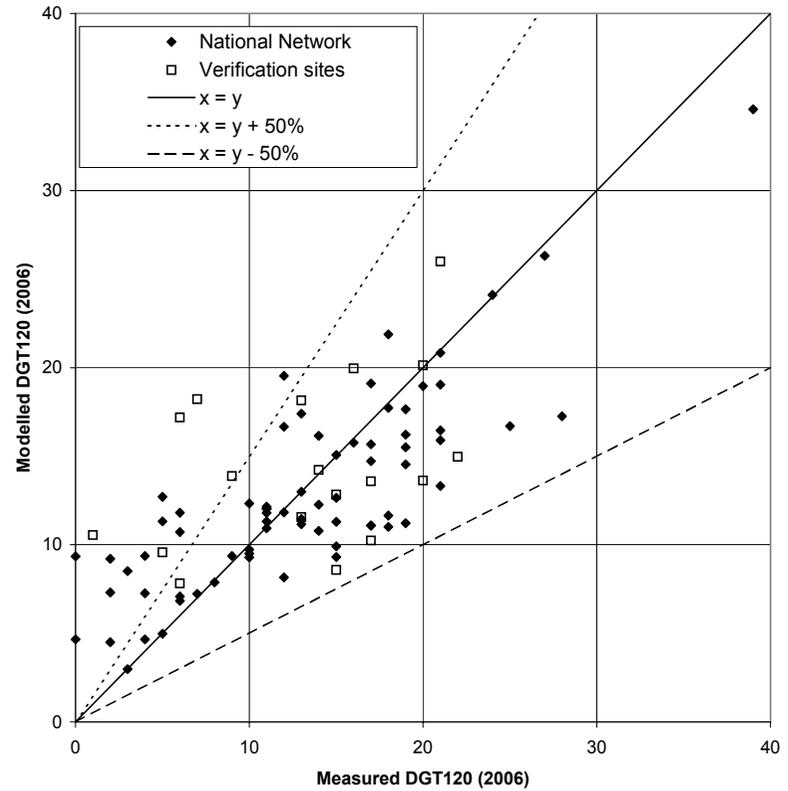
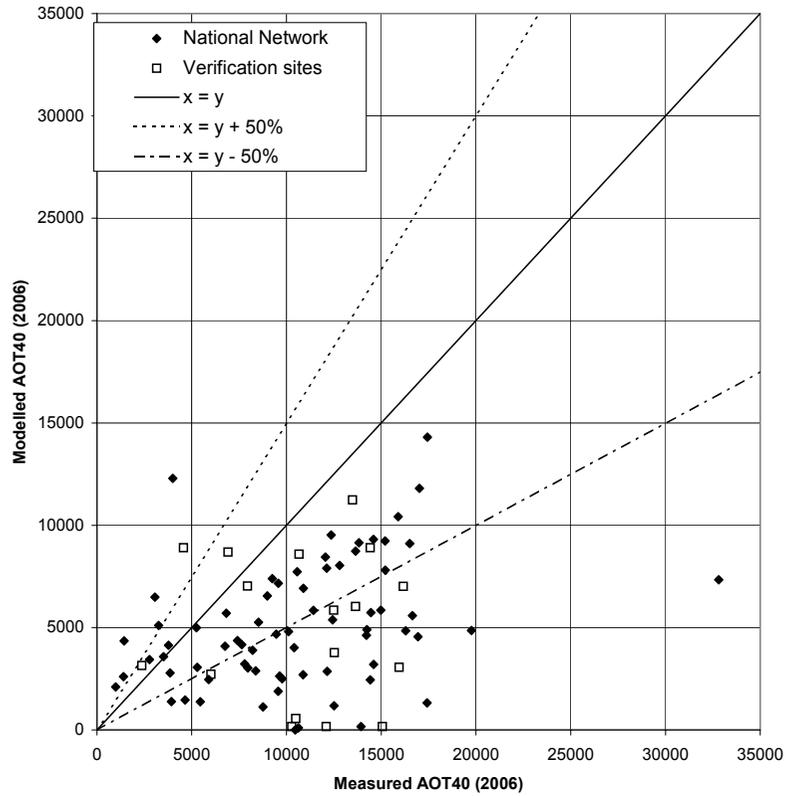**Figure 6.9. OSRM verification (AOT40, µg m^{-3}.hours)**

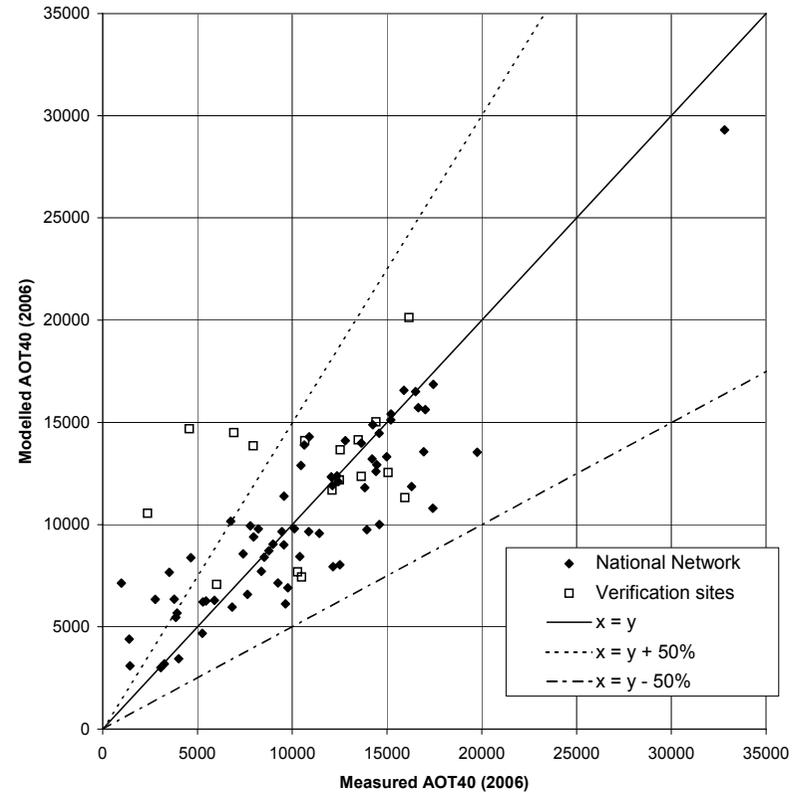**Figure 6.10. PCM empirical model verification (AOT40, µg m^{-3}.hours)**

Table 6.7: OSRM verification summary, days greater than 120 µg m⁻³ (2006)

DGT 120 metric	Year	Mean of measurements (days)	Mean of model estimates (days)	R^2	% outside DQO	No. sites used in assessment
National network	2006	13.1	8.1	0.11	57%	72
Verification sites	2006	13.2	8.4	0.002	58%	19

Table 6.8: PCM empirical model verification summary, days greater than 120 µg m⁻³ (2006)

DGT 120 metric	Year	Mean of measurements (days)	Mean of model estimates (days)	R^2	% outside DQO	No. sites used in assessment
National network	2006	13.1	12.8	0.68	18%	72
Verification sites	2006	13.2	14.5	0.17	28%	18

Table 6.9: OSRM verification summary – AOT40 metric (2006)

AOT40 metric	Year	Mean of measurements (µg m⁻³.hours)	Mean of model estimates (days)	R^2	% outside DQO	No. sites used in assessment
National network	2006	10497	5043	0.13	58%	71
Verification sites	2006	10887	5061	0.001	61%	18

Table 6.10: PCM empirical model verification summary – AOT40 metric (2006)

AOT40 metric	Year	Mean of measurements (days)	Mean of model estimates (days)	R^2	% outside DQO	No. sites used in assessment
National network	2006	10497	10252	0.80	11%	70
Verification sites	2006	10887	12528	0.11	24%	17

In addition to the verification plots, the model outputs from the OSRM and the PCM empirical model at each monitoring station have been plotted against one another for both metrics as shown in Figures 6.11 and 6.12. Both charts illustrate that OSRM estimates lower concentrations than the PCM empirical model. Figure 6.11 (the days greater than 120 µg m⁻³ metric) shows that OSRM estimates lower concentrations than the PCM empirical model in both the national network and verification sites. However, Figure 6.12 (the AOT40 metric) suggests a clearer difference between national network sites (that are almost all lower in the OSRM than the PCM empirical model) and the verification sites, which are more evenly represented by OSRM compared with the PCM empirical model.

Past analysis (Hayman, 2006c) has shown that the OSRM has slightly under predicted measured concentrations in some cases and slightly over predicted measured concentrations in other cases during "low ozone" years like 2004 and 2005. In general, it underpredicts ozone metrics and the significant underprediction found in 2006 was also observed in 2003, another "high ozone" year with photochemical summer episodes (Bush and Targe, 2005).

Tables 6.11 and 6.12 below present the average measured and averaged modelled results from OSRM for the years 2004, 2005 and 2006. These illustrate the model performance during high (2006) and low (2004, 2005) ozone years in both metrics. The difference between the concentrations predicted by the OSRM and the measured concentrations is larger for 2006 than for 2004 and 2005.

Figure 6.11. Comparison of OSRM against PCM empirical model (Days greater than 120 μg m⁻³)
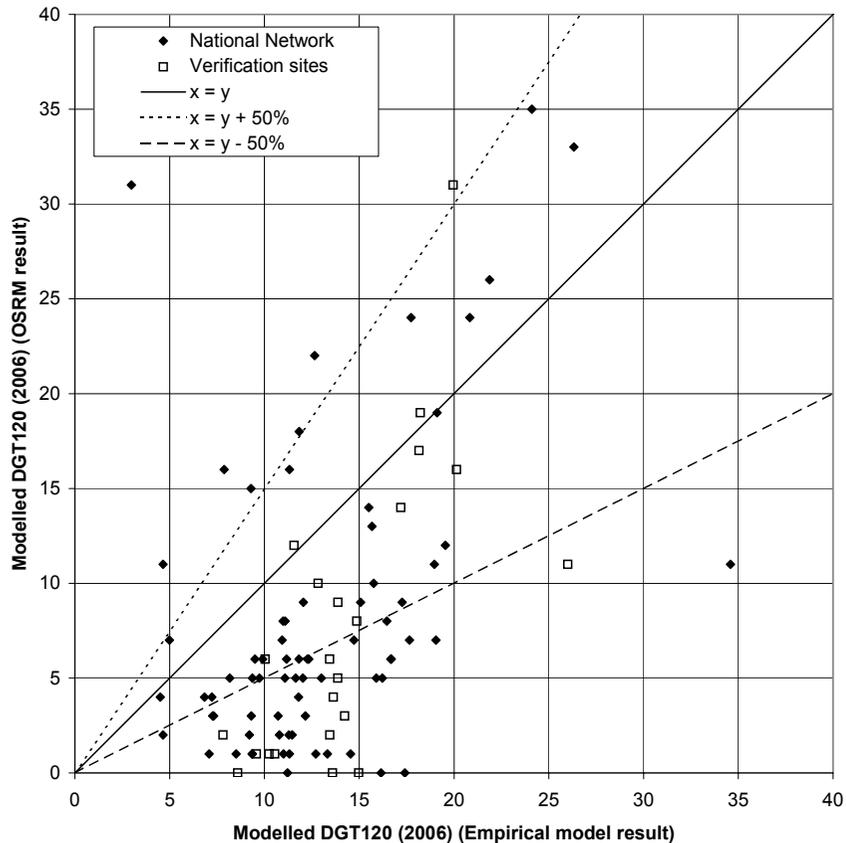
Figure 6.12. Comparison of OSRM against PCM empirical model (AOT40, μg m⁻³.hours)
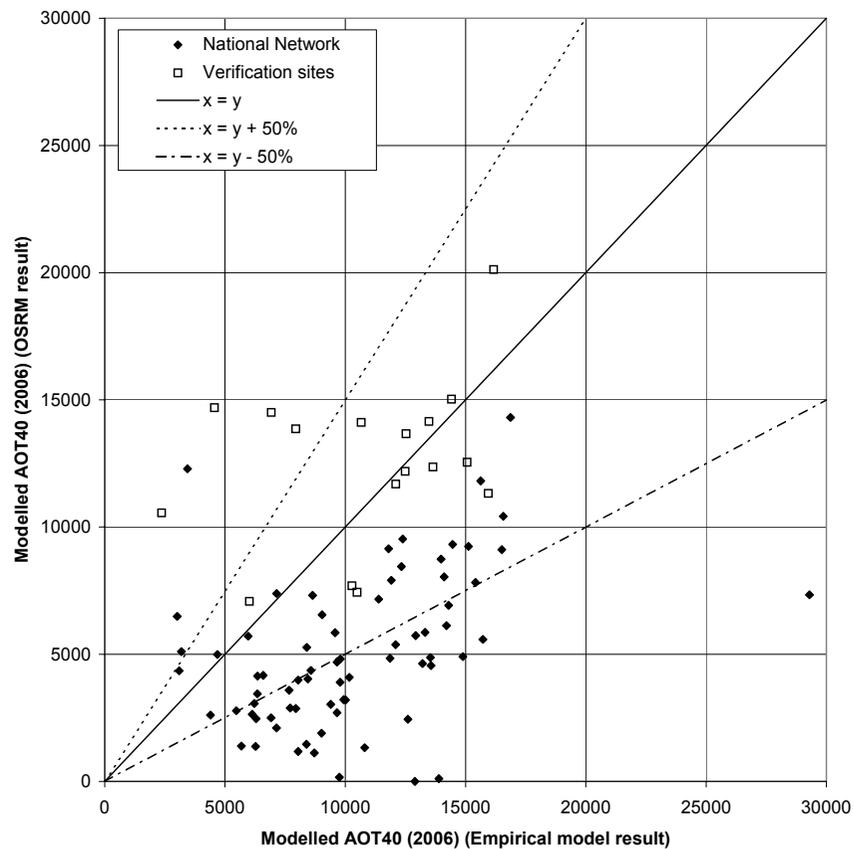
Table 6.11. Days greater than 120 µg m⁻³ OSRM results from 2004-2006

Year modelled	NAEI Year	National network		Verification sites	
		Mean of measured	Mean of modelled	Mean of measured	Mean of modelled
2004	2004	13	12	7	6
2005	2004	3	6	4	5
2005	2005	3	6	4	5
2006	2005	13	8	8	8

Table 6.12. AOT40 (µg m⁻³.hours) OSRM results from 2004-2006

Year modelled	NAEI Year	National network		Verification sites	
		Mean of measured	Mean of modelled	Mean of measured	Mean of modelled
2004	2004	2888	2056	3681	2256
2005	2004	3650	4165	3810	3088
2005	2005	3650	4099	3810	3372
2006	2005	10497	5043	5061	6574

For this report the ozone concentrations for 2005 were remodelled using the 2005 NAEI in order to find out whether the difference between the performance of the OSRM in 2006 and in previous years was due to particularly high or low ozone conditions or due to using NAEI inventories from different years. The model performance in predicting concentrations in 2005 was slightly improved (modelled closer to measured values) by using the 2005 NAEI emissions rather than using the projected emissions from the 2004 NAEI, but the differences made by using the later inventory were not significant. The results in Tables 6.11 and 6.12 indicate that the difference between model performance in 2006 compared to 2005 is due to the high/low ozone years rather than the use of different NAEI inventory versions. The OSRM results do at least show that, although generally underpredicting ozone concentrations compared with measurements and PCM model data, 2006 was a more ozone active year than 2005.

6.2.3   Conclusions for OSRM Performance in Modelling 2006 Ozone

- As has been shown previously, the OSRM in 2006 has generally underestimated ozone metrics compared with measured data.

- The difference between the concentrations predicted by OSRM and the measured concentrations were larger for the high ozone year (2006) than in previous (low ozone) years (2004 and 2005). This had been observed for a previous high ozone year (2003)

- The PCM empirical model continues to produce results that are closer to the measured concentrations than the OSRM and should continue to be used in its current capacity (contributing modelled data in fulfilment of UK reporting obligations to the European Commission).

7 Detailed Assessment of Relationship Between Ozone, Nitrogen Oxide and Nitrogen Dioxide Levels, and Factors Controlling Them (Objective 2)

It is well-established that the behaviour of ozone (O_3), NO and NO_2 in the atmosphere is coupled by the following reactions,

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

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

and it is because of this strong chemical coupling that the term "oxidant" is sometimes used as a collective term for NO_2 and O_3. This reaction cycle partitions NO_X between its component forms of NO and NO_2, and oxidant between its component forms of O_3 and NO_2, but conserves both NO_X and oxidant. As a result, oxidant derived from background O_3 is partitioned between the forms of NO_2 and O_3, with a progressively greater proportion in the form of NO_2 as NO_X increases as a result of received emissions. In urban areas, oxidant can also be derived significantly from directly emitted NO_2, and this is also partitioned between the forms of NO_2 and O_3, with a progressively greater proportion in the form of O_3 as NO_X decreases with dilution.

Owing to this local-scale 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, 2004; 2007), 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.

Annual mean monitoring data from 56 urban UK sites reporting co-located measurements of O_3 and NOx have previously been analysed to provide a method of describing NO_2/NOx partitioning as a function of NOx (Jenkin, 2004). It was demonstrated that consideration of O_3, NO and NO_2 as a set of chemically coupled species (rather than NO and NO_2 alone) provides additional information to assist the prediction and interpretation of how the level of NO_2 (and O_3) varies with that of NOx. The method involves defining (i) linear expressions describing how the level of oxidant varies with the level of NOx, and (ii) algebraic expressions describing how the fractional contribution of NO_2 to oxidant (i.e., [NO_2]/[oxidant]) varies with NOx. The product of these two quantities yields the dependence of NO_2 levels as a function of NOx. The advantage of this semi-empirical approach (usually termed the "*oxidant partitioning model*") is that it allows the derived NO_2 vs NOx relationships to be rationalised in terms of sources of oxidant and well-understood chemical processes. In this way it also enables predictions that take account of possible changes in the magnitudes of oxidant sources, such as the background O_3 level or the fractional contribution of NO_2 to NOx emissions (i.e. "primary NO_2").

In the present programme, a number of analyses of monitoring data have been undertaken to provide more information on local, regional and global contributions to oxidant at UK locations, and to improve the description of the partitioning of oxidant into its component species (i.e., O_3 and NO_2).

The main purpose of this work is to improve and update the representation of the oxidant partitioning method in the Pollution Climate Mapping model (PCM) and the surface conversion algorithm of the OSRM, in relation to assessments of annual mean NO_2 and O_3 levels. The current method is incorporated in the Netcen Primary NO_2 Model, which was developed from the OSRM surface conversion algorithm, and is used in the PCM to simulate the interaction between the primary NO_2 ratio and NO_x, NO_2 and O_3 concentrations at roadside locations.

7.1 Analysis of Temporal and Spatial Trends in Background Oxidant Sources

7.1.1 Long-Term Temporal Trends in Background Oxidant Sources

Previous analyses have shown that the level of oxidant at a given location is made up of a combination of a background (NOx-independent) source and a local (NOx-dependent) source (e.g., Clapp and Jenkin, 2001; Jenkin 2004). The former effectively equates to the background ozone concentration, and the latter is derived from primary NO_2 emissions. The background contribution thus provides an estimate of the ozone concentration which would exist at the given location in the notional absence of NOx, i.e. when the local-scale chemical coupling described above has not occurred.

Data from the rural site at Lullington Heath for the period 1991-2006, have been analysed to estimate the relative contributions to background oxidant which derives from "regional" and "global" sources. Figures 7.1 and 7.2 show the seasonal variation and long-term trend in the background oxidant concentration, with this background being further separated into estimated global (hemispheric) and regional contributions. These quantities have been determined by, first, removing the (comparatively small) local contribution from the measured oxidant, based on the observed concentration of NOx and an inferred average fractional contribution of NO_2 to NOx emissions of 9.3 % (Jenkin, 2004). This allowed the background oxidant concentration to be determined. The background was then separated into the hemispheric baseline and a regional modification to this baseline, on the basis of air mass histories described by four-day back trajectories for each day of the 16 year time period (those arriving from the west being used to define the baseline, with the regional modification being obtained by difference). These quantities thus provide an estimate of the baseline ozone concentration, upon which the regional modification is superimposed.

Figure 7.1 shows the seasonal variation as monthly mean values averaged over the whole period 1991-2006 (upper panel), and for the average of the heat-wave years, 1995, 2003 and 2006 (lower panel). The regional modification results from a combination of regional scale photochemical ozone formation, and increased removal of ozone through deposition when air masses have travelled over the continent prior to arrival. The regional modification is thus notably positive in the summer months, when photochemical formation is the dominant influence, but negative in the wintertime when net removal through deposition occurs. The summertime regional enhancement is, on average, greatest in July and August when most photochemical episodes occur, with average monthly-mean contributions over the whole period of ca. 10 μg m^{-3}. The seasonal variation of the inferred hemispheric baseline shows the springtime maximum typically observed for O_3 at remote sites, as discussed elsewhere (e.g., Monks, 2000; Derwent et al., 2007).

Figure 7.2 shows the time series of the oxidant components on an annual mean basis over the sixteen year period. The regional modification shows year-on-year variability owing to variation in the meteorological conditions experienced, but with net regional-scale ozone formation occurring in most years. A general decreasing trend in the regional oxidant contribution is apparent, consistent with the impact of EU controls on VOC and NOx emissions. The heat-wave year of 1995 shows the largest regional contribution in the early part of the time series, with 2003 and 2006 having the largest contributions in the later years. The inferred annual mean hemispheric baseline ozone concentration has a barely significant upward trend of 0.08 μg m^{-3} annum^{-1}. However, consideration of data over the period 1991-1999 yields a more notable upward trend of 0.4 μg m^{-3} annum^{-1} with no clear trend subsequently. The variation in the inferred hemispheric baseline thus shows some of the features reported for baseline air at the Mace Head site on the west coast of Ireland, as discussed in detail by Derwent et al. (2007).

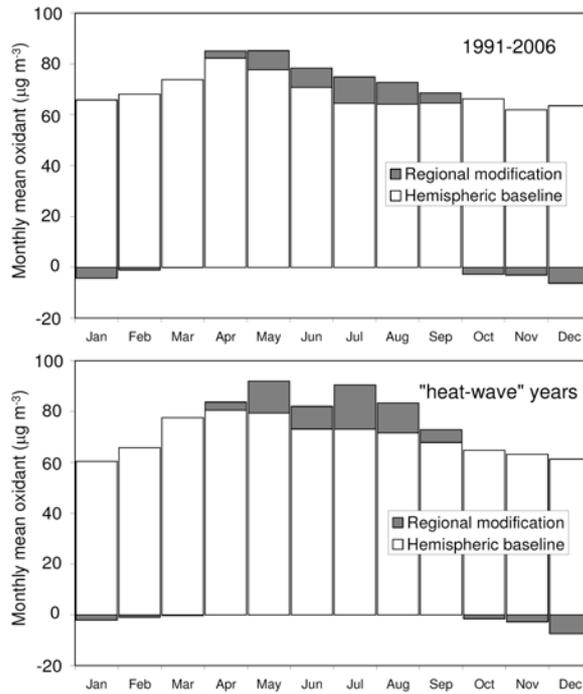**Figure 7.1: Seasonal variation of monthly mean background oxidant contributions at Lullington Heath, based on data averaged over the period 1991-2006 (upper panel) and for the average of the heat-wave years, 1995, 2003 and 2006 (lower panel).**
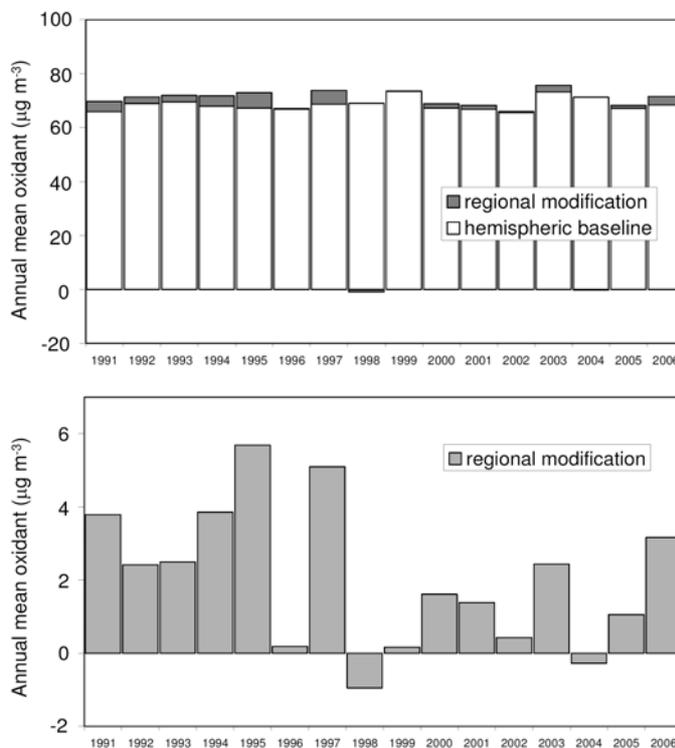

Figure 7.2: Time series of the annual mean background oxidant contributions at Lullington Heath. The regional contribution is shown on an expanded scale in the lower panel.

7.1.2　　Spatial Trend in the Regional Oxidant Source

The regional oxidant source derives from substantial short-term elevations during summertime episodes, which are a consequence of the formation of additional oxidant from regional-scale photochemical processing of emitted VOC and NOx over north-west Europe. Such events are characterised by stable anticyclonic conditions, when slow moving air resides in the boundary layer for a period of up to several days. Under such conditions, the air-mass circulates slowly over north-west Europe, receiving VOC and NOx emissions, when both temperature and solar intensity are elevated, thereby promoting efficient photochemical processing. This general picture of the conditions associated with photochemical episodes in the UK has been supported, for example, by an analysis of air-mass back trajectories associated with events when hourly-mean ozone concentrations have reached or exceeded the public information threshold, 180 μg m^{-3} (Jenkin et al., 2002).

General information on the temporal and spatial trends in the regional-scale oxidant source is also apparent from consideration of such events. Figure 7.3 (upper panel) shows data from 13 long-running rural sites, which have data since 1990 and which provide reasonable geographical coverage over the UK. The number of hours with mean ozone concentrations ≥ 180 μg m^{-3} at these sites combined (and individually) shows year-on year variability due to the requirement for appropriate meteorological conditions, but with a general decreasing trend over the period similar to that described for Lullington Heath above. This is apparent from considering only the "heat-wave" years of 1990, 1995, 2003 and 2006, in which meteorological conditions particularly conducive to regional-scale photochemical ozone formation were experienced. The information also demonstrates that, although no two years are identical, the number of hours exceedence tends to decrease towards the north and west of the UK. Locations towards the south and east are more prone to elevated photochemical ozone because trajectories during anticyclones tend to arrive from continental Europe with greater probability of passing over regions of high ozone precursor emissions.

This spatial variation is illustrated further in Figure 7.3 (lower panel), which shows the mean number of hours ≥ 180 μg m^{-3} annually, based on the average of the data over the period 1990-2006 for the complete set of rural sites. The data are presented in relation to a north-westerly co-ordinate, starting from Lullington Heath in the south-east. The data show a general decreasing trend with distance north-west, but also display a degree of scatter. As indicated in the figure, this scatter can be broadly related to the altitude of the site, with higher altitude sites at a given distance north-west showing a tendency towards a greater number of hours exceedence. As discussed previously by PORG (1997), the lower altitude sites are more likely to become decoupled from the air aloft when a shallow night-time inversion layer forms, and are therefore more influenced by ozone removal via deposition. Consequently, elevated ozone concentrations during photochemical events tend to persist for a smaller proportion of the diurnal cycle at such locations.

Further information on the temporal and spatial trends in elevated ozone concentrations is apparent from consideration of the annual maximum hourly-mean ozone concentrations recorded at the same set of 13 long-running sites over the period 1990-2006. Figure 7.4a shows that the maximum concentrations show an approximately linear decline with distance north-west, as illustrated for 1990 and for the average of all years in the time series. A significant average decreasing trend in the annual maximum ozone concentration is apparent over the period at all sites except Strath Vaich (Figure 7.4b), indicative of a decreasing intensity of regional-scale ozone pollution episodes. The observed decrease in the frequency and severity of photochemical ozone events in the UK, illustrated in Figures 7.4 and 7.6, is consistent with that expected from reductions in the emissions of anthropogenic VOC and NOx in the EU since the early 1990s (Derwent et al., 2003). Figure 7.4b also shows that the absolute magnitude of the decreasing trend diminishes with distance north-west, as the sites become less impacted by the regional-scale processes, as discussed above. These linear relationships therefore suggest a simple south-east to north-west gradient in the regional oxidant source.
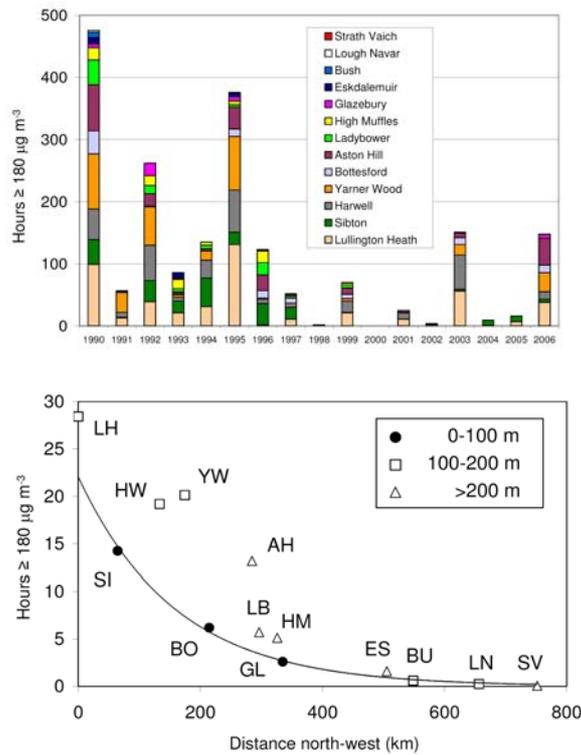
Figure 7.3: (Upper panel) Number of hours with [ozone] ≥ 180 μg m^{-3} at 13 UK rural sites in each year over the period 1990-2006. (Lower panel) Annual number of hours with [ozone] ≥ 180 μg m^{-3} at UK rural sites (based on data averaged over the period 1990-2006) as a function of distance along a north-westerly co-ordinate. Sites are also classified in terms of altitude intervals, with the displayed line being an exponential fit to the three low altitude sites.
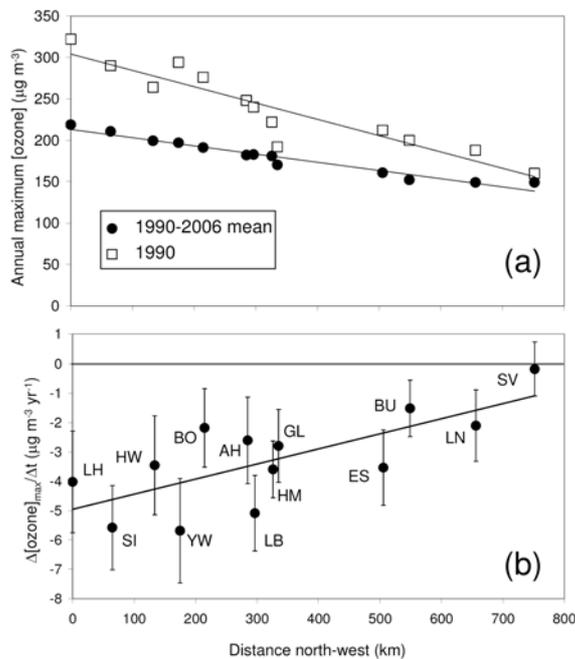
Figure 7.4: (a) Annual maximum hourly mean [ozone] at UK rural sites, as a function of distance along a north-westerly co-ordinate. Data are shown for 1990 and averaged over the period 1990-2006. Lines are regressions of the data. (b) Corresponding average rate of change in annual maximum [ozone] over the period 1990-2006. Displayed error bars are 1σ, and the line is a regression of the data.
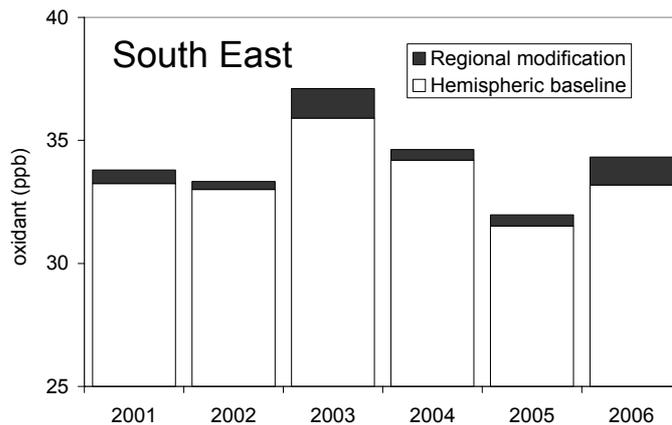
Figure 7.5: Recent time series of the annual mean background oxidant contributions in south-east England, based on data from the rural sites at Harwell, Lullington Heath and Rochester.

7.1.3 Recent Background Oxidant Time Series in South-East England

The analysis method described in Section 7.1.1 is being applied to sites throughout the UK to obtain a more direct evaluation of the geographical dependence of the contributions of hemispheric and regional oxidant sources for available years. Average data for south-east England over the period 2001-2006 (based on data from the rural sites at Harwell, Lullington Heath and Rochester) are shown in Figure 7.5 (to facilitate use of the data in the analysis described further below, these data are presented in ppb units). Similarly to the discussion for Lullington Heath above, this shows that the hemispheric baseline contribution has demonstrated no clear trend in recent years, but that it was elevated in 2003. The variation in the time series is consistent with observations of baseline ozone over the same period at Mace Head, as reported by Derwent et al. (2007), but the levels are consistently about 5 ppb lower than at Mace Head. This lowering is probably due to loss by deposition during passage of the baseline air over the UK, and its influence can probably therefore be related to the distance across land from the Atlantic ocean that baseline air has travelled under prevailing westerly conditions (the will be investigated further in the ongoing analysis). Similarly to the analyses presented in the previous sections, the regional modification is greatest during the heat-wave years of 2003 and 2006.

The data in Figure 7.5 lead to an average annual mean background oxidant level of 34.2 ppb for south-east England over the period 2001-2006, which is made up of a hemispheric baseline contribution of 33.5 ppb and a regional modification of 0.7 ppb. As discussed above, it is reasonable to infer that the regional modification diminishes with distance north-west, and that the hemispheric baseline contribution varies in relation to the distance across land from the Atlantic ocean that baseline air has travelled under prevailing westerly conditions.

7.2 Analysis of Temporal Trends in the Local Oxidant Source

Annual mean data from 13 London sites have been used to investigate the trends in the local oxidant source (i.e. primary NO_2) over the period 2001-2006, as summarised in Figure 7.6. The local oxidant contributions have been determined from the observed total oxidant (i.e., O_3 and NO_2) by subtraction of the average background oxidant levels for south-east England shown in Figure 7.5. Figure 7.6 (upper panel) shows the temporal trend in the local oxidant contribution, normalised in relation to the level of NOx, for each of the sites. This quantity is therefore an estimate of the fraction of NOx emitted in the form of NO_2. The data show a clear increasing trend at all the sites, consistent with previous analyses (e.g., AQEG, 2007). At the Marylebone Road kerbside site, this primary NO_2 fraction has increased steadily from about 10 % at the start of the time series to just over 20 % in 2005 and 2006. At the other sites, the majority of the increase appears to have occurred over the period 2004-2006. The lower panel of Figure 7.6 shows the oxidant data from these sites plotted as a function of NOx.

Regression analysis of the data suggest that the average emitted NO_2/NOx fractions increased slowly from ca. 10 % in 2001 to ca. 13 % in 2004, and then more rapidly to ca. 17% and 19 % in 2005 and 2006, respectively.
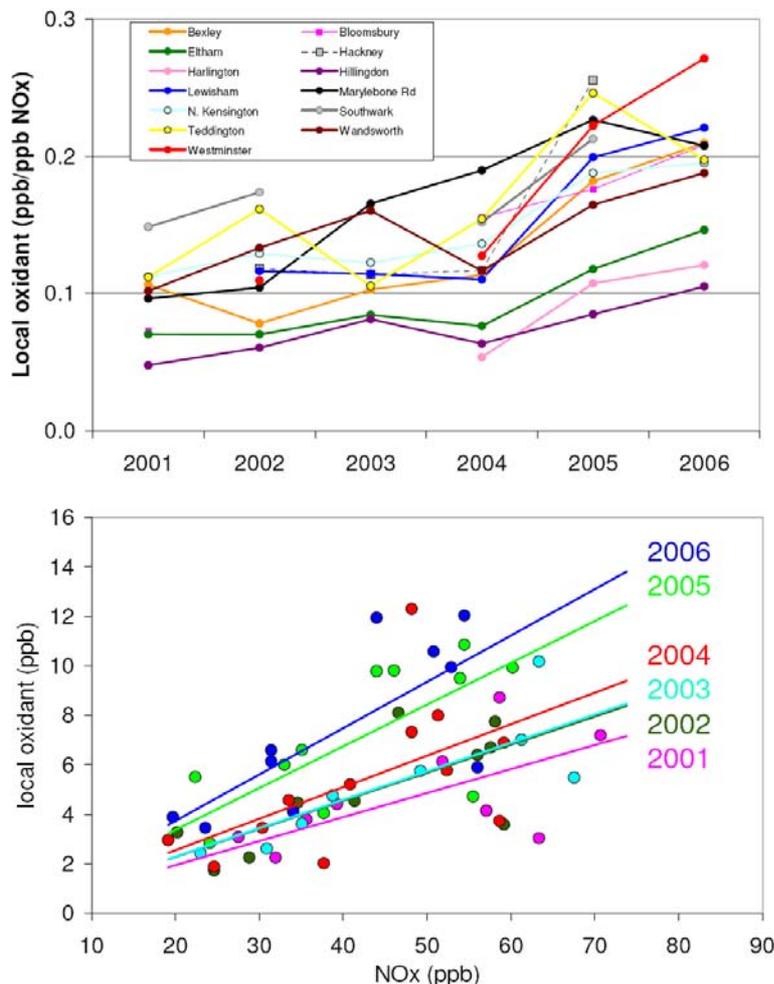
Figure 7.6: (Upper panel) Recent times series of annual mean local oxidant contribution (as a fraction of NOx) at London sites. (Lower panel) Recent local oxidant levels plotted as a function of NOx for all sites in the upper panel except Marylebone Rd. The lines are linear regressions of the data for each year, which provide the following estimates of the average NO_2/NOx emissions fraction: 0.097 (2001), 0.114 (2002), 0.115 (2003), 0.127 (2004), 0.169 (2005) and 0.187 (2006).

7.3 Development of Improved Oxidant Partitioning Expressions

Previous analyses have made use of two polynomial expressions to describe the partitioning of oxidant into its component forms of O_3 and NO_2 on an annual mean basis (e.g., Clapp and Jenkin, 2001; Jenkin, 2004). These were based on fits to subsets of sites which were designated "road influenced" and "without immediate road influence". The expressions were then used for larger sets of sites, with the choice of category based on the closest match to the observed data for each of the additional sites. The observed data, and therefore the fitted expressions, invariably display values of $[NO_2]/[oxidant]$ at a given level of NOx which fall below predictions which are based on known rate parameters for reactions (1) and (2), and the assumption of instantaneous photochemical steady state (see Figure 7.7). As discussed previously (Jenkin, 2004) this is believed to be at least partially because an annual mean data-point is, by definition, an average of data collected over a range of NOx levels, such that this average must lie below the idealised curve which describes the data as a

function of NOx. The extent to which the average is displaced from the curve will also depend on the variability of NOx experienced, which is a site-dependent characteristic. Logically, sites closer to source would be expected to show greater variability such that their data-points would be more displaced from the idealised curve. This reasoning therefore qualitatively explains why the previous "road influenced" polynomial was further displaced from ideality than the "without immediate road influence" polynomial (see Figure 7.7).

A detailed analysis has been carried out of annual mean [NO_2]/[oxidant] ratios at 75 urban and 13 rural UK sites where the necessary co-located measurements are made, considering data up to 2006. The complete set of observed data are also shown in Figure 7.7. The variability of NOx levels at each of the sites has been investigated, and the ratio of the upper to lower quartiles of the annual mean distribution of hourly mean NOx levels has been selected as a practical indicator of this variability (see Figure 7.8).
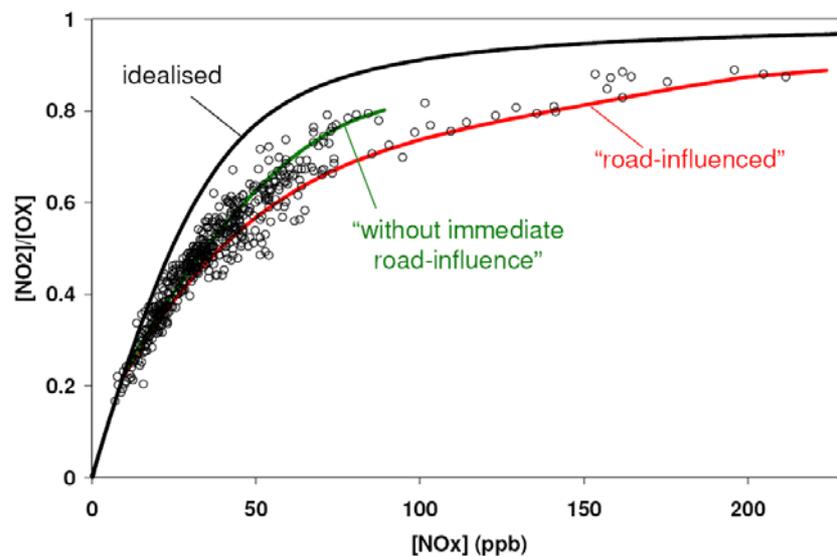
Figure 7.7: Points are annual mean [NO_2]/[OX] data as a function of [NOx] for 75 UK urban sites, considering data up to 2006. Lines represent the idealised dependence, based on the NOx-O_3 photostationary state under average conditions, and two polynomial expressions applied previously in the oxidant partitioning model (see Jenkin, 2004).

Figure 7.8 shows the annual quartile ratio observed at the 75 urban sites, based on the average of the data for available years at each site. The quartile ratio varies over the approximate range 2.3-4.5 at these sites, with a mean value of 3.1 ± 0.5 (1σ). The ratios show some year to year variability at a given site, but are generally reasonably consistent. For categorisation and examination of [NO_2]/[OX] data, the sites were subdivided into three categories, as shown in Figure 7.8 (lower panel). Category I (consisting of sites with a quartile ratio < 2.5), is dominated by central London locations, the urban centre and background sites at Bloomsbury, Bridge Place and Southwark all falling into this group. This can be rationalised by the existence of a larger background NOx level at the centre of a large urban conurbation, such that the variability associated with processes which are comparatively local to the site is effectively "diluted" by this background. Category III (consisting of sites with a quartile ratio $\geq$ 3.5) has a selection of urban centre and roadside sites. The intermediate category (category II: $2.5 \leq$ quartile ratio < 3.5) contains the majority of sites, and consists of a selection of urban background, urban centre and roadside sites, including Marylebone Road (quartile ratio = 3.0). In general terms, sites closer to NOx sources tend to display greater ratios than local background locations, although each category contains a variety of nominal site types.
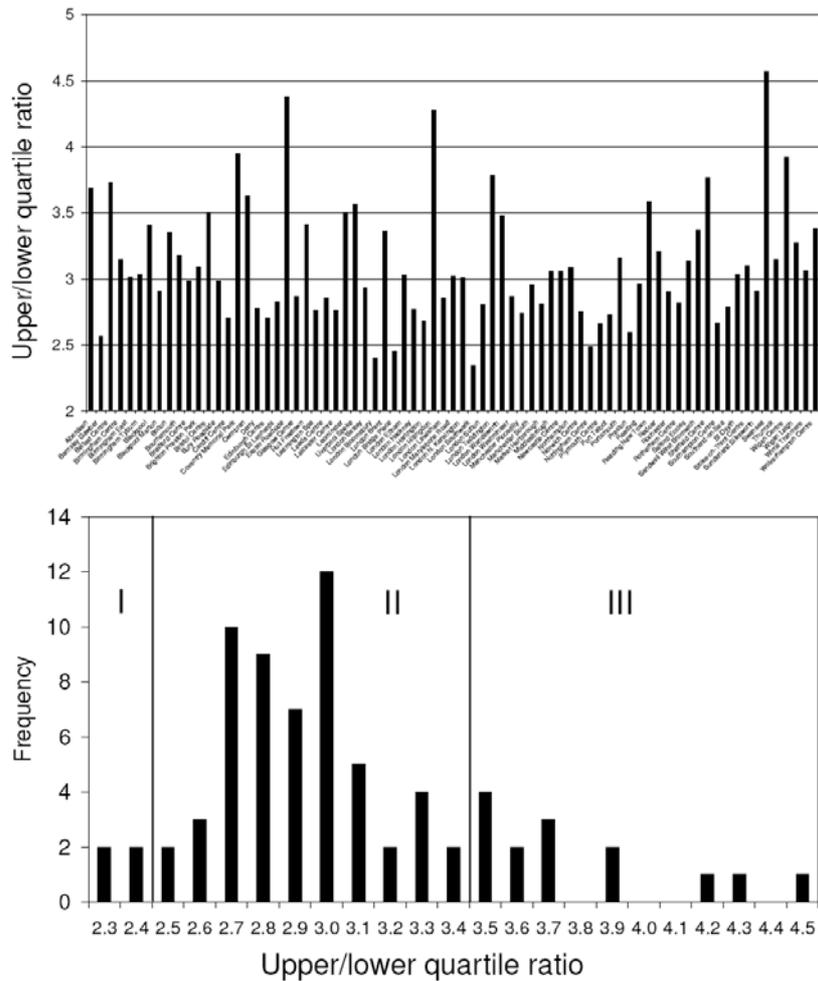
Figure 7.8: (Upper panel) Ratio of the upper to lower quartiles of the annual mean distribution of hourly mean NOx levels at the 75 urban sites considered in the oxidant analysis, based on the average of the data for available years. (Lower panel) Associated frequency distribution of upper/lower quartile ratios, and their subdivision into three intervals representing site categories for illustration.

Figure 7.9 shows the annual mean [NO$_2$]/[oxidant] ratios observed at the 75 urban sites, subdivided in terms of the NOx quartile ratio categories I-III. This confirms that an increase in the NOx quartile ratio is accompanied by a general lowering of the data away from the idealised [NO$_2$]/[oxidant] vs [NOx] curve, suggesting that quartile ratio represents an observable quantity which can be used to define site characteristics. Figure 7.9 also shows that averaging the idealised curve over concentration ranges for NOx (assuming a logarithmic concentration distribution) generates [NO$_2$]/[oxidant] vs [NOx] curves which can provide a reasonable general description of the observed data in each category. The relationship between the NOx quartile ratio and the required averaging factor is being examined further in ongoing work, which aims to determine site-specific averaging factors for all 75 sites. In the meantime, a series of polynomial expressions describing the NOx-averaged curves have been recommended for use in PCM studies, as summarised in Table 7.1.
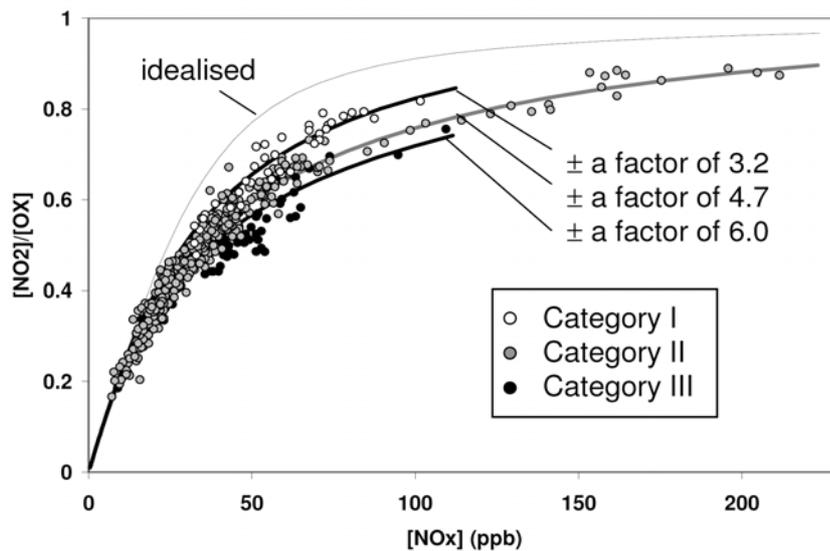
Figure 7.9: Points are annual mean [NO$_2$]/[oxidant] data as a function of [NOx] for 75 UK urban sites, separated into three groups on the basis of the annual quartile ratio of the hourly mean NOx distribution. Lines represent the idealised dependence (as in Figure 7), and the dependence obtained by averaging the idealised curve over NOx concentration ranges of ± the factors shown. These factors were optimised to obtain a reasonable representation of the data in the three groups.

Table 7.1: Polynomial expressions describing the NOx-averaged curves for [NO$_2$]/[oxidant] vs [NOx] as a function of [NOx] in relation to annual quartile ratio of the hourly mean NOx distribution.

Category	Average quartile ratio	NOx range averaging factor	Coefficients for 6th order polynomial describing [NO$_2$]/[oxidant] [a]					
			$[NOx]^6$	$[NOx]^5$	$[NOx]^4$	$[NOx]^3$	$[NOx]^2$	$[NOx]$
I	2.4	3.2	4.856E-14	- 3.290E-13	- 9.371E-09	2.824E-06	- 3.684E-04	2.582E-02
II	3.0	4.7	-1.673E-13	1.195E-10	- 3.469E-08	5.305E-06	- 4.692E-04	2.595E-02
III	3.8	6.0	-2.881E-13	1.857E-10	- 4.843E-08	6.620E-06	- 5.211E-04	2.591E-02
IIIa [b]	3.5	5.5	-2.423E-13	1.607E-10	- 4.329E-08	6.132E-06	- 5.020E-04	2.593E-02
Notes								
a: [NOx] in ppb units; expressions are valid for 0-160 ppb. b: additional category supplied on request.								

7.4 Trends in f-NO₂ at UK Monitoring Sites Calculated Using the Netcen Primary NO₂ Model

Two different approaches to controlling oxides of nitrogen in air have resulted in a legislation gap where vehicle manufacturers have reduced NO_X emissions in compliance with the Euro standards and other directives without yielding a corresponding reduction in ambient NO_2 concentrations to below the EU First Daughter Directive limit values for NO_2 in many locations.

One possible reason for this gap relates to the proportion of NO_X emitted directly as NO_2 from vehicle exhausts (this is the primary NO_2 fraction, f-NO_2, often expressed as a percentage).
f-NO_2 in many locations in the UK may be rising as a result of changes in the composition of the national vehicle fleet and the introduction of new exhaust technologies that have been brought in to meet the emission limits for various pollutants. For petrol-fuelled vehicles f-NO_2 is less than 5%, whereas f-NO_2 in diesel vehicles not fitted with new exhaust treatment technology is higher at around 10-12%. The continuing increase in the proportion of diesel-engine vehicles in the national fleet will therefore have a significant impact on the ambient NO_2 concentrations, particularly in roadside environments. Furthermore, the pressure to fit diesel vehicles with after exhaust treatment technology such as particulate traps and oxidation catalysts is likely to further increase f-NO_2. Some catalyst-based particulate filters achieve the catalytic action by oxidising a portion of the NO in the exhaust to NO_2 in order to promote the oxidation of soot collected in the filter and so potentially emit a higher proportion of NO_X as NO_2.

The potential implications of increases in f-NO_2 within the UK on likely compliance with the ambient NO_2 limit values in 2010 mean there is a growing interest in identifying and understanding trends in f-NO_2. Understanding how f-NO_2 is changing and having up-to-date information on f-NO_2 levels is particularly important for incorporating f-NO_2 into models designed to predict future ambient NO_2 concentrations (e.g. the PCM model) and models for predicting ozone in urban areas (e.g. OSRM) where there are significant interactions with local NO_x sources.

In this project, trends in f-NO_2 have been calculated for a selection of roadside monitoring sites across the UK, from several different networks, using the Netcen Primary NO_2 model. Analysis of how modelled f-NO_2 varies geographically across the UK and how f-NO_2 trends have changed in the past few years is presented. Further potential routes for model improvements and development are given.

7.4.1 Methodology

To carry out the modelling, the Netcen Primary NO_2 model has been used combined with monitoring data from a selection of roadside and background monitoring sites.

7.4.1.1 The Netcen Primary NO₂ Model

The Netcen Primary NO_2 Model is a one-dimensional model of the relationships between f-NO_2 and NO_X, NO_2 and O_3 concentrations at roadside locations. Abbott (2005) gives a detailed description of the model and an example of its application using data at a selection of UK AURN monitoring sites.

Several relationships and assumptions underpin the model. These include:

- A background site can be chosen to be 'paired' with each roadside monitoring site such that the NO_x, NO_2 and O_3 measured at the background site are representative of the background concentrations at the roadside site.

- Total oxidant at roadside locations $[Ox] = [O_3] + [NO_2]$;

- $[Ox]_1 - [Ox]_0 = A ([NO_x]_1 – [NO_x]_0) + B^*$ where A is the primary NO_2 ratio, Ox is the total oxidant (the subscript 1 is for roadside, 0 is for background) and B^* represents the net effect of other reactions and deposition and excludes the background oxidant concentration.

The model has three modules depending on what input data is available and what output information is needed. Two of these modules are used in the analysis of recent trends in f-NO$_2$ presented here. These are:

Module 1: The analysis module. This calculates f-NO$_2$ for roadside monitoring sites using hourly NO$_X$, NO$_2$ and O$_3$ measurements from this site and hourly NO$_X$, NO$_2$ and O$_3$ measurements from its paired background site. The annual f-NO$_2$ component is derived directly from the monitoring data by regressing the hourly roadside increment of oxidant (dependant variable) against the hourly roadside increment of NO$_X$ (independent variable). The annual f-NO$_2$ is calculated as the gradient of the regression line.

Module 2: The ozone module. The ozone concentration at the roadside is calculated using a one-dimensional finite difference model of the chemistry and turbulent diffusion in the surface boundary layer. f-NO$_2$ is then derived from the monitoring data by regression analysis as in the analysis module. There are relatively few roadside monitoring sites across the UK where ozone is measured. The ozone module has therefore been used in the analysis of recent time series data so as to prevent being limited to analysing roadside sites with ozone monitoring.

7.4.1.2 Model Set-Up

When running the analysis and ozone modules, the model loops through each hour of the year and then calculates the annual mean f-NO$_2$ through regression analysis of hourly f-NO$_2$ for all the hours modelled. The model requires the following data channels to run: measured NO$_X$, NO$_2$ and O$_3$ at the background site and measured NO$_X$, NO$_2$ and O$_3$ (or modelled O$_3$ if the ozone module is in use) at the roadside site. If any input data is missing for any hour that hour will not be modelled. The model is currently configured to use default met data settings in the ozone module if met data is missing for a given hour. If the modelled f-NO$_2$ >100% for any given hour, this hour is not included in the regression analysis. This is because f-NO$_2$ >100% is not physically realistic because the maximum possible proportion of NO$_X$ that can be NO$_2$ is 100%. Where f-NO$_2$ >100% occurs, it suggests that the model assumptions are not holding true. This may occur as a result of reactions occurring between the background and roadside site that added extra total oxidant to the air mass. It is also possible, for any given hour that the air mass at the background site is not representative of the behaviour of the non-traffic related component of the roadside site.

The analysis module performs better where there is a significant NO$_X$ roadside increment as a higher NO$_X$ roadside increment means there is a bigger f-NO$_2$ signal for the model to detect. Therefore, a minimum roadside increment was set at 10µg m^{-3}. For hours with a roadside increment less than this, the model did not run and no result was included in the regression analysis to calculate the annual f-NO$_2$.

7.4.1.3 Model Runs

For the model runs carried out for the analysis presented here, monitoring data has been used from sites from a range of networks including the AURN, LAQN and other contract sites managed by AEA. Details of which roadside sites have been used in the model and the background sites they have been paired with are given on the graphs presented in the results section.

For all UK sites Heathrow met data has been used in the ozone module.

Model runs have been carried out for years with available data up to and including 2006.

7.4.2   Results of f-NO$_2$ Trends

Figures 7.10-7.16 present plots of modelled f-NO$_2$ for a selection of sites across different of regions in England. Figures 7.17-7.19 present similar plots for selected sites in Wales, Scotland and Northern Ireland. Each point on the graphs represents an annual average f-NO$_2$ at the roadside site being modelled. Black points have a data capture of >30% and are therefore considered reliable for this modelling. Points with data capture of between 10 and 30% are shaded grey and points with less than

10% data capture are coloured white. The name of the paired background site assumed to represent background concentrations at each roadside site is given in brackets after the roadside site name.

7.4.2.1 London
Figures 7.10 and 7.11 show a general upwards trend in f-NO$_2$ at most of the sites modelled in London. However at some, but not all sites, there is evidence of a levelling off or even slight decrease in f-NO$_2$ levels between 2005 and 2006. Compared with other sites across the UK, f-NO$_2$ at sites in London has generally shown greater upward trends in recent years and is therefore generally higher by 2006, although there are some exceptions to this.

At the AURN sites modelled (Figure 7.10), the highest f-NO$_2$ of 29.8% occurred in 1998 at Hounslow roadside. It is unclear why this peak has occurred at a site which otherwise has fairly modest f-NO$_2$ levels, or whether it has occurred due to some artefact of the model. Other AURN sites with particularly noteworthy trends include London Marylebone Road where there is clear evidence of step change in f-NO$_2$ between 2002 and 2003. f-NO$_2$ levels at this site then continued to rise until 2005 where f-NO$_2$ peaked at 27.1% before dropping slightly in 2006 to 25.1%. At London A3 roadside, the maximum modelled f-NO$_2$ was 15.4% in 2005. While this is not particularly high relative to other London sites, modelled f-NO$_2$ in both 1997 and 1998 was less than 1.0% so there has been a very significant increase in f-NO$_2$ over the past 7 years at this site. By contrast, London Cromwell Road 2 is noteworthy because it had unusually high f-NO$_2$ in the late 1990s with f-NO$_2$ as high as 15.6% in 1998. f-NO$_2$ levels at this site have increased to 23.0% by 2006, but the upwards trend in the last three years shows evidence of levelling off.

The highest modelled f-NO$_2$ from LAQN sites selected occurred at Lambeth 4, where the three years with good data capture show a slight upward trend from 28.5% in 2004 to 31.8% in 2006. Other sites with high f-NO$_2$ values include Barnet 1 – Tally Ho Corner, which showed a very steep increase in f-NO$_2$ between 2000 and 2003, after which the increase has more or less levelled off. The maximum modelled f-NO$_2$ value at this site was 28.5% in 2006. f-NO$_2$ at Croydon 4 – George Street also reached a high level in 2006 of 26.2%.

Several of the LAQN sites show evidence of a slight down turn in f-NO$_2$ in 2006 relative to 2005 (e.g. Hammersmith and Fulham 1 – Broadway, Islington 2 – Holloway Road, Hounslow 4 – Chiswick High Rd). This change in trend is not apparent at many of the AURN sites in London.

7.4.2.2 The South East
Both AURN sites in the South East, Brighton Roadside and Hove Roadside (Figure 7.12), showed an increase in f-NO$_2$ between the first year of measurements and 2006, without ever exceeding 20% f-NO$_2$. Canterbury Roadside reached the highest f-NO$_2$ of the sites modelled in the South East with a big increase from 17.8% in 2005 to 35.5% in 2006. It will be informative to see how f-NO$_2$ at this site behaves in 2007 in terms of whether f-NO$_2$ remains this high, levels off or continues to increase.

At the majority of the other sites modelled in the South East, there are insufficient years of data to pick out any strong trends. f-NO$_2$ values between 10 and 20% in the South East region seem to be typical.

7.4.2.3 The South West
There is clear evidence of an upward trend in f-NO$_2$ at all three sites (all AURN) modelled in the South West region (Figure 7.13). However, this trend has been relatively gentle at Bath Roadside and Bristol Old Market where modelled f-NO$_2$ had not reached 20.0% by 2006. The upward trend at Exeter Roadside between 2001 and 2006 has been steeper with a maximum modelled f-NO$_2$ of 24.1% in 2006.

7.4.2.4 The Midlands
Figure 7.14 shows that f-NO$_2$ has gradually increased at Oxford Centre Roadside from 6.3% in 1998 to 16.9% in 2006. This increase is not apparent at the nearby contract site, Oxford High St. The modelled f-NO$_2$ at West Chipping Norton in 2006 is relatively high at 28.7%.

7.4.2.5 East Anglia
The AURN sites in East Anglia (Figure 7.15) show little evidence of any significant increase in f-NO$_2$. However, at the contract sites, there is a more mixed picture. Two sets of model runs for these contract sites have been carried out using two background sites: Wicken Fen and Norwich Centre. The reason for using two background sites here was to check whether using Wicken Fen (where total

oxidant seems to have increased in recent years in contrast to other rural sites) as a background site would have a significant impact on modelled f-NO_2. Generally the results suggest that the model is not particularly sensitive to this. Modelled f-NO_2 at Cambridge Gonville Place using both background sites showed a clear upward trend since between 2003 and 2006. The model suggests there was a very high f-NO_2 at Cambridge Silver Street in 2002/2003, but it is unclear as to why this occurred or whether it is actually an artefact of the model. The two other roadside sites in Cambridge don't show such high f-NO_2 levels.

7.4.2.6 The North
Figure 7.16 shows modelled f-NO_2 at Bury Roadside increased very gradually between 1997 and 2004 from 4.6 - 8.2% before increasing more rapidly to 18.2% in 2007. At the other sites modelled in the North, the length of the time series is insufficient to detect any overall trends, but generally the f-NO_2 levels are relatively low with no annual f-NO_2 values above 12.5% and the majority below 10%.

7.4.2.7 Wales
Modelled f-NO_2 at sites selected in Wales (Figure 7.17) is generally relatively low in comparison with many other sites across the UK. One exception to this is at Swansea Roadside where modelled f-NO_2 in 2006 was 18.3%. The other Swansea sites modelled show evidence of a gradual upward trend, but because initial f-NO_2 was so low in the late 1990s/early 2000s by 2006 f-NO_2 values were still only 11.1 and 11.2% at these sites.

Data capture of modelled f-NO_2 was relatively poor for at least some of the years at the majority of Welsh sites included in the modelling (a lot of the data points have less than 30% data capture). This may be caused by a relatively low NO_X roadside increment at some of these sites. The model is set up to only run for hours when the roadside increment is at least 10µg m^{-3} because at lower roadside increments the f-NO_2 signal is not sufficiently clear for the model to detect.

7.4.2.8 Scotland
Of the Scottish sites where f-NO_2 has been modelled (Figure 7.18), only Inverness shows any clear upward trend. This site has very low data capture – probably reflecting the low NO_X roadside increment at the roadside site – and only reached a maximum f-NO_2 of 13.7% in 2005. The only Scottish site with good data capture, Glasgow Kerbside has a very flat trend in f-NO_2 from 1999 onwards. Generally f-NO_2 at the small selection of sites modelled did not exceed 15%

7.4.2.9 Northern Ireland
In Northern Ireland (Figure 7.19), as in Wales and Scotland, there are issues with reliability of the model results at many of the sites considered due to low data capture. This again probably results from the relatively low NO_X roadside increment experienced along the roads on which the monitoring sites are located. The general picture from the results, however, suggests that f-NO_2 on many roads remains low with small upward trends apparent in some locations and no trend apparent in others. Derry Dales Corner (maximum modelled f-NO_2 of 29.0%), Castlereagh Lough View Drive (maximum f-NO_2 of 17.1%) and Belfast Roadside (maximum f-NO_2 of 14.5%) have the highest modelled f-NO_2 from the sites modelled in Northern Ireland. Otherwise modelled f-NO_2 values are typically in the region of approximately 10%.

Figure 7.10. f-NO$_2$ trends at selected sites in England – London (AURN sites).
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture

Figure 7.11. f-NO₂ trends at selected sites in England – London (LAQN sites).
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture
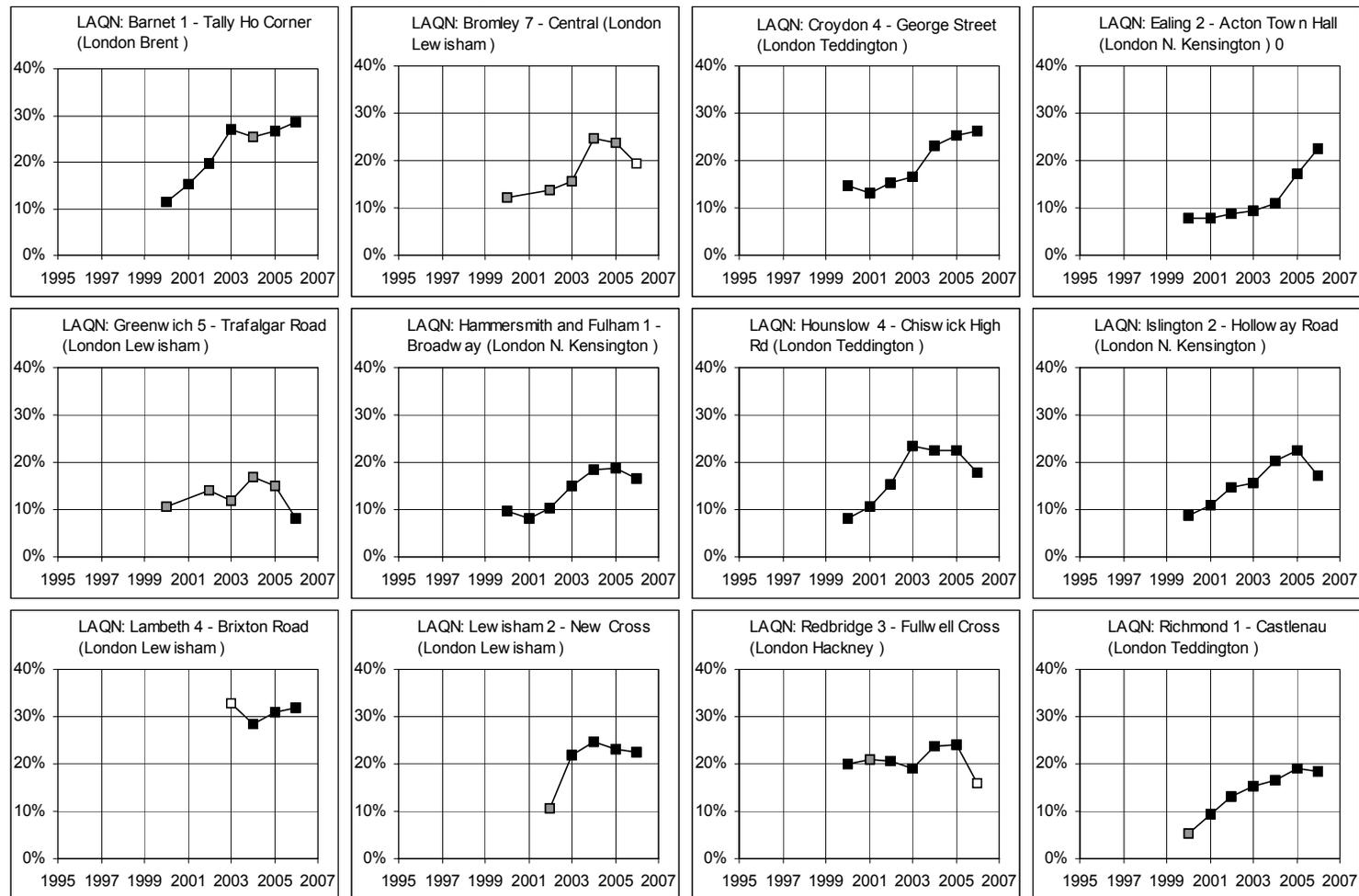
Figure 7.12. f-NO$_2$ trends at selected sites in England – The South East
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture
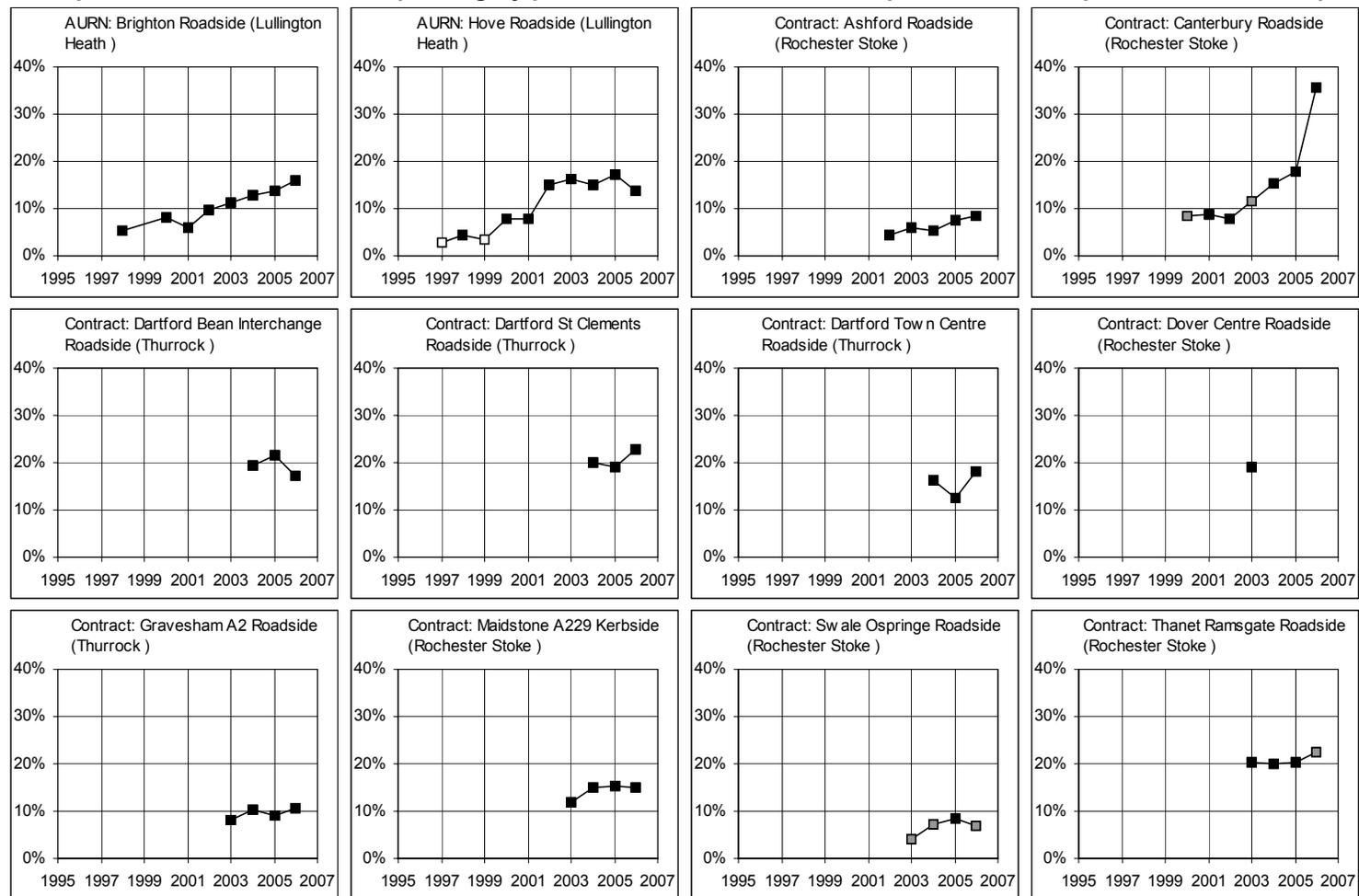
Figure 7.13. f-NO$_2$ trends at selected sites in England – The South West
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture
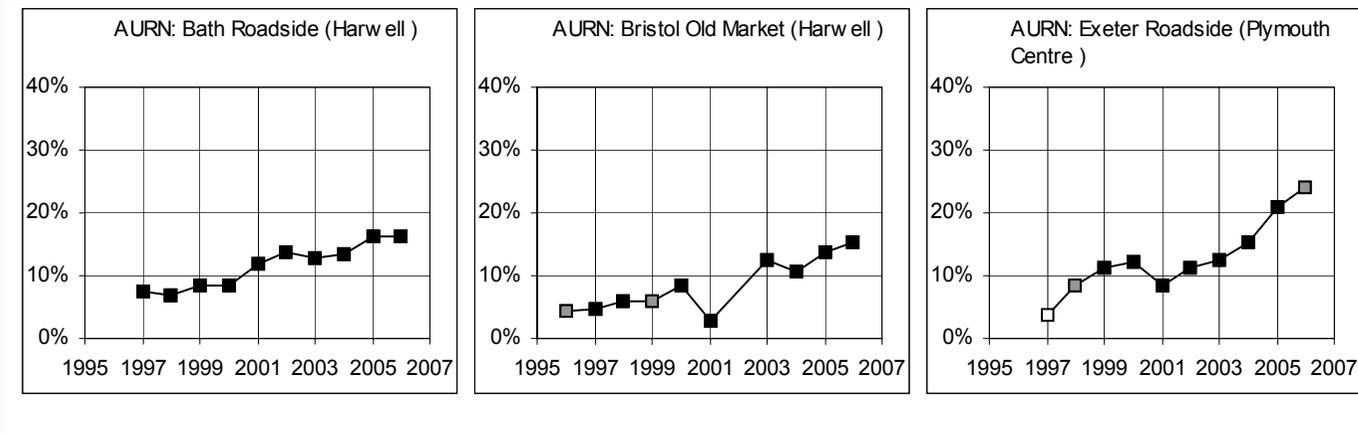
Figure 7.14. f-NO$_2$ trends at selected sites in England – The Midlands
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture
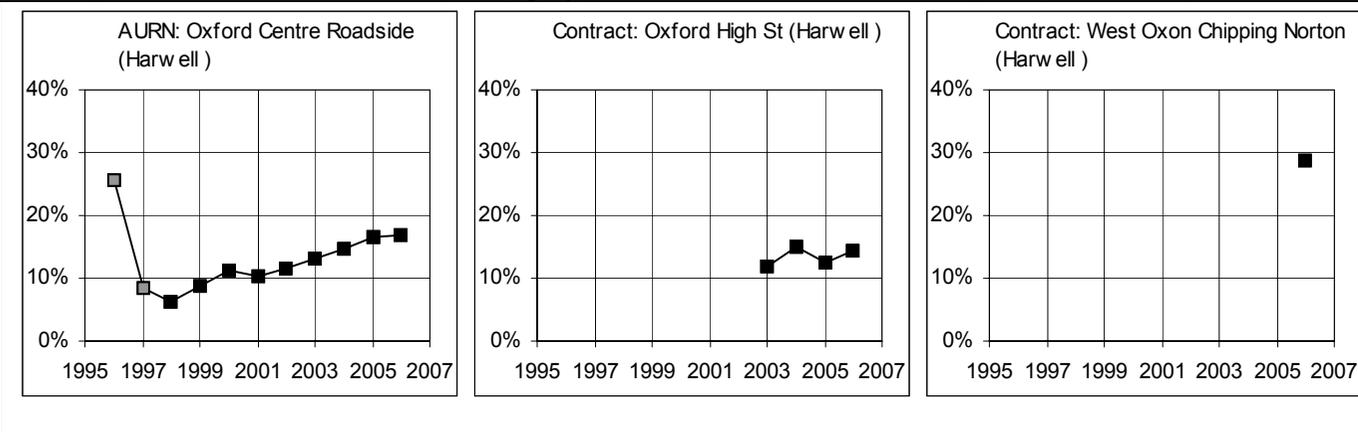
Figure 7.15. f-NO$_2$ trends at selected sites in England –East Anglia
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture
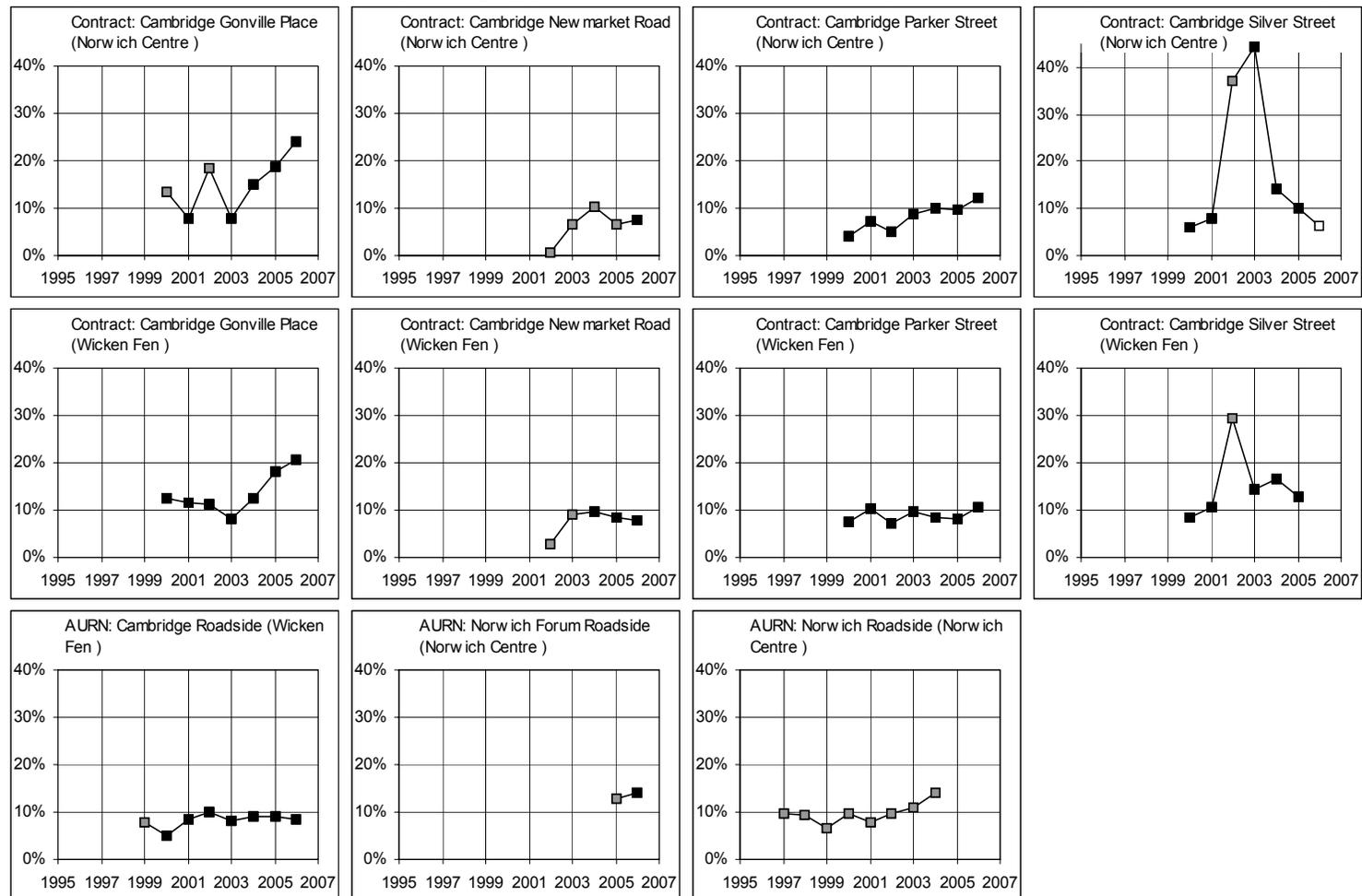
Figure 7.16. f-NO$_2$ trends at selected sites in England – The North
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture

AURN: Lincoln Roadside (Wicken Fen)

AURN: Stockton-on-Tees Yarm (High Muffles)

AURN: Bury Roadside (Bolton)

Contract: Wakefield Horbury Road (Barnsley Gawber)

Contract: Rotherham Wales (Rotherham Centre)

Figure 7.17. f-NO₂ trends at selected sites in Wales
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture
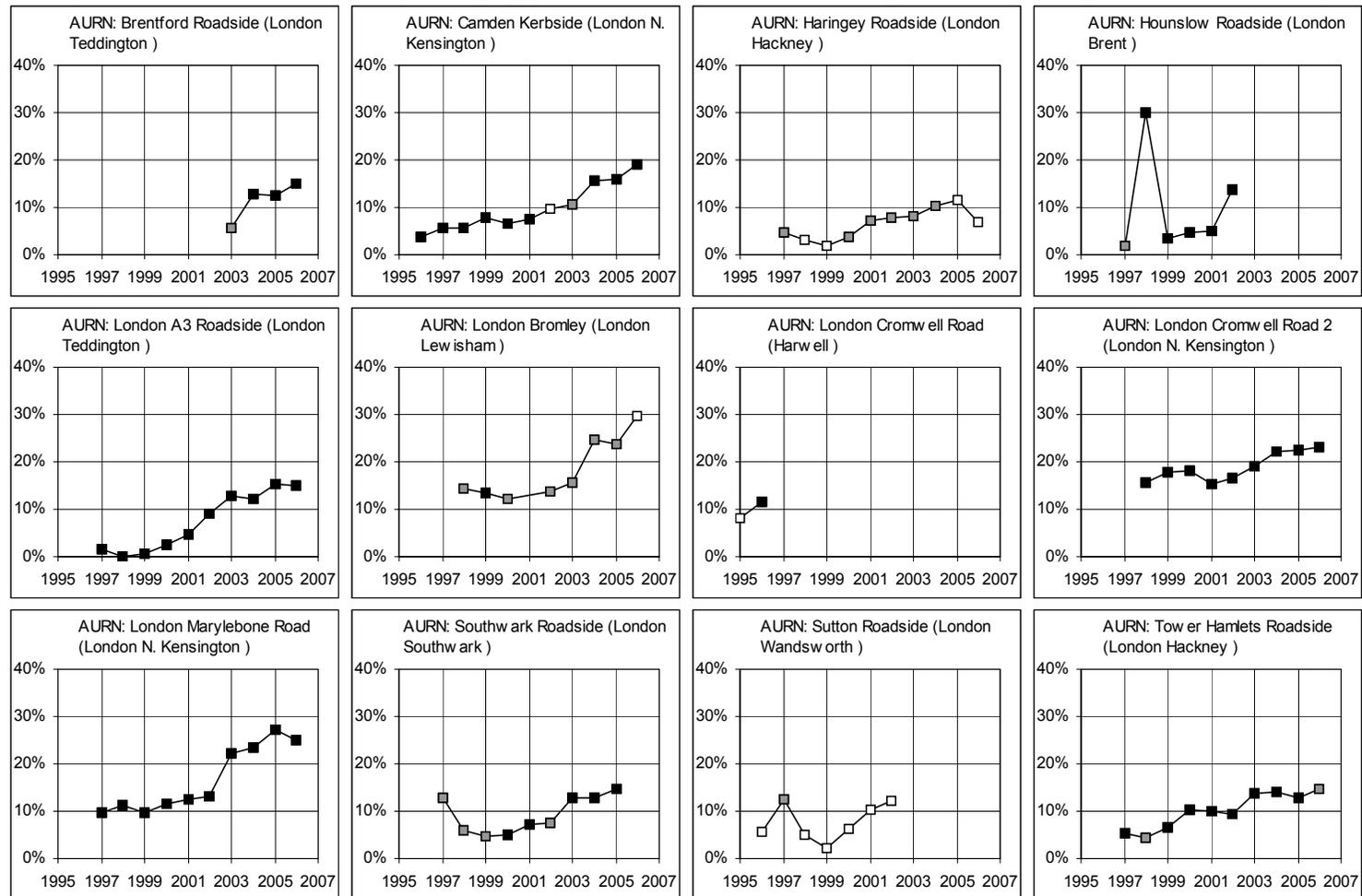
Figure 7.18. f-NO₂ trends at selected sites in Scotland
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture

Figure 7.19. f-NO$_2$ trends at selected sites in Northern Ireland
Labelling convention Network: roadside site name (paired background site name)
Black points denote >30% data capture; grey points <30% and >10% data capture; and white points <10% data capture
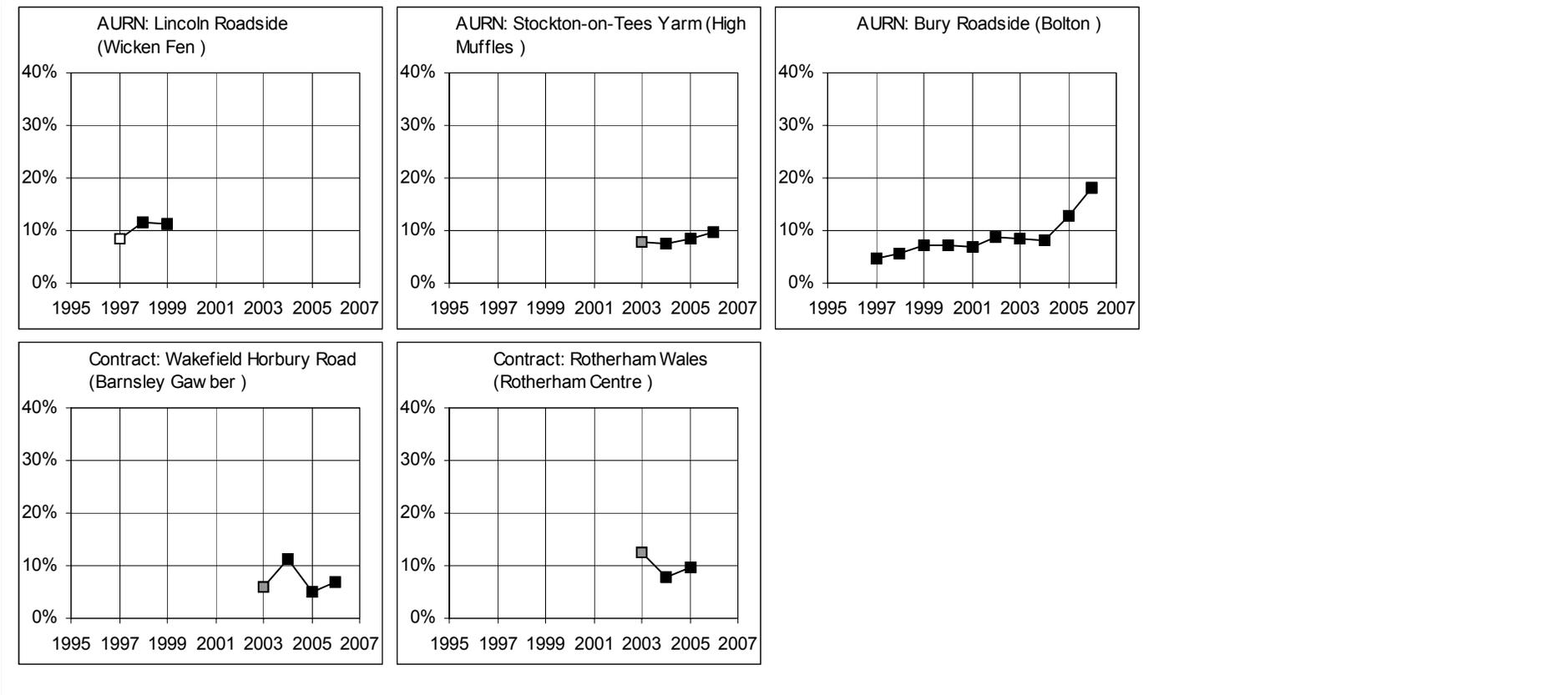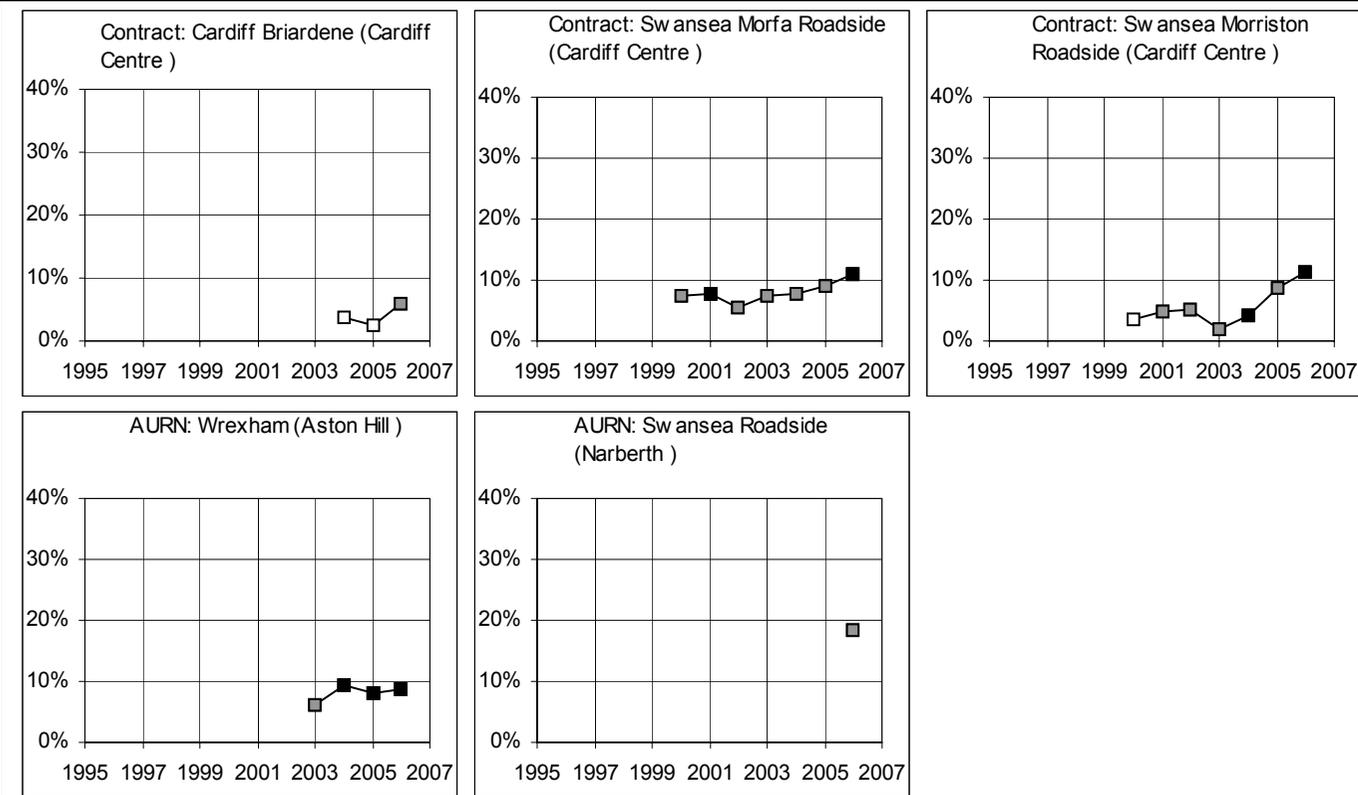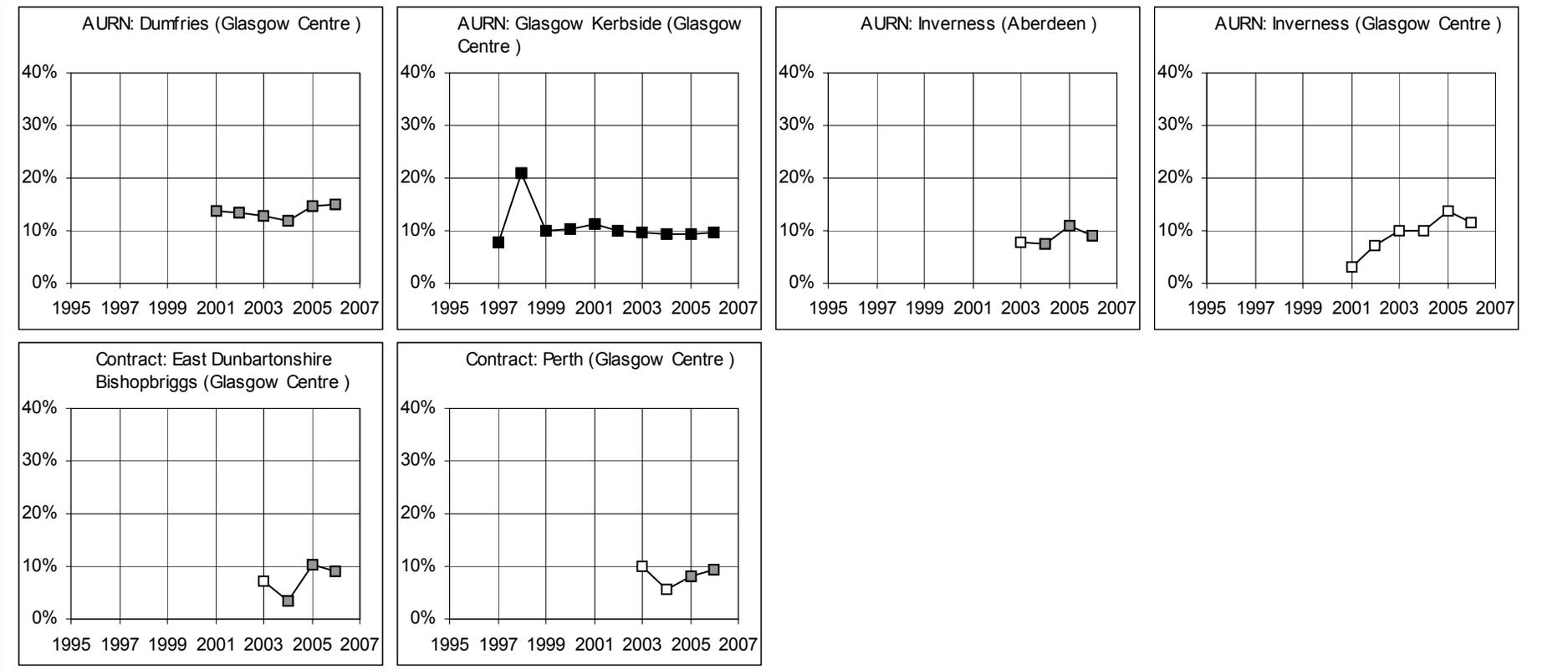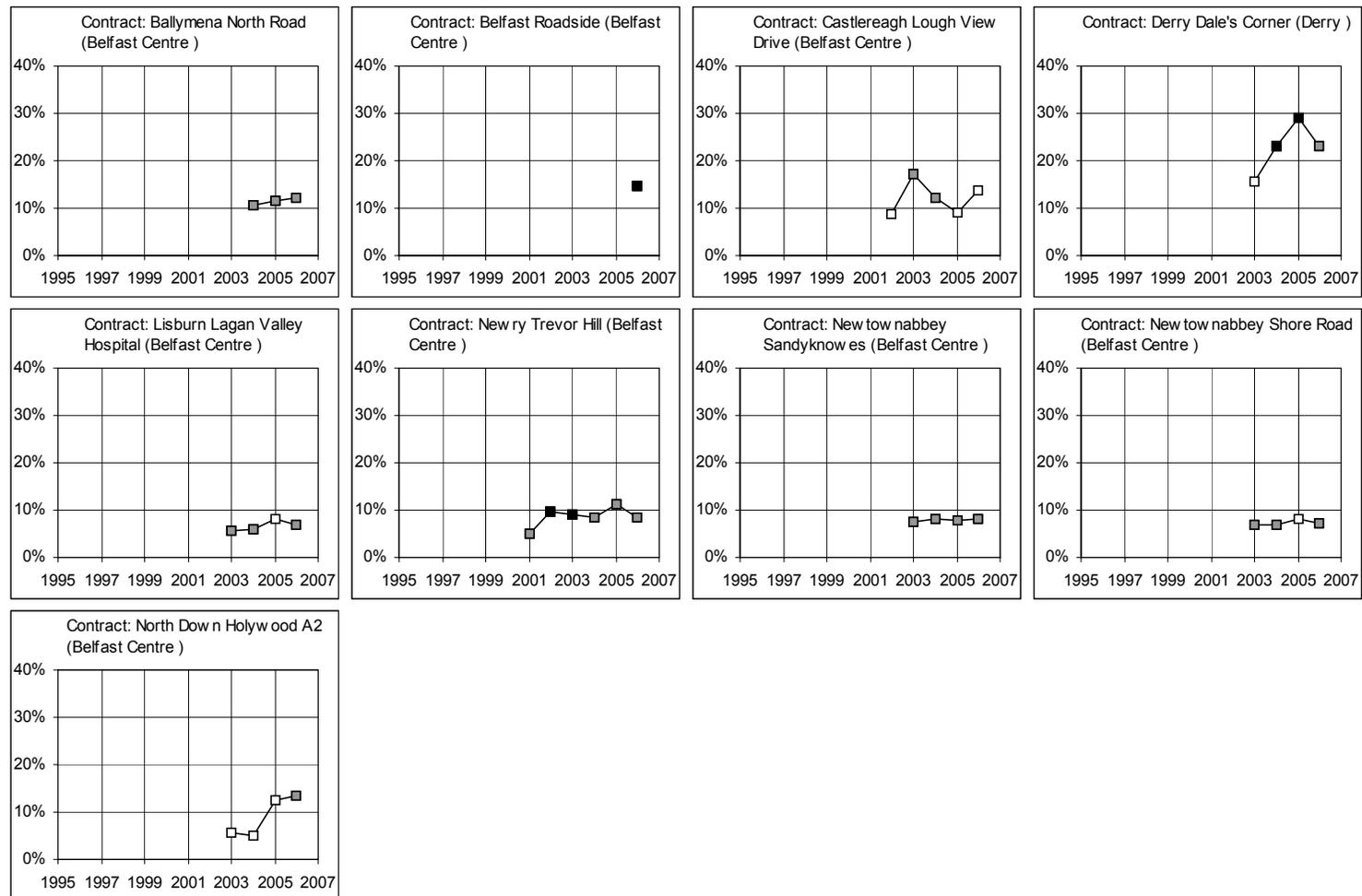
7.4.3   Discussion on f-NO$_2$ Trends

7.4.3.1 Geographical Distribution of f-NO$_2$

The results presented above provide evidence of regional geographical variations across the UK in terms of f-NO$_2$ at roadside locations. The highest f-NO$_2$ values tend to be found in London, which also contains many of the sites where the steepest upward trends in f-NO$_2$ have been modelled. Many, but not all, sites considered in this analysis across the South of England, the Midlands and East Anglia also exhibit upward trends in f-NO$_2$, although the maximum modelled f-NO$_2$ at these sites do not typically reach the levels found at some of the higher sites in London. The sites selected in the North of England, Wales, Scotland and Northern Ireland collectively suggest there is less of a general increase in roadside f-NO$_2$ in these areas, although there are a few sites within these regions where f-NO$_2$ has risen significantly in the past few years.

It is important to note that there are a number of caveats that should be applied to the general geographical distribution of f-NO$_2$ described above. Firstly, the model is a local scale model, which applies only in the immediate vicinity of the roadside monitoring site for which it has been run. For example, the two Oxford sites are located on adjoining roads in the city centre, but f-NO$_2$ at these sites from 2003-2006 has increased at one without showing a clear trend at the other (although the absolute f-NO$_2$ values are broadly similar at the two sites). Given the different behaviours of sites within the same cities/regions (e.g. within London and within Cambride), it is difficult to generalise f-NO$_2$ results, even across roads within a very small area.

Secondly, the coverage of the sites used in this modelling exercise in some regions is relatively poor and there are large areas across the country that are not represented by even one site. Where there are a good number of sites in a region, often the length of time series is insufficient to detect trends in the modelled f-NO$_2$.

Thirdly, particularly at sites in Scotland, Northern Ireland and to a lesser extent Wales, low data capture has been an issue in this modelling exercise because of the relatively low roadside increment on roads next to the monitoring sites. Points with low data capture are more uncertain and therefore less confidence can be placed in these results.

7.4.3.2 Trends in f-NO$_2$ up to and including 2006

At sites where the model suggests f-NO$_2$ has increased over time, it is possible to identify three groups of sites:

Sites where f-NO$_2$ has continued to rise between 2005 and 2006
Sites where f-NO$_2$ has levelled off
Sites where f-NO$_2$ has fallen between 2005 and 2006

Sites where f-NO$_2$ has continued to rise between 2005 and 2006 include sites where significant increases are still occurring (e.g. Canterbury Roadside, Ealing 2 – Acton Town Hall). f-NO$_2$ at other sites (e.g. Brighton Roadside) has risen more slowly, while at some sites (e.g. London A3 roadside) f-NO$_2$ increases have levelled off entirely. A significant number of the sites modelled in London from the LAQN network suggest f-NO$_2$ has peaked in 2004-2005 and are now declining again (e.g. Islington 2 – Holloway Road, Hammersmith and Fulham 1 - Broadway). Notably London Marylebone Road is one of the sites where f-NO$_2$ has fallen between 2005 and 2006.

The modelling presented above therefore presents a very mixed picture in terms of how f-NO$_2$ has changed in the past year or so. This suggests that predicting future changes in f-NO$_2$ across the UK for national scale models like the PCM model will be difficult as it is going up in some places, but coming down in others.

7.4.3.3 Model development options

Summer heat waves can present several potential problems for the model as follows.

Firstly, currently the ozone module of the Netcen Primary NO_2 model uses default meteorological parameters (e.g. for temperature, height of boundary layer) for hours where there is missing data. Sensitivity tests using default met data for the whole year in 2000 showed that the modelled annual f-NO_2 is not particularly sensitive to the met data used. However, default met data can present problems during big summer ozone episodes associated with heat waves, for example 9th June 2006, as the model run failed in this instance using default met data. One possibility for model development would therefore be to change what default met data the model uses where measured data are missing. This could be done through setting seasonal default met values for hours with missing met data, or by using met data from the last hour for which measurements were available.

Secondly, the model may produce less representative f-NO_2 results during summer heat waves at some sites because of spatial variability in regional oxidant between a given roadside site and its 'paired' background site. This spatial variability will be more significant during summer heat waves because regional oxidant levels will be higher than under normal conditions. Because the amount that regional oxidant levels are elevated may not be uniform across the country differences between paired sites may be more significant than normal. This may be responsible for the difference in the modelled f-NO_2 at Cambridge Silver Street in 2003 using Norwich Centre and Wicken Fen as the background site. For the run using Norwich Centre there was good data capture all year including in the summer heat wave, which may have skewed the annual f-NO_2. For the run with Wicken Fen, the data capture over the summer months was low so the heat wave was not included in the modelled annual f-NO_2. More work would be required to confirm whether this is the cause of the anomously high values at Cambridge Silver Street.

It is also possible that summer heat waves affect the frequency distribution of the hourly modelled f-NO_2, and therefore the annual f-NO_2, for other reasons. Investigating exactly what causes the impact of summer heat waves on modelled f-NO_2 at certain sites is another possible route for further model development.

7.4.3.4 Comparison of modelled f-NO_2 with f-NO_2 derived using an emissions inventory

One alternative method of estimating f-NO_2 is to generate an actual NO_2 emissions inventory. This has been calculated for the 2005 NAEI on the basis of the NO_X emissions inventory for traffic combined with f-NO_2 values taken from a review of actual tailpipe emission measurement studies presented in Grice et al (2007). Average f-NO_2 values across different areas of the UK for urban roads have then been calculated as the ratio of NO_2/NO_X emissions for these areas. This is a national scale estimate of f-NO_2 rather than a local scale estimate as is calculated using the Netcen Primary NO_2 model.

Figure 7.20 shows the resulting calculations of how f-NO_2 has changed across all the UK's urban roads, and how it is predicted to change with time. f-NO_2 is estimated to have increased at a relatively steady rate from 7.7% in 2001 to 10.8% in 2006. This increase is then predicted to continue into the future with a slight levelling off of the upward trend near 2020.

Given the cross-section of roads that the f-NO_2 values represent – both in London and those from across other urban areas in the UK – this graph seems to broadly agree with the general trend of increasing f-NO_2 at many roadside locations in the UK. However, a comparison between the UK urban roads trend shown in Figure 7.20 and the trends at individual sites in Figures 7.10-7.19 does illustrate the extent to which f-NO_2 on individual roads may not be adequately represented by the national average, especially in London.

Figure 7.20. Emissions based calculations of f-NO$_2$ on UK urban roads (2001-2020)
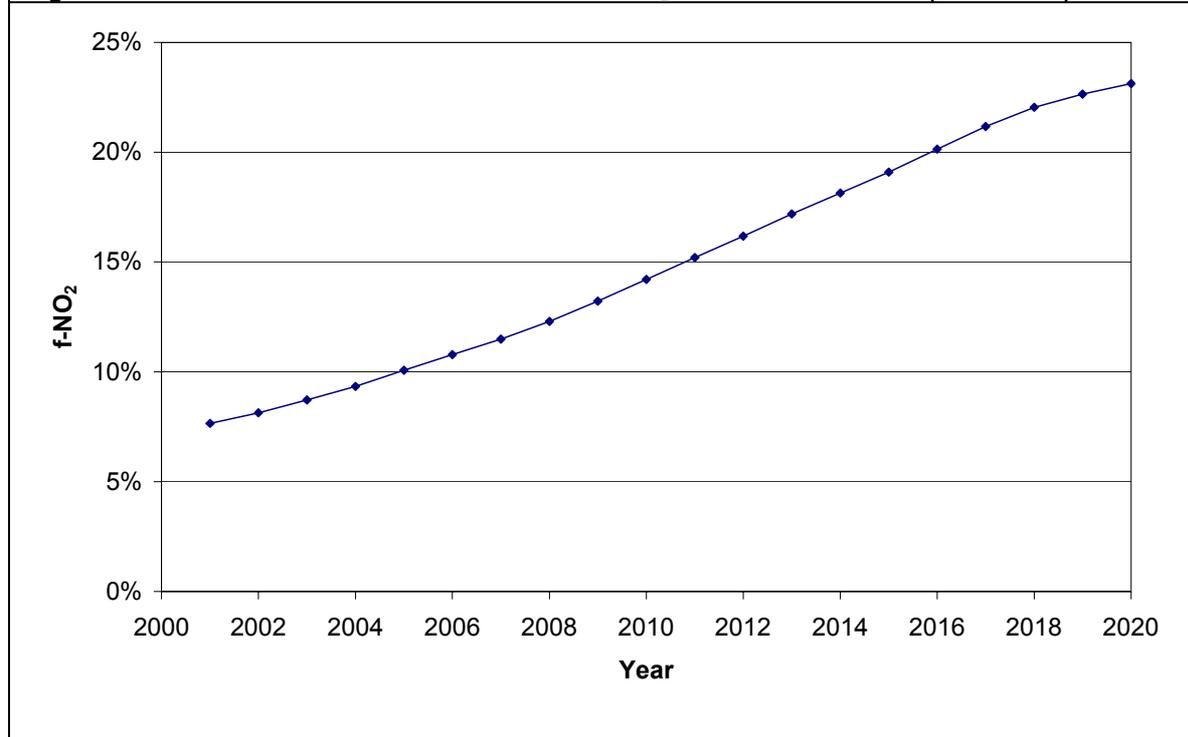
7.5 Conclusions on NO$_x$-NO$_2$-O$_3$ Relationships

A lot can be gathered from research based on the analysis and interpretation of ozone and oxidant monitoring data and the spatial and temporal (monthly and annual) trends that provide clues about sources and loss processes, in addition to the type of full-scale process modelling using tools like the OSRM and PTM. The work undertaken so far will help to improve the treatment of NO$_x$-NO$_2$-O$_3$ relationships in the PCM and the surface conversion algorithm of the OSRM, helping to improve predictions of ozone concentrations in urban environments. Such analysis includes further insight into the contribution made by direct emissions of NO$_2$ principally from traffic sources in urban areas providing a direct additional source of oxidant.

Work is currently underway in the Pollution Climate Mapping Programme on incorporating these findings to date into the PCM models.

8 Improvements to Photochemical Reaction Schemes (Objective 3)

There are a large number of volatile organic compounds emitted from both anthropogenic and natural sources which contribute to ground-level ozone production. For instance, the 2000 UK VOC emission inventory considered 664 VOCs emitted from 249 source sectors. The contributions of individual compounds to ozone formation vary, a result of differing chemical reactivities and structures. VOC control policies will be more effective from the point of view of reducing ozone formation if they are based on assessments using models that can take full account of the different reactivities of different VOC species. A major thrust in development of ozone models has been to improve and/or expand the information available on key groups of compounds contributing to ozone formation

Over the past decade, the Department's Ozone Research Programme has supported the development of detailed chemical mechanisms representing the breakdown of individual volatile organic compounds in the atmosphere. This has culminated in the **Master Chemical Mechanism (MCM)**, the latest version of which treats 135 emitted volatile organic compounds from both manmade and natural sources, producing ~5,900 chemical species involved in nearly 13,500 thermal and photochemical reactions. Generally speaking, the purpose of a chemical mechanism in any policy modelling tool addressing ozone or other air pollutants is to convert the emissions of the organic compounds into estimates of the concentrations of the pollutants. The modelling tool itself may address the urban, regional or global atmosphere and the damaging pollutants addressed may be ozone and the other atmospheric oxidants, together with fine particulate matter. In each case, the chemical mechanism is required to quantify the conversion rates of the emitted organic compounds into ozone, other oxidants and fine particulate matter and, in turn, to describe quantitatively their atmospheric destruction and removal rates.

The MCM has played a critical role in the development of the Photochemical Ozone Creation Potential (POCP) concept, an index to rank the contribution of individual VOCs to ozone formation, and the calculation of POCPs on different timescales including multi-day timescales characteristic of photochemical episodes in Europe.

Using the knowledge and understanding gained from developing the MCM, a reduced mechanism - the Common Representative Intermediate (CRI) mechanism - has been derived from the Master Chemical Mechanism, v3.1. Models such as the OSRM currently use other reduced chemical mechanisms not linked directly to the MCM.

8.1 Review of the Master Chemical Mechanism

Having undergone some years of development and application, Defra requested a review of the MCM to enable the Department to assess future funding for further development. The review was carried out in the first year of this project by the members of the project consortium who have been responsible for the development of the MCM over the past 15 years, namely Dr Mike Jenkin, Professor Dick Derwent, Professor Mike Pilling and Dr Andrew Rickard. The review covered:

- The aims of the MCM
- An introduction to the MCM and its policy background
- MCM protocols
- Current status of the MCM and on-going developmets
- The MCM website
- Comparison of the MCM with other chemical mechanisms
- Policy and other applications of the MCM
- Recommended future activities of the MCM including those requied to improve and maintain the status of the MCM.

A report "*A Review of the Master Chemical Mechanism*" (RG Derwent, ME Jenkin, TP Murrells, MJ Pilling and AR Rickard) was submitted to Defra in July 2007. The report was independently peer-reviewed by three reviewers selected by Defra and the report authors given the opportunity to respond

to the comments made by the reviewers. The peer-review comments were all very positive about the report and rated very highly the progress made with the development of the MCM, but also provided some helpful pointers for future development of MCM.

In response to these comments, the review's authors prepared a set of revised recommendations for future development and activities with the MCM and submitted these to Defra in November 2007 with approximate timescales and resources needed to undertake them. Section 8.2 summarises the recommendations of the MCM review team for future work. Note that the text in Section 8.2 is taken directly from the review and the list of references cited here are given in the original review document and are not repeated in the list of references at the end of this report.

8.2   Review's Recommendations for Future Work with the MCM

Activities that are required to improve and maintain the status of the MCM, and more generally to help guide the representation of organic degradation chemistry in atmospheric models, can be broadly subdivided into the following categories:

8.2.1   Major Revision of the MCM Protocol

A strategy has been defined by the international ACCENT panel (described in section 5 of the review), which provides a framework for revising and updating the basic rules on which the MCM is based. The overall aim of this activity is to make the MCM construction methodology robust and sustainable, and to ensure that it continues to be fully recognised and endorsed by the international community. This is believed to be an essential activity to ensure the long term stability of the mechanism, which will require support from a number of sources, as yet not fully identified. Some Defra support is requested for this initial activity (i.e. the update to the protocol) so that it can be forewarned of any major revisions in our understanding of the mechanism of photochemical ozone formation that may have knock-on effects for policy; and for subsequent initial application of the protocol.

As indicated in section 5 (of the review), the procedure devised by the ACCENT panel will involve consultation of series of individuals or groups with appropriate expertise, who will provide supplementary advice on updates which are required to the MCM protocol. It is therefore not possible to provide an exhaustive list of recommendations prior to those activities. However, Annex 3 (of the review) provides a detailed preliminary survey carried out by the core MCM team, which identifies a systematic series of suggested revisions which will almost certainly form a major component of the updates to the protocol.

8.2.2   Development and Application of Interim Updates to the Current MCM

The full revision of the MCM protocol described in Section 8.2.1, followed by its subsequent implementation, is necessarily a long-term activity. It is recognised that parallel interim improvements to the MCM can be made in the shorter term, based on the current mechanistic framework. Such improvements will ensure that the MCM continues to evolve in line with recent developments in understanding, and will allow the impact of such developments on science and policy applications (e.g., VOC reactivity and reactivity scales, see section 8 of the Review) to be assessed. This will also help to inform the activities in Section 8.2.1. Based on the information in Annex 3 (of the review), the following specific interim improvements have been identified:

a) *Initiation reactions for VOC with OH, O_3 and NO_3,and the inorganic reaction set*: Where the initiation reactions for emitted VOC, and oxygenated products have been studied experimentally, the rate coefficients and branching ratios would be updated in line with the latest evaluations (e.g., Atkinson et al., 2006, www.iupac-kinetic.ch.cam.ac.uk; Calvert et al., 2007). The set of inorganic reactions in MCM would also be updated in the same way.

b) *Initiation by photolysis*: The representation of the photolysis reactions in the MCM would

be updated to include additional processes (e.g., the photolysis of nitrophenols: Bejan et al., 2006) and additional product channels, where appropriate (e.g., for the photolysis of long chain aldehydes). The standard rates of the photolysis reactions in models on the MCM website would be revised to be consistent with the latest evaluations of absorption cross-sections and quantum yields (e.g., Atkinson et al., 2006, www.iupackinetic.ch.cam.ac.uk; Calvert et al., 2007), where appropriate. The associated wavelength interval averaged data would be made available on the website to allow consistent photolysis rates to be used in other applications.

c) *Reactions of RO$_2$ radicals*: (i) The reactions of HO$_2$ with selected RO$_2$ classes (e.g. acylperoxy radicals) would be revised to include radical-forming channels (e.g., Hasson et al., 2004; Jenkin et al., 2007). (ii) The reactions of NO$_2$ with selected acylperoxy radicals (e.g., HC(O)C(O)O$_2$) would be revised to generate RO and NO$_3$ in preference to stabilised peroxyacyl nitrate formation (e.g., Orlando and Tyndall, 2001). (iii) The reactions of RO$_2$ with NO would be revised to implement the latest information of the branching ratios for organic nitrate (RONO$_2$) formation (e.g., Calvert et al., 2007). (iv) The generic rate coefficients assigned to the parameterised RO$_2$ permutation reactions would be updated to reflect the larger kinetics database of self- and cross-reactions of RO$_2$ radicals (e.g.,Boyd et al., 2003).

d) *Reactions of RO radicals*: Within the current mechanistic framework, the relative importance of the fates of RO radicals (reaction with O$_2$, thermal decomposition and isomerisation) would be revised in line with the latest method of Atkinson (2007). Where appropriate, the formation of chemically activated RO radicals from reactions of RO$_2$ with NO would be represented (e.g., Orlando et al., 1998).

e) *Degradation of organic nitrates (RONO$_2$) and hydroperoxides (ROOH)*: The MCM currently includes a simplified representation of the degradation of RONO$_2$ and ROOH following reaction with OH. In the case of RONO$_2$, this leads to release of NO$_2$ at the primary step. In practice, the chemistry may lead to retention of oxidised nitrogen in the organic product, or the sequestering of additional NOx, which will have an impact on assessments of O$_3$ formation as conditions become more NOx-limited (e.g. see sections 8.5 and 8.6 of the review). The degradation chemistry for RONO$_2$ should be improved to include appropriate representation of bi- and multifunctional oxidised nitrogen products, particularly for more reactive RONO$_2$ species (e.g., those formed from longer chain alkanes, and from dienes such as isoprene and 1,3-butadiene). For the unsaturated RONO$_2$ formed from the dienes, reaction with O$_3$ and NO$_3$ should also be considered. For ROOH, attack of OH at the carbon D to the –OOH group leads to prompt OH regeneration. ROOH formation becomes more important as conditions become more NOx-limited, such that representation of such reactions will have an increasing impact on assessments of O$_3$ formation.

In each case, the policy importance of these revisions would be illustrated by documenting the changes in the respective POCP values (see section 8.3 of the review).

8.2.3 Development and Testing of Mechanistic Variants

It is widely recognised that gaps and uncertainties remain in the detailed understanding of the degradation of some VOC classes, and this is often indicated by the inability of established mechanisms to explain the results observed in environmental chambers. Although such shortcomings can sometimes be resolved by tuning parameters within the acceptable limits of uncertainty (e.g., Zádor et al., 2005; Pinho et al., 2007), they often indicate the omission of unknown or only partially understood processes. Within the strict MCM construction methodology, it is not possible to address such shortcomings until there is at least a rudimentary understanding of the elementary processes involved, and this clearly must await the emergence of new and informative experimental studies. Nevertheless, previous activities with the MCM (e.g., Bloss et al., 2005a) have proposed and tested possible mechanistic variants in relation to chamber data, although the impacts of such variants in broader science and policy applications has not been assessed. It should also be noted that policy mechanisms based on chamber data routinely apply speculative fixes to "optimise" their performance.

This issue would be addressed by development of a series of specific formal mechanistic variants to the MCM. Such variants would provide a preliminary representation of processes which allow improved descriptions of chamber data, but which have not been fully confirmed by experimental understanding of elementary reactions. In addition to providing a basis for making progress in policy assessments, such activities would highlight areas for focussed

study by the science community, such that the variants can ultimately be endorsed and fully implemented in the MCM, or rejected. The mechanistic variants would be fully documented, and available on request in the form of appropriate reaction listings (e.g., a FACSIMILE deck). Examples of processes which could appear in mechanistic variants are as follows:

a) *OH regeneration from complex RO_2 radical isomerisation in aromatic systems*: This process has been shown to provide an improved description of aromatic hydrocarbon removal and O_3 formation in chamber studies (e.g., Bloss et al., 2005a), but no mechanism has yet been identified.

b) *Photosensitised reaction of NO_2 with aromatic organic aerosol*: This process has been shown to provide an improved description of aromatic hydrocarbon removal and O_3 formation in chamber studies (e.g., Bloss et al., 2005a), and is partially endorsed by experimental study (e.g., George et al., 2005). Its implementation also requires secondary organic aerosol (SOA) code development (see Section 8.2.4).

c) *Implementation of cyclisation reactions of 1,4-hydroxycarbonyls formed from long chain alkanes*: The formation of reactive dihydrofurans from these cyclisation processes, followed by dehydration, has been observed (Martin et al., 2002), with the impact of water vapour studied by Holt et al. (2005). Atkinson et al. (2007) have recently demonstrated that this occurs by an acid-catalysed surface mechanism, which can potentially occur on ambient particulate. Representation of this chemistry should be implemented and tested on the basis of these studies.

d) *Isomerisation of δ-hydroxyperoxy radicals:* A number of studies (Heiss and Sahetchian, 1996; Perrin et al., 1998; Jorand et al., 2003; Atkinson et al., 2007) have obtained evidence for H-shift isomerisation reactions of δ -hydroxyperoxy radicals formed from longer chain alkanes, which lead to the generation of hydroperoxy carbonyl products, with this chemistry potentially having an increasing impact as conditions become more NOx-limited. Representation of this chemistry should be implemented and tested on the basis of these studies.

e) *Reduction of radical yields from longer chain alkene ozonolysis*: Chamber evaluations have identified that the observed O3 formation rate requires parameters to be adjusted to outside the reported range (Pinho et al., 2006).

The POCP indices would be determined for each mechanistic variant for the range of relevant VOC to elucidate the policy importance of the modified descriptions of VOC chemistry.

8.2.4   Development of New MCM Schemes

The range of reactivity and structure of emitted anthropogenic VOCs (AVOC) is very well represented by the 100 + species degraded in the MCM. In contrast, there are only four biogenic VOCs (BVOC) treated, with most applications to date emitting three of these. In practice, the emitted speciation of BVOC includes contributions from isoprene, monoterpenes (isomeric formula $C_{10}H_{16}$), sesquiterpenes (isomeric formula, $C_{15}H_{24}$) and oxygenated VOCs (e.g., He et al., 2000; Llusia et al., 2000; Owen et al., 2001; Boissard et al., 2001; Spänke et al., 2001), with typically more than 20 significant contributors identified in a given study. Owing to wide variations in reactivity, these species are oxidised on a variety of temporal and associated spatial scales in the atmosphere (lifetimes range from minutes to days), and detection of the more reactive BVOC (some monoterpenes and sesquiterpenes) is therefore non-trivial. The chemical structure of these compounds also has implications for degradation pathways, which can differ dramatically between BVOC, with corresponding variability in their ability to generate O_3 (and secondary organic aerosol, SOA). As a result of EU controls on AVOC emissions over the last decade, BVOC have an increasing relative impact on regional scale photochemistry in Europe, and have potential additional significance in relation to biofuel production.

As a result, the MCM would benefit from the inclusion of schemes for additional terpenes, with the specific aim of increasing the reactivity range of the species represented. The selection of the particular species to be treated would take account of information on the speciation of emissions within the European region. Based on an initial appraisal of species emitted from oilseed rape, it is anticipated that the selection might include compounds such as limonene, linalool, β-caryophyllene, myrcene, α-terpinene, 1,8-cineole and p-cymene. The resultant mechanism in appropriate models,

such as the UK PTM, would then be used to generate a more complete picture of the biogenic contribution to regional ozone formation in the UK and North West Europe.

In addition to the above biogenic hydrocarbons, a scheme for the important biogenic organosulphur compound, dimethyl sulphide (DMS), should be included. It has been routinely detected at coastal locations in the UK (e.g., Carslaw et al., 1997; Allan et al., 1997) and has a potential impact on oxidant chemistry and on particulate formation.

8.2.5 Development and Application of Secondary Organic Aerosol (SOA) Code

Previous investigations of secondary organic aerosol (SOA) formation have established that there are broadly three mechanisms responsible for the transfer of organic material from the gaseous to the aerosol phase (i) Partitioning into the condensed organic phase, characterised by speciesdependent equilibrium absorptive partitioning coefficients, Kp (Pankow, 1994);
(ii) Partitioning into the condensed aqueous phase, characterised by species-dependent Henry coefficients, H (Baum, 1998); and (iii) Enhancement of mechanisms "(i)" and "(ii)" driven by accretion reactions in the condensed phase, leading to the formation of oligomeric compounds of lower volatility (e.g., Tobias and Ziemann, 2000; Kalberer et al., 2004; Tolocka et al., 2004). Previous studies based on the MCM (e.g., Jenkin, 2004; Johnson et al., 2004; 2005; 2006) have considered mechanism "(i)" explicitly, with mechanisms "(ii)" and "(iii)" notionally accounted for by an empirically-derived scaling factor applied globally to the values of Kp. The previous work should be extended as follows:

a) *Policy calculations with existing code*: The existing code would be applied to policyrelated calculations which help to develop understanding of the roles of individual anthropogenic and biogenic VOC and VOC emissions sectors in the generation of organic fine particulate matter.

b) *SOA code improvement*: The work would be extended to provide a more rigorous representation of mechanisms "(ii)" and "(iii)" described above. Mechanism "(ii)" will require values of H to be estimated for the complete series of closed-shell oxygenated organic products generated from the gas phase chemistry. This would allow a code to be developed to represent bulk partitioning of the "monomeric" oxygenated products into the condensed organic and aqueous phases, allowing a basis for representation of total mass concentrations present in the gaseous and aerosol phases. The code would need to be further refined to account for the formation of oligomeric species in the condensed organic phase (i.e., mechanism "(iii)"). A practical method could involve implementation of speciesdependent scaling factors for each of the partitioning species, with these values related to the functional group content of each species. This would take account of existing laboratory information on the identities of high molecular weight adducts in SOA (e.g., Tobias and Ziemann, 2000; Kalberer et al., 2004), and also on recent theoretical assessments of the thermodynamics of accretion reactions for specific oxygenate classes (e.g., Barsanti and Pankow, 2004; 2005; 2006).

c) *Policy calculations with refined code*: The activities identified in (a) above would be repeated with the refined code, to assess the impact of implementation of the additional mechanisms.

8.2.6 Development of a Hierarchy of Traceable Reduced Mechanisms

The development of the latest version of the Common Representative Intermediates mechanism, CRI v2, has provided a reduced mechanism which is traceable to the MCM. It
therefore provides the initial basis for the development of a hierarchy of traceable reduced mechanisms which can be tailored to a range of applications. The following possible activities
for future developments have been identified:

a) *Testing and application of CRI v2 in a policy environment*: CRI v2 would be fully tested in a series of policy-related calculations, to assess its performance against MCM v3.1. Such calculations could include calculation of Photochemical Ozone Creation Potentials (POCP), investigation of multi-day ozone formation and examination of its ability to represent source sector reactivity contributions (see section 8 of the review).

b) *Reduction of CRI v2*: The further reduction of the mechanism would be carried out using a series of emissions lumping strategies. The aim of this activity would be to lump emitted VOC on the basis of

chemical class and POCP, with the lumping strategy systematically tested in relation to mechanism performance for a range of conditions. The ultimate goal of this activity would be to obtain a traceable streamlined mechanism which can be used economically is models applied to ozone policy assessments, e.g. OSRM and NAME.

c) *Development of SOA capability*: In conjunction with the SOA code development activities described above for the MCM (section 8.2.5), a traceable method to represent SOA formation using the CRI mechanism would be developed. The aim of this activity would be to enable models such as OSRM and NAME to provide model estimates of particulate organic carbon for the current and future situations. Currently, secondary particulates (PM) are not handled well in Defra's policy assessments carried out as part of its Pollution Climate Modelling Contract. This focus of secondary organic particulates would complement work recently commissioned by Defra in this project on the secondary inorganic components (sulphate and nitrate), as discussed in Section 5.2.

8.3 The Next Stage in the MCM Review

The recommendations made by the MCM review team are currently being considered by the Department in parallel with the recommendations of a wider review of Defra's ozone modelling activities that had been commissioned independently by the Department at about the same time. As part of this, Defra have recently commissioned a further study within the current tropospheric ozone modelling project to examine the wider issues of solvent reduction and substitutions policies. The aim of this study is to develop a methodology for assessing the costs, benefits and trade-offs of such policies and with, the use of case studies, to feed this into the current review of the MCM.

8.4 Maintenance of the MCM Website

The MCM is available on the internet website maintained by the University of Leeds for the wider scientific community (http://mcm.leeds.ac.uk/MCM/). The MCM database and the website has continued to be maintained and developed during the first year of this project.

Knowledge Transfer funding has been obtained from NERC for complementary developments of the MCM database and the IUPAC evaluated database at Cambridge (http://www.iupac-kinetic.ch.cam.ac.uk/). The project involves the Universities of Cambridge and Leeds and BADC. The main objectives of the project work packages are briefly outlined below:

- The IUPAC summary table is being converted into a more comprehensive searchable and flexible database taking the design of the new MCM online database as a starting point.

- Common web-based tools are being developed for clear simultaneous searching of both databases and easy extraction of data.

- The ease of maintenance of the MCM and its accuracy will be enhanced by linking of IUPAC datasheets to the appropriate reactions in the MCM database. Both databases are being developed further and synchronised in line with developments being made by other chemo-informatics communities using standardised formats and nomenclature so that data can be shared across each database as well as with other community databases.

- Web-based tools are being developed to improve interactions and collaborations with the user community and to facilitate the exchange of new data and tools.

The above KT activities are only supported through the existing project until November 2008. Further funding to help support the development, maintenance and linkage of both websites/databases will be required subsequently.

Ongoing activities as part the EU EUROCHAMP Programme (http://www.eurochamp.org/) involve the development of tools to facilitate the evaluation of the MCM and will promote its wider use, these include:

- A simplified generic box model, based on the MCM and using a FORTRAN code, has been developed which is aimed at laboratory, field and chamber scientists. The current version is now in the testing phase at the EUPHORE chamber in Valencia.

- The development of a "precursor subset back extraction" tool which will enable the user to determine the sources (and sinks) of specific species of interest in their model calculations. A visualisation tool for this back extractor is also being developed in collaboration with the Department of Computing, University of Leeds.

9 Other Project Activities

Other project activities have been carried out in the first year of the project involving the project consortium members.

9.1 Defra's External Review of Tools for Modelling Tropospheric Ozone

Defra commissioned a team led by Professor Paul Monks (University of Leicester) to undertake an independent review of tools for modelling tropospheric ozone formation and assessing impacts on human health and ecosystems. The aim of the review was to identify key development opportunities for Defra funding – to improve value of each model to Defra's policy needs and to prioritise development opportunities identified.

As part of that review process, Professor Monks solicited feedback from various ozone modellers, by completion of a *pro-forma* Model Information Sheet providing details and status of models currently used under Defra research contracts. Members of the project consortium were involved in providing the necessary feedback. Professor Derwent completed such a sheet for the PTM; Dr Murrells completed a sheet for the OSRM. The completed sheets for the OSRM model submitted for the modelling review is given in Appendix 1.

The first draft of the Review report was completed in October 2007 and presented at a User's Workshop at Defra on 19th October 2007. Members of the project consortium at AEA involved with the OSRM (Tim Murrells, Sally Cooke and John Abbott) and Professor Derwent took part in the workshop. The final version of the Review report has since been submitted to Defra (Monks et al, 2007).

9.2 Support to the Royal Society Initiative "*Ground Level Ozone in the 21st Century*"

The Royal Society has launched a study to assess and synthesise existing information on ground-level ozone and its impacts, and their coupling to climate change. The study is assessing the potential impacts of ground-level ozone concentrations on human health and the environment over the next century. It will identify options for reducing emissions and mitigating impacts, and will identify gaps in policy and research. The study, which will be global in scope, invited Professor Derwent to contribute to its assessment. It was agreed that Professor Derwent will report outputs to this project. Professor Derwent has attended initial Royal Society meetings.

9.3 Air Quality Expert Group Report on Ozone

Professor Pilling (Chair), Professor Derwent, Dr Jenkin and Dr Murrells (*ex-officio*) are member of Defra's Air Quality Expert Group (AQEG). AQEG is currently preparing a report on "*Ozone in the UK*", the first draft of which is near completion. These members of the project consortium have contributed in various ways to the report building on research carried out in this project and attended several AQEG meeting during 2007.

9.4   Project Meetings, Reports and *Ad-hoc* Requests

A kick-off meeting for the project was held at Defra on 27th February 2007 attended by all the project consortium members and Defra. A series of presentations were given on the current state-of-play of ozone modelling and the work programme for the project discussed.

The Project Manager gave a presentation on the purpose, scientific aims and objectives of the project at Defra AEQ's Annual Modelling meeting held at Ashdown House in 9th March 2007. The presentation to Defra's other air quality modelling contractors covered the modelling framework and approaches used in the project, covering the OSRM and the Photochemical Trajectory Model (PTM), and identification of knowledge gaps.

Additional meetings of the project partners have been held during 2007. On 31st July 2007, the project partners involved with the MCM Review (Chapter 8) met with Dr Amin-Hanjani (Defra) to discuss the next stage for the MCM review. The possibility was discussed of going to another stage in demonstrating the potential of the MCM for assisting Defra on policies such as solvent control. This ultimately led to the commissioning at the end of the first year of the project of some further work by external consultants, to be done within the current tropospheric ozone modelling project, but involving the project team, to examine the wider issues of solvent reduction and substitutions policies. The aim of this study is to develop a methodology for assessing the costs, benefits and trade-offs of such policies and with, the use of case studies, to feed this into the current review of the MCM.

AEA Energy & Environment and Professor Derwent have attended to three *ad-hoc* queries from Defra on the following matters:

- ***VOC emission trends from the industrial coatings industry and its impacts on ozone***. The UK emission time-series expressed as POCP-weighted emissions from the sector were provided. Long time-series trends in ozone concentrations and exceedences back to 1980 were also provided for this query.

- ***Ozone consequences of reductions in natural gas leakage***. Following a query by Ofgem, some advice was given to Defra on how to potentially quantify the reductions in UK ozone levels that would arise if greater controls were placed on the leakage of natural gas from gas distribution systems.

- ***VOC emissions from paints and their contribution to ozone formation***. Time-series data from the NAEI showing trends in emissions from the paints industry were provided, together with POCP values for paint solvent emissions and their contribution to episodic ozone concentrations.

Three quarterly progress reports were prepared for Defra providing a summary of the progress made on each of the various project objectives and project management related issues.

9.5   Technical Reports and Publications

The following technical reports have been prepared by the project consortium in the first year of the project:

Climate Change Consequences of VOC Emission Controls. T Murrells and RG Derwent. Report to the Department for Environment, Food and Rural Affairs, Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland. AEA Report AEAT/ENV/R/2475 - Issue 3, September 2007.

NAME Modelling to Support Empirical Modelling of Secondary PM Projections.
A Redington. Report by the Met Office, November 2007

Emission Sensitivities for PM Components for Harwell, Oxfordshire Estimated Using a Photochemical Trajectory Model for 2006. RG Derwent. Report by rdscientific, September 2007

UK air quality modelling for annual reporting 2006 on ambient air quality assessment under Council Directives 96/62/EC and 2002/3/EC relating to ozone in ambient air. A.J. Kent and J.R. Stedman (2008). Report to the Department for Environment, Food and Rural Affairs, Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland. AEA Report AEAT/ENV/R/2499 (2008)

A Review of the Master Chemical Mechanism. R.G. Derwent, M.E. Jenkin, T.P. Murrells, M.J. Pilling and A.R. Read. Report to Defra, July 2007.

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

Modelling the impact of elevated primary NO_2 and HONO emissions on regional scale oxidant formation in the UK. Jenkin M.E., Utembe S.R. and Derwent R.G. Atmospheric Environment, 42, 323–336 (2008).

Trends in ozone concentration distributions in the UK since 1990: local, regional and global influences. Jenkin M.E. Submitted to Atmospheric Environment.

A publication has been prepared by Professor Derwent containing the UK PTM model results. A presentation was also given at the International Aerosol Modelling Algorithms Conference at University of California, Davis during December 2007.

10   Conclusions and Policy Relevance

Work has been carried out in the first year of the project on three of the project's main objectives. The work can be broadly categorised as **application** of existing models of tropospheric ozone for policy purposes and further **research and development** of the models and the underpinning science. The main conclusions from the work and the policy relevance are as follows:

10.1   Application of Tropospheric Ozone Models and Policy Support

UK Ozone Climate in 2006

The UK ground-level ozone climate for 2006 has been characterised by the Pollution Climate Mapping (PCM) empirical modelling approach and the Ozone Source Receptor Model (OSRM). Both models indicated 2006 was a relatively high ozone year, with elevated concentrations measured in the summer when peak episodic conditions prevailed.

Results from the PCM, that are based on 2006 ozone monitoring data, are summaried for the EU Target Value for ozone concentration metrics for human health and vegetation in 2010 (an average over the past 3 years) and the Long-term Objectives for ozone in Tables 10.1 and 10.2, respectively.

Table 10.1: UK summary results of air quality assessment relative to the Target Values for ozone for 2010

Target Value	Number of zones exceeding
Max Daily 8-hour mean Target Value	none
AOT40 Target Value	none

Table 10.2: UK summary results of air quality assessment relative to the Long-term Objectives for ozone

Long-term Objective	Number of zones exceeding
Max Daily 8-hour mean Long-term Objective	43 zones (41 measured + 2 modelled)
AOT40 Long-term Objective	41 zones (32 measured + 9 modelled)

There were particularly high numbers of exceedences of the 120 µg m^{-3} Long-term Objective value in East Anglia and the South-East.

The OSRM is a process model calculating the formation of ozone in the UK based on a chemical transport modelling approach using emissions inventory and real meteorological data for 2006. It shows broadly similar patterns compared with the empirical maps in terms of these ozone metrics for 2006, identifying significantly higher concentrations in the south and east of the UK, however there are some specific spatial differences and overall, as has been shown previously, the OSRM in 2006 has generally under estimated ozone concentration metrics compared with measured data. Furthermore, the difference between the concentrations predicted by OSRM and the measured concentrations were larger for the high ozone year (2006) than in previous (low ozone) years (2004 and 2005). This had been observed for a previous high ozone year (2003).

Modelling Impacts of Emission Scenarios on Future UK Ozone

The process modelling capability of the OSRM has been used to model a number of future emission scenarios relevant to policy.

- The impact on UK ozone concentrations of four additional transport emission reduction measures were modelled for the Air Quality Strategy Review (AQSR). For the road transport

measures that involved reductions in NO_x emissions due to tighter Euro 5/6(VI) standards on vehicle emissions, the results tended to show a worsening in the health-based ozone metrics. A slight improvement in ozone was observed when measures reducing NO_x emissions from shipping were included.

- A separate study looked at the impact of reducing shipping emissions alone, using assumptions used in the Air Quality Strategy Review. All metrics show that reducing NO_x emissions from shipping by 9% leads to a reduction in ozone concentrations. Reducing SO_2 emissions by 33% also leads to a small beneficial effect on ozone, but the impact is considerably smaller than the effect of reducing NO_x emissions. It was recommended that the effect of shipping emissions on ozone concentrations be given a more detailed analysis.

- The OSRM was used to model the impacts of changing VOC emissions from road transport across Europe arising from the EU Fuel Quality Directive and the uptake of bioethanol-petrol blends. The focus was on the impacts of potential increases in acetaldehyde emissions from engine exhausts and an increase in evaporative emissions from cars as a consequence of the relaxation of volatility limits of summer blends of petrol to enable the market penetration of bioethanol blends across Europe. The overall conclusion from the modelling study was that the effect of introducing up to 10% bioethanol petrol blends in Europe is unlikely to show any effect on UK ozone levels in the UK up to 2020.

Climate Change Consequences of VOC Emission Controls

A report entitled "*Climate Change Consequences of VOC Emission Controls*" was prepared for Defra to be used as a guide for industry, providing a simple approach, with worked examples, for quantitatively assessing the climate change consequences of VOC emission control by incineration. Defra expect the report to be used as supplementary background technical information for a wider set of guidelines for industry operators and regulators covering the issue of VOC abatement and its environmental consequences.

10.2   Research and Development of Ozone Models

Chemical Mechanisms in Ozone Models

A substantial and in-depth review of the **Master Chemical Mechanism** was carried out by members of the project consortium. The review report was independently peer-reviewed and in response to this, the review's authors prepared a set of revised recommendations for future development of the MCM. The direct policy relevance of the MCM as a crucial tool and source of chemical reactivity information in models for assessing the affect of VOC control options on ozone and other transboundary air pollutant formation in Europe was demonstrated in the review and this demonstration is now being extended.

NO_x-NO_2-O_3 Relationships

A number of analyses of monitoring data have been undertaken to provide more information on local, regional and global contributions to oxidant at UK locations, and to improve the description of the partitioning of oxidant into its component species (i.e., O_3 and NO_2). The work undertaken so far will help to improve the treatment of NO_x-NO_2-O_3 relationships in the PCM empirical model and the surface conversion algorithm of the OSRM, helping to improve predictions of ozone concentrations in urban environments. Such analysis includes further insight into the contribution made by direct emissions of NO_2 principally from traffic sources in urban areas providing a direct additional source of oxidant. Work is currently underway in the Pollution Climate Mapping Programme on incorporating these findings to date into the PCM models.

Modelling Secondary Particulate Matter

Whilst this project is primarily focused on modelling of tropospheric ozone, there is considerable overlap with approaches used to model secondary particulate matter (PM). Process models for forecasting the response of secondary PM formation to changes in precursor emissions (NO_x, SO_2, NH_3, NMVOCs) require similar chemical transport models to the types used for predicting ozone concentrations and there is overlap in terms of evaluating policies affecting the formation of both pollutants. Work was undertaken in this project using the Photochemical Trajectory Model (PTM) and the Met Office NAME model to examine the sensitivity of secondary PM component concentrations to changes in the emissions of PM precursors. The aim was to develop scaling factors that could be used in the PCM to gauge the importance of these non-linearities for policy-making in relation to changes in precursor emissions.

Work in the coming year of the project will have a focus on Objective 4 and the treatment of meteorological processes in the OSRM. The precise details of the work plan are still to be agreed with Defra in light of the recommendations of the recent independent review of Defra's ozone modelling requirements. This is likely to help define the best way forward for improving the treatment of meteorological processes in the OSRM. There is also likely to be an emphasis on improving the use of emission inventories in the OSRM.

Work on improving the chemical mechanisms in ozone models, including the OSRM, is also not yet defined, but will in part be influenced by the MCM Review's recommendations and may involve evaluation of alternative condensed chemical mechanisms to the one currently used in the OSRM. Further demonstrations of the policy relevance of the MCM is also to be undertaken in 2008.

Finally, further analysis of NO_x-NO_2-O_3 relationships will be carried out to improve the treatment of these relationships in the PCM empirical model and the surface conversion algorithm of the OSRM.

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Appendices

CONTENTS

Appendix 1
Model Information Sheet for the Ozone Source
Receptor Model Completed for Defra's External Review
of Tools for Modelling Tropospheric Ozone

Model	**Ozone Source-Receptor Model (OSRM)**
Institution/s	AEA Energy & Environment
Possible contacts	Tim Murrells (AEA)
Email	tim.p.murrells@aeat.co.uk
Type & scale	Lagrangian trajectory model (EMEP domain) 10km x 10km (UK-scale runs), 1 km x 1 km (London runs), 50km x 50km.
	Uses a Surface Conversion Algorithm in OSRM post-processor to convert hourly mid-boundary layer concentrations to surface concentrations with corrections allowing for local NO_x emission rates.
Chemistry	STOCHEM (not evaluated) with additional reactions added to represent (i) HONO chemistry; (ii) reactions of peroxy radicals with NO_3 and (iii) formation of organic nitrates [70 species, 200 thermal and photochemical reactions]
Treatment of VOCs	12 man-made VOCs + isoprene
	C_2H_6, C_3H_8, nC_4H_{10}, C_2H_4, C_3H_6, C_7H_8, C_8H_{10}, CH_3OH, acetone, MEK, HCHO, CH_3CHO
Meteorology	UK Met Office NAME archive (1999-2005)
Emission Inventories	(a) NAEI 1km x 1km emission inventories aggregated to 10 km x 10 km for the UK by sector, with representative temporal profiles applied for each pollutant and sector (diurnal, day of week, month of year)
	(b) EMEP emission inventories at 50 km x 50 km for the non-UK emissions
	(c) Bespoke emission potential inventory for biogenic VOC emissions comprising 8 emission potentials for isoprene and terpenes from deciduous and evergreen trees (50 km x 50 km).
Computer Resources (*super; mainframe; PC*) and typical run time	Cluster of dual-processor workstations
	4.5 days for a UK-scale model run to a 10 km x 10 km grid covering the UK (~3,000 receptor sites). This typically involves a total of ~26 million trajectories to simulate each hour in a calendar year.
Policy relevance	UK policy applications and regulatory impact assessments (e.g., EU Decorative Paints and Petrol Vapour Recovery Directives, Vehicle Emission Directives)

Producible metrics
(hourly, eight hourly, daily,
seasonal, AOT40 etc.)

A post-processor code is used to process the hourly concentrations generated by the OSRM and to calculate a large number of metrics for ozone and nitrogen dioxide (see Annex). The code also produces output datafiles for generating maps of these metrics.

Comments

The OSRM is currently the Defra tool for assessing ozone control policies.

The model was extensively used to assess future ozone concentrations and the effectiveness of measures for the Review of the Air Quality Strategy.

Would benefit from use of a reduced chemical mechanism that can be directly traceable to the Master Chemical Mechanism

Annex - Metrics Calculated by the OSRM

Ozone:

(1)   annual mean concentration

(2)   AOT30 for the protection of crops (EU and UN ECE[1])

(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)   annual mean of the difference between the maximum of the 24 possible 8-hour running mean concentrations in each day and 35 ppb (or 70 $\mu g\ m^{-3}$) for the protection of human health

(19)   annual mean of the difference between the maximum of the 24 possible 8-hour running mean concentrations in each day and 50 ppb (or 100 $\mu g\ m^{-3}$) for the protection of human health

Nitric Oxide: (20)   annual mean concentration

Nitrogen Dioxide: (21)   annual mean concentration

(22)   maximum hourly concentration in the year

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[1] The EU methodology uses fixed hours (08:00-20:00 Central European Time) during the relative accumulation period, whereas the UN ECE calculation uses daylight hours, defined by the incident UV radiation being greater than 50 mW m^{-2}.

Appendix 2

Worked Example (E) for Method for Assessing the Climate Change Consequences of VOC Emission Control and tables of GWPs and fuel CO_2 conversion factors (taken from report by Murrells and Derwent (2007)

Worked Examples for Quantifying the Climate Change Consequences of VOC Emission Controls

The following worked example show how the CO_2 equivalent emissions can be calculated from a given set of input conditions in order to weigh up the climate changes consequences of direct release of the VOCs to be disposed of compared with climate changes consequences of their incineration. The worked example (Case E) was taken from the report "***Climate Change Consequences of VOC Emission Controls***" (T Murrells and RG Derwent. Report to the Department for Environment, Food and Rural Affairs, Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland. AEA Report AEAT/ENV/R/2475 - Issue 3, September 2007). It is not necessarily meant to be realistic in terms of practicalities of incineration, but are meant to illustrate how CO_2 equivalent calculations can be done for different types of input data scenarios.

The GWPs and fuel CO_2 conversion factor are taken from the original report.

Scenario:
In this case, 150 tonnes of a hydrocarbon solvent manufactured from a renewable source with a molecular formula C_6H_{12} are to be disposed of in an incinerator fired by 1100 tonnes of gas oil. Heat may be recovered from the incinerator such that 500 tonnes gas oil can be saved from other parts of the installation. The fuel is not from a renewable source.

CO_2 equivalent emissions from direct release to air
The GWP of the solvent is not given in Annex B, but a value of 10 is assumed due to the indirect effect of the VOC.
Therefore, from equation (1):

$CO_{2\ primary}$ = 10 x 150 = **1,500 tonnes CO_2 equivalent** due to the indirect GWP of the hydrocarbon.

The solvent is from a renewable source, so the carbon it is made up from does not contribute to climate change and hence:

$CO_{2\ secondary}$ = 0, and the total CO_2 equivalent emissions from direct release to air (Eqn 4) is

$CO_{2\ equiv}$ = $CO_{2\ primary}$ = **1,500 tonnes CO_2 equivalent**

CO_2 equivalent emissions from incineration
The CO_2 equivalent emissions arising from the carbon in the VOC that is incinerated (Eqn 5) is:

$CO_{2\ incin}$ = $CO_{2\ secondary}$ = **0 tonnes CO_2 equivalent**

because the VOC is from a renewable source.

Gas oil is used to fire the incinerator with a fuel CO_2 conversion factor, F_{fuel}, taken from Annex C of 3.19 tonnes CO_2 per tonne gas oil.
The CO_2 emissions arising from the 1100 tonnes of gas oil used in the incinerator is (Eqn 6)

$CO_{2\ fuel}$ =   3.19 x 1100 = **3,509 tonnes CO_2 equivalent**

The installation's CO_2 offset from the heat recovery is based on a 500 tonnes gas oil saved is Δm_{fuel}
From Equation 7:

$CO_{2\ offset}$ =   3.19 x 500 = **1,595 tonnes CO_2 equivalent**

Then the total CO_2 equivalent emissions from incineration is (Eqn 8):

$CO_{2\ equiv}$ = 0 + 3,509 – 1,595 = **1,914 tonnes CO_2 equivalent**

Difference in CO_2 equivalent emissions from incineration compared with direct release
The difference is:
$\Delta CO_{2\ equiv}$ = 1,914 – 1,500 = **414 tonnes CO_2 equivalent**

In this case, because the solvent has a low indirect GWP and was being incinerated with a large amount of fossil fuel, the difference has a positive value indicating overall climate change disbenefits in incineration under these conditions compared with direct release of the solvent

Global Warming Potentials (GWPs) of some common VOCs.

VOC Common name	Chemical formula	Other name	GWP, 100 year time horizon
dimethylether	CH_3OCH_3		1[a]
methylene dichloride	CH_2Cl_2	Dichloromethane	10[a]
methyl chloride	CH_3Cl	Chloromethane	16[a]
methyl bromide	CH_3Br	Bromomethane	5[a]
methylchloroform	CH_3CCl_3	1,1,1-Trichloroethane	144[a]
HCFC-22	$CHClF_2$	Chlorodifluoromethane	1,780[a]
HCFC-123	$CHCl_2CF_3$	Dichlorotrifluoroethane	76[a]
HCFC-124	$CHClFCF_3$	Chlorotetrafluoroethane	599[a]
HCFC-141b	CH_3CCl_2F	Dichlorofluoroethane	713[a]
HCFC-142b	CH_3CClF_2	Chlorodifluoroethane	2,270[a]
HCFC-225ca	$CHCl_2CF_2CF_3$	Dichloropentafluoropropane	120[a]
HCFC-225cb	$CHClFCF_2CClF_2$	Dichloropentafluoropropane	586[a]
HFC-23	CHF_3	Trifluoromethane	14,310[a]
HFC-32	CH_2F_2	Difluoromethane	670[a]
HFC-125	CHF_2CF_3	Pentafluoroethane	3,450[a]
HFC-134a	CH_2FCF_3	1,1,1,2-Tetrafluoroethane	1,410[a]
HFC-143a	CH_3CF_3	1,1,1-Trifluoroethane	4,400[a]
HFC-152a	CH_3CHF_2	1,1-Difluoroethane	122[a]
HFC-227ea	CF_3CHFCF_3	1,1,1,2,3,3,3-Heptafluoropropane	3,140[a]
HFC-236fa	$CF_3CH_2CF_3$	1,1,1,3,3,3-Hexafluoropropane	9,500[a]
HFC-245fa	$CHF_2CH_2CF_3$	1,1,1,3,3-Pentafluoropropane	1,020[a]
HFC-365mfc	$CH_3CF_2CH_2CF_3$	1,1,1,3,3-Pentafluorobutane	782[a]
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	1,1,1,2,3,4,4,5,5,5-Decafluoropentane	1,610[a]
HFE-449s1	$CH_3O(CF_2)_3CF_3$		397[a]
HFE-569sf2	$CH_3CH_2O(CF_2)_3CF_3$		56[a]
HFE-347pcf2	$CF_3CH_2OCF_2CHF_2$		540[a]
ethane			8.4[b]
propane			6.3[b]
butane			7.0[b]
ethylene			6.8[b]
propylene			4.9[b]

Notes:

a) Taken from Table 2.6 (pp160-161) in IPCC (2005) calculated using the methodologies therein

b) Indirect GWPs taken from Collins et al. (2002) and Table 2.8 in IPCC (2005) representing the impact of the VOC on the global distribution of methane and ozone

c) If the VOC of interest is not listed, assume default values of 0.1 and 10 for a hydrocarbon, spanning the range between its likely direct and indirect effects, and 100 to 5,000 for a fluorocarbon

Fuel CO$_2$ conversion factors for different fuel types

Fuel type	Fuel factor (tonnes CO$_2$)	Fuel consumption units
Natural gas	0.206	per MWh gas[1]
	6.023	per ktherm gas[1]
Gas oil	3.19	per tonne gas oil
	0.265	per MWh gas oil[1]
	2.674	per thousand litres gas oil
Fuel oil	3.223	per tonne fuel oil
	0.281	per MWh fuel oil[1]
Coal	2.457	per tonne coal
	0.346	per MWh coal[1]
Electricity	0.523	per MWh electricity

[1] Based on Net Calorific Values.

These conversion factors refer to fuels used in 2005 and are based on the 2005 UK Greenhouse Gas Inventory compiled by AEA Energy & Environment (Baggott et al, 2007, http://www.airquality.co.uk/archive/reports/cat07/0704261626_ukghgi-90-05_main_chapters_final.pdf)

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