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Consultation on Ozone in the United Kingdom

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Terms of Reference

The Air Quality Expert Group was set-up in 2001, to provide independent scientific advice on air quality, in particular the air pollutants contained in the Air Quality Strategy (AQS) for England, Scotland, Wales and Northern Ireland and those covered by the EU Directive on ambient air quality assessment and management (the Air Quality Framework Directive). AQEG replaces the Airborne Particles Expert Group, who published their report on 'Source apportionment of airborne particulate matter in the UK' in January 1999.

AQEG reports to the Secretary of State for Environment, Food and Rural Affairs, Scottish Ministers, the National Assembly for Wales and the Department of the Environment in Northern Ireland (the Government and Devolved Administrations). AQEG is an advisory non-departmental public body in England, Wales and Northern Ireland. In terms of the Scotland Act 1998, the Group is a jointly established body.

AQEG's main functions are:

- to give advice to ministers on levels, sources and characteristics of air pollutants in the UK;
- to assess the extent of exceedences of Air Quality Strategy objectives and proposed objectives, EU limit values and proposed or possible objectives and limit values, where monitoring data is not available;
- to analyse trends in pollutant concentrations;
- to assess current and future ambient concentrations of air pollutants in the UK; and
- to suggest potential priority areas for future research aimed at providing a better understanding of the issues that need to be addressed in setting air quality objectives.

The Group will not give approval for products or equipment.

Further information on AQEG can be found on the Group's website at: http://www.defra.gov.uk/environment/airquality/panels/aqeg/index.htm. Information on these pages includes the dates, agendas, and minutes of meetings as they become available, a list of the members, the Register of Interests, and draft and final reports as they become available.

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Executive Summary

High ozone concentrations in the atmosphere near the ground are of concern because of potential effects on human health and damage to vegetation. Air quality strategies in Europe and elsewhere in the world have been directed towards measures to limit ozone levels. However, ozone presents a difficult control problem because it is a gas created in the atmosphere, and not one directly emitted from processes that can be regulated, and its creation can take place over a wide range of time and distance scales. This report by the AQEG provides scientific evidence to inform UK control strategies for ozone.

A network of ozone monitors exists in the UK and has been used to measure ozone continuously since the last authoritative review of ground-level ozone in the UK was published by the Photochemical Oxidant Review Group report in 1997. The measurements indicate variability from hour to hour, day to day and from season to season. This report recognises that there are a number of ways of summarising the ozone concentrations. However uncertainty regarding health and ecological effects means that there is no preferred summary ozone statistic (known as an ozone metric) with which to describe ozone effects. A number of ozone metrics are therefore used in this report. Both long-term and short-term average ozone concentrations (for example annual and hourly averages) need to be considered and so ozone metrics broadly fall into these two categories. AQEG was not able to propose a method of simplifying the analysis and interpretation of ozone metrics.

The ozone metrics are related to standards for protecting health or vegetation. Current levels are not below what would be generally regarded as a safe level. The uncertainty regarding the most suitable choice of metric means that the focus in this report has been on interpreting recent ozone trends and predicting future trends, rather than focusing on exceedences. Changes in ozone concentrations are subject to influences related to ozone producing sources, meteorology and chemical reactions over urban, regional and hemispherical distances.

A detailed analysis of measurements over the last few years shows there is some variability from year to year because of fluctuations in the occurrence of fine weather conditions, associated with episodes of high ozone lasting a few days. However there is evidence of an increase in hemispheric baseline ozone concentrations, expressed as an annual average trend, as a result of increases in global emissions. At the same time, control of NO_x emissions in the UK has led to an increase in ozone in urban areas.

In the future, up to 2030, these trends may continue. Most uncertainty is attached to the trend in hemispheric background ozone. It depends on whether global emissions of ozone-precursors will increase or decrease. If the latter occurred it could lead to a decrease in the annual mean background concentration.

The complexity and spatial scale of processes leading to ozone production means that interpretation and forecasting of ozone has depended on calculations. Some of these calculations have made use of both measurements and mathematical models, in combination, to predict future ozone levels at urban monitoring sites in the UK. Other theoretical models rely on the best current understanding of the chemical and physical processes, leading to predictions of ozone concentrations over regions and globally. These process models can be very complex, making full use of available computing power, especially when aspects of climate change are included. A full evaluation of these models has not been made by AQEG. However confidence in models is such that AQEG would accept the use of simple, intermediate and complex models, when they are used to identify the magnitude of changes in ozone as a result of moderate changes in emissions (that is changes within foreseeable emission scenarios). There has been encouraging agreement between different types of model.

In urban areas where most of the UK population lives, AQEG conclude that over the next two decades urban ozone will rise and tend towards levels in the rural areas that surround urban areas. This is because road traffic NO_x emissions will no longer depress urban ozone concentrations. This effect will be superimposed on any regional and global trends in rural ozone.

Complex global models provide boundary conditions for models of ozone behaviour on a regional scale. They also help to identify climate change processes leading to changes in future global ozone concentrations, but the models cannot incorporate all known processes. For predictions to 2030 the influence of climate change is uncertain, but is thought to be small compared with the direct effect of changes in regional and global emissions of ozone producing gases. Care must be taken with regional and global models that results are not applied where they are not appropriate. For example, they may not be applied without further corrections to urban areas. Further development of more complex urban, regional and global models is likely in future, but full evaluation is necessary before a model is used to determine an emissions control strategy.

Chemical transport models can be used to determine the impact of a source in one location on the concentration of ozone in another. However, for ozone, such relationships can be very complex, because of the way different chemical species interact and the way ozone metrics are applied. Instead this report has looked at the most effective control options to reduce ozone using a number of metrics, where the control option is a broad measure, that is, a reduction of all emissions in one sector, rather than control of a specified source. It turns out that for some of the ozone metrics considered, levels are unlikely to show much change as a result of foreseeable emission reductions. This is partly because these ozone metrics depend on influences over urban, regional and global scales. Regional influences are dependent on combined natural and man-made VOC emissions and the implementation of measures to reduce natural VOC emissions would be difficult to apply. Studies of the impact of foreseeable measures on UK emissions to reduce ozone within the UK also indicate that there is little scope to easily make large ozone reductions. AQEG consider that it is important to understand the factors which influence an ozone metric, before making emission control choices.

An annex to the report shows a range of possible future UK and global emission scenarios. AQEG have considered the additional measures needed, beyond foreseeable measures, to achieve compliance with standards for a range of ozone metrics, including the scenario involving the maximum feasible reduction of VOC and NO_x emissions in the UK and Europe. For some of the emission scenarios considered there would be a worsening of the health-related ozone metrics caused by the increase in urban ozone. There is firm evidence from both modelling and measurement that local action has limited impact on air pollution episodes of high ozone. Large scale reductions of 60% or more, in both the UK and Europe, of VOC and NO_x would be necessary to reduce ozone concentrations in urban areas. Only some of the scenarios approach the scale of reduction needed to bring about the reduction of ozone in urban areas, so that further careful assessment of practical policy options is needed. These should take into account the impact of future global methane and CO emissions, emissions of NO_x from shipping worldwide and natural emissions of VOCs in Europe.

The main chapters of this report answer seven questions posed by Defra. Each chapter takes the form of a short answer, followed by a more detailed answer and then by supporting evidence. The following box contains the questions and the short answers.

Question 1: A large quantity of urban and rural monitoring data have been collected since the last PORG report, by Defra's own networks, local authority stations, and elsewhere. What does this reveal in terms of trends (using metrics considered relevant to effects) and spatial concentration patterns?

Annual mean ozone concentrations have generally increased over the last 10 years or so in urban areas, while the changes in concentrations in rural areas are less marked and show variations with location and time. Ozone concentrations are generally lower in urban areas than in the surrounding rural areas due to reaction with NO_x (mostly NO) emissions, which are greatest in urban areas. The main cause of the increase in urban areas is the reduction in NO_x emissions, which has led to a decrease in this "urban decrement", reducing the differences between urban and rural concentrations.

Reductions in precursor emissions in the European region have led to reductions in peak ozone concentrations at rural sites, although there are significant variations from year to year due to the weather, with higher concentrations generally measured in years with hotter summers (such as 1995, 2003 and 2006). The trends in some of the health-based ozone metrics are influenced by both changes in mean and peak concentrations.

Question 2: Observations since the 1970s have shown that global background ozone concentrations have been rising throughout this period. What is the strength of these data, and what is the evidence concerning the trends and likely projections of precursor emissions, and the resultant ozone concentrations?

There is strong evidence that background or, more strictly, baseline surface ozone concentrations in the northern hemisphere have increased by up to 10 μg m^{-3} per decade over the last 20 to 30 years. This increase has been attributed to the growth in man-made ozone-precursor emissions from industry, road, air and ship transport, homes and agriculture. Future ozone concentrations depend on which of the possible future emission scenarios is followed. Future annual mean surface ozone concentrations in the southern half of the United Kingdom are simulated to increase by about 6 μg m^{-3} in a "current legislation" (IIASA CLE) scenario and to decrease by about 4 μg m^{-3} in a "maximum feasible reduction" (IIASA MFR) scenario between 2000 and 2030. Observed baseline ozone concentrations over the 2000 – 2006 period have remained level and have shown no overall trend.

Question 3: What is the likely impact of climate change on future ozone levels in Europe, over the next two decades? What is the significance of such impacts compared to other influences, such as inter-annual variability or (global and regional) emission trends?

The net impact of climate change on mean surface ozone levels over Europe on the 2030 time horizon is not known with any confidence but is likely to be small compared with the most important influence. This is the trends in the anthropogenic emissions in Europe and throughout the whole northern hemisphere of the important precursor gases to ozone formation: nitrogen oxides (NO_x), methane (CH_4), and non-methane volatile organic compounds (NMVOC), in particular, and carbon monoxide (CO). Climate change may have relatively greater influence on future peak episodic ozone in particular geographic areas through a number of different mechanisms such as changes in precursor emissions, ozone loss by deposition, and meteorology. Inter-annual variability in annual mean surface ozone at a given location is large compared with the likely magnitude of net ozone change by 2030, so multi-year data series are necessary for unravelling the competing influences on ozone concentration at different locations.

Question 4: What are the likely future trends in urban ozone concentrations over the next two decades and what is driving them?

Urban ozone concentrations are expected to rise over the next two decades and to tend towards the levels found in the rural areas that surround them. The increases in urban ozone concentrations are largely driven by vehicle emission controls that have brought about a reduction in NO_x emissions in urban areas. Road traffic NO_x emissions have previously depressed urban ozone levels below rural levels and although this titration effect is being diminished by pollution controls, many urban areas in the UK are still expected to have lower ozone concentrations in 2020. Urban ozone concentrations will also respond to the changes occurring to ozone in the surrounding rural areas, largely driven by changes on the hemispheric/global scale. Depending on the strength of these trends, these could also cause increases in urban ozone, which will be in addition to the NO_x-titration effect.

Question 5: Ozone is currently modelled on a number of spatial and temporal scales. What are the main uncertainties associated with such work, and what research is required to reduce these uncertainties?

Although a number of models address ozone on a range of temporal and spatial scales across the UK, there is no consistent and comprehensive understanding of model performance and the uncertainties that affect them. Research is required to understand and intercompare the influence of different spatial and temporal resolutions, chemical mechanisms and parameterisations upon predicted concentrations and their policy implications. This process would involve harmonising model performance evaluation and collecting information on uncertainties of the various model formulations. Research is also required to evaluate the relative importance of man-made and natural biogenic sources of ozone-precursors.

Question 6: Integrated assessment modelling to support the European Commission's Thematic Strategy for Air Quality suggests that regional ozone levels in the UK are likely to remain relatively steady regardless of foreseeable emission reductions across Europe. Does the Group agree with this analysis and what is the explanation for this lack of response to reductions in precursor emissions?

The Air Quality Expert Group agrees that under the specific emission scenarios considered within the European Union's CAFE strategy, regional ozone levels in the UK are likely to remain steady in the foreseeable future. However, the Group disagrees that regional ozone levels in the UK are likely to remain steady regardless of all foreseeable emission reduction scenarios across Europe or that the CAFE strategy findings indicate a lack of response in regional ozone levels to precursor emissions more generally.

Question 7: What are likely to be the most effective control options to reduce UK population exposure to ozone (in terms of precursors to be targeted), and on what scale should they operate? The Group may include discussion of the types of controls they consider to be feasible, but do not need to consider the policy implications of such measures.

The ozone-precursor compounds of relevance are methane, non-methane volatile organic compounds (NMVOC), oxides of nitrogen and carbon monoxide. While UK action can be beneficial, effective control of ozone concentrations in the UK requires emission reductions to be implemented throughout Europe and increasingly the entire northern hemisphere. Local actions, especially those of a short-term nature to address episodes of high ozone concentrations, have generally had, or been simulated to have, limited benefits.
Control of NMVOC emissions will almost always lead to an improvement in ozone air quality and a reduction in population exposure. Additional benefits result from concerted international action and from focussing the emission control on those source sectors making the largest

contributions.
Methane mitigation is seen as a cost-effective strategy in international ozone management, bringing multiple benefits for air quality, public health, agriculture and the climate system.
Less attention has been paid to global CO emissions but reduction of these emissions also has the potential to improve ozone air quality.
The picture is more complicated for control of NO_x emissions; large emission reductions are generally needed in urban areas to overcome the initial ozone disbenefit. Control of the rising emissions of NO_x from shipping would also be beneficial to annual and summer-time mean ozone in Western Europe.

Chapter 1

Introduction

1. The Department for Environment, Food and Rural Affairs and the Devolved Administrations commissioned this, the fifth report from the Air Quality Expert Group (AQEG), in order to inform ozone policy considerations. The report investigates the recent historic trends, current status and likely future changes to tropospheric ozone concentrations in the UK. The main focus is on human exposure to ozone pollution, particularly in urban areas, and it largely excludes damage to vegetation and ecosystems. By necessity, AQEG has also considered trends and changes to ozone-precursor emissions on the European and global scales, as a background to the main focus of the report. These aspects are relevant to ozone's role as an important greenhouse gas, which was discussed in detail in the third AQEG report *Air Quality and Climate Change: A UK Perspective.* Defra requested that the report should be structured as a series of short answers to seven questions, plus supporting evidence where necessary. The questions and short answers are listed in the Executive Summary.

2. Much of the background material needed for this report may be found in the fourth report of the Photochemical Oxidants Review Group (PORG), published in 1997. PORG was an official body of experts, set up by the then Department of Environment, to review current knowledge on the physical and chemical aspects of photochemical oxidants and associated precursors.

3. Ozone is one of the more important photochemical oxidants. It is a secondary pollutant formed photochemically from the sunlight-initiated oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides, NO_x (= NO + NO_2). The chemistry of ozone formation is discussed in some detail in Chapter 2 of the fourth PORG report. The timescale of VOC oxidation, and hence of ozone formation, is quite long – hours, days, or even longer – so that ozone is formed many kilometres downwind of the emissions of its precursors. Ozone formation is a transboundary process and international agreements are required for its control. The human health impacts of ozone derive from its irritant properties and its induction of an inflammatory response in the lung. Ozone also has adverse effects on crop yields, on tree growth and on the composition of natural plant communities.

4. Episodes of high ozone concentrations typically occur in summer, when the solar intensity is higher, leading to increased rates of photochemical oxidation of VOCs. Under anticyclonic conditions, the airflow in the UK is usually from the east and continental sources of ozone-precursor emissions are important. There is a substantial year to year variability in summer ozone concentrations, because of the variability in the weather. There has also been a decrease in UK peak ozone concentrations over the last 20 to 30 years, because of reductions in emissions of precursor species in Europe.

5. Ozone concentrations are generally lower in urban regions than in surrounding rural regions because of the effects of emissions of NO_x, which are greatest in urban regions. NO reacts rapidly with ozone to form nitrogen dioxide, leading to this urban decrement. Reductions in NO_x emissions over the last 10 to 15 years have led to a reduction in this decrement, so that ozone concentrations in urban areas have generally increased.

6. Intercontinental transport of ozone and of ozone-precursors has an important impact on ozone concentrations on regional and local scales. Ozone is formed in the background troposphere, especially in the northern hemisphere, mainly by the oxidation of methane and also CO. NO_x is again essential for ozone formation and derives from anthropogenic emissions, but also from natural sources such as lightning and from soil emissions.

Transport of ozone from the stratosphere, where mixing ratios are higher, provides a further source of ground level ozone.

7. There has been more than a doubling of the tropospheric background ozone concentration since 1850, reflecting the anthropogenic influence. An increase was seen in the background ozone concentration in the latter part of the 20th century monitored at suitably placed stations both in Europe and elsewhere. This increase is ascribed to import of ozone from across the North Atlantic. It has a direct influence on the ozone budget, which is further augmented by regional ozone formation. An increase in background ozone reduces the magnitude of the regional contribution required for exceedence of ozone standards.

8. The Air Quality Strategy (2007) confirmed the air quality objective, which applies from the end of 2005, of 100 μg m^{-3} measured as the daily maximum of a running 8-hour mean ozone concentration, not to be exceeded more than 10 times a year. The European Union has a less stringent target of a daily maximum of a running 8-hour mean of 120 μg m^{-3}, not to be exceeded more than 25 times a year, averaged over three years. The date for achievement of this target is 31 December 2010. Target values for the protection of vegetation and ecosystems are based on critical levels and cumulative exposure. The AOT40 index is based on exposure over 40 ppb (80 μg m^{-3}) during daylight hours in the growing season. The current Air Quality Strategy and EU targets for AOT40 are 18,000 μg m^{-3} h, calculated from one hour values from May to July and to be achieved, so far as possible, by 2010.

9. The National Emissions Ceiling Directive, NECD (2001/81/EC) sets ceilings for each member state of the EU for emissions, *inter alia*, of the ozone-precursors NO_x and non methane VOCs, to be met by 2010. Member States are obliged to report each year their national emissions inventories and projections for 2010. A consultation draft on the updated UK national programme to meet the NECD was published in October 2006. Wider international agreements on emissions of ozone-precursors are negotiated through the UNECE Convention on Long Range Transboundary Air Pollution (CLRTAP). The 1999 Gothenburg Protocol sets emissions ceilings for NO_x and VOCs for 2010. The percentage reductions required vary from country to country, but, once fully implemented, they should cut European emissions of NO_x by 41% and of VOCs by 40%, compared to 1990.

10. Three other reports on ozone are in preparation:

- Defra has commissioned a report on ozone impacts on vegetation and ecosystems. This report will update the NEGTAP report (2001) and is likely to be published in 2009.
- The Royal Society's project on Ground Level Ozone in the 21st Century complements the two Defra reports. It examines likely changes in ozone on a 50 to 100 year timeframe, and will specifically address the effects of climate change. The report will be published in late 2008.
- UNECE has set up a Task Force on Hemispheric Transport of Air Pollution which will report by 2009 to inform CLRTAP on hemispheric air pollution and, in particular, on source receptor relationships for transcontinental transport of air pollution. An interim report was published in 2007 to inform the review of the Gothenburg Protocol.

11. This report from AQEG addresses the seven questions posed by Defra and laid out in the Executive Summary. It examines a shorter timeframe than the Royal Society report, and is limited to the next two decades. The chapters of the report each address a specific question. A short answer is provided, together with a fuller answer, followed by the

supporting evidence. The Executive Summary includes the short answer to each question. The supporting evidence is substantial for Chapter 2 and Chapter 8, because of the need to analyse and assess monitoring data and to examine model results.

12. In discussing global and regional emission projections, this report refers, in a number of places, to the IPCC Special Report on Emission Scenarios (SRES) and the scenarios developed by the International Institute for Applied Systems Analysis (IIASA) for the Regional Air Pollution Information and Simulation (RAINS) model. A brief summary of these emission projection scenarios is given in Box 1.1.

Box 1.1 The IPCC SRES and IIASA RAINS Global Emission Projection Scenarios

The SRES scenarios (IPCC, 2001) provide global emission projections of ozone-precursor gases for a wide range of scenarios covering the main emission driving forces, from demographic to technical and economic development. The Terms of Reference for the SRES scenarios did not require consideration of any future policies that explicitly address climate change. The SRES scenarios are broadly grouped into four families following different "storylines", each assuming a distinctly different direction for future developments.

The A1 storyline is for a future world with very rapid economic growth, global population that peaks in mid-century and declines thereafter, the rapid introduction of new and more efficient technologies and with a substantial reduction in regional differences in per capita income. Within this family are three sub-scenarios with different technological emphasis:

A1FI – A1, fossil fuel intensive
A1T – A1, with non-fossil energy source emphasis
A1B – A1, with a balance across energy sources.

The A2 storyline is a more pessimistic scenario, describing a very heterogeneous world based on self-reliance, regional differences in economic and technological development and continuous increase in global population.

The B1 storyline describes a convergent world like A1, with global population peaking in mid-century, but with rapid changes in economic structures, introduction of clean and resource-efficient technologies, emphasis on global solutions to social and environmental sustainability.

The B2 storyline describes a world with emphasis on local solutions to social and environmental sustainability, less rapid and more diverse than in B1 and A1, with continuously increasing global population, but at a lower rate than A2.

Emission projections for the SRES scenarios and further details can be found at http://www.grida.no/climate/ipcc_tar/wg1/519.htm

Two main emission projection scenarios have been developed by IIASA: the "Current Legislation" (CLE) scenario and the "Maximum Technically Feasible Reduction" (MFR) scenario. These have been developed for a global version of the Regional Air Pollution Information and Simulation model (RAINS, Schöpp *et al*., 1999) and the model used to forecast ozone-precursor emissions by region and source sector to 2030.

The "Current Legislation" (CLE) scenario reflects the current perspectives of individual countries on future economic development and takes into account the anticipated effects of presently decided emission control legislation in the individual countries. The CLE scenario considers the state of national emissions legislation in each country as of the end of 2002 and the evolution of emission controls in the coming years as laid down in the legislation. International and national fuel quality and emission standards currently in force in Europe and North America were considered and information and standards were collected for other countries and world regions. Country-, sector- and technology-specific impacts of emission control measures were

considered. These included combustion modification and secondary measures like Selective Catalytic Reduction (SCR) for reduction of NOx emissions from stationary combustion; lower sulphur fuels and flue gas desulphurisation for reduction of SO_2 emissions; engine modification and catalyst- and filter-based exhaust after-treatment systems on mobile sources. Emission controls for methane include modified practices in agriculture, technologies for waste treatment (e.g. landfill gas recovery), energy production and reducing natural gas leakage.

The "Maximum Technically Feasible Reduction" (MFR) scenario is a more optimistic emission reduction scenario based on the full implementation of all presently available best technical emission control measures while maintaining the same projected level of anthropogenic activities worldwide. The focus is on the theoretical potential of today's most advanced emission control technologies and the MFR scenario does not take into account their practical limitations and the high costs associated with their global penetration. But it also does not take account of the potential benefits of non-technical measures that modify energy demand or human behaviour such as increased energy efficiency measures, fuel substitution and reduced transport demand.

Further details of the IIASA RAINS model and the CLE and MFR emission scenarios and their application to tropospheric ozone modelling can be found in Amann *et al.* (2004), Cofala *et al*. (2006), Dentener *et al.* (2005) and Schöpp *et al.* (1999).

1.1 Ozone metrics of relevance to human health

13. A number of ozone metrics have been used in this report and those relevant to human health are shown in Table 1-1.

14. Ambient concentrations of primary air pollutants (that are emitted directly into the atmosphere) typically have highly skewed distributions of hourly concentrations with the mode at low concentrations and a small number of hours with high concentrations. Ozone is a secondary pollutant with a non-zero hemispheric background concentration and frequency distributions are therefore very different from those found for primary pollutants. Similarly annual mean concentrations can be made up from very different frequency distributions and the annual mean does not capture all of the features of ambient concentrations that may be of concern in terms of the impact on human health, such as short periods of high concentrations. A range of different metrics are therefore used for ozone and these metrics reflect different features of the frequency distribution of hourly concentrations. These frequency distributions in turn vary with location and reflect the differing influences of local, regional and global factors determining ozone concentrations. Examples of these different frequency distributions are given in the supporting evidence for Chapter 2.

15. Several of the metrics listed in Table 1-1 are based on the annual average of the daily maximum of the running 8-hour mean concentration. (The running 8-hour mean is assigned the date of the last hour of the running mean using GMT.) The metrics are calculated using cut-off concentrations of zero (that is, including all days), 70 µg m^{-3} and 100 µg m^{-3}. For the metrics with cut-offs, the cut-off concentration is subtracted from the daily maximum of the running 8-hour mean concentration and the value set to zero if the result is zero or negative. The average across all of the days in the year is then calculated. These metrics have been recommended as appropriate for the assessment of the impact of the daily variation in ozone concentration on human health. The range of cut-offs reflects uncertainty as to whether there is a threshold for ozone (COMEAP, 1998). WHO concluded that there was evidence that associations existed below the current guideline value (120 µg m^{-3}), but their confidence in the existence of associations with health outcomes decreased as the concentrations decreased (WHO, 2004). The cut-off at 70 µg m^{-3} is not based on direct evidence of a threshold for health effects at this value. It was recommended (UNECE/WHO, 2004) for use in cost-benefit analysis and integrated

assessment modelling on the basis of a combination of the uncertainty in the shape of the concentration response function at low ozone concentrations, the seasonal cycle and geographical distribution of ozone concentrations and the range of concentrations for which European scale ozone modelling was able to provide reliable estimates.

16. The metric of the annual average of the daily maximum of the running 8-hour mean with a cut-off at 70 µg m^{-3} is closely related to the SOMO35 (sum of means over 35 ppb) metric adopted for European scale integrated assessment modelling. It can be calculated by multiplying the 70 µg m^{-3} cut-off metric by the number of days in the year and the application of a factor to take account of the different units used. We have calculated the 70 µg m^{-3} cut-off metric in µg m^{-3}, SOMO35 is typically quoted in ppb.days or ppm.days. The 70 µg m^{-3} cut-off metric is preferred over SOMO35 because the units are easier to interpret and compare with other metrics and the magnitude of the metric is not unduly influenced by low data capture in a year.

17. The metric most sensitive to peak concentrations during photochemical episodes is the maximum 1-hour average during the year. This metric is thus likely to show a response to reductions in relevant precursor emissions. It is, however, highly variable from year to year and from site to site and is particularly subject to instrument malfunction or interference. High percentiles of the hourly concentration, such as 99.9th or 99th percentile are therefore sometimes preferred for data analysis.

Table 1-1 The ozone metrics of relevance to human health considered in this report

Metric	Relevance	Key influences on the values of this metric at urban locations
Annual average	Basic metric used to show long-term trends.	Includes all of the hours in the year. Strongly influenced by the magnitude of local NO_x emissions
Annual average of the daily maximum of the running 8-hour mean	Used as "basic metric" for many of the health metrics. Also used as for Defra's air quality indicator.	Strongly influenced by the magnitude of local NO_x emissions
Annual average of the daily maximum of the running 8-hour mean with a 70 µg m^{-3} cut-off	Health impact, related to SOMO35	Influenced by the magnitude of local NO_x emissions and by photochemical episodes
Annual average of the daily maximum of the running 8-hour mean with a 100 µg m^{-3} cut-off	Health impact	Strongly influenced by photochemical episodes and to a lesser extent the magnitude of local NO_x emissions
Maximum 1-hour average (peak hour in the year)	Used as the basis for some epidemiological studies, although has been suggested that 8 hour is more representative. Also an indicator of short term peaks.	The metric most sensitive to peak concentrations during photochemical episodes and thus likely to show a response to reductions in relevant precursor emissions.
Number of days with daily maximum of running 8-hour mean exceeding 100 µg m^{-3}	Equates to the number of exceedences of the UK ozone standard (AQS objective is no more than 10 exceedences per year)	Strongly influenced by photochemical episodes and to a lesser extent the magnitude of local NO_x emissions

Number of days with daily maximum of running 8-hour mean exceeding 120 µg m^{-3}	Equates to the number of exceedences of the EU Target Value (no more than 25 days, averaged over 3 years) and Long Term Objective (no exceedences) from the 3rd Daughter Directive	Strongly influenced by photochemical episodes and to a lesser extent the magnitude of local NO_x emissions
SOMO35 (sum of means over 35 ppb)	Used as a metric by IIASA, for CAFE and NECD revision, related to Annual average of the daily maximum of the running 8-hour mean with a 70 µg m^{-3} cut-off	Influenced by the magnitude of local NO_x emissions and by photochemical episodes

1.2 Units

18. Concentration units of µg m^{-3}, where the volume of air is standardised to 20°C and a pressure of 101.3 kPa, are used where possible in this report, as these are the units used in current legislation. On occasion, and especially in the supporting evidence for the answer to Question 3, ozone mixing ratio, in units of ppb (parts per billion, i.e. the number of ozone molecules within a sample of air containing 1,000,000,000 molecules in total) has been used. Much of the evidence for this answer relies on global atmospheric models of trace species concentrations. Modelling studies use mixing ratio to describe trace species abundance because the chemical processes, for example, reactions with NO and NO_2, are much clearer with ppb than with µg m^{-3} units. The ppb unit also features in the ozone metric SOMO35.

19. There is a simple conversion between the two units as defined here, with:

$$1 \text{ ppb of ozone} \equiv 2.00 \text{ µg } m^{-3}.$$

Chapter 2

Temporal trends and spatial distributions in ozone concentrations determined from monitoring data

Question 1: *A large quantity of urban and rural monitoring data have been collected since the last PORG report, by Defra's own networks, local authority stations, and elsewhere. What does this reveal in terms of trends (using metrics considered relevant to effects) and spatial concentration patterns?*

Short answer to question 1

20. **Annual mean ozone concentrations have generally increased over the last 10 years or so in urban areas, while the changes in concentrations in rural areas are less marked and show variations with location and time. Ozone concentrations are generally lower in urban areas than in the surrounding rural areas due to reaction with NO_x (mostly NO) emissions, which are greatest in urban areas. The main cause of the increase in urban areas is the reduction in NO_x emissions, which has led to a decrease in this "urban decrement" (see Box 2.1 below), reducing the differences between urban and rural concentrations.**

21. **Reductions in precursor emissions in the European region have led to reductions in peak ozone concentrations at rural sites, although there are significant variations from year to year due to the weather, with higher concentrations generally measured in years with hotter summers (such as 1995, 2003 and 2006). The trends in some of the health based ozone metrics are influenced by both changes in mean and peak concentrations.**

Box 2.1 Urban Decrement

The focus of this report is on ozone concentrations in urban areas. Ozone concentrations in urban areas are typically lower than those in the surrounding countryside as a result of its removal by reaction with NO, for which emissions are greatest in urban areas. We have used the term "urban decrement" to describe the amount by which ozone concentrations are lower in an urban area than in surrounding rural locations. An urban decrement can be defined for the annual mean ozone concentration or any of the other human health related ozone metrics that we have considered.

Detailed answer to question 1

2.1 Introduction

22. The main influences on urban ozone concentrations have been described in the introduction. They are:

- Regional photochemical ozone production
- An urban decrement due to local emissions of NO
- The hemispheric background

23. Changes in hemispheric background ozone concentrations are discussed in detail in Chapter 3.

2.2 Temporal trends

2.2.1 Annual means

24. Annual mean ozone concentrations at urban sites generally show an increase in concentration over the last 10 years or so due to the reduction in local emissions of NO in urban areas. This is generally the strongest influence on annual means in urban areas. This increase is due to the change in the partitioning of the total oxidant between NO_2 and ozone as NO emissions have reduced. The magnitude of the increase is generally greatest at the locations with the largest reduction in NO concentrations. These are typically the urban background locations with the highest initial local NO_x emissions. Roadside locations with very high emissions generally do not show as large an increase in ozone concentrations. A site-specific model combining emission inventories for NO_x and the oxidant partitioning model of Jenkin (2004) can explain the trends in measured annual mean ozone concentrations at urban sites with considerable success.

25. Annual mean ozone concentrations are also influenced by the magnitude of the regional photochemical generation of ozone and the years with higher annual means such as 1995, 2003 and 2006 correspond to warmer summers with more frequent photochemical episodes.

26. The trends in annual mean ozone concentration at rural sites are generally less steep and are variable from site to site. This is because the influences of the changes in hemispheric background concentrations, regional photochemistry and the reduction in NO titration vary from site to site. Remote sites in the north west are most likely to show the influence of changes in hemispheric background concentrations in terms of overall trends and year to year variability, although these influences can also be detected at sites in the south east and urban sites using modelling methods to isolate the different influences.

27. The influences on ozone concentrations also vary according to season. The seasonal variation is much more pronounced for air masses that are influenced by regional emissions. This results in ozone concentrations lower than the hemispheric background in the winter due to titration with NO and higher in the summer due to photochemical ozone production.

2.2.2 Peak concentrations

28. The trend in the annual maximum of 1-hour ozone concentrations (peak ozone concentrations) is generally downwards at rural sites as a result of the control of regional anthropogenic VOC and NO_x emissions, although there is considerable year-to-year variability due to the weather. The trends in high percentile 1-hour ozone concentrations (99.9^{th} percentile, for example) and in maximum and high percentile 8-hour concentrations are similar. This is consistent with ambient measurement data for VOCs, which show a consistent downward trend in the concentrations of the more reactive anthropogenic VOCs associated with ozone formation at monitoring sites in the UK. The recent downward trends in the emissions and ambient concentrations of NO_x have been described in AQEG's reports on NO_2 (AQEG 2004, 2007). Observations of the reactive hydrocarbon isoprene in the UK are indicative of elevated inputs of biogenic hydrocarbons during summertime (particularly during heat-waves), although the inferred biogenic isoprene input is substantially greater than current assessments of biogenic isoprene sources in the UK.

29. The trends in peak ozone concentrations at urban sites are generally flatter because the reduction in local NO_x emissions has tended to decrease the urban decrement during photochemical ozone episodes at the same time as the peak ozone concentrations at rural sites have declined.

30. A comparison of measured peak ozone concentrations at rural sites and those in central London over the last 15 years or so illustrates this well (see Figure 2.18).

2.2.3 Exceedence metrics

31. The trends in the number of days with the daily maximum of running 8-hour mean ozone concentration above 100 µg m^{-3} and 120 µg m^{-3} are generally strongly influenced by photochemical episodes and to a lesser extent by the magnitude of local NO_x emissions. The number of exceedence days is highly variable from year-to-year due to variations in meteorology but is generally downwards at rural sites, although to a lesser extent than the peak ozone concentration. A reduction in the urban decrement in the number of exceedences per year at urban sites compared with that at nearby rural sites might have been expected as NO_x emissions have declined, although such a trend is not readily apparent from the measurement data.

2.2.4 Health based metrics based on the annual average of the daily maximum running 8-hour concentration with various cut-offs

32. The trends in the annual average of the daily maximum of the running 8-hour mean concentration generally follow the trends in annual mean concentration, although the value of this metric for a given year is higher, since it is based on the daily maximum concentration.

33. Trends in the annual average of the daily maximum of the running 8-hour mean with a 100 µg m^{-3} cut-off are sensitive to both photochemical episodes and the magnitude of local NO_x emissions, especially in urban areas. This metric generally shows a decline at rural sites due to the reductions in the emissions of precursor species but with considerable year-to-year variability. The trends at urban sites are unclear with competing influences of the reduction in regional photochemical ozone and the reduction in local NO_x emissions. The trends in annual average of the daily maximum of the running 8-hour mean with a 70 µg m^{-3} cut-off and thus SOMO35 are somewhat clearer at urban sites with many sites showing an increase as local NO_x emissions have reduced. The trend in this metric at rural sites is less clear with considerable year-to-year variability since the cut-off for this metric is very close to typical hemispheric background concentrations.

2.3 Spatial patterns

34. The spatial pattern of ozone concentrations across the UK varies depending on the metric illustrated and from year to year due to variation in the weather and changes in emissions. Maps of a range of ozone metrics have been calculated using empirical measurement based PCM models for the years 1995, 2003 and 2005. These years have been chosen to illustrate two recent years with high and low photochemical ozone contributions (2003 and 2005, respectively) and a year with high photochemical ozone contributions combined with high urban NO_x emissions (1995).

2.3.1 Annual means

35. The hemispheric background is a major contributor to annual mean ozone concentration across the UK. Upland areas tend to have the highest annual mean ozone concentrations

due to topographic effects, as has been described by PORG (1997). There is also a significant decrement in urban areas, as discussed above. Annual mean concentrations in rural areas were highest in 2003 and lowest in 2005 at most locations due to the photochemical episodes during 2003 and perhaps a higher hemispheric background in 2003. Urban concentrations were lowest in 1995 due to the greater local NO_x emissions at the time, as illustrated by the results of a transect across London (see Figure 2.32).

2.3.2 Exceedence metrics

36. The spatial distribution of the number of days with running 8-hour mean ozone concentrations greater than 100 µg m^{-3} and greater than 120 µg m^{-3} is dominated by the contribution from photochemical episodes and therefore highly variable from year to year. The number of days above 100 µg m^{-3} was highest in the south and south west and Wales in 1995, highest in the south east in 2003 (and also high in the north of Scotland in 2003 due to the higher background) and highest in East Anglia in 2005 although values were generally much lower. There are also clear urban decrements for these metrics.

2.3.3 Health based metrics based on the annual average of the daily maximum running 8-hour concentration with various cut-offs

37. The maps of the annual average of the daily maximum of the running 8-hour mean concentration have been calculated from the annual mean maps using a non-linear function and thus show a similar spatial pattern.

38. Values of the annual average of the daily maximum of the running 8-hour mean concentration with a cut-off of 100 µg m^{-3} metric were much higher in 2003 than in 2005. Values were higher in south and south west England and Wales in 1995 than in 2003 for this metric. This is in contrast to the annual mean, which was higher in 2003 in these areas. The contribution from photochemical episodes and an urban decrement are the most important factors influencing the spatial distribution for this metric.

39. Maps of the annual average of the daily maximum of the running 8-hour mean concentration with a cut-off of 70 µg m^{-3} show highest concentrations in the south of the UK, where the contribution from photochemically generated ozone is greatest and in northern Scotland, where the impact of the hemispheric background is most pronounced due to the low regional NO_x emissions in this area. There is also an urban decrement for this metric. Concentrations were generally highest in 2003 and lowest in 2005 due to the larger contribution from photochemical ozone episodes in 2003 and 1995. Urban concentrations were lowest in 1995 due to the greater local NO_x emissions at the time.

2.3.4 Transects

40. A comparison of the modelled transects of ozone concentrations for the annual mean and other health based metrics across London with data from monitoring sites close to the transect confirms that the empirically generated maps include a reasonably realistic description of the urban decrements.

2.4 Concluding remarks

41. It is clear that the temporal trends and spatial patterns are different for the different ozone metrics and respond in different ways to changes in the key influences on ozone concentrations. Any consideration of the impact of possible future measures on urban ozone concentrations should therefore consider a range of metrics, and this is the approach that we have adopted in answering Question 7.

Supporting evidence for question 1

2.5 Overview

42. Data from the UK automatic monitoring network and elsewhere indicate that the concentration of ozone at a given location in the UK can be influenced by a combination of global (hemispheric), regional and local scale effects. As a result, the observed trend in ozone concentrations, concentration distributions and related metrics is determined from the net trend of these three influences, the relative contributions of which can vary both spatially and temporally. Specifically, the data demonstrate the following three major influences:

I. The hemispheric baseline ozone concentration has been gradually increasing as a result of global-scale effects, thereby influencing the background or baseline levels of ozone brought into the UK from the Atlantic Ocean.

II. Substantial short-term elevations in ozone concentrations during summertime episodes are a consequence of the formation of additional ozone from regional-scale photochemical processing of emitted VOC and NO_x, with such events tending to be more frequent and intense towards the south of the UK. Their severity has progressively decreased since about 1990 as a result of EU controls of anthropogenic VOC and NO_x emissions.

III. The control of NO_x emissions in the UK has reduced local-scale removal of ozone by reaction with emitted NO, contributing to a general increase in ozone concentrations since about 1990. This has most relevance to urban areas, where NO_x emissions are higher.

43. In the following sections, the effects of the above influences are illustrated by a systematic consideration of ozone observations at remote, rural and urban locations. Trends in the observed concentrations of hydrocarbons and NO_x are also presented, with specific reference to trends in VOC and NO_x emissions. Additional information is given in Annex 3.

2.6 Ozone observations at remote network locations

44. Figure 2.1 demonstrates the trend in the hourly mean ozone distributions (illustrated by the annual maximum, annual minimum and selected percentiles of the hourly-mean ozone concentrations) at Strath Vaich, a remote site in north Scotland, for the period 1990-2006. This site is characterized by very low NO_x levels, the annual mean typically being 1 µg m^{-3} or less. There has been little change in the maximum ozone concentration at this site although, similarly to other locations described below, it displays substantial scatter. However, the 95th through to the 5th percentiles of the ozone concentrations all display statistically significant upward trends in the range 0.3-0.5 µg m^{-3} yr^{-1}, with a small upward trend also observed in the minimum. The reasonably similar upward trend across the majority of the distribution is consistent with observations at this remote location being dominated by the trend in the hemispheric ozone baseline, which is described and discussed in more detail in Chapter 3. The seasonal cycle of ozone concentrations at Strath Vaich thus typically displays the springtime maximum, characteristic of baseline air. To illustrate this, Figure 2.2 shows daily ozone concentrations (as the maximum of the 8-hour running mean) for the example year of 2005.

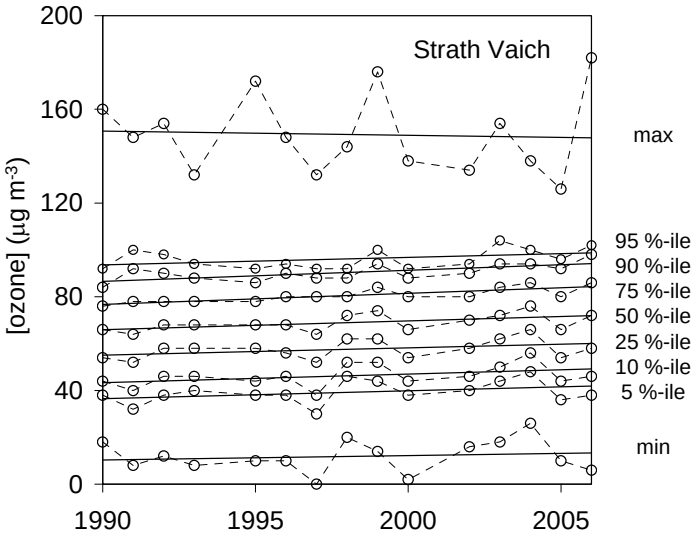


Figure 2.1 Trend in hourly-mean ozone distributions at Strath Vaich (a remote site in northern Scotland), based on data over the period 1990-2006. Solid lines are linear regressions of data indicating the average trend over the period.

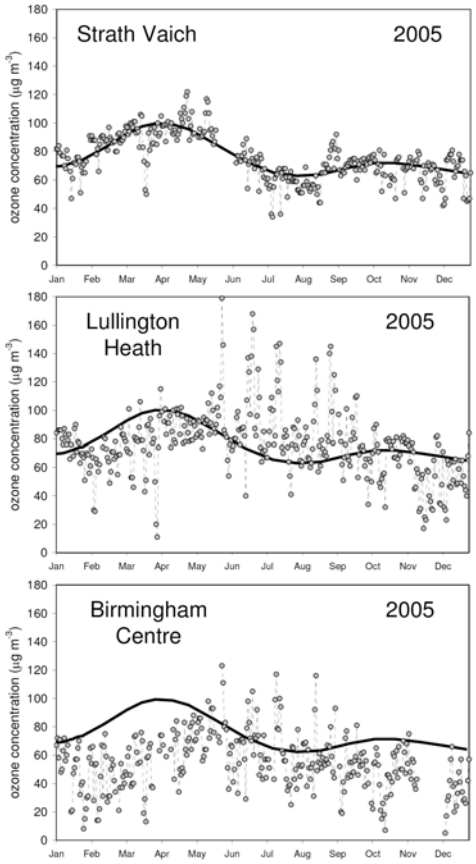


Figure 2.2 Daily maximum of the 8-hour running mean ozone concentrations in 2005 at Strath Vaich (a remote site in N. Scotland), Lullington Heath (a rural site in S. England) and Birmingham Centre. The curve is an approximate fit to the Strath Vaich data, which is reproduced in the panels for the other sites to facilitate comparison.

2.7 Ozone observations at rural network locations

2.7.1 Temporal and spatial trends in elevated ozone events at rural locations

45. The hemispheric baseline influences concentrations of ozone throughout the UK, but with the observed concentrations further modified by processes occurring on regional and local scales, which can both increase and decrease ozone. Data from rural sites, in particular, show substantial short-term elevations in ozone concentrations during summertime episodes, which are a consequence of the formation of additional ozone from regional-scale photochemical processing of emitted VOC and NO_x over north-west Europe. This is illustrated in Figure 2.2 Lullington Heath, a rural site in southern England, for the example year of 2005. 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 emissions of the ozone-precursors, when both temperature and solar intensity are elevated, thereby promoting efficient photochemical processing. This general picture of the conditions associated with photochemical ozone 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).

46. General information on the temporal and spatial trends in regional-scale ozone formation is also apparent from consideration of such events. Figure 2.3 (upper panel) shows data from 13 long-running rural and remote 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. 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 of exceedences 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 is apparent from satellite measurements of NO_2 (Figure 2.4), which clearly shows the region of elevated anthropogenic emissions in north-west Europe.

47. The spatial variation is illustrated further in Figure 2.3 (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 series 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.

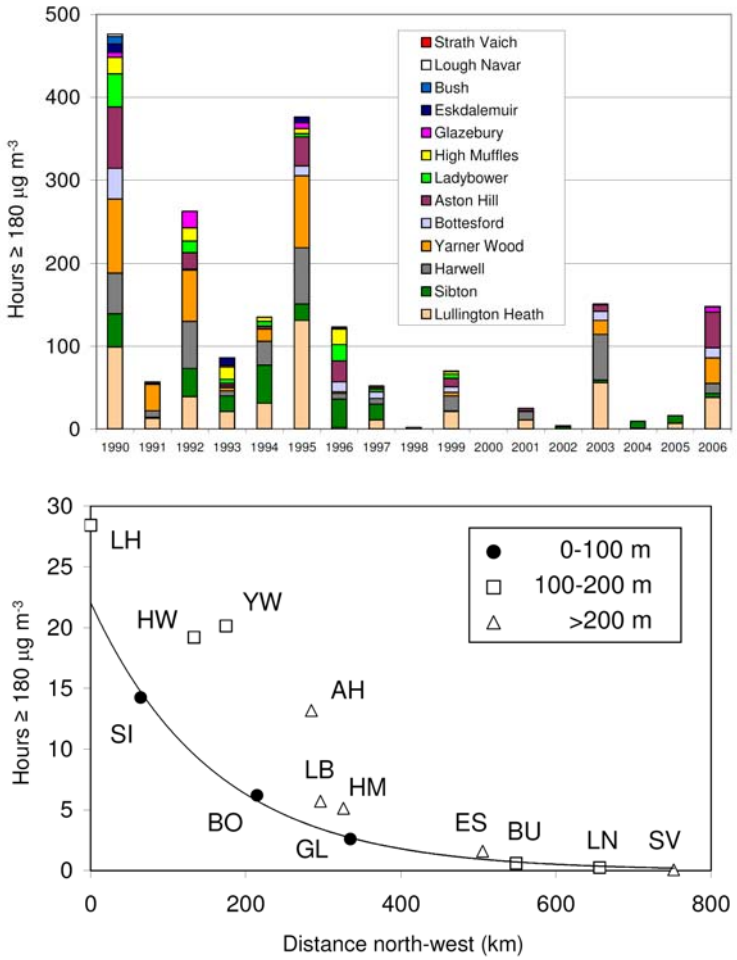


Figure 2.3 (Upper panel) Number of hours with [ozone] ≥ 180 µg m^{-3} at 13 UK rural and remote sites in each year over the period 1990-2006. (Lower panel) Annual number of hours with [ozone] ≥ 180 µg m^{-3} at UK rural sites (based on data averaged over the period 1990-2006) as a function of distance 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.

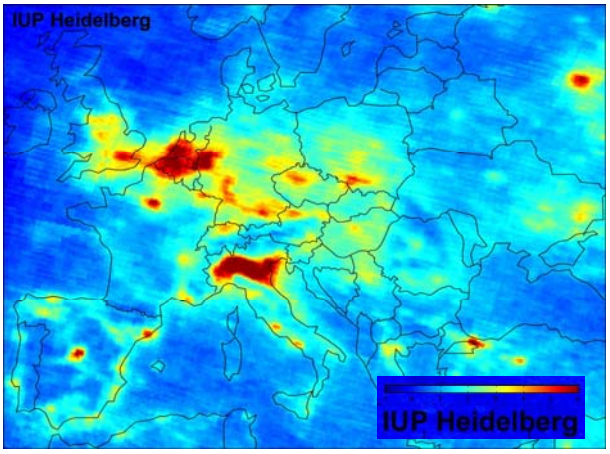


Figure 2.4 European mean tropospheric nitrogen dioxide vertical column density (VCD) between January 2003 and June 2004, as measured by the SCIAMACHY instrument on ESA's Envisat. The scale is in 10^{15} molecules.cm^{-2}. S. Beirle, U. Platt and T. Wagner, Institute for Environmental Physics, University of Heidelberg.

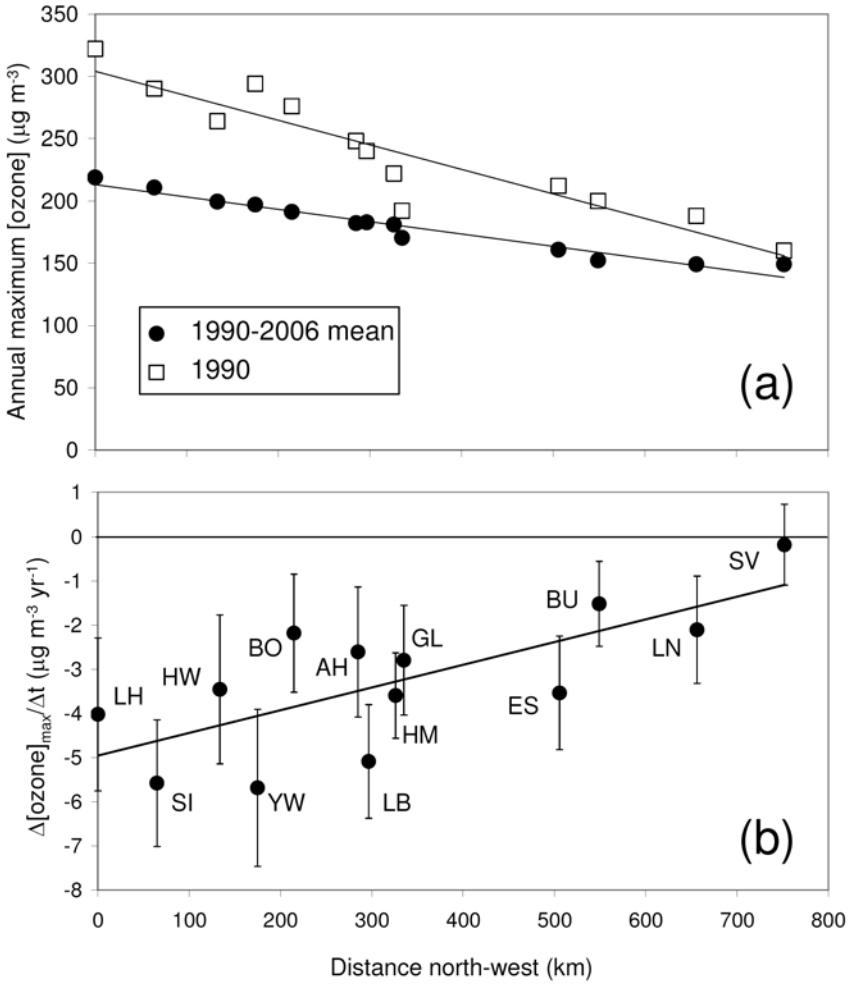


Figure 2.5 (a) Annual maximum hourly-mean [ozone] at 13 UK rural and remote sites, as a function of distance along a north-westerly co-ordinate (sites are identified in Figure 2.3). Data are shown for 1990 and averaged over the period 1990-2006. Lines are regressions of the data. (b) Corresponding average 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.

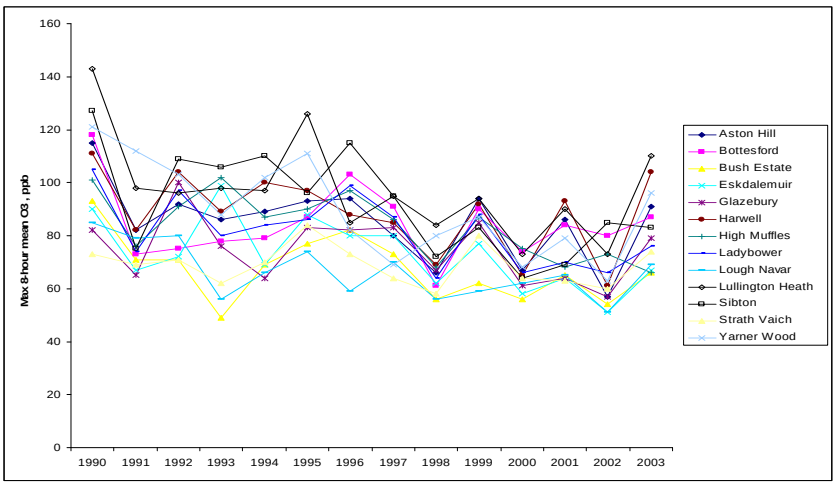


Figure 2.6 Time series of the maximum 8-hourly-mean ozone concentrations monitored at a selection of long-running rural EMEP background sites between 1990 and 2003.

48. 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 2.5a 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 decreasing trend in the annual maximum ozone concentration is apparent over the period at all sites except Strath Vaich (Figure 2.5b), indicative of a decreasing intensity of regional-scale ozone pollution episodes. This observed decrease in the frequency and severity of photochemical ozone events in the UK, is consistent with that expected from reductions in the emissions of anthropogenic VOC and NO_x in the EU since the early 1990s (Derwent *et al.*, 2003), as will be discussed further below. Figure 2.5b 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. Figure 2.6 shows that the decreasing intensity of the regional-scale ozone pollution episodes can also be illustrated using the annual trends in the maximum 8-hour mean ozone concentrations monitored during each year at the selection of long-running rural sites, with the majority showing downwards trends that are statistically significant.

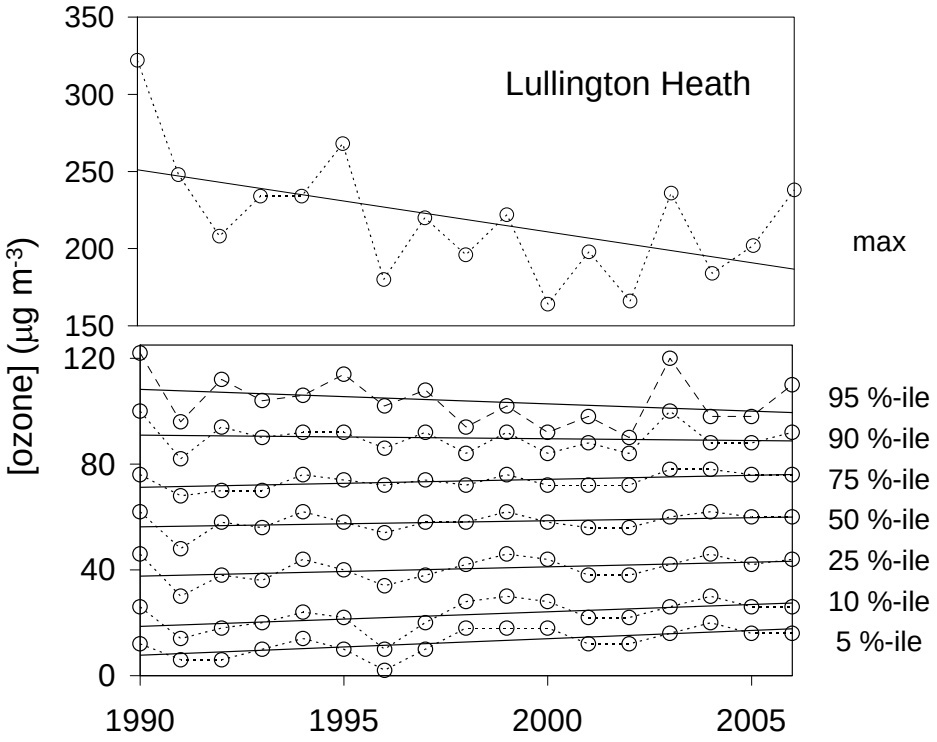


Figure 2.7 Trend in hourly-mean ozone distribution at Lullington Heath (a rural site in southern England), based on data over the period 1990-2006. Solid lines are linear regressions of data indicating the average trend over the period.

2.7.2 Temporal trends in ozone distributions at rural locations

49. Figure 2.7 demonstrates the trend in the hourly-mean ozone distribution at Lullington Heath over the period 1990-2006. Figure 2.8 presents the associated rates of change in the annual maximum, annual minimum and selected percentiles of the hourly-mean ozone concentrations, in comparison with those observed at a number of other locations, including the remote site at Strath Vaich discussed above (section 2.6). The progressive decreases in the maximum and the 95th and 90th percentiles at Lullington Heath reflect the general decrease in regional-scale ozone formation, these statistics corresponding to elevated ozone concentrations during summertime photochemical episode events, as discussed above. As indicated in Figure 2.8, similar trends have also been observed at other long-running rural sites in the southern UK. As a result of this decreasing regional component, the trends in the percentiles at these sites remain more negative than those observed at the remote site at Strath Vaich down to about the 50th percentile.

50. The upward trends in the lower percentiles at the rural sites tend to exceed slightly those observed at Strath Vaich, which can be explained by an additional contribution (i.e. over and above the increasing hemispheric baseline) resulting from a decreasing trend in removal by reaction with locally emitted NO, these statistics probably corresponding to wintertime minima when a shallow inversion layer can cause elevated NO_X concentrations, even at such rural sites (e.g., see ozone depletion events in Figure 2.2 for Lullington Heath). The annual minimum hourly-mean ozone concentration shows no trend because the concentration is essentially zero in each of the years.

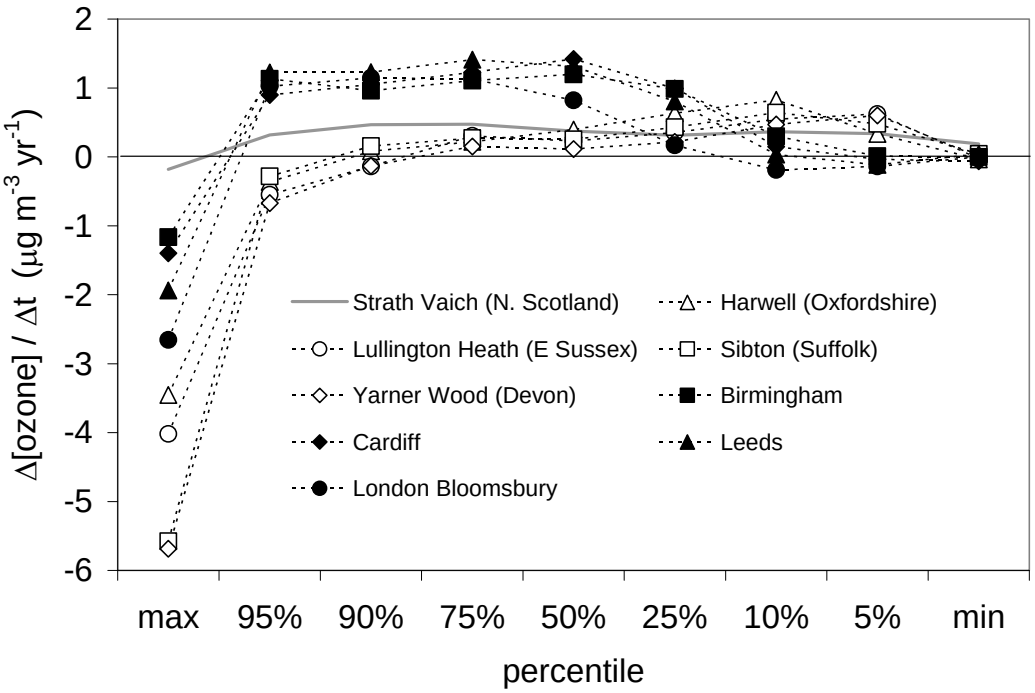


Figure 2.8 Rate of change in hourly-mean ozone concentration at a number of locations based on annual maximum, annual minimum and selected percentiles. The grey line represents observations from the remote site at Strath Vaich (1990-2006). Open symbols are selected rural sites in southern England (1990-2006) and closed symbols are selected urban sites (1993-2006).

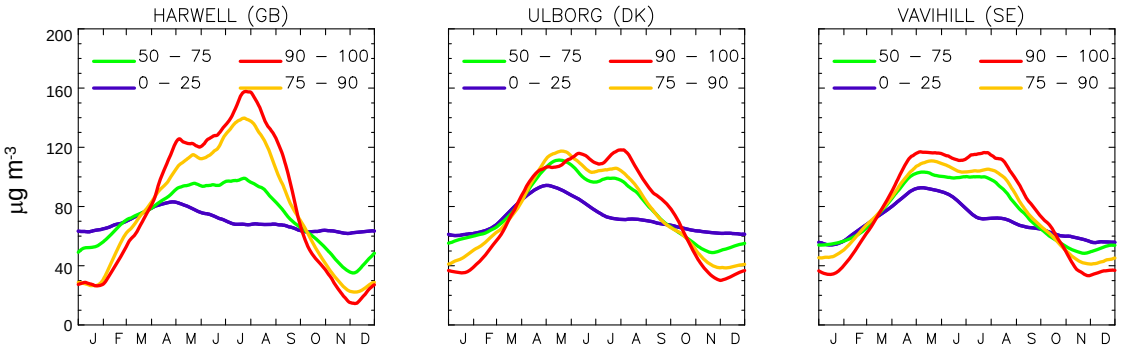


Figure 2.9 Smoothed seasonal cycles of ozone concentrations (based on 1988-1996 data) at three surface sites in Europe as a function of the NO_x emissions integrated along back trajectories from the time of measurement. The different curves represent seasonal cycle for the different quartiles of the trajectory integrated NO_x (adapted from the synthesis and integration report of the TROTREP project).

51. The distribution trend at Lullington Heath (Figure 2.7), and other similar sites, is thus clearly influenced by the local, regional and global scale effects indicated above, with a general narrowing of the distribution with time. Some additional evidence for the role of chemical processes in elevating ozone concentrations in the summer (through photochemistry involving VOC and NO_x) and removing ozone in the winter (through direct reaction with emitted NO) comes from the observations of seasonal ozone concentrations at rural sites in relation to pollutant input. Figure 2.9 shows smoothed data for Harwell (Oxfordshire) and for rural sites in Denmark and Sweden, averaged over the period 1988-1996. The data have been categorised in terms of integrated NO_x emissions along trajectories arriving at the given location, and demonstrate that polluted air masses showed a summer surplus and a winter deficit in ozone with increasing seasonal amplitude associated with increased anthropogenic emissions. The difference between the "polluted" and "clean" seasonal cycles therefore quantifies the impact of the chemical modification which, over the period considered at Harwell, maximised at about -40 µg m^{-3} in winter and +80 µg m^{-3} in summer. The time series in Figure 2.7 shows that the magnitude of these modifications at Lullington Heath (and other similar rural UK sites) has progressively diminished since the early 1990s, in response to EU VOC and NO_x emissions controls, resulting in the narrowing of the ozone distribution referred to above.

52. Figure 2.5 and Figure 2.8 show that the average trends in the maximum ozone concentrations at the rural southern UK sites over the period 1990-2006 are typically in the region of -4 to -6 µg m^{-3} yr^{-1}. The trends in the 99.9th percentile of the hourly-mean ozone concentrations at a larger series of 18 rural and remote sites in the UK have also been analysed, based on data from all available years up to 2005. The results are summarised in the histogram in Figure 2.10, with the detailed site-specific information presented in Annex 3.1. The 99.9th percentile at a given site typically shows comparable, but slightly smaller, rates of decrease compared with the maxima. The average trend of the longer-running rural and remote sites (located throughout the UK) is -2.4 µg m^{-3} yr^{-1}, with eight sites showing statistically significant downward trends. The data for these sites are presented geographically in Figure 2.11. Consistent with the data for the annual maxima discussed in the previous section, these tend to show a north-south gradient in the rate of decline.

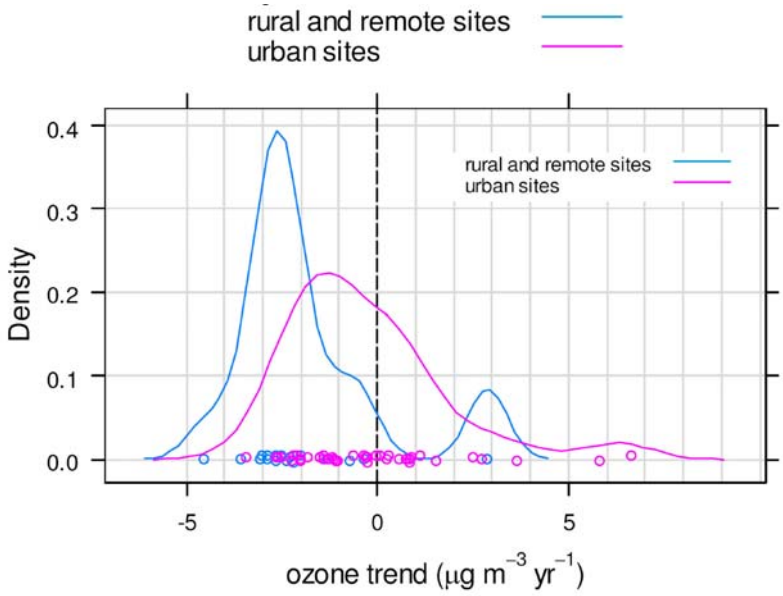


Figure 2.10 Distribution of trends in the 99.9th percentile of the hourly-mean ozone concentration at 18 rural/remote and 45 urban locations in the UK, based on data up to 2005. The site-specific information is presented in Annex 3.

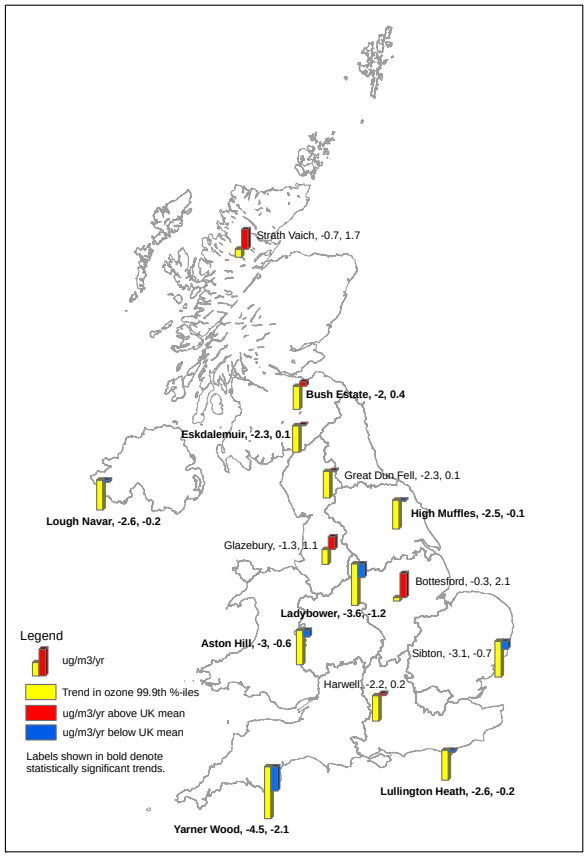


Figure 2.11 Spatial patterns in the average trends in 99.9th percentile hourly-mean ozone concentration at rural and remote sites (yellow bar) and their relationship to the UK mean of -2.4 µg m^{-3} yr^{-1}, based on data up to 2005.

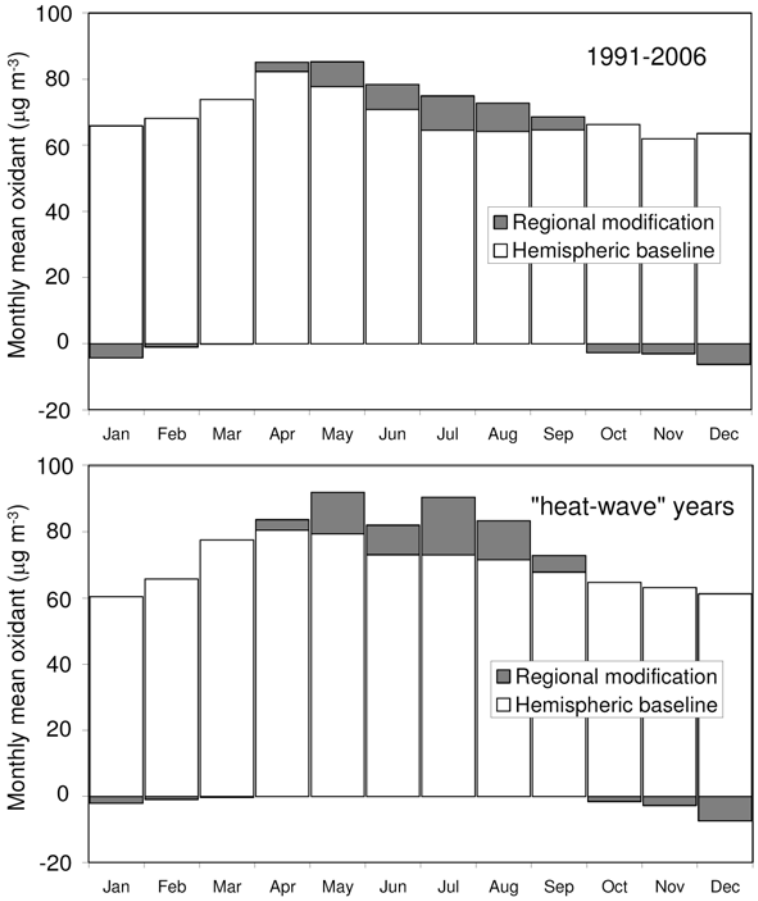


Figure 2.12 Seasonal variation of monthly mean background oxidant (i.e. ozone) contributions at Lullington Heath, based on data averaged over the period 1991-2006 (upper panel) and for the average of the heat-wave years, 1995, 2003 and 2006 (lower panel).

2.7.3 Temporal trends in background oxidant sources at Lullington Heath

53. Data from the rural site at Lullington Heath, for the period 1991-2006, have been analysed to estimate the relative contributions of sources of oxidant. As described in detail elsewhere (e.g. AQEG, 2004), the oxidant concentration is defined as the sum of the concentrations of ozone and NO_2. This quantity has been shown to be made up of a combination of a background (NO_x-independent) source and a local (NO_x-dependent) source (Clapp and Jenkin, 2001). 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 NO_x, i.e. when local removal by reaction with emitted NO, and (less significantly) local production from emitted NO_2, has not occurred.

54. Figure 2.12 and Figure 2.13 show the seasonal variation and long-term trend in the background oxidant (i.e. ozone) concentration at Lullington Heath, with this background being further separated into estimated “global (hemispheric)” and “regional” contributions. These quantities have been determined by, first, removing the “local” contribution from the measured oxidant, based on the observed concentration of NO_x and an inferred average fractional contribution of NO_2 to NO_x emissions of 9.3 % (Jenkin, 2004). This allowed the background oxidant (i.e. ozone) 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.

55. Figure 2.12 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 ozone at remote sites, as discussed above and in Chapter 3.

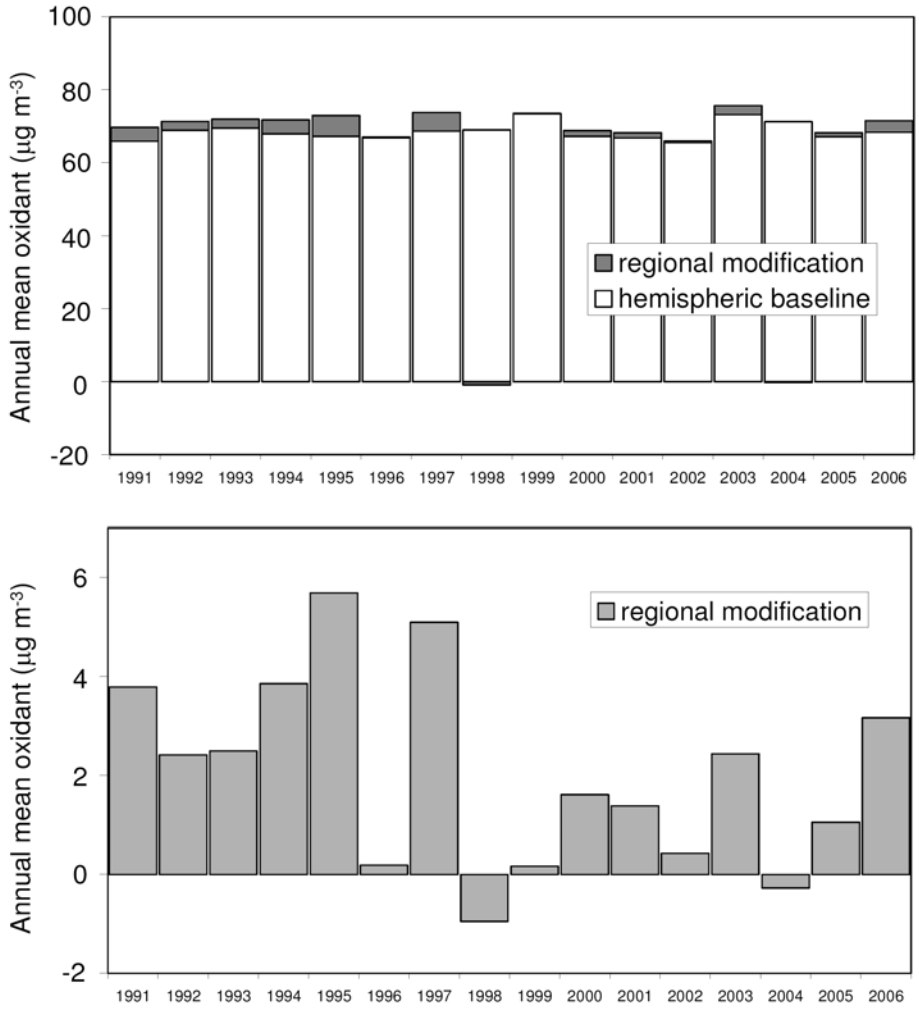


Figure 2.13 Time series of the annual mean background oxidant (i.e. ozone) contributions at Lullington Heath. The regional contribution is shown on an expanded scale in the lower panel.

56. Figure 2.13 shows the time series of the oxidant components on an annual mean basis over the 16-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 NO_x 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} yr^{-1}. However, consideration of data over the period 1991-1999 yields a more notable upward trend of 0.4 µg m^{-3} yr^{-1} with no clear trend subsequently. The variation in the inferred hemispheric baseline thus shows some of the features observed at Strath Vaich (see section 2.7) and at the Mace Head site on the west coast of Ireland, as discussed in detail in Chapter 3.

Box 2.2 Daily metrics of ozone exposure.

Hourly-mean ozone concentrations show characteristic diurnal cycles with lowest levels during the early morning and highest levels during the mid-afternoon. Daily metrics are single numbers chosen to represent this wide dynamic range in concentrations. The daily metrics most commonly used in ozone air quality studies are: maximum hourly-mean concentration, maximum 8-hourly-mean concentration, and daily mean concentration.

Each of these commonly used metrics is equally well able to describe the observed dynamic range in ozone concentrations. This is because they are strongly correlated with each other, though the detailed nature of these correlations may vary from site to site and from year to year. For example, at a typical urban background monitoring site in central London during 1993 there were 350 days with valid daily ozone metrics and these were correlated as follows:

Max 1-hour mean = 1.195 x max 8-hour mean r^2=0.93
Daily mean = 0.56 x max 8-hour mean r^2=0.85

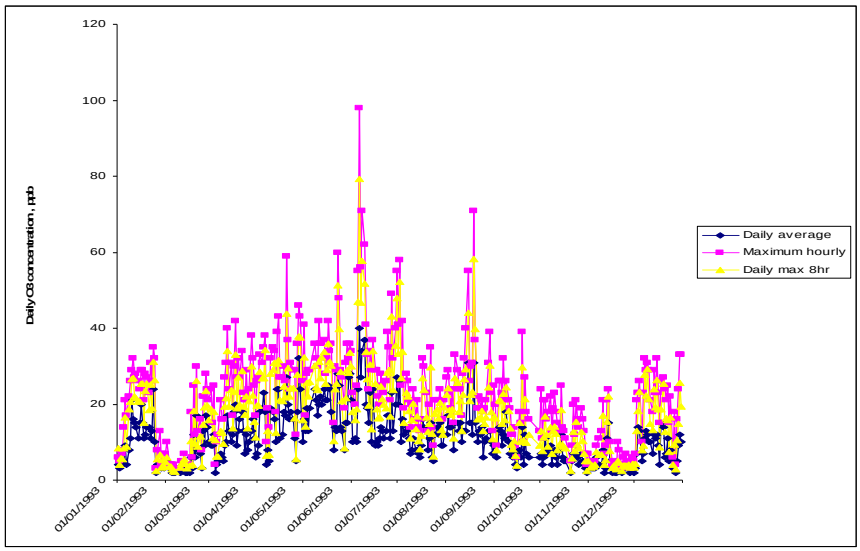


Figure 2.14 The time series of three daily ozone metrics for the urban background site in central London during 1993.

2.7.4 Temporal trends in human health ozone metrics at rural locations

57. Making the assumption that there is no threshold for ozone and human health effects, there remains an important question concerning the relevant ozone metric against which ozone monitoring data should be compared, to derive policy-relevant conclusions concerning recent air quality trends. Box 2.2 describes some of the more commonly used daily ozone metrics, with Figure 2.14 illustrating the close correlation observed between maximum hourly-mean, maximum 8-hourly-mean and daily mean concentrations at a typical urban background site in central London. Figure 2.15 shows that the annual mean of the daily maximum 8-hour running mean concentration is closely correlated with the annual mean ozone concentration for a series of site types, and this is illustrated further using trend data for 18 rural and remote UK sites up to 2005, in Annex 3A3.1.

58. In the following discussion, we consider that the annual average of the daily maximum 8-hour mean ozone concentrations is an appropriate ozone metric, and the EMEP ozone database has been recompiled on this basis. There are 46 EMEP rural sites, located at elevations below 500 m, that have long enough observational records to enable robust trend analysis. An analysis of the trends in the annual averages of daily maximum 8-hour mean ozone concentrations for the period from 1990 through to 2002 has been carried out, the detailed results of this analysis being presented in 0. Of the 46 EMEP sites, 17 showed downwards trends and 29 showed upwards trends. Of these, 11 sites showed highly statistically significant upwards trends and two showed similarly significant downwards trends. Taking all the sites together, the average trend was (0.3 ± 0.6) μg m^{-3} yr^{-1}. For comparison, an analysis of the trends in the annual mean concentrations at 18 rural and remote sites in the UK, based on data from all available years up to 2005, has also been carried out. The results are summarised in the histogram in Figure 2.16, with the detailed site-specific information presented in Annex 3A3.1. On average there has been an increase in annual mean ozone at these rural and remote sites (located throughout the UK) of 0.4 μg m^{-3} yr^{-1}, with six of the 18 sites showing statistically significant increases in the trend.

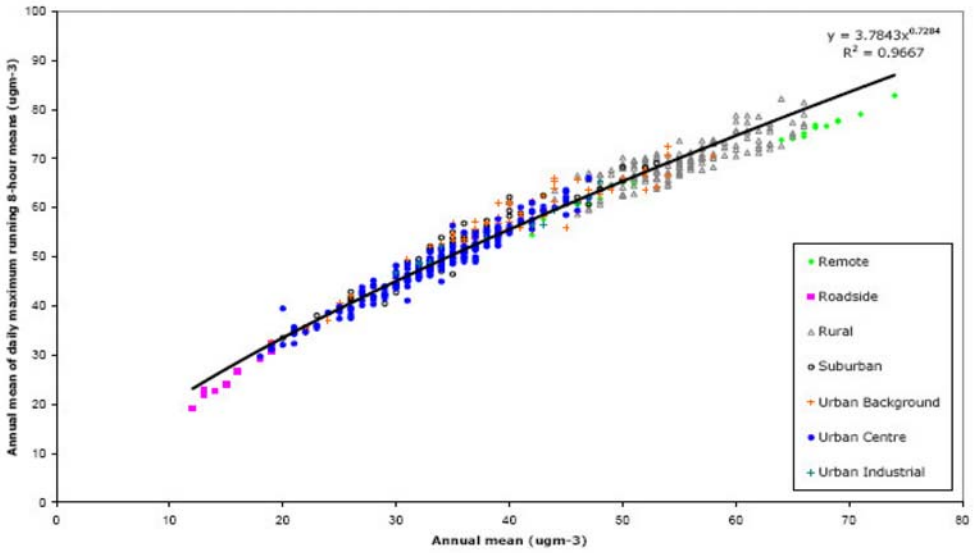


Figure 2.15 Relationship between measured annual mean of the maximum daily 8-hour running mean ozone concentration and the annual mean ozone concentration, for a series of site classifications.

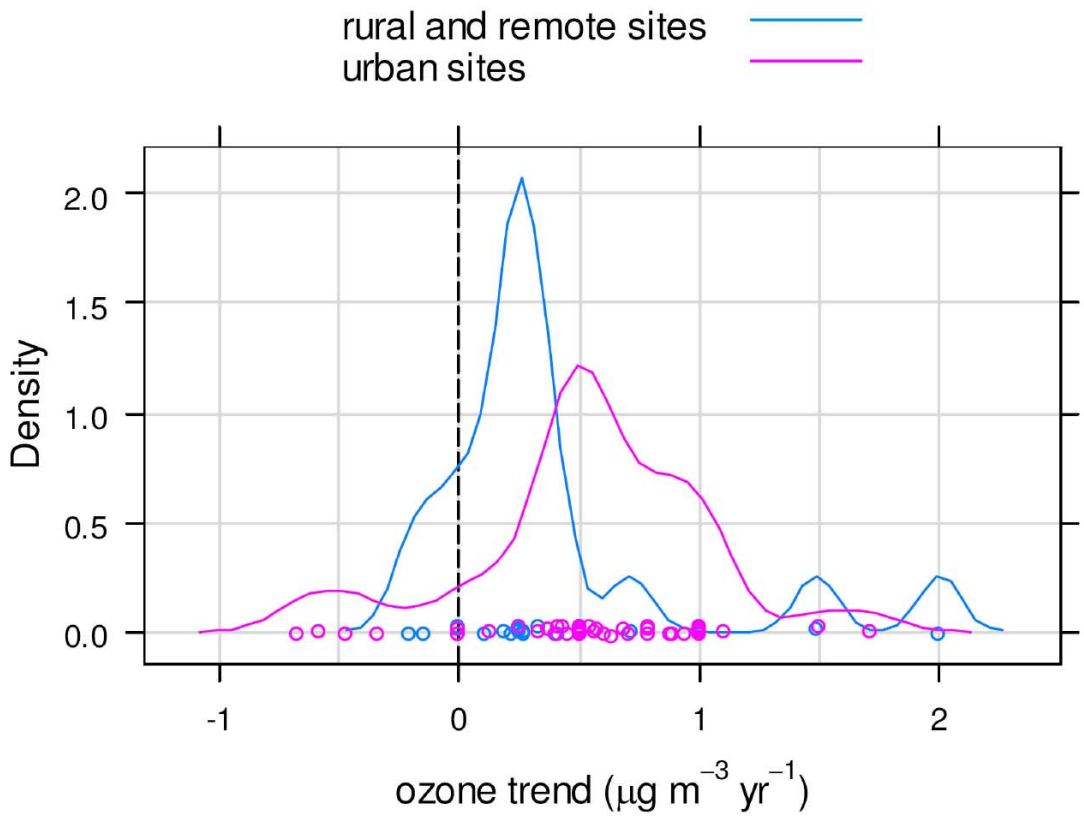


Figure 2.16 Distribution of trends in the annual mean ozone concentration at 18 rural/remote and 45 urban locations in the UK, based on data up to 2005. The site-specific information is presented in Annex 3.

59. To sort out what have been the major influences on the observed long term trends in the annual average daily maximum 8-hour mean ozone concentrations at the 46 EMEP rural sites, Figure 2.17 plots out the observed trends for the sites identified in 0 over the 1990-2002 period, against the initial 1990 value of the ozone metric. This shows that there is a correlation between the magnitude of the observed ozone trend and the initial 1990 value of the ozone metric. Those EMEP sites with low initial values of the ozone metric, such as those shown in Figure 2.17 in Germany and Belgium, show strong upwards trends. These are sites which were influenced by traffic emissions initially. As NO_x emissions have decreased across Europe, NO_x-driven depletion of ozone has steadily reduced and levels of the ozone metric have increased. At sites heavily influenced by long range transboundary transport, such as the Netherlands site in Figure 2.17, initial levels of the ozone metric were high because the sites were located away from traffic. Europe-wide measures to reduce ozone-precursor VOC and NO_x emissions have steadily reduced levels of the ozone metric, leading to the observed downwards trends over the 1990-2002 period. Sites such as Mace Head, see Figure 2.17, that are on the Atlantic Ocean seaboard of Europe, are strongly influenced by the increasing hemispheric and global ozone baseline and show increasing trends over the 1990-2002 period.

60. The observations of rural ozone levels in Europe can therefore be rationalised in terms of the net effect of the three major influences on ozone concentrations identified above. Overall, an approximate balance has been maintained between these influences over the 1990-2002 period at the rural EMEP sites.

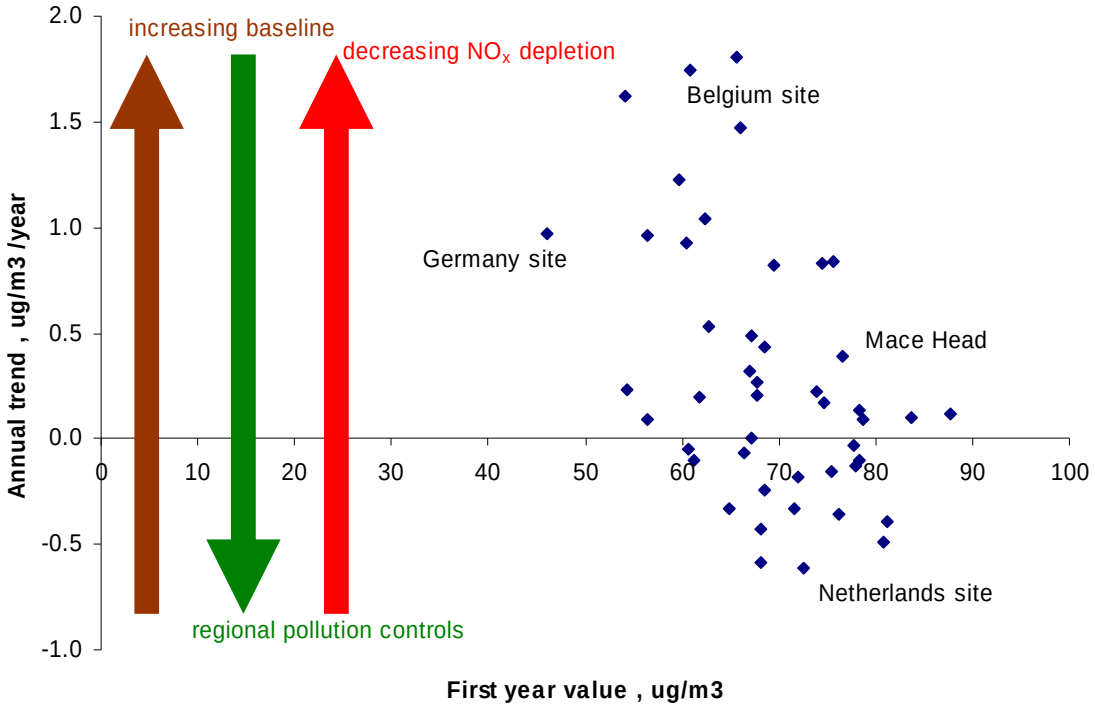


Figure 2.17 A scatter plot of the trends in the annual average daily maximum 8-hour mean ozone concentrations observed at 46 EMEP rural sites over the period 1990-2002 plotted against the initial 1990 value of the ozone metric.

2.8 Ozone observations at urban network locations

2.8.1 Temporal trends in elevated ozone events at urban locations

61. Urban locations are typically characterised by higher concentrations of NO_x than surrounding rural areas, and the balance between ozone production and loss (compared with the hemispheric baseline) is shifted as a result of the increased impact of local scavenging of ozone by reaction with emitted NO. This is apparent in Figure 2.2 for the Birmingham Centre site, for which the daily ozone concentrations are generally lower than those observed at the Lullington Heath rural site throughout the year. Despite this, the short term elevations in ozone concentrations during regional-scale episodes in the summertime are still apparent, such that the levels on such occasions are typically observed to be greater at urban locations within the UK than those observed remote north-westerly sites such as Strath Vaich, which are less impacted by regional-scale European pollution.

62. Figure 2.18 shows the maximum hourly-mean ozone concentration recorded at London sites over the period 1989-2006, compared with the trend at long-running rural sites. A notable urban decrement is apparent in the early part of the time series, but with the maxima at the rural sites and the London sites being comparable in more recent years. This demonstrates the reducing impact of local ozone scavenging by reaction with NO as NO_x emissions have declined over the period. As a result, the effect of EU-wide reductions in VOC and NO_x emissions in reducing peak ozone levels is almost cancelled out by the increasing impact of local NO_x reduction at urban sites, such that the decline in the maximum values at urban sites (if any) is much more subtle than that observed at rural locations.

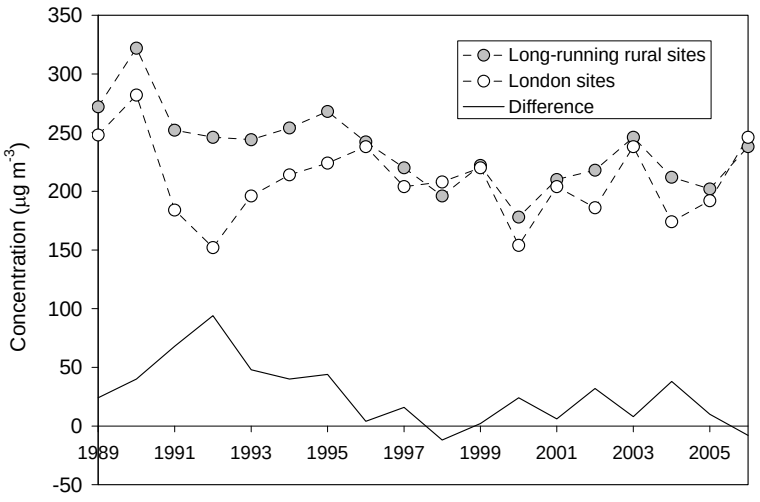


Figure 2.18 Maximum hourly-mean ozone concentrations in each year at the long-running rural sites identified in Figure 2.3, and at London sites, over the period 1989-2006. The difference between the rural and London sites for the given ozone metric is termed the "urban decrement".

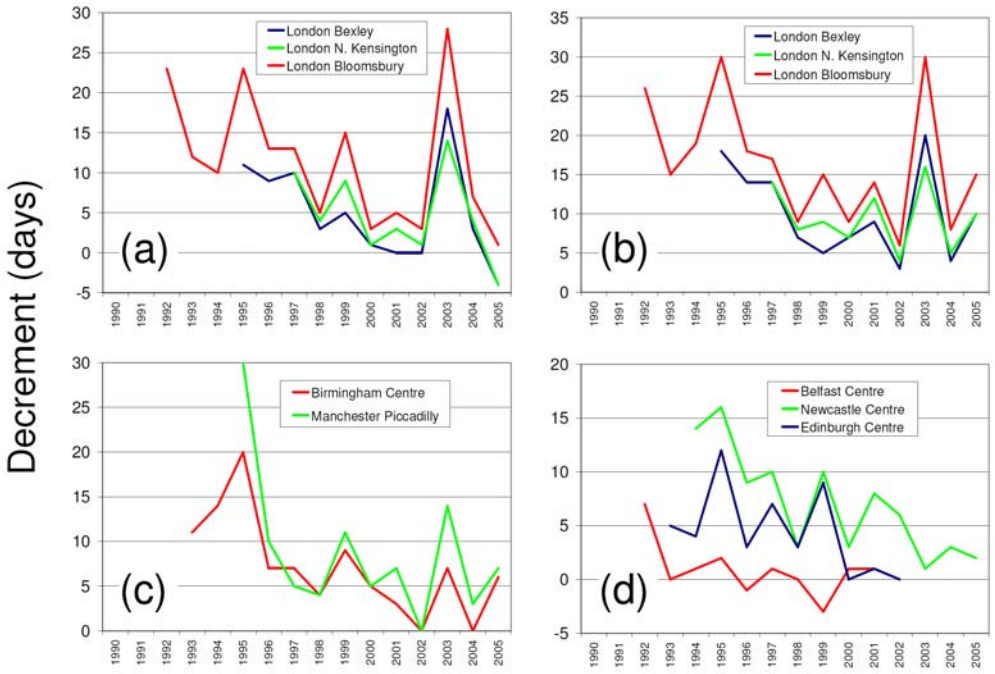


Figure 2.19 The decrement in the number of days the daily maximum 8-hour running mean concentration exceeds 120 µg m^{-3} at urban sites compared with paired rural sites, since the early 1990s. (a) Selected London sites, relative to Harwell; (b) Selected London sites, relative to Lullington Heath; (c) Birmingham Centre and Manchester Piccadilly, relative to Aston Hill; (d) Belfast Centre, relative to Lough Navar; Newcastle Centre, relative to High Huffles; Edinburgh Centre, relative to Eskdalemuir.

63. The general reducing trend in the urban ozone decrement is also apparent from an analysis of daily maximum 8-hour running mean concentrations. Figure 2.19 shows that the number of days the daily maximum 8-hour running mean concentration exceeds 120 µg m^{-3} at selected urban sites in a given year has tended towards the number observed at paired rural sites in the same region since the early 1990s.

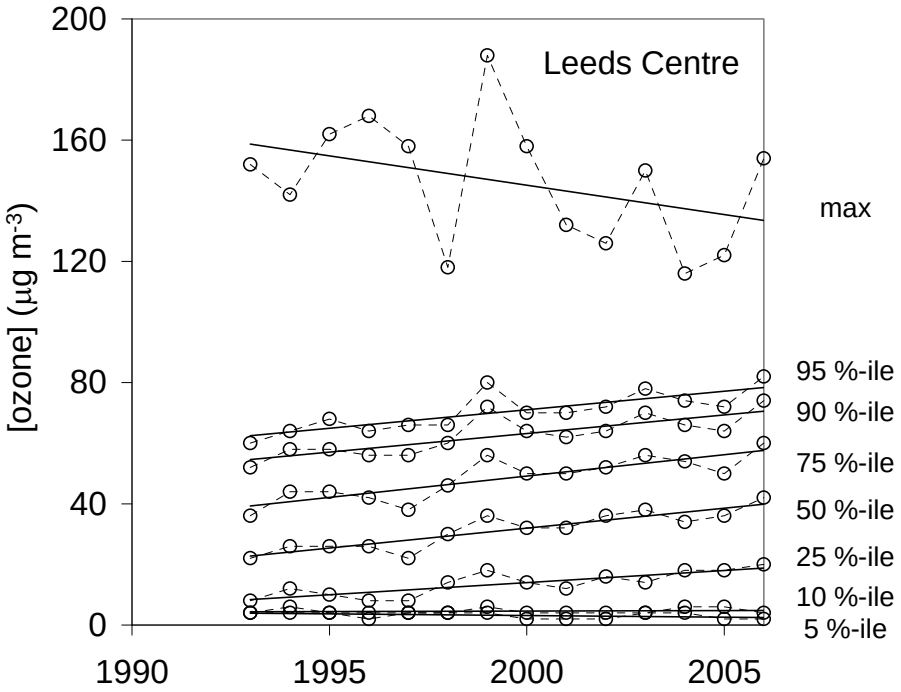


Figure 2.20 Trend in the hourly-mean ozone distributions at the Leeds Centre urban site, based on data over the period 1993-2006. Solid lines are linear regressions of data indicating the average trend over the period.

2.8.2 Temporal trends in ozone distributions at urban locations

64. Figure 2.20 demonstrates the trend in the hourly-mean ozone distribution at an example urban location, Leeds Centre, over the period 1993-2006. Figure 2.8 presents the associated rates of change in the annual maximum, annual minimum and selected percentiles of the hourly-mean ozone concentrations, in comparison with those observed at a number of other urban locations, and at the remote and rural sites discussed above in sections 2.6 and 2.7. At Leeds Centre (Figure 2.20), a general decrease in the annual maximum hourly-mean ozone concentration is discernable. This indicates that the effects of regional-scale ozone-precursor controls can be observed at comparatively polluted urban locations. As shown in Figure 2.8, similar observations are apparent at other long-running urban sites in England and Wales (Birmingham, Cardiff and London Bloomsbury). However, the lower percentiles at all these sites show an increasing trend, with the influences of decreasing removal by reaction with NO locally having the overriding effect on the distribution as a whole. As shown in Figure 2.8, the upward trends in the 95th through to the 25th percentiles at Leeds, Birmingham and Cardiff are of the order of 1 µg m^{-3} yr^{-1}, notably greater than observed at the rural sites. The low end of the percentile range (≤ 10th percentile) are concentrations which are at, or close to, zero and show very little trend. These correspond to conditions where the NO_X concentration is sufficiently high that there is enough NO effectively to remove all ozone, so that even decreasing emissions does not lead to a notable increase in ozone concentration (i.e. the distribution is truncated because it hits zero). At the Bloomsbury site in central London, the maximum upward trend is also of the order of 1 µg m^{-3} yr^{-1}, but the trend collapses to zero at a higher percentile because the NO_x concentrations are generally greater, compared with the other urban centre sites.

65. Further evidence for the generally increasing trend across the distribution is shown in Figure 2.21. This presents the frequency distributions of the 8760 hourly ozone mean concentrations measured at an urban background site in central London during 1991 and

1998. These data also show a marked shift in the frequency distribution of ozone concentrations over this period, bringing a much reduced frequency of low ozone concentrations < 20 µg m^{-3} and a much increased frequency of ozone concentrations in the 20-80 µg m^{-3} range. This is likely to be due mainly to reduced NO_x emissions which deplete urban ozone, but will also reflect the steadily increasing ozone background, especially during wintertime. Similar behaviour is anticipated in most towns and cities in north-west Europe.

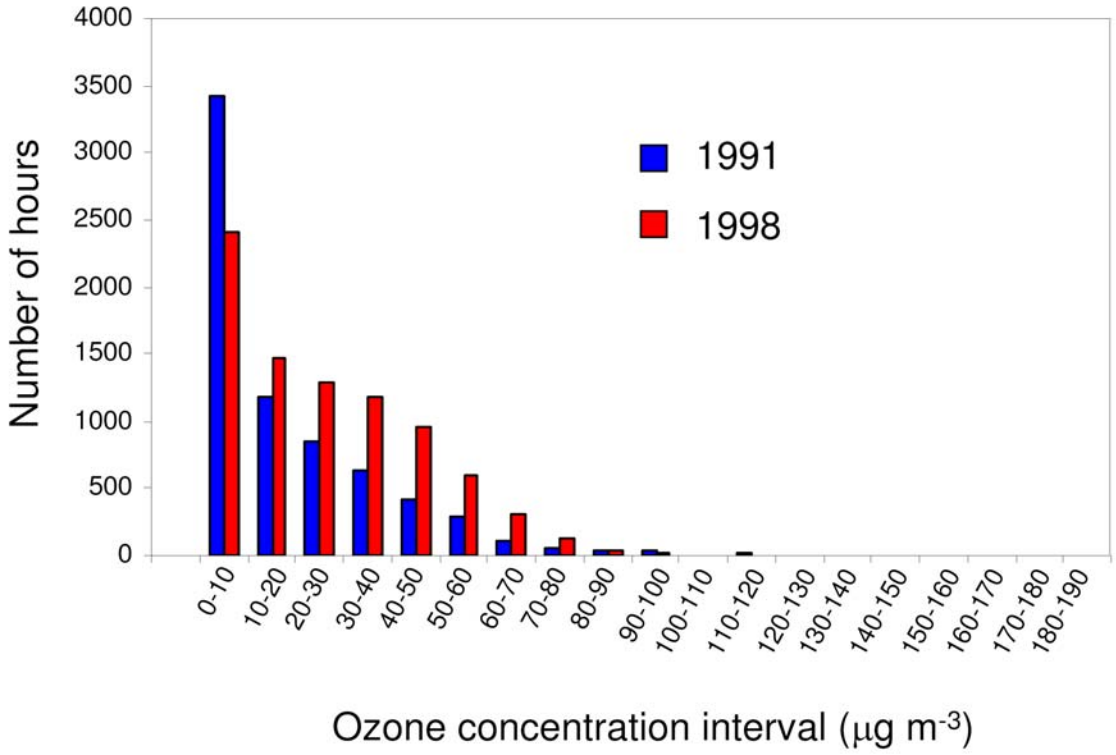


Figure 2.21 The frequency distributions of the hourly ozone concentrations measured during 1991 and 1998 at a typical urban background site in central London.

66. The data in Figure 2.8 demonstrate that maximum ozone concentrations at the selected urban UK sites have tended to show some decline since the early 1990s, although the rate of decrease at individual sites is generally not statistically significant. Analysis of a wider dataset also shows a range of average trends in the maximum, partly because the impact of summertime regional scale ozone formation has less of an impact at urban sites to the north and west of the UK, such that the decreasing regional component is expected to be less apparent. Figure 2.10 shows a summary of the trends in the 99.9th percentile of the hourly-mean ozone concentrations at 45 urban sites in the UK, based on data from all available years up to 2005, with the detailed site-specific information presented in Annex.1.1. Although none of the individual sites shows a significant trend in the 99.9th percentile, the average trend is -0.3 µg m^{-3} yr^{-1}. As shown in Figure 2.10, the absolute rate of decline in these top end ozone concentrations at urban sites is systematically lower than those observed at rural and remote locations, consistent with the discussion in the previous section.

67. Although the distributions of ozone concentrations at urban locations have displayed logical trends, primarily in response to the general decreasing trend in local and regional scale emissions, it is also apparent that some degree of year-to-year variability results from the different meteorological conditions experienced. Figure 2.22 shows the ozone distributions and annual mean concentrations for the London Bloomsbury and Leeds

Centre sites for the heat-wave years of 1995 and 2003, and for the more typical meteorological year of 2005. The distributions for the Lullington Heath (rural) and Strath Vaich (remote) sites are also shown for comparison. The data for 2003 at the urban sites show a general shift to higher concentrations when compared with the 1995 data, owing to the reducing impact of local ozone removal by reaction with NO. However, the data for 2005 are generally shifted back to lower concentrations than observed in 2003, because of the lower frequency of regional-scale photochemical ozone episodes in 2005, compared with both 2003 and 1995. The year-to-year variability in the hemispheric baseline (discussed in the Chapter 3) also has an underlying effect. This is particularly apparent for the annual mean concentrations at the rural and remote sites, which show a clear elevation in 2003 compared with the other years. The data in Figure 2.22 therefore demonstrate once again that ozone concentrations at UK locations are influenced by trends and variability in processes on local, regional and global scales.

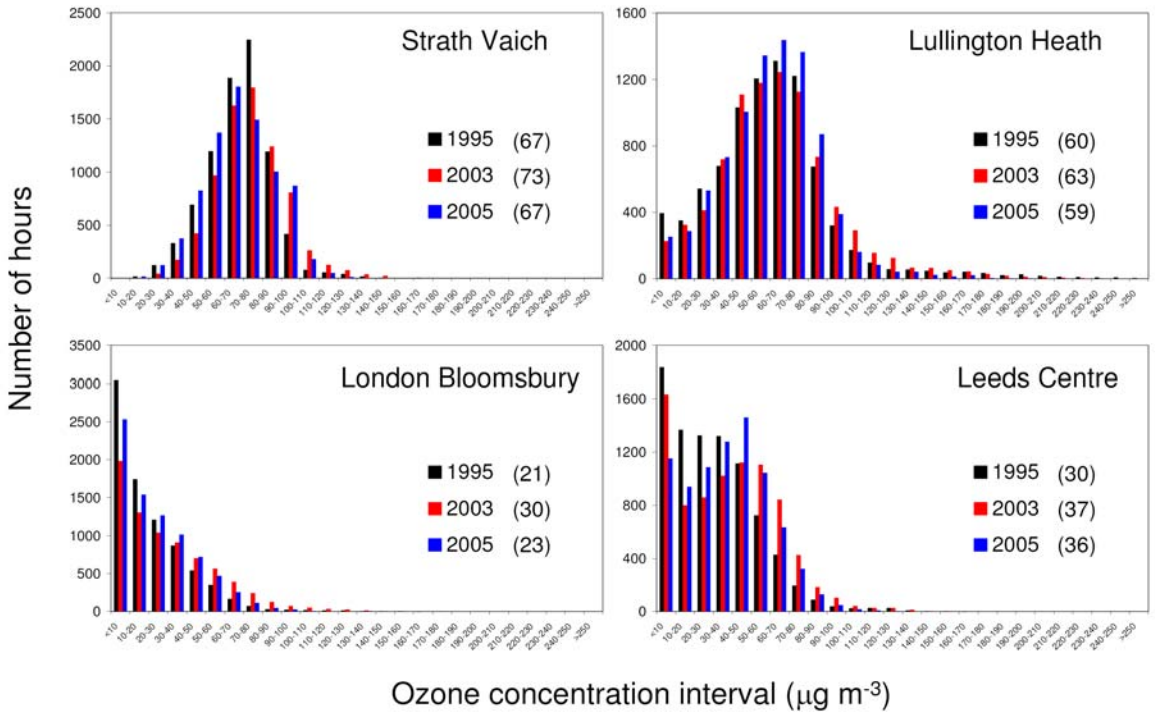


Figure 2.22 Frequency distributions of the hourly-mean ozone concentrations measured during 1995, 2003 and 2005 at selected urban, rural and remote locations in the UK. Annual mean concentrations (in µg m^{-3}) are also given in brackets.

2.8.3 Temporal trends in human health ozone metrics at urban locations

68. Following on from the analysis presented for rural sites in section 2.7.4, here we consider trends in urban ozone levels in terms of the human health metrics, the annual mean of the daily maximum 8-hour running mean concentration and the annual mean concentration. Similarly to the conclusion for rural sites, Figure 2.15 shows that the two metrics are closely correlated, and this is illustrated further using trend data for 45 UK sites, in Annex A3.1.

69. Although monitoring of the ozone levels in rural locations in Europe began during the 1970s, monitoring in urban locations is a relatively recent activity. There are over 1000 urban ozone monitoring sites contributing to the AIRBASE database of the EU during the 2000s. With this large increase in urban ozone monitoring, it is clear that urban ozone levels are substantially reduced below rural levels by NO_x-driven depletion processes. This depletion is increasingly more apparent when comparing suburban with urban background and traffic-influenced sites.

70. In view of the importance of urban exposure levels, a clear understanding of urban ozone trends is required. As an example, trends in the urban ozone metrics are examined for the UK over the period from 1994-2003. It is anticipated that the ozone behaviour found is typical of that experienced in most of the European towns and cities. The trends in the annual average daily maximum 8-hour mean ozone concentration at the UK urban sites are shown in Table 2-1. Upwards trends are found at the vast majority of the urban sites, 47 out of 49, and downwards trends at only two sites. A total of 19 sites showed trends that are highly statistically significant (> 90% confidence). The London Marylebone Road site is the most heavily trafficked and most heavily polluted site of all in Table 2-1 and the site which has the lowest annual mean daily maximum 8-hour mean ozone concentrations. The low ozone levels at this site are caused by NO_x depletion and the strong upwards trend of 1.4 µg m^{-3} yr^{-1} observed at this site has been caused by the diminution of this NO_x depletion by the reduction of NO_x emissions from petrol-engined vehicles due to the fitting of exhaust gas catalysts. This same influence is apparent across all the other urban sites in Table 2-1.

71. The strong upwards trends in the ozone metric observed at almost all of the UK urban sites have been caused by the diminution of the depletion of ozone by chemical reactions with NO_x which has been caused, in turn, by the reduction of NO_x emissions from petrol-engined vehicles due to the fitting of exhaust gas catalysts. At these urban sites there appears to have been little influence of the decrease in intensity of regional pollution episodes on annual mean daily maximum 8-hour mean ozone concentrations. Similar behaviour is anticipated in most European towns and cities during the 1990s and 2000s.

72. Trends in annual mean ozone concentrations at 45 urban background, urban centre and suburban sites, based on data from all available years up to 2005, have also been analysed. The results are summarised in the histogram in Figure 2.16, with the detailed site-specific information presented in Annex 3.1. The majority of these show upwards trends, with 17 showing statistically significant increases. The mean trend of the 45 sites is an increase in ozone of 0.3 µg m^{-3} yr^{-1}. As also shown in Figure 2.16, the rate of increase in the annual mean concentrations at urban sites is systematically greater than those observed at rural and remote locations, due to the decreasing scavenging from locally emitted NO. As a result of decreasing NO_x emissions since the early 1990s, the less polluted urban sites are, in some respects, now tending towards “rural” character, at least in terms of their NO_x levels. This is illustrated in Figure 2.23, which shows a comparison of mapped annual mean NO_x concentrations in the UK in 1996 and 2005, based on empirical modelling activities (Kent *et al.*, 2007). This comparison clearly demonstrates the shrinkage of the high NO_x zones, which is accompanied by greater infiltration of ozone into urban areas.

Table 2-1 Trends and their statistical significance in the annual mean daily maximum 8-hour mean ozone concentrations observed at rural, suburban, urban and roadside sites in the United Kingdom during the period from 1990 onwards.

Urban sites 1994-2003	Statistical significance	Trend $\mu g\ m^{-3}\ yr^{-1}$	Urban sites 1997-2003	Statistical significance	Trend $\mu g\ m^{-3}\ yr^{-1}$
Belfast Centre		+0.62	Barnsley Gawber		+1.10
Birmingham Centre	*	+0.90	Bolton	+	+1.76
Birmingham East		+0.34	Bradford Centre		+1.70
Bristol Centre		+0.36	Derry		+1.58
Cardiff Centre	+	+0.90	Glasgow Centre	*	+1.16
Edinburgh Centre		+0.64	Leamington Spa		+1.44
Hull Centre		+0.18	London Brent		+1.54
Leeds Centre	*	+1.14	London Eltham		+0.42
Leicester Centre		+0.78	London Hackney		+0.96
Liverpool Centre	+	+1.50	London Haringey		+1.70
London Bexley	**	+0.98	London Hillingdon	+	+1.98
London Bloomsbury	*	+0.80	London N. Kensington		+2.02
Middlesbrough	**	+1.62	London Southwark		+1.36
Southampton Centre		+0.88	London Sutton		+1.08
Swansea	*	+1.08	London Teddington	*	+1.66
Wolverhampton Centre	+	+0.96	London Wandsworth	+	+1.62
			Manchester Piccadilly		+0.68
average	+	+0.70	Manchester South	+	+1.30
			Newcastle Centre		+1.08
Roadside sites 1997-2003			Norwich Centre		+3.72
			Nottingham Centre		+0.74
Bury Roadside	+	+1.10	Plymouth Centre		+1.90
London Marylebone Road	**	+1.42	Port Talbot		+1.14
			Reading		-0.80
			Redcar	*	+2.18
			Rotherham Centre		+1.32
			Salford Eccles		+0.62
			Sheffield Centre		+0.68
			Stoke-on-Trent Centre		0
			Swansea		+0.74
			Thurrock		+1.48
			Average		+1.52

Notes: Statistical significance is based on the non-parametric Mann-Kendall test and Sen's slope estimates and is indicated by: ** at the 0.01 level of significance, * at the 0.05 level of significance, + at the 0.1 level of significance and blank means less than the 0.1 level.

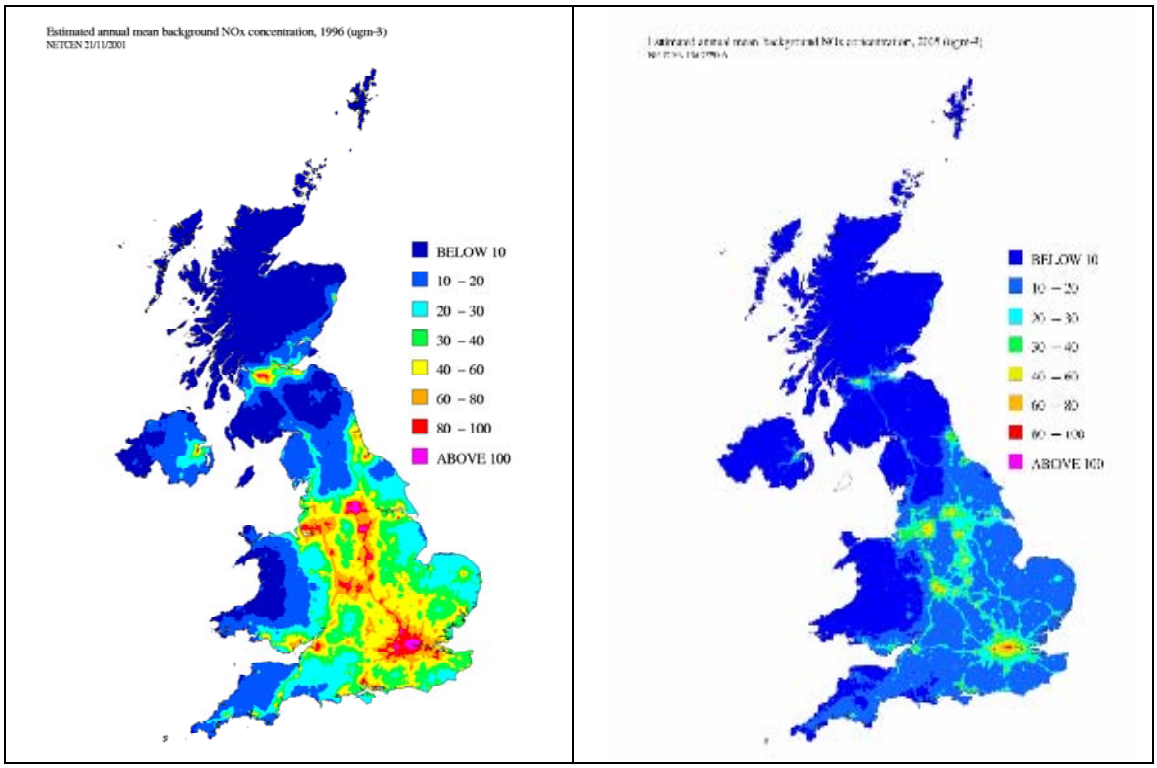


Figure 2.23 Estimated annual mean background concentrations of NO_x in the UK in 1996 and 2005.

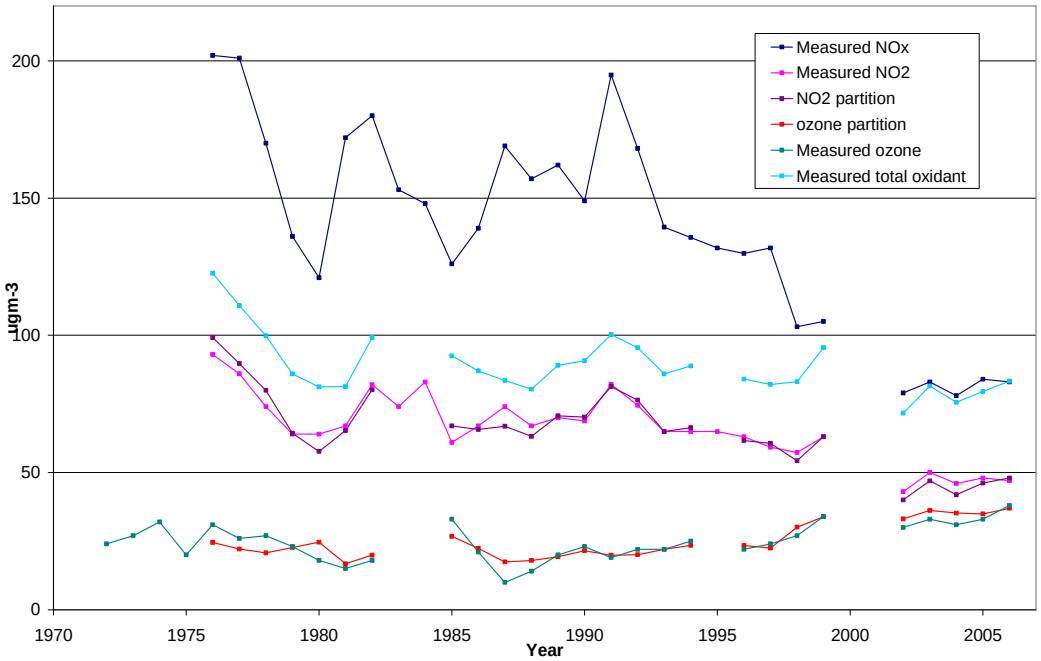


Figure 2.24 Measured annual mean concentrations of ozone, NO_2 and NO_x at Central London, London Bridge Place and London Westminster along with predictions from the oxidant partitioning model (µg m^{-3}).

2.8.4 Site-specific projections of annual mean ozone concentrations at urban sites in the national monitoring network

73. The trends in annual mean ozone concentrations in the urban environment have been explored in terms of the partitioning of oxidant between its component forms of ozone and NO_2, and how this varies with trends in the availability of NO_x. Figure 2.24 shows measured annual mean concentrations of ozone, NO_2, total oxidant (OX) and NO_x in central London from 1972 to 2006 (2006 data are provisional, OX is expressed as μg m^{-3}, as NO_2). A simplified version of the oxidant partitioning model (Jenkin, 2004) has been applied here to partition the OX concentration between ozone and NO_2 as a function of the measured NO_x concentration. The OX concentration includes contributions from background oxidant and local primary NO_2. OX concentrations were highest in the mid 1970s when photochemical ozone concentrations were likely to have peaked and measured NO_x concentrations were high. There was an additional peak in OX in 1991, which coincided with the high NO_x concentrations and a major NO_2 episode (Bower *et al.*, 1994) in that year. The fit of the predicted and measured ozone and NO_2 concentrations is very good, suggesting that the function within the oxidant partitioning model provides a good fit to the data. Annual mean ozone concentrations declined from the mid 1970s to a minimum in the late 1980s, followed by an increase to current levels as NO_x emissions and concentrations have declined considerably.

74. The more recent trends in annual mean urban ozone concentrations have been examined at a range of monitoring sites using the site-specific projections model (Stedman *et al.*, 2001). In this model we have tried to explain the trends in measured ozone resulting from a combination of the changes in NO_x described by emission inventories and the resulting changes in the partitioning of OX. The site-specific projections of NO_x have been calculated both backwards and forwards in time from a base year of 2003 using sector specific emission projections from the NAEI and a source apportionment of local sources derived from the mapped inventory. NO_2 and ozone projections have been calculated from a combination of these NO_x projections and estimates of regional and local oxidant concentrations using the oxidant partitioning model to assign OX between NO_2 and ozone. The background oxidant concentration has been assumed to remain constant in all years. The local oxidant has been assumed to be a constant proportion of the total NO_x concentration, the value of the primary NO_2 emissions fraction (f-NO_2) has been held constant at the values derived by Jenkin (2004) from monitoring data up to and including 2001 (14 % in central London and about 9 % elsewhere).

75. Figure 2.25(a) shows the results of this assessment for the London Bloomsbury site. The predicted increase in annual mean ozone concentration is in good agreement with the measurements at this site. Emission inventory projections out to 2020 suggest that NO_x concentrations are likely to remain sufficiently high that NO_2 concentrations will remain higher than those of ozone.

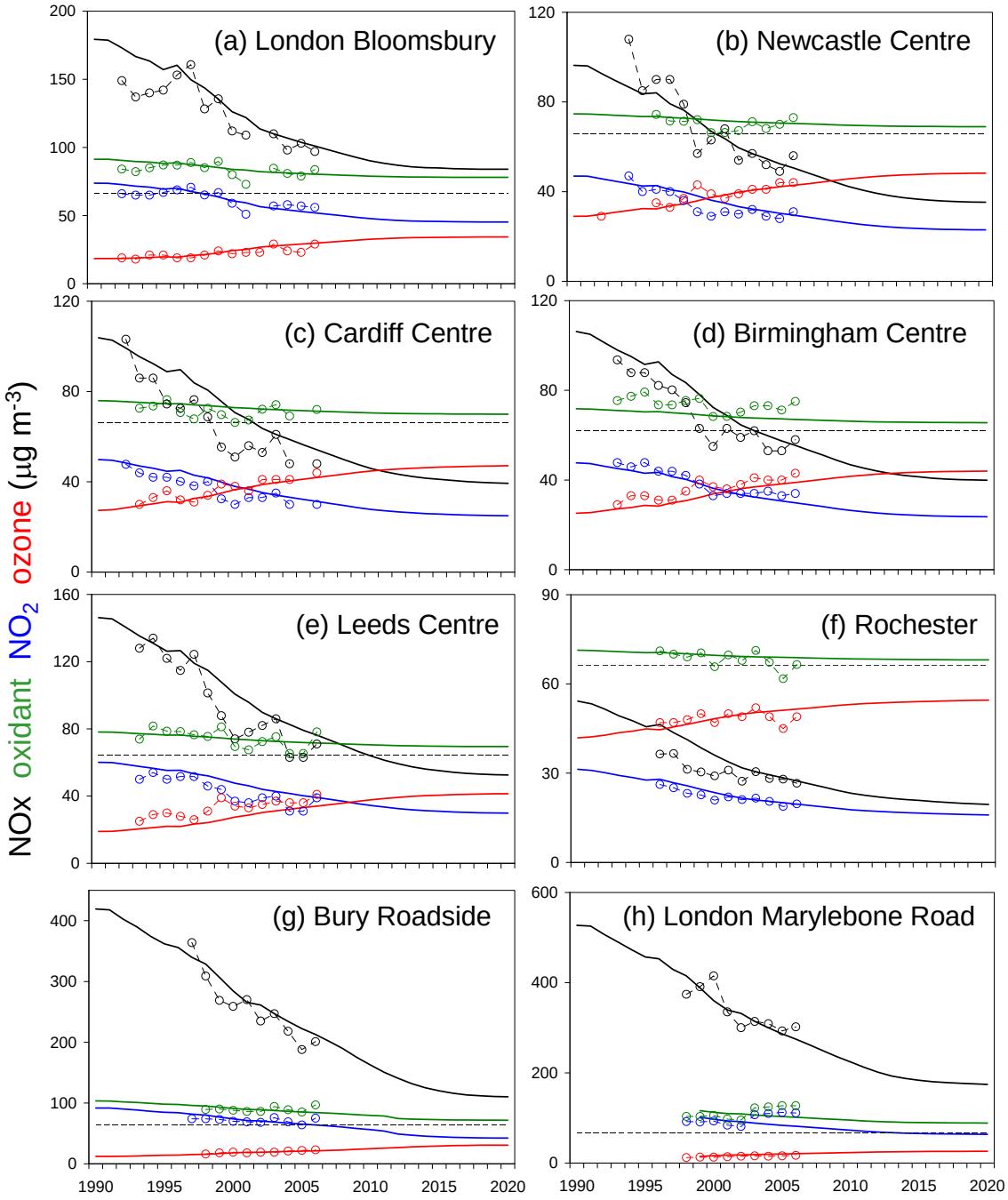


Figure 2.25 Site-specific predictions of NO_x, NO_2, ozone and oxidant at selected urban centre and roadside sites. The lines are the modelled projections and the points are measured annual mean data. The broken line in each panel indicates the level of regional oxidant specified in the model.

76. Figure 2.25(b-e) shows similar plots for the Newcastle Centre, Cardiff Centre, Birmingham Centre and Leeds Centre sites. Once again there is reasonably good agreement between the predictions and the measured trends in NO_x, NO_2 and ozone at these sites. NO_x concentrations have declined sufficiently that annual mean ozone concentrations are now higher than annual NO_2 concentrations at a number of these urban monitoring sites. It is also interesting to note that about three quarters of the predicted increase in annual mean ozone concentrations between the early 1990s and 2015 had already taken place by 2006.

77. Figure 2.25(f) shows the results of a similar analysis for the semi-rural site at Rochester. While the trend in annual mean NO_x is somewhat less steep than implied by the model the predicted trends in ozone and NO_2 are explained well.

78. Figure 2.25(g-h) show the trends in ozone, NO_2 and NO_x at the roadside sites at Bury Roadside and London Marylebone Road. The measured ozone concentrations are lower at these roadside locations because NO_x concentrations are much higher. The predicted concentrations and trends in ozone concentrations are in good agreement with the measurements at these two sites. NO_2 concentrations are predicted less well and this is discussed in the AQEG report on trends in primary NO_2 (AQEG, 2007a). Primary NO_2 emission fractions have been assumed to remain unchanged, as have the levels of regional oxidant in the simple analysis shown here. The main message from this analysis is that the broad patterns of the increase in annual mean ozone concentrations at urban sites can be explained by a combination of changes in NO_x emissions and the partitioning of oxidant, such that a progressively greater fraction is in the form of ozone and the NO_x concentration decreases.

2.9 Observations of trends in concentrations of ozone-precursors

79. The observed trends in ozone concentrations, concentration distributions and related metrics described in the previous sections has been interpreted in terms of the modification of a baseline ozone level by chemical processes occurring on local and regional scales. These processes involve either the production of ozone from the regional scale photochemical processing of emitted VOC and NO_x, or the removal of ozone by local reaction with emitted NO. The observed ozone trends have thus been rationalised in terms of substantial reductions in the emissions of anthropogenic VOC and NO_x since the early 1990s, which have been driven, in particular, by Europe-wide controls on the emissions from petrol-engined motor vehicles through the fitting of three-way gas catalysts to reduce exhaust emissions, and canisters to reduce petrol evaporation emissions.

80. The site-specific analysis and interpretation of annual mean ozone trends presented in the previous section demonstrates the progressive reduction in NO_x concentrations at a selection of UK sites, and confirms that these observations are fully consistent with those predicted on the basis of the NAEI (e.g. as presented in AQEG 2007b). In this section, trends in the concentrations of hydrocarbons at UK sites are examined, allowing assessment of the effectiveness of EU control measures implemented to reduce VOC emissions, and how well they are represented in the NAEI.

81. Dollard *et al.* (2007) have recently carried out a comprehensive analysis of concentrations of up to 26 C_2 to C_8 hydrocarbons monitored for varying subsets of the period 1993-2004 at 11 urban background, one rural and one kerbside site within the UK hydrocarbon network. The results demonstrate significant and sustained reductions in the concentrations of the majority of species over this period, with the more reactive VOC implicated in ozone formation typically declining at rates between about 15% and 25% per year, as illustrated for selected species and sites in Figure 2.26, for the period 1993-2004. As discussed by Dollard *et al.* (2007), the magnitude of these reductions is compatible

with the declines in VOC emissions from relevant sources, as represented in the NAEI for the same period, and it is reasonable to infer that similar trends have occurred for other emitted, but unmeasured, VOC which contribute to the same sectors. This therefore confirms the assessment of the impact of control measures designed to limit the emissions of anthropogenic VOC in the EU, and the contribution this has made to the decline in regional-scale ozone formation described in previous sections.

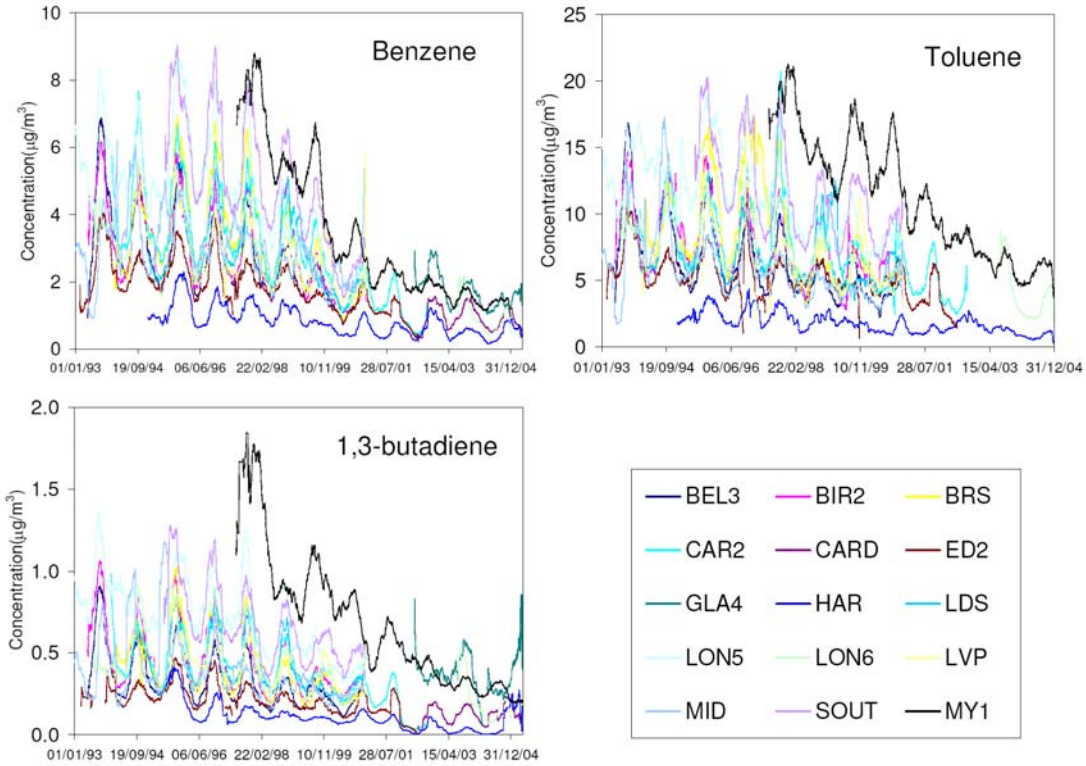


Figure 2.26 Ninety-day running mean concentrations of benzene, toluene and 1,3-butadiene at 15 UK hydrocarbon network sites over the period 1993-2004. The concentrations for Marylebone Road (MY1) have been divided by two to facilitate presentation of the data.

82. The measured series of hydrocarbons includes isoprene (2-methyl-1,3-butadiene), which is known to be emitted from both anthropogenic and biogenic sources, and has therefore been used to provide a marker for biogenic emissions activity. Previous studies have demonstrated that its anthropogenic source (dominated by exhaust emissions) is well correlated with that of the structurally-similar hydrocarbon 1,3-butadiene, with isoprene/1,3-butadiene emissions ratios of ca. 0.4-0.5 on a µg / µg basis (e.g. Derwent *et al.*, 1995; Reimann *et al.*, 2000). Figure 2.27 shows a correlation of daily mean isoprene and 1,3-butadiene concentrations at Marylebone Road over the period 2000-2005, which confirms a limiting anthropogenic ratio of this magnitude, such that the variable excess contribution can be attributed to background biogenic sources. These observations provide a basis for separating isoprene into its anthropogenic and biogenic contributions, as shown in Figure 2.27 and Figure 2.28. Figure 2.28 confirms the steady decline in the anthropogenic contribution, which is 23% per year on average over this six year period, with the biogenic contribution displaying a characteristic seasonal cycle resulting primarily from the light and temperature dependence of isoprene emissions. This shows that the inferred summertime monthly mean biogenic contribution at the end of the time series is comparable to the anthropogenic contribution, and also similar to that inferred previously for the Eltham and Bloomsbury (UCL) sites, as reported in AQEG (2007b). Closer inspection of the daily mean data for August 2003, and hourly-mean data for 10th August

2003 (Figure 2.29), the highest temperature day on record, demonstrates a dominance of the background biogenic contribution under these favourable conditions, even at a busy roadside location. This suggests that biogenic emissions of isoprene (and probably other unmeasured biogenic hydrocarbons) could be playing an increasingly important role in urban scale photo-oxidation processes under such conditions, as the emissions of anthropogenic NMVOC decline.

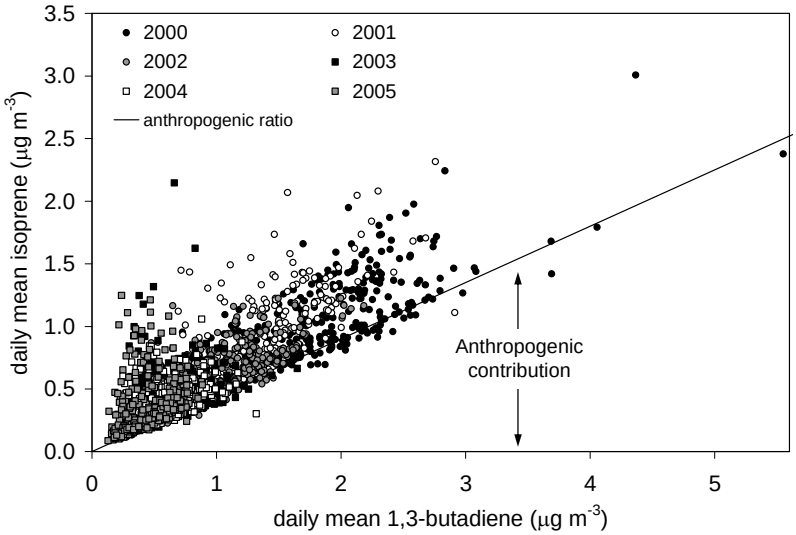


Figure 2.27 Correlation of daily mean concentrations of isoprene and 1,3-butadiene at Marylebone Road over the period 2000-2005. The line indicates a concentration ratio [isoprene]/[1,3-butadiene] = 0.45, which is representative of the limiting anthropogenic ratio.

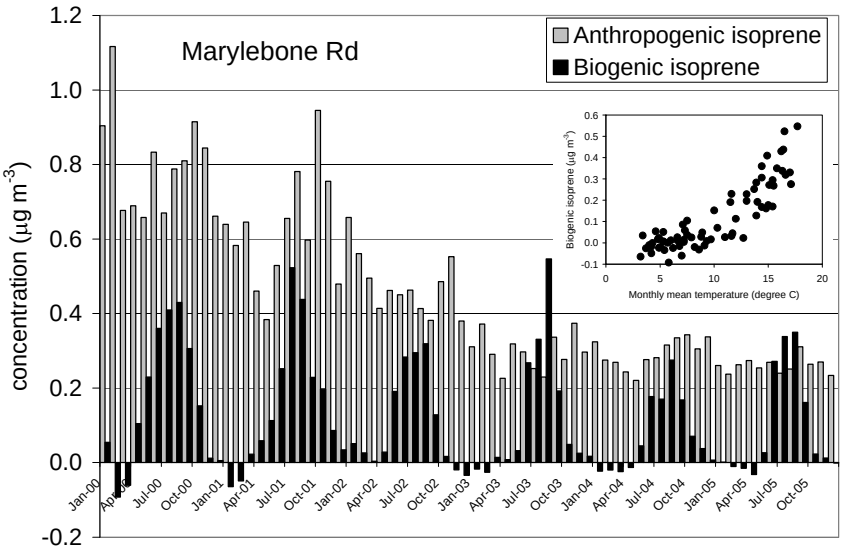


Figure 2.28 Monthly mean anthropogenic and biogenic isoprene concentrations over the period 2000-2005 at Marylebone Road. The anthropogenic contribution to the total was inferred from 1,3-butadiene concentrations, using limiting isoprene/1,3-butadiene ratios in the ratios in the range ca. 0.45 – 0.55 derived from wintertime (Jan, Feb, Nov and Dec) data in each year. The inset shows a correlation of the biogenic isoprene concentration with monthly mean temperature for England and Wales (source UK Meteorological Office).

83. It is important to note, however, that these inferred biogenic isoprene concentrations, and others measured in southern England during the August 2003 heat-wave (i.e. at the AURN site at Harwell, and at Writtle in Essex as part of the NERC TORCH campaign, Lee *et al.*, 2006), cannot be reconciled with current assessments of biogenic isoprene emissions in the UK (e.g., Stewart *et al.*, 2003). The possibility of elevated anthropogenic

evaporative emissions contributing to the inferred biogenic contribution has therefore been considered by AQEG, but the low total diene content of gasoline (which actually has contributions from both 1,3-butadiene and isoprene), are not consistent with a major input of isoprene from this source. This conclusion is also supported by a principle component analysis of long-term observations at sites in Lille, northern France, presented by Borbon *et al.* (2003), who concluded that isoprene was derived significantly from exhaust emissions, and from a second unique (biogenic) source displaying a dependence on temperature and insolation, not observed for any of the other 40 measured C_2-C_9 hydrocarbons. Further work therefore appears necessary to characterise the biogenic sources of isoprene and other more complex hydrocarbons in the UK, so that their impact on ozone formation can be fully assessed.

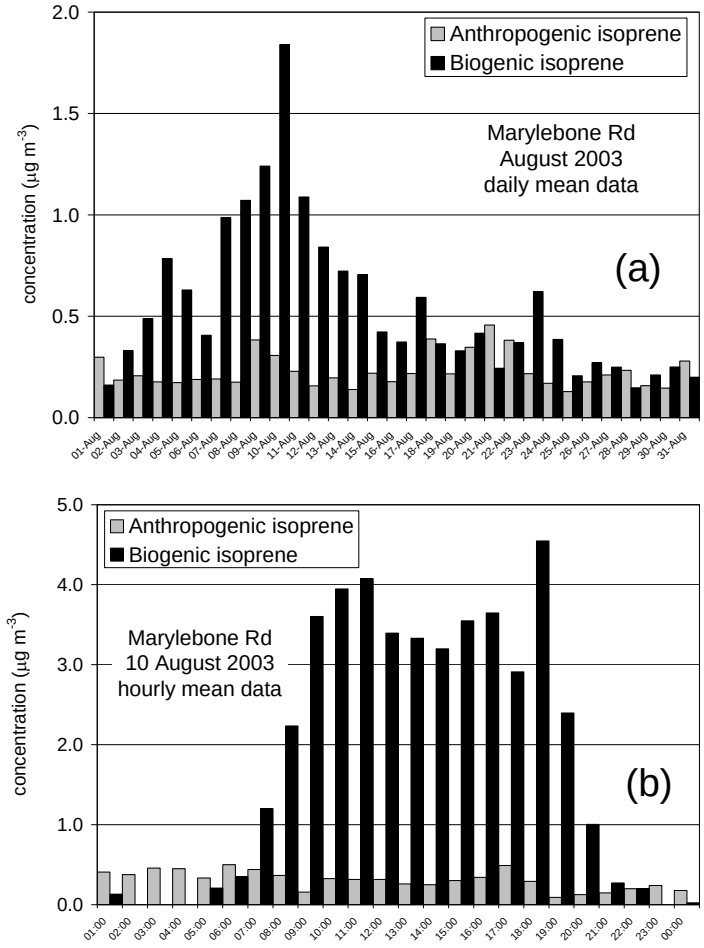


Figure 2.29 Estimated anthropogenic and biogenic isoprene concentrations at Marylebone Road as (a) daily means in August 2003, and (b) hourly-means on 10th August 2003. The anthropogenic contribution to the total was inferred from 1,3-butadiene concentrations, using a limiting isoprene/1,3-butadiene ratio of 0.463 derived from wintertime (Jan, Feb, Nov and Dec) data in 2003.

2.10 Spatial concentration patterns of ozone in the UK

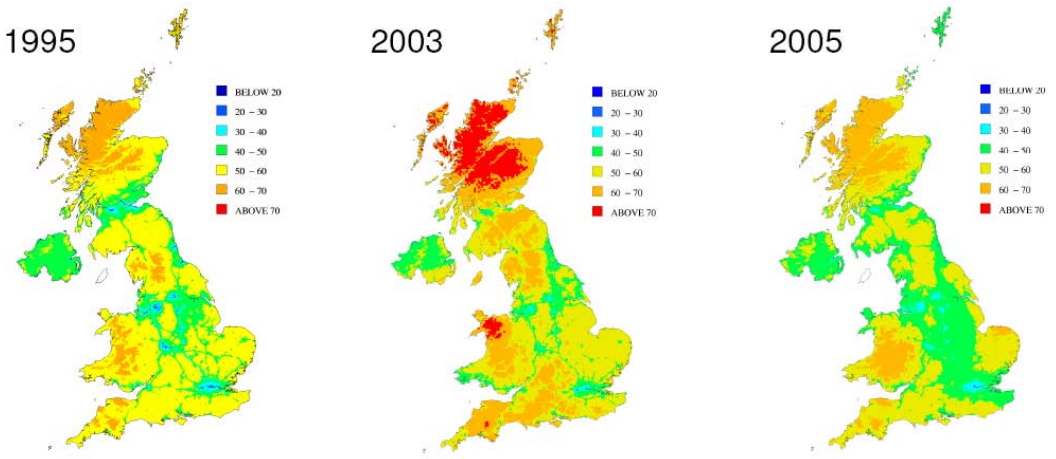
2.10.1 Empirical maps

84. Maps of a range of ozone metrics have been calculated using empirical measurements based Pollution Climate Models (PCM) for the years 1995, 2003 and 2005 (Stedman and Kent, 2008). These years have been chosen to illustrate two recent years with higher and lower photochemical ozone contributions (2003 and 2005) and a year with higher photochemical ozone contributions combined with higher urban NO emissions (1995). These maps are shown in Figure 2.30.

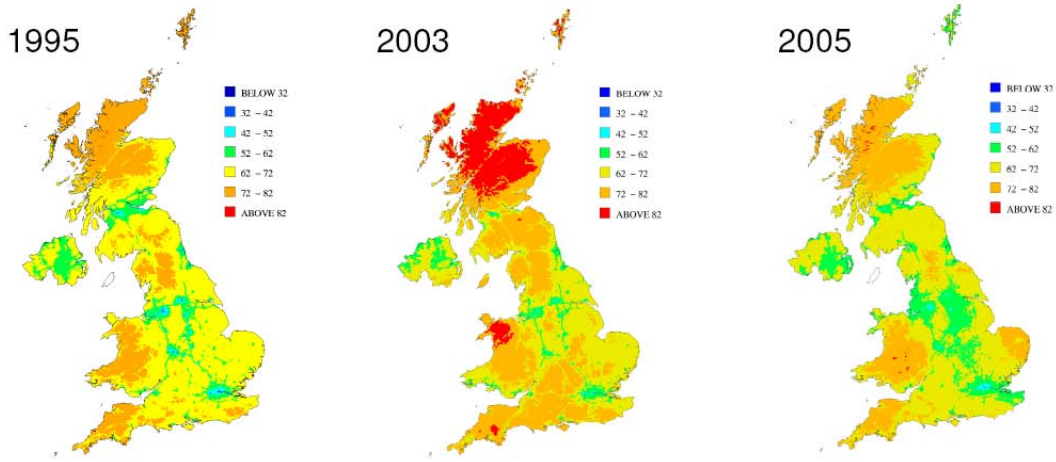
85. The empirical PCM mapping methods used to calculate the maps presented here have been described by Coyle *et al.* (2002), Kent *et al.* (2006) and Bush *et al.* (2005). The maps of annual mean concentration have been calculated by interpolation of monitoring data from rural monitoring sites for the well-mixed period in the afternoon. Two corrections were then applied. Firstly an altitude correction was applied to take account of the effects of topography (Coyle *et al.*, 2002). Topographic effects are important for some ozone metrics, such as the annual mean, because of the disconnection of a shallow boundary layer from air aloft during the night at lowland locations. Surface ozone concentrations are lower at night in these locations due to a combination of dry deposition and titration with NO emissions. This effect is much less marked at higher altitudes and at coastal locations, where wind is generally stronger and a shallow boundary layer does not form. An urban decrement was then calculated using the oxidant partitioning model of Jenkin (2004). Maps of regional oxidant were calculated as the sum of altitude corrected ozone and rural NO_2 as interpolated from measurements at rural sites. The partitioning of oxidant between ozone and NO_2 was then calculated as a function of modelled local NO_x concentrations (the sum of the contributions to modelled NO_x concentration for the appropriate year from local area and point sources from Kent *et al.* 2007). The maps of annual average of the daily maximum of the running 8-hour mean ozone concentration were calculated from the annual mean using a non-linear function derived from monitoring data (see Figure 2.15). We recognise that this metric would not be expected to have a significant altitude dependence as has been implied by our methods in which values have been estimated from the annual mean. The focus of this report is on ozone impacts in urban areas. We therefore chose to base our estimates on the annual mean for which the urban decrement can be calculated using the oxidant partitioning model, rather than the more empirical relationships with NO_x concentrations which we have had to use for the remaining metrics.

86. The maps for the remaining health based metrics were calculated by the interpolation of measurement at rural sites in rural areas followed by the calculation of an urban decrement. The urban decrement has been applied based on empirical linear relationships between the decrement and modelled local NO_x concentrations, which is described in Chapter 5.

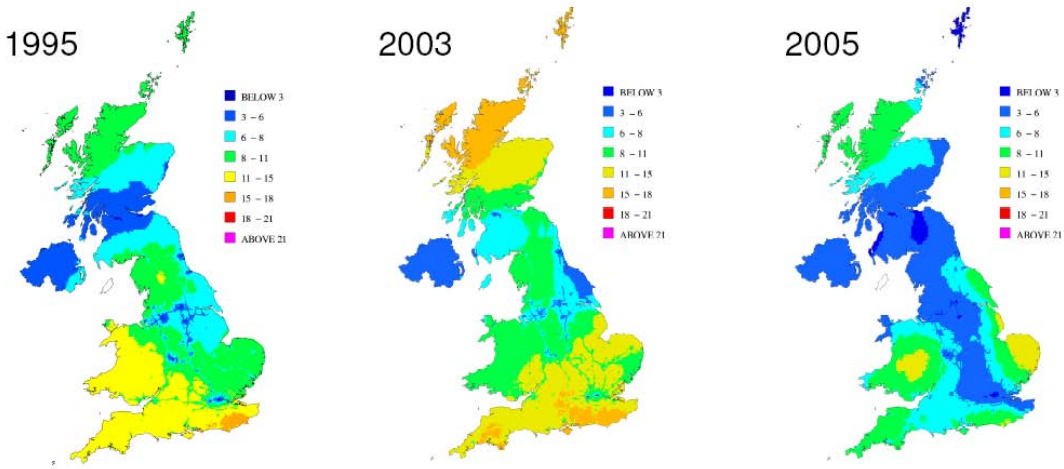
87. The hemispheric background is a major contributor to annual mean ozone concentration across the UK. Upland areas tend to have the highest annual mean ozone concentrations due to topographic effects, as has been described by PORG (1997). There is also a significant decrement in urban areas, as discussed above. Annual mean concentrations in rural areas were highest in 2003 and lowest in 2005 at most locations due to the photochemical episodes during 2003 and perhaps a higher hemispheric background in 2003. Urban concentrations were lowest in 1995 due to the greater local NO emissions at the time. The maps of the annual average of the daily maximum of the running 8-hour mean concentration have been calculated from the annual mean maps using a non-linear function and thus show a similar spatial pattern.



(a) Annual mean ozone concentration (μg m^{-3})

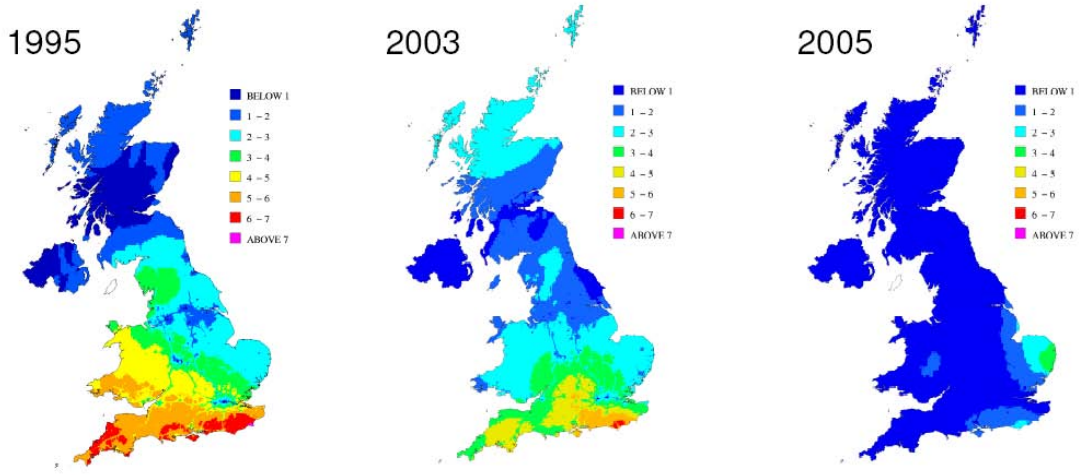


(b) Annual mean of the daily maximum of the running 8-hour mean ozone concentration (μg m^{-3})

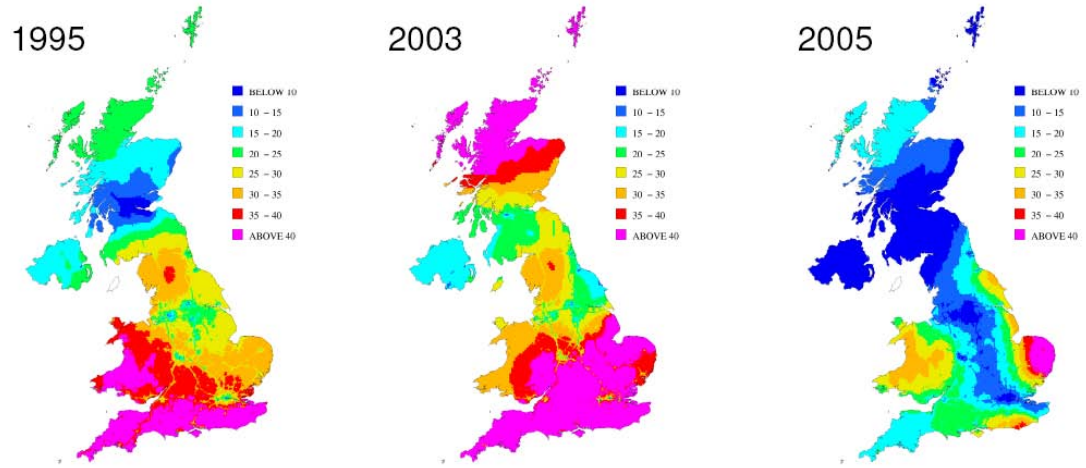


(c) Annual mean of the daily maximum of the running 8-hour mean with a 70 μg m^{-3} cut-off (μg m^{-3})

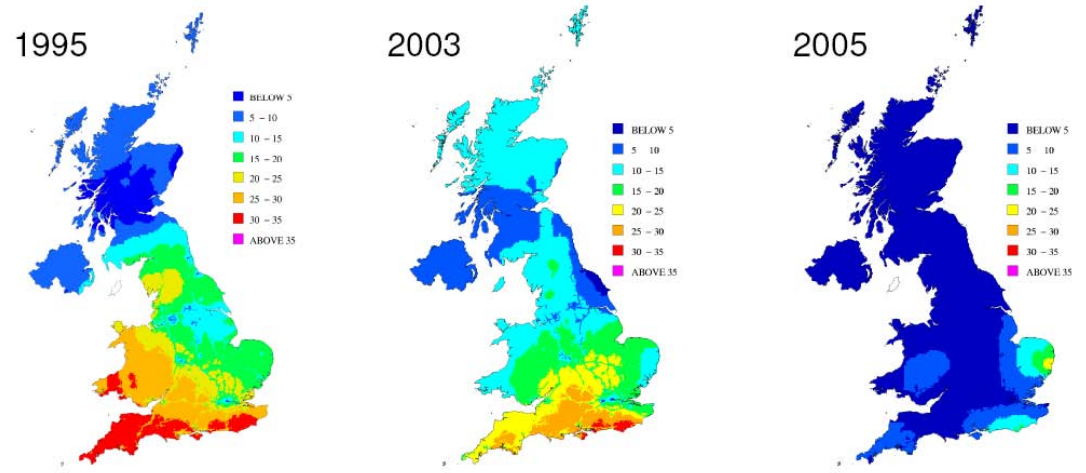
Figure 2.30 Maps for a range of ozone metrics, calculated using empirical measurements-based PCM models for the years 1995, 2003 and 2005. The darkest blue area in Figure 2.30(e) identifies where the AQS objective of less than 10 days >100 μg m^{-3} is achieved.



(d) Annual mean of the daily maximum of the running 8-hour mean with a 100 μg m^{-3} cut-off (μg m^{-3})



(e) Number of days with maximum 8-hour running mean ozone concentration greater than 100 μg m^{-3}



(f) Number of days with maximum 8-hour running mean ozone concentration greater than 120 μg m^{-3}

Figure 2.30 (cont.): Maps for a range of ozone metrics, calculated using empirical measurements based PCM models for the years 1995, 2003 and 2005. The darkest blue area in Figure 2.30(e) identifies where the AQS objective of less than 10 days >100 μg m^{-3} is achieved.

88. Maps of the annual average of the daily maximum of the running 8-hour mean concentration with a cut-off of 70 µg m^{-3} show highest concentrations in the south of the UK, where the contribution from photochemically generated ozone is greatest in northern Scotland, where the impact of the hemispheric background is most pronounced due to the low regional NO_x emissions in this area. There is also an urban decrement for this metric. Concentrations were generally highest in 2003 and lowest in 2005 due to the larger contribution from photochemical ozone episodes in 2003 and 1995. Urban concentrations were lowest in 1995 due to the greater local NO emissions at the time.

89. Values of the annual average of the daily maximum of the running 8-hour mean concentration with a cut-off of 100 µg m^{-3} metric were much higher in 2003 than in 2005. Values were higher in south and south west England and Wales in 1995 than in 2003 for this metric. This is in contrast to the annual mean, which was higher in 2003 in these areas. The contribution from photochemical episodes and an urban decrement are the most important factors influencing the spatial distribution for this metric.

90. The spatial distribution of the number of days with the maximum 8-hour running mean ozone concentrations greater than 100 µg m^{-3} and greater than 120 µg m^{-3} is dominated by the contribution from photochemical episodes and therefore highly variable from year to year. The number of days above 100 µg m^{-3} was highest in the south and south west and Wales in 1995, and highest in the south east in 2003 (and also high in the north of Scotland in 2003 due to the higher background) and highest in East Anglia in 2005 although values were generally much lower. There are also clear urban decrements for these metrics.

91. The results of this mapping exercise are summarised in Table 2-2 in terms of the population-weighted mean values of each of the metrics. The population-weighted mean has been calculated by multiplying the 1 km x 1 km background maps by 1 km x 1 km population statistics from the 2001 census. The values for all of the grid squares are summed and then divided by the total population to calculate the population-weighted mean. This is a useful summary statistic, which for the metrics derived as the annual mean of the daily maximum of running 8-hour means is related to human health impacts if the dose response function is assumed to be linear. The health impact can be estimated by multiplying the population-weighted mean by the dose response coefficient (expressed as a percentage change in impact per µg m^{-3}) and by a baseline rate of the health impact in the absence of the air pollutant (e.g. Defra, 2006c). Thus the maps calculated here would enable health effects to be estimated if the dose response function is assumed to apply from either 0, 70 or 100 µg m^{-3}. Population-weighted means have been calculated for the UK as a whole and for each of the devolved administrations and for London and the rest of England.

92. Figure 2.31 shows the UK population-weighted mean for each metric compared to the value in 1995. The metrics fall into three groups. The number of days with running 8-hour mean ozone concentrations greater than 120 µg m^{-3} and annual mean and the daily maximum of the running 8-hour mean concentration with a cut-off of 100 µg m^{-3} were both highest in 1995 and lowest in 2005. These are the metrics most strongly influenced by regional photochemical ozone production. The annual mean and the daily maximum of the running 8-hour mean concentration with a cut-off of 0 µg m^{-3} were both highest in 2003 and slightly higher in 2005 than in 1995. These metrics are strongly influenced by the hemispheric background (which was high in 2003) and the urban decrement (which was greatest in 1995). The number of days with running 8-hour mean ozone concentrations greater than 100 µg m^{-3} and the daily maximum of the running 8-hour mean concentration with a cut-off of µg m^{-3} were highest in 2003 and lowest in 2005. These metrics are influenced by both regional photochemical ozone production (high in 1995 and 2003) and the urban decrement (which was greatest in 1995).

Table 2-2 Population-weighted mean values calculated from the maps of ozone metrics.

a) 1995

	Annual Mean (µg m^{-3})	0 µg m^{-3} cut-off metric (µg m^{-3})	70 µg m^{-3} cut-off metric (µg m^{-3})	100 µg m^{-3} cut-off metric (µg m^{-3})	Days greater than 100 µg m^{-3} (days)	Days greater than 120 µg m^{-3} (days)
Scotland	40.9	56.3	4.6	0.7	11.6	4.3
Wales	49.7	65.0	11.2	4.3	36.0	25.7
Northern Ireland	42.8	58.3	5.2	1.1	18.9	6.7
Inner London	31.9	47.0	5.3	2.0	22.7	13.0
Outer London	36.4	51.8	7.3	2.8	27.7	16.5
Rest of England	44.5	59.9	8.5	3.1	29.6	18.6
UK	43.2	58.6	7.9	2.8	27.6	17.0

b) 2003

	Annual Mean (µg m^{-3})	0 µg m^{-3} cut-off metric (µg m^{-3})	70 µg m^{-3} cut-off metric (µg m^{-3})	100 µg m^{-3} cut-off metric (µg m^{-3})	Days greater than 100 µg m^{-3} (days)	Days greater than 120 µg m^{-3} (days)
Scotland	51.1	66.3	8.1	1.0	24.5	7.9
Wales	51.3	66.5	9.2	2.3	33.9	15.2
Northern Ireland	45.2	60.7	4.7	0.5	16.5	7.1
Inner London	38.1	53.6	7.6	2.1	31.4	11.8
Outer London	42.2	57.8	9.5	2.7	38.1	15.1
Rest of England	48.6	64.0	9.4	2.5	34.9	15.6
UK	47.9	63.2	9.0	2.3	33.5	14.4

c) 2005

	Annual Mean (µg m^{-3})	0 µg m^{-3} cut-off metric (µg m^{-3})	70 µg m^{-3} cut-off metric (µg m^{-3})	100 µg m^{-3} cut-off metric (µg m^{-3})	Days greater than 100 µg m^{-3} (days)	Days greater than 120 µg m^{-3} (days)
Scotland	43.6	59.1	3.7	0.1	4.5	0.1
Wales	51.2	66.5	8.1	0.7	23.3	3.8
Northern Ireland	42.5	58.0	3.8	0.1	3.0	0.2
Inner London	33.4	48.7	2.6	0.3	5.9	2.5
Outer London	37.5	53.0	3.8	0.5	9.6	3.6
Rest of England	44.9	60.4	5.9	0.7	16.1	3.7
UK	44.0	59.4	5.4	0.6	14.1	3.2

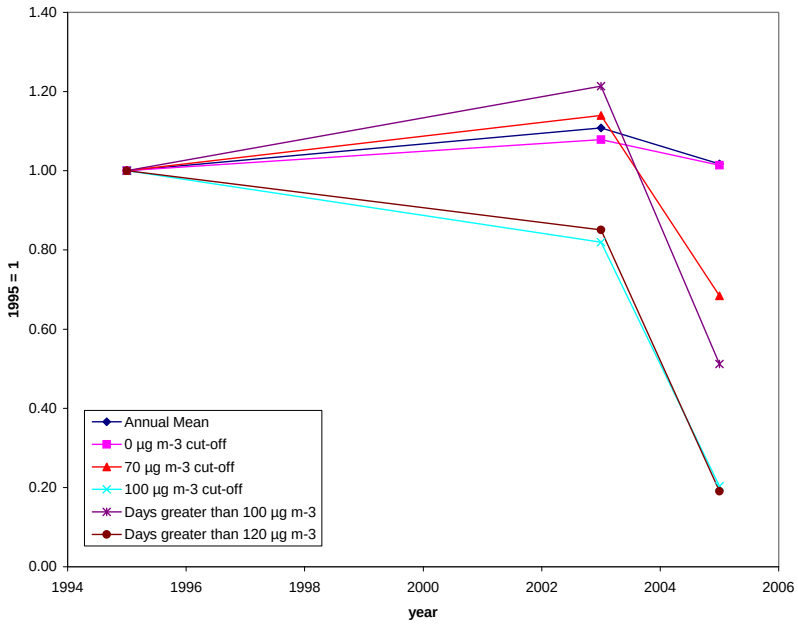


Figure 2.31 Changes in UK population-weighted mean values of the different ozone metrics.

2.10.2 Transects across the London conurbation

93. The results of this mapping exercise for 1995, 2003 and 2005 have been further examined by plotting a transect of modelled ozone concentrations across the London area from west to east through central London. The annual means for the three years (Figure 2.32(a)) were reasonably similar and illustrate the urban decrement very well. The annual mean was generally highest in 2003 across London. The annual means in suburban areas were lowest in 2005 but the annual means in central London were lowest in 1995 due to the greater NO_x emission density in the city centre in 1995.

94. Monitoring data for non-roadside sites close to the transect (which is at northing 183500) are also included in the figure. Data for the AURN have been included for 1995 (only two sites are available) and 2005, for 2003 we have also included a wider set of data from the LAQN. Figure 2.33 shows the location of the transect and the monitoring sites for both the AURN and the LAQN. The agreement between the modelled transect and the measurements is very good, differences could be caused by uncertainties in the modelling, and the fact that the monitoring sites do not lie directly on the transect. Both the ranking of the years and the magnitude of the urban decrement are confirmed by the measurements.

95. Figure 2.32(b) shows a similar plot for the daily maximum of the running 8-hour mean concentration with a cut-off of 70 µg m^{-3}. Values of this metric were highest in 2003 across the whole of London and only a little lower in 1995. Values of this metric were much lower in 2005 when there was less photochemically generated ozone. Once again the monitoring data confirm the results of the modelling assessment. Data from the AURN only have been included for this metric and the metric with a cut-off of 100 µg m^{-3}.

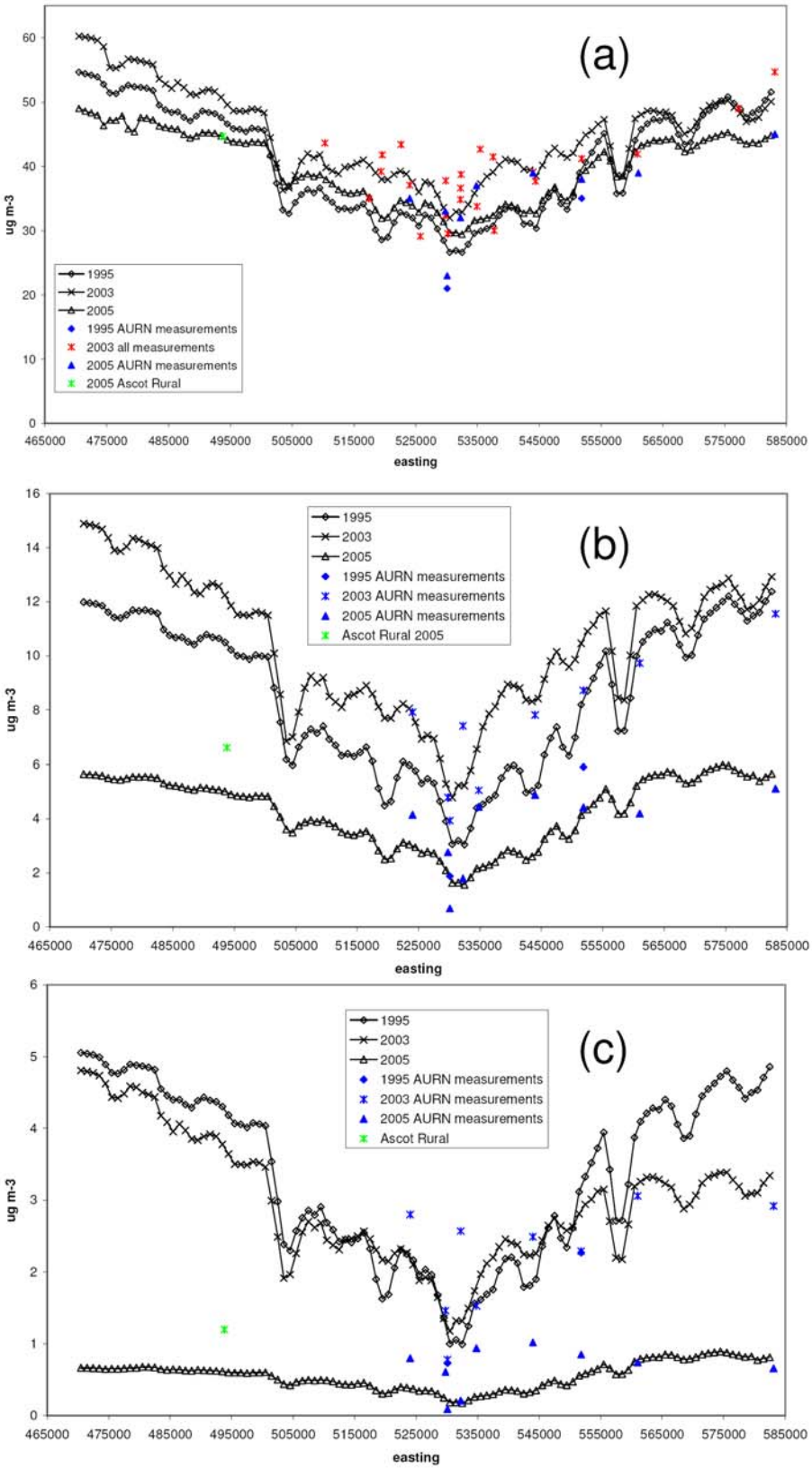
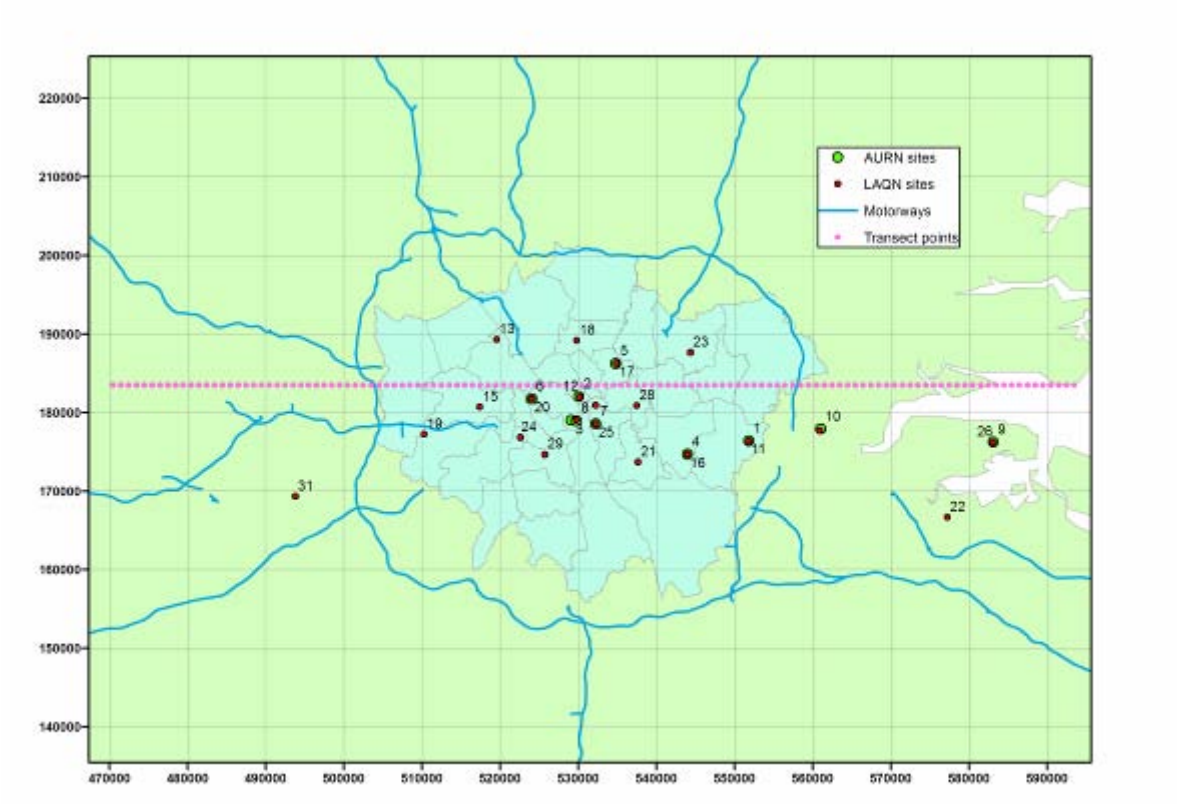


Figure 2.32 Transects of ozone metrics across London. (a) Annual mean ozone concentration; (b) Annual mean of the daily maximum of the running 8-hour mean ozone concentration with a 70 µg m^{-3} cut-off; and (c) Annual mean of the daily maximum of the running 8-hour mean ozone concentration with a 100 µg m^{-3} cut-off.



Site	Network	Code		Site	Network	Code
London Bexley	AURN	1		Hackney 4 - Clapton	LAQN	17
London Bloomsbury	AURN	2		Haringey 2 - Priory Park	LAQN	18
London Bridge Place	AURN	3		Hounslow 2 - Cranford	LAQN	19
London Eltham	AURN	4		Kens and Chelsea 1 - North Kensington	LAQN	20
London Hackney	AURN	5		Lewisham 1 - Catford	LAQN	21
London N. Kensington	AURN	6		Luton Background	LAQN	22
London Southwark	AURN	7		Redbridge 1 - Perth Terrace	LAQN	23
London Westminster	AURN	8		Richmond 2 - Barnes Wetlands	LAQN	24
Rochester	AURN	9		Southwark 1 - Elephant and Castle	LAQN	25
Thurrock	AURN	10		Stoke Rural (AURN)	LAQN	26
Bexley 1 – Slade Green (AURN)	LAQN	11		Thurrock	LAQN	27
Bloomsbury - AURN	LAQN	12		Tower Hamlets 1 - Poplar	LAQN	28
Brent 1 - Kingsbury (AURN)	LAQN	13		Wandsworth 2 - Town Hall	LAQN	29
City of London 1 - Senator House	LAQN	14		Westminster – AURN	LAQN	30
Ealing 1 – Ealing Town Hall	LAQN	15		Ascot Rural	LAQN	31
Greenwich 4 - Eltham	LAQN	16				

Figure 2.33 The locations of the London transect and monitoring sites included in the analysis.

96. The transect for the daily maximum of the running 8-hour mean concentration with a cut-off of 100 µg m^{-3} is shown in Figure 2.32(c). This figure also shows the impact of the urban decrement superimposed on the impact of photochemically generated ozone. Values of this metric were very low in 2005 and were somewhat higher in 1995 than in 2003 in suburban areas. The greater urban decrement in 1995 lead to values of this metric being similar in 1995 and 2003 in the centre of London. Once again there is reasonably good agreement between the model and available measurements.

97. Figure 2.34 shows the results of a more detailed assessment of data from the LAQN for 2003. This figure shows the transects for the annual mean, monthly mean for August 2003, mean for the 9th of August 2003 and the values for 15:00 GMT on this day (which was the peak of a major photochemical episode). The maximum urban decrement is about 25 µg m^{-3} for the annual mean, 35 µg m^{-3} for the monthly mean, 50 µg m^{-3} for the daily mean and 85 µg m^{-3} for the 15:00 value. Thus the maximum urban decrement is about 30% to 40% of the rural values.

98. The analysis of monitoring data transect for London confirms that the empirically generated maps include a reasonably realistic description of the urban decrements.

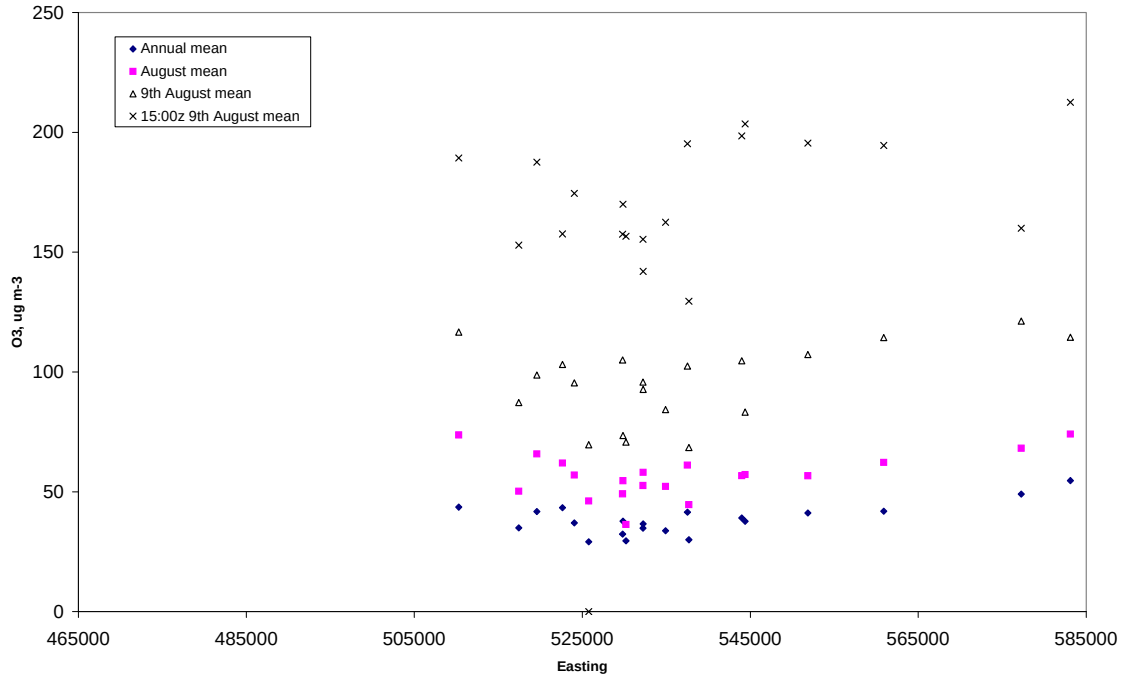


Figure 2.34 Ozone transect across London in 2003 (µg m^{-3})

Chapter 3

Trends in background ozone concentrations

Question 2: *Observations since the 1970s have shown that global background ozone concentrations have been rising throughout this period. What is the strength of these data, and what is the evidence concerning the trends and likely projections of precursor emissions, and the resultant ozone concentrations?*

Short answer to question 2

99. **There is strong evidence that background or, more strictly, baseline* surface ozone concentrations in the northern hemisphere have increased by up to 10 µg m^{-3} per decade over the last 20 - 30 years. This increase has been attributed to the growth in man-made ozone-precursor emissions from industry, road, air and ship transport, homes and agriculture. Future ozone concentrations depend on which of the possible future emission scenarios is followed. Future annual mean surface ozone concentrations in the southern half of the United Kingdom are simulated to increase by about 6 µg m^{-3} in a "current legislation" (IIASA CLE) scenario and to decrease by about 4 µg m^{-3} in a "maximum feasible reduction" (IIASA MFR) scenario between 2000 and 2030. Observed baseline ozone concentrations over the 2000 – 2006 period have remained level and have shown no overall trend.**

Detailed answer to question 2

100. There is a substantial body of evidence that points to a more than doubling in surface ozone levels in the northern hemisphere since pre-industrial times. Modern ozone measurements began in the 1960s and many background and remote northern hemisphere monitoring stations have recorded upwards trends over the main continental regions. At some sites, these upwards trends slowed and levelled off during the 1980s, some during the 1990s and almost all by the 2000s. The trends revealed by ozone sondes for the middle and upper troposphere broadly agree with those from the surface observations. These trends since pre-industrial times have been driven by increasing emissions of man-made tropospheric ozone-precursor gases, particularly methane, VOCs, carbon monoxide and NO_x.

101. There is, however, no agreed picture of the growth in global ozone background concentrations from the 1970s onwards that covers all the surface sites and all the main continents. With photochemistry producing local ozone lifetimes as short as a few days in the boundary layer, local measurement of tropospheric ozone does not reflect the abundance over the same continent and a surface measurement is not representative of the bulk troposphere above. Thus, it is not contradictory for ozone trends in different atmospheric regions to be different because there may well be different trends in regional pollutants driven particularly by changes in NO_x emissions. The continuity of some of the ozone records has been compromised by changes in measurement and calibration techniques, relocation of sites and by changes in local influences from road traffic and development at the stations.

Footnote*

Baseline or background ozone concentrations require careful definition, see Box 3.1

102. The ozone record at Mace Head, on the west coast of Ireland, for the period from 1987 – 2007 is relatively unique, however, in that it has been collected from only two instruments, quality assurance has been maintained consistently to a high standard and data capture has been excellent. Furthermore, the hourly measurements have been sorted by air mass origins to separate the data record into a dataset for baseline northern hemisphere air masses and one for European regionally-polluted air masses. The unsorted data show little overall trend from 1987 – 2006 in common with most remote European monitoring stations. This is because the observed downwards trend in the polluted air masses have more or less compensated for the observed upwards trends in baseline data, leaving little overall trend. Baseline ozone levels as recorded at Mace Head are of some policy significance because they characterise the background levels in the British Isles upon which regional-scale pollution episodes are superimposed. The definition of baseline in this context is explained in Box 3.1.

103. The observed trend in the ozone mixing ratios in baseline air masses at Mace Head, Ireland is highly statistically significant over the 1987 – 2006 period and amounts to +0.7 µg m^{-3} per year. The trend has been significantly higher in winter and spring, compared with the summer months. The seasonal cycle in ozone mixing ratios has therefore increased in amplitude over this period. Observations at Pacific coast sites in North America show similar upwards trends to this Atlantic coast site in Europe. It is possible that such inflow sites show up the influence of intercontinental ozone transport much more effectively compared with surface sites in continental regions.

104. Examination of the 1995 – 2006 period shows that monthly mean baseline ozone concentrations rose steadily to unprecedented levels of over 100 µg m^{-3} during the winter of 1998-1999 before falling somewhat thereafter, interrupted temporarily by a secondary peak in 2002-2003. During 2006, 12-month running mean baseline ozone concentrations showed evidence of levelling out and re-establishing the former upwards trend. Over the 1995 – 2006 period annual mean baseline ozone mixing concentrations showed an upwards trend of +0.4 µg m^{-3} per year. The peaks in 1998-1999 and 2002-2003 have been identified as due to boreal biomass burning in Alaska, Yukon and Siberia from an examination of simultaneous changes in the annual growth rates of carbon dioxide, methane and carbon monoxide. Over recent years since 2000, 12-month rolling mean monthly mean baseline ozone abundances have remained relatively constant and have shown little evidence of significant trends either positive or negative. Over this same period, baseline methane abundances have also levelled-off from their previous extended period of rising levels. Observations therefore show that the period of steadily rising ozone and methane baseline levels has given way to a period of relatively constant methane and ozone baseline levels, although predictions of future trends are highly uncertain.

105. Global chemistry-transport models have been used to verify the general picture described above for the growth in northern hemisphere background ozone levels, in general, and at Mace Head, in particular. These studies have benefited from the significant improvements that have been made in the gridded global emission inventories of man-made tropospheric ozone-precursor gases as a result of the UN FCCC and IIASA activities. Further details of the emission inventories and emission scenarios used here are given in the Annex 2. Models are able to account for much of the observed growth in observed background ozone and methane levels up to the present-day. Model-predicted trends for surface ozone up to 2030 vary spatially across Europe and are scenario dependent. Future annual mean ozone abundances for the southern United Kingdom in the STOCHEM model increase from 66 µg m^{-3} in 2000 to 72 µg m^{-3} in 2030 in the IIASA CLE scenario corresponding to an annual increase of +0.3 % per year. In contrast, in the IIASA MFR scenario, rolling mean ozone abundances fall to 63 µg m^{-3} in 2030, corresponding to a decline of -0.2% per year. Observed baseline ozone abundances over the 2000 – 2006

period have remained level and shown no overall trend, in the middle of the range of the STOCHEM model simulations.

Supporting evidence for question 2

3.1 Overview

106. Chapter 2 addresses the trends in global background ozone, the strengths of these data and the likely projections in future ozone concentrations. The supporting evidence assembled here deals with the ozone trends since the pre-industrial era, the growth in the global ozone background, observations of the ozone baseline trend at Mace Head, Ireland, modelling the global background trend and the projections of future background ozone concentrations in the British Isles.

107. Ozone is present in surface air at every monitoring site across Europe, on almost every hour of the day. As an illustration, Figure 3.1 presents the frequency distribution of the observed ozone concentrations at the Harwell, Oxfordshire site during 2006. The most frequent hourly concentrations lie in the range from about 50 to 75 µg m^{-3}.

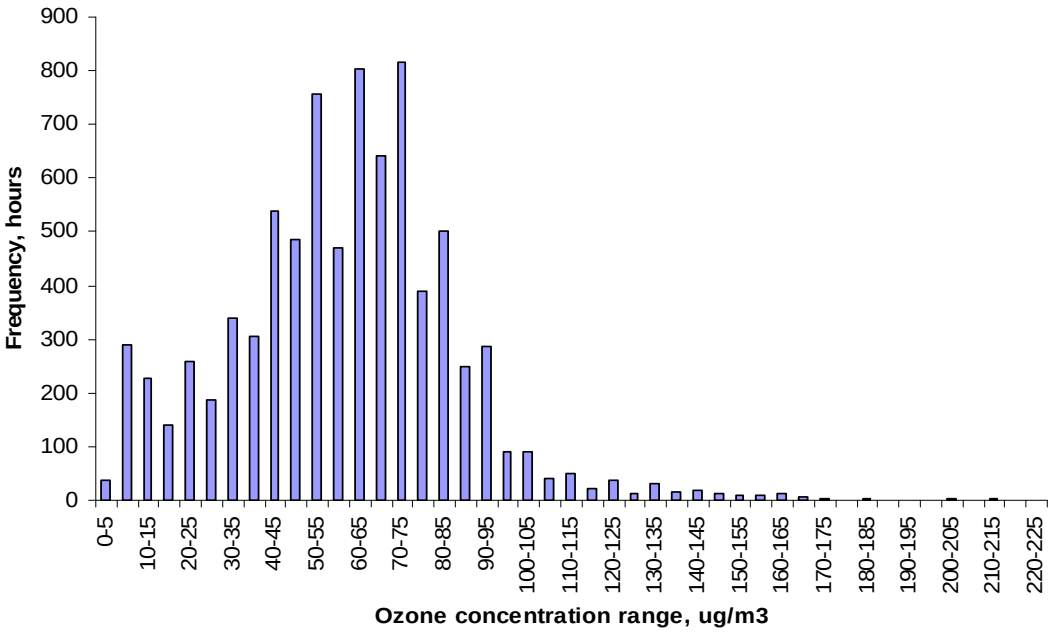


Figure 3.1 Frequency distribution of the hourly-mean ozone concentrations observed at Harwell, Oxfordshire during 2006 in µg m^{-3}.

108. The presence of pollution episodes is clearly seen as a 'tail' extending to high concentrations and there is evidence of a 'tail' extending to low concentrations. This behaviour carries the implication that there is a background source of ozone so that even in the cleanest of situations, the air masses arriving at the Harwell site almost always contain ozone. Further details of ozone frequency distributions and their trends are given in the answer to Chapter 2.

109. Background ozone concentrations are not usually accessible from observations, see Box 3.1. Generally speaking, observations in the cleanest of situations, when the influence of local man-made source is minimal, are employed to define baseline concentrations. Hence those observations at Mace Head, Ireland that have been made in air masses that have recently been transported many thousands of kilometres across the North Atlantic Ocean, would be termed baseline observations. Baseline and global background

concentrations are thus not the same because of their different roots in observations and modelling, respectively. Further explanations concerning the terms global background and baseline concentrations are given in Box 3.1.

Box 3.1. Global background and global baseline concentrations.

For the air quality pollutants such as SO_2, NO_2 and NO_x, the term background concentrations implies concentrations observed at locations away from the immediate influence of local sources of pollution. There is gradation in pollution level between urban background, rural or regional background and global background concentrations of an air quality pollutant. Urban background concentrations are those observed in urban areas away from the direct influence of heavily-trafficked roads and chimney stacks. Rural or regional background concentrations are those observed at locations where there is little influence from urban sources of pollution. Global background concentrations are those monitored in pristine locations where there is little or no influence at all from man-made sources of pollution on the urban or regional scales.

These definitions of urban, rural and global background concentrations are somewhat subjective and this leads to difficulties particularly in ensuring the comparability of urban background concentrations between different networks. Rural background locations are more straightforward to define and to ensure comparability between networks. Generally speaking, the siting criteria promulgated by EMEP are stricter than those generally accepted for rural locations and so EMEP sites generally report remote rural background concentrations. Global background sites are usually established on mountain-tops or on islands surrounded by oceans and have the greatest degree of isolation from man-made sources of pollution.

For pollutants with atmospheric lifetimes longer than days and for secondary pollutants, the above definitions that have worked so well for air quality pollutants are fraught with difficulties and there are major operational problems. For the long-lived greenhouse gases that build up in the atmosphere, it is not possible to find a location in the northern hemisphere that is free of the influence of continental emissions because their lifetimes are longer than the time taken to advect the emissions around a latitude circle. For ozone, it is also not possible to find a location in the northern hemisphere that is free from the influence of man-made emissions because tropospheric precursor emissions from each continent form ozone on the hemispheric scale. As a result, it is not possible to observe the global background concentrations of ozone and the long-lived greenhouse gases because there are no locations with the required degree of isolation from man-made sources.

For ozone and the long-lived greenhouse gases, operational expediency has brought into use the terms baseline site or monitoring station and hence baseline concentration. A baseline site is one that is not influenced by recent, local sources of man-made pollution. This is the approach adopted by WMO in its Global Atmosphere Watch programme. Observations may be made continuously and subsequently sorted or air samples taken only when meteorological conditions are such that the recorded concentrations are free from the recent, local influence of man-made sources. Observations made at the baseline monitoring station at Mace Head, Ireland are carefully sorted by air mass origins. Those observations made when the air masses have recently traversed the North Atlantic Ocean are classified as baseline observations, whereas those made when the air masses arrive from continental Europe are classified as regionally-polluted. On average, for about two-thirds of the time the Mace Head monitoring site monitors baseline air masses off the North Atlantic Ocean.

Baseline concentrations and global background concentrations differ significantly in magnitude for ozone and the long-lived greenhouse gases, though it is not possible by observation to quantify these differences for each trace gas. Baseline concentrations will always be higher than global background concentrations because of the influence of man-made sources of pollution on the hemispheric and global scales on the former.
The operational difficulties associated with the observation of global background concentrations of ozone and the long-lived greenhouse gases do not arise in modelling studies. It is a straightforward modelling exercise to quantify global background concentrations of any trace gas using a variety of source-apportionment and labelling techniques.

Global background and baseline concentrations are terms that are often used interchangeably. Strictly speaking, the term baseline should be used for observations and global background for modelled ozone in the absence of all man-made sources.

In summary, urban background and rural background concentrations of the air quality pollutants are straightforwardly observed using pollution monitoring networks. The global background concentration of an air quality pollutant is that concentration that would be observed in the absence of all man-made sources. For ozone and the long-lived greenhouse gases, it is not possible to find a location that would be free from the influence of man-made sources of pollution. Baseline concentrations are those observed free from the influence of recent, local sources of pollution.

3.1.1 Ozone trends since the pre-industrial era.

110. The change in tropospheric ozone since the pre-industrial era is difficult to evaluate on the basis of observations alone because ozone is highly reactive and atmospheric abundances cannot be retrieved from ice cores. Recent evaluations of surface observations in the 19th and early 20th centuries in Europe indicate much lower ozone abundances than today (Volz and Kley, 1988; Marenco *et al.*, 1994; Staehelin *et al.*, 1994, 1998). Volz and Kley (1988), for example, report ozone abundances for the Montsouris Observatory in Paris in the range 10 – 32 µg m^{-3} for the period between 1876 and 1910. It is not straightforward to scale these few measurements to establish global or even northern hemisphere abundances but it is likely that ozone abundances in the northern hemisphere have doubled since the pre-industrial era.

111. Chemical-transport models (CTMs) predict that current man-made emissions of NO_x, VOCs, and CO, as well as the increase in global methane burdens, should have increased tropospheric ozone by a similar amount as the observations, primarily in the northern hemisphere. IPCC (2001) provides a summary of 11 CTM studies of the growth in tropospheric ozone since the pre-industrial era. Comparisons of these model results with the reconstructed 19th century observations at continental sites indicate a systematic model overestimation of about 10 µg m^{-3} (Wang and Jacob, 1998). There are also issues regarding seasonal cycles that are difficult to reconcile between the models and the pre-industrial observations. Correcting these systematic overestimations would require either a large missing sink for ozone or a downwards revision of the natural NO_x sources from lightning in the 19th century. Either of these is considered unlikely. There are also problems in reconciling model estimates of pre-industrial CO concentrations with observations derived from ice cores, suggesting considerable problems with the emission inventories for the pre-industrial era, particularly of biomass burning.

3.1.2 Growth in the global ozone background

112. Reliable tropospheric ozone monitoring began at the surface and with ozone sondes during the International Geophysical Year in 1957. However, it is difficult to put a consistent picture together of the growth in background ozone since the 1960s. With photochemistry producing local ozone lifetimes as short as a few days in the boundary layer, local measurement of tropospheric ozone does not reflect the abundance over the same continent and a surface measurement is not representative of the bulk troposphere above (IPCC, 2001). Thus it is not contradictory for ozone trends in different atmospheric regions to be different because there may well be different trends in regional pollutants driven particularly by changes in NO_x emissions.

113. Surface ozone data collected at Arosa, Switzerland during the 1950s are characterised by annual ozone abundances of about 36 µg m^{-3} (Staehelin *et al.*, 1994). Measurements at the same location between 1989 – 1991 indicate an approximate doubling over a period of three decades.

114. Ozone sondes offer the best record of ozone throughout the troposphere. Weekly continuous data since 1970 are available from only nine stations in the latitude range from 36^{o}N to 59^{o}N (Logan, 1999). Most stations show an increase from 1970 to 1980 but no

clear trend from 1980 to 1996. Of the 14 stations with records since 1980, only two, one in Japan and one in Europe, had statistically significant increases in the mid-troposphere between 1980 and 1995. In contrast, the four Canadian stations all showed significant decreases.

115. The ozone sonde record at Hohenpeissenberg, an alpine location in southern Germany extends from 1966 to the present day. The pattern of long-term change in the mid-troposphere layer shows large increases from the mid-1960s to the mid 1980s, with smaller increases and even declines, thereafter. The small declines seen in the 2000s at Hohenpeissenberg have not been seen at the high altitude Zugspitze site (also in the Alps), although they have been seen at the nearby alpine site of Wank (Oltmans *et al.*, 2006).

116. Surface ozone measurements from 17 background stations up to the mid-1990s also show no clear and consistent trend even in northern latitudes (Oltmans *et al.*, 1998). The largest negative trend in surface ozone was -0.7 ± 0.2 % per year at the South Pole (1975 to 1997), while the largest positive trend was +1.5 ± 0.5 % per year at the mountain-top Zugspitz site in southern Germany from 1978 to 1995.

117. Two stations in the eastern North Atlantic, Izana, Canaries and Mace Head, Ireland show increasing ozone abundances over their period of record since 1987 (Oltmans *et al.*, 2006). While increases are seen in most months, the statistically significant changes are during the winter and spring months. The mid Atlantic station in Bermuda also shows evidence of an increase during the winter and spring months and fits the pattern of the other two North Atlantic sites (Oltmans *et al.*, 2006). In contrast, Lelieveld *et al.* (2004) present results from ship cruises from 1977 to 2002 that show no statistically significant trends in the 40^{o}N to 50^{o}N latitude range.

118. Vingarazan (2004) details 21 near-surface or lower troposphere background locations that have reported increasing ozone trends over the period from 1967 to 2001. Mace Head, Ireland was included in this collection of sites. In contrast, eight surface or near-surface sites reported downwards trends over a similar period. Downwards trends have been reported for some Canadian arctic sites that have reversed during the 1991 – 2001 period (Vingarazan, 2004).

119. Background ozone has increased by up to 10 µg m^{-3} per decade over the last 20 to 30 years, according to measurements at sea level and on mountain tops that are less influenced by European sources (Raes and Hjorth, 2006). This has been attributed to the world-wide increase in anthropogenic activities, including growth in ozone-precursor emissions from industry, road, air and ship transport, households and agriculture. In addition, to an upwards trend, background ozone shows considerable year-to-year variability, partly due to precursor emissions such as forest fires, but also due to meteorological variability, which can alter the efficiency of long-range transport from particular sources (Raes and Hjorth, 2006).

120. Trend analyses for surface ozone in Europe have been restricted to northern and western Europe where the time series are long enough for meaningful studies (Monks *et al.*, 2003; Solberg *et al.*, 2004). Apart from the background sites on the western fringes of Europe, trends in surface ozone are not uniform across central Europe (Jonson *et al.*, 2006).

121. The differences in the reported trends between the ozone sondes, surface observations, mountain-top sites and other ozone records are difficult to resolve. There may be inherent difficulties with ozone sondes for long-term trend detection (Jonson *et al.*, 2006). There may well be different local site influences at mountain-top sites compared with surface sites that mean that surface sites are not fully representative of the lower and mid-

troposphere (IPCC, 2001). However, surface sites are more relevant to policy formulation and for the assessment of environmental effects.

3.1.3 Observations of the trend in baseline ozone at Mace Head, Ireland

122. A number of analyses have been published of the long-term ozone monitoring data at the baseline site at Mace Head, Ireland (Simmonds *et al.*, 1997; Simmonds *et al.*, 2004; Carslaw, 2005; Derwent *et al.*, 2007). In all these analyses, care has been taken to separate the ozone data by air mass origins, whether maritime from across the North Atlantic Ocean or regionally-influenced from continental Europe. The basic unsorted monthly mean ozone data from 1987 – 2007 have shown no statistically significant trends. Attention is directed in the paragraphs below only to the baseline data since these only have shown evidence of trends over time.

123. During most years, around two-thirds of the time, the air masses arriving at the Mace Head, Ireland baseline station have travelled across the North Atlantic Ocean directly to the station and have had no influence from man-made pollutant emissions from Europe. These air masses are considered to be representative of northern hemisphere baseline conditions. Simmonds *et al.*, (1997) used the simultaneous observations of man-made halocarbons, CO and methane and back-track air mass trajectories to sort the hourly ozone observations into two categories: baseline and regionally-influenced. Over the 1987 – 1995 period, Simmonds *et al.* (1997) reported an upwards trend of +0.4 µg m^{-3} per year in the annual mean baseline ozone abundance.

124. Simmonds *et al.*, (2004) using similar sorting techniques, reported trends in baseline ozone abundances over an extended period from 1987 – 2003. Annual mean trends were +1.0 µg m^{-3} per year, with winter trends +1.2 µg m^{-3} per year and summer trends +0.8 µg m^{-3} per year. It has become apparent subsequently that these trends have been influenced by unprecedented biomass burning during 1997-1998 as revealed by simultaneous observations of the biomass burning gases: CO_2, CO, CH_4, CH_3Cl and CH_3Br (Simmonds *et al.*, 2005). The 1997-1998 biomass burning came towards the end of the 1987 – 2003 record and has apparently exaggerated the observed upwards trend in the baseline ozone data.

125. Analysis of the 20-year baseline record over the period from 1987 – 2007 has recently been performed by Derwent *et al.*, (2007) in which an additional air mass origin sorting technique has been applied to the data post 1995 (based on the NAME Lagrangian dispersion model). Because of the reductions in European emissions, the original sorting method has been increasingly unreliable. Based on a six-year overlap period from 1995 – 2001, the 1987 – 1994 data have been rescaled and the 1995 – 2006 data have been sorted using the NAME dispersion model. The combined 1987 – 2006 data are presented in Figure 3.2. Baseline ozone levels increased at about +0.2 to +0.4 µg m^{-3} per year during the early period of the record as previously reported by Simmonds *et al.*, (1997). The ozone record was then strongly perturbed by global scale biomass burning events that appear to have shifted up the data during the 1997 – 1999 period as reported by Simmonds *et al.*, (2004). The figure shows a rise to the all-time maximum baseline concentration of 104 µg m^{-3} in March 1999 followed subsequently by a slight decline, although the average concentrations subsequent to 2000 are significantly higher than those in the 1990s. Derwent *et al.* argued that periods before and after the biomass burning are different with the period before showing a statistically significant increase and the period after showing a slight decrease which is not statistically significant. They noted, however, that the trend during the period 1987 – 1997, is dominated by the unusually low concentration in the incomplete year of 1987. If this year is eliminated from the analysis, the trend is reduced and is no longer statistically significant.

126. The period since 2000, shows a decline from the maximum in the spring of 1999, followed by a period of relatively constant ozone baseline levels. Further biomass burning events perturbed ozone during 2002 – 2003 as reported by Simmonds *et al.*, (2005). Over this same period, baseline methane abundances have also stabilised and their 20-year period of rising levels has been halted.

127. The overall conclusion from the observations and analyses at Mace Head is that there has been a significant increase in the annual mean concentration over the past 20 years, with a springtime maximum that has also increased. The interannual increase is quite variable; some individual years show a strong increase while several consecutive years show little change. The period from 2000 has shown, if anything, a slight decrease in the annual mean. Predictions of future changes in baseline ozone are clearly subject to significant uncertainties; the present trend suggests a period of stabilisation.

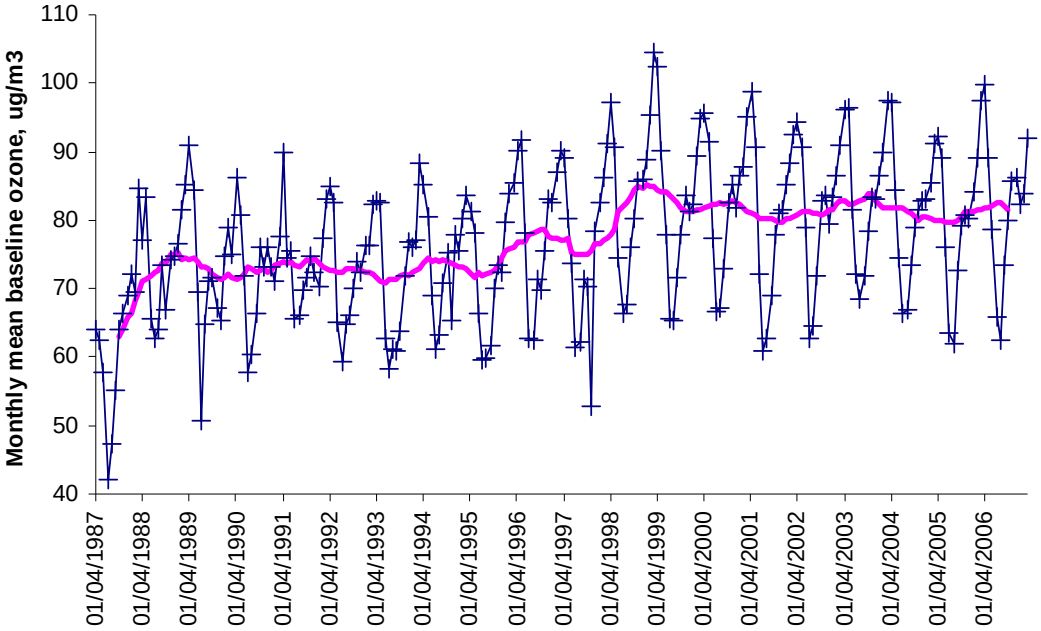


Figure 3.2 Monthly mean (blue line with + signs) and 12-month rolling mean (pink line) baseline ozone abundances at Mace Head, Ireland from 1987 to 2006.

128. Along the west coast of North America, three sets of observations have shown similar strong springtime increases in ozone as observed at Mace Head, Ireland. The marine boundary layer surface sites at Lassen National Park in northern California and from aircraft have indicated a positive trend in ozone of +0.8 to +1.4 µg m^{-3} yr^{-1} depending on season between 1984 and 2002 (Jaffe *et al.*, 2003). Parrish *et al.*, (2004) identify the cause of this increase as increasing emissions of ozone-precursors at northern temperate latitudes.

3.1.4 Relevance of the Mace Head baseline observations to the UK and Europe

129. The Mace Head observations define the trace gas concentrations in air masses that have recently been advected across the North Atlantic Ocean and on into Europe, the United Kingdom and Ireland included. Because of the large expanse of the North Atlantic Ocean,

the Mace Head baseline site can be taken as representative of the Atlantic seaboard of Europe over a significant latitude range.

130. Back-track trajectories confirm that on most days, including most ozone episode days, the air masses arriving at UK monitoring sites and a significant number across north west Europe, can be back-tracked eventually to the North Atlantic region. This may take up to 10 days under anticyclonic conditions. On this basis, the Mace Head baseline observations provide a reliable guide to the trace gas concentrations upon which European regional-scale pollution events are superimposed. Mace Head observations are, for example, used to set the initial and boundary conditions for the Unified EMEP model (Simpson *et al.*, 2005).

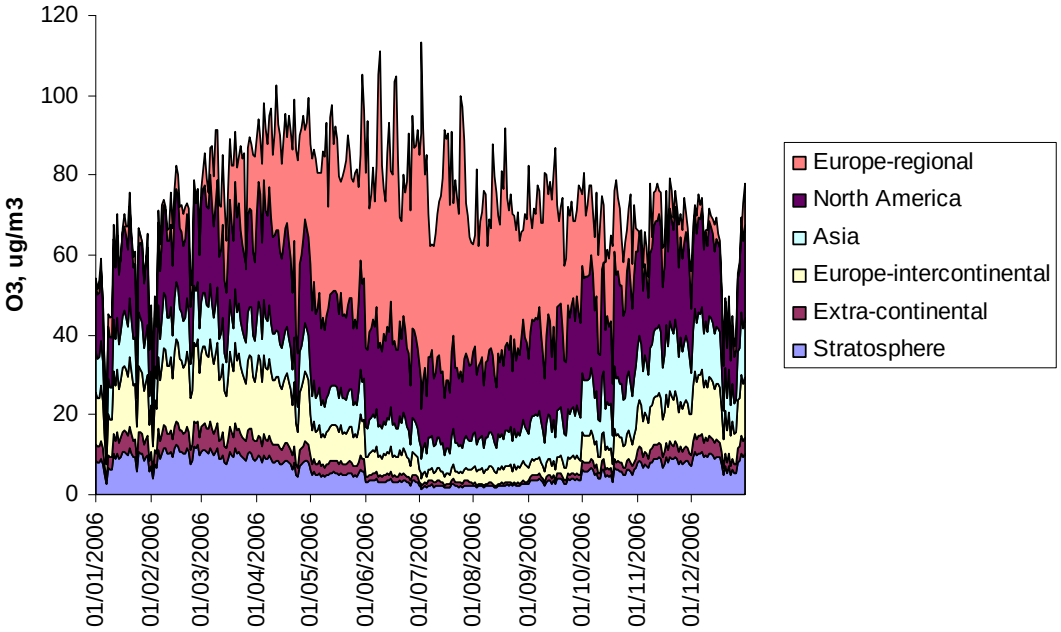


Figure 3.3 Source attribution of the ozone found at a rural location in southern England during each afternoon of 2006 using the UK PTM and STOCHEM models. Europe-regional refers to the ozone advected directly; North America to that formed over that continent and over the western Pacific; Europe-intercontinental to that advected around latitude circles and back into Europe.

131. Using the UK Photochemical Trajectory model and the global model STOCHEM, it has been possible to provide an attribution for the ozone modelled for Harwell, a rural location in Oxfordshire, during each afternoon of 2006, see Figure 3.3. The plot shows the daily contribution to ozone from regional-scale ozone formation within the model domain and from background sources, including exchange with the stratosphere and transport across the North Atlantic Ocean from sources in North America, Asia and ultimately from Europe, having travelled around a latitude circle. Regional-scale ozone formation makes its largest contribution during the summer months whereas background sources contribute most during springtime. On an annual average basis, regional-scale ozone formation accounts for about 22 µg m^{-3} and background sources about 52 µg m^{-3} of the 74 µg m^{-3} annual mean daily maximum 1-hour mean ozone concentration estimated in the model.

132. Figure 3.3 and the annual average source attribution figures in the paragraph above are highly site-specific. Generally speaking, it is anticipated that regional-scale ozone

formation increases and background sources decrease relative to the Harwell case when moving eastwards and southwards into Europe. This is because the increasing frequency of photochemical episodes increases the former term and the increasing travel time and hence dry deposition losses of background ozone increases the latter term.

133. Because of the dominant contribution from background sources to the source attribution of ozone at Harwell illustrated in Figure 3.3, it is apparent why the trend in baseline ozone levels is so important for the UK and for north west Europe. The trend up to the year 2000 has apparently been stronger during the spring months when background sources are dominant. Equally well, regional-scale ozone-precursor emission controls have strongly reduced regional-scale ozone formation, particularly during the summer months, when this term dominates.

3.1.5 Modelling the global ozone background trend at Mace Head, Ireland

134. During the last few years, global CTM model studies of tropospheric ozone have advanced significantly because of the availability of accurate, consistent gridded emission inventories for the tropospheric ozone-precursors that have resulted from the activities of the UN FCCC and of IIASA. These emission inventories have been used to complete multi-model ensemble simulations of present-day and near-future tropospheric ozone burdens (Stevenson *et al.*, 2006) and of CO (Shindell *et al.*, 2006) under the aegis of the EU ACCENT programme; the ACCENT output is discussed in further detail in Chapter 4. A detailed comparison has also been completed of two CTMs that participated in the EU ACCENT intercomparison, STOCHEM and TM3. Generally, both TM3 and STOCHEM represented well the surface ozone concentrations observed at six baseline stations (Dentener *et al.*, 2005). This study has been used to compile an analysis of the evolution of the methane, CO and tropospheric ozone burden from 1990 – 2030 at Mace Head, Ireland from 1990 – 2030 using STOCHEM (Derwent *et al.*, 2006).

135. The STOCHEM study showed striking similarities between the model and observed abundances of methane, CO and ozone over the period from 1990 through to 2002. Seasonal cycles were exactly in phase between the model and observations and model biases were minimal. Model trends in methane overestimated those observed as did those in CO. Model and observed CO abundances diverged particularly during 1998-1999 when the observed record had been influenced by unprecedented levels of biomass burning which had not been included in the global emission inventories. Model seasonal cycles for ozone faithfully reproduced those observed in the baseline record at Mace Head. Again, the model failed to show the ozone anomaly observed during the winter of 1998-1999 due to biomass burning.

136. Over the 1990 – 2002 period the STOCHEM model indicated an upwards trend in ozone at Mace Head of +0.32 µg m^{-3} yr^{-1}. The STOCHEM study only considered the trends driven by man-made tropospheric ozone-precursors and made no allowances for any trends in natural sources such as wetlands, tundra, natural fires, lightning, soil and vegetation emissions. The observed trend over the period from 1987 – 1995 was reported as +0.38 µg m^{-3} yr^{-1} by Simmonds *et al.* (1997) during the period where there was no apparent influence from global biomass burning events. It is therefore likely that the STOCHEM model may well have been able to account for much of the observed rise in baseline ozone levels during the 1987 – 1995 period.

137. Whilst it is generally accepted that increasing global man-made emissions of ozone-precursors are an important, likely cause of the growth in background ozone levels (IPCC, 2001; Parrish *et al.*, 2004), other explanations are not ruled out. Lelieveld and Dentener (2000) point to the possibility that the observed interannual variability in lower tropospheric ozone is influenced by changes in stratospheric ozone. Ordonez *et al.* (2007) demonstrate an impact of northern mid-latitude lowermost stratospheric ozone changes

on background ozone in the lower troposphere at the Jungfraujoch and Zugspitze mountain-top sites in the Alps. Using the SLIMCAT model they are able to explain the time trend in lower tropospheric ozone anomalies from 1990 through to 2004 based on the upwards trend and year-to-year variability in lowermost stratospheric ozone. Oltmans *et al.* (2006) drew attention to the disparity in the annual growths in ozone between Mace Head, Ireland (+8.2% per decade) and Zugspitze (+12.6% per decade) and this stratospheric ozone signal found by Ordonez *et al.*, (2007) may well be an explanation.

3.1.6 Forecasts of future background ozone levels in the British Isles

138. Looking into the future, the STOCHEM study pointed to future ozone trends for Mace Head, Ireland, of +0.18 - +0.24 µg m^{-3} yr^{-1} in the IIASA CLE scenario over the period to 2030 and -0.28 µg m^{-3} yr^{-1} in the IIASA MFR scenario (Derwent *et al.*, 2006). Further details of these emission scenarios are given in the Emissions Annex and the multi-model ensemble calculations for the whole of Europe are given in Chapter 4. For the southern United Kingdom, STOCHEM model experiments give an impression of the ozone trends for these global emission scenarios, see Figure 3.4. This plot shows the observed annual mean ozone abundances from the seven Defra rural ozone monitoring network sites in southern England for 1990 – 2003, together with the model trends out to 2030. 60-month rolling mean ozone abundances increase from 66.4 µg m^{-3} in 2000 to 72.6 µg m^{-3} in 2030 in the IIASA CLE scenario, corresponding to an annual increase of +0.3 % per year. In contrast, in the IIASA MFR scenario, rolling mean ozone abundances fall from 66.4 µg m^{-3} in 2000 to 62.8 µg m^{-3} in 2030, corresponding to a decline of -0.2% per year. Observed baseline ozone abundances over the 2000 – 2006 period have remained level and shown no overall trend, in the middle of the range of the STOCHEM model predictions (Derwent *et al.*, 2007).

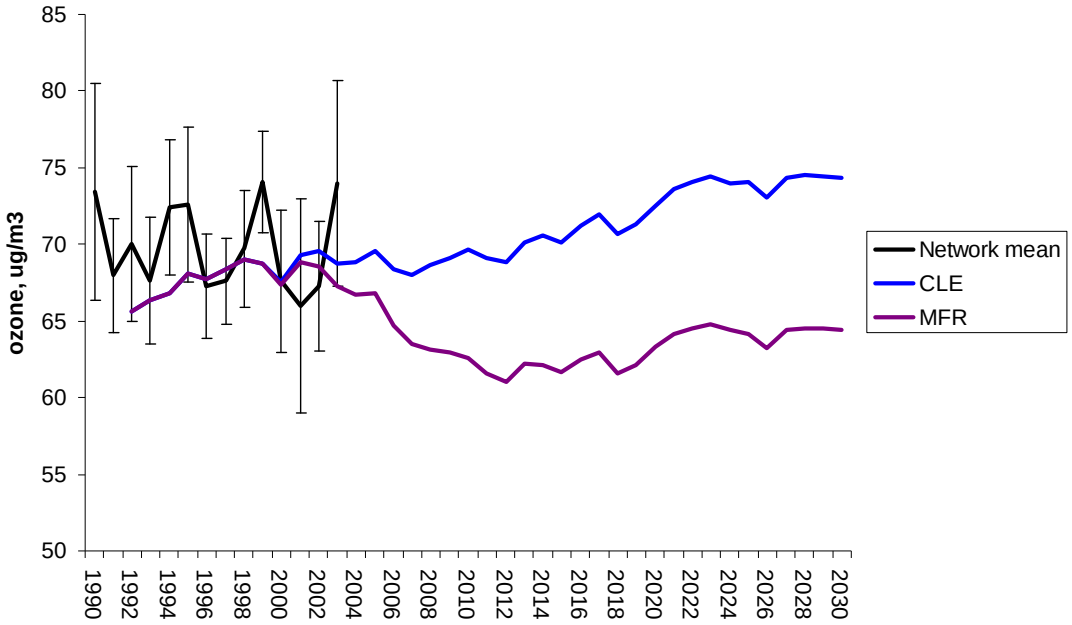


Figure 3.4 Observed annual mean rural ozone network concentrations and 60-month rolling mean STOCHEM model results for southern England in the IIASA CLE and MFR scenarios for 1990 through to 2030.

Chapter 4

Short term impact of climate change on ozone concentrations in Europe

Question 3*: What is the likely impact of climate change on future ozone levels in Europe, over the next two decades? What is the significance of such impacts compared to other influences, such as inter-annual variability or (global and regional) emission trends?*

Short answer to question 3

139. **The net impact of climate change on mean surface ozone levels over Europe on the 2030 time horizon is not known with any confidence but is likely to be small compared with the most important influence. This is the trends in the anthropogenic emissions in Europe and throughout the whole northern hemisphere of the important precursor gases to ozone formation: nitrogen oxides (NO_x), methane (CH_4), and non-methane volatile organic compounds (NMVOC), in particular, and carbon monoxide (CO). Climate change may have relatively greater influence on future peak episodic ozone in particular geographic areas through a number of different mechanisms such as changes in precursor emissions, ozone loss by deposition, and meteorology. Inter-annual variability in annual mean surface ozone at a given location is large compared with the likely magnitude of net ozone change by 2030, so multi-year data series are necessary for unravelling the competing influences on ozone concentration at different locations.**

Detailed answer to question 3

140. Assuming trends in anthropogenic emissions of precursor gases around the world follow the projections of presently-planned controls ("current legislation"), then an ensemble of global models simulate an increase in annual-mean surface ozone over Europe as a whole of 1.8 ppbv between the years 2000 and 2030. For a more optimistic scenario in which all possible technical control options are implemented worldwide, the models simulate a decrease in average surface ozone over Europe of −2.8 ppbv over this period. In contrast, for a more pessimistic high-growth scenario, average surface ozone over Europe is simulated to increase by 3.9 ppbv. Precursor emission projections are continually re-evaluated, and actual emissions may vary from those projected for a given scenario, so the above simulations indicate the range in possible future annual mean surface ozone change over Europe over this time period.

141. The models show that the benefit to mean European ozone levels of current legislation control measures on European emissions of precursor gases is more than offset by increasing hemispheric and global ozone levels, driven by increasing precursor emissions elsewhere, and its subsequent long-range transport into Europe. However, projected ozone changes vary spatially across the region and with season, with the UK having an "ozone climate" that is often somewhat different to that of Europe as a whole. There is a general tendency for absolute ozone levels to be greater in southern and central Europe and for beneficial change to be more marked in these regions than in north-west Europe. Also, although simulations of the current legislation scenario project an increase in ozone over Europe on average, they project a decrease in summertime ozone episode extremes but an increase in winter ozone levels. This will increase the metrics of long-term exposure to ozone such as SOMO35 and AOT40 but is not expected to have an important impact on ozone metrics that are sensitive to short-term high peaks.

142. The net sign of the additional impact of climate change on ozone across particular geographic regions such as Europe, let alone the magnitude of the impact, is highly uncertain. This is because, although many different processes have been identified through which climate change can influence future ozone levels (e.g. effects on anthropogenic and biogenic precursor emissions, atmospheric chemistry, synoptic meteorology, deposition and stratospheric-tropospheric exchange), only a limited number of coupled climate-chemistry models have been run and many known climate impacts have yet to be included. The most substantive impacts quantified so far on global tropospheric ozone are increased gas-phase chemical destruction of ozone driven by increased atmospheric humidity, and increased downward transport of ozone from the stratosphere. Some model simulations suggest a pattern of net negative feedback of climate on surface ozone over the oceans, but a net positive feedback over polluted land surfaces, the latter likely driven, at least in part, by the net dominance of increased ozone production with water vapour concentration in high-NO_x environments. Overall, however, the size of modelled impacts of climate change on European surface ozone to 2030 in model simulations to date are small compared with the modelled changes in ozone arising from anthropogenic precursor emission changes, and insignificant in comparison with the uncertainties in these emissions projections and with inter-model variability. This does not exclude the possibility that climate change may have proportionally larger influence on regional peak summertime surface ozone through, for example, drought-related depression of ozone dry deposition, increased incidence of wild fires, or extended air-mass residence time in the boundary layer. Also, the climate change signal on surface ozone is likely to increase significantly beyond the 2030 time horizon specified for this report.

143. Changes in natural sources of ozone-precursors in Europe to 2030 are anticipated to be of less influence on future mean ozone levels in Europe than the changes in the man-made precursor emissions of NO_x, NMVOC, CH_4 and CO over this period. Biogenic NMVOC emissions may increase in the future with increasing temperatures under climate change, although other factors will certainly also be influential, such as future changes to the vegetation mix caused by human activities or by environmental change itself. NMVOC emissions are found to contribute to ozone production in the UK and near-European continent, but may be less important to ozone generation in the NO_x-limited atmosphere of southern Europe. The relationship between biogenic emissions and major episodes of poor air quality in the context of both a changing climate and other precursor emission changes remains an area of major uncertainty.

144. Although there is variation in model simulations of future ozone, these inter-model differences are generally smaller (to the 2030 time horizon) than the differences in average simulations of future ozone for different emission scenarios; so the main source of uncertainty in predicting future ozone is in projecting the emissions, rather than in the modelling. Uncertainty increases substantially when trying to model effects of climate change also, because of deficiency in what is currently incorporated within global- and regional-scale models.

145. Large-scale climate variability phenomena such as the North Atlantic Oscillation impose inter-annual variability on annual surface ozone concentrations at a given European location which is likely to be of comparable magnitude to the net trend over the next 2 to 3 decades caused by the other influences described above.

Supporting evidence for question 3

4.1 Overview

146. **Note on units:** In this chapter, concentrations of model-simulated ozone are expressed in parts per billion volumetric mixing ratio (ppbv, 1 part in 10^9), for the reasons explained in Chapter 1. For ozone close to the surface, at ambient temperature and pressure, the conversion is 1 ppbv ≡ 2 µg m^{-3}.

147. AQEG's Third Report *Air Quality and Climate Change: a UK Perspective* (AQEG, 2007) has previously summarised considerable background information on this question. The answer to Question 7 in Chapter 8 of this report also provides complementary information, as does a concurrent report from the Royal Society on ozone in the 21st century (Royal Society, 2008).

148. The concentrations of ozone over Europe are dependent on the clean-air hemispheric background of ozone (due to photochemical formation of ozone throughout the troposphere and downward transport from the stratosphere), on the local and regional emissions of ozone-precursors within Europe, and on meteorology (via its influence on long-range transport of ozone and on regional air pollution episodes). Chapter 21 provides further information on the factors influencing ozone and the temporal and spatial scales on which they operate.

149. The most important precursors of ozone are methane (CH_4) and carbon monoxide (CO), which are long-lived gases, and nitrogen oxides (NO_x) and non-methane volatile organic compounds (NMVOC), which are relatively short-lived gases. Model calculations indicate that approximately half of the increase of tropospheric ozone from pre-industrial times to the present-day is due to changes in the chemistry of the atmosphere induced by the increase in NO_x and approximately half to the combined increase of CH_4, CO and NMVOC emissions (~25% for CH_4, and ~25% for CO and NMVOC together) (Wang and Jacob, 1998).

150. Models, described below, indicate that the most important influence on changes in surface ozone over the period to 2030 will continue to be the global and regional mix in anthropogenic emissions of these short- and long-lived ozone-precursor gases, which in turn is consequent on the particular trajectory of economic growth, and of air quality and climate change legislation implementation, that is followed. Changes in natural sources of ozone-precursors within Europe, predominantly biogenic NMVOCs from natural vegetation, are likely to be less influential on the 2030 timescale. Biogenic NMVOC emissions may increase in the future with increasing temperatures under climate change, although other factors will certainly also be influential, such as the future anthropogenically-driven or climate change-driven vegetation mix. NMVOC emissions are observed to contribute to episodic ozone production in the UK and near-European continent, but may be less important to ozone generation in the NO_x-limited atmosphere of southern Europe.

151. A recent model intercomparison organised under the auspices of ACCENT has compared the results from 26 differently formulated chemistry models (Stevenson *et al.*, 2006; Dentener *et al.*, 2006). The models investigated the effect on global ozone levels in the year 2030 compared with the year 2000 of three different scenarios for future worldwide emissions available at the time of the research: "central", "optimistic" and "pessimistic" (Table 4-1). A subset of 10 of the models also investigated the effect of climate change on atmospheric chemistry for the "central" emissions scenario, using a simulated climate for 2030 as described in Stevenson *et al*. (2006). Further detail on ozone-precursor emissions projections is given in Annex 2.

Table 4-1 ACCENT CTM (Chemical Transport Model) and CCM (Coupled Climate Model) model intercomparison experiments. (Adapted from Dentener et al. (2006)). SSTs: Sea surface temperatures. IIASA: International Institute of Applied Systems Analysis. IPCC: Intergovernmental Panel on Climate Change. SRES: Special Report on Emissions Scenarios.

Run	Descriptor	Meteorology	Emissions
S1	Y2000 (Baseline)	CTM 2000 GCM SSTs 1990s	2000
S2	CLE (Central)	CTM 2000 GCM SSTs 1990s	IIASA current legislation, to 2030
S3	MFR (Optimistic)	CTM 2000 GCM SSTs 1990s	IIASA maximum feasible reduction, to 2030
S4	A2 (Pessimistic)	CTM 2000 GCM SSTs 1990s	SRES A2, most pessimistic IPCC scenario, to 2030
S5	CLEc (Central + climate change)	GCM (General Circulation Model) SSTs 2030s only	IIASA current legislation, to 2030

152. For the current legislation scenario ("central"), annual-mean surface ozone averaged over Europe as a whole is simulated to increase by 1.8 ppbv between 2000 and 2030 (+0.6 ppbv/decade) (Dentener *et al.*, 2006). For the maximum feasible reduction scenario ("optimistic"), in which all possible technical control options are implemented worldwide, average surface ozone over Europe is simulated to decrease by –2.8 ppbv (–0.9 ppbv per decade). In contrast, under the more pessimistic high growth scenario of the IPCC SRES A2, average surface ozone over Europe is simulated to increase by 3.9 ppbv (+1.3 ppbv per decade).

153. Europe-wide averages obscure the fact that the magnitude of the modelled changes in future ozone vary significantly geographically across Europe and with season. The spatial variation in the changes in annual mean and seasonal mean surface ozone over Europe for the year 2030 compared with the year 2000 are shown in the left hand side of Figures 4.1-4.3 for the three different projections of global emissions. The extent of inter-model variation is illustrated by the corresponding maps of the model-ensemble standard deviations of simulated ozone changes.

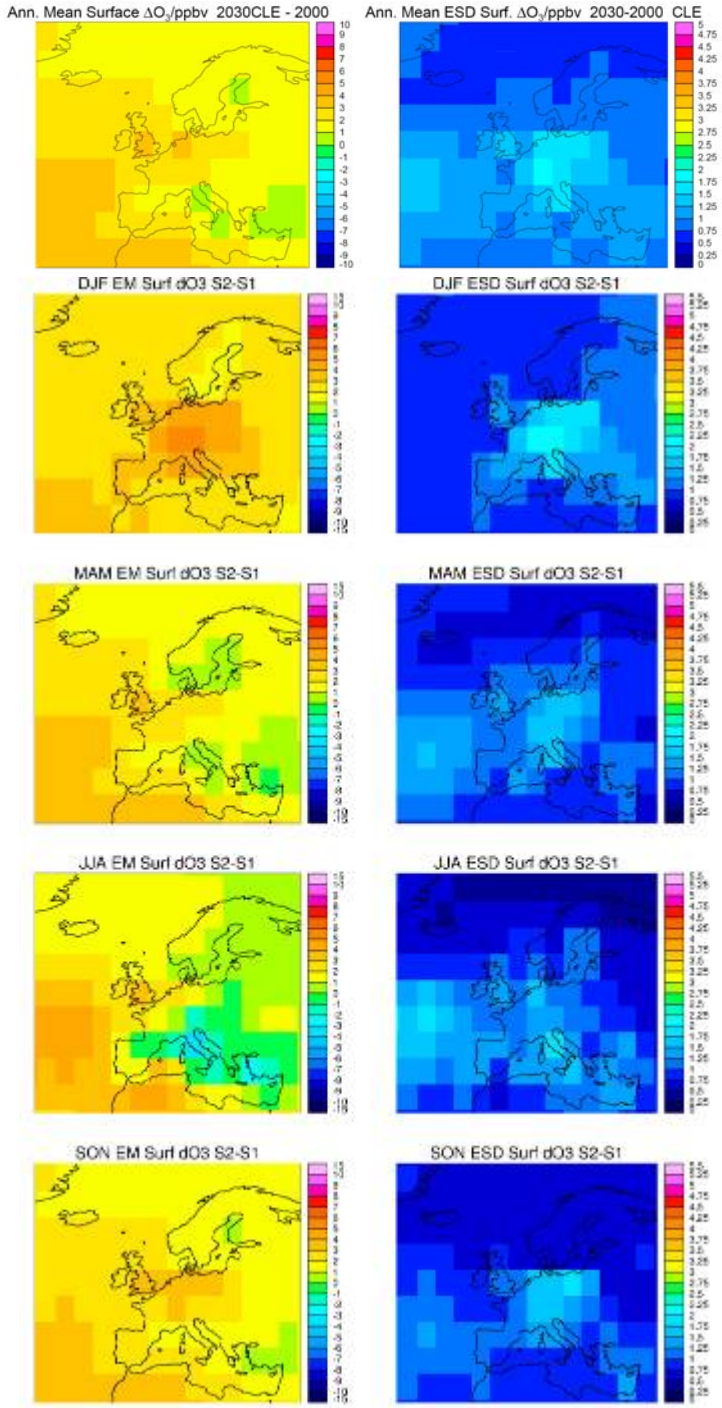


Figure 4.1 Left column: 26-model ensemble-mean change in annual mean surface ozone (top row) and 3-month seasonal mean surface ozone (subsequent rows) for year 2030 compared with base year 2000 for "central" emissions scenario CLE (climate unchanged). Right column: standard deviation of ensemble simulations. Units are ppbv (1 ppbv $O_3 \cong 2$ μg m^{-3} O_3). The models have been interpolated to a common resolution (5° × 5° horizontal); lowest model level depth is ~100 m. Source: Stevenson (pers. comm.) from data of Dentener *et al.* (2006).

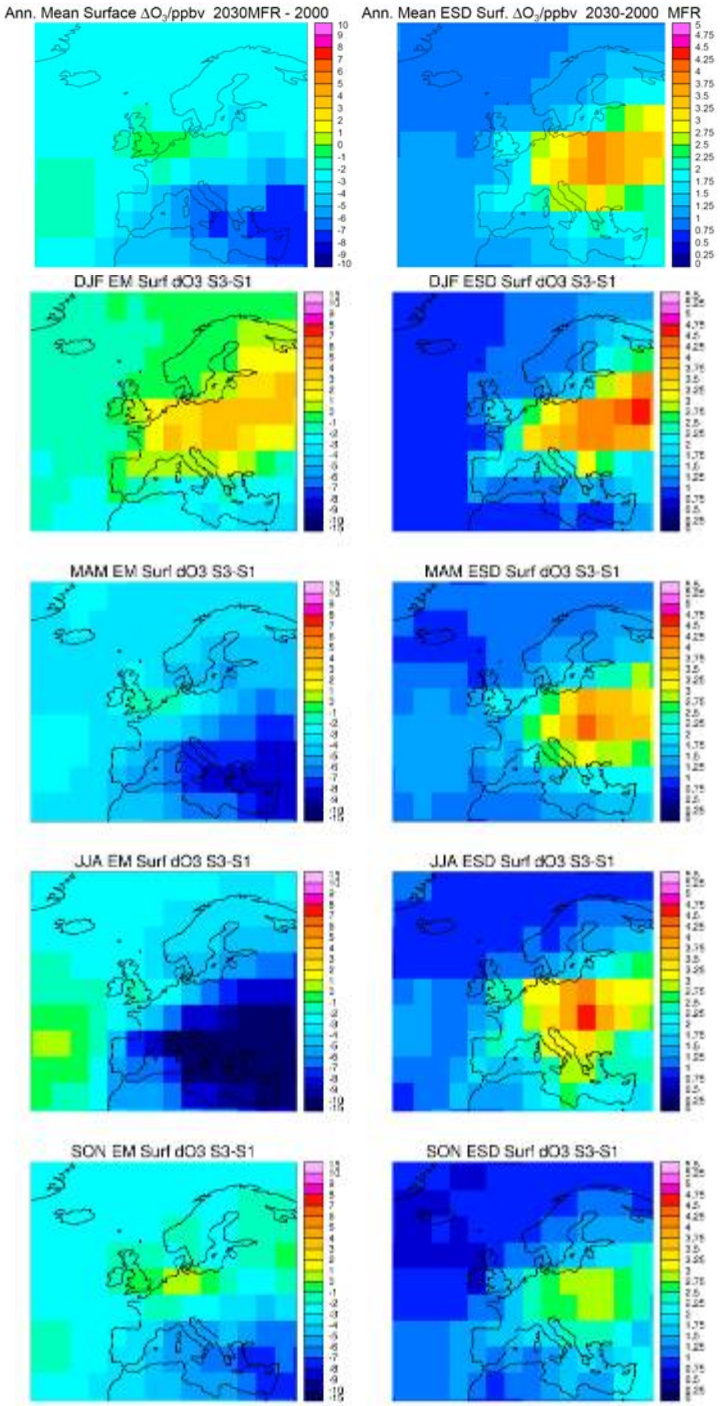


Figure 4.2 Left column: 26-model ensemble-mean change in annual mean surface ozone (top row) and 3-month seasonal mean surface ozone (subsequent rows) for year 2030 compared with base year 2000 for "optimistic" emissions scenario MFR (climate unchanged). Right column: standard deviation of ensemble simulations. Units are ppbv (1 ppbv $O_3 \cong 2$ μg m^{-3} O_3). The models have been interpolated to a common resolution (5° × 5° horizontal); lowest model level depth is ~100 m. Source: Stevenson (pers. comm.) from data of Dentener *et al.* (2006).

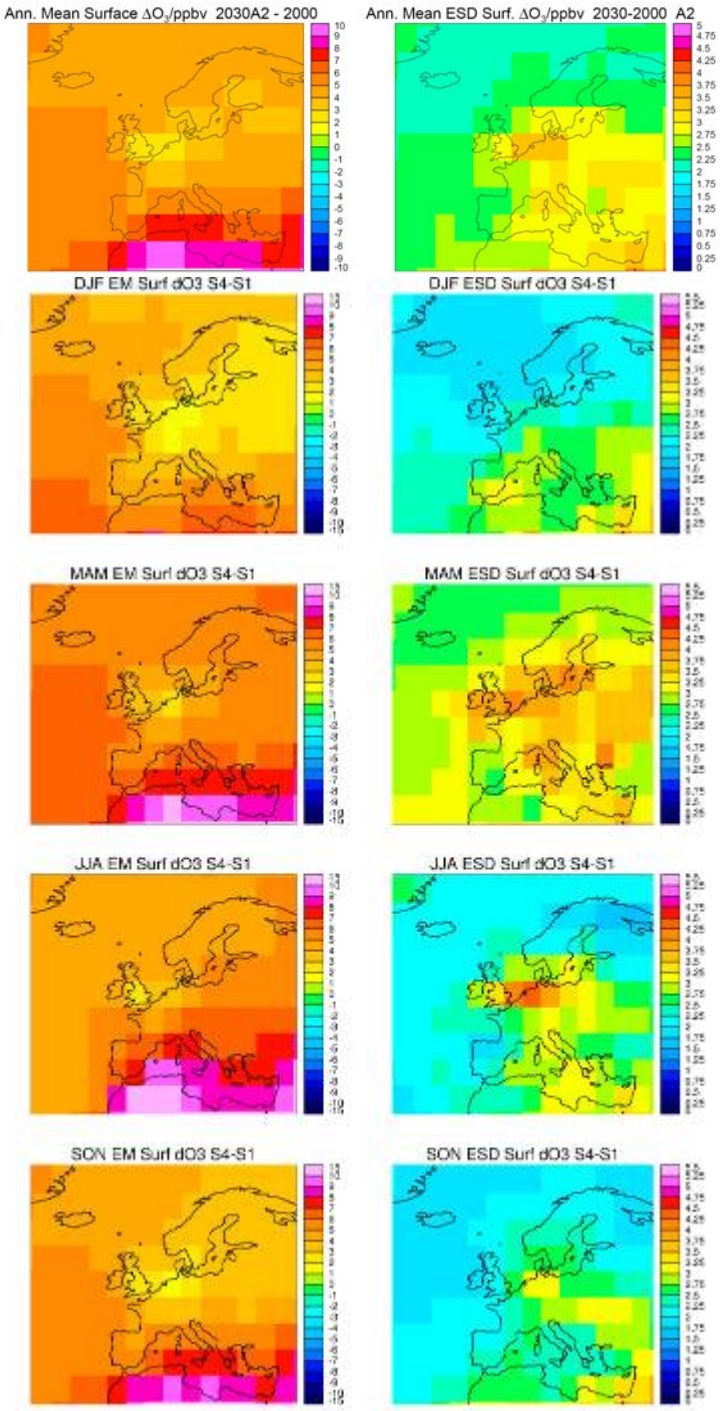


Figure 4.3 Left column: 26-model ensemble-mean change in annual mean surface ozone (top row) and 3-month seasonal mean surface ozone (subsequent rows) for year 2030 compared with base year 2000 for "pessimistic" emissions scenario SRES A2 (climate unchanged). Right column: standard deviation of ensemble simulations. Units are ppbv (1 ppbv $O_3 \cong 2$ µg m^{-3} O_3). The models have been interpolated to a common resolution (5° × 5° horizontal); lowest model level depth is ~100 m. Source: Stevenson (pers. comm.) from data of Dentener *et al.* (2006).

154. There is a strong gradient of greater annual average ozone from north to south across Europe reflecting gradients in ozone photochemistry, the transport patterns of ozone and its precursors into Europe, and the decreased removal of ozone by dry deposition over the Mediterranean Sea as compared with over land. The interplay between the factors determining future ozone is complex. For example, ozone levels over southern and

eastern Europe are simulated to increase less (or actually to decrease) compared with the simulated increases in ozone levels over northern Europe for the CLE scenario (particularly in summer, Figure 4.1), but to increase more than ozone levels over northern Europe for the pessimistic SRES A2 emissions scenario (Figure 4.3). Also, although the optimistic MFR scenario is simulated to lead to substantial declines in summertime surface ozone across most of Europe, this scenario gives rise only to marginal improvement in ozone over the southern UK and near continent (Figure 4.2). These latter simulations illustrate the consequence of the NO_x-saturated chemistry in this region (Collins *et al.*, 2007). In winter, in northern Europe, NO_x emissions generally decrease ozone production by removing HO_x radicals through the reaction $NO_2 + OH \rightarrow HNO_3$. For the CLE and MFR scenarios the local NO_x emission reductions increase wintertime ozone. For the SRES A2 scenario an expected local decrease in European winter ozone production is swamped by the import of increased ozone from outside Europe (Figure 4.3). The transport of ozone is most efficient in winter due to its increased lifetime.

155. In areas that better represent background conditions, and where inter-model agreement is generally better (such as over the Atlantic Ocean off the coast of the European continent away from the shipping lanes) the simulated changes in annual average ozone between 2000 and 2030 are up to +4, –3 and +6 ppbv for the central, optimistic and pessimistic emissions scenarios, respectively.

156. The current modelling activity indicates that the benefit to average ozone over Europe from current legislation reductions on European emissions of precursor gases is more than offset by increasing hemispheric and global ozone levels, caused by increasing precursor emissions elsewhere, and its subsequent long-range transport into Europe (Derwent *et al.*, 2006). Again it is important to note that there is considerable geographical and seasonal variability within this overall statement. A decrease in summertime average surface ozone of –3 ppbv is calculated for 2030 for the CLE scenario over southern areas of Europe, whereas an increase up to 4 ppbv is calculated over northwestern Europe (Szopa *et al.*, 2006). On the other hand, the CLE scenario is expected to lead to a decrease in extreme summertime ozone episodes everywhere, but to an increase in wintertime ozone levels.

157. The offsetting effect of hemispheric ozone on average European ozone levels in the current legislation emissions scenario is illustrated in model estimates for changes to human health indices for exposure to ozone by 2030. The ensemble-mean data from the 26 model intercomparison is for the SOMO35 metric for the central Europe region (7º-17ºE, 48º-54ºN) to increase by 341 ppb.days by 2030 from the year 2000 modelled estimate of 2795 ppb.days; and for SOMO35 for the central Mediterranean region (5º-30ºE, 35º-45ºN) also to increase by 234 ppb.days by 2030 from the year 2000 estimate of 5559 ppb.days (Ellingsen *et al.*, 2008). (No objective is currently defined for this metric). In contrast, the ensemble-mean simulation for the effect of the current legislation emissions scenario on the EU60 health metric (the number of days in the year with maximum 8-hour average exceeding 60 ppbv), which has greater emphasis on ozone extremes, is for a decrease of 4 days by 2030 from 26 days in year 2000 in the central Europe region, and for a decrease of 2 days from 75 days in the central Mediterranean regions. (The currently-defined threshold for this metric is 25 days per year as an average over 3 years). Under the MFR scenario, the model-ensemble average change in the SOMO35 metric is a decrease of 935 ppb.days in the central Europe region and a decrease of 2318 ppb.days in the central Mediterranean region, and the model-ensemble average change in the EU60 metric is a decrease of 23 days in the central Europe region and a decrease of 55 days in the central Mediterranean region (Ellingsen *et al.*, 2008).

158. The magnitude of all these simulated changes should be set in the context in the spread of model results. The uncertainty in the calculations of future European ozone obtained by comparing results from the ensemble of different models is relatively large, of the order of

30% or 1-2 ppbv in the simulated ozone changes for 2030 (Stevenson *et al.*, 2006; Dentener *et al.*, 2006). Inter-model uncertainty for individual grid domains is much larger (right hand panels of Figures 4.1-4.3) than the inter-model uncertainty for European-scale averaged values, as expected. The inter-model uncertainty is also not spatially uniform, being generally substantially greater over eastern and southern Europe than elsewhere.

159. The individual model estimates for the values of the health metrics vary widely but is substantially less for the SOMO35 metric than for the EU60 metric, suggesting that the former is probably the more robust indicator of changes in ozone exposure when considering results from individual models (Ellingsen *et al.*, 2008).

160. On a European-averaged spatial scale, inter-model variations are smaller than the differences in average simulations for future ozone for different emission scenarios, so the main source of uncertainty in simulating future ozone are the future trends in global and regional precursor emissions, rather than the models. However, it should also be recognised that the majority of simulations so far are derived from global models, and results may be different if deploying higher resolution regional models.

161. Subsequent to the ACCENT model intercomparison described above, IIASA have provided updated estimates for ozone-precursor emissions for year 2000 and into the future under the “current legislation” (CLE) scenario (Rafaj and Amann, 2007). The IIASA projections are only for anthropogenic emissions. The new IIASA emissions estimates, plus updated shipping emissions estimates with greater spatial disaggregation, have been incorporated into new model simulations of future ozone (Royal Society, 2008). The new 2000 global emissions totals for NO_x and CO are now ~11% and ~15% higher, respectively, than the global totals for 2000 used in the published ACCENT intercomparison. On the other hand, the new scenario suggests that the initial projections of future precursor emissions under a CLE scenario may have been too high and that a commitment to implementation of emissions reduction technology has occurred more rapidly worldwide than was previously envisaged. Global emissions projections of NO_x and NMVOC in the updated CLE scenario now lie somewhere between the old CLE and MFR scenarios, although still closer to the former in 2030 because the impact of the new CLE scenario on these precursors emissions is relatively small before 2030 but greater thereafter. (See also note below about assumed global CH_4 concentrations in the scenarios).

162. The preliminary model simulations indicate that, as expected, the lower future precursor emissions in the updated CLE scenario lead to lower surface ozone increase by 2050 than was obtained by 2030 using the old CLE scenario. Figure 4.4 compares model simulations of European ozone using the updated emissions with the ACCENT simulations (Royal Society, 2008). By 2050, simulations using the updated CLE scenario show European-averaged annual-average ozone to be lower than in 2000 (white solid and black solid lines, respectively, in Figure 4.4) although this is not uniform throughout the year – spring and summertime ozone is lower in 2050, but ozone in winter is higher. Model results are not available for the updated CLE scenario for 2030 but, given the relative values of the emissions estimates, simulated European surface ozone in 2030 would have values between the solid and dashed white lines in Figure 4.4.

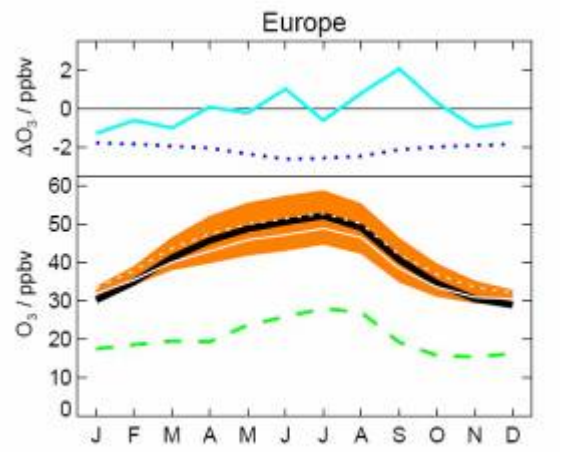


Figure 4.4 Lower panel: Seasonal cycle in future surface ozone averaged over Europe from various model simulations. The dashed green line is from simulation of a pre-industrial emissions scenario. The solid black line is for year 2000 using the updated IIASA year 2000 emissions. The solid white line is for year 2050 using the updated IIASA CLE emissions scenario. The shaded orange region shows the range of the ensemble-mean ACCENT-simulated European surface ozone for year 2030 using the "old" IIASA scenarios as already discussed in the text and illustrated in detail in Figures 4.1-4.3 (the white dashed line is the ACCENT simulation for 2030 using the "old" IIASA CLE scenario). Upper panel: Change in European surface ozone relative to the updated 2050 IIASA CLE scenario for two cases; inclusion of 2000-2050 climate change (solid cyan), and for methane fixed at 2000 levels (dotted blue). For the non-ACCENT data, between three and five different global models were used. Source: Royal Society (2008).

163. Model-simulated future ozone is also very sensitive to assumed future global CH_4 concentration, which is perhaps even harder to project than anthropogenic NO_x, NMVOC and CO emissions, and which is projected to be higher than it is presently. Although global CH_4 concentrations have levelled off in recent years (at ~1760 ppbv), it appears this may have been due to transient counteracting factors and that anthropogenic CH_4 emissions are again on the increase (Bousquet *et al.*, 2006).

164. This sensitivity of ozone to global CH_4 is clearly illustrated by the dotted blue line in the upper panel of Figure 4.4 which shows the substantial (~ –2 ppbv) decrease in European-averaged surface ozone that might be anticipated in 2050 for the updated CLE scenario but with a year 2000 CH_4 concentration of 1760 ppbv rather than the year 2050 projected CH_4 concentration of 2363 ppbv used in these simulations (Royal Society, 2008). For comparison, the ACCENT intercomparison used an estimate of 2088 ppbv for CH_4 concentration in their simulations of ozone in 2030.

165. The key messages to be taken from the revised IIASA projections is that they illustrate the uncertainty surrounding predictions of future global and regional precursor emissions (including CH_4) and that this is the major uncertainty in predicting future surface ozone. Also, that surface ozone in Europe is impacted by emissions in the rest of the hemisphere. The optimistic (MFR) and pessimistic (SRES A2) emissions scenarios used in the ACCENT modelling remain a guide to the range in changes in European surface ozone that may occur in the future depending on which trajectory of precursor emissions is ultimately followed. If the CLE scenario is taken up worldwide as per the latest IIASA projections then ozone in Europe in the longer term, i.e. beyond 2030, is likely to decrease. On the other hand, if some countries worldwide do not follow the CLE course, then background ozone in the longer term, including over Europe, is likely to increase.

166. Climate change will additionally influence future ozone levels through its impact on many different natural processes. Identified processes include those related to:
   I. Emission fluxes of ozone-precursors (e.g. NMVOC from vegetation, NO_x from soil and from lightning, CH_4 from wetlands, and NO_x, CO and NMVOC from wild fires);
   II. Atmospheric chemistry (e.g. via changes in temperature and atmospheric water vapour content);
   III. Atmospheric dynamics (e.g. boundary layer ventilation, convective mixing, prevalence of anticyclonic blocking highs, precipitation, and stratosphere-troposphere exchange);
   IV. Loss of ozone by dry deposition to vegetation. This depends on soil moisture content and CO_2 concentrations. Under dry soil conditions the stomata of vegetation are almost completely closed because the plants are conserving water, so loss of ozone by dry deposition decreases and ozone levels increase. Similarly, if CO_2 levels rise the stomata can open less for the same level of photosynthesis. For example, Sanderson *et al.* (2007) calculated an increase in surface ozone over Europe of 2-6 ppbv solely due to the effect of doubling CO_2 concentrations on plant stomata.

   Climate change may also influence future anthropogenic emissions of ozone-precursors indirectly through mitigation and adaptation responses such as reduced energy demand for space heating in winter but greater energy demand for air-conditioning in summer.

167. Although these (and other) processes and feedbacks of climate change acting on future ozone levels have been identified, only a small number of coupled climate-chemistry models have been run and many known climate feedbacks have yet to be included.

168. Stevenson *et al*. (2005) performed a detailed investigation of climate change and variability on future tropospheric ozone using the IPCC IS92a emissions scenario ("business as usual") and comparing results for the period 1990-2030 for a fixed climate and for a projected climate from HadCM3 with a global mean surface warming of ~1 K. They specifically investigated the impact of changes in temperature (on reaction rates and changes in isoprene emissions), humidity (on the $O^1D + H_2O$ reaction), convection (affecting mixing and lightning NO_x emissions), precipitation (wet removal processes) and large-scale circulation (e.g. stratosphere-troposphere exchange). In this study the largest influence on the tropospheric ozone burden was the increase in humidity, reducing ozone lifetime, together with enhanced oxidants leading to a decrease in methane lifetime and influence on ozone production. The influence of increased stratospheric-tropospheric exchange of ozone was less important.

169. Other model studies, for example Collins *et al.* (2003), Sudo *et al.* (2003), Zeng and Pyle (2003), have found a greater impact on tropospheric ozone from increased mid-latitude stratosphere-troposphere exchange of ozone. A recent interpretation of European free-troposphere ozone trends has suggested that European ozone may have been more strongly influenced by downward transport from the lower stratosphere of air more concentrated in ozone than was previously recognised (Ordóñez *et al.*, 2007). Climate change and reductions in anthropogenic emissions of ozone depleting substances are also projected to contribute to an increase in stratospheric ozone which, combined with the projected increase in transport to the surface, will lead to an increase in background ozone independent of the impact of precursor emissions.

170. Ten of the 26 global models in the ACCENT intercomparison were used to produce year 2030 global ozone fields for the current legislation (CLE) scenario and a simulated 2030 climate (Table 4-1). The ensemble-mean difference in European seasonal surface ozone calculated with and without climate change is shown in Figure 4.5. Climate change is simulated to reduce the 2030 annual-mean surface ozone averaged over Europe by 0.4 ppbv, i.e. average surface ozone over Europe increases by 1.4 ppbv for this emissions scenario rather than by the 1.8 ppbv calculated for 2030 using a year 2000 climate (Dentener *et al.*, 2006). However, the magnitude of this projected impact of climate

change on this time horizon is not significant in comparison with the magnitude of the spread in model simulations shown in the right-hand panels of Figure 4.5.

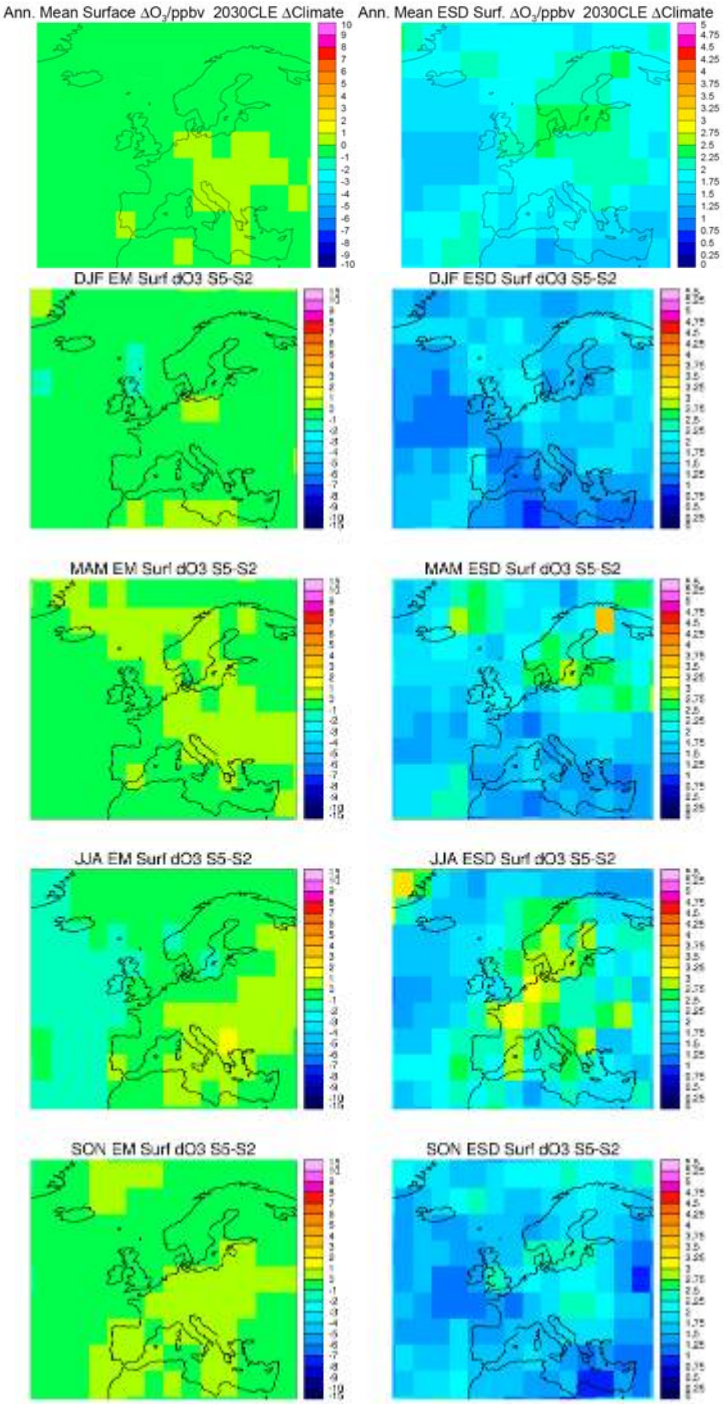


Figure 4.5 Left column: 10-model ensemble-mean change in annual mean surface ozone (top row) and 3-month seasonal mean surface ozone (subsequent rows) for year 2030 for "central" emissions scenario CLE using a simulated 2030 climate in 2030 as compared with using 2000 climate in 2030, i.e. this figure illustrates the additional perturbation caused by modelled impacts of climate change between 2000 and 2030 to the simulated ozone changes for this period already illustrated in Fig. 4.1. Right column: standard deviation of ensemble simulations. Units are ppbv (1 ppbv $O_3 \cong 2$ μg m^{-3} O_3). The models have been interpolated to a common resolution (5° × 5° horizontal); lowest model level depth is ~100 m. Source: Stevenson (pers. comm.) from data of Dentener *et al.* (2006).

171. There is some evidence from this model intercomparison, and other global model simulations including climate change effects (e.g. Royal Society, 2008), for a pattern of negative feedback of climate on surface ozone over the oceans, but positive feedback over polluted land surfaces (Figure 4.5). The negative climate feedback for lower altitude ozone in the models appears to be driven by the increased specific water vapour content of a warmer atmosphere increasing the rate of chemical ozone loss through the sequence of reactions:

$$O_3 + h\nu\,(\lambda < 310\ \text{nm}) \rightarrow O_2\,(a^1\Delta g) + O(^1D)$$
$$O(^1D) + H_2O \rightarrow 2OH$$

This loss process dominates particularly in low-NO_x environments, such as over the oceans, and offsets the increased rate of photochemical ozone production via increased temperature, and the increased influx of ozone via stratospheric-tropospheric exchange, although these latter processes are also important. The impact of climate change on surface ozone over polluted continents appears to have a positive net effect. In these areas increases in surface ozone may arise because of a decrease in formation of the NO_x reservoir compound peroxyacetyl nitrate (PAN) with temperature as shown, for example, for the US by Murazaki and Hess (2006)), or because of an increase in ozone production with increasing water vapour in a high-NO_x environment.

172. Many climate feedbacks, however, have generally not been included in these models. One important potential climate effect, for example, is the impact of temperature on emissions of NMVOC from vegetation. High concentrations of ozone were observed in northern Europe during the summer heat-wave of 2003 (Solberg *et al.*, 2005). Detailed analysis of measured species concentrations and chemical and meteorological modelling has indicated that the peaks in ozone experienced at the surface were due to regional scale accumulation of pollutants entrained into the boundary layer each day (including, for example, from extensive forest fires caused by the drought and heat on the Iberian Peninsula (Solberg *et al.*, 2005)), coupled to strong additional stimulation of ozone production from the oxidation of biogenic NMVOC (Lee *et al.*, 2006). This strongly non-linear influence of high temperatures on isoprene emissions occurred in a geographic region where biogenic emissions are normally considered not to be significant (Stewart *et al.*, 2003). At present it is not possible fully to reconcile the biogenic NMVOC concentrations observed in south east England during this episode with the national biogenic NMVOC inventory for the UK (Utembe *et al.*, 2005). See also Section 2.9.

173. Two issues regarding future ozone arise from the experience of 2003. First, the extent of occurrence of meteorological conditions in the future which cause extended residence time of pollutants in the atmospheric boundary layer (regardless of changes in pollutant emissions), and secondly, the future response of biogenic NMVOC emissions to climate change and their impact on future ozone generation.

174. The evidence is currently equivocal regarding the future frequency of summertime blocking high pressure systems, which cause import of air westwards into the UK and stagnation, but it is possible that such conditions will increase in frequency (Barnes *et al*. unpublished, cited in Royal Society, 2008), with consequent adverse impact on peak ozone metrics.

175. On the other hand there is more confidence that periods with temperatures of the magnitude encountered in 2003 will rise both in frequency and duration across Europe as a consequence of climate change (Stott *et al.*, 2004; Meehl and Tebaldi, 2004; Schar *et al.*, 2004). However, such a strong response of biogenic emissions to high temperature as observed in northern Europe in 2003 may not be observed in future decades or across all regions, for example, in the Mediterranean, where the plants are better adapted for water and temperature stress. Many other environment-related factors, in addition to temperature, influence biogenic NMVOC emissions and it is not clear what the net effect

will be on biogenic emissions, in particular regions as the environment changes. Example factors influencing biogenic NMVOC emission include:

- Increasing CO_2 levels. Experiments in chambers (Possell *et al.*, 2004; Possell *et al.*, 2005) and in "free air enrichment experiments" (Centritto *et al.*, 2004) have shown that isoprene emission rates from some species decrease with increasing CO_2 concentration. The degree of suppression caused by increasing CO_2 can be large, but there is disagreement on the net effect on total biogenic emissions from all species regionally and globally. Some model studies predict that the CO_2 suppression effect more or less offsets the increase in emissions predicted with increasing temperature in the future both globally (Lathiere *et al.* unpublished, cited in Royal Society, 2008) and for Europe (Arneth *et al.*, 2007) whilst other studies predict substantial future increases in global isoprene (Guenther *et al.*, 2006).
- Changes to net primary productivity (NPP), and on NPP-CO_2 feedbacks, through direct impact on plant health by ozone (Sitch *et al.*, 2007), or through indirect impact on stomatal conductance of changes in soil moisture (Sanderson *et al.*, 2007).
- Changes in individual species' tolerance as environmental conditions change.
- Changes in the species mix as environmental conditions change, i.e. successional changes in vegetation land-type.
- Response of species emissions to changes in insect herbivory as environmental conditions change.

176. It is also possible that anthropogenically-driven changes in land-use species mix (whether directly policy driven or otherwise) could have as much or greater influence on the total biogenic NMVOC emission flux going forward as the net effect of climate change-driven influences on the plant emission processes *per se*.

177. Future changes in biogenic NMVOC emissions will be occurring alongside changes in anthropogenic precursor emissions (NMVOC and NO_x, in particular). Therefore, in addition to uncertainty on future biogenic emission rates, the extent to which any future increase in emissions of biogenic NMVOC increases future ozone will depend on the extent to which the future air-shed into which these emissions occur is VOC rather than NO_x sensitive, which will likely vary with region.

178. In summary, the net sign of the additional impact of climate change on surface ozone at the European and sub-European spatial scale, let alone the magnitude of the impact, is not known with confidence. Current level of understanding suggests that the climate change feedback on annual-average surface ozone over polluted land masses will be positive. However, the additional effects of climate change on precursor emissions, atmospheric chemistry, downward transport of stratospheric ozone, synoptic meteorology etc. are currently anticipated to be a smaller influence on annual mean surface ozone levels on the 2030 time horizon than the effects of human-led changes in regional and global emissions of precursor gases already discussed. This does not exclude the possibility that climate change may have proportionally larger influence on regional peak summertime surface ozone through, for example, enhanced biogenic NMVOC emissions, drought-related depression of ozone dry deposition, increased incidence of wild fires, or extended air-mass residence time in the boundary layer. Also, for time horizons longer than 2030, benefits to continental surface ozone levels accrued from precursor emissions controls may be reversed by climate change impacts and by consequences of land-use change.

179. Inter-annual variability in European ozone is driven mainly by variations in the frequency of zonal air flows (westerlies) versus blocking high pressures (as mentioned above) which, in winters, is determined by the North Atlantic Oscillation. In summer this variation only occurs over northern Europe; summers with predominantly zonal flow have lower ozone and fewer episodes than summers with predominantly blocked flow. There is

evidence that variations in the thermohaline circulation, leading to changes in the Atlantic (Ocean) Multi-decadal Oscillation (AMO), may have been an important driver of multi-decadal variations in the summertime climate of western Europe (Sutton and Hodson, 2005). Such large-scale climate phenomena impose considerable variability on the year by year levels of ozone at different locations, as illustrated in the historic time-series of ozone measurements from UK rural network monitoring sites provided in Chapter 2.6-2.8.

180. The magnitude of inter-annual variability is likely to be large compared with the net change in mean ozone over the next 2 to 3 decades caused by the other influences described above. This adds to the uncertainty in ascribing the various influences on ozone and emphasises the need for multi-year observational data and simulations.

Chapter 5

Likely future trends in urban ozone concentrations

Question 4: *What are the likely future trends in urban ozone concentrations, over the next two decades and what is driving them?*

Short answer to question 4

181. **Urban ozone concentrations are expected to rise over the next two decades and to tend towards the levels found in the rural areas that surround them. The increases in urban ozone concentrations are largely driven by vehicle emission controls that have brought about a reduction in NO_x emissions in urban areas. Road traffic NO_x emissions have previously depressed urban ozone levels below rural levels and although this titration effect is being diminished by pollution controls, many urban areas in the UK are still expected to have lower ozone concentrations in 2020. Urban ozone concentrations will also respond to the changes occurring to ozone in the surrounding rural areas, largely driven by changes on the hemispheric/global scale. Depending on the strength of these trends, these could also cause increases in urban ozone, which will be in addition to the NO_x-titration effect.**

Detailed answer to question 4

182. To answer this question on future urban ozone levels in the United Kingdom, we need to understand what have been the main lessons learnt from the vast expansion that has taken place in urban ozone monitoring during the last decade. As the response and supporting evidence to Chapter 2 indicated, almost all of the 49 urban centre, urban background, roadside and kerbside AURN sites have shown upwards trends in the annual mean of the daily maximum 8-hour mean ozone concentrations over the period since monitoring began through until 2003. Broadly speaking, these upwards trends are greatest for the most polluted sites and lowest for the least polluted sites. This behaviour has been explained by the progressive diminution of the NO_x-driven titration of ozone following the implementation of 3-way exhaust gas catalysts on petrol-engined motor vehicles mandated by the European Commission.

183. What happens to future urban ozone levels at a given location can be considered to depend on the NO_x emission density (strictly NO_x concentrations) in the immediate surrounding area. Once NO_x emission densities fall much below 10 tonnes per 1 km x 1 km grid square per year, then NO_x titration ceases to act as dominant sink for ozone, compared with dry deposition, and the urban ozone concentrations approach those of the surrounding rural area. Under these conditions, it becomes increasingly unlikely that further NO_x emission controls will bring about further ozone increases. For grid squares above this threshold, further NO_x emission reductions would still bring about further urban ozone increases. The further above this threshold a grid square is then the greater the potential for ozone increases. Whether urban ozone levels continue to increase over the next decade in the grid squares with emission densities above the threshold, will depend on further road traffic NO_x emission reductions. This depends crucially on the extent to which diesel NO_x exhaust emission controls are introduced through EU legislation and penetrate through the respective vehicle fleets. Experience in London has shown how important it will be to understand the fraction of the NO_x that is emitted as NO_2 as primary NO_2 emissions are a source of oxidant and hence O_3 in urban areas.

184. Modelling using the process-based ADMS-Urban and Ozone Source-receptor Models provides further confirmation of the decrease in the local NO_x-titration effect and increases

in ozone concentrations (i.e., a decrease in the urban ozone decrement). For example, calculations using the ADMS-Urban model gave annual mean ozone concentrations in 2001, which varied from 40 µg m^{-3} on the outskirts of London to less than 20 µg m^{-3} in central London. In 2020, using projected changes in London emissions and trends in oxides of nitrogen but with no change in meteorology, annual mean concentrations were predicted to have risen to more than 52 µg m^{-3} on the outskirts of London. Furthermore, the two models gave comparable percentage decreases for a number of ozone metrics as a function of the modelled NO_x concentration and these decrements were also comparable to those derived from the empirically based approach used in the Pollution Climate Model.

185. There has always been a concern as to whether there may be photochemical ozone formation hot spots in UK urban areas. As indicated in Chapter 2 (see for example Figure 2.29 and Figure 2.31), urban ozone monitoring network data from the London Air Quality Network (LAQN) during the intense photochemical ozone episode in August 2003 showed no evidence of elevated ozone concentrations within the London conurbation compared with rural levels. This was found to be the case on a monthly, highest daily and highest hourly basis during August 2003. Intense urban-scale ozone production does not therefore appear to be as widespread a phenomenon in London as it is in Atlanta, Houston and Los Angeles in the USA. On this basis, it appears that urban ozone levels are always lower than the levels in the surrounding rural areas and that this deficit is driven by depletion of ozone by NO_x emissions within the urban areas. The bulk of the ozone monitored in urban areas therefore had its origins in the surrounding rural areas and was made by regional scale ozone formation. This urban-rural relationship is expected to continue in the future and regional-scale ozone levels are expected to continue to control future urban levels.

186. Urban ozone concentrations will therefore also respond to the changes occurring to ozone in the surrounding rural areas. Model results obtained using the Ozone Source-receptor Model showed that, depending on the strength of the ozone trends on the hemispheric/global scale, these changes could also cause increases of a similar magnitude in urban ozone to the changes in the NO_x-titration effect.

187. Analysis of the $NO\text{-}NO_2\text{-}O_3\text{-}O_x$ relationships for a number of years and urban locations has revealed the presence of anomalously elevated regional background oxidant contributions for 1999. These elevated background oxidant levels appear to be associated with the 20-year maximum monthly mean baseline ozone concentration of 51.8 ppb (~103.6 µg m^{-3}) reported for Mace Head, Ireland during March 1999. Indeed, this ozone anomaly is present in the records of 55 sites (located largely in rural locations) in the EMEP ozone-monitoring network during the winter and early spring of 1998-1999 (see Figure 2.12 and Figure 2.18 in Chapter 2). The origin of this anomaly appears to have been tropical and boreal biomass burning elsewhere in the northern hemisphere. Hemispheric scale events have the capacity therefore to influence regional and hence urban ozone concentrations and are likely to contribute to year-on-year variability in the future.

188. On this basis, it is concluded that the main drivers for future urban ozone are likely to be:

- Local scale NO_x emissions and the extent to which the diminution of NO_x titration of ozone due to the control of road traffic NO_x emissions continues in the future,
- Regional ozone levels, and the balance between any rise in hemispheric background ozone and any decline due to the control of regional-scale ozone-precursor emissions,
- The occurrence of hemispheric scale events such as biomass burning.

189. Any changes to UK ozone arising from other aspects of climate change (temperature, humidity) are most likely to affect urban ozone through changes to regional ozone concentrations. Given the absence of local photochemical production of ozone in London during the 2003 episodes, it is unlikely that photochemical production of ozone in urban areas will become more significant in future when the frequency of such episodes is expected to increase.

Supporting evidence for question 4

5.1 Overview

190. As shown in Chapter 2, urban ozone levels are lower than those in the rural areas surrounding them because of higher NO_x emissions, mostly from low-level vehicular traffic sources, which act as local ozone sinks. It is then straightforward to understand how measures to control vehicular NO_x emissions have led to a diminution in these local ozone sinks and hence to rising urban ozone levels. This difference between the values of the ozone concentration or metric at the urban location and the corresponding quantity at a surrounding rural site (taken to be representative of the regional ozone field) defines an urban ozone decrement.

191. The issue is then the extent to which rising ozone levels will continue into the future. In this supporting evidence, information is presented on diurnal cycles in ozone, ozone sinks and on projections of future low-level NO_x emissions. An analysis has been undertaken to determine the significance of the local NO_x titration effect in 2020 and model calculations are also presented for the Greater London area for current and future years using the ADMS-Urban model.

192. As Chapters 2, 3 and 4 have indicated, in addition to a reduction in the NO_x titration effect, there are two other main drivers determining UK ozone concentrations and their frequency distribution:

I. regional controls on NO_x and VOC emissions at the European level, reducing peak ozone concentrations (i.e., reduced photochemical ozone production).
II. an increasing background concentration arising from global changes in atmospheric composition and hemispheric circulation.

193. The Ozone Source-receptor Model (OSRM) has been used to investigate the significance of these other drivers on future UK urban ozone concentrations compared to the NO_x-titration effect.

194. A comparison of the urban ozone decrements derived from UK process-based models (OSRM and ADMS-Urban) and empirical approaches is then made. The supporting information concludes with a summary of recent European activities to model urban ozone. A technical annex to this question is given in Annex 4.

5.2 The NO_x titration driver

5.2.1 Ozone diurnal cycles and sinks

195. At almost all UK ozone-monitoring sites, both rural and urban, ozone exhibits a characteristic diurnal cycle. Figure 5.1 illustrates these diurnal cycles for a pair of sites, a rural site at Harwell, Oxfordshire and an urban background site, London Bloomsbury. Average diurnal cycles are presented for two years, 1995 and 2006, two strongly photochemically active years, widely spaced in time. The average diurnal cycles for both

sites and years are clearly evident in Figure 5.1 and show highest average concentrations in the mid-afternoon and lowest levels in the early morning.

196. Garland and Derwent (1979) have shown that the average diurnal cycle at the rural monitoring site is controlled by the diurnal cycle in the atmospheric boundary layer depth and the strength of turbulent mixing processes. The atmospheric boundary layer is generally well mixed during the mid-afternoon and surface ozone monitoring data are representative of those present in a considerable depth of the atmosphere. At night, boundary layer depths are generally considerably smaller and ozone levels close to the surface become depleted by surface deposition and local NO_x sources because they are not efficiently replenished by turbulent transport and exchange. The average diurnal curves at the rural site have been shifted to higher concentration during the early morning and evening, reflecting the diminution in local NO_x sources due to vehicle emission controls. Nocturnal depletion is still evident in 2006 because surface deposition under the shallow night time stable layer is the dominant night time sink for ozone. Diminution of NO_x titration between 1995 and 2006 has led to a reduction in the urban ozone deficit in London and urban levels have clearly risen towards the rural levels immediately outside of London.

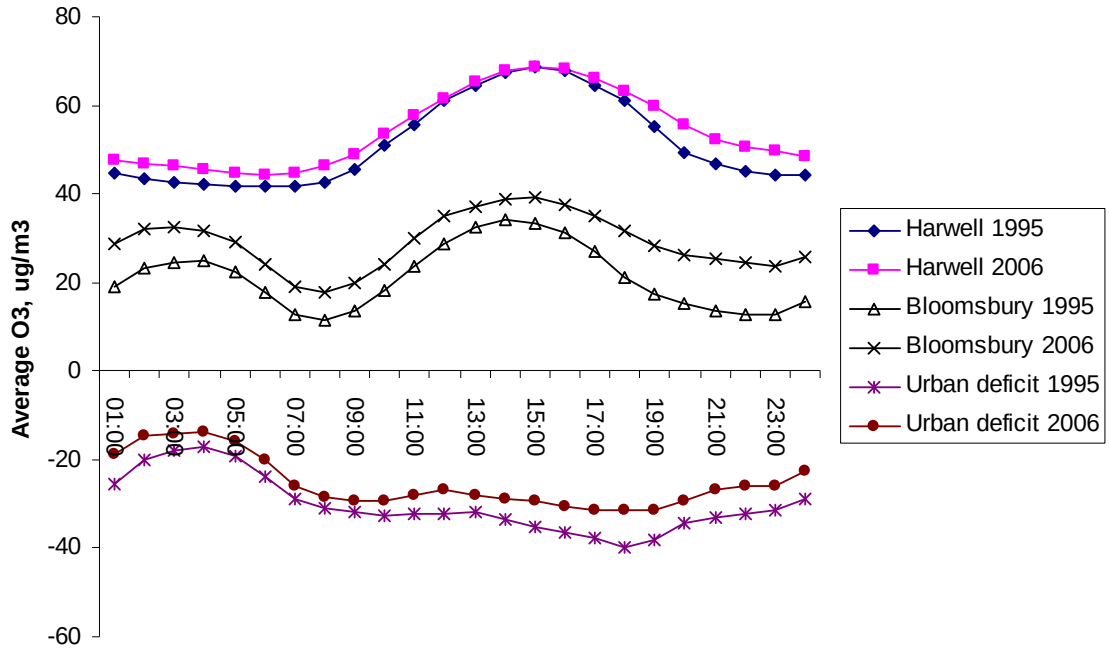


Figure 5.1 Average diurnal cycles in ozone at a rural and a London urban background site in 1995 and 2006, together with the London urban deficit in both years.

197. The average diurnal cycle at the London urban background site, see Figure 5.1, exhibits the same mid-afternoon maximum as the rural site. However, London urban background levels are clearly depressed relative to rural levels and there is a London urban decrement of about 30–40 µg m^{-3} during the mid-afternoon, due largely to London-wide and local NOx emissions. Over the period from 1995 to 2006, NO_x emission controls have reduced the strength of NO_x titration, reducing the London urban ozone decrement by about 10 µg m^{-3}, that is by about one quarter.

198. It is evident from Figure 5.1 that ozone concentrations at the London urban background site have been raising from 1995 to 2006 due to a diminution in NO_x titration because of NO_x emission reductions. London urban background ozone concentrations have been rising relative to rural levels and urban ozone decrements have been falling. Similar behaviour has been observed in most urban areas. Further details of urban ozone trends were given in the response to Question 1 (see Chapter 2).

5.2.2 Changes in the NO_x titration effect

199. Over the period from 1995 to 2006, it would appear that the NO_x sink for ozone at the London urban background site has been reduced by about one quarter due to NO_x emission controls. As further NO_x controls are enacted and promulgated, the average diurnal curve will rise further until it meets the average diurnal curve for the rural Harwell site and the London urban ozone decrement is eroded away. At that point, NO_x depletion will have become of negligible importance in comparison with surface depletion and the difference between rural and urban areas, at least as far as ozone sinks are concerned, will have disappeared.

200. Turbulent transport to a vehicular NO_x-driven ozone sink or to a vegetated surface become of roughly similar magnitudes for a NO_x emission density of about 10 tonne km^{-2} yr^{-1}, making reasonable assumptions of deposition velocities (5 mm s^{-1}), aerodynamic resistances (0.1 cm s^{-1}) and nocturnal atmospheric boundary layer depths (100 metres). Hence, this value can be used as an indicator of the relative importance of NO_x-driven and surface deposition sinks for ozone. Strictly, it is the NO-NO_2-NO_x concentrations that determine the threshold and this will vary throughout the year and from site to site.

201. For the purposes of this analysis, the threshold of 10 tonne km^{-2} yr^{-1} has been used to identify those urban areas in which local vehicular traffic sources will dominate over surface deposition as the major ozone sink. In these locations, urban ozone concentrations are expected to be depressed relative to rural levels and further NO_x emission controls will lead to increasing urban ozone concentrations. For urban areas with local NO_x emission densities below this level, NO_x depletion is expected to be relatively unimportant and the impact of further NO_x emission controls is likely to be small.

202. Figure 5.2 shows the spatial distribution of the low-level NO_x emissions across the United Kingdom in 2004 (left-hand panel) and 2020 (right-hand panel), highlighting the areas with emission densities in excess of 10 tonne km^{-2} yr^{-1}. The analysis used the latest emission estimates available at the time from the NAEI for these years. From these figures, it is apparent the area with emission in excess of 10 tonne km^{-2} yr^{-1} shrinks between 2004 and 2020 in response to further NO_x emission reductions. On this basis, it is likely that the upwards trends in annual mean ozone concentrations in the urban areas with NO_x emissions below this threshold will cease relative to rural areas immediately surrounding them. Furthermore, there are a number of rural areas containing important road links that will also shift below this critical emission density, carrying the implication that ozone concentrations will cease rising in these grid squares relative to the rural areas,. When this happens, the trends in the rural and urban will become the same and the future prospects for both will be determined by those of the rural areas. The influence of the diminution of NO_x titration will drop out, leaving European pollution controls and the growth in northern hemisphere ozone baseline as the main controlling influences on ozone in the 'white' areas of the right-hand panel of Figure 5.2.

203. Table 5-1 presents details of the urban locations where ozone levels are depleted relative to the rural areas immediately surrounding them in 2004 and 2020, using the NO_x emission threshold of 10 tonne km^{-2} yr^{-1}. The prospects are that significant areas of the UK and significant populations, will still have depleted ozone levels in 2020, despite the NO_x emissions reductions form vehicle traffic that are projected to occur between 2004 and 2020. Urban ozone levels will continue to rise in these areas up to 2020 and beyond. This conclusion is confirmed by the calculations of process-based models in subsequent sections of this supporting evidence.

204. The further above the threshold a grid square is then the greater the potential for ozone increases. Whether urban ozone levels continue to increase over the next decade in the

grid squares with emission densities above the threshold, will depend on further road traffic NO_x emission reductions. This depends crucially on the extent to which diesel NO_x exhaust emission controls are introduced through EU legislation and penetrate through the respective vehicle fleets. Experience in London has shown how important it will be to understand the fraction of the NO_x that is emitted as NO_2 with these new technology diesel vehicles as primary NO_2 emissions are a source of oxidant and hence O_3 in urban areas [Clapp and Jenkin, 2001; Jenkin, 2004].

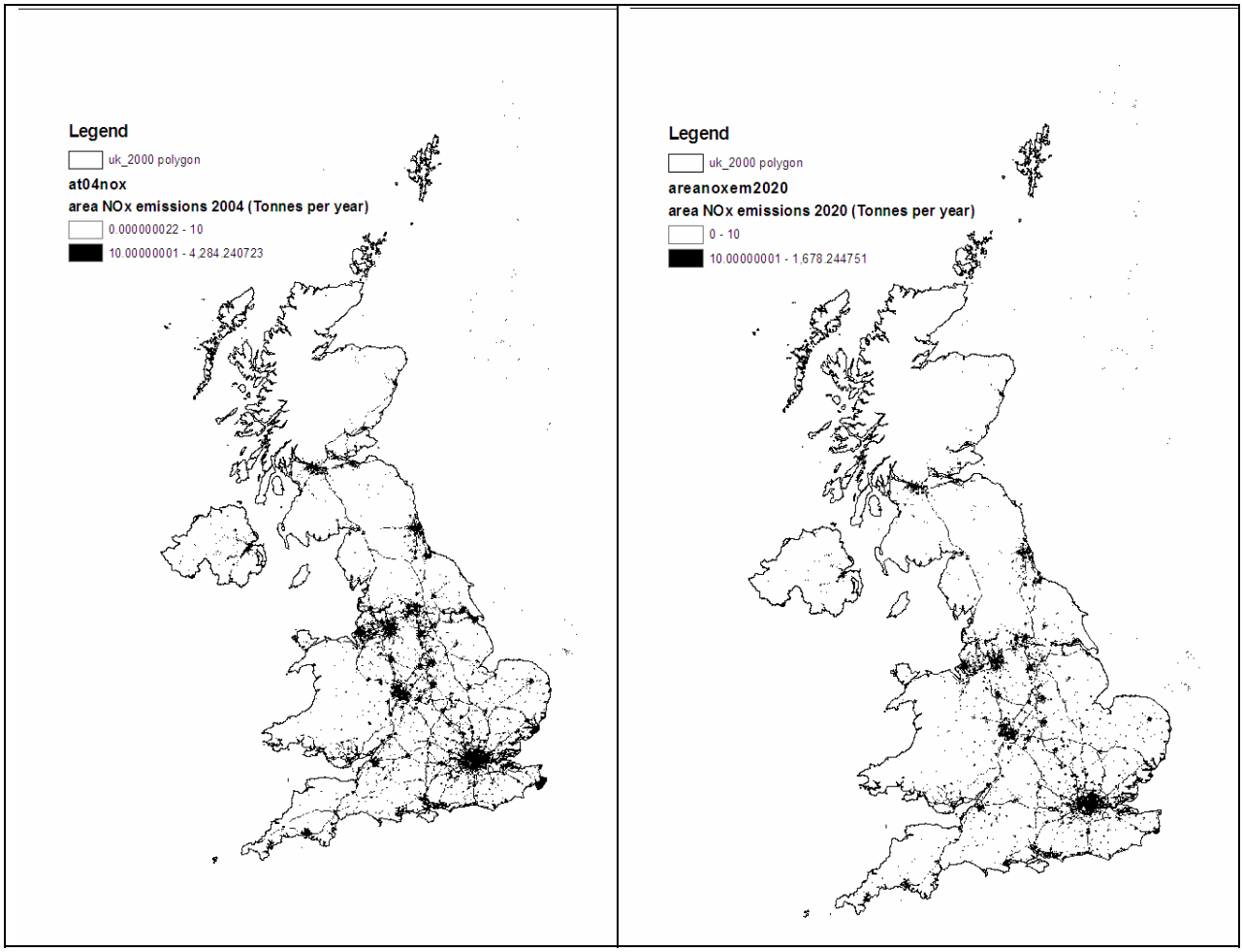


Figure 5.2 NO_x Emission Densities (tonnes km^{-2} y^{-1}) across the UK in 2004 (left-hand panel) and 2020 (right-hand panel).

Table 5-1 Populated Areas of the United Kingdom and Likely Occurrence of Depleted Ozone Levels relative to the Rural Areas immediately surrounding them in 2004 and 2020. The Percentage of the Area with Depleted Ozone Levels and the Percentage of the Population Resident in these Depleted Areas have been estimated using the 10 tonne km^{-2} yr^{-1} Threshold Emission Density, see text. Data for the regions in the lower part of the Table excludes any urban areas in the regions listed separately in the Table.

Urban Area/Region	Total Area, (km^2)	Percentage of Area with Depleted Ozone, (km^2)		Total Population	Percentage of Population in Area with Depleted Ozone	
		2004	2020		2004	2020
Greater London	1632	92.9%	82.7%	7784707	98.8%	94.6%
West Midlands	594	96.3%	86.7%	2083891	98.9%	92.5%
Greater Manchester	557	96.2%	85.8%	1846479	98.9%	91.8%
West Yorkshire	363	90.6%	77.7%	1150737	96.0%	86.1%
Tyneside	217	97.2%	87.6%	714326	99.1%	93.1%
Liverpool	185	93.5%	84.9%	697197	98.3%	92.5%
Sheffield	165	93.9%	83.0%	521984	97.5%	89.8%
Nottingham	169	94.1%	82.8%	558935	98.5%	90.4%
Bristol	142	91.5%	78.9%	488798	98.2%	85.7%
Brighton/Worthing/Littlehampton	98	83.7%	66.3%	387431	91.9%	81.7%
Leicester	102	94.1%	77.5%	374314	97.5%	84.7%
Portsmouth	93	83.9%	75.3%	355516	92.5%	84.6%
Teesside	113	84.1%	68.1%	301290	98.0%	82.6%
The Potteries	91	92.3%	85.7%	266188	96.2%	92.2%
Bournemouth	113	85.0%	66.4%	338103	91.6%	75.9%
Reading/Wokingham	97	86.6%	74.2%	305786	94.4%	83.4%
Coventry/Bedworth	76	94.7%	84.2%	277475	98.8%	91.5%
Kingston upon Hull	80	88.8%	75.0%	260201	94.3%	81.0%
Southampton	78	89.7%	82.1%	265011	94.0%	89.6%
Birkenhead	88	88.6%	75.0%	265019	98.5%	88.3%
Southend	64	85.9%	70.3%	217874	95.3%	84.7%
Blackpool	63	93.7%	77.8%	212909	99.1%	90.8%
Preston	58	93.1%	81.0%	180687	96.7%	88.3%
Glasgow	366	86.3%	73.2%	1083323	95.2%	85.4%
Edinburgh	118	85.6%	65.3%	429071	94.7%	84.0%
Cardiff	74	93.2%	81.1%	264259	97.6%	89.1%
Swansea	85	80.0%	60.0%	190228	92.4%	69.7%
Belfast Metropolitan	196	75.5%	58.2%	515484	85.8%	68.7%
Eastern	19137	11.2%	7.3%	4909876	60.6%	47.9%
South West	23546	6.4%	4.0%	4039462	49.0%	38.5%
South East	18664	14.0%	9.8%	6160629	60.4%	48.8%
East Midlands	15492	10.5%	6.6%	3261327	56.9%	42.1%
North West & Merseyside	13743	12.0%	8.2%	3470622	68.6%	52.5%
Yorkshire & Humberside	14792	9.4%	6.6%	3003872	58.6%	44.9%
West Midlands	12192	10.9%	7.1%	2624016	60.9%	45.9%
North East	8288	8.0%	4.9%	1443912	65.2%	51.1%
Central Scotland	9352	8.7%	5.8%	1883014	58.7%	45.2%
North East Scotland	18625	2.1%	1.1%	976022	55.7%	46.4%
Highland	39170	0.1%	0.1%	341329	19.8%	14.3%
Scottish Borders	11182	1.1%	0.8%	250529	38.2%	29.9%
South Wales	12236	5.0%	3.5%	1698082	48.1%	39.8%
North Wales	8372	3.1%	1.9%	702506	39.6%	30.0%
Northern Ireland	13969	2.1%	0.9%	1149153	24.4%	12.2%
Total	244837	8.6%	6.1%	58251571	72.4%	61.7%

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5.2.3 Modelling of the Greater London Area

205. Williams *et al*. (2006) have used the ADMS-Urban model to calculate ozone concentrations for the Greater London area for current (2001) and future (2010 and 2020) years. The model runs used traffic flow and emissions data from the 2001 London Atmospheric Emissions Inventory, together with meteorological data from Heathrow and background data from rural monitoring sites around London. The modelling of future years allowed for changes to traffic flows, pollutant emission rates and background concentrations.

206. Background NO_x concentrations for 2010 and 2020 were derived by multiplying the 2001 data by factors of 0.68 and 0.53, respectively, based on trends in national emission projections. To obtain future concentrations of NO_2, a best-fit curve was derived to relate NO_x and NO_2 concentrations in 2001 and this was applied to the projected 2010 and 2020 NO_x concentrations. Future ozone concentrations were calculated by assuming conservation of total oxidant (Oxidant = NO_2 + O_3), i.e., no allowance was made for changes in global or hemispheric ozone concentrations.

207. The model uses the generalised reaction chemistry scheme (GRS). Comparison with measurements has shown good performance for annual means but some underestimate (typically 10%) in the peaks. Table 5-2 shows the annual average ozone concentration predicted at each of the AURN monitoring sites for 2001, 2010 and 2020. In 2001, annual mean ozone concentrations were calculated to vary from 40 µg m^{-3} in the outskirts of London to less than 20 µg m^{-3} in central London. In future years, ozone concentrations in London were predicted to increase and will be greater than 52 µg m^{-3} by 2020 in the outskirts of London. Concentrations will be greater than approximately 20 µg m^{-3} along major roads in central London.

Table 5-2 Measured and Modelled Annual Average Ozone Concentrations (µg m^{-3}) for AURN Sites in London for 2001, 2010 and 2020. The model results are from ADMS Urban calculations.

Site	2001 Obs	2001 Model	2010 Model	2020 Model
Marylebone Road	14	11	12	15
Bloomsbury	23	21	26	28
Hackney	29	27	32	35
London Southwark	29	26	30	32
North Kensington	34	28	32	34
Wandsworth	27	25	30	34
Eltham	37	36	41	44
Bexley	38	34	39	42
Brent	37	37	42	45
Hillingdon	26	24	32	36
Teddington	44	40	45	47
Average	31	28	33	36

208. As an example, Figure 5.3 shows the annual mean of the daily maximum 8-hour rolling average concentrations with a cut-off of 70 µg m^{-3} for 2001, as a current year, and 2010 and 2020. The increase in this metric for these base case runs is clear and is driven by the reduction in local NO_x titration as the model runs assumed no change in background O_3 concentrations.

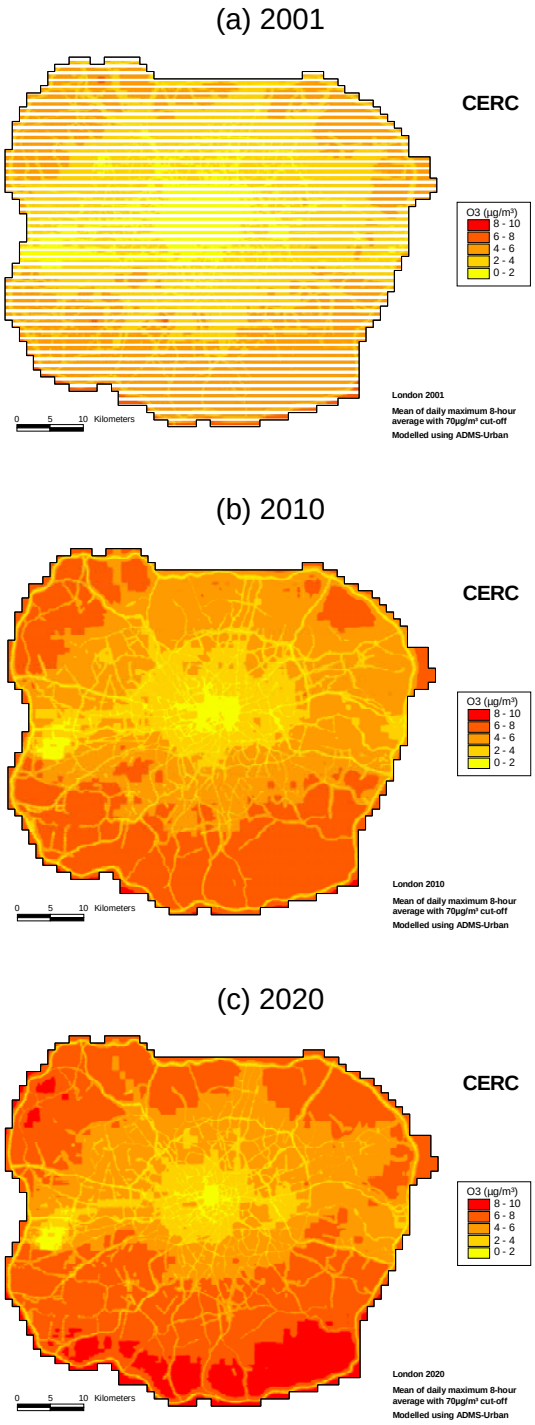
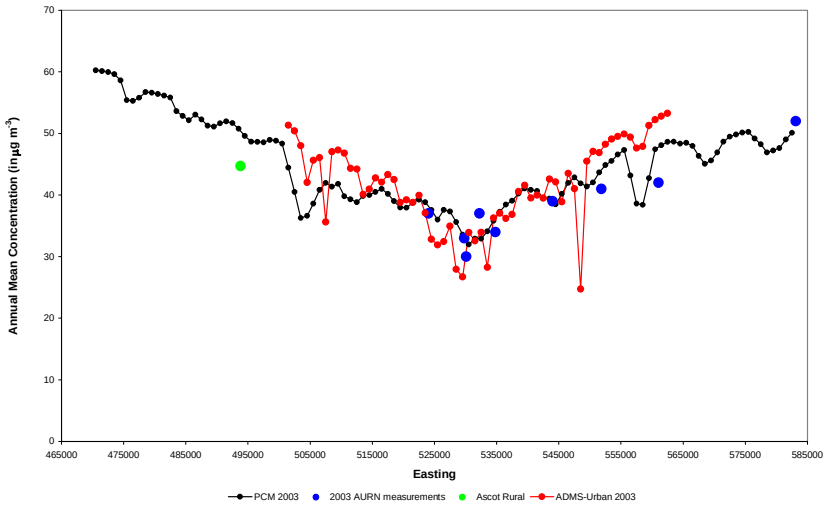


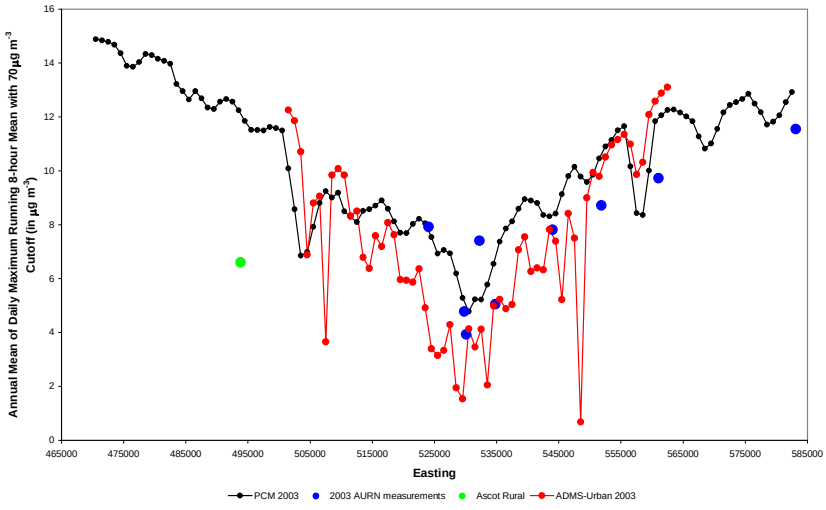
Figure 5.3 Maps of the Annual Mean of the Daily Maximum 8-hour Average Ozone Concentrations with a cut-off of 70 µg m^{-3} (in µg m^{-3}) calculated for London for 2001 and 2010 and 2020 Base Cases, using ADMS-Urban.

209. In the supporting evidence to Question 1, Figure 2.29 presented the variation in three ozone metrics, as derived by the empirical mapping methods used in the Pollution Climate Model, along a transect from west to east across London for the years 1995, 2003 and 2005. Figure 5.4 illustrates the ozone metrics derived along the same transect (see Figure 2.33 for a map of the transect) for 2003 using the ADMS-Urban model. Figure 5.4 also includes the observed ozone metrics and those derived for 2003 using the empirical approaches. The figure again provides an illustration of the urban decrement and indicates a broad level of agreement between the two approaches. The ozone

metrics are lowest (and thus the urban decrement are highest) in regions of highest NO_x emission density in central London.



(a)



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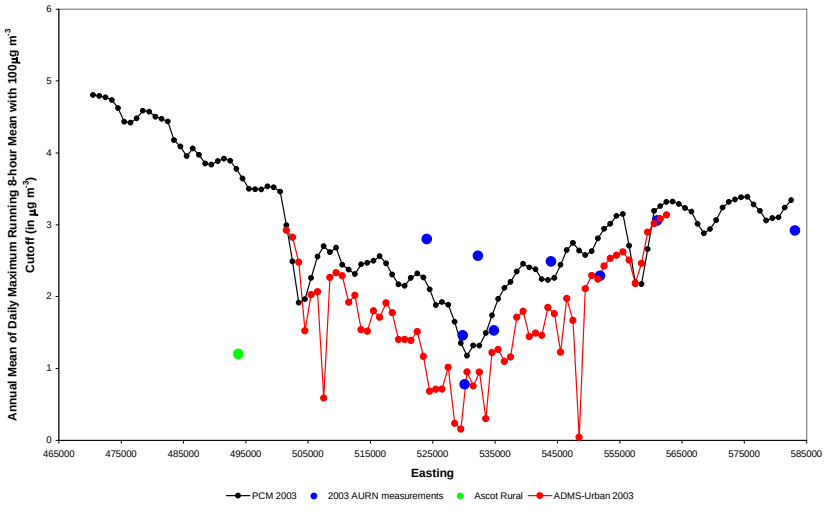

(c)

Figure 5.4 Transects of modelled (ADMS-Urban [red] and Pollution Climate Model [black]) and observed ozone metrics across London for 2003: (a) annual mean ozone concentration; (b) annual mean of the daily maximum of the running 8-hour mean ozone concentration with a 70 µ µg m^{-3} cut-off; and (c) annual mean of the daily maximum of the running 8-hour mean ozone concentration with a 100 µg m^{-3} cut-off.

5.3 The regional and global determinants of ozone

210. In addition to a reduction in the NO_x titration effect, there are two other drivers determining ozone concentrations in the UK: (a) regional controls on NO_x and VOC emissions at the European level, reducing peak ozone concentrations and (b) an increasing background concentration arising from global changes in atmospheric composition and hemispheric circulation. The Ozone Source-receptor Model (OSRM) has been used to investigate the significance of these other drivers on future UK urban ozone concentrations compared to the NO_x-titration effect (Hayman *et al*., 2006; 2008a, 2008b).

211. Two sets of OSRM model runs were undertaken to 41 receptor sites - representing the locations of 20 rural, 10 London and 11 other urban background O_3 monitoring sites - for the years 1990, 1995, 2000, 2003, 2005, 2010, 2015 and 2020. Year-specific emission inventories based on the 2004 NAEI and EMEP inventories were used in these calculations and the same meteorology - that of 2003 - was used to avoid complications arising from year-to-year variations in meteorology. Two sets of model runs were performed:
    I. The first set were initialised using daily concentration fields of O_3 and key trace species (Hayman *et al*., 2008a) derived from the STOCHEM model and modified for ozone to take account of the trend in baseline concentrations derived for a business-as-usual scenario with climate change (Hayman, 2008a).
    II. The second set of runs, for the same years, used the same initial concentrations as used for the 2003 model run, to illustrate the effect of changing atmospheric composition.

    All other model parameters were set to those used in the ozone modelling runs undertaken for the Review of the Air Quality Strategy (Hayman *et al*., 2008a, 2008b).

212. The hourly ozone concentrations were processed to derive the ozone metrics of interest. A surface conversion algorithm using site-specific hourly parameters has been developed to improve the performance of the model for urban ozone (Hayman *et al.*, 2008a). The difference between the 'unconverted' and 'converted' outputs is a measure of the ozone decrement at the location and reflects *inter alia* the effects of the local NO_x emissions.

213. The results for London Bloomsbury, London Bexley and Rochester, three closely related sites in urban, suburban and rural locations respectively, have been chosen to illustrate the model results. Figure 5.5 shows the values of two metrics
    I. The annual mean of the maximum daily running 8-hour average ozone concentration [upper panel – metric A]
    II. annual mean of the difference between the maximum daily running 8-hour average ozone concentration and a 100 µg m^{-3} (or 50 ppb) cut-off [lower panel - metric B].

    Both metrics were calculated for the two sets of model runs. The runs with changing atmospheric composition are shown in the figure as solid lines and the runs with fixed composition use dotted lines. It is clear that the changes in atmospheric composition assumed are calculated to have a significant effect on the values of the metrics.

214. The two metrics shown in Figure 5.5 were selected because of their relevance to human health and also because of their differing sensitivity to peak ozone concentrations. As discussed In the supporting evidence to Question 1, emission controls on NO_x and NMVOCs across Europe have largely reduced peak ozone concentrations and this can be seen in the downward trend at Rochester for metric B [lower panel of Figure 5.5] from 1990 to 2005. Metric A is more sensitive to changes in baseline ozone concentrations. The effect of the assumed changes in atmospheric composition was to increase future ozone concentrations and hence the values of metric A by ~3-5 µg m^{-3} in 2020 compared to the constant composition case (see upper panel of Figure 5.5). Conversely, years prior to 2003 show lower values of metric A (a reduction of ~3-5 µg m^{-3} in 1990), for variable

composition. 2003, the year used for the constant initial composition case, is in the middle of the time period considered.

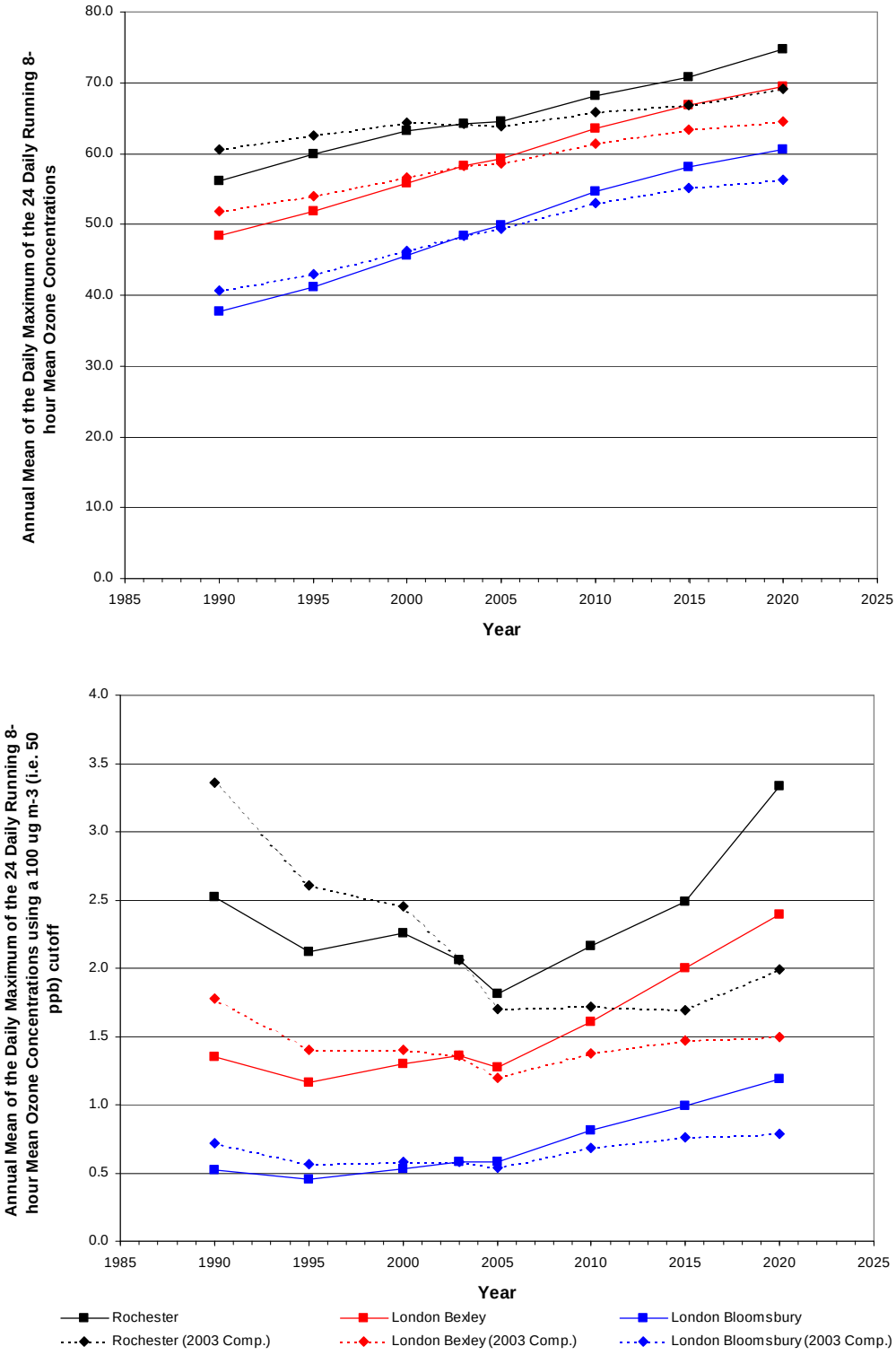

Figure 5.5 Annual mean of the maximum daily running 8-hour average ozone concentration [upper panel] and annual mean of the difference between the maximum daily running 8-hour average ozone concentration and a 100 μg m^{-3} (50 ppb) Cut-off [lower panel] as calculated using the OSRM for changing (squares/solid lines) and constant (diamonds/dashed lines) atmospheric composition for selected years between 1990-2020 using 2003 meteorology for the 3 Sites: Rochester (black), London Bexley (red) and London Bloomsbury (blue).

215. Figure 5.5 also shows the decreasing values of the two ozone metrics in moving from Rochester to the suburban London Bexley to the urban London Bloomsbury sites, consistent with the increase in the NO_x emission densities and hence local NO_x titration effect. To illustrate the change in the NO_x titration effect more clearly, the modelled percentage ozone decrements, defined as 100*(converted-unconverted)/unconverted (see paragraph 212), are shown in Figure 5.6 for the London Bexley and Bloomsbury sites for the two metrics.

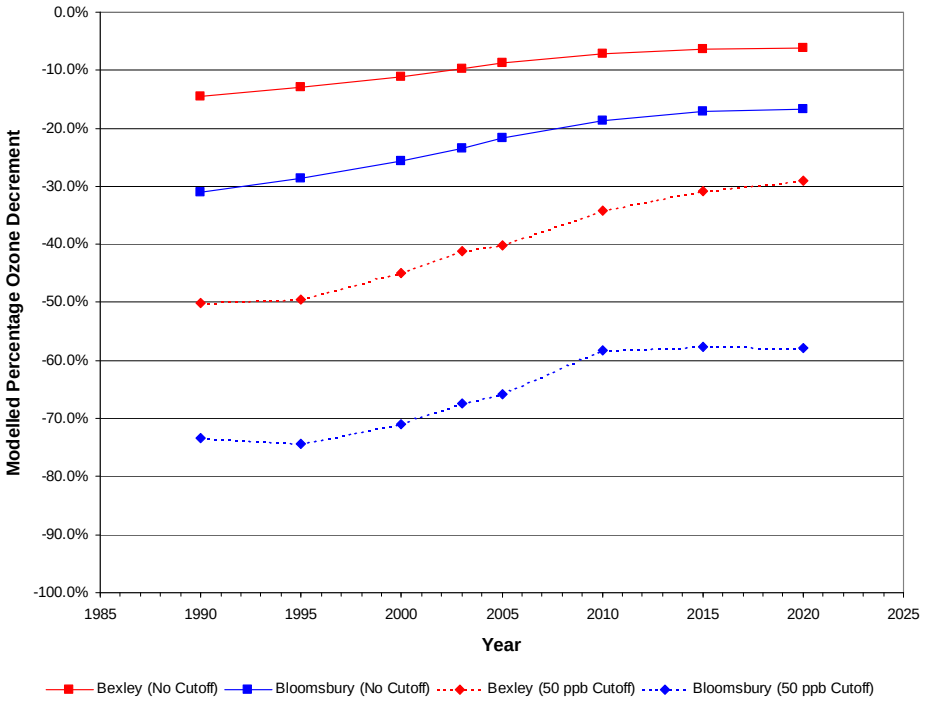

Figure 5.6 Modelled percentage decrement in the annual mean of the maximum daily running 8-hour average ozone concentration [squares/solid lines] and annual mean of the difference between the maximum daily running 8-hour average ozone concentration and a 100 μg m^{-3} (50 ppb) cut-off [diamonds/dotted lines] as calculated using the OSRM for changing atmospheric composition for selected years between 1990-2020 using 2003 meteorology for the London Bexley (red) and London Bloomsbury (blue).

216. As expected, the decrements for both metrics, as measured by the differences between the three sites, decrease between 1990 and 2020, reflecting the reduction in NO_x emissions and hence the NO_x titration effect. There is a difference however between the two metrics. As indicated in Figure 5.6, the urban decrements for metric B as a fraction of the rural value, appear larger than those for metric A. At London Bloomsbury, local NO_x titration causes a ~30% reduction in metric A in 1990 (reducing to ~17% in 2020) but an ~75% reduction in the metric with 100 μg m^{-3} cutoff in 1990 (reducing to ~60% in 2020). The corresponding values at London Bexley in 1990 are reductions of 15% (7% in 2020) and 50% (30% in 2020), respectively. The larger changes in the decrement for the metric B is a result of the sensitivity of this metric to relatively small changes in ozone concentrations close to the cut-off concentration (this high sensitivity was discussed by Sofiev and Tuovinen (2001) for the case of the AOT40 metric). The fractional decrements for the metric with the 70 μg m^{-3} (or 35 ppb) cut-off lie between the other two.

217. To conclude this section, it can be seen that, depending on their strength, ozone trends assumed on the hemispheric/global scale could, by 2020, cause increases in urban ozone of a similar magnitude to the changes expected from the NO_x-titration effect. As discussed in Chapter 4, the trend in the ozone background over this period is very uncertain. The results in this section show the differences in responses of ozone metrics, depending on their sensitivities to the different ozone determinants.

5.4 Modelling UK Urban Ozone Decrements

218. The OSRM calculations presented in the previous section (Section 5.3) support the view that ozone can be represented by a regional component and an urban ozone decrement (see Clapp and Jenkin, 2001; Jenkin, 2004). In this report, the urban ozone decrement is taken to be the difference between the values of the ozone concentration or metric at the urban location and the corresponding quantity at a surrounding rural site (taken to be representative of the regional component).

219. Urban decrements in ozone concentrations have been explored for a range of metrics using two UK process-based models (the Ozone Source-receptor Model (OSRM) (Hayman *et al.*, 2007a, b) and ADMS-Urban models (Williams *et al.*, 2006)) and an empirical approach based on monitoring data (Pollution Climate Model, PCM (Kent *et al.,* 2006)). The relationships between the urban decrements and local NO_x concentrations have been examined and the results of the analysis indicate that the empirical approach to estimating urban ozone decrements currently used in mapping studies (as presented in the supporting evidence to Chapter 2) is in reasonably good agreement with process based models. This section provides a short summary of the modelling and uses annual mean ozone to illustrate the results obtained. An accompanying technical annex to the report provides further information and also results for a wider range of ozone metrics.

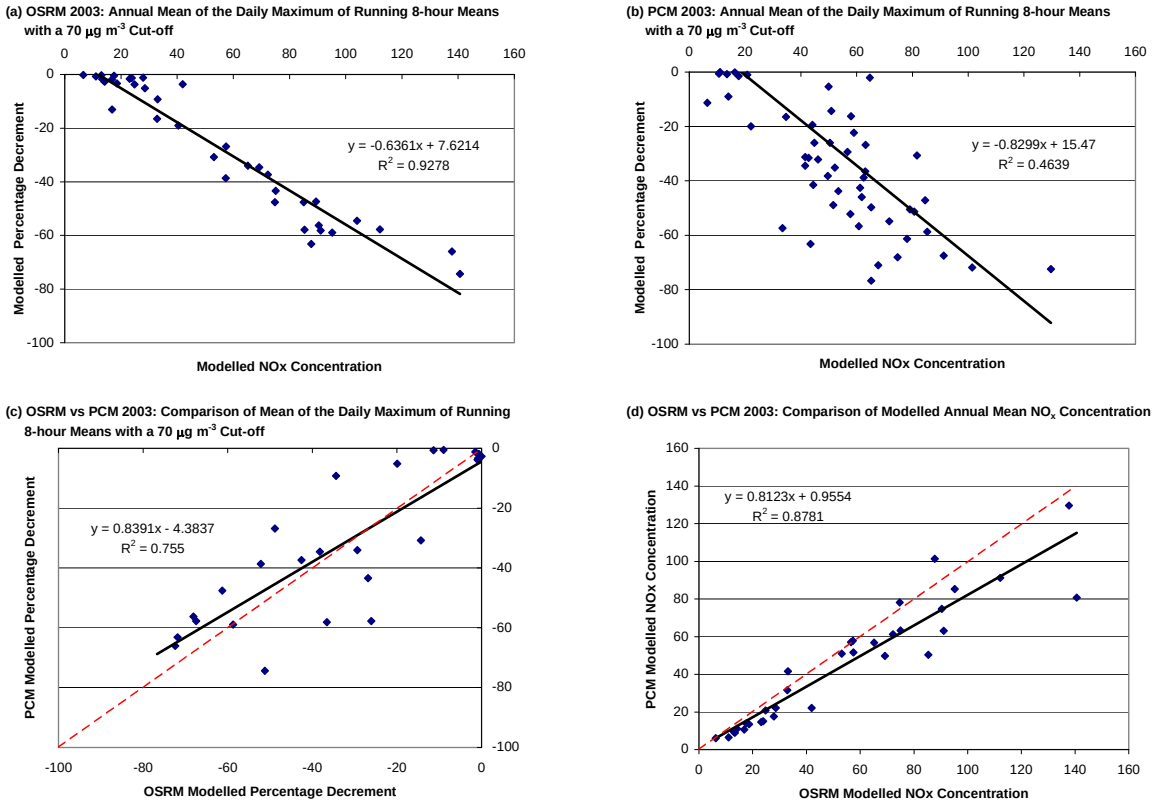

Figure 5.7 Ozone decrements calculated for UK ozone monitoring sites in 2003 using the Pollution Climate Model, as a function of the modelled NO_x concentration (µg m^{-3}, as NO_2).

220. The upper panels of Figure 5.7 show the dependence of the modelled percentage decrement in the metric, the annual mean of the daily maximum of the running 8-hour mean ozone concentrations with a 70 µg m^{-3} cut-off, on the modelled local NO_x annual mean concentration, as calculated using the OSRM (panel a) and PCM (panel b). This linear dependence is also seen for other ozone metrics (see Annex 4). The lower panels

of Figure 5.7 show a show scatter plots of the PCM results against the corresponding OSRM results for this ozone metric (panel c) and for the NO_x concentrations (panel d).

221. The results presented in Figure 5.7 support the assumption in the empirical modelling approach that the urban decrement in ozone concentration varies approximately linearly with annual mean NO_x concentration (the regression lines are shown here for illustrative purposes only) but also show a good degree of agreement. There is, however, considerable scatter in these plots, which is to be expected since the regional ozone field will incorporate uncertainties associated with the interpolation procedure and very local effects may affect the measured ozone concentrations. The positive outliers are due to measured urban ozone metrics exceeding the values measured at rural sites in the same region.

222. Urban ozone decrements have also been calculated for monitoring site locations in London for the same ozone metrics using ADMS-Urban. These results again compare well with those derived by the OSRM and PCM, as indicated in Annex 4. The OSRM model seems to generally predict a lesser decrement for the ozone metrics than ADMS-Urban. The PCM derived values are based on ambient monitoring data and also incorporate additional uncertainties associated with spatial interpolation of data from rural monitoring sites and therefore show greater scatter than the process model based estimates. These results provides additional evidence that process-based models are now available which can provide a good description of how the decrement in ozone varies spatially across urban areas.

Table 5-3 A comparison of the absolute decrements for metrics and sites for which estimates have been calculated using the OSRM and ADMS-Urban, and from ambient monitoring data using the empirical PCM approach.

	annual mean $\mu g\ m^{-3}$	mean >70 $\mu g\ m^{-3}$ $\mu g\ m^{-3}$	mean >100 $\mu g\ m^{-3}$ $\mu g\ m^{-3}$	days >120 $\mu g\ m^{-3}$ days
Absolute Ozone Decrements: ADMS				
Rural Value of Metric	59.2	14.3	3.5	21.0
London Bloomsbury	-33.1	-12.9	-3.3	-20.0
London Teddington	-10.7	-3.7	-1.0	-6.0
London Brent	-14.6	-6.1	-1.6	-8.0
London Eltham	-16.0	-6.9	-1.9	-11.0
London Bexley	-14.6	-6.2	-1.7	-9.0
Absolute Ozone Decrements: PCM				
Rural Value of Metric	56.5	14.7	4.1	24.8
London Bloomsbury	-26.5	-10.6	-3.2	-19.8
London Teddington	-8.2	-2.2	-0.4	1.7
London Brent	-16.8	-4.3	-0.2	-2.6
London Eltham	-18.4	-7.2	-1.8	-12.6
London Bexley	-14.1	-5.5	-1.4	-7.8
Absolute Ozone Decrements: OSRM				
Rural Value of Metric	50.4	10.5	2.2	13.0
London Bloomsbury	-14.0	-5.6	-1.2	-8.0
London Teddington	-5.2	-3.2	-0.7	-2.0
London Brent	-5.7	-3.2	-0.6	-1.0
London Eltham	-4.1	-2.7	-0.7	-1.0
London Bexley	-5.4	-3.4	-1.0	-5.0

223. Table 5-3 shows a comparison of the absolute decrements (in µg m^{-3} or days) for metrics and sites for which estimates are available from all three methods. Once again there is reasonably good agreement between the different methods, with the OSRM model tending to predict smaller absolute decrements. The lower absolute decrements derived by the OSRM appear to arise from the lower rural values used to derive the decrements. While the rural values given for the ADMS and Pollution Climate models are based on measured values of the metrics (actual or interpolated), the values for the OSRM are those calculated by the model and these were generally lower than the observed values particularly for sites in the southern part of the UK.

5.5 The City-Delta study and integrated assessment modelling

224. The City-Delta study is the most relevant recent study on urban ozone in Europe. The City-Delta study was an open model intercomparison exercise, sponsored by a number of international bodies, as a contribution to the modelling activities in the Clean Air for Europe (CAFE) programme (see http://aqm.jrc.it/citydelta/). The aim of the study was to assess the changes in urban air quality predicted by different atmospheric chemistry-transport (CTM) dispersion models for ozone (and particulate matter) in response to changes in urban emissions. Eight European cities were selected for the study: Berlin, Copenhagen, Katowice, London, Marseille, Milan, Paris and Prague. Scientific drivers (distinct differences in climatic conditions, the vicinity of the sea, differences in meteorological situations, and emission densities) and practical considerations (the availability of suitable models, of emission inventories for gaseous and particulate pollutants, of sufficient meteorological information, and monitoring data) were important in the choice of these cities. The results of the study have been published in a number of recent papers (e.g., Cuvelier *et al.*, 2007; Thunis *et al.*, 2007; van Loon *et al.*, 2007; Vautard *et al.*, 2007).

225. In the paper by Vautard *et al.* (2007), six different models were used to simulate concentrations of ozone and particulate matter for 1999 over domains encompassing a large area around four major European cities: Berlin, Milan, Paris and Prague. Three of the models produced results at large-scale (typically 50 km) and small-scale spatial (5 km) resolution. For ozone, the study concluded that the models were able to capture *fairly well* (*sic.*) the mean, daily maxima and variability of ozone concentrations, as well as the time and intercity variability. However, there was a significant overestimation of ozone concentrations and hence metrics in city centres, especially for the large-scale models.

226. The City-Delta study used the SOMO35 metric to assess the impact of ozone on human health. It was ultimately intended that the City-Delta study would assist the development of a methodology for treating urban ozone in the integrated assessment modelling of IIASA (Amann *et al*., 2006). The IIASA integrated assessment model uses source-receptor relationships derived from the EMEP Eulerian model at a 50km x 50km resolution to relate regional-scale changes in ozone to reductions in NO_x and VOC emissions. Although it was recognised that urban ozone levels would be lower through the NO_x-titration effect, the magnitude of this effect could not be quantified systematically for cities in different parts in Europe (see Figure 5.8) (Amann *et al*., 2006). The influence of the determining factors (such as meteorological conditions, emission densities, NO_x/VOC ratios, etc.) have not yet been determined in a Europe-wide context. The implications of these issues for integrated assessment modelling and UK ozone are discussed further in Chapter 6.

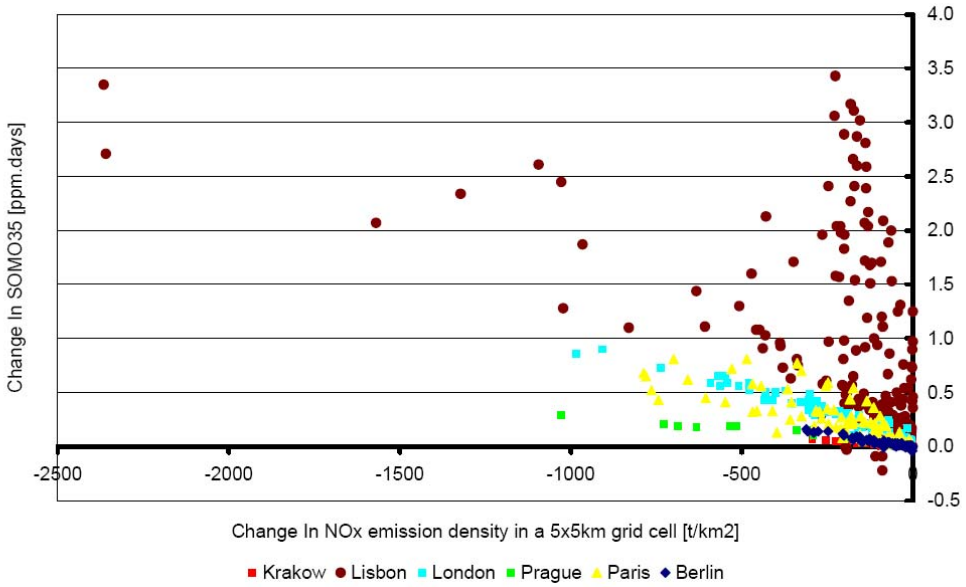

Figure 5.8 Change in the SOMO35 indicator in response to reductions of urban NO_x emissions as computed by the CAMx model for six European cities participating in the City-Delta project (taken from Amman *et al.*, 2006).

5.6 Urban ozone and climate change

227. AQEG has considered the impact of climate change on air quality in a previous report (AQEG, 2007). The response to Question 3 addressed the impact of climate change on UK ozone concentrations. In an earlier section, the influence of changing atmospheric composition arising from climate change was considered and shown to be a significant driver on UK ozone. Here, we consider other influences arising from climate change. Given that urban ozone in the UK can be represented in terms of a regional component and an urban decrement, any changes to the regional component arising from changes in temperature, humidity, etc will produce accompanying changes in ozone in the urban centre.

228. As indicated in the AQEG report on Air Quality and Climate Change: A UK Perspective (AQEG, 2007), there is likely to be an increasing frequency of summertime photochemical pollution episodes and the summer of 2003 in Europe was expected to become 'typical' by the 2040s in terms of temperature. Even under these conditions, it is unlikely that the intense urban ozone production, typical of Los Angeles, would occur in the UK. As indicated in Chapter 2, there was no evidence for local photochemical production of ozone in London in 2003.

Chapter 6

Uncertainties in ozone models

Question 5: *Ozone is currently modelled on a number of spatial and temporal scales. What are the main uncertainties associated with such work, and what research is required to reduce these uncertainties?*

Short answer to question 5

229. **Although a number of models address ozone on a range of temporal and spatial scales across the UK, there is no consistent and comprehensive understanding of model performance and the uncertainties that affect them. Research is required to understand and intercompare the influence of different spatial and temporal resolutions, chemical mechanisms and parameterisations upon predicted concentrations and their policy implications. This process would involve harmonising model performance evaluation and collecting information on uncertainties of the various model formulations. Research is also required to evaluate the relative importance of man-made and natural biogenic sources of ozone-precursors.**

Supporting evidence for question 5

230. A number of model studies have been performed and applied with the aim of understanding ozone formation in Europe and in the United Kingdom. A survey of some of the principal models used in these studies has been compiled and is available in the supporting evidence to this question. Some of these models have been used to support Defra in its policy development and air quality strategy formulation, in particular the PCM, OSRM and UK PTM models. The EMEP model is the main tool for policy formulation within Europe through the aegis of the UN ECE and the Commission of the European Communities. The complexity and spatial scale of processes leading to ozone production means that it is difficult to evaluate the accuracy of ozone calculations, although decisions on how to reduce ozone concentrations have relied on the interpretation and forecasting of ozone models. The use of models is an accepted way of including understanding of the underlying science in environmental decision making, however the complexity and spatial scale of processes leading to ozone production means that it is difficult to evaluate the accuracy of ozone models even though decisions on how to reduce ozone concentrations have relied on the interpretation and forecasting of such models.

231. Ozone models have a long history of helping to explain observations such as the long-range transboundary transport of ozone, the diurnal cycle in ozone concentrations and in predicting outcomes where observations have a limited usefulness or availability. They have demonstrated that each different organic compound exhibits a different propensity to form ozone. They have shown how the observed downwards trends in urban concentrations of organic compounds and NO_x due to vehicle emission controls can account for the observed downwards trends in episodic peak ozone levels. They have also been used to great effect in the underpinning of the integrated assessment models used to formulate air quality policies at the EU and UN ECE levels.

232. Defra employs ozone models to predict the outcomes of particular control measures in support of its air quality strategy and policy development. It also uses modelling to supplement observations in its reporting under the EU Daughter Directives. This activity is an alternative to obtaining a comprehensive set of observations for the UK which would

not be feasible because of resource constraints. Ozone models are thus critical tools that help inform and set priorities within Defra. As a result, it is essential that these tools are fit for purpose, that the results are robust and produced in a timely manner and that Defra's applications are consistent with the model's intended purpose and formulation.

233. The models detailed in the supporting evidence cover a wide range in complexity from the simple empirical and interpolation-based mapping models to highly sophisticated Eulerian grid-based 3-D airshed models. Models are always incomplete and efforts to make them more complex can be problematic. Increasing the complexity of a model by adding new features and capabilities may introduce more model parameters whose values are uncertain. More complex models may contain more parameters than can be estimated or calibrated with the available observations. Scientific advances will never make it possible to build a perfect ozone model. Models are necessarily simplifications and approximations of the real world and are inherently uncertain (National Academy of Sciences, 2007, Oreskes *et al.*,1994). The NAS report recognises the limitations of models but still recommends their use in environmental decision making. It recognises the difference between research and regulatory applications of models. It contains general warnings and guidance on how this should be done, especially that evaluation should continue throughout the life of a model. In particular the report cites the history of ozone control policies to draw lessons about models use. The policy response to ozone issues in North America has been subject to step changes as the science and modelling has developed and this is something to be avoided. A more complete evaluation of uncertainties in modelling should have been undertaken before policy was initiated.

234. The ozone models reviewed in the supporting evidence, in common with all environmental models, contain a large number of simplifications in their formulation which for the purposes of this discussion may be grouped into four categories as follows:
    - Simplifications to the modelling system arising from theoretical aspects of the system that are not fully understood or from model parameterisations,
    - Boundary conditions and model input,
    - Empirical aspects of the system that are difficult or impossible to measure,
    - Temporal and spatial averaging within the modelling system.

235. The first area of model uncertainty concerns the theoretical aspects of ozone modelling that are not fully understood or processes which are simplified by model parameterisations. This includes both dynamical processes, for example the mixing of stratospheric ozone into the troposphere or mixing of free tropospheric air into the atmospheric boundary layer and chemical processes, for example, simplified models of natural biogenic emissions of isoprene and other VOCs, and hence uncertainty in their contribution to ozone formation in the United Kingdom. Increased theoretical understanding also impacts on the best choice of model for a particular application. Broadly speaking, two major regimes of ozone formation have been identified: intense VOC-limited ozone formation in urban plumes and steady NO_x-limited ozone formation on the regional and trans-boundary scales. Whilst the extremes of these regimes have been well studied in field studies carried out elsewhere in Europe, for example in Milan and Berlin and in Los Angeles and Texas in North America, it is not at all clear in which regime the ozone observed in a given episode in the UK has been formed. This lack of understanding precludes a definitive choice between the different model approaches, say Eulerian grid versus Lagrangian trajectory approaches, for example. Eulerian models are well suited to describing the competition between vertical mixing and rapid chemistry that drives urban scale ozone formation. In contrast, trajectory models, because they can handle more complex chemical mechanisms, are more suited to the description of ozone formation on the regional scale under low-NO_x conditions.

236. The second area of model uncertainty arises because of the uncertainties inherent in the large amount of input data that is used to set up and drive ozone models. This includes

the boundary conditions for both the meteorological models and transport and chemical transformation models (if both models are utilised), model initialisation and data assimilation (if utilised). Both the data themselves, which may come from measurements or other larger area model outputs, and the implementation of these data in the ozone model have a degree of uncertainty associated with them. Further uncertainty may arise because the process descriptions in the models are themselves simplifications of real-world behaviour. The photolysis rate coefficients are a good example of this. These coefficients control the rate of photochemical ozone formation and should depend on cloud cover and take photochemical haze formation into account. Rarely are the large amounts of solar radiation data required for this purpose available, and clear-sky conditions are commonly assumed.

237. The third area of model uncertainty concerns those empirical aspects of ozone formation that are difficult or impossible to measure or observe and then to represent in ozone models. Many of these empirical uncertainties involve the measurement of the atmospheric concentrations of the many reactive free radical species, the emitted VOCs and their secondary organic reaction products that together control ozone formation over Europe. Even if all these measurements were available, it is not clear that the different ozone models would necessarily have the capacity to handle the detailed chemical mechanisms that would be needed to calculate the resulting ozone formation. This a particularly pressing issue for Eulerian-grid models because they necessarily require highly compact and concise chemical mechanisms because of the limited computer resources available.

238. The fourth area of model uncertainty arises from the temporal and spatial averaging which is a feature of all models to a greater or lesser extent. The greater the temporal averaging in a model the less it is able to take account of aspects of the system and processes which vary with time, because the processes and the parameters that drive them are implicitly assumed to be constant over the averaging time considered, when in reality they may be highly variable or sporadic. Scavenging by precipitation, resuspension and fires are classic examples of sporadic processes. Man-made emissions are most accurately quantified as annual and national totals. These totals have then to be broken down to an hourly basis and gridded at a spatial scale of 1km x 1km or down to individual road-links, across the country. In the real world, however, emissions from a single 1km x 1km grid square or a single road link are highly variable and unpredictable and this variability may introduce significant uncertainties in ozone model predictions and their evaluation against observations. Spatial averaging both in model input (e.g. emissions) and model formulation introduces further uncertainty since at scales similar to or smaller than the relevant input or model grid resolution the model will not be able to predict spatial variations in concentrations. This is particularly relevant to urban areas where there are sharper gradients in ozone concentrations, and requires due consideration when model calculations are compared with monitored data measured at a point.

239. Whilst it is relatively straightforward to characterise the main sources of uncertainty in ozone models in general terms, it is another matter to quantify their importance in a particular ozone modelling system, let alone in a particular model application. The effects of some sources of model uncertainty, such as those in the initial and boundary conditions, may reduce as the model calculation progresses, but the effects of others, such as those in meteorology or emissions, may grow. Some sources of uncertainty are crucial to the accuracy of an individual case but drop out when looking at the relative responses to emission controls and other policy measures. Such sources of uncertainty include photolysis rates and natural biogenic emissions. Uncertainties are best reduced by continual improvements to process descriptions, participation in model intercomparisons, development of real-time forecasting capabilities and continued comparisons against observations.

240. Comparisons against observations give an invaluable guide to overall model performance. Understandably, policy-makers expect modellers to establish the trustworthiness of their models. For ozone models, this almost always involves some form of comparison of model predictions against measured ozone concentrations. However, the ability of an ozone model to reproduce measured ozone concentrations from the past does not guarantee its adequacy for the future or for predicting the response to ozone control strategies. Agreement with observations is inherently partial. Models agree with some observations but not all. A model can certainly perform well against observations and the precision and accuracy of the fit can be quantified. The performance of models can be evaluated relative to observations, relative to other models or against our own theoretical expectations, but the performance of a model, especially for future projections of concentrations, cannot be ascertained precisely. Nevertheless, comparison against observations is a good first step in the evaluation of model performance.

241. The term *validation* is widely used to describe evaluation of model performance against measured data. Oreskes *et al.* (1994) argue that validation and verification of models of natural environmental systems are not possible. This is because there are always input parameters that are poorly known, fine scale details of crucial importance which are inadequately understood, and assumptions and inferences which may not be valid under all circumstances. Such views apply to the *complete validation* of models, applicable to all possible circumstances and scenarios. In practice, the term *validation* is frequently used in a more restricted sense to describe the evaluation of model predictions against measured data, which might more appropriately be described as *partial*, or *conditional validation*, as it applies only to a limited range of input variables, and hence outputs. The distinction between *complete* and *partial* model validation is an important one, as a model giving excellent predictions from within a limited range of input variables may perform poorly when used beyond that range of inputs. Such limitations need to be clearly recognised, and the term model *evaluation* is to be preferred to *validation*, as it more accurately describes the process undertaken.

242. Assuming that the model code faithfully represents the model specification there are three general questions to be answered when evaluating environmental or mathematical models, which following Beck (2002) and Britter and Schatzmann (2007) can broadly be expressed as follows:
    - Is the scientific formulation of the model broadly accepted and does it use state-of-the-art process descriptions?
    - Does the model replicate observations adequately?
    - Does the model reflect the needs and responsibilities of the model user and is it suitable for answering policy questions and fulfilling its designated tasks?

243. These questions apply well to ozone models and should lie at the heart of a review and evaluation of such models.

244. When relying on models to draw conclusions, AQEG generally support an approach which uses a range of available ozone models, including simple and advanced ones, in combination with measurements. The ozone model should be used to determine the relative response of ozone to estimated future emissions from a baseline determined from recent measurements. This assumes that current emissions and emission projections are reliable.(U.S. Environmental Protection Agency, 2007)

245. The survey of the principal ozone models given in the supporting evidence starts to gather some of this basic information together. Defra is carrying out a review of these models to assist their overall assessment (Monks *et al.*, 2007). It is recommended that this work is extended by:

- Exchanging the experiences gained with different chemical mechanisms and model parameterisations,
- Investigating further central policy issues such as the relative importance of man-made and natural biogenic sources of VOCs,
- assembling information on uncertainties and,
- setting out a protocol for a model intercomparison activity.

Table 6-1 Ozone models

Model	Type and Resolution	Chemistry	Treatment of VOCs	Meteorology	Policy Relevance
OSRM AEA Technology& Environment	Lagrangian trajectory with surface post processing. Emissions: NAEI 10km x 10km, EMEP 50km x 50km emissions	STOCHEM 70 species, 180 reactions	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, MEK, acetone, HCHO, CH_3CHO)	UK Met Office NAME archive	UK policy applications Current DEFRA ozone tool Used for scenarios in the DEFRA Air Quality Strategy.
MODELS-3/CMAQ Imperial College London	Eulerian grid Fully nested: 4km x 4km, 12km x 12km, 48km x 48km Emissions: NAEI 10km x 10km, EMEP 50km x 50km emissions	CB4* 36 species, 93 reactions	7 man-made VOCs +isoprene ETH, PAR, OLE, TOL, XYL, FORM, ALD2	UK Met Office BADC archive	Most heavily used research and policy model in USA.
MODELS-3/CMAQ University of Manchester, Edinburgh, Hertfordshire. Eon	Eulerian grid Fully nested: 5km x 5km, 45km x 45km Emissions: NAEI 10km x 10km, EMEP 50km x 50km emissions	CB4* 36 species, 93 reactions RADM2* 57 species,158 reactions SAPRC-99* 72 species, 214 reactions	7 man-made VOCs +isoprene ETH, PAR, OLE, TOL, XYL, FORM, ALD2	MM5 – 5th generation 3-D meteorological fields	Most heavily used research and policy model in USA.
CHIMERE INERIS, Paris	Eulerian grid 0.5^o x 0.5^o 50km x 50km emissions	MELCHIOR 80 species, 300 reactions	12 man-made VOCs +isoprene	Meteo France	ozone and PM forecast model for Europe
EMEP MSC-W	Eulerian grid 50km x 50km, 4km x 4km Emissions: EMEP 50km x 50km	EMEP 80 species, 140 reactions	9 man-made VOCs +isoprene (C_2H_6,nC_4H_{10},C_2H_4, C_3H_6,C_8H_{10},HCHO, MEK,CH_3OH, C_2H_5OH)	HIRLAM-PS	Policy formulation for UN ECE LRTAP Input to RAINS CAFE and NEC policy analyses

UK PTM rdscientific, Imperial College London, University of: Leeds, Birmingham.	Lagrangian trajectory Emissions: NAEI 10km x 10km, EMEP 50km x 50km emissions	Master Chemical Mechanism* 4,414 species, 12,871 reactions CB4* 36 species, 93 reactions	175 man-made VOCs from NAEI + isoprene, α-pinene, β-pinene	UK Met Office NAME archive HYSPLIT/NCEP BADC/UK MO	UK policy applications for O_3 and PM modelling
HARM/ELMO University of Nottingham, Lancaster	Lagrangian trajectory Emissions: NAEI 10km x 10km, EMEP 50km x 50km emissions	STOCHEM + secondary organic aerosol formation	12 man-made VOCs + isoprene, terpenes (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)	HYSPLIT/NCEP	DEFRA mapping for SOA EU & UNECE assessments
NAME Met Office	Lagrangian dispersion Source- or receptor-oriented Emissions: NAEI 10km x 10km, EMEP 50km x 50km emissions	STOCHEM + reactive VOCs	13 man-made VOCs + isoprene (C_2H_6,C_3H_8,nC_4H_{10}, C_2H_4,C_3H_6,C_4H_6, C_7H_8,C_8H_{10},CH_3OH, acetone, MEK, HCHO, CH_3CHO)	UK MO NAME archive 1995-2007 ECMWF 1957-onwards	Basic model (without ozone) used as DEFRA air quality forecast model. Emergency response (without chemistry)
POLLUTION CLIMATE MODEL AEA Technology&Environment	Empirical and interpolation based mapping models	Parameterised treatment of oxidant partitioning	No VOC chemistry	n/a	Reporting for ozone Daughter Directives Interpretation of observations
ADMS-Urban CERC	Gaussian type nested in trajectory model. Variable resolution down to 10m.	GRS* 6 reactions Or CB4* 95 reactions and 36 species	GRS – 1 surrogate VOC CB4 7 man-made VOCs +isoprene	Standard met data from one measurement site or mesoscale model	Policy including for UK. Air quality forecasting for AirTEXT (London) - nested within Prevair.

Notes:
a. * denotes that this chemical mechanism has been compared against smog chamber data.
b. Table 6-1 does not summarise all features of each model and is not intended to be authoritative.

Chapter 7

Impact of European emissions reductions on ozone in the UK

Question 6: *Integrated assessment modelling to support the European Commission's Thematic Strategy for Air Quality suggests that regional ozone levels in the UK are likely to remain relatively steady regardless of foreseeable emission reductions across Europe. Does the Group agree with this analysis and what is the explanation for this lack of response to reductions in precursor emissions?*

Short answer to question 6

246. **The Air Quality Expert Group agrees that under the specific emission scenarios considered for the European Commission's Thematic Strategy, regional ozone levels in the UK (based on the SOMO35 metric) would be likely to remain steady in the foreseeable future. However, the Group disagrees that this indicates a lack of response of regional ozone levels in the UK to precursor emissions in European countries and the surrounding sea, especially for episodes of higher concentration.**

Detailed answer to question 6

247. In order to understand why regional ozone levels in the UK were predicted to remain relatively steady within the integrated modelling carried out for the European Commission's Clean Air for Europe (CAFE) Thematic Strategy, it is firstly necessary to understand how potential future precursor emission reductions were handled. Some potential future precursor emission reductions were taken on board and incorporated into the 'CAFE baseline' emissions scenario. The remaining potential emission controls were made available to the optimisation routines within the integrated assessment model, to be taken up when and if required to achieve the identified targets. Owing to the manner in which the different contributions to environmental damage were weighted by the choice of gap closure targets[1], optimisations that reduced acid rain and eutrophication, together with PM levels, were generally favoured, rather than optimisations that reduced ground-level ozone formation.

248. The potential emission controls that came out strongly in the CAFE analysis turned out to be measures that focussed primarily on the emissions of NO_X and of particulate matter (PM). NO_x reductions would be expected to offset the effects of wider emissions controls because they lead to locally higher urban ozone levels. Reductions in PM emissions offer cost-effective reductions in days of lost life expectancy across Europe. They also offer side benefits of small reductions in NO_x emissions.

249. The next issue to understand is the impact of the additional CAFE measures on *regional* ozone, through the selection of SOMO35 as the index of the human health effects and AOT40 for crops and vegetation damage. Both SOMO35 and AOT40 are strongly influenced by changes in northern hemisphere ozone background concentrations and so the influence of changes in regional ozone formation are heavily damped. This damping is greatest for countries on the Atlantic Ocean seaboard of Europe, such as the United Kingdom, Ireland, Norway and Portugal and smallest for the countries in central Europe,

[1] Intended to close the gap between the projected current legislation (CLE) scenario and the scenario corresponding to the maximum technical feasible reduction (MTFR) by 60%; that is to achieve 60% of the maximum possible improvement implied by the MTFR scenario.

such as Germany, where the influence of the northern hemisphere ozone baseline is least and the contribution from regional ozone formation greatest. In urban areas, any reductions in the NO_x emissions from road traffic would lead to higher SOMO35 levels, counteracting any benefits from reduced regional-scale ozone formation. As has been observed elsewhere in this report, ozone levels appear to behave differently, depending on the metric used.

250. The integrated assessment modelling carried out for the CAFE strategy reveals little about the response of regional ozone to foreseeable NMVOC emission reductions, because many of the projected control measures such as the EU Directives addressing solvent emissions and petrol vapour recovery, for example, were already implemented in the CAFE baseline. Furthermore, the NMVOC control measures available to the optimisation routines were relatively costly and had few side benefits for primary PM emissions and hence would not be seen as attractive in any optimisation that was, understandably, weighted towards reducing urban PM health effects rather than regional ozone. EMEP simulations show that NMVOC reductions show greater reductions in SOMO35 throughout EUROPE, and including the UK, than do equivalent percentage reductions in NO_x. However, the reductions in NMVOCs included in the RAINS analysis were signifcantly smaller than those in NO_x

251. This combination of reasons explains why regional ozone levels over the United Kingdom have appeared to remain relatively steady in the European Commission's CAFE strategy regardless of the implementation of a number of additional measures in the foreseeable future. The results are related to the sensitivity of the UK to the Northern Hemisphere background, coupled with the increases in ozone that are projected in urban regions on reducing NO_x. European emissions have the greatest effect in the UK on high episodic concentrations of ozone experienced under anticyclonic conditions. As a result of this combination of circumstances, measures which lead to significant reductions in ozone in central Europe, are less effective in the UK, when assessed against a low threshold metric such as SOMO35. A key issue in the CAFE assessment is that in a combined strategy designed to address several pollutants, the measures which win out are those that reduce PM simply because of the greater health effects/benefits. Measures purely directed at ozone are less attractive in cost-benefit terms. Strategies for reducing ozone in the UK are addressed in Chapter 8, but a full cost-benefit analysis has not been performed.

Supporting evidence for question 6

7.1 Overview

252. Chapter 7 addresses the results of the integrated assessment modelling carried out to support the European Commission's Thematic Strategy for Air Quality, CAFE (Commission of the European Communities, 2005). This modelling work was undertaken using the RAINS integrated assessment model based at IIASA in Austria, which in turn used source-receptor relationships from the Unified EMEP model, operated at the Meteorological Synthesising Centre-West (MSC-W) in Norway. The supporting evidence assembled here deals with the salient features of the Unified EMEP model. An overview is then provided of the RAINS model together with the CAFE strategy analyses. Some remarks are then made about the various policy relevant ozone metrics. Finally, the supporting evidence contains some comments on the relative effects of NMVOC vs. NO_x controls on ozone formation.

7.2 Salient features of the Unified EMEP model

253. The European-scale integrated assessment modelling carried out to support the United Nations Economic Commission for Europe UN ECE international Convention on Long-range Transport of Air Pollution CLRTAP has always been based on an understanding of the transboundary fluxes and origins of the pollutants in question. At the time of the formulation of the multi-pollutant multi-effect Gothenburg Protocol, these transboundary fluxes were quantified using the EMEP Lagrangian model (Simpson 1993, 1995). In the intervening period since the Gothenburg Protocol, EMEP has developed the Unified Eulerian model (Simpson *et al.,* 2003). This new model has the same basic representations of the emissions, chemistry and deposition processes as the original Lagrangian model but differs in that they are assembled into a three-dimensional modelling framework on a 50 km x 50 km grid (see also Chapter 6). The performance of the EMEP Unified model has been reviewed by national experts as part of the EMEP Task Force on Measurement and Modelling (TFMM) at a workshop in Oslo during 2004 (UN ECE, 2004). It was this version of the EMEP model that would be ultimately employed in the determination of the source-receptor relationships for the integrated assessment modelling to be carried out within the CAFE Thematic Strategy. Model performance against observations for acidifying substances and ground-level ozone appeared adequate for policy purposes on the regional scale. Preliminary evaluation of the source-receptor relationships determined with the EMEP Unified model against those determined with other European models also appeared satisfactory. However, problems were found in the modelling of some PM components. Further work was recommended to improve model performance for these PM components and to address urban ozone and PM.

254. During the CAFE process, further changes to the Unified Eulerian model were made by EMEP. They initially used two main metrics for ozone, AOT40 and AOT60. The former was used to assess ozone impacts on crops and vegetation whereas the latter was used for human health impacts. Later, following advice from WHO, it was decided that SOMO35 provided a better metric for the assessment of human health effects, and so EMEP and hence IIASA (for the integrated assessment model) switched to the SOMO35. A description of ozone metrics is given in the introduction to this report and is also discussed in section 7.4 below.

255. Until 2005, EMEP maintained a constant background tropospheric ozone concentration in its modelling and did not account for rising trends in hemispheric ozone. However, in 2006, EMEP introduced new assumptions concerning ozone background concentrations, including an increase of 6 µg m^{-3} in the annual mean over the mean 1990 level when calculating 2010 ozone concentrations, and an increase of 9 µg m^{-3} in the annual mean for year 2020 simulations. A comparison of maps of SOMO35 produced by the EMEP model with and without this increase illustrates how the higher hemispheric background leads to higher values of SOMO35 across the whole of the UK, indicating the sensitivity to changes in the global background (EMEP, 2006).

256. With this trend in northern hemispheric background included, modelled trends in SOMO35 averaged over the UK show a slight reduction between 1990 and 2000 with a subsequent increase to slightly higher levels between 2000 and 2010. This apparent slight increase can be explained by the influence of the increasing northern hemispheric background acting to offset the reductions in ozone caused by regional-scale pollution controls. This can be contrasted with the situation in Germany where average SOMO35 levels are much higher, but show a more marked decrease between 1990 and 2010. Since the relative contribution from hemispheric background ozone is much smaller in central Europe, the hemispheric background increase is not enough to offset the decrease due to regional pollution controls.

257. The RAINS analysis for the UK is sensitive to the assumed increase in background ozone. Chapter 3 shows that, while concentrations of baseline ozone, as measured at Mace Head, have increased significantly since 1987, the concentration has been steady since 2000, so that the increases anticipated in the EMEP analysis, and their effect on UK ozone, may not be realistic.

7.3 IIASA RAINS integrated assessment model

258. Integrated assessment modelling, in particular the RAINS model of IIASA, has played an influential role in both the UN ECE and development of the Gothenburg Protocol (1999), and the Clean Air for Europe (CAFE) programme of the European Union. The RAINS model (Amann *et al.*, 2004) is based on the atmospheric modelling of EMEP to simulate pollutant concentrations and deposition across Europe on a grid of spatial resolution 50 km x 50 km, together with the response of these concentrations and depositions to the scaling of national emissions from each country to represent the effect of emission reductions. The RAINS model links these data to emission projections and uses a database on potential emission reductions and their costs in each country to deduce the least cost solution to achieving targets set for improved environmental protection across Europe. Such optimisation procedures were used to derive proposed emission ceilings for NO_x, VOCs, SO_2, NH_3 and primary $PM_{2.5}$ in a series of scenarios for the CAFE programme in 2005 towards drafting of the EC's Thematic Strategy for Air Quality.

259. At the inception of the CAFE Strategy analyses, the RAINS model was subject to peer review and the documentation prepared for that review fully details the methodologies and input data employed (Amann *et al.*, 2005a). Subsequently, as with the Unified EMEP model, further changes have been made to the RAINS model and these have had a major impact on the results of the scenario analyses (Amann *et al.*, 2005b,c,d).

260. Paralleling EMEP, there has been a switch from AOT60 to SOMO35 in characterising human health impacts (see section 7.4, below). IIASA used a linear relationship between SOMO35 in each grid square and changes in NO_x and VOC emissions in each country based on the blame matrices[2] calculated using the EMEP Unified model (Tarrason *et al*., 2006). IIASA justified this linear relationship by assuming that in 2020 NO_x emission reductions will be sufficient to get over the non-linear 'hump' situation whereby reductions in NO_x can lead to enhanced ozone. As discussed in this report, and especially in the response to Chapter 5, these may not be good assumptions for parts of the UK, and also the Netherlands and Belgium. Nevertheless, with these assumptions, the change in SOMO35 in any EMEP grid square is represented as a weighted sum of emission changes in NO_x and VOCs in each country in the RAINS model.

261. Recognising that ozone levels are lower within urban areas, IIASA distinguish between urban and rural populations in deriving a population weighted average. However in a regional model, it was not possible to model realistically these sub-grid scale phenomena in the SOMO35 values derived by EMEP, and no simple relationship was suggested by urban scale modelling in the City-Delta project (Amann *et al.,* 2006). Because of the resolution used (50 km x 50 km) in the RAINS model, any implied reduction in SOMO35 in an urban grid-square is set to zero for the population in that square. Conversely for rural populations any implied increase in SOMO35 due to reduction of NO_x emissions is also set to zero. Hence in the RAINS model this reduces any response of SOMO35 to emission changes, and does not truly reflect the urban ozone decrement (see Chapter 5 section 5.5), or allow for situations where NO_x concentrations may still be high in other areas of Europe.

262. The CAFE Thematic Strategy aimed to close the gap between the projected current legislation (CLE) scenario and the scenario corresponding to the maximum technical feasible reduction (MTFR) by 60%; that is to achieve 60% of the maximum possible improvement implied by the MTFR scenario. However, whereas the RAINS optimised

[2] EMEP's "blame matrices" assign the proportion of emissions by country of origin that give rise to the concentrations of a given pollutant seen in each individual country, i.e. the origin of the pollution in each country in the model domain.

scenario for the CAFE Scenario Analysis Report implied a 22% reduction in SOMO35 for the EU-25 by 2020 relative to the year 2000, for the UK it indicated a 17% increase. The UK was the only country to show such an increase, albeit from a lower start point than many other areas of Europe. One effect of this increase is an projected increase in the premature deaths in the UK attributable to ozone exposure between 2000 and 2020 (Amann *et al.*, 2005c). The reduction in SOMO35 in the UK from the additional effort beyond the CLE for the Thematic Strategy (involving emissions reductions from 817 (CLE) to 646 kT of NO_x, and from 878 (CLE) to 766 kT of VOCs, for the UK) is modest (~3%) compared with the average improvement in the EU-25(~7.3%). Ireland also remains very much the same.

Table 7-1 Estimates of premature deaths attributable to the exposure to ozone (cases per year). These calculations are based on regional scale ozone calculations (50km x 50 km) and for the meteorological conditions of 1997. A cut-off value of 35 ppb has been applied

	2000	2020	
		Baseline Current Legislation	The Thematic Strategy scenario
Austria	422	316	287
Belgium	381	345	337
Cyprus	33	32	31
Czech Rep.	535	390	348
Denmark	179	161	153
Estonia	21	22	21
Finland	58	60	56
France	2663	2171	1973
Germany	4258	3316	3057
Greece	627	568	542
Hungary	748	573	511
Ireland	74	79	76
Italy	4507	3556	3328
Latvia	65	65	61
Lithuania	66	64	60
Luxembourg	31	26	24
Malta	22	20	19
Netherlands	416	369	356
Poland	1399	1112	1005
Portugal	450	437	412
Slovakia	239	177	157
Slovenia	112	82	75
Spain	2002	1687	1518
Sweden	197	189	178
UK	1423	1705	1665
EU-25	**20927**	**17522**	**16246**

7.4 Ozone metrics

263. In response to advice from the World Health Organization and the UN ECE Task Force on Health (TFH, 2008), changes were made to the ozone metrics employed in the integrated assessment modelling for the assessment of human health effects within the CAFE programme. This advice recommended moving away from formulations based on the AOT concept and moving towards daily metrics such as the annual mean of the maximum 8-hour mean ozone concentrations. On this basis, the integrated assessment models have replaced AOT60 with SOMO35, a metric that includes a specific 70 µg m^{-3} threshold (see also Chapter 1 for an explanation of ozone metrics).

264. Observations of the behaviour of SOMO35 show a definite inter-annual variability at UK monitoring sites. Thus in general higher levels are indicated in more photochemically-active years such as 2006 compared with 2005, suggesting that SOMO35 is responsive to meteorology and regional scale ozone formation, and is consequently sensitive to the occurrence of more severe episodes such as those occurring in 2003 and 2006. (See Chapter 2).

265. Measurements at rural sites clearly indicate a mixture of contributions with the peak episodes of large exceedences superimposed on a large number of days with relatively modest exceedences of the 70 µg m^{-3} threshold, which even occur in winter. In urban areas there are clear indications of local scale removal of ozone, leading to near or complete elimination of many of the days of lesser exceedence and large reductions relative to the peak ozone level observed during episodes, consistent with the behaviour of the urban decrement.

7.5 VOC vs NO_x controls

266. Table 7-2 (EMEP 2006) indicates the response of SOMO35 in each country to 15% reductions in emissions of NO_X and VOC in each other country and source region. It includes shipping, and provides an insight into the differing effects of NO_X vs. VOC controls. The Table indicates that the response of SOMO35 to reducing UK emissions of NO_X is negative, indicating a suggested worsening of health effects. The extent of the negative change outweighs the benefits to the UK of NO_X emissions reductions in some other countries (such as France) with a net negative effect from the EU-25 as a whole. This is in contrast to central European countries such as Germany, where reductions in NO_X both in Germany and other EU-25 countries give a clear improvement. It is also evident that changes in shipping emissions of NO_X in the Atlantic and North Sea have an impact, with reductions in the Atlantic reducing UK ozone, because of reduced ozone production and reductions in the North Sea increasing ozone because of the reduced ozone titration. Note that while land-based emissions are being reduced shipping emissions are continue to increase steadily. In this context, the effect of increases in shipping NO_x emissions in the Atlantic are significant from an ozone exposure perspective.

267. Table 7-2 shows that reducing NMVOC emissions by 15% results in either no change or a positive change in SOMO35. As with NO_X, it is also evident that the effects of emissions reductions in the EU-25 has greater benefits in central European countries, such as Germany than it does for countries at the western edge of Europe such as the UK. The Table shows that, on an equivalent percentage reduction basis, NMVOC emissions reductions are more beneficial than NO_X emissions reductions. However it is important to note that the additional emission reductions in the CAFE Thematic Strategy scenario beyond the CLE scenario were relatively modest for NMVOCs compared with NO_x (equivalent to ~8% of 2010 emissions of VOCs from the EU-25 as opposed to 15% of NO_x emissions in 2010).

Table 7-2 Source-receptor tables indicating effects of 15% reductions in NOx or VOCs in different countries/sea areas on SOMO35 and on AOT40 taken from EMEP (2006). Positive values indicate improvements in ozone health effects, i.e. reductions in SOMO35.

Country in which emissions are reduced by 15%	Effect of cutting NO_x on SOMO35 in: UK	Germany	Effect of cutting VOCs on SOMO35 in: UK	Germany
UK	-36	3	49	22
Germany	1	47	5	48
France	6	28	7	74
EU-25	-20	111	74	128
Atlantic	19	11	0	0
North Sea	-7	3	0	0

	Effect of cutting NO_x on AOT40 in: UK	Germany	Effect of cutting VOCs on AOT40 in: UK	Germany
UK	-140	48	351	177
Germany	21	651	42	341
France	71	311	55	116
EU-25	29	1371	537	926
Atlantic	101	77	0	0
North Sea	-38	101	0	0

Notes:

a. SOMO35 data are provided in ppb.days from EMEP (2006).
b. AOT40 data are provided in ppb.hours from EMEP (2006).

268. For comparison, corresponding figures are given for the response of AOT40, showing the effect of a higher threshold and less sensitivity to the influence of the hemispheric background concentrations. For AOT40, although the effect of reducing UK NO_x emissions is still negative for the UK, the EMEP model results imply that equivalent reductions in other countries outweigh this; although they still have much more benefit for central European countries.

269. It is concluded that the EMEP model indicates a number of negative and positive responses of ozone levels in the UK to changes in NO_x emissions from the UK itself, from other countries, and from shipping; and that the global background also influences SOMO35. The net effect of projected changes depends on how much these different influences cancel out.

Chapter 8

Control options for reduction of exposure to ozone in the UK

Question 7: *What are likely to be the most effective control options to reduce UK population exposure to ozone (in terms of precursors to be targeted), and on what scale should they operate? The Group may include discussion of the types of controls they consider to be feasible, but do not need to consider the policy implications of such measures.*

Short answer to question 7

270. **The ozone-precursor compounds of relevance are methane, non-methane volatile organic compounds (NMVOC), oxides of nitrogen and carbon monoxide. While UK action can be beneficial, effective control of ozone concentrations in the UK requires emission reductions to be implemented throughout Europe and increasingly the entire northern hemisphere. Local actions, especially those of a short-term nature to address episodes of high ozone concentrations, have generally had or been simulated to have limited benefits.**

- **Control of NMVOC emissions will almost always lead to an improvement in ozone air quality and a reduction in population exposure. Additional benefits result from concerted international action and from focussing the emission control on those source sectors making the largest contributions.**
- **Methane mitigation is seen as a cost-effective strategy in international ozone management, bringing multiple benefits for air quality, public health, agriculture and the climate system.**
- **Less attention has been paid to global CO emissions but reduction of these emissions also has the potential to improve ozone air quality.**
- **The picture is more complicated for control of NO_x emissions; large emission reductions are generally needed in urban areas to overcome the initial ozone disbenefit. Control of the rising emissions of NO_x from shipping would also be beneficial to annual and summer-time mean ozone in western Europe.**

Detailed answer to question 7

271. Improvements in ozone air quality across Europe are expected as a result of the Gothenburg Protocol to the UN ECE Convention on Long-range Transboundary Air Pollution, the European Union's National Emission Ceilings (NEC) Directive and its draft Air Quality Directive, implementing the Clean Air for Europe (CAFE) Thematic Strategy. As Question 6 stated, the emission reductions proposed in the CAFE strategy do not however improve ozone air quality over the UK. The aim of this question is to identify additional measures, over and above those agreed in current baseline scenarios for 2010-2020, which would be effective in reducing UK population exposure to ozone.

272. A number of additional control measures were considered as part of the latest UK Air Quality Strategy (published in July 2007), although not all those originally identified were subsequently taken forward. It should be noted that only one of the original measures specifically addressed ozone. All the other measures were designed to reduce concentrations of oxides of nitrogen (and/or particulate matter) and as such would potentially have an adverse impact on ozone concentrations. This was mainly because of

a reduction in the NO_x titration effect, especially in urban areas (see Chapter 2 and Chapter 45).

273. The measure designed to reduce ozone exposure sought to control NMVOC emissions, largely through implementation of Stage II petrol vapour recovery and abatement of emissions from onshore/offshore oil tanker loading operations (the reductions were equivalent to ~9% reduction in UK annual NMVOC emissions). There was a reduction in ozone concentrations and hence metrics compared to the corresponding base case for all metrics considered but the improvements were very modest (<0.2%). Slightly larger improvements were seen if the same level of NMVOC emission reduction occurred across the board from all UK anthropogenic source sectors, a result of the spatial distribution of the NMVOC emissions and the reactivity of the NMVOC emitted from different source sectors.

274. The CAFE Thematic Strategy also considered a Maximum Feasible Reduction (MFR) scenario, suggesting scope for additional control of UK (and European) NMVOC and NO_x emissions. Using the same assumptions and input datasets as those undertaken for the Review of the Air Quality Strategy, a limited set of further model runs were carried out to investigate the effect of larger reductions in these emissions. The emission reductions used were not associated with specific measures but were selected simply to illustrate their effect on ozone concentrations. Reductions in NMVOC emissions in both the UK and the rest of Europe (from a 2020 base) led to a monotonic reduction in O_3 concentrations in rural and urban areas of the UK. Reductions in NO_x emissions in both the UK and the rest of Europe would generally reduce O_3 concentrations in rural areas of the UK, but would initially lead to increases in O_3 concentrations in urban areas. This trend would be reversed in urban areas for reductions in NO_x emissions in excess of ~30% (~60% in London) from the 2020 base. Although these reductions reverse the O_3 concentration increases, they would not necessarily be sufficient to bring the values of the O_3 metrics to levels below those modelled for 2003. The most effective way of doing this would be to reduce both NO_x and NMVOC emissions in the UK and the rest of Europe by at least 60%.

275. Reductions of NO_x and NMVOC emissions in Europe will not only reduce further high (peak) ozone levels over Europe but will also reduce Europe's contribution to hemispheric ozone. However, effective control of hemispheric ozone, and its contribution to background ozone, requires the reduction of the emissions of NO_x, NMVOC, CH_4 and CO throughout the entire northern hemisphere:

- Reductions in global emissions of methane, in particular, are effective at reducing levels of background ozone. There are the additional climate benefits since both ozone and methane are greenhouse gases. A 20% reduction in global methane concentrations is simulated to have the same impact on background surface ozone in Europe as a 20% reduction in both European NO_x and NMVOC emissions, although the latter has more immediate impact. Although global methane concentrations have levelled off in recent years, there is no clear explanation of this change and it may be transient. Projected trends in anthropogenically-influenced sources of methane show a continuing increase, driven by increasing population and industrialisation. Regardless of future trends, however, methane mitigation is a cost-effective strategy in international ozone management, bringing multiple benefits for air quality, public health, agriculture and the climate.
- Over northern Europe (including the UK), reduction of NO_x alone (i.e., without reduction in NMVOC) may lead to increased ozone, particularly in winter and/or in areas close to busy shipping waters. Various studies have highlighted the importance of NO_x emissions from shipping. The exact spatial pattern of shipping's impact on ozone depends on the particular "photochemical climate". Whilst reduction in shipping emissions of NO_x is simulated to yield net benefit overall on

surface ozone over Europe, in some localities (English Channel, southern North Sea and Baltic), NO_x emissions from shipping currently reduce local ozone by NO_x titration such that reducing these emissions may lead to an increase in ozone in these areas.

- Less attention has been paid to the assessment of CO emissions and to their potential to influence background ozone concentrations and radiative forcing. Models suggest that emissions of CO in the northern hemisphere are currently substantially underestimated. However, since CO has a lifetime of several months it is clear that, as for methane, the trajectory of future hemispheric CO emissions has the potential to influence hemispheric ozone air quality significantly.

276. Within the EU, transport is currently the dominant source of ozone-precursor emissions. Because of the marked reductions in NMVOC emissions from the transport sector by 2020, a different range of source categories was found to be responsible for summertime photochemical ozone formation; these were stationary sources in sectors associated with the chemical, oil and gas industries and the manufacturing industries that use solvents. Subsequent work also investigated the ozone benefits resulting from the replacement of highly reactive aromatic species by low reactivity species and concluded that a much more focussed approach on the most important solvent sub-sectors identified by their Photochemical Ozone Creation Potential would appear to be more effective than unselective reduction of NMVOC emissions.

277. As NMVOC emissions reduce from man-made sources, biogenic sources will become more significant. The extent of any changes in future O_3 concentrations will be increasingly influenced by such biogenic emissions. In addition, if the incidence of high temperature episodes increases, then the very strong temperature dependence of biogenic emissions may lead to increases over current levels (although other factors related to environmental change will also certainly affect future emissions, as discussed in greater detail in Chapter 4). Human influence in determining which tree species are planted could be significant as emissions vary considerably between species.

278. The modelling results described in the preceding paragraphs are generally based on reductions in annual emissions of ozone-precursor species. Article 7 of the 3rd Air Quality Daughter Directive on ozone addresses the issue of short-term action plans when hourly ozone concentrations exceed the alert threshold of 240 µg m^{-3}. There have been few exceedences of this threshold in the UK in recent years. A study of an episode that occurred in the UK in July 1999 concluded that it was difficult to identify any realistic and beneficial short-term actions in the UK. Although this conclusion was based on a single episode at a single site, it concurred with the outcome of experiments in Germany and France that concerted large-scale interventions were needed for decisive reductions of peak ozone concentrations. More recent calculations again show that NMVOC emission control reduces ozone concentrations throughout the year but control of NO_x emissions has a more complex effect with day-to-day differences.

Supporting evidence for question 7

8.1 Overview

279. Controls on NO_x and NMVOC emissions introduced throughout Europe since the late 1980s have been effective in reducing photochemical ozone production and peak ozone concentrations in both the UK and across Europe (see responses to Questions 1 and 4; NEPAP, 2005; Jonson *et al.*, 2006) but there are still widespread exceedences of ozone air quality objectives across Europe (e.g., EEA, 2007). Further improvements in ozone air quality across Europe are expected as a result of the Gothenburg Protocol to the UN ECE Convention on Long-range Transboundary Air Pollution, the European Union's National

Emission Ceilings (NEC) Directive and its draft Air Quality Directive, implementing the Clean Air for Europe (CAFE) Thematic Strategy. As Chapter 7 indicates, the emission reductions proposed in the CAFE strategy do not, however, improve ozone air quality over the UK. The aim of this question is to identify additional specific measures (where possible), over and above those agreed in current baseline scenarios for 2010-2020, which would be effective in reducing UK population exposure to ozone.

280. A reduction in the UK population exposure to ozone implies a focus on suburban and urban areas, although exposures are still higher in the surrounding rural areas. As indicated in Chapter 2 and Chapter 5, the reduction in NO_x emissions in urban areas has led to increased ozone concentrations and hence exposure[3]. The existence, or otherwise, of a threshold for effects on human health is critical as it will determine (a) the ozone metric to use for the assessment and (b) the extent to which the increases in urban areas drive the policy response. The ozone metrics with and without the cut-offs are likely to respond differently both spatially and to the level of emission reductions that may be required. The increasing background concentration arising from global changes clearly indicates that future policy action on ozone air quality is inextricably linked to that on climate change and greenhouse gas emissions.

281. The UK's particular geographic position on the north west, and generally upwind, coastal fringe of Europe is a further important consideration. It means that, with the exception of South East England, the UK's "chemical climatology" can frequently be somewhat different from that of central and southern Europe. This has a major influence in determining the level of the emission reductions needed and whether these need to be implemented at the national, European or global scales.

282. Ground-level ozone not only affects human health but also crops and other vegetation. These impacts will shift the focus away from urban areas. Further, different ozone metrics are used to assess the impact and the response of these metrics may again differ from those used to assess the impact on human health, both spatially and the level of emission reductions required to achieve ozone air quality standards and objectives.

283. In this supporting evidence, we start by considering additional specific measures (where possible), which would reduce ozone exposure over extended periods. The ozone modelling undertaken on the national scale and for London for the UK Air Quality Strategy published in 2007 is reviewed. There is scope for additional reductions of NO_x and NMVOC emissions beyond those considered in the Air Quality Strategy and model calculations are presented to show the effect of further UK and UK/European emission reductions of these species in 2020. Other modelling studies emphasise the significant changes expected in the contribution and hence importance of different NMVOC source sectors to ozone formation. With the increasing recognition of the influence of global and hemispheric changes in ozone on national and local concentrations, modelling studies investigating possible regional or hemispheric controls on ozone-precursor emissions (i.e. methane, oxides of nitrogen, carbon monoxide) are summarised. As NMVOC emissions from man-made sources are reduced, biogenic NMVOCs will become more significant and a section is included on this topic. The supporting information concludes with a consideration of exposure during ozone pollution episodes. Model results are presented that describe the sensitivity to reductions of NO_x or NMVOC emissions and the limited effectiveness of possible short-term actions to reduce ozone concentrations during such episodes.

[3] The reduction of NO_x emissions has been driven largely to reduce the impact of NO_2 on human health but this has had an adverse effect on ozone air quality (albeit from a generally low base). While urban ozone air quality would improve if NO_x emissions were allowed to increase, this is not seen as a desirable outcome. The integrated assessment modelling undertaken for the CAFE strategy specifically excluded this outcome.

284. The studies described in this supporting information present results of emission reduction calculations. It should be noted that many of the emission reductions used were not necessarily associated with specific measures but to indicate the response or sensitivity to a significant emission reduction. Additional information is given in Annex 5.

8.2 Ozone Exposure over Extended Periods

8.2.1 Ozone Policy Options at the National Scale

8.2.1.1 The UK Air Quality Strategy

285. As part of the Review of the UK Air Quality Strategy[4], modelling was undertaken to assess the impact on ground-level ozone for future base case scenarios (2010, 2015 and 2020) and a number of additional measures developed for the Review (Defra, 2006; Hayman *et al.*, 2006a, Williams *et al.*, 2006). It should be noted that only one of the original measures (Measure M) was specifically designed to address ozone through control of NMVOC emissions. Most of the other measures were designed to reduce concentrations of oxides of nitrogen (and/or particulate matter) and as such would potentially have an adverse impact of ozone (see Table 8-1 for a list of the measures and the emission reductions associated with the measures).

286. Hayman *et al.* (2006a) used the Ozone Source-receptor model (OSRM) to assess the impact on ozone at the national scale. UK emission projections for 2010, 2015 and 2020 were taken from the UK National Atmospheric Emission Inventory (NAEI) programme (see Table 8-1) and the non-UK emissions were based on the IIASA scenario – Current Legislation including Climate Change. Allowance was made for a change to atmospheric composition arising from climate change. Using the monthly trends provided by Derwent *et al*., 2006, this would cause a change in the initial daily ozone concentrations from 2003 values ranging from -1.7 to +3.2 µg m^{-3} by 2010 and from -3.1 to +5.9 µg m^{-3} by 2020. The calculations were undertaken to a 10 km x 10 km grid covering the UK and the model runs used meteorology for 2003, a photochemically-active year (although some runs were undertaken with 2000 or 2002 meteorology to assess the sensitivity to year-to-year variability in meteorology).

287. Seven ozone metrics were derived from the calculated hourly ozone concentration, of which four were related to impacts on human health. The results for these four metrics were presented as population-weighted means for the whole of the UK and for specific regions, as shown in Tables A5-1 - A5-4 of Annex 5. The full set of results for all the metrics calculated can be found in Hayman *et al.* (2006a). The population-weighted mean values were combined with risk functions in subsequent cost-benefit analyses to determine the population affected. The population exposure results were presented in the main consultation document for the Review of the Air Quality Strategy (Defra, 2006).

[4] The UK Government and the Devolved Administrations published the latest Air Quality Strategy for England, Scotland, Wales and Northern Ireland on 17th July 2007 (Defra, 2007). This followed a consultation on the Review of the Air Quality Strategy in 2006.

Table 8-1 Projected UK NO_x and NMVOC emissions for the base case and the measures in the Review of the UK Air Quality Strategy modelled using the OSRM for 2010, 2015 and 2020.

Measure(s)	Description	Total UK NO_x Emissions (kilo tonne per annum)		
		2010	2015	2020
Base	Base case projections	1118.5	992.1	869.1
A	Introduction of EURO V/VI (low reduction scenario)	1115.9	958.3	803.7
B	Introduction of EURO V/VI (high reduction scenario)	1109.6	914.1	727.8
B*	An earlier version of the Introduction of EURO V/VI (high reduction scenario)	1109.6	911.6	712.7
C	Early uptake of EURO V/VI	1107.8	946.5	799.4
E	Introduction of low emission vehicles	1117.0	986.6	857.9
J	Domestic combustion	1115.6	984.3	856.2
K & L	Control on power stations, iron and steel and oil refineries	924.1	796.0	785.0
L	Control on small combustion plant (20-50 MW) (= base case in 2010 as no NO_x emission reduction until 2013)	1118.5	976.4	852.9
M	Petrol vapour recovery from petrol stations and abatement of NMVOC emissions from on and offshore loading of crude oil (= base case emissions as only NMVOC emission reduction)	1118.5	992.1	869.1
O	A combination of Measures C and E	1106.4	941.8	790.1
P	A combination of Measures C and L	1107.8	930.8	783.2
Q	A combination of Measures C, E and L	1106.4	926.1	773.9
M & Q	A combination of Measures C, E, L (=Q) and M	1106.4	926.1	773.9
Measure(s)	**Description**	**Total UK NMVOC Emissions (kilo tonne per annum)**		
		2010	**2015**	**2020**
Base	Base Case projections	1026.2	1034.7	1061.3
M	Petrol vapour recovery from petrol stations and abatement of NMVOC emissions from on and offshore loading of crude oil	952.2	958.4	983.0
M & Q	Combination of selected NO_x and NMVOC control measures	952.2	958.4	983.0

Notes: The above NMVOC emission totals include a contribution from natural sources of 178 kilo tonne per annum. This sectoral source was not used in the OSRM modelling and the NMVOC emissions were generated using a biogenic emission potential inventory.

288. As shown in Tables A5-1 - A5-4 of Annex 5, there is a progressive increase in ozone concentrations for the base case runs and hence the values of all the ozone metrics (i.e. a decline in ozone air quality) from 2003 through to 2020. As most of the measures that were modelled were focussed on control of NO_x (and particulate matter) emissions, the model results generally showed further increases in ozone concentrations and increases in the population-weighted metrics and hence population exposure. This was mainly because of a reduction in the NO_x titration effect in urban areas (see Chapter 2 and Chapter 5).

289. The exception was Measure M, which addressed reduction of UK NMVOC emissions (equivalent to ~9% of all UK emissions), largely through implementation of Stage II petrol vapour recovery and abatement of emissions from onshore/offshore oil tanker loading

operations. There was a reduction in ozone concentrations (i.e. an improvement in ozone air quality) over the corresponding base case for all metrics considered but the improvements were very modest (<0.2% reduction in the value of the metric) and insufficient to offset the underlying increases in ozone concentrations from 2003 to 2020. This is illustrated in Figure 8.1 for the metric, the annual mean of the difference between the maximum daily running 8-hour average ozone concentration and a 70 μg m^{-3} (or 35 ppb) cut-off. As also shown in this figure, slightly larger improvements were however seen if the same level of emission reduction occurred from (i) all UK anthropogenic source sectors (0.5%-0.6% reductions in the value of the metrics) and (ii) all UK and European anthropogenic source sectors (1.3%-1.6% reductions). In part, this reflects differences in (a) the spatial pattern of the emissions and (b) the NMVOC speciation and hence reactivity profiles of the source sectors.

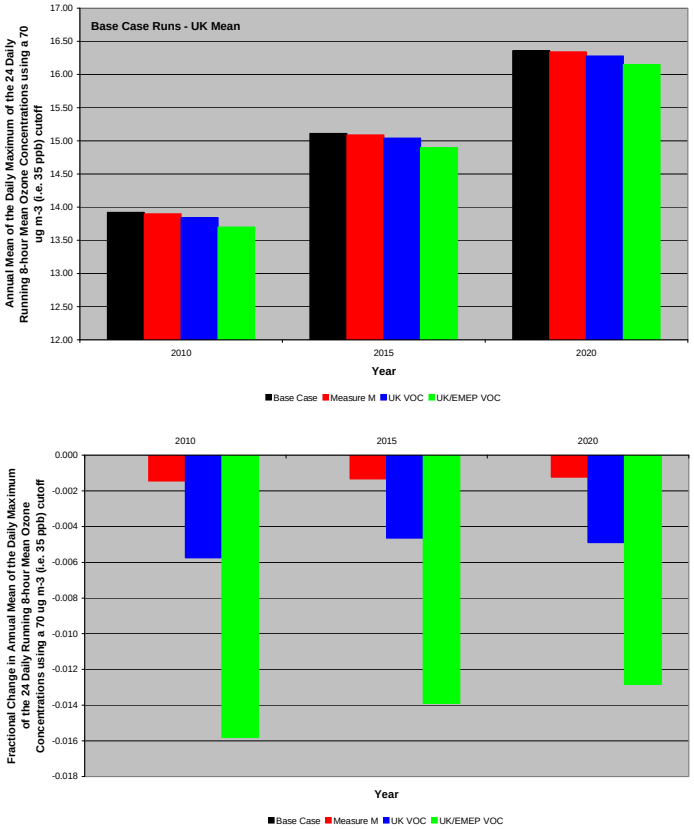

Figure 8.1 The response (upper panel) and fractional response (relative to base case =1, lower panels) of the metric - annual mean of the daily maximum of the 24 daily running 8-hour mean ozone concentrations using a 70 μg m^{-3} (i.e. 35 ppb) cut-off - calculated by the OSRM for the base case and for three NMVOC emission reduction scenarios (a) Measure M in the Review of the UK Air Quality Strategy, (b) equivalent 9% across-the-board reductions of UK NMVOC emissions and (c) 9% across-the-board reductions of UK and non-UK NMVOC emissions.

290. For the Review of the Air Quality Strategy, limited modelling of ozone concentrations was also undertaken using the ADMS-Urban model for the Greater London area (Williams *et al*., 2006). As described in the response to Question 4, the model runs used traffic flow and emissions data from the 2001 London Atmospheric Emissions Inventory, together with meteorological data from Heathrow and background data from rural monitoring sites around London. The modelling of ozone in future years took into account changes to traffic flows, pollutant emission rates and background concentrations. A single additional measure - Measure Q - was investigated. This measure represented a combination of other measures: the early uptake of EURO V/VI (Measure C, see Table 8-1), the introduction of low emission vehicles (Measure E) and the control on small combustion

plant (20-50 MW) (Measure L). As presented in Table 8-2, the ADMS-Urban calculations also showed an increase in ozone for all four metrics used to assess human-health impacts. These results are not directly comparable with those of the OSRM because of differences in the emission inventories, meteorology and assumptions of atmospheric composition. The results do however give an indication of the range of potential future ozone concentrations and metrics.

Table 8-2 Population-weighted means calculated for Greater London for the Review of the Air Quality Strategy by ADMS-Urban for the four ozone metrics used to assess human-health impacts for 2001, 2010 and 2020 base cases and for Measure Q in 2020.

	2001 Base	2010 Base	2020 Base	2020 Measure Q
Annual mean of daily maximum running 8-hr ozone concentrations	47.3	55.7	58.5	59.6
Annual mean of daily maximum running 8-hr ozone concentrations with a cut-off of 70 µg m^{-3}	2.42	3.96	4.67	4.88
Annual mean of daily maximum running 8-hr ozone concentrations with a cut-off of 100 µg m^{-3}	0.28	0.56	0.69	0.72
Number of Days on which a running 8-hr ozone concentration exceeds 100 µg m^{-3}	7.6	13.1	15.6	16.0

291. In summary, the modelling of future O_3 concentrations for the Review of the Air Quality Strategy indicated that, without additional measures, O_3 air quality would deteriorate for both average and peak levels. Concentrations will still exceed the Air Quality Strategy's objective in 2020. Average levels are likely to rise in urban and rural areas.

8.2.1.2 Beyond the Review of the Air Quality Strategy

292. The CAFE Thematic Strategy considered larger reductions in both NMVOC and NO_x emissions in both the UK and Europe. UK NO_x and NMVOC emissions in the Maximum Feasible Reduction (MFR) scenario for 2020 were 518 and 663 kilo tonne per annum respectively, whereas the lowest levels modelled in the Review of the Air Quality Strategy were 713 and 805[5] kilo tonne per annum respectively. The reduction in NMVOC emissions considered in Measure M of the Review of the UK Air Quality Strategy was about a third of that of the MFR scenario, suggesting scope for additional reduction.

293. A limited set of site-specific OSRM runs were subsequently undertaken to investigate the level of emission reduction needed to achieve ozone air quality objectives and target values. 41 receptor locations, corresponding to UK ozone monitoring sites, were modelled using the same assumptions and input datasets as the OSRM runs undertaken for the Review of the Air Quality Strategy. The site-specific calculations considered additional across-the-board emission reductions (20% to 80%) in 2020 NO_x and/or NMVOC emissions. Two series of runs were undertaken (i) UK action alone and (ii) combined UK and European action. These emission reductions were not associated with specific measures but simply to scope the scale of the reductions needed.

[5] This does not include the contribution of 178 kilo tonne per annum from biogenic sources, which is included in the UK totals given in **Error! Reference source not found.**.

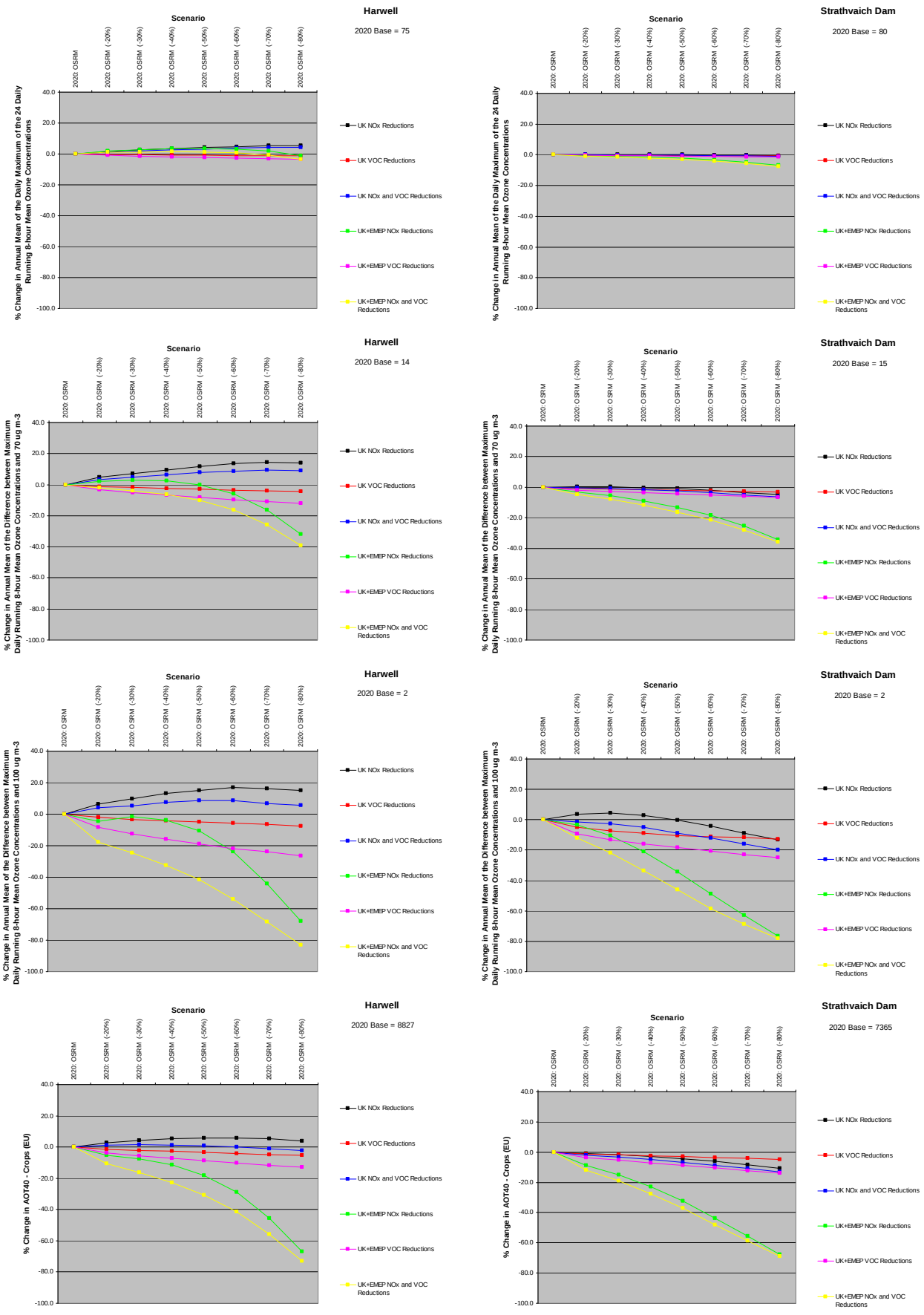

Figure 8.2 The percentage change in different ozone metrics for additional post-2020 across-the-board reductions of NO_x and/or NMVOC emissions at the Harwell (left-hand panels) and Strathvaich Dam (right-hand panels), as calculated using the OSRM.

294. As shown in Chapter 5, urban ozone concentrations can be represented by a regional component and an urban ozone decrement. Hence, results for rural sites are considered initially. Figure 8.2 presents the response at the Harwell and Strathvaich Dam sites of a number of ozone metrics: (a, b, c) annual mean of the difference between maximum daily running 8-hour mean ozone concentrations with no cut-off and cut-offs of 70 and 100 μg m^{-3} and (d) AOT40 – crops.

295. Although the model results indicated that the effectiveness of the emission reduction was dependent on site and the ozone metric chosen, a number of general comments can however be made:
    - Metrics sensitive to higher ozone concentrations in the concentration distribution, such as the annual mean of the difference between maximum daily running 8-hour mean ozone concentrations with a cut-off or AOT40 – crops, show a larger response to emission reduction than metrics sensitive to the entire concentration distribution (e.g. annual mean of the maximum daily running 8-hour mean ozone concentrations);
    - There are a range of responses to the reduction of UK NO_x emissions, which depend on the site and metric. For some sites, there is an initial increase in the metric and substantial reductions in NO_x emissions are needed before there is a decrease in the metric;
    - NMVOC emission reductions alone always improve ozone air quality;
    - Combined reductions of NMVOC and NO_x emissions are more effective than reducing NO_x emissions alone;
    - UK and European action is always more effective than UK action alone.

296. The influence of the higher NO_x emissions in urban areas is illustrated in Figure 8.3 for the sites: London Bloomsbury, London Bexley and Rochester, in rural, suburban and urban locations, respectively. As expected, the rural site at Rochester has higher ozone concentrations (and hence a higher value of the metric) than the suburban site at London Bexley, which is also higher than the urban site at London Bloomsbury. The ozone metrics at the urban sites do however tend towards the surrounding rural value as the local NO_x titration effect decreases (see Chapter 5).

297. Overall, the results suggested that, as in the CAFE work, health-related O_3 metrics would increase in the baseline scenario between now and 2020. As above, reductions in NMVOC emissions in both the UK and in the rest of Europe (from a 2020 base) led to a monotonic improvement in O_3 in rural and urban areas of the UK, with this combined action being more effective than UK action alone. Reductions in NO_x emissions alone in both the UK and the rest of Europe will reduce O_3 levels in rural areas of the UK, but will lead to increases in urban areas until this trend is reversed in urban areas for reductions in excess of ~30% (~60% in London) from a 2020 base. Although these reductions reverse the increasing O_3 trend, they are not necessarily sufficient to bring the O_3 metric to levels below those modelled for 2003. The most efficient way of doing this is to reduce both NO_x and NMVOC emissions in both the UK and the rest of Europe. The results suggest that reductions of the order of 60% or more for both pollutants will achieve this in rural and urban areas of the UK, whereas reductions of ~60%-70% would be required to achieve this in London.

8.2.2 Ozone policy options at the European scale

298. The Gothenburg Protocol to the UN ECE Convention on Long-range Transboundary Air Pollution, the European Union's National Emission Ceilings (NEC) Directive and its draft Air Quality Directive implementing the Clean Air for Europe (CAFE) Thematic Strategy have been agreed to reduce the impacts of ozone on human health and ecosystems. The Gothenburg Protocol and the NEC Directive mandate country-specific emission limits to be achieved by 2010 for oxides of nitrogen (NO_x) and volatile organic compounds (NMVOCs). Emission limits are also defined for sulphur dioxide (SO_2) and ammonia (NH_3). The Gothenburg Protocol and the National Emissions Ceilings Directive are subject to periodic reviews, which are currently in progress.

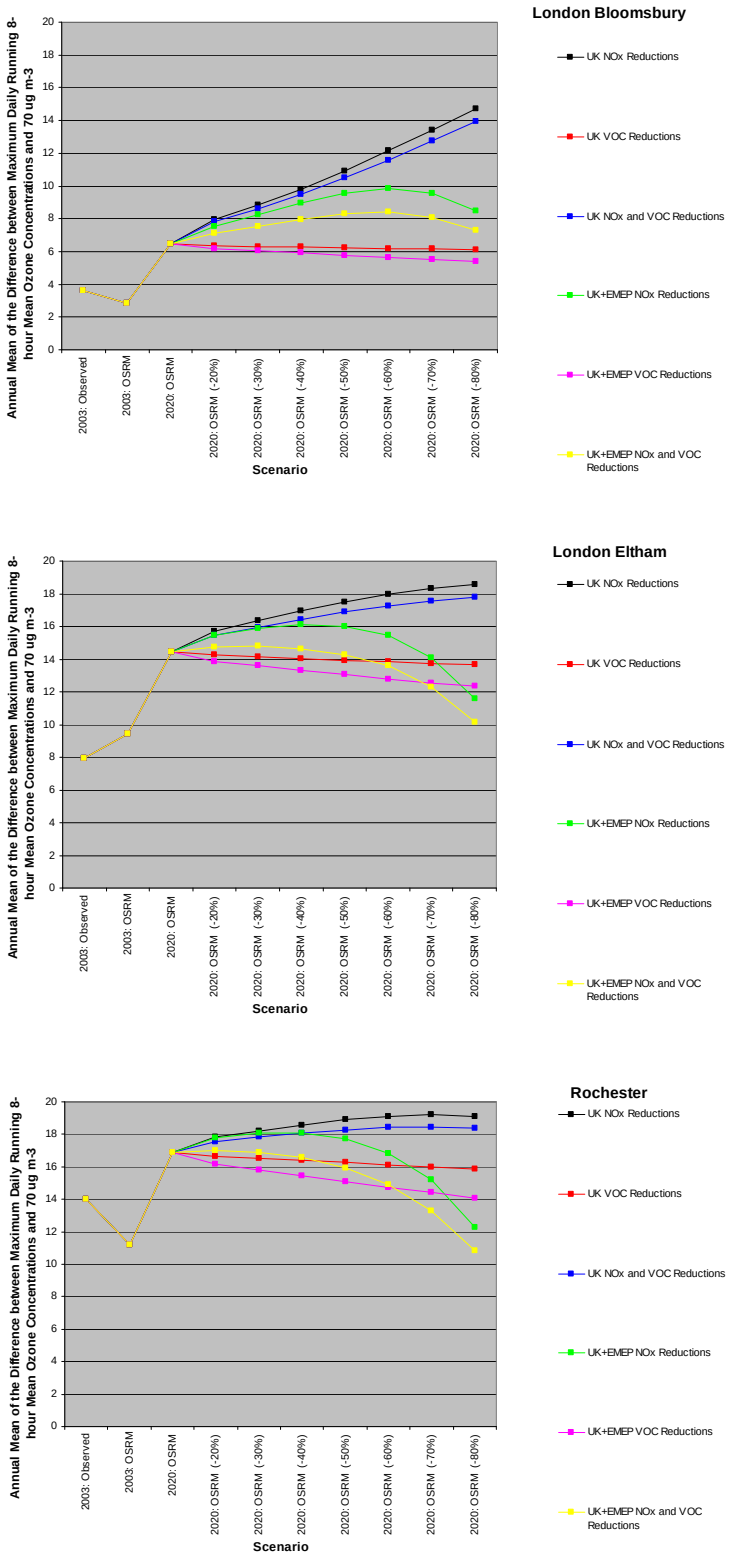

Figure 8.3 The effect of across-the-board reductions of 2020 NO_x and/or NMVOC emissions on the ozone metric - annual mean of the difference between maximum daily running 8-hour mean ozone concentrations and 70 µg m^{-3}, as calculated by the OSRM.

299. The CAFE strategy aimed to cut mortality from ozone pollution by 10% by 2020 compared with the 2000 levels (as well as reducing the impacts on ecosystems). This would be achieved by reducing total emissions of nitrogen oxides by 60% and total NMVOC emissions by 51% within the EU between 2000 and 2020.

300. These European policy actions have been underpinned by the integrated assessment modelling of IIASA. The integrated assessment modelling was the subject of Question 6 and is not considered further here.

301. The focus of this section is on the contribution to ozone formation by different NMVOC source sectors and how the relative contributions and hence the importance of the sectors will change by 2020 because of planned emission controls. Subsequent studies have investigated the benefits to ozone resulting from the replacement of highly reactive aromatic species by low reactivity species.

8.2.2.1 Ozone formation from different NMVOC source sectors

302. Within the European Union, transport is currently the dominant source of ozone-precursor emissions. Figure 8.4 shows the sector split of emissions of ozone-precursors for member countries of the European Environment Agency.

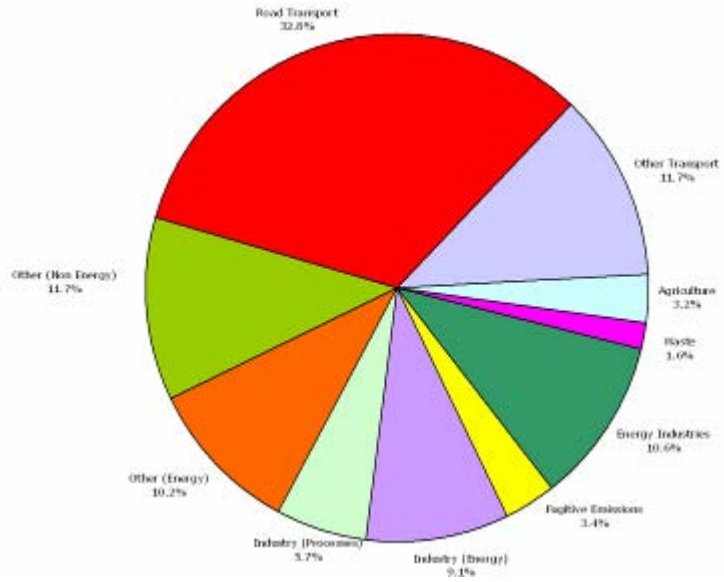

Figure 8.4 Sector split of weighted emissions of ozone-precursors for Member Countries of the European Environment Agency used to derive the EEA's Core Indicator CSI002 on ozone-precursor emissions (taken from http://themes.eea.europa.eu/IMS/CSI).

303. As part of the UK National Atmospheric Emission Inventory programme, speciated NMVOC emission inventories (664 NMVOCs from 248 source sectors) have been derived for the years 2000, 2010 and 2020 (based on the 2002 NAEI inventory year). Derwent and co-workers (see Section 8.5 of Hayman *et al.*, 2006b) used these inventories in the UK Photochemical Trajectory model (UK PTM). The model incorporated an extended version of the Master Chemical Mechanism, which considered 176 of the 664 NMVOCs, accounting for ~90% of the total mass emission in the 2000 inventory.

304. The model described photochemical ozone formation along the idealised photochemical episode trajectory giving the highest ozone concentration over the UK. The same speciation of the NMVOC emissions was assumed along the trajectory as that derived

from the NAEI emission inventory. A series of sensitivity experiments was performed. At each point along the trajectory, the emissions of the NMVOC contributing to a specific source sector were increased by a nominal fraction (the choice of 7.3% was completely arbitrary and had no policy significance) and these additional emissions increased photochemical ozone production over the base case experiment. The additional ozone present at the end-point of the trajectory was taken as a measure of the propensity for regional scale ozone formation from that source category and was used to derive the incremental reactivity of that source category.

305. The source categories that made the largest contribution to photochemical ozone formation in 2000 were associated with road transport (cars with and without catalysts). These categories were in first and second places by virtue of their large percentage contributions to total NMVOC emissions and their relatively high incremental reactivities. The source category with the largest incremental reactivity was chemical waste incineration but, because of its relatively low percentage contribution to total NMVOC emissions, it contributed little to ozone formation.

306. Assuming that there would be no change in the incremental reactivities between 2000 and 2010, peak ozone was reduced by 25.3 µg m^{-3} on the standard base case UK PTM model trajectory from Austria to the United Kingdom, when the 2000 NMVOC inventory was substituted by that for 2010 (i.e. this reflects the overall mass emission reduction that has occurred between 2000 and 2010). The reduction was somewhat smaller at 24.4 µg m^{-3} when the substitution was made with the 2020 inventory (corresponding to the trend in the total NMVOC emissions, see Table 8-1).

307. Table 8-3 gives the NMVOC emission source categories that contributed most to the decrease in episodic peak ozone concentrations between the years 2000 and 2010 using these Defra NMVOC emission projections. By far the largest contribution to the decline in ozone of 13.2 µg m^{-3}, or more than about one half of the total, came from the reduction in NMVOC emissions in the road transport sector (cars with and without catalysts, LGVs and HGVs). The next largest combined contribution, amounting to about 15% of the ozone decline, came from NMVOC emission reductions in the stationary source sectors of the chemicals, oil and gas industries.

Table 8-3 The NMVOC emission source categories that gave the greatest contributions to the decline in episodic peak ozone concentrations between the years 2000 and 2010.

Source Category	Contribution to the Decrease in Peak Ozone Concentrations between 2000 and 2010 (in µg m^{-3})
- Cars without catalysts	9.6
- Cars with catalysts	2.2
- LGVs without catalysts	0.8
- Rigid HGVs	0.6
All Road transport	13.2
Onshore Loading of crude oil	1.4
Offshore Loading of crude oil	1.0
Surface Cleaning with trichloroethene	0.6
Domestic Combustion of coal	0.6
Offshore Oil and Gas Industries	0.6
Chemical Industry	0.6
Decorative Paint Trade	0.6
Gas Leakage	0.6
House and Garden Machinery	0.6

308. In 2020, because of the marked reductions in NMVOC emissions in the transport sector, a different range of source categories will be responsible for the bulk of the ozone formation. Table 8-4 shows, in order of importance, the major ozone producing sectors in 2020. The entries are dominated by stationary NMVOC sources in industries, associated with the chemical, oil and gas industries and the manufacturing industries that use solvents. The only sector listed associated with road transport, is that of petrol stations and the emission of NMVOC from refuelling motor vehicles with unleaded petrol. Table 8-4 points to a major shift in policy if ozone levels are to be reduced beyond 2010 levels so that stationary NMVOC sources are targeted rather than motor vehicles.

Table 8-4 The NMVOC emission source categories that gave the greatest contributions to episodic peak ozone concentrations in 2020.

Source Category	Contribution to Peak Ozone Concentrations in 2020 (in µg m^{-3})
Chemical Industry	3.2
Spirit Manufacture (maturation)	2.2
Onshore Loading of crude oil	1.8
Road Transport (cars with catalysts)	1.4
Refineries (process fugitives)	1.4
Industrial Adhesives	1.4
Petrol Stations (vehicle refuelling with up)	1.4
Offshore Loading of crude oil	1.4
Industrial Coatings (metal plastic)	1.2
Aerosols (cosmetics and toiletries)	1.2
Other Solvent Use	1.2
Aerosols (car care)	1.0

Notes: up = unleaded petrol

309. Derwent *et al.* (2007a, b) have also investigated the ozone benefits resulting from the replacement of highly reactive aromatic species by low reactivity species. Three simple illustrative strategies were formulated in which the emissions of the xylenes, trimethylbenzenes and all aromatic species were replaced or substituted by the emission of one of a potential range of 94 organic compounds. Of these, eight alcohols, six esters, six ketones, three ethers, a cycloalkane and a glycol ether were found to give greater ozone reductions on substitution for the aromatic compounds than would be obtained

from the corresponding mass-based control policy. Derwent *et al.* (2007b) concluded that a much more focussed approach on the most important solvent sub-sectors identified by their POCP indices would appear to be more effective, environmentally and financially.

310. It is also worth noting an earlier study by Derwent and Nelson (2003) for the Environment Agency. The UK PTM, with a previous version of the Master Chemical Mechanism, was used to derive an Integrated Downwind Ozone Potential (IDOP) for ~120 VOCs. The IDOP was defined as the excess ozone production, integrated over the downwind environment, for a 1 tonne hr^{-1} industrial emission source. This ozone production can also be expressed as an ozone-equivalent emission ceiling for each emitted VOC species (in tonne hr^{-1}), which, when exceeded, would lead to ozone concentrations in the downwind environment that were ~10 µg m^{-3} higher than in the absence of that industrial VOC source. The IDOP and POCP have similar rankings of VOC reactivity.

311. Houston, Texas is noted for some of the highest ozone levels in the USA and measurement campaigns have linked these ozone excursions to emissions of ethene and propene from industrial sources. As part of the Texas 2000 Air Quality Study, Ryerson *et al.* (2003) drew upon the work of Derwent and Nelson (2003) and its conclusion that downwind ozone production was dependent upon only a limited set of all the possible organic compounds known to be emitted from petrochemical sources. Furthermore, the ozone productivities of ethene and propene defined in the Agency study were able to account qualitatively for the formation of the ozone excursions in Houston.

8.2.3 Ozone policy options at the global scale

312. Allowance was made in the OSRM model runs for the Review of the Air Quality Strategy for a change to atmospheric composition arising from global changes and this had a significant impact on the calculated future ozone air quality. Sensitivity runs were undertaken for the emission projections for 2010 and 2020 with a current atmosphere (2003) and future atmospheric composition based on the business-as-usual scenario with climate change (see Section 4.4.2 of Hayman *et al.* (2006a)). The changes in the initial daily ozone concentrations from the 2003 values ranged from -1.7 to +3.2 µg m^{-3} in 2010 and from -3.1 to +5.9 µg m^{-3} in 2020. Figure 8.5, shows the sensitivity of the different population and area-weighted ozone and nitrogen dioxide metrics for the UK for the 2010 and 2020 base case runs, with and without changing atmospheric composition, relative to the 2003 current year (=1).

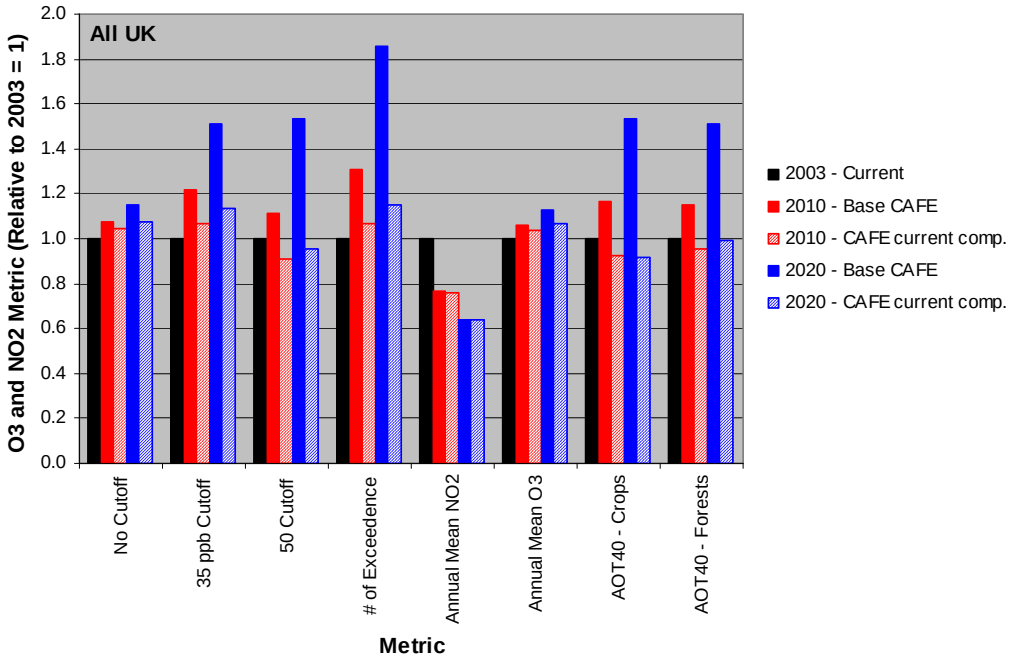

Figure 8.5 The sensitivity of different ozone and nitrogen dioxide metrics calculated by the OSRM for the 2010 [red] and 2020 [blue] base case runs (with changing [solid bars] and current [hashed bars] atmospheric composition) relative to 2003 (=1, solid black bars) for the UK.

313. There are significant and increasing differences for the ozone metrics between the two sets of runs. The greatest differences occur for the ozone metrics with an exceedence of a threshold, i.e. annual mean of the maximum daily running 8-hour average ozone concentration with a 70 or 100 µg m^{-3} cut-off, the number of days when the maximum of the 24 possible 8-hour running mean concentrations in each day exceeds 100 µg m^{-3} and the two AOT40 metrics. There is little effect on the annual mean NO_2 concentrations between the runs with and without a changing atmospheric composition.

314. The increasing background concentration arising from global changes clearly indicates that future policy action on ozone air quality is inextricably linked to that on climate change and greenhouse gas emissions.

8.2.3.1 Methane

315. Background (hemispheric) concentrations of tropospheric ozone are sensitive to methane emissions, yet methane mitigation is predominantly considered in respect of its impact on radiative forcing, rather than its impact on air quality. Methane is relatively long-lived in the atmosphere (~8-9 years) so controls on global methane will produce ozone reductions that are widespread globally, and which are sustained on the same timescale (West and Fiore, 2005). Model simulations show that, globally, tropospheric ozone responds approximately linearly to anthropogenic methane emissions changes. For example, reducing global anthropogenic methane emissions by 20% beginning in 2010 is simulated to decrease the average daily maximum 8 hourly surface ozone concentrations by approximately 2 µg m^{-3} on average globally by 2030. This strategy is estimated to be cost effective in terms of avoided global ozone-related mortality alone (West *et al.*, 2006).

316. Observations now clearly reveal a slow-down in the rate of increase of global methane, with atmospheric concentrations currently levelling off at ~1750 ppbv (Khalil *et al.*, 2007). The reasons for the trend towards apparent steady state (constant emission rates) are not

entirely clear but a strong possibility is that decreased emissions from agriculture, particularly from rice growing in China (Khalil and Shearer, 2006) and from fossil-fuel processing following the break-up of the Soviet Union (Bousquet *et al.*, 2006) have offset increases from other sectors. Other suggestions include an increased prevalence of tropical thunderstorms creating more NO_x that has enhanced methane destruction, and a decline in total methane emissions from tropical land plants because of deforestation (Keppler *et al.*, 2006; Houweling *et al.*, 2006). However, despite the current observations, recent analyses suggest that anthropogenically-influenced sources of methane are on the increase again (Bousquet *et al.*, 2006), driven by increasing population and industrialisation, so that global methane control remains a viable option for control of background ozone (and of an important contribution to radiative forcing).

8.2.3.2 NO_x and NMVOCs

317. In contrast to methane, controls on NO_x and NMVOC emissions, which are relatively short-lived in the atmosphere, tend to impact more on local and regional ozone generation, rather than hemispheric background ozone, and consequently predominantly act to reduce regional high-ozone episodes in regions where emissions of these precursors are relatively high. At the same time however, reductions of NO_x and NMVOC also increase the lifetime of methane (by decreasing the average OH radical concentration), which in turn causes an increase in average ozone in the long-term, thereby offsetting some of the benefits to background ozone reduction derived from methane emission reductions (Dentener *et al.*, 2005; West *et al.*, 2007).

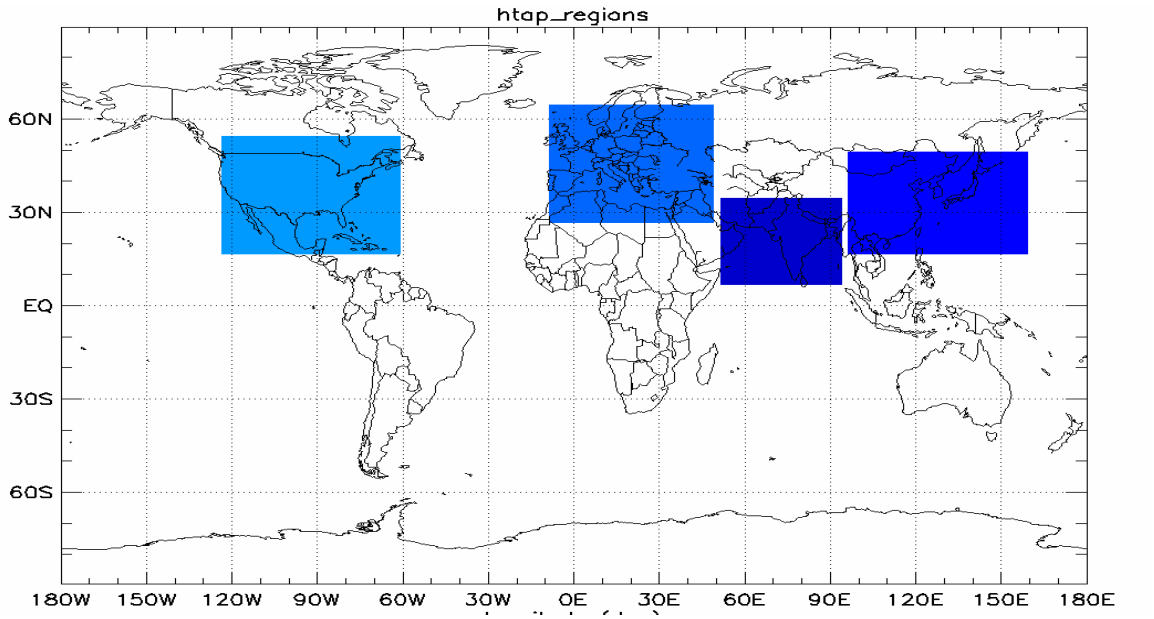

Figure 8.6 Source receptor regions defined by the HTAP taskforce: North America – NA, Europe - EU, South Asia – SA, and East Asia. Source: (LRTAP, 2007).

318. The UN Taskforce on Hemispheric Transport of Air Pollution (HTAP) has compiled results from more than 20 global models that have simulated the impact on surface ozone over Europe (and other receptor regions) of a 20% reduction in NO_x, NMVOC and CO emissions from each of a number of industrialised source regions of these pollutants (LRTAP, 2007). The geographical regions defined in the HTAP study are illustrated in Figure 8.6, and the mean model-simulated decreases in average surface ozone over the Europe source region for the months of March, April and May are shown in Figure 8.7.

319. Figure 8.7 shows that, when considering these particular ozone-precursor species, springtime surface ozone in Europe is most sensitive to reductions of precursors within

Europe itself, as expected. The next greatest sensitivity is to reductions in emissions in North America, reflecting the prevailing west-east air-mass transport at these latitudes. Nevertheless, even for these relatively short-lived precursors, the ensemble-mean sensitivity of European springtime ozone to 20% decreases in ozone-precursors in the three non-Europe source regions together is always greater than half the ozone response to the equivalent decreases within Europe. (In the case of CO, the response of European ozone to CO reductions in the three non-Europe source regions is as great as the response to CO reduction in Europe alone). The response of annual mean surface ozone in Europe to reductions of precursors from the three non-Europe source regions is even greater than the response of peak-season ozone.

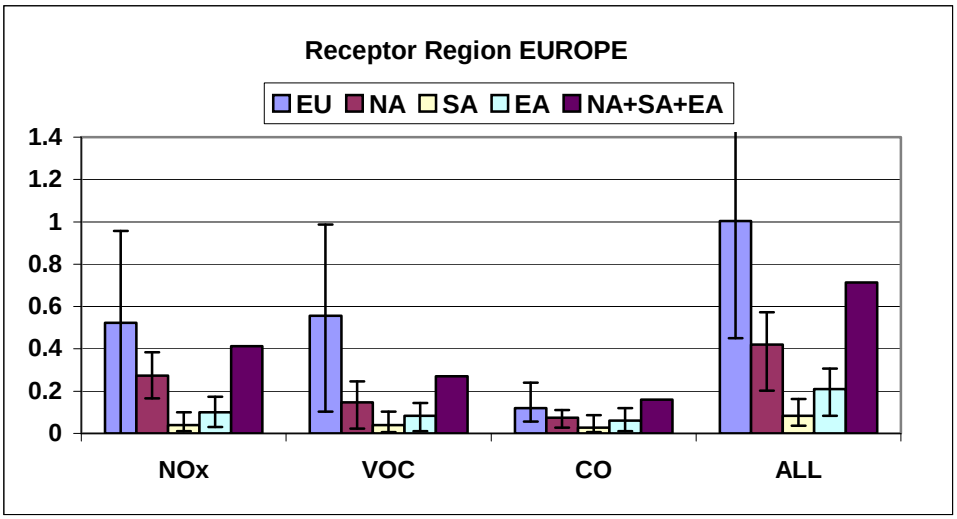

Figure 8.7 The decrease in springtime (March-April-May) mean surface ozone (ppbv) in the Europe HTAP Receptor Region resulting from 20% lower emissions of ozone-precursors NOx, NMVOC and CO in each of the four source regions (EU-Europe, i.e. application of "domestic" emissions reductions only; NA-North America; SA-South Asia; EA-East Asia). The ALL category is the result of applying the 20% reduction to all NOx, NMVOC and CO emissions simultaneously in the stated source region. The 5th bar in each group is the impact on European ozone of precursor reductions in the three non-European source regions together. The bars denote the Multi-Model Mean Response and the whiskers span the full range of the individual model responses. Source: (LRTAP, 2007).

320. A key observation is that European surface ozone is as sensitive to NMVOC emission reductions as to NO_x emission reductions, particularly with respect to domestic NMVOC emissions. This greater sensitivity to NMVOC emissions across Europe as a whole is in contrast to the NO_x-limited regime that exists in the other three HTAP receptor regions. It is also important to note that the model outputs are for net changes in simulated mean surface ozone across Europe as a whole, and these mask the spatial variations within Europe in the response of ozone to NO_x and NMVOC emissions reductions. For example, winter ozone is simulated to increase over northern Europe in the scenario of a 20% reduction in NO_x alone.

321. The magnitude of the reductions in European average springtime surface ozone shown in Figure 8.7 for 20% reductions in NOx, NMVOC (and CO) emissions should be compared with the simulations showing that a 20% reduction in global methane concentration alone leads to a reduction in background surface ozone, in the long-term, of ~2 μg m^{-3}. Figure 8.7 shows that European reductions of 20% in both NO_x and NMVOC emissions together are necessary to achieve the same impact on average European ozone as a 20%

reduction in global methane concentrations (but the timescales on which the different emissions reductions impact on ozone are different).

322. In the ACCENT intercomparison of 26 global models (see response to Question 3 for more detail and illustrations), the ensemble-mean simulation for a scenario in which all possible technical control options on ozone-precursors are implemented worldwide (the MFR scenario) is a reduction of –5.6 μg m^{-3} in average surface ozone over Europe between the years 2000 and 2030 (Dentener *et al.*, 2006). This net reduction is predominantly driven by the significant reductions (of several μg m^{-3}) in the concentration of hemispheric background ozone in the air masses entering Europe (Derwent *et al.*, 2006). The reduction in European ozone under the MFR scenario should be compared with the ensemble-mean simulated increase of 3.6 μg m^{-3} in average surface ozone across Europe by 2030 for implementation of the current legislation scenario on precursor emissions (Dentener *et al.*, 2006). The MFR scenario illustrates the significant benefit to European ozone levels of implementation of stringent global-scale precursor emission control acting in addition to improvements brought about by precursor emission control at the regional scale.

8.2.3.3 NO_x emissions from shipping

323. One important, and comparatively under-regulated, source of ozone-precursors (principally NO_x) is shipping (Lawrence and Crutzen, 1999; Endresen *et al.,* 2003; Derwent *et al.*, 2005; Eyring *et al.*, 2005, 2007). World shipping has increased by 35% over the last 50 years, and model simulations suggest that shipping currently contributes ~12 μg m^{-3} to annual mean and summertime surface ozone over the North Atlantic and western Europe (Derwent *et al.*, 2005; Eyring *et al.*, 2007). The exact impact of shipping on ozone at a more local scale in particularly congested sea-ways (e.g. English Channel, North Sea, Mediterranean, etc.) will depend on the particular local NO_x emission densities and photochemical climate. In some localities, NO_x emissions from shipping may currently limit local ozone generation such that reducing emissions may lead to an increase in ozone in these areas.

324. Emission scenarios predict that if no further control measures are implemented beyond existing International Maritime Organisation regulations, global NO_x emissions from shipping might increase with an annual growth rate of 1.7% between 2000 and 2030, becoming comparable in magnitude to global NO_x emissions from road traffic by 2050 (Eyring *et al.*, 2005). On the other hand, this is a sector with large potential for NO_x reduction, and aggressive application of abatement measures that is suggested could reduce shipping NO_x emissions by 85% from year 2000 emissions by 2050, despite a growing fleet (Eyring *et al.*, 2005).

325. The impact of different shipping emission scenarios on future European surface ozone, derived from the ACCENT intercomparison of output from 10 chemical-transport (CTMs) or general circulation models (GCMs), is shown in Figure 8.8 (Eyring *et al.*, 2007). The panels show the simulated changes in ozone in 2030 compared with 2000 assuming, from left to right, complete abatement of all shipping emissions in 2030, the same shipping emissions in 2030 as in 2000, and a flat rate increase of 2.2% per year in shipping emissions between 2000 and 2030. (Other emissions in the models follow the IPCC SRES A2 scenario.) Surface ozone increases in all three scenarios in 2030 (due to the increased emissions of precursors from other sources both regionally and globally under the SRES A2 scenario – see Chapter 4), but there is some additional sensitivity of ozone levels to shipping emissions. The sensitivity is greatest over the near-Atlantic areas, the British Isles and the North and Baltic Seas, and there are important contrasting trends. For example, ozone over the near-Atlantic in 2030 is simulated to increase by ~4 μg m^{-3} less if shipping emissions are entirely removed (*c.f.* year 2000 emissions) and by ~4 μg m^{-3} more if shipping emissions increase. In contrast, ozone over the English

Channel, southern North Sea and Baltic areas is simulated to increase more in 2030 if shipping emissions are removed, and to increase less, or not at all, if shipping emissions increase. The latter reflects the sensitivity of ozone formation to the whole chemistry mix. Where NO_x is already relatively high, further NO_x (such as from shipping) limits ozone directly by titration ($NO + O_3$) and/or indirectly by reducing oxidant capacity (NO_2 + OH).

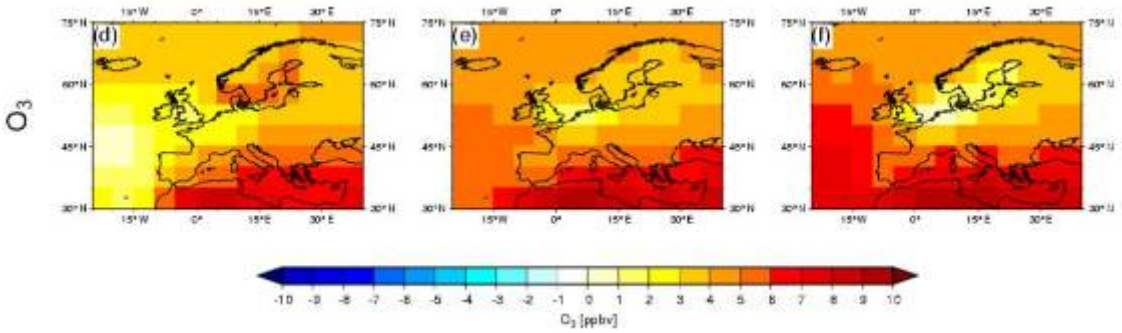

Figure 8.8 Changes 2030–2000 over Europe under the IPCC SRES A2 scenario with different assumptions for ship emissions. Left, changes in a world without ship emissions in 2030; middle, changes in a world with ship emissions remaining at 2000 levels; right, changes under a constant growth scenario of a flat increase of 2.2% per year compared to the year 2000. Data are ensemble mean values from 10 global atmospheric chemistry models. Source: (Eyring *et al.*, 2007).

8.2.3.4 Carbon Monoxide

326. The influence of global and regional trends in carbon monoxide emissions on global and regional ozone has been less extensively studied. The ACCENT model intercomparison, using best estimates of present-day CO emissions, showed large underestimates in simulated northern hemisphere extratropical CO compared with both surface observations and satellite observations from the MOPITT instrument (Shindell *et al.*, 2006). The interpretation is that year-round emissions, probably from fossil fuel burning in east Asia, and seasonal biomass burning emissions in south-central Africa, are greatly underestimated in current inventories, such as those from IIASA. Although CO has a shorter atmospheric lifetime (of only a few months) than methane, it is sufficiently long-lived to have an impact on both hemispheric and regional-scale ozone concentrations, for example by scavenging the OH radical and increasing the lifetime of methane. Control of hemispheric CO emissions will therefore also reduce background concentrations of ozone, and its associated contribution to radiative forcing.

327. IIASA has recently prepared a revised set of emission projections for methane, oxides of nitrogen and carbon monoxide to inform the report by Royal Society on Ozone in the 21st Century (Rafaj and Amman, 2007). The NO_x and CO emissions are lower than those given in previous emission projections as the effects of recent air pollution control measures have been incorporated. These new emission projections could have a significant implication for future global ozone concentrations and emission control policies.

8.3 Natural vs man-made emission sources

328. The extent of any changes in future O_3 concentrations will increasingly be influenced by biogenic NMVOC emissions. As man-made emissions reduce, biogenic sources will contribute an increasing proportion of O_3 precursors. Biogenic NMVOCs describe a wide range of compounds, of which only a few are generally of interest and represented in chemical-transport models. Isoprene is the compound of most importance for ozone modelling for example. Emissions of the various terpenes (e.g. α- and β-pinene) are also

important, for both ozone and aerosol formation. The remaining NMVOC species ('other VOC', or OVOC) play some role, but little is known about the chemistry of many components or the quantitative emissions of individual species. Emissions may be large, however.

329. The emission flux of biogenic NMVOCs for all types of vegetation is most often described on an hourly basis (Guenther *et al.*, 1995, 1996) by:

$$\text{Flux } (\mu g\ m^{-2}\ yr^{-1}) = \int \varepsilon\ D\ \gamma\ dt$$

330. where ε is the average emission potential ($\mu g\ g^{-1}\ h^{-1}$) for the particular species, D is the foliar biomass density (g dry weight foliage m^{-2}), and γ is a dimensionless environmental correction factor representing the effects of short-term (e.g. hourly) temperature and solar radiation changes on emissions. This approach is used in most current models for ozone (including 'one-atmosphere' models such as the EMEP Unified and the US CMAQ models). As such, annual emission estimates are not a routine input or output, making it difficult (if not impossible) to compare the emission estimates used in different models. The Annex on Emissions of Ozone-precursors provides further information on the compilation and comparison of different biogenic NMVOC emission inventories.

331. As an example, Table 8-5 gives the biogenic NMVOC emissions derived by Winiwarter *et al.* (2001) in the EU PELCOM project by country for nine tree species classes, using the country environmental correction factors derived by Simpson *et al.* (1999). The table also includes the emission estimates of Simpson *et al.* and, for comparison, the reported national estimates of NMVOC emissions from man-made sources in 1990 and the National Emission Ceilings for 2010 agreed in the Gothenburg Protocol.

332. If the incidence of high temperature episodes increases as a result of climate change, then the very strong temperature dependence of biogenic emissions may lead to increases over current levels (although other factors related to environmental change will also certainly affect future emissions, see Chapter 4). Human influence in determining which tree species are planted could be significant in this context as emissions vary considerably between species. Some of these changes were considered by Donovan *et al.* (2005) in their study to quantify the effects of trees on urban air quality in scenarios of high photochemical pollution.

333. Donovan *et al.* (2005) used a trajectory model to evaluate the effects of the emissions of biogenic volatile organic compounds from the urban forest in the West Midlands metropolitan area (as well as their effects on pollutant deposition of O_3, NO_2, CO and HNO_3). While all tree species investigated were found to be beneficial to air quality in terms of pollutant deposition, some tree species were found to have the potential for photochemical production of ozone. An urban tree air quality score (UTAQS) was developed to ranks tree species in order of their potential to improve air quality. Of the 30 species considered, pine, larch, and silver birch were calculated to have the greatest potential to improve urban air quality, while oaks, willows, and poplars could worsen downwind air quality if planted in very large numbers.

Table 8-5 Comparison of the emissions of volatile organic compounds by tree species and country derived in the PELCOM Project with the estimate of Simpson *et al*. (1999), national estimates of NMVOCs from man-made sources in 1990 and the National Emission Ceilings as given in the Gothenburg Protocol for 2010. Units: kilo tonnes per year.

Emission	Coniferous				Deciduous					Total	Simpson et al.	Anthropogenic	
Species / Country	*Pine*	*Spruce Fir*	*Larch*	*Other*	*Quercus ssp.*	*Quercus ilex*	*Beech*	*Birch, Poplar*	*Other*			*1990*	*2010*
Albania	1	2	1	-	28	14	1	-	2	51	54	-	-
Austria	8	95	9	-	14	2	2	-	1	132	125	351	159
Belarus	117	57	-	-	45	-	-	35	5	260	150	533	309
Belgium	2	10	1	-	23	-	1	-	-	38	34	324	144
Bosnia and Herzegovina	2	20	5	1	28	4	5	-	4	68	72	-	-
Bulgaria	25	12	2	-	173	12	5	-	4	234	104	217	185
Croatia	3	13	2	1	42	9	6	-	4	80	47	105	90
Czech Republic	18	83	5	1	18	-	1	-	1	127	108	435	220
Denmark	1	10	-	1	3	-	-	-	-	15	15	178	85
Estonia	19	22	-	-	4	-	-	-	2	47	4	-	-
Finland	149	146	-	-	-	-	-	12	2	309	341	209	130
France	119	71	49	8	593	66	11	2	17	935	1050	2957	1100
Germany	84	236	25	1	88	1	9	1	3	448	377	3195	995
Greece	24	13	9	1	136	61	2	-	2	248	153	373	261
Hungary	6	18	2	-	74	-	2	-	4	107	101	205	137
Ireland	2	7	-	-	1	-	-	-	-	11	13	197	55
Italy	25	57	19	1	210	70	10	-	13	405	114	2213	1159
Latvia	32	22	-	-	5	-	-	3	2	64	59	152	136
Lithuania	22	21	-	-	5	-	-	2	1	52	0	103	92
Luxembourg	-	1	-	-	3	-	-	-	-	5	3	20	9
Macedonia	3	1	-	-	25	11	1	-	1	43	30	-	-
Netherlands	4	2	1	-	5	-	-	-	-	12	7	502	191
Norway	30	60	-	-	2	-	-	3	1	95	160	310	195
Poland	164	61	11	-	42	1	3	2	5	288	232	831	800
Portugal	62	-	-	2	138	45	-	-	3	251	140	640	202
Republic of Moldova	-	1	-	0	24	-	-	-	1	27	-	157	100
Romania	1	118	17	0	167	-	12	-	9	323	197	616	523
Russia	732	1452	6	5	282	-	2	3033	23	5534	5125	3566	-
Russia - PEMA	-	-	-	-	-	-	-	-	-	-	-	203	165
Serbia and Montenegro	6	16	4	1	105	9	9	-	7	158	112	-	-
Slovakia	7	40	6	1	24	-	3	-	2	83	86	149	140
Slovenia	3	17	2	-	12	4	2	-	1	41	19	42	40
Spain	337	-	11	9	406	302	5	1	12	1083	511	1094	669
Sweden	120	285	-	-	17	-	1	14	4	441	581	526	241
Switzerland	1	16	6	1	3	1	1	-	-	29	31	292	144
Turkey	115	19	25	11	248	11	4	-	9	443	-	-	-
Ukraine	98	90	12	-	243	-	5	24	11	484	474	1369	797
United Kingdom	15	36	7	1	6	-	1	1	1	67	77	2555	1200
Sum	**2357**	**3130**	**237**	**46**	**3242**	**623**	**104**	**3133**	**157**	**13038**	**10716**		
Sum without Turkey	2242	3111	212	35	2994	612	100	3133	148	12595			
Sum Simpson (without Turkey)	2036	4356	137	159	2408	360	56	994	211	10716			

8.4 Exposure during ozone pollution episodes

8.4.1 Action plans

334. The EU 3rd Daughter Directive makes provision for 'short-term action plans' specifically for extreme episodic ozone events, where there is a risk of exceedence of the alert threshold (240 µg m^{-3} ≈120 ppbv) for three or more consecutive hours. As reported by Jenkin (see Section 5.3.2 in Hayman *et al.*, 2002), a version of the UK Photochemical Trajectory Model (PTM) has previously been used to investigate the impact of a series of UK precursor control measures on the peak ozone concentration at the Barnsley Gawber site at 13:00 hr on 1 August 1999. This event was selected because an exceedence of 240 µg m^{-3} was recorded, within a more general and widespread UK ozone episode, which persisted from 30 July – 2 August 1999.

8.4.1.1 Modelling of a UK episode at Barnsley

335. Figure 8.9 shows the 96-hour trajectory arriving at Barnsley Gawber at 13:00 hr on 1 August 1999. The event was characterised by airflow from the European continent (as typically experienced during ozone episodes), with the trajectory passing over the UK for the final 18 hours prior to arrival. For much of this time, the trajectory path travelled over rural areas of Suffolk, Norfolk and Lincolnshire and therefore did not receive particularly significant precursor emissions. However, the final six hours travel involved passage over the general area of Worksop (Nottinghamshire) and Rotherham (S. Yorkshire) and into the M1 corridor, prior to arrival at Barnsley Gawber, about 1 hour downwind of Rotherham.

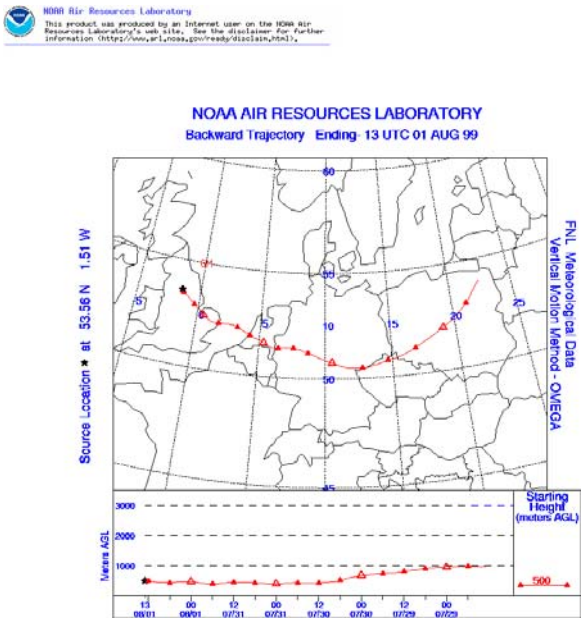

Figure 8.9 96-hour trajectories to Barnsley Gawber (1300 hr on 1st August 1999), which correspond to reported hourly average ozone ≥ 120 ppbv at this site. The trajectories were obtained from the NOAA interactive on-line trajectory service (http://www.arl.noaa.gov/ready/hysplit4.html).

336. The PTM, containing the Common Representative Intermediates (CRI) mechanism, was used to simulate the ozone concentration along this trajectory for the base case scenario, employing mapped emissions based on the 1998 NAEI (this is described subsequently in Table 8-7). The simulated ozone concentration at the trajectory end point, 236 µg m^{-3}, was slightly lower than the observed value of 248 µg m^{-3}. In order to provide a base case simulation in which the 240 µg m^{-3} threshold was exceeded, the VOC emissions throughout the model domain were slightly increased (by *ca.* 6%), to bring the simulated concentration at the end point up to the observed value of 248 µg m^{-3}.

337. A set of 11 precursor control measures was investigated, as listed in Table 8-6. Of these, only two were realistically feasible: the remainder were to test the sensitivity of the simulated ozone level to purely illustrative measures.

Table 8-6 Summary of precursor control measures investigated. Measures 1–9 are illustrative. Measures 10 and 11 represent a potentially achievable action.

Control measure	
1	No UK emissions of anthropogenic NMVOC or NO_X
2	UK emissions of anthropogenic NMVOC and NO_X doubled
3	No anthropogenic NMVOC emissions in the region of Rotherham/M1 [1]
4	No NO_X emissions in the region of Rotherham/M1 [1]
5	No anthropogenic NMVOC or NO_X emissions in region of Rotherham/M1 [1]
6	No anthropogenic NMVOC emissions in Nottinghamshire or South Yorkshire [2]
7	No NO_X emissions in Nottinghamshire or South Yorkshire [2]
8	22.3% anthropogenic NMVOC reduction in Nottinghamshire or South Yorkshire [2,3]
9	23.8% NO_X reduction in Nottinghamshire or South Yorkshire [2,3]
10	**No cars in the region of Rotherham/M1 [1,4]**
11	**No cars in Nottinghamshire or South Yorkshire [2,4]**

Notes [1] Region of Rotherham/M1 corresponds to the final 2 hours of the trajectory; [2] Nottinghamshire/S. Yorkshire corresponds to final 6 hours of the trajectory; [3] Level of control equates to the contribution of cars to NMVOC or NO_X emissions independently; [4] Control involves simultaneously reducing NMVOC emissions by 22.3% and NO_X emissions by 23.8%.

338. Figure 8.10 shows the change in the simulated ozone levels at the trajectory endpoint that result from these 11 control measures. It should be noted that none of the measures results in a large change. Even eliminating all UK anthropogenic emissions of VOC and NO_X (measure 1) only lowers the simulated concentration by 5.4 µg m^{-3}. Interestingly, a similar effect is achieved by doubling UK emissions (measure 2). This is because the Barnsley Gawber site is directly downwind of Rotherham under the conditions of 1 August 1999, and the ozone level is reduced as a result of increasing the NO_x emissions shortly before the air mass arrives at the end point.

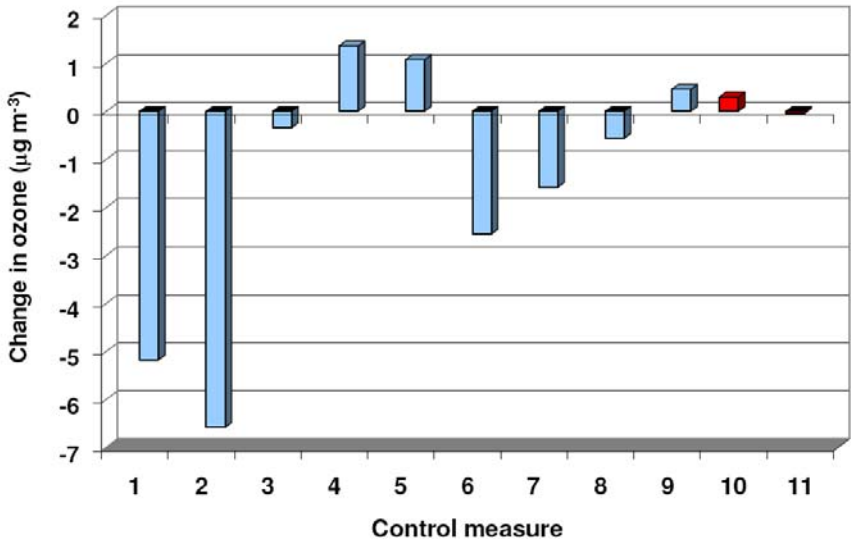

Figure 8.10 Illustration of the influence of the UK precursor controls listed in Table 8-6 on the simulated peak ozone level at Barnsley Gawber (1 August 1999 trajectory with assumed Friday arrival: base case ozone mixing ratio = 244.8 µg m^{-3}). Measures 1–9 are illustrative. Measures 10 and 11 represent potentially achievable actions.

339. The specific influence of control measures 3, 4 and 5 involving Rotherham and the M1 (i.e. the final two hours of the trajectory) confirmed that the air mass was strongly VOC-limited and also inhibited by elevated NO_x levels in a comparatively polluted plume. Thus removal of VOC emissions (measure 3) led to a reduction of ozone, removal of NO_X emissions (measure 4) led to an ozone increase, and removal of both (measure 5) led to

a smaller increase. Expanding the scope of the illustrative measures to Nottinghamshire and South Yorkshire (i.e. the final six hours of the trajectory) led to ozone reductions when either VOC or NO_X emissions were eliminated (measures 6 and 7). However, partial elimination of NO_X over the widened area (measure 9) still resulted in increased ozone. Measures 10 and 11 represented actions that were potentially feasible. The elimination of car traffic in Rotherham and on the M1 resulted in a small simulated increase in the ozone concentration of 0.3 µg m^{-3}, whereas the elimination throughout Nottinghamshire and South Yorkshire led to a very small simulated decrease of 0.04 µg m^{-3}. The magnitude and sense of the influence of these controls were logical, within the context of the effects of the illustrative measures described above.

340. The results of these model simulations provided a series of peak ozone concentrations, from which the duration of the exceedence of the alert threshold was inferred. This was achieved on the basis of a relationship between these two quantities, derived from archived monitoring data. The results indicated that none of the measures listed in Table 8-6 would lead to changes in the exceedence duration of more than 27 minutes, and the potentially achievable actions 10 and 11 would result in changes of only +70 and -10 seconds, respectively.

341. The study concluded that it was difficult to identify any realistic and beneficial UK short-term actions for the type of extreme ozone events that had been recorded in the UK. The calculations also showed that some local measures (especially those affecting NO_x emissions) could increase ozone levels under certain circumstances.

8.4.1.2 UK vs European action

342. The PTM, described above, was also applied to assess the effectiveness of a series of emission reduction scenarios related to the NECD, on simulated peak ozone concentrations over a wider geographical area in the southern UK during the same ozone episode (see Section 8.3.2 in Hayman *et al.*, 2002). The emissions scenarios are summarised in Table 8-7, with the 1998 emissions used as the base case (referred to as the “1998 ref” scenario). The remaining scenarios refer to 2010, and represent either emission reductions within the UK only, or throughout Europe.

343. In this case, the model was used to simulate the chemical development over a 96 hour period along the trajectories arriving at 16:00 hr (on 31 July 1999) at eight southern UK sites: Yarner Wood, Aston Hill, Somerton, Harwell, Lullington Heath, Wicken Fen, Rochester and Sibton. The 31 July 1999 was selected because the highest ozone concentrations were generally observed on that day. The calculation was carried out for each of the emissions scenarios summarised in Table 8-7. The results showed some variability from one site to another, particularly for those scenarios in which only UK controls were implemented. Figure 8.11 summarises the information in terms of the percentage reduction in simulated peak ozone at each site, relative to the 1998 base case. The sites are presented in order of location from west to east to emphasise the geographical dependence of the effectiveness of the control measures..

Table 8-7 Summary of NECD-related emissions scenarios used for investigation of the influence of precursor emission controls on episodic ozone levels.

Abbreviation	Description	UK NMVOC Emissions (kt per annum)	UK NO_X Emissions (kt per annum)
1998 ref (base case)	1998 UK emissions of CO, NO_X, SO_2 and NMVOC as defined by NAEI[1]. Other relevant country total scaled to latest EMEP values[2].	1958	1753
2010 UK ref	2010 UK emissions of CO, NO_X, SO_2 and NMVOC as projected by NAEI[3]. Emissions outside UK unchanged from 1998 ref.	1252	1167 (NECD)
2010 UK 1200	UK NMVOC emissions reduced to meet NECD according to NAEI scenario[3]. Emissions outside UK unchanged from 1998 ref.	1200 (NECD)	1167 (NECD)
2010 UK 1150	UK NMVOC emissions further reduced according to NAEI scenario[3]. Emissions outside UK unchanged from 1998 ref.	1150	1167 (NECD)
2010 NECD	As 2010 UK 1200, with other EU country totals set at NECD values. Other relevant country totals set to EMEP 2010 projection[2].	1200 (NECD)	1167 (NECD)
Notes: (1) 1998 emissions available from National Atmospheric Emissions Inventory, NAEI; (http://www.naei.co.uk); (2) EMEP website (http://www.emep.int/index.html) accessed August 2000. 'Latest' values generally corresponded to 1997. Projections for 2010 based on reduction plans in force at that time; (3) NAEI 2010 reference scenario supplied by J. Goodwin, AEA Technology; NMVOC reduction scenarios based on cost curve analysis supplied by N. Passant and J. Goodwin, AEA Technology.			

344. Relative to the 1998 reference, there was generally a clear decreasing trend in percentage ozone reduction from west to east as a result of purely UK measures, reflecting that the prevailing airflow is broadly from the east. In the limit, the Sibton site was totally unaffected by any UK reductions under the meteorological conditions of the present case study. The Harwell site was an exceptional case, in that the corresponding trajectory passed directly over London prior to arrival, and therefore received substantial UK emissions. As a result, the simulated influence of UK reductions was significantly greater than for sites further west (e.g. Aston Hill). Under the precise conditions of 31 July 1999, Harwell could be regarded as being representative of sites directly downwind of major UK population centres during an ozone episode.

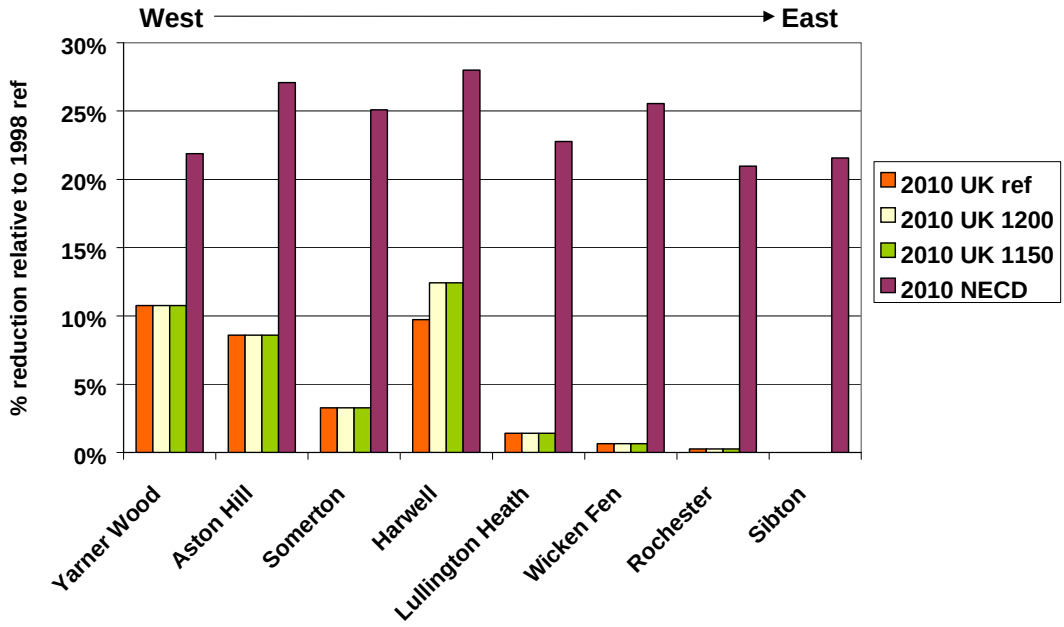

Figure 8.11 The percentage reduction in simulated peak ozone at each site, relative to the 1998 reference, for each of the scenarios in Table 8-7. Results represent the average of the results for each day of the week.

345. Figure 8.11 demonstrates that the reduction of precursor emissions to the 2010 NECD scenario (involving controls throughout Europe) was accompanied by notable reductions (*ca.* 20%-25%) in the simulated peak ozone concentrations at all eight southern UK sites. This emphasises the transboundary nature of the ground level ozone problem, and the importance of internationally co-ordinated strategies. The results indicated that the influence of the agreed precursor controls outside the UK had a greater influence on the simulated peak ozone than those within the UK at all eight sites, and that controls outside the UK would be essential for any significant reduction in peak values at locations to the east/south east of the country.

346. The conclusions from the above model runs mirror the outcome of the Heilbronn ozone field experiment in Germany in June 1994 [e.g. Moussiopoulos *et al*., 1997]. The aim of the study was to investigate if peak ozone concentrations during summer smog periods could be reduced by the aid of short-term local scale interventions. The measurements made during the experiment showed that local interventions led to lower concentrations of the emitted pollutants but only to minor changes in peak ozone concentrations. The main conclusion from the Heilbronn ozone experiment was that concerted large-scale interventions to the primary pollutant sources are needed for decisive reductions of peak ozone concentrations in Central Europe.

8.4.2 Ozone formation during the August 2003 episode

347. In conjunction with the NERC TORCH project, a modified version of the PTM was used to simulate regional scale ozone formation during late July and August 2003. The model is based on that of Derwent *et al.* (1996), with recent updates described by Utembe *et al.* (2005) and Johnson *et al.* (2006).

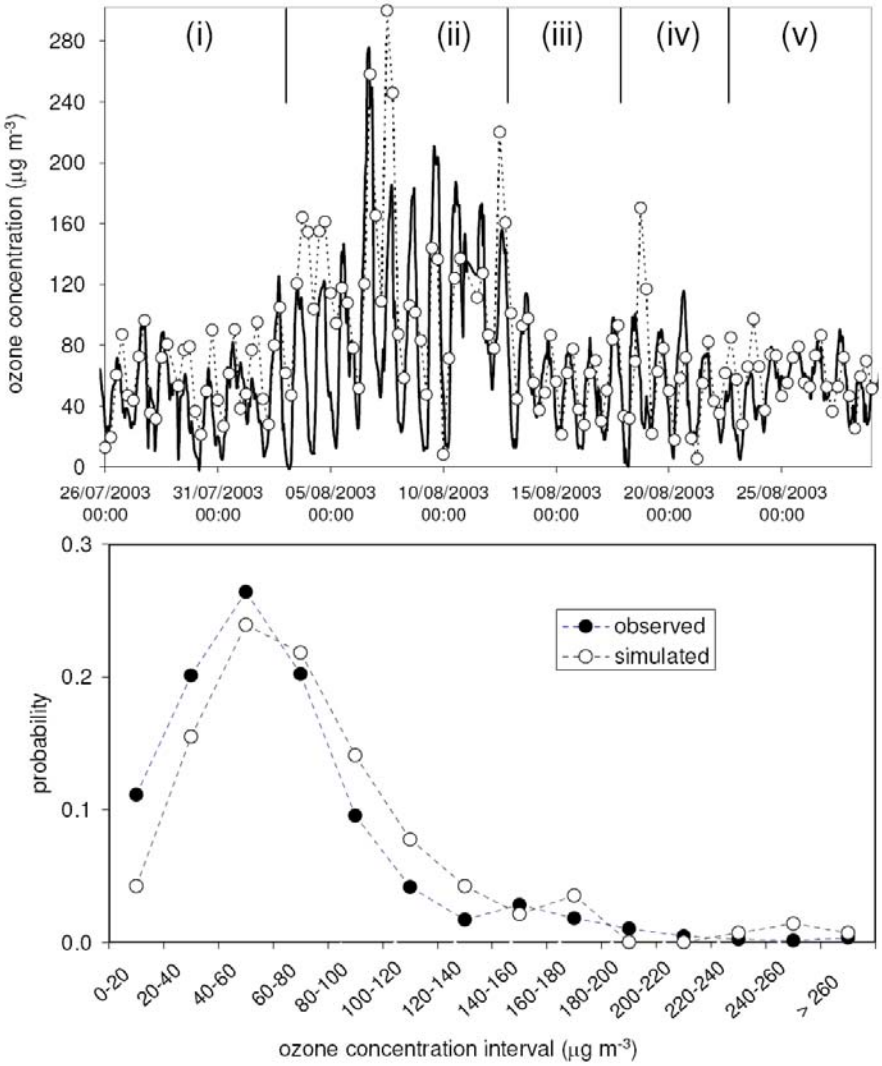

Figure 8.12 (Upper panel) comparison of observed ozone concentrations (line) and those simulated in the base case (open points) for the period of the TORCH campaign. The broken line joining the simulated points is to guide the eye, and is not intended to infer intermediate simulated concentrations. The campaign period (ii) identifies the anticyclonic period of the campaign. (Lower panel) comparison of the observed and simulated distributions of ozone concentrations for the campaign period. The ozone concentrations were measured by the University of York, as reported in Utembe *et al.* (2005).

8.4.2.1 Sensitivity to emission variations over the period 1990-2020

348. The 2003 campaign has also been simulated using historical emissions of NO_X, anthropogenic NMVOC, CO and SO_2 appropriate to the years 1990, 1995 and 2000 (based on NAEI and EMEP), and projected emissions for the years 2005, 2010, 2015 and 2020, based on relative UK figures reported in AQEG (2004; 2005). Figure 8.13 shows the trend in the simulated ozone distribution, which indicates that the same conditions in earlier years would have been accompanied by broader ozone distributions with greater daytime maxima and increased overnight depletion. The decreasing trend in the top-end ozone concentrations is driven primarily by reductions in emissions of anthropogenic VOC since 1990. The simulated campaign maximum concentration is ca. 30 % lower for 2005 conditions, compared with 1990 conditions, which agrees well with the observed decline at long-running rural sites, as presented in Chapter 2. The maximum ozone concentration is projected to show some modest decline with future emissions trends, followed by a

slight increase towards the end of the period. This is a consequence of the increasing trend in the emitted VOC/NOx ratio (i.e. as VOC emissions level off and NOx emissions continue to fall), and the fact that ozone formation generally tends to be VOC limited for the conditions of this campaign (see below).

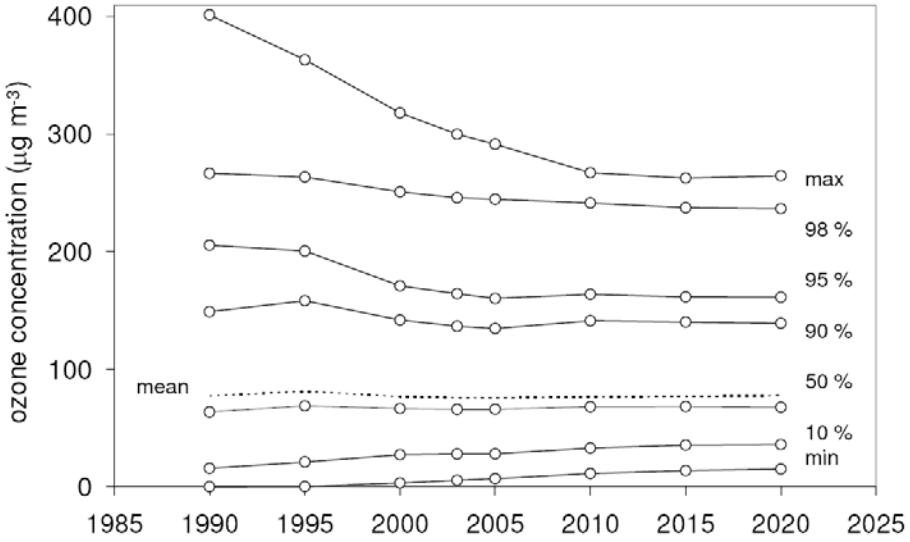

Figure 8.13 Simulated trend in ozone distribution statistics for the August 2003 episode at Writtle (Essex) as a function of emissions for the period 1990-2020.

349. The increasing (night-time) minima are a consequence of associated NO_X emissions reductions, resulting from decreased local removal of ozone by reaction with NO emitted into the shallow night-time boundary layer. The trend in the distribution thus shows similar features to those observed at rural sites (Chapter 2 evidence), although the observations relate to measurements throughout the year.

350. Figure 8.14 presents the same data in terms of the number of hours that ozone concentrations reached or exceeded 180 µg m^{-3}. Once again, the simulations with the earlier years' emissions show a greater number of exceedences, and display a similar trend to that observed at long-running rural sites in the UK, particularly for the heat-wave years of 1990 and 1995 relative to 2003. This elevated ozone metric is projected to show no further decline with future emissions trends (consistent with the 2006 heat-wave year observations), but a slight increase towards the end of the period owing to the increasing trend in the emitted VOC/NO_x ratio, as indicated above.

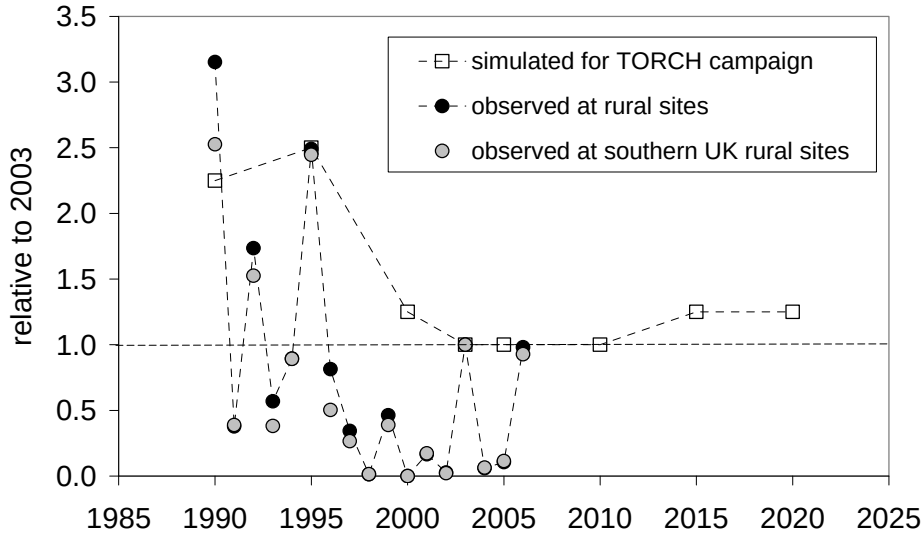

Figure 8.14 Simulated trend in the number of hours with ozone ≥ 180 µg m^{-3} for the August 2003 episode at Writtle (Essex) as a function of emissions for the period 1990-2020 (squares), compared with observed statistics at long-running UK rural sites (black circles) and at southern UK long-running rural sites (grey circles) for the period 1990-2006. Data are presented relative to the value simulated or observed in the reference 2003 case. The 11 Long-running rural sites which contribute to the data are identified in the Question 2 evidence. The southern UK sites are Lullington Heath, Sibton, Harwell, Yarner Wood and Aston Hill.

8.4.2.2 Effects of Incremental NOx and VOC Emissions Reductions

351. The effects of 10% incremental reductions in the emissions of NO_X and anthropogenic VOC for the years 1990, 2003 and 2020 were modelled to investigate whether ozone formation is limited by the availability of NO_X or VOC. Figure 8.15 shows the resultant simulated changes in ozone concentrations for the three years:
    - The 1990 scenario demonstrates strong VOC limitation throughout the campaign period, with NO_x reductions almost always leading to an increase in ozone concentration, such that VOC emissions controls are clearly the favoured option for reducing ozone concentrations. The approximately compensating influences of VOC and NO_X reductions also qualitatively explain the small change in the simulated 180 µg m^{-3} exceedence in the early part of the time series (Figure 8.14).
    - The results for the 2003 scenario demonstrate a shift towards NO_X-limitation, with an increased number of days (relative to 1990) where the NO_X control leads to a reduction in ozone concentration. Although there are two days within the campaign period where 10% NO_X control leads to slightly greater ozone reduction than 10% VOC control, it is clear that the campaign period is still dominated by VOC limited conditions.
    - The results for the 2020 scenario show that 10% NO_X control leads to comparable numbers of days when the ozone concentration is increased and decreased, and a further increase in the number of days (relative to 2003 and 1990) when NO_X control is more beneficial in reducing ozone concentrations than VOC control. Despite this, VOC reductions remain the favoured option when the whole campaign is considered.

352. The results therefore demonstrate that ozone formation for the conditions of the campaign at this location was predominantly VOC-limited for the complete time series, but shows a trend towards NO_x-limitation. Although this is in general agreement with previous assessments for south-east England, this sensitivity study also shows that VOC- and NO_X-limitation are not intrinsic properties of a location, and that it is possible to get events when either condition prevails.

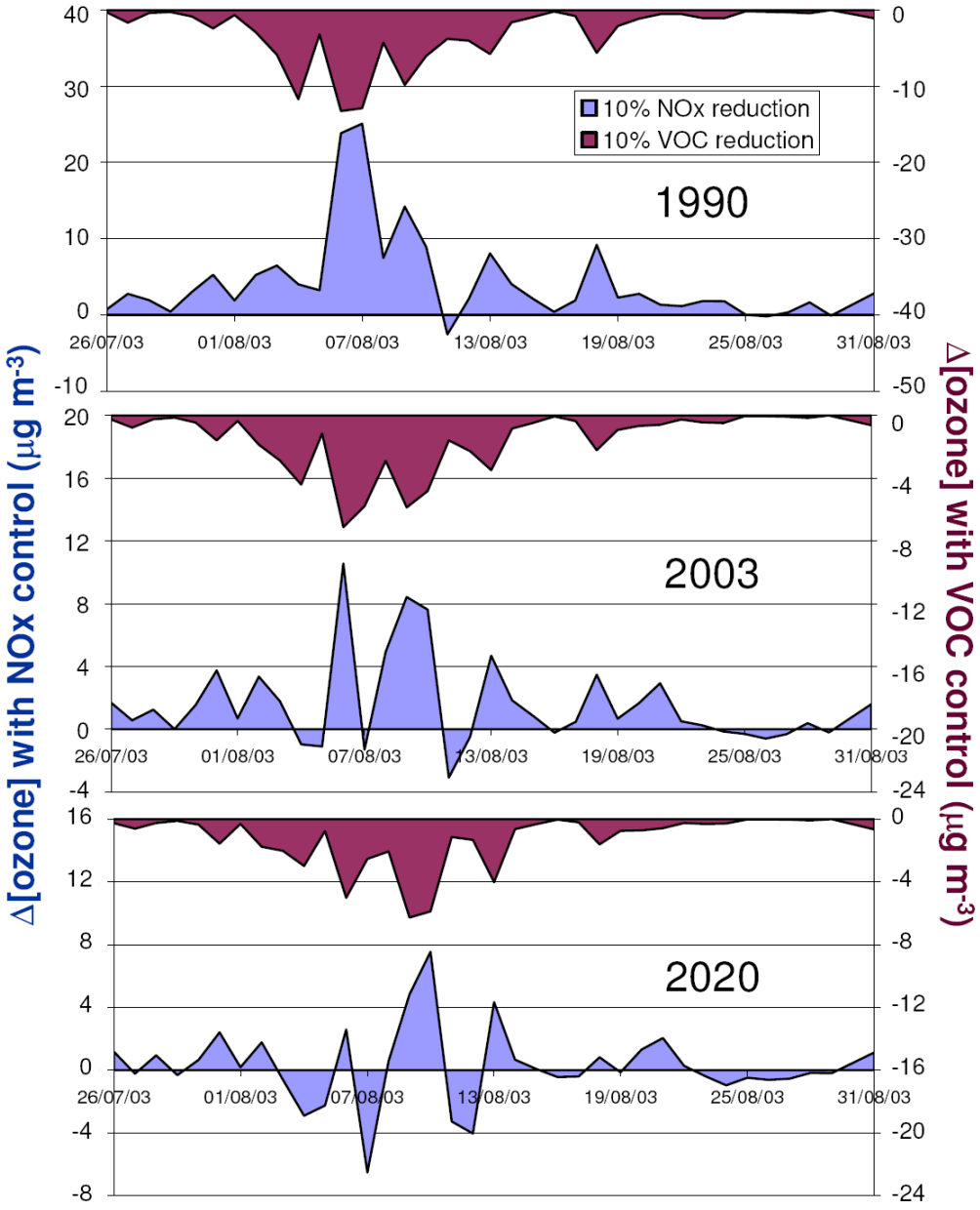

Figure 8.15 Simulated change in ozone concentration at the arrival point (Writtle, Essex) resulting from an incremental decrease of 10% in emissions of NO_X and anthropogenic VOC (AVOC) for the 1990 (upper panel), 2003 (middle panel) and 2020 (lower panel) emission scenario.

8.4.3 Further assessment of emissions reduction scenarios

353. Derwent (2008) has performed a similar study to that of the TORCH campaign by Jenkin (see Section 8.4.2). Derwent used the UK Photochemical Trajectory Model (UK PTM) to calculate ozone concentrations at Harwell for each day of 2005. The model made use of 3-dimensional 96-hour back trajectories provided by the Met Office NAME atmospheric dispersion model. Thirty trajectories were used for 15:00 each day because a single trajectory may not be a reliable guide to air-mass origins. The chemical mechanism employed was Carbon Bond IV. Base case emissions were taken for 1999 using EMEP and NAEI inventories.

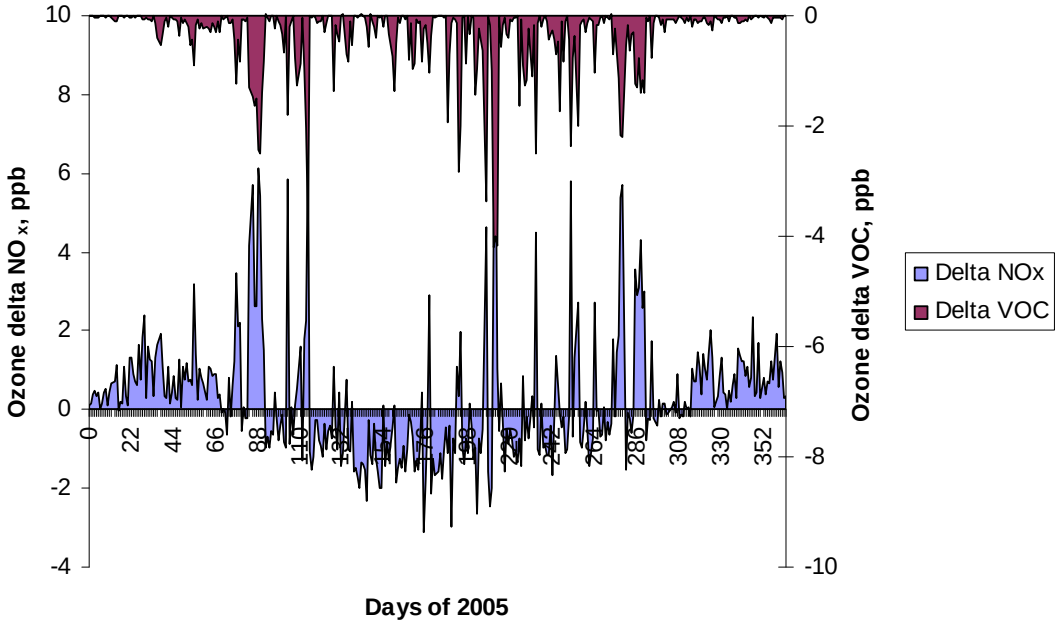

Figure 8.16 Changes in the maximum daily ozone concentration (in ppb) calculated at Harwell for 2005 for 30% reductions in the emissions of (a) oxides of nitrogen and (b) volatile organic compounds.

354. NO_x and NMVOC emissions were then separately reduced by 30% across the board and the ozone changes were calculated for each day of the year, as shown in Figure 8.16. In response to NOx reductions, daily maximum ozone levels sometimes increased and sometimes decreased. Ozone increases tend to occur during the winter and ozone decreases tended to occur during summer. On the other hand, daily maximum ozone levels only decreased in response to NMVOC reductions. Overall, the average of the daily ozone maximum values increased from 64.2 µg m^{-3} in the base case to 64.6 µg m^{-3} with 30% reduction in NO_x emissions but decreased to 63.4 µg m^{-3} with a 30% reduction in NMVOC emissions. This complements the scenario calculations based on the results from the TORCH campaign in 2003 (see Section 8.4.2).

355. Yu *et al.* (2007) have used the US one-atmosphere MODELS-3 modelling system to investigate three UK air pollution episodes (occurring in September 1998, June and December 2001), as part of a project for the Environment Agency. The overall aim of the study was to assess the use of advanced models as a tool to evaluate contributions of the Agency regulated sources to regional ozone production (and also SO_2 and NO_2 concentrations) under a range of episodic and typical situations. For ozone, the model was used to simulate the June 2001 episode and the effect of a notional additional VOC source, located in the Thames Estuary area, was investigated. Even with the notional source emitting only a very reactive VOC (ethene) at a constant rate of 10 tonnes per hour, the overall contribution of this point source to ground level O_3 concentrations was found to be very small. This more sophisticated modelling approach based on an actual air pollution episode again confirmed the limited impact of local action on local ozone concentrations.