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Ozone in Central England: the impact of 20 years of precursor emission controls in Europe

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ABSTRACT

Episodic peak ozone levels over the 1990–2007 period appear to have declined strongly whilst annual mean daily maximum levels have risen over the same period at monitoring sites within the midlands regions of the UK. Sensitivity studies carried out with a photochemical trajectory model have shown that European policies to control Volatile Organic Compound (VOC) and Nitrogen Oxides (NO_x) emissions are the likely cause of the decline in episodic peak levels. There appeared to have been little influence on the episodic peak from changes in intercontinental trans-Atlantic transport but an overwhelming influence on the annual mean daily maximum levels. Non-linear relationships between VOC and NO_x emission controls and ozone, together with the ambition level set by policy-makers, appear to explain why ozone levels in Central England still do not meet internationally accepted air quality guidelines despite two decades of policy actions within Europe.

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1. Introduction

Elevated ozone (O₃) levels have been the subject of much concern for European air quality policy-makers over the last 20 years. Policy actions to reduce O₃ levels began with the Nitrogen Oxides (NO_x) and Volatile Organic Compounds (VOCs) Protocols to the United Nations Economic Commission for Europe (UN ECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP) during the late 1980s (UN ECE, 2006). The reductions in O₃ precursor emissions required in these Protocols have been secured largely through vehicle emissions directives promulgated by the Commission of the European Communities, now the European Union (EU). During the 1990s, the UN ECE added the Gothenburg Protocol to abate acidifica-

tion, eutrophication and ground-level ozone. The EU implemented directives controlling emissions from large combustion plants, solvents and petrol evaporation. During the 2000s, the EU has sought to unify VOC and NO_x policy actions in its Clean Air for Europe (CAFÉ) Thematic Strategy on Air Pollution (Commission of the European Communities, 2005). One of these policy actions was to renegotiate the national emissions ceilings for SO₂, NO_x, VOCs and PM set within the EU National Emissions Ceilings (NEC) Directive (EU, 2001).

Here, we use a modelling approach to assess the impact of the last 20 years of O₃ precursor emissions controls in Europe on ground-level O₃. Central England has been chosen as the study area because it is a highly populated region of the UK

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where O₃ levels exceed internationally accepted air quality guidelines by wide margins (AQEG, 2009). There are a variety of O₃ metrics that could have been chosen for such a study (AQEG, 2009). Here, metrics have been chosen to represent both episodic peak O₃ levels and annual mean O₃ levels, reflecting acute and chronic exposures and their respective human health impacts (WHO, 2006, 2008). Assessments of O₃ trends in the UK point to a significant decline in episodic peak ozone levels but little overall trends in annual mean levels (AQEG, 2009).

The aim has been to use model sensitivity studies to determine those factors that have been most influential in shaping the observed trends with time in the chosen episodic peak and annual mean O₃ metrics. At the outset, four factors have been proposed and assessed in this study, including the NO_x vs VOC precursor emission reductions achieved, non-linearities in photochemical O₃ formation, the ambition level set by policy-makers in international policy negotiations and the influence of intercontinental trans-Atlantic O₃ transport.

2. The Photochemical Trajectory Model (PTM)

The Photochemical Trajectory Model used in the present study has previously been used to describe photochemical O₃ formation (Derwent et al., 1996, 1998) as well as secondary inorganic and organic aerosol formation (Abdalmogith et al., 2006; Johnson et al., 2006) in north-western Europe. Full details of the PTM are given elsewhere (Derwent et al., 2009) but a brief description of the extensions and improvements made is given below.

2.1. Model description

The model describes the chemical development within an air parcel that follows an air parcel trajectory for up to 10 days, forwards in time, reaching the chosen arrival point. The rate of change of the concentration of species, c_i , in molecule cm⁻³ s⁻¹ was described by a series of differential equations of the form in Eq. (1) below:

$$\frac{dc_i}{dt} = P_i - L_i c_i - \frac{V_i c_i}{h} + \frac{E_i}{h} \quad (1)$$

where P_i is the instantaneous production of species i from photochemistry, $L_i c_i$ is the instantaneous loss rate from photochemistry, V_i is the species-dependent dry deposition velocity, h , the time-dependent boundary layer depth and E_i the local areal emission rate of the pollutant sources in molecule cm⁻² s⁻¹. The systems of simultaneous stiff differential equations were integrated with a variable order Gear's method program FACSIMILE (Curtis and Sweetenham, 1987).

2.2. Treatment of meteorological processes

To capture the inherent variability in the meteorological processes, a Lagrangian or moving air parcel approach has been adopted. For each mid-afternoon of each day a large number of equally probable and randomly selected 96-h air parcel trajectories have been generated using the Met Office Numerical Atmospheric dispersion Model Environment

(NAME) model, a sophisticated Lagrangian atmospheric dispersion model (Manning et al., 2003). The NAME model was driven by meteorology from the Met Office numerical weather prediction model (Cullen et al., 1997; Davies et al., 2005) at 60 km horizontal resolution with between 26 and 33 vertical levels. Each trajectory was randomly selected from the many thousands of air parcel tracks simulated by NAME that described the histories of air parcels that had passed over the chosen arrival point. In this way, we have been able to describe the inherent variability in the atmospheric transport processes. Each air parcel trajectory was fully three-dimensional with information on the latitude, longitude and height of the air parcel and the temperature and atmospheric boundary layer depth at the air parcel location, recorded at hourly intervals backwards in time. If the air parcel height was less than the atmospheric boundary layer height, then the air parcel was assumed to be in the boundary layer and all deposition and emission processes were switched on. Otherwise, the deposition and emission processes were switched off. The trajectory length of 96 h was chosen to ensure that, on the occasions studied here, the starting point of each trajectory was over the North Atlantic Ocean or over a relatively unpolluted region in the northern or western fringes of Europe.

2.3. Treatment of emissions

The PTM used four coordinate systems to identify the location of the air parcel at any point along each air mass trajectory:

- (a) Latitude and longitude were used to fix the solar zenith angle and hence the photolysis rates. This coordinate system was also used to describe the emissions of α -pinene from natural biogenic sources, together with their variation with month of the year, based on the inventories provided by Guenther et al. (1995).
- (b) A 150 km \times 150 km grid defined for the European Monitoring and Evaluation Programme EMEP region.
- (c) A 50 km \times 50 km coordinate system which was used to fix the local instantaneous areal emission rates, E_i , of SO₂, CO, NO_x, VOCs, methane from man-made sources (Tuovinen et al., 1994), of ammonia and primary PM (EMEP, 2007) and of isoprene from natural biogenic sources (Simpson et al., 1995) when the air parcels were over the continent of Europe closest to the UK.
- (d) The UK Ordnance Survey 10 km \times 10 km grid system was utilised to fix areal emission rates over the United Kingdom based on the National Atmospheric Emission Inventory (Dore et al., 2007).

All gridded emissions were scaled over each country and for each pollutant, separately, to reproduce the national emissions totals for 1990, 1993, 1996, 1999, 2002 and 2006 from EMEP (2007). Forecast emission totals for 2010 were taken to be the country emission totals as set out in the NEC Directive (EU, 2001). Emissions were assumed to be constant throughout the year at the annual rate, except for the emissions of α -pinene from natural biogenic sources for which monthly gridded emissions were available. For the entire European continent, independent of location, and for all years, the speciation of the

total VOC emissions was taken from Passant (2002). Natural biogenic emissions of isoprene and α -pinene were held constant throughout the 1990–2010 period and so did not contribute any of the model O₃ trends.

2.4. Gas-phase chemical mechanisms

Three chemical mechanisms have been employed in this study and they span over two orders of magnitude in chemical complexity. The first is the Master Chemical Mechanism (MCM), a near-explicit chemical mechanism describing the detailed degradation of a large number of emitted organic compounds. This has been employed to describe formation of ozone and other secondary pollutants under conditions appropriate to the atmospheric boundary layer. The MCM can be accessed via the University of Leeds website (<http://mcm.leeds.ac.uk/MCM>). The degradation chemistry used in the MCM has been developed using published protocols (Saunders et al., 2003; Jenkin et al., 2003; Bloss et al., 2005). The MCM version used addressed 124 emitted VOC species and employed 4355 reactive compounds taking part in 12,723 chemical reactions. We have also employed the Common Representative Intermediates mechanism version 2 (CRI v2), a reduced mechanism of intermediate complexity which is directly traceable to the MCM (Jenkin et al., 2008). This mechanism addressed 99 emitted VOC species and employed 455 reactive compounds taking part in 1168 chemical reactions. In addition, the Carbon Bond Mechanism (CBM) has also been employed as an example of a highly condensed chemical mechanism (Gery et al., 1989). The version used here addressed 6 emitted VOC species, 51 reactive compounds and 100 chemical reactions. No changes were made in the VOC speciation with time or with location across Europe because of the dearth of available speciation data (see for example Vautard et al., 2007).

The VOC speciation from Passant (2002) was used without modification for the model runs employing the MCM since the VOCs treated in the MCM represented up to 90% of the total VOC mass emission. A scaling factor of 1.10 was used for the CRI mechanism because of the slightly reduced overlap between the VOC species in the CRI and the VOC speciation. The 665 emitted VOC species were converted directly into CBM VOC species: ETH, OLE, PAR, ALD2, TOL and XYL as described by Gery et al. (1989).

2.5. Photolysis reactions

The rates of the photolysis reactions, J , for all of the photochemically labile species were calculated from the instantaneous solar zenith angle, Z , using expressions of the form in Eq. (2):

$$J = l \times (\cos Z)^m \exp(-n \sec Z) \quad (2)$$

where the coefficients, l , m , n are available from the Master Chemical Mechanism website (<http://mcm.leeds.ac.uk/MCM>) for each photolysis reaction.

2.6. Deposition

Dry deposition was represented using a species-dependent dry deposition velocity approach. Deposition velocities for the

gas-phase chemical components were unchanged from previous work (Derwent et al., 1996). In addition, the dry deposition of up to 205 members of the peroxyacylnitrate family was given the same deposition velocity as peroxyacetylnitrate PAN. No allowance was made for the wet removal of PM components and organic hydroperoxides.

2.7. Initial and boundary conditions

The initial concentrations for most model species were set to zero. For ozone, methane (CH₄) and carbon monoxide (CO) initial concentrations were taken from the monthly mean baseline observations for each month of 1990, 1993, 1996, 1999, 2002 and 2005 for the atmospheric research station at Mace Head, Ireland (Derwent et al., 2007). For NO₂, SO₂, HNO₃ + NO₃⁻, NH₃ + NH₄⁺ initial concentrations were established based on the annual mean observations reported for the Valentia Observatory, Ireland in the EMEP monitoring network (Fjaeraa, 2006). The concentrations recorded at both these sites can be taken to be representative of North Atlantic maritime air masses. In this manner, we have been able to take into account quantitatively the impact of increasing background O₃ concentrations driven by intercontinental trans-Atlantic Ocean transport on European O₃ levels.

2.8. Observations

Hourly observations of O₃ were taken from an Air Quality Archive http://www.airquality.co.uk/archive/data_and_statistics.php for the Central England for each year from 1990 to 2007. A sketch map of Central England is shown in Fig. 1, giving the locations of the selected monitoring sites.

3. Modelling O₃ levels during photochemical episodes from 1990 to 2010

3.1. Modelling a photochemical episode in Central England during 1999

The PTM has been employed and developed to simulate the O₃ levels observed during the summer PUMA campaign (Pollution in the Urban Midlands Atmosphere) held during June and July 1999 within Central England (Harrison et al., 2006). From previous studies of this campaign (Walker et al., 2009), it has been learnt that the PTM gives an acceptable reproduction of the O₃ observations and that much of the observed O₃ was of regional rather than local origins. Furthermore, local Central England natural biogenic sources of VOCs were found to be a relatively minor source of O₃ compared with man-made VOC sources within the London area, Netherlands, Belgium and France (Walker et al., 2009). This photochemical episode was therefore considered an ideal choice for a modelling study of the trends in episodic O₃ over the last 20 years.

For each mid-afternoon, 1000 equal probability 96-h back-track air mass trajectories were generated for the arrival point at Pritchatts Road, Birmingham (52°27.4'N, 1°56.0'W) (star symbol, Fig. 1) using the NAME atmospheric dispersion model. At each hourly time point, the weighted mean of each trajectory parameter was calculated for each day's trajectory.

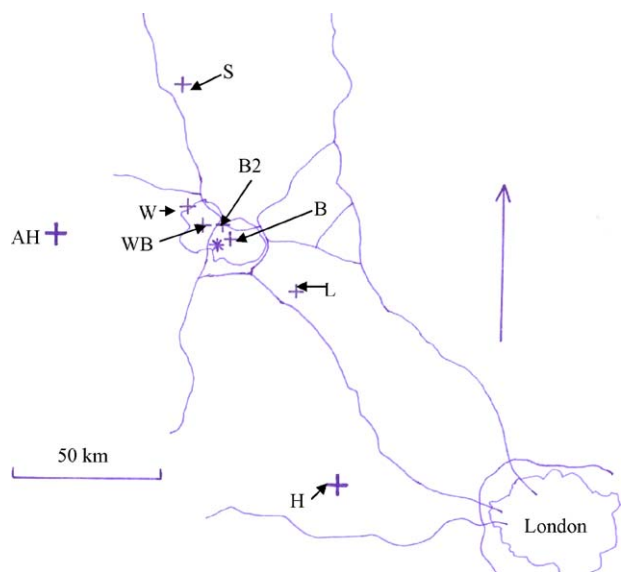


Fig. 1 – Sketch map of Central England showing the Birmingham and London conurbations and the trunk road system. Selected O₃ monitoring sites are shown as large + signs: EMEP stations, AH, Aston Hill, H, Harwell and urban monitoring stations as small + signs: B, Birmingham Centre, B2, Birmingham 2, L, Leamington, S, Stoke-on-Trent, W, Wolverhampton, WB, West Bromwich. The star symbol shows the location of Pritchatts Road, Birmingham.

Weighting employed the mixing ratio at the end of each of the 1000 trajectories of an inert tracer emitted with unit emission density across the land area of Europe calculated with the PTM. The weighted mean trajectory was then used to

represent the transport processes for each day of the PUMA campaign.

Fig. 2 illustrates the PTM performance for O₃ during the summer PUMA campaign. The model results (shown as circles for the MCM and + signs for the CRI mechanisms, respectively) are presented for the University of Birmingham, Pritchatts Road field site from the 20th June to 1st July 1999 as mid-afternoon 15.00 UTC mixing ratios. Also shown (as lines) are the observed mid-afternoon maximum O₃ mixing ratios observed at six urban monitoring sites (small + signs, Fig. 1) within a 60 km radius of the centre of the city of Birmingham and at two remote rural EMEP monitoring sites (large + signs, Fig. 1). Both the model and the observations exhibited periods of background O₃ levels in the range 20–50 ppb from 20th to 25th June and from 27th June to 1st July with an O₃ episode on 26th June in between.

On the 26th June, the PTM predicted 15.00 UTC O₃ mixing ratios of 94.3 and 94.6 ppb, respectively, with the MCM and CRI mechanisms. These compare closely with the maximum mid-afternoon hourly levels of 92 ppb observed at the Stoke-on-Trent and Leamington Spa urban monitoring sites and the range 76–92 ppb observed across all eight sites. Inspection of the inert tracer-weighted back-track air mass trajectory for the 26th June showed that it had passed over the Shetland Isles, the North Sea and the more populated and industrial regions of the Netherlands, Belgium, France and the south-east of the UK en route to the West Midlands as reported by Walker et al. (2009).

Over the 12-day period the PTM showed a small bias for O₃ (–1.6 ppb with the MCM and +2.5 ppb with the CRI mechanisms, respectively), a small mean normalised bias (–0.04 MCM and 0.06 CRI), root mean square errors of about 10 ppb and all model results within a factor of two of the observations. On this basis, the PTM performance was considered acceptable and furthermore it was concluded that there were no

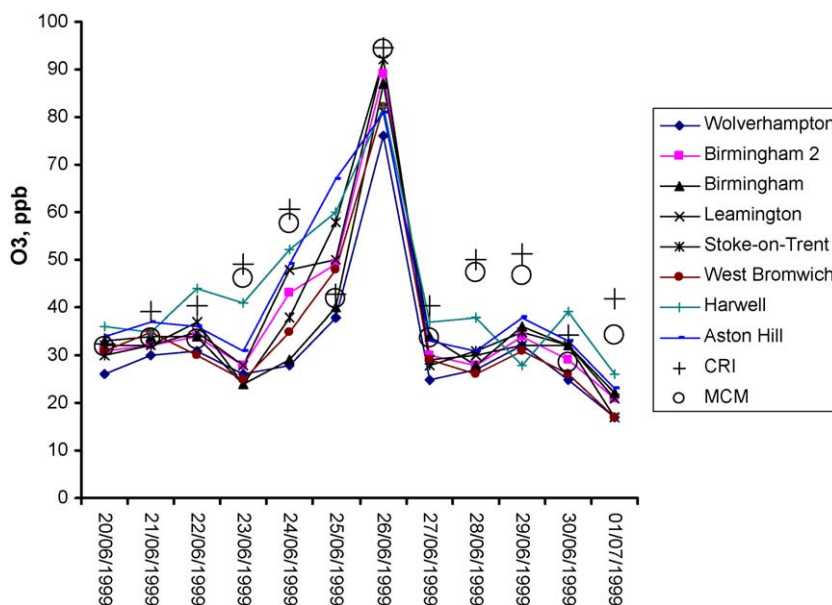


Fig. 2 – Daily maximum hourly mean ozone mixing ratios observed (lines with symbols) at six urban background and two rural monitoring sites in the West Midlands of the UK together with 15.00 UTC predictions from the PTM model using the MCM (circles) and CRI (plus signs) chemical mechanisms for summer PUMA campaign in 1999.

discernible differences between the model results with either of the chemical mechanisms: MCM or CRI.

3.2. Modelling episodic peak O₃ trends from 1990 to 2010

O₃ trends over the 1990–2010 period were examined using the PTM model by studying seven snapshot years: 1990, 1993, 1996, 1999, 2002, 2005 and 2010, as sensitivity cases. For each snapshot, the model input emissions data for SO₂, NO_x, VOCs, CO and NH₃ were set by changing the scaling factors from the base case 1999 values according to the national totals from EMEP (2007). The initial and boundary conditions for O₃ were also set to the appropriate June monthly mean baseline mixing ratios for Mace Head, Ireland for each snapshot year as reported by Derwent et al. (2007). In this way we have been able to take into account intercontinental O₃ transport and the growth in the O₃ background. Four of the equal probability 96-h back-track air mass trajectories that arrived at Pritchatts Road, Birmingham on the 26th June 1999 and gave PTM O₃ predictions within the observed range of 76–92 ppb were selected as the base case meteorology. Model concentrations were taken as the average over the four calculations to include some measure of meteorological variability. All other model input parameters remained unchanged from their base case values for each of the snapshot years, including the meteorological input data and natural biogenic emissions. That is to say, the episodic O₃ trends that have been examined are those which have arisen from changes in O₃ precursor emissions and changes in initial and boundary conditions. These trends have been examined as input parameter sensitivity studies relative to the 1999 base case and no attempt has been made to model the influence of year-on-year changes in meteorology and other factors, despite their likely importance.

Fig. 3 shows the influence of changes in O₃ precursor emissions and boundary and initial conditions on the 15.00

UTC mixing ratios calculated for the meteorological conditions of 26th June 1999 for each of the snapshot years. The observed annual maximum hourly O₃ mixing ratios for two rural EMEP monitoring sites in the UK Midlands: Aston Hill and Harwell over the 1990–2007 period are also shown in this figure. The observations at Harwell and Aston Hill show marked year-on-year variability superimposed on statistically significant downwards trends of -1.4 and -1.3 ppb per year. The influence of the two recent strongly photochemical years: 2003 and 2006 is evident as well as that of the poor summer of 2002. There has been a strong influence of UK and European O₃ precursor emission reductions on episodic O₃ formation as shown by the decline in the PTM predictions. The observations also exhibit significant year-on-year variability which has not been represented in the PTM. Nevertheless, there is a striking similarity between the downwards trends found in the model, -1.7 ppb per year, and in the observations.

A sensitivity case was run 'with' and 'without' solvent controls, revealing a significant change in model trend (see Fig. 3), confirming the importance of VOC emission reductions on the model predictions. A further sensitivity case was run in which the influence of the changes in the intercontinental trans-Atlantic O₃ transport was removed by resetting all the initial and boundary conditions to their 2005 values and rerunning all of the snapshot years. No significant change was found in the model predicted O₃ downwards trend.

A final sensitivity case was examined for the year 2010 in which the VOC, NO_x and SO₂ emissions were set everywhere at the EU NEC Directive emission ceilings and the initial and boundary conditions set at 2005 values. The PTM result is shown as the filled circle in Fig. 3. Even with the full implementation of the EU NEC Directive, episodic peak O₃ levels remain above internationally accepted air quality guidelines (WHO, 2006) (broken line, Fig. 3, expressed as 55.6 ppb which is the 1-h maximum mixing ratio equivalent to the 50 ppb 8-h maximum). Indeed, a slight rise can be seen

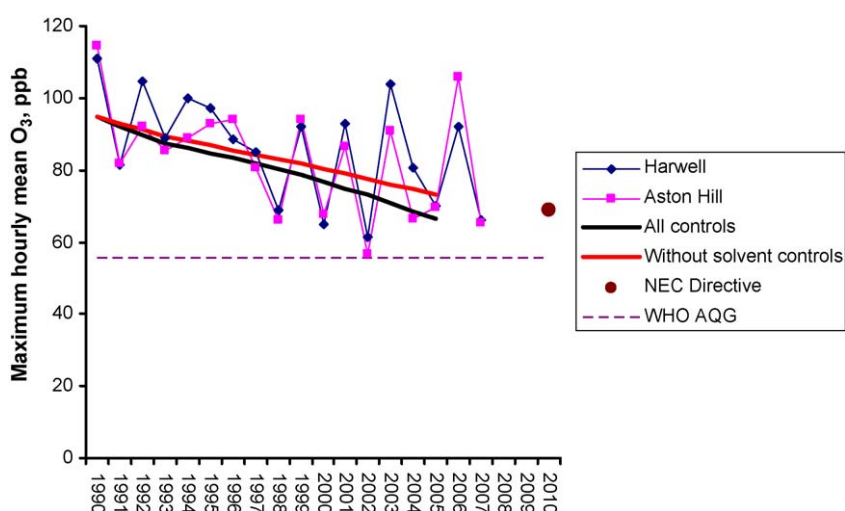


Fig. 3 – Time development of the annual maximum hourly mean ozone mixing ratios from 1990 to 2010 in the observations (lines with symbols) at two rural EMEP monitoring stations and in the PTM (solid lines: MCM, for all controls and without solvent controls). The filled circle shows the PTM model results for 2010 with the NEC Directive fully implemented. The broken line shows the WHO maximum 8-h mean air quality guideline for ozone expressed as the equivalent maximum 1-h mean.

between the end of the 'all controls' line at 66.4 ppb and the 2010 point at 68.9 ppb. This has been caused by a mis-match in the timing of the VOC controls which have largely been completed by 2005 and the NO_x controls which are expected later in the study period. This late NO_x reduction has caused a slight increase in model episodic O₃ levels. NO_x controls may sometimes cause an increase in O₃ due to a reduction in NO_x inhibition of photochemical O₃ formation.

There is a policy issue concerning the contributions made to the decline in episodic peak O₃ levels from emission controls applied to the road transport and stationary VOC sources. Fig. 3 shows the contribution to the ozone trend resulting from controls to both road transport and stationary VOC sectors ('all controls') and without any controls applied to the solvents sector ('without solvent controls') but with road transport and other stationary sources fully controlled. The difference between these lines shows the contribution made by controlling solvent emissions. On this basis, 'all controls' reduced episodic peak O₃ by about 28.2 ppb over the 1990–2005 period, of which about 6.7 ppb reduction came from solvent emission controls on their own. A further sensitivity study (not shown in Fig. 3) identified the contribution to the O₃ trend that had come from controls applied to decorative paint usage alone to be 0.9 ppb. Paints are thus a relatively minor component of solvents.

4. Annual mean O₃

4.1. Modelling O₃ on a daily basis through 2005 at a location in Central England

For the annual ozone metric, focus has been given to the year 2005 which was neither extremely photochemically active compared to the year 2003, nor was it heavily influenced by natural sources, such as agricultural burning, as was 2006. The chosen observational metric was the mean monthly daily maximum 8-h running mean O₃ mixing ratio and the model metric was the mean monthly daily mid-afternoon maximum ozone mixing ratio. Attention has been focussed on the observed and model behaviour for the Central England rural EMEP monitoring site at Harwell, Oxfordshire. Fig. 4 presents a comparison of the mean monthly observations and model results for each month of 2005. The model follows the observed seasonal cycle closely, except for the overestimation of the November and December 2005 values. No significant differences were found in model performance between the PTM results obtained with the CRI or CBM mechanisms.

Model monthly mean biases varied from 1 to 3 ppb during the spring months, –3 to –6 ppb during the summer months, to 2–8 ppb during the winter months. Mean fractional biases varied between –0.09 and 0.2 except during November and December. Model results were generally well within the range of a factor of 2 of the observations, with less than 3 days per month outside of this range. The exception being November and December, when 5 days or less were outside of this range. On this basis, PTM model performance was considered satisfactory for the annual metric, except during November and December 2005. It is likely that the O₃ observations were unduly influenced by NO_x emissions from local construction

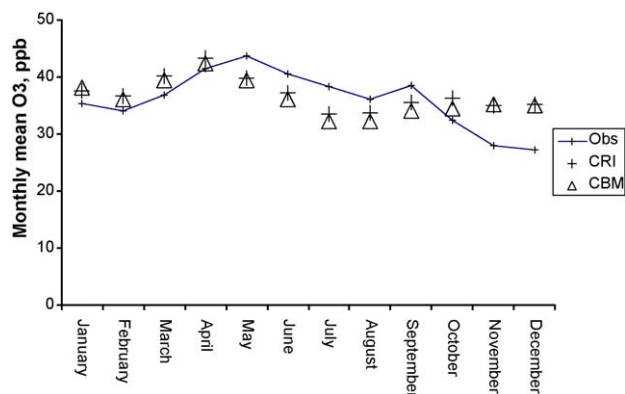


Fig. 4 – Monthly mean daily maximum 8-h rolling mean ozone observations at the rural EMEP monitoring site at Harwell, Oxfordshire together with the monthly mean 15.00 UTC ozone mixing ratios estimated with the PTM employing the CRI and CBM mechanisms.

activity during these months. These sources were not included in the emission inventories used.

4.2. Modelling annual O₃ trends from 1990 to 2010

Ozone trends over the 1990–2010 period were studied using the 7 snapshot years by examining the sensitivity of the base case 2005 results to changes in European VOC and NO_x emissions and initial and boundary conditions to allow for changes in intercontinental trans-Atlantic O₃ transport. Fig. 5 presents the PTM results for the Harwell, Oxfordshire site employing the CRI and CBM mechanisms. Also shown are the observations for the Central England rural EMEP monitoring sites at Aston Hill and Harwell. The observations exhibit a significant amount of site-to-site variability as well as year-on-year variability over the 1990–2007 period. Generally speaking, the levels at Harwell and Aston Hill track each other closely but with an offset of about 2–3 ppb that is consistent with the broad spatial patterns across the UK characterised by Jenkin (2008). The years 2003 and 2006 show significant apparent year-on-year variability. The elevated O₃ levels associated with the 2003 heat-wave did not strongly influence the more northerly and westerly Aston Hill site and those associated with the 2006 agricultural fires did not strongly impact the more southerly Harwell site. In contrast, the model results show a rise to a maximum in 1999, followed by a decline through to 2005 and 2010. There are year-on-year influences in the observations involving meteorological variability and other factors such as natural biogenic emissions that are not captured by the model which employs constant 2005 meteorology.

Fig. 5 shows the influence of the selection of the chemical mechanism. The PTM results with the CRI (solid red line) and CBM (solid black line) mechanisms showed the same trends with time, though with a small offset that declined somewhat through the study period. The differences between the two sets of model results are small compared with the root mean squares errors found in the comparison with the 2005 observations.

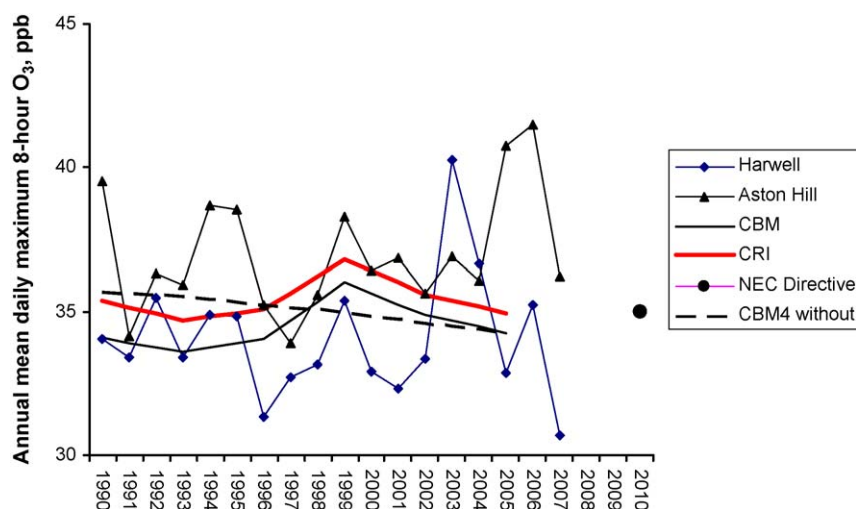


Fig. 5 – Trends in the annual ozone metric from observations at the rural EMEP monitoring sites at Aston Hill and Harwell in the UK Midlands and from the PTM employing the CRI and CBM mechanisms.

The annual mean metrics show increases of 0.02 and 0.09 ppb per year over the 1990–2007 period at the Harwell and Aston Hill sites, respectively, which compare reasonably well with the 0.09 ppb per year trend found with the PTM model. Also shown in Fig. 4 (broken black line) are the results from a sensitivity study in which the boundary and initial conditions were held constant at their 2005 values to represent the situation with unchanging intercontinental trans-Atlantic O₃ transport. In this case, the PTM model shows a downwards trend of –0.1 ppb per year due to emission changes alone. On this basis, it is concluded that the changing intercontinental transport has exerted a major influence of model O₃ trends and has over-ridden the downwards trend that would have occurred from emission reductions and produced an overall upwards trend in the annual mean metric.

Fig. 5 (filled circle) also shows the impact of meeting the EU NEC Directive in 2010 on the annual mean ozone metric. The PTM model shows a rise of 0.7 ppb between 2005 and 2010 showing that the full implementation of the EU NEC Directive may not bring about a decrease in the annual mean metric despite maintaining constant initial and boundary conditions between 2005 and 2010. This rise results from the markedly different impacts of VOC and NO_x controls on the annual mean metric. Because VOC controls always act to decrease ozone and only during the summer months, they act to decrease the metric. However, because NO_x controls act to increase O₃ during the spring, autumn and winter months and may increase or decrease O₃ during the summer months, they generally act to increase the metric. Because the impact of the EU NEC Directive between 2005 and 2010 is to bring more NO_x controls, then the metric exhibits an overall increase.

5. Discussion and conclusions

In this study, sensitivity analyses have been employed to determine the likely main influences on O₃ trends over the

close to 20-year period from 1990. Focus has been given to the following issues:

- NO_x vs VOC precursor emission reductions achieved,
- non-linearities in photochemical O₃ formation,
- intercontinental trans-Atlantic O₃ transport,
- the ambition level achieved in international policy negotiations.

Episodic peak O₃ levels exert an important influence on human health (WHO, 2006, 2008). Observed peak O₃ levels, see Fig. 3, in Central England have declined steadily since 1990 but this decline has not been enough by 2007 to meet internationally accepted air quality guidelines set by WHO (2006). The analysis has focussed on rural O₃ levels, despite the human health perspective, because rural levels indicate maximum population exposure levels since O₃ levels in UK urban areas have always been found to be lower than those in the rural areas surrounding them (AQEG, 2009).

Sensitivity studies using the PTM have shown that much of the observed decline in episodic peak O₃ levels is likely to have resulted from reductions in VOC and NO_x emissions across Europe. This conclusion is based on the similarity between the observed trend (about –1.4 ppb per year) and the model emission sensitivity (–1.7 ppb per year). The PTM modelling should not be taken as a full scenario analysis covering the 1990–2007 period. Account has not been taken of meteorological variability as has been the case in Andersson et al. (2006), for example, or of changes in a number of model input parameters including the O₃ dry deposition velocity, natural biogenic emissions of isoprene and α-pinene, precursor emissions from wild fires and other non-inventoried sources (see Solberg et al., 2008 for a full discussion of such issues). If changes in the initial and boundary conditions were not included, model O₃ trends were not significantly altered showing that they had not strongly influenced trends in episodic peak O₃.

An important question is why have episodic peak O₃ levels not declined enough to meet WHO (2006) air quality guidelines by 2007. Whilst NO_x and VOC precursor emissions have declined by about 50–60%, episodic O₃ levels have only declined by 30%. This is an indication of the importance of non-linearities inherent in the O₃ vs NO_x and VOC source–receptor relationships. This is an important scientific issue which should have been taken into account in the design and formulation of the UN ECE Protocols and EU air quality policies. The underlying reason therefore for not meeting the WHO air quality guideline is that the policy-makers have not set a high enough ambition level for the agreed reductions in European NO_x and VOC emissions. VOC and NO_x emission reductions would have had to have been reduced by about 70% by 2010 rather than the 50–60% achieved, for the WHO air quality guideline to have been achieved in Central England.

Annual O₃ levels in Central England appear to have increased slightly with an upwards trend of +0.02 to +0.09 ppb per year over the period from 1990 to 2007. Model sensitivity studies to changes in both regional precursor emission changes and changes in initial and boundary conditions also indicate an upwards trend of +0.09 ppb per year. Again, it must be emphasised that these studies are not full scenario analyses but are merely emission sensitivity studies with meteorological and all other model input data held constant. If the model trend is examined with and without changes in the initial and boundary conditions due to intercontinental trans-Atlantic transport, the model trend reverses in sign from +0.09 ppb per year to –0.10 ppb per year. On this basis, it is concluded that the observed behaviour in the annual metric at Central England sites could only have been achieved if the change in intercontinental trans-Atlantic transport had acted to offset the downward trend due to precursor emission reductions. Inspection of the annual PTM simulations shows that the reductions in VOC emissions have led largely to decreasing summertime levels. NO_x reductions on the other hand have also led to reductions in summertime levels but accompanied by increases in wintertime levels. As a result, the combined reductions in European VOC and NO_x emissions since 1990 have led to a less than linear reduction in the annual metric, thus explaining the relatively weak trend of –0.10 ppb per year found for precursor emission changes alone. Non-linearity appears to have been a significant issue because of the different seasonal influences of the NO_x and VOC precursors on the annual metric.

WHO (2006) suggests that whilst there is some evidence that long-term exposure to O₃ may have chronic effects, it is not sufficient to recommend an annual guideline. WHO (2008) points to a number of uncertainties that mean that it will not be possible in the near term to define a no-effects O₃ concentration for the general population. For the purposes of this study, we propose that a reasonable policy target for the annual metric should be one of a decreasing trend beyond 2010. Further emission sensitivity studies looking at the situation beyond 2010 pointed to decreasing values of the annual metric being more likely with further emission reductions of VOCs of about 30%, about 60% for NO_x or about 30% for VOC and NO_x combined, making reasonable assumptions concerning future levels of intercontinental trans-Atlantic O₃ transport.

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