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## **particles in the United Kingdom Photochemical generation of secondary**

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R. G. Derwent and A. L. Malcolm

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# $\frac{1}{\text{Beta}.2000.0674}$ <br>Photochemical generation of secondary<br>particles in the United Kingdom particles in the United Kingdom particles in the United Kingdom<br>BY R. G. DERWENT AND A. L. MALCOLM

BY R. G. DERWENT AND A. L. MALCOLM<br>*Climate Research Division, Meteorological Office,*<br>*London Boad, Brasknell BC19 9SZ, IIK* R. G. DERWENT AND A. L. MALCOLM<br>*Late Research Division, Meteorological Office,*<br>*London Road, Bracknell RG12 2SZ, UK* 

Bohaon Road, Brackhell RG12 252, UR<br>While much of the suspended particulate matter found in the ambient air in urban<br>areas has been emitted directly into the atmosphere, some has been formed there by While much of the suspended particulate matter found in the ambient air in urban<br>areas has been emitted directly into the atmosphere, some has been formed there by<br>photochemical reactions from gaseous precursor species. Tw While much of the suspended particulate matter found in the ambient air in urban<br>areas has been emitted directly into the atmosphere, some has been formed there by<br>photochemical reactions from gaseous precursor species. Tw areas has been emitted directly into the atmosphere, some has been formed there by<br>photochemical reactions from gaseous precursor species. Two major components of<br>this secondary particulate matter have been selected for de this secondary particulate matter have been selected for detailed study in the United Kingdom context. These are particulate sulphate, formed from the precursor, sulphur dioxide, and secondary organic aerosols, formed from Kingdom context. These are particulate sulphate, formed from the precursor, sularomatic hydrocarbons. A Lagrangian dispersion model has been used to describe phur dioxide, and secondary organic aerosols, formed from oxidation of terpenes and<br>aromatic hydrocarbons. A Lagrangian dispersion model has been used to describe<br>the emissions, transport and transformation of  $SO_2$  into aromatic hydrocarbons. A Lagrangian dispersion model has been used to describe<br>the emissions, transport and transformation of  $SO_2$  into particulate sulphate. The<br>origins of the particulate sulphate are delineated in two the emissions, transport and transformation of  $SO_2$  into particulate sulphate. The origins of the particulate sulphate are delineated in two separate pollution episodes which occurred during 1996. A photochemical traject origins of the particulate sulphate are delineated in two separate pollution episodes<br>which occurred during 1996. A photochemical trajectory model is used to describe<br>the formation of secondary organic aerosols and to asse which occurred during 1996. A photochemical trajectory model is used to describe<br>the formation of secondary organic aerosols and to assess the relative contributions<br>from natural biogenic and man-made precursor sources dur the formation of secondary organic<br>from natural biogenic and man-mac<br>photochemical pollution episodes. photochemical pollution episodes.<br>Keywords: suspended particulate matter; particulate sulphate;

secondary organic aerosols; terpenes; aromatic hydrocarbons; SO<sub>2</sub>

### 1. Introduction

1. Introduction<br>Human health concerns about ambient concentrations of suspended particulate mat-<br>ter particularly in our cities are not new Recently the application of sophisticated the Human health concerns about ambient concentrations of suspended particulate mat-<br>ter, particularly in our cities, are not new. Recently, the application of sophisticated<br>statistical techniques to daily medical records Human health concerns about ambient concentrations of suspended particulate matter, particularly in our cities, are not new. Recently, the application of sophisticated statistical techniques to daily medical records has re ter, particularly in our cities, are not new. Recently, the application of sophisticated statistical techniques to daily medical records has revealed links between suspended particulate matter and adverse health outcomes statistical techniques to daily medical records has revealed links between suspended particulate matter and adverse health outcomes at current levels in many cities worldwide (Dockery *et al.* 1993; Pope *et al.* 1995). This has prompted far-reaching reassessments of the potential importance of urban part reassessments of the potential importance of urban particulate pollution in future assessments of the potential importance of urban particulate pollution in future<br>c-quality policy.<br>While much of the suspended particulate matter found in urban areas has been<br>rectly injected into the atmosphere from pollu

air-quality policy.<br>While much of the suspended particulate matter found in urban areas has been<br>directly injected into the atmosphere from pollution sources such as industrial boilers,<br>furnaces domestic fires and motor ve While much of the suspended particulate matter found in urban areas has been<br>directly injected into the atmosphere from pollution sources such as industrial boilers,<br>furnaces, domestic fires and motor vehicles, some of thi directly injected into the atmosphere from pollution sources such as industrial boilers, furnaces, domestic fires and motor vehicles, some of this material has been formed in the atmosphere by chemical reactions (QUARG 199 the atmosphere by chemical reactions (QUARG 1996). Since most of these chemical the atmosphere by chemical reactions (QUARG 1996). Since most of these chemical reactions are driven by sunlight, they are termed photochemical reactions. The suspended particulate matter formed in the atmosphere is termed reactions are driven by sunlight, they are termed photochemical reactions. The sus-<br>pended particulate matter formed in the atmosphere is termed secondary particulate<br>matter, or secondary particles, to distinguish it from pended particulate matter formed in the atmosphere is termed secondary particulate<br>matter, or secondary particles, to distinguish it from the primary emitted material.<br>In air-quality policy terms, this distinction is param matter, or secondary particles, to distinguish it from the primary emitted material.<br>In air-quality policy terms, this distinction is paramount. For emission controls to be effective against secondary particles, they have In air-quality policy terms, this distinction is paramount. For emission controls to be particles.

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<sup>2644</sup> *R. G.DerwentandA.L.Malcolm*

2644 R. G. Derwent and A. L. Malcolm<br>The term 'generation of secondary particulate matter' refers to a rather general and unspecific process which must be split down at the outset into a more spe-The term 'generation of secondary particulate matter' refers to a rather general<br>and unspecific process which must be split down at the outset into a more spe-<br>cific set of clearly defined atmospheric processes. The term d and unspecific process which must be split down at the outset into a more specific set of clearly defined atmospheric processes. The term describes primarily the processes whereby gas-phase chemical reactions involving spe cific set of clearly defined atmospheric processes. The term describes primarily the<br>processes whereby gas-phase chemical reactions involving specific precursor gases<br>produce low-volatility products which are capable of ho processes whereby gas-phase chemical reactions involving specific precursor gases<br>produce low-volatility products which are capable of homogeneous nucleation to<br>form tiny new particles that can then increase in size by coa produce low-volatility products which are capable of homogeneous nucleation to<br>form tiny new particles that can then increase in size by coagulation and capture<br>by pre-existing ambient particles. The term also describes th form tiny new particles that can then increase in size by coagulation and capture<br>by pre-existing ambient particles. The term also describes the processes whereby<br>the low-volatility gas-phase reaction products condense ont by pre-existing ambient particles. The term also describes the processes whereby<br>the low-volatility gas-phase reaction products condense onto pre-existing ambient<br>particles, the so-called heterogeneous nucleation process. the low-volatility gas-phase reaction products condense onto pre-existing ambient<br>particles, the so-called heterogeneous nucleation process. While homogeneous nucle-<br>ation may potentially increase both the number of aeroso particles, the so-called heterogeneous nucleation process. While homogeneous nucleation may potentially increase both the number of aerosol particles and the mass of the aerosol particles per unit volume. Homogeneous nucle ation may potentially increase both the number of aerosol particles and the mass of<br>the aerosol particles per unit volume in the atmosphere, heterogeneous nucleation<br>can only increase the mass of the aerosol particles per the aerosol particles per unit volume in the atmosphere, heterogeneous nucleation<br>can only increase the mass of the aerosol particles per unit volume. Homogeneous<br>nucleation operates in the ultrafine particle size range, a can only increase the mass of the aerosol particle<br>nucleation operates in the ultrafine particle size ranges.<br>across the ultrafine and fine particle size ranges.<br>The main chemical constituents of secondary r cleation operates in the ultrafine particle size range, and heterogeneous nucleation<br>ross the ultrafine and fine particle size ranges.<br>The main chemical constituents of secondary particulate matter that have been<br>entified

fields across the ultrafine and fine particle size ranges.<br>The main chemical constituents of secondary particulate matter that have been<br>identified generally in urban locations include sulphuric acid and ammonium sul-<br>pha The main chemical constituents of secondary particulate matter that have been<br>identified generally in urban locations include sulphuric acid and ammonium sul-<br>phate, ammonium and other nitrates and organic compounds (Finl phate, ammonium and other nitrates and organic compounds (Finlayson-Pitts  $\&$  Pitts 1986). The sulphur- and nitrogen-containing secondary particulate constituents phate, ammonium and other nitrates and organic compounds (Finlayson-Pitts & Pitts 1986). The sulphur- and nitrogen-containing secondary particulate constituents are largely derived from the photochemical oxidation of manare largely derived from the<br>precursors. In contrast, the o<br>natural biogenic precursors.<br>This paper focuses on quali ecursors. In contrast, the organic constituents appear to have been derived from<br>tural biogenic precursors.<br>This paper focuses on quality policy for the United Kingdom and aims to address<br>e two following questions.

natural biogenic precursors.<br>This paper focuses on quali<br>the two following questions. the two following questions.<br>(1) Is it possible to attribute the origins of the secondary particulate sulphate

- For interestigally solutions.<br>Is it possible to attribute the origins of the secondary particulate sulphate<br>observed in the UK to UK  $SO_2$  sources alone or are European  $SO_2$  sources also<br>making a contribution? Is it possible to attribute<br>observed in the UK to UK<br>making a contribution?
- % observed in the UK to UK  $SO_2$  sources alone or are European  $SO_2$  sources also<br>making a contribution?<br>(2) Is it possible to assess the likely contribution from natural biogenic sources to<br>secondary organic aerosol leve making a contribution?<br>Is it possible to assess the likely contribution fi<br>secondary organic aerosol levels in the UK? secondary organic aerosol levels in the UK?<br>The approach adopted in our study deals with secondary particles in the fine

secondary organic aerosol levels in the UK?<br>The approach adopted in our study deals with secondary particles in the fine<br>particle size range as a whole and does not deal directly the very smallest of particles<br>in the ultra The approach adopted in our study deals with secondary particles in the fine<br>particle size range as a whole and does not deal directly the very smallest of particles<br>in the ultrafine particle size range per se. There are a particle size range as a whole and does not deal directly the very smallest of particles<br>in the ultrafine particle size range per se. There are a number of reasons why we have<br>chosen to address fine particles, generally, r in the ultrafine particle size range per se. There are a number of reasons why we have<br>chosen to address fine particles, generally, rather then ultrafine particles in particular.<br>Currently, the modelling tools that we have chosen to address fine particles, generally, rather then ultrafine particles in particular.<br>Currently, the modelling tools that we have at our disposal are rudimentary, the gaps<br>in our understanding are wide, and the uncer Currently, the modelling tools that we have at our disposal are rudimentary, the gaps<br>in our understanding are wide, and the uncertainties are huge. While there are many<br>years of measurements of fine particles against whic in our understanding are wide, and the uncertainties are huge. While there are many<br>years of measurements of fine particles against which our models can be verified,<br>there are few corresponding measurements of ultrafine pa years of measurements of fine particles against which our models can be verified,<br>there are few corresponding measurements of ultrafine particles. It is not possible, at<br>present, to quantify accurately how much of the seco there are few corresponding measurements of ultrafine particles. It is not possible, at<br>present, to quantify accurately how much of the secondary particulate matter in UK<br>urban areas was formed by the homogeneous and heter present, to quantify accurately how much of the secondary particulate matter in UK<br>urban areas was formed by the homogeneous and heterogeneous nucleation routes.<br>Furthermore, there are internationally accepted air-quality urban areas was formed by the homogeneous and heterogeneous nucleation routes.<br>Furthermore, there are internationally accepted air-quality standards and criteria<br>values for fine particles with which to judge public-health Furthermore, there are internationally accepted air-quality standards and criteria<br>values for fine particles with which to judge public-health significance but none yet<br>exist for ultrafine particles. However, in addressing values for fine particles with which to judge public-health significance but none yet<br>exist for ultrafine particles. However, in addressing the above two questions for fine<br>particles, we are necessarily producing answers t exist for ultrafine particles. However, in addressing the above particles, we are necessarily producing answers that are relev<br>of ultrafine particles and their importance to public health. of ultrafine particles and their importance to public health.<br>2. Source attribution of particulate sulphate in the UK

2. Source attribution of particulate sulphate in the UK<br>Of all the chemical constituents of secondary suspended particulate matter, easily the<br>best quantified are sulphuric acid and ammonium sulphate aerosols, known collec **best quantified are sulphuric acid and ammonium sulphate aerosols, known collections** best quantified are sulphuric acid and ammonium sulphate aerosols, known collec-<br>*Phil. Trans. R. Soc. Lond.* A (2000)

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*Photochemical generationofsecondaryparticles in the UK* <sup>2645</sup>

In this study, we address the origins of the particulate sulphate observed in the United Kingdom and ask whether it has been derived from UK  $SO_2$  sources or whether European  $SO_2$  sources also make a contribution. We have employed the United Kingdom and ask whether it has been derived from UK  $SO_2$  sources or whether European  $SO_2$  sources also make a contribution. We have employed the Meteorological Office dispersion model, NAME, to model the formatio whether European  $SO_2$  sources also make a contribution. We have employed the Meteorological Office dispersion model, NAME, to model the formation of particulate sulphate over a European area and provide information on th Meteorological Office dispersion model, NAME, to model the formation of particulate sulphate over a European area and provide information on the likely source of the aerosols arriving at particular receptor points within ulate sulphate over a European area and provide information on the likely source<br>of the aerosols arriving at particular receptor points within the UK. Previous work<br>(Malcolm *et al.* 2000) studied the year 1996 and in part of the aerosols arriving at particular receptor points within the UK. Previous work (Malcolm *et al.* 2000) studied the year 1996 and in particular two pollution episodes, one in March and the other in July. The model ind (Malcolm *et al.* 2000) studied the year 1996 and in particular two pollution episodes, one in March and the other in July. The model indicated that a high proportion of the particulate sulphate observed during the March one in March and the other in July. The model indicated that a high proportion of the particulate sulphate observed during the March episode was due to the import of sulphate aerosols from the rest of Europe, whereas the J the particulate su<br>sulphate aerosols<br>by UK sources.<br>The aqueous p Iphate aerosols from the rest of Europe, whereas the July episode was dominated<br>UK sources.<br>The aqueous phase oxidation scheme has subsequently been revised, and the pre-<br>pusly discussed model's underprediction of particul

by UK sources.<br>The aqueous phase oxidation scheme has subsequently been revised, and the previously discussed model's underprediction of particulate sulphate in the winter has<br>improved. We have repeated the model run for 1 The aqueous phase oxidation scheme has subsequently been revised, and the previously discussed model's underprediction of particulate sulphate in the winter has improved. We have repeated the model run for 1996 for this st viously discussed model's underprediction of particulate sulphate in the winter has<br>improved. We have repeated the model run for 1996 for this study and have compared<br>the model results with observations from five rural sul improved. We have repeated the model run for 1996 for this study and have compared<br>the model results with observations from five rural sulphate measurement sites. Attri-<br>bution plots during the two episodes are also presen the model results with observations from<br>bution plots during the two episodes a<br>of the observed particulate sulphate. % of the observed particulate sulphate.<br>(a) *The NAME model* 

NAME is a Lagrangian model in which emissions are simulated by releasing large numbers of particles into a three-dimensional model atmosphere. Detailed descriptions of the model can be found in Physick & Maryon (1995) and Ryall & Maryon (1998).

Meteorological data (such as wind and temperature fields, precipitation and cloud (1998).<br>Meteorological data (such as wind and temperature fields, precipitation and cloud<br>information) are obtained from the Meteorological Office's numerical weather pre-<br>diction model, the Unified Model (UM) (Cullen 199 Meteorological data (such as wind and temperature fields, precipitation and cloud<br>information) are obtained from the Meteorological Office's numerical weather pre-<br>diction model, the Unified Model (UM) (Cullen 1993). The t information) are obtained from the Meteorological Office's numerical weather prediction model, the Unified Model (UM) (Cullen 1993). The three-dimensional wind field passively carries the released particles, with turbulent diction model, the Unified Model (UM) (Cullen 1993). The three-dimensional wind<br>field passively carries the released particles, with turbulent dispersion simulated by<br>random walk techniques. Boundary-layer depth is time va field passively carries the released particles, with turbulent dispersion simulated by<br>random walk techniques. Boundary-layer depth is time varying and is calculated in<br>NAME from wind and temperature profiles. Dry and wet random walk techniques. Boundary-layer depth is time varying and is calculated in NAME from wind and temperature profiles. Dry and wet deposition processes act on the pollutant mass carried by each particle. The dry deposi NAME from wind and temperature profiles. Dry and wet deposition processes act<br>on the pollutant mass carried by each particle. The dry deposition scheme is based<br>on a resistance analogy parametrization to determine the depo on the pollutant mass carried by each particle. The dry deposition scheme is based on a resistance analogy parametrization to determine the deposition velocity and<br>wet deposition is parametrized by washout and rainout processes using a scavenging<br>coefficient method. Cloud fraction and cloud liquid water wet deposition is parametrized by washout and rain<br>coefficient method. Cloud fraction and cloud liquid<br>used to drive the aqueous phase of the chemistry.<br>Every particle is labelled with its release location efficient method. Cloud fraction and cloud liquid water output from the UM are<br>ed to drive the aqueous phase of the chemistry.<br>Every particle is labelled with its release location and time of origin, which makes<br>possible t

used to drive the aqueous phase of the chemistry.<br>Every particle is labelled with its release location and time of origin, which makes<br>it possible to identify which sources have contributed to a particular receptor area. Every particle is labelled with its release location and time of origin, which makes<br>it possible to identify which sources have contributed to a particular receptor area.<br>Each particle is released with an initial mass of p it possible to identify which sources have contributed to a particular receptor area.<br>Each particle is released with an initial mass of pollutant (both sulphur dioxide and ammonia in this study) and exists for as long as i Each particle is released with an initial<br>ammonia in this study) and exists for a<br>remains inside the model boundaries. ammonia in this study) and exists for as long as it carries mass of any species and it<br>remains inside the model boundaries.<br>(*b*) *Oxidation of sulphur dioxide* 

(b) Oxidation of sulphur dioxide<br>In the atmosphere the gas-phase oxidation of sulphur dioxide  $(SO_2)$  is dominated<br>its reaction with the hydroxyl radical OH The hydroxyl radical plays an impor-In the atmosphere the gas-phase oxidation of sulphur dioxide  $(SO_2)$  is dominated<br>by its reaction with the hydroxyl radical, OH. The hydroxyl radical plays an impor*by* its reaction with the hydroxyl radical, OH. The hydroxyl radical plays an impor-<br>*Phil. Trans. R. Soc. Lond.* A (2000)

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site	correlation	bias	NMSE	$%$ (within a factor of $2)$
Yarner Wood	0.40	$-1.16$	1.82	51.2
Eskdalemuir	0.39	$-1.40$	3.23	36.3
High Muffles	0.34	$-1.03$	1.84	52.5
Strathvaich	0.49	$-1.24$	6.74	10.8
Lough Navar	0.72	$-1.63$	5.27	10.1

Table 1. *Statistics for a comparison of modelled versus measured particulate sulphate for 1996*

tant part in tropospheric chemistry due to both its high reactivity with trace species<br>such as  $SO<sub>2</sub>$  and because of its photochemical regeneration in the atmosphere. In tant part in tropospheric chemistry due to both its high reactivity with trace species<br>such as  $SO_2$  and because of its photochemical regeneration in the atmosphere. In<br>the aqueous phase there are two main oxidation pathw tant part in tropospheric chemistry due to both its high reactivity with trace species<br>such as  $SO_2$  and because of its photochemical regeneration in the atmosphere. In<br>the aqueous phase there are two main oxidation pathw such as  $SO_2$  and because of its photochemical regeneration in the atmosphere. In<br>the aqueous phase there are two main oxidation pathways, namely those via hydro-<br>gen peroxide,  $H_2O_2$ , and ozone. These routes are both p the aqueous phase there are two main oxidation pathways, namely those via hydrogen peroxide,  $H_2O_2$ , and ozone. These routes are both parametrized in NAME. The reaction with hydrogen peroxide is very rapid and the oxida gen peroxide,  $H_2O_2$ , and ozone. These routes are both parametrized in NAME. The reaction with hydrogen peroxide is very rapid and the oxidant can be completely exhausted before there has been time for regeneration of reaction with hydrogen peroxide is very rapid and the oxidant can be completely exhausted before there has been time for regeneration of  $H_2O_2$  via the recombination of the hydroperoxy radical,  $HO_2$ . The oxidation of exhausted before there has been time for regeneration of  $H_2O_2$  via the recombina-<br>tion of the hydroperoxy radical,  $HO_2$ . The oxidation of  $SO_2$  with  $O_3$  is dependent on<br>the acidity of the cloud droplets and is much tion of the hydroperoxy radical,  $HO_2$ . The oxidation of  $SO_2$  with  $O_3$  is dependent on<br>the acidity of the cloud droplets and is much more likely to be limited by high acidity<br>(at which point the reaction proceeds very the acidity of the cloud droplets and is much more likely to be limited by high acidity<br>(at which point the reaction proceeds very slowly) than low ozone concentrations. In<br>order to parametrize the oxidation of  $SO_2$  by (at which point the reaction proceeds very slowly) than low ozone concentrations. In order to parametrize the oxidation of  $SO_2$  by  $O_3$  it is therefore necessary to model the ammonia life cycle so that the concentration order to parametrize the oxidati<br>the ammonia life cycle so that the<br>in the calculation of cloud pH.<br>In the NAME study presente e ammonia life cycle so that the concentration of this base species can be included<br>the calculation of cloud pH.<br>In the NAME study presented here, both  $SO_2$  and  $NH_3$  are emitted into the<br>odel atmosphere using emissions

in the calculation of cloud pH.<br>In the NAME study presented here, both  $SO_2$  and NH<sub>3</sub> are emitted into the model atmosphere using emissions obtained from the EMEP 50 km  $\times$  50 km area<br>database (EMEP 1997) The other chem In the NAME study presented here, both  $SO_2$  and  $NH_3$  are emitted into the model atmosphere using emissions obtained from the EMEP  $50 \text{ km } \times 50 \text{ km}$  are database (EMEP 1997). The other chemical species required are all model atmosphere using emissions obtained from the EMEP  $50 \text{ km} \times 50 \text{ km}$  area<br>database (EMEP 1997). The other chemical species required are all obtained from the<br>Meteorological Office global chemistry model, STOCHEM, a database (EMEP 1997). The other chemical species required are all obtained from the Meteorological Office global chemistry model, STOCHEM, as monthly average fields. STOCHEM is a three-dimensional Lagrangian tropospheric c Meteorological Office global chemistry model, STOCHEM, as monthly average fields.<br>STOCHEM is a three-dimensional Lagrangian tropospheric chemistry model which<br>is driven by global meteorological data from the UM and runs o STOCHEM is a three-dimensional Lagrangian tropospheric chemistry model which<br>is driven by global meteorological data from the UM and runs on a much larger scale<br>than NAME (a  $5^{\circ} \times 5^{\circ}$  grid square is used, which give is driven by global meteorological data from the UM and runs on a much larger scale<br>than NAME (a  $5^{\circ} \times 5^{\circ}$  grid square is used, which gives a resolution of *ca*. 600 km  $\times$ <br>400 km at mid-latitudes), and, hence, is than NAME (a  $5^{\circ} \times 5^{\circ}$  grid square is used, which gives a resolution of *ca*. 600 km  $\times$  400 km at mid-latitudes), and, hence, is unable to produce the same degree of fine spatial and temporal resolution that can b 400 km at mid-latitudes), and, hence, is unable to produce the same degree of fine<br>spatial and temporal resolution that can be achieved in NAME. A full description<br>can be found in Collins *et al.* (1997). The fields of OH spatial and temporal resolution that can be achieved in NAME. A full description<br>can be found in Collins *et al.* (1997). The fields of OH,  $O_3$  and  $HO_2$  radicals are<br>treated as fixed, their values only changing monthly can be found in Collins *et al.* (1997). The fields of OH,  $O_3$  and  $HO_2$  radicals are treated as fixed, their values only changing monthly. The  $H_2O_2$  is initialized using the monthly average field from STOCHEM and th treated as fixed, their values only changing monthly. The  $H_2O_2$  is initialized using<br>the monthly average field from STOCHEM and thereafter is modelled in NAME as<br>a three-dimensional field.

#### (*c*) *NAME results for 1996*

Five rural measurement sites (Yarner Wood, Eskdalemuir, High Muffles, Strath-Five rural measurement sites (Yarner Wood, Eskdalemuir, High Muffles, Strath-<br>vaich and Lough Navar) produce daily values of ambient particulate sulphate, and<br>these data have been compared with output from the NAME model f Five rural measurement sites (Yarner Wood, Eskdalemuir, High Muffles, Strath-<br>vaich and Lough Navar) produce daily values of ambient particulate sulphate, and<br>these data have been compared with output from the NAME model f these data have been compared with output from the NAME model for 1996. The measurement data are obtained from the National Air Quality Information Archive these data have been compared with output from the NAME model for 1996. The measurement data are obtained from the National Air Quality Information Archive provided by the National Environmental Technology Centre (NETCEN) measurement data are obtained from the National Air Quality Information Archive<br>provided by the National Environmental Technology Centre (NETCEN) on behalf<br>of the Department of the Environment, Transport and the Regions (D http://www.aeat.co.uk/netcen/airqual/index.html. theDepartment of the Environment, Transport and the Regions (DETR) at<br>tp://www.aeat.co.uk/netcen/airqual/index.html.<br>The model was run over a domain of longitude 15.0° W to 20.0° E and latitude<br>0° N to 65.0° N. Modelled

 $43.0^{\circ}$  N to  $65.0^{\circ}$  N. Modelled sulphuric acid has been added to modelled ammonium ://www.aeat.co.uk/netcen/airqual/index.html.<br>he model was run over a domain of longitude 15.0° W to 20.0° E and latitude<br>° N to 65.0° N. Modelled sulphuric acid has been added to modelled ammonium<br>hate to give particulate sulphate to give particulate sulphate in  $\mu$ g m<sup>-3</sup> of SO<sub>4</sub>. Table 1 shows a set of four



Figure 1. NAME model daily sulphate aerosols plotted against measured sulphate aerosols at Lough Navar and High Muffles for 1996.

Lough Navar and High Muffles for 1996.<br>
standard statistics (correlation, bias, normalized mean square error (NMSE), and<br>
percentage within a factor of two) calculated on daily values for the five sites over standard statistics (correlation, bias, normalized mean square error (NMSE), and<br>percentage within a factor of two) calculated on daily values for the five sites over<br>1996 1996. percentage within a factor of two) calculated on daily values for the five sites over 1996.<br>Comparison with a previous model run for this period (Malcolm *et al.* 2000) shows

1996.<br>Comparison with a previous model run for this period (Malcolm *et al.* 2000) shows<br>that the average correlation over the five sites for the year remains the same at 0.47,<br>the average bias is less negative by 0.37 (r Comparison with a previous model run for this period (Malcolm *et al.* 2000) shows<br>that the average correlation over the five sites for the year remains the same at 0.47,<br>the average bias is less negative by 0.37 (reflect that the average correlation over the five sites for the year remains the same at 0.47, the average bias is less negative by 0.37 (reflecting the improved magnitudes during the winter months), the average NMSE is reduced the average bias is less negative by 0.37 (reflecting the improved magnitudes during the winter months), the average NMSE is reduced by 5.41 and the average percentage within a factor of two is increased by  $21.6\%$ . e winter months), the average NMSE is reduced by 5.41 and the average percentage<br>thin a factor of two is increased by 21.6%.<br>Yearly time-series of daily model particulate sulphate versus observation are pre-<br>nted in figure

within a factor of two is increased by 21.6%.<br>Yearly time-series of daily model particulate sulphate versus observation are pre-<br>sented in figure 1 for Lough Navar and High Muffles. Despite the improved perfor-<br>mance of th Yearly time-series of daily model particulate sulphate versus observation are presented in figure 1 for Lough Navar and High Muffles. Despite the improved performance of the model in the winter months, the exceptional epis sented in figure 1 for Lough Navar and High Muffles. Despite the improved perfor-<br>mance of the model in the winter months, the exceptional episode in March is still<br>not fully captured. The negative biases at all sites indi mance of the model in the winter months, the exceptional episode in March is still<br>not fully captured. The negative biases at all sites indicate that the model is gener-<br>ally underpredicting. The obtained correlations are not fully captured. The negative biases at all sites indicate that the model is generally underpredicting. The obtained correlations are still somewhat low, but given the inherent difficulty of modelling both formation and ally underpredicting. The obtained correlations are still somewhat low, but given the<br>inherent difficulty of modelling both formation and transport of particulate sulphate,<br>perhaps that is to be expected. To improve model inherent difficulty of modelling both formation and transport of particulate sulphate,<br>perhaps that is to be expected. To improve model performance significantly, we would<br>need more detailed resolution  $SO_2$  emissions (bo perhaps that is to be expected. To improve model performance significantly, we would<br>need more detailed resolution  $SO_2$  emissions (both spatially and temporally) and also<br>to be able to represent the nonlinear chemical co meed more detailed resolution  $SO_2$  emissions (both spatially and temporally) and also<br>to be able to represent the nonlinear chemical conversion more precisely. It should<br>also be remembered that the meteorology is varying to be able to represent the nonlinear chemical conversion more precisely. It should also be remembered that the meteorology is varying over a 50 km grid scale on a three hourly basis, which means it is unable to resolve su variations (for example, due to local topography).

### (*d*) *Source attribution*

Two periods have been selected from both the March and July episodes in order to demonstrate the origin of the material seen in the modelled data in figure 1. The periods selected were from midnight to midnight for  $14{\text -}16$  March 1996 and 19 $-$ 

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UKMO NAME v4.3 Dispersion Model: re run9603 Attribution - Receptor: HIGH MUFFLES Species: SULPHATE Grid: Custom1 From 0000UTC 14/03/1996 to 0000UTC 16/03/1996 BL particles



Figure 2. Attribution plots for two days during March 1996 at Lough Navar and High Muffles.

21 July 1996. All of the particles released in the model contributing to the material 21 July 1996. All of the particles released in the model contributing to the material arriving at the measurement sites during these periods have been plotted as a number on a map of the model domain (figures 2 and 3). Th 21 July 1996. All of the particles released in the model contributing to the material arriving at the measurement sites during these periods have been plotted as a number on a map of the model domain (figures 2 and 3). The on a map of the model domain (figures 2 and 3). The number (where legible, as most are overplotted) represents the number of days it took to travel from the point shown to the receptor point (i.e. either Lough Navar or Hig are overplotted) represents the number of days it took to travel from the point shown

Figure 2 shows Lough Navar (in the west of Northern Ireland) receiving particulate to the receptor point (i.e. either Lough Navar or High Muffles in these examples).<br>Figure 2 shows Lough Navar (in the west of Northern Ireland) receiving particulate<br>sulphate during the two-day period generated as a result Figure 2 shows Lough Navar (in the west of Northern Ireland) receiving particulate sulphate during the two-day period generated as a result of emissions throughout southern England and the industrial regions of northern E *Phil. Trans. R. Soc. Lond.* A (2000)

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PHILOSOPHICAL<br>TRANSACTIONS

#### *Photochemical generationofsecondaryparticles in the UK* <sup>2649</sup>



Figure 3. Attribution plots for three days during July 1996 at Lough Navar and High Muffles.

had been emitted several days earlier, before undergoing chemical conversion and thad been emitted several days earlier, before undergoing chemical conversion and<br>transport to Northern Ireland. High Muffles is dominated by the European sources<br>during this period, with the only UK contribution being fro had been emitted several days earlier, before undergoing chemical conversion and<br>transport to Northern Ireland. High Muffles is dominated by the European sources<br>during this period, with the only UK contribution being from transport to Northern Ireland. High Muffles is dominated by the Euduring this period, with the only UK contribution being from coasts<br>the measurement site. Again, travel times of several days are seen.<br>In figure 3 the part during this period, with the only UK contribution being from coastal areas near to<br>the measurement site. Again, travel times of several days are seen.<br>In figure 3 the particulate sulphate modelled at Lough Navar during thi

the measurement site. Again, travel times of several days are seen.<br>In figure 3 the particulate sulphate modelled at Lough Navar during this two-<br>day period in July originated from  $SO_2$  emissions in Ireland and Southern In figure 3 the particulate sulphate modelled at Lough Navar during this two-<br>day period in July originated from  $SO_2$  emissions in Ireland and Southern England,<br>with just a few sources on the French, Belgian and Dutch co day period in July originated from  $SO_2$  emissions in Ireland and Southern England, with just a few sources on the French, Belgian and Dutch coasts contributing. High Muffles, however, is dominated by UK sources, mainly i *Phil. Trans. R. Soc. Lond.* A (2000)

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**MATHEMATICAL,<br>PHYSICAL<br>& ENGINEERING**<br>SCIENCES

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PHILOSOPHICAL<br>TRANSACTIONS

2650  $R. G. Derwent and A. L. Malcolm$ <br>March episode was dominated by a southeasterly wind flow and the July episode by March episode was dominated by a southeasterly wind flow and the July episode by a high pressure resulting in a slack wind field. A detailed account of the meteorology during these two episodes can be found in Malcolm *et* March episode was dominated by a southeasterly wind flow and the<br>a high pressure resulting in a slack wind field. A detailed account of<br>during these two episodes can be found in Malcolm *et al.* (2000).<br>The Lagrangian natu during these two episodes can be found in Malcolm  $et$  al. (2000).<br>The Lagrangian nature of the NAME model makes it possible to attribute modelled

during these two episodes can be found in Malcolm *et al.* (2000).<br>The Lagrangian nature of the NAME model makes it possible to attribute modelled<br>sulphate aerosols to the  $SO_2$  emission from which it was generated. This The Lagrangian nature of the NAME model makes it possible to attribute modelled<br>sulphate aerosols to the  $SO_2$  emission from which it was generated. This facility has<br>shown that the elevated levels of particulate sulphate sulphate aerosols to the  $SO_2$  emission from which it was generated. This facility has<br>shown that the elevated levels of particulate sulphate recorded during March 1996<br>at rural measurement sites were dominated by transpo shown that the elevated levels of particulate sulphate recorded during March 1996 at rural measurement sites were dominated by transport from Europe. In contrast, the smaller peak in particulate sulphate seen in July 1996 at rural measurement sites were dominated by transport from Europe. In contrast,<br>the smaller peak in particulate sulphate seen in July 1996 was dominated by UK<br>emissions. This study serves to highlight the need for policy the smaller peak in particulate sulphate seen in July 1996 was dominated by UK emissions. This study serves to highlight the need for policy makers to seriously consider the impact of secondary aerosol precursors emitted i consider the impact of secondary aerosol precursors emitted in countries other than their own when devising future air-quality strategies.

### 3. Source attribution of secondary organic aerosols in the UK

It was noted originally by Went (1960) that natural biogenic hydrocarbons play It was noted originally by Went (1960) that natural biogenic hydrocarbons play<br>an important role in the formation of tropospheric aerosols. The sunlight-driven<br>atmospheric photo-oxidation of high-molecular-weight hydrocarb It was noted originally by Went (1960) that natural biogenic hydrocarbons play<br>an important role in the formation of tropospheric aerosols. The sunlight-driven<br>atmospheric photo-oxidation of high-molecular-weight hydrocarb an important role in the formation of tropospheric aerosols. The sunlight-driven<br>atmospheric photo-oxidation of high-molecular-weight hydrocarbons has been shown<br>to produce low vapour pressure reaction products that parti atmospheric photo-oxidation of high-molecular-weight hydrocarbons has been shown<br>to produce low vapour pressure reaction products that partition between the gas<br>and aerosol phases (Pandis *et al.* 1992). These reaction pro to produce low vapour pressure reaction products that partition between the gas<br>and aerosol phases (Pandis *et al.* 1992). These reaction products are known as semi-<br>volatile organic compounds because of their ability to and aerosol phases (Pandis *et al.* 1992). These reaction products are known as semi-<br>volatile organic compounds because of their ability to pass between the gas and<br>aerosol phases (Kamens *et al.* 1999). In the aerosol ph volatile organic compounds because of their ability to pass between the gas and<br>aerosol phases (Kamens *et al.* 1999). In the aerosol phase, these reaction products are<br>known as secondary organic aerosols (SOAs). Of the n aerosol phases (Kamens *et al.* 1999). In the aerosol phase, these reaction products are<br>known as secondary organic aerosols (SOAs). Of the natural biogenic hydrocarbons,<br>terpenes have been found to be effective sources of known as secondary organic aerosols (SOAs). Of the natural biogenic hydrocarbons, terpenes have been found to be effective sources of SOAs (Hoffmann *et al.* 1997), whereas, of the man-made hydrocarbons, aromatics are the terpenes have been for<br>whereas, of the man-1<br>(Odum *et al.* 1996).<br>These consideration nereas, of the man-made hydrocarbons, aromatics are the most important source<br>dum *et al.* 1996).<br>These considerations have prompted questions about the relative importance of<br>tural biogenic sources as opposed to man-made

(Odum *et al.* 1996).<br>These considerations have prompted questions about the relative importance of natural biogenic sources as opposed to man-made sources of SOA levels in the United These considerations have prompted questions about the relative importance of natural biogenic sources as opposed to man-made sources of SOA levels in the United Kingdom. To begin to answer these questions, a photochemical natural biogenic sources as opposed to man-made sources of SOA levels in the United<br>Kingdom. To begin to answer these questions, a photochemical trajectory model has<br>been used to investigate the formation of semi-volatile Kingdom. To begin to answer these questions, a photochemical trajectory model has<br>been used to investigate the formation of semi-volatile organic degradation products<br>from the photo-oxidation of both natural biogenic terpe head to investigate the formation of semi-volatile organic degradation products from the photo-oxidation of both natural biogenic terpene and man-made aromatic hydrocarbon compounds during a summertime regional ozone pollu

### (*a*) *Application of the UK photochemical trajectory model*

The formation of SOAs during a summertime regional scale pollution episode The formation of SOAs during a summertime regional scale pollution episode<br>has been described using the UK Photochemical Trajectory Model (UK PTM). This<br>model addresses the detailed chemical development in an air parcel a The formation of SOAs during a summertime regional scale pollution episode<br>has been described using the UK Photochemical Trajectory Model (UK PTM). This<br>model addresses the detailed chemical development in an air parcel as has been described using the UK Photochemical Trajectory Model (UK PTM). This<br>model addresses the detailed chemical development in an air parcel as it moves across<br>the European emissions grid following a six-day trajectory model addresses the detailed chemical development in an air parcel as it moves across<br>the European emissions grid following a six-day trajectory from Austria through to<br>its arrival point in Wales (Derwent *et al.* 1996). T the European emissions grid following a six-day trajectory from Austria through to<br>its arrival point in Wales (Derwent *et al.* 1996). The chemistry is described for a<br>single air parcel whose base is at the surface and wh its arrival point in Wales (Derwent *et al.* 1996). The chemistry is described for a single air parcel whose base is at the surface and whose upper boundary is at the top of the atmospheric boundary layer. Temperatures, h single air parcel whose base is at the surface and whose upper boundary is at the<br>top of the atmospheric boundary layer. Temperatures, humidities, boundary-layer<br>depths, wind speeds and wind directions were all diurnally v top of the atmospheric boundary layer. Temperatures, humidities<br>depths, wind speeds and wind directions were all diurnally varying<br>appropriate to the conditions of regional scale pollution episodes.<br>The UK PTM employs the pths, wind speeds and wind directions were all diurnally varying and given values<br>propriate to the conditions of regional scale pollution episodes.<br>The UK PTM employs the Master Chemical Mechanism (MCM) to describe the<br>oto

appropriate to the conditions of regional scale pollution episodes.<br>The UK PTM employs the Master Chemical Mechanism (MCM) to describe the photochemical ozone production from 123 emitted organic compounds that gener-The UK PTM employs the Master Chemical Mechanism (MCM) to describe the<br>photochemical ozone production from 123 emitted organic compounds that gener-<br>ate 3482 reaction and degradation products and take part in over 10 500 photochemical ozone production from 123 emitted organic compounds that generate 3482 reaction and degradation products and take part in over 10 500 chemical reaction processes (Jenkin *et al.* 1999). The MCM also includes ate 3482 reaction and degradation products and take part in over  $10\,500$  chemical reaction processes (Jenkin *et al.* 1999). The MCM also includes the reactions of the simple atoms and radicals containing oxygen, hydrog *Phil. Trans. R. Soc. Lond.* A (2000)

CO,  $SO_2$  and  $H_2O_2$  that together describe the fast photochemistry of the polluted CO,  $SO_2$  and  $H_2O_2$  that together describe the fast photochemistry of the polluted<br>atmospheric boundary layer. The MCM version 2.0 may be downloaded from the<br>World Wide Web at http://chem.leeds.ac.uk/Atmospheric/MCM/mc  $CO$ ,  $SO_2$  and  $H_2O_2$  that together describe the fast photochemistry of the polluted atmospheric boundary layer. The MCM version 2.0 may be downloaded from the World Wide Web at http://chem.leeds.ac.uk/Atmospheric/MCM/m WorldWide Web at http://chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html.<br>The fast photochemistry and regional photochemical ozone production occurring

World Wide Web at http://chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html.<br>The fast photochemistry and regional photochemical ozone production occurring<br>in the UK PTM are driven by the emissions picked up by the air parcel a The fast photochemistry and regional photochemical ozone production occurring<br>in the UK PTM are driven by the emissions picked up by the air parcel as it traverses<br>Europe. The emissions of  $NO_x$ ,  $CO$ ,  $SO_2$ , isoprene and v in the UK PTM are driven by the emissions picked up by the air parcel as it traverses<br>Europe. The emissions of  $NO_x$ ,  $CO$ ,  $SO_2$ , isoprene and volatile organic compounds<br>(VOCs) were employed at 150 km  $\times$  150 km scale acr Europe. The emissions of  $NO_x$ ,  $CO$ ,  $SO_2$ , isoprene and volatile organic compounds (VOCs) were employed at 150 km  $\times$  150 km scale across Europe based on EMEP emissions (Mylona 1999), at 50 km  $\times$  50 km where available (VOCs) were employed at 150 km  $\times$  150 km scale across Europe based on EMEP emissions (Mylona 1999), at 50 km  $\times$  50 km where available from either EMEP or EC CORINAIR (Bouscaren & Cornaert 1995) and at 10 km  $\times$  10 km emissions (Mylona 1999), at 50 km  $\times$  50 km where available from either EMEP or EC CORINAIR (Bouscaren & Cornaert 1995) and at 10 km  $\times$  10 km within the United Kingdom from Salway *et al.* (1996). European emission inv EC CORINAIR (Bouscaren & Cornaert 1995) and at 10 km  $\times$  10 km within t<br>United Kingdom from Salway *et al.* (1996). European emission inventories (Mylc<br>1999) may be downloaded from the World Wide Web at http://www.emep.i UnitedKingdom from Salway *et al.* (1996). European emission inventories (Mylona 1999) may be downloaded from the World Wide Web at http://www.emep.int.<br>The emissions of all VOCs were split into the emissions of individu

pounds using the detailed speciated emission inventory available for the United King-The emissions of all VOCs were split into the emissions of individual organic compounds using the detailed speciated emission inventory available for the United King-<br>dom from the NAEI, and this same speciation was assume pounds using the detailed speciated emission inventory available for the United King-<br>dom from the NAEI, and this same speciation was assumed to hold across Europe<br>and is given in Derwent *et al.* (1996). The model also tr dom from the NAEI, and this same speciation was assumed to hold across Europe and is given in Derwent *et al.* (1996). The model also treated the dry deposition and surface removal of ozone, nitric acid, hydrogen peroxide surface removal of ozone, nitric acid, hydrogen peroxide and the peroxyacylnitrates.<br>(*b*) *Model treatment of SOAs* 

The formation of SOAs in the UK PTM was driven by the emissions of terpenes The formation of SOAs in the UK PTM was driven by the emissions of terpenes<br>from natural biogenic emissions and aromatic hydrocarbons as the air parcel tra-<br>versed Europe. Emissions of terpenes at a spatial resolution of The formation of SOAs in the UK PTM was driven by the emissions of<br>from natural biogenic emissions and aromatic hydrocarbons as the air p<br>versed Europe. Emissions of terpenes at a spatial resolution of  $1^{\circ} \times 1^{\circ}$  are is of terpenes<br>
ir parcel tra-<br>
° and for the<br>
tory Activity from natural biogenic emissions and aromatic hydrocarbons as the air parcel tra-<br>versed Europe. Emissions of terpenes at a spatial resolution of  $1^{\circ} \times 1^{\circ}$  and for the<br>month of July for Europe were taken from the Glo versed Europe. Emissions of terpenes at a spatial resolution<br>month of July for Europe were taken from the Global Emiss<br>emissions database (http://blueskies.sprl.umich.edu/geia/).<br>It was assumed that all the terpene emissio

monthof July for Europe were taken from the Global Emission Inventory Activity<br>emissions database (http://blueskies.sprl.umich.edu/geia/).<br>It was assumed that all the terpene emissions occurred into the UK PTM as  $\alpha$ -<br>p It was assumed that all the terpene emissions occurred into the UK PTM as  $\alpha$ pinene. No explicit temperature or time dependence was assumed for these emissions,<br>and the emissions from a particular grid square were held constant at the monthly<br>average emission rate. Emissions of each of the aromatic and the emissions from a particular grid square were held constant at the monthly<br>average emission rate. Emissions of each of the aromatic hydrocarbons was taken<br>from the EMEP (Mylona 1999), EC CORINAIR (G. McInnes 1994, p average emission rate. Emissions of each of the aromatic hydrocarbons was taken<br>from the EMEP (Mylona 1999), EC CORINAIR (G. McInnes 1994, personal com-<br>munication) and UK NAEI inventories using the VOC speciation taken f from the EMEP (Mylona 1999), EC CORINAIR (G. McInnes 1994, personal com-<br>munication) and UK NAEI inventories using the VOC speciation taken from Derwent<br>*et al.* (1996). The MCM version 2.0 was used to describe the reacti munication) and UK NAEI inventories using the VOC speciation taken from Derwent

radicals and ozone during daylight and with  $NO<sub>3</sub>$  radicals and ozone during nighttime The MCM version 2.0 was used to describe the reactions of  $\alpha$ -pinene with OH radicals and ozone during daylight and with  $NO_3$  radicals and ozone during nighttime (Jenkin *et al.* 2000). Altogether the  $\alpha$ -pinene degrad radicals and ozone during daylight and with  $NO_3$  radicals and ozone during nighttime (Jenkin *et al.* 2000). Altogether the  $\alpha$ -pinene degradation scheme contained over 329 reactions and formed a number of low-volatilit (Jenkin *et al.* 2000). Altogether the  $\alpha$ -pinene degradation scheme contained over 329 reactions and formed a number of low-volatility degradation products, which are classed as semi-volatile organic compounds, includin reactions and formed a number of low-volatility degradation products, which are classed as semi-volatile organic compounds, including pinonaldehyde, peroxypinonic acid, pinonic acid, norpinonaldehyde and hydroperoxypinonal classed as semi-volatile organic compounds, including pinonaldehyde, peroxypinonic<br>acid, pinonic acid, norpinonaldehyde and hydroperoxypinonaldehyde. These semi-<br>volatile organic compounds have been scavenged in the UK PTM acid, pinonic acid, norpinonaldehyde and hydroperoxypinonaldehyde. These semivolatile organic compounds have been scavenged in the UK PTM by pre-existing<br>aerosol species in competition with their subsequent atmospheric degradation. No<br>loss of semi-volatile organic matter from the aerosol back into aerosol species in competition with their subsequent atmospheric deg<br>loss of semi-volatile organic matter from the aerosol back into the g<br>allowed in order to simulate the upper limit concentrations of SOAs.<br>The MCM versio Somether Sometively in the series of solution and the series of solution and solved in order to simulate the upper limit concentrations of SOAs.<br>The MCM version 2.0 was also used to describe the reactions of aromatic hydro

allowed in order to simulate the upper limit concentrations of SOAs.<br>The MCM version 2.0 was also used to describe the reactions of aromatic hydro-<br>carbons with OH radicals which generate SOAs. A small fraction of chemical The MCM version 2.0 was also used to describe the reactions of aromatic hydro-<br>carbons with OH radicals which generate SOAs. A small fraction of chemical flux<br>through these reactions was assumed to generate low-volatility carbons with OH radicals which generate SOAs. A small fraction of chemical flux<br>through these reactions was assumed to generate low-volatility reaction products,<br>which would be present in the atmosphere as semi-volatile or through these reactions was assumed to generate low-volatility reaction products,<br>which would be present in the atmosphere as semi-volatile organic compounds. These<br>fractions have been quantified in table 2 for each of th which would be present in the atmosphere as semi-volatile organic compounds. These fractions have been quantified in table 2 for each of the aromatic hydrocarbons where these are available from the literature (Odum *et al* fractions have been quantified in table 2 for each of the aromatic hydrocarbons where these are available from the literature (Odum  $et$   $al$ . 1997), otherwise they have been set to zero. Again, these semi-volatile organic

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Table 2. *The assumed fractions by mass of each aromatic hydrocarbon oxidized in the UK Photochemical Trajectory Model, which produces SOAs and their percentage contribution to SOA formation*

formation<br>formation<br>(Mass fractions of SOAs produced from each aromatic hydrocarbon oxidized were taken from<br>Odum et al. (1997). No SOA was assumed to be formed from the photo-oxidation of benformation<br>(Mass fractions of SOAs produced from each aromatic hydrocarbon oxidized were taken from<br>Odum *et al.* (1997). No SOA was assumed to be formed from the photo-oxidation of ben-<br>zene, styrene, benzaldebyde, i-propy Odum *et al.* (1997). No SOA was assumed to be formed from the photo-oxidation of benzene, styrene, benzaldehyde, i-propylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 3.5-dimethylbenzene and 3.5-diethyltoluene zene, styrene, benzaldehyde, i-propylbenzene,  $1,2,3$ -trimethylbenzene,  $1,2,4$ -trimethylbenzene,



UK PTM by pre-existing aerosol species. No loss of semi-volatile organic matter from UK PTM by pre-existing aerosol species. No loss of semi-volatile organic matter from<br>the aerosol back into the gas phase was allowed to simulate an upper limit concen-<br>tration of SOAs. The semi-volatile organic compounds f UK PTM by pre-existing aerosol species. No loss of semi-volatile organic matter from<br>the aerosol back into the gas phase was allowed to simulate an upper limit concen-<br>tration of SOAs. The semi-volatile organic compounds f the aerosol back into the gas phase was allowed to simulate an upper limit concentration of SOAs. The semi-volatile organic compounds formed from aromatic hydrocarbon photo-oxidation are thought to be species such as 2,5*et al.* 1997).<br>*et al.* 1997).

### (*c*) *Model results for SOAs*

Figure 4 presents the calculated concentrations of SOAs in the UK PTM as the Figure 4 presents the calculated concentrations of SOAs in the UK PTM as the<br>air parcel traverses Europe from Austria across to Wales. Because no loss of semi-<br>volatile organic matter from the aerosol once scavenged has be Figure 4 presents the calculated concentrations of SOAs in the UK PTM as the air parcel traverses Europe from Austria across to Wales. Because no loss of semi-<br>volatile organic matter from the aerosol once scavenged has be volatile organic matter from the aerosol once scavenged has been allowed, the convolatile organic matter from the aerosol once scavenged has been allowed, the concentrations of SOAs represent an upper limit to those anticipated in the real atmo-<br>spheric boundary layer. The figure shows the concentratio centrations of SOAs represent an upper limit to those anticipated in the real atmo-<br>spheric boundary layer. The figure shows the concentrations of SOAs formed from<br>the photo-oxidation of both natural biogenic hydrocarbons spheric boundary layer. The figure shows the concentrations of SOAs formed from<br>the photo-oxidation of both natural biogenic hydrocarbons and man-made aromatic<br>hydrocarbons. The conclusion is that the SOA formed from terpe the photo-oxidation of both natural biogenic hydrocarbons and man-made aromatic<br>hydrocarbons. The conclusion is that the SOA formed from terpene photo-oxidation<br>is several times greater in concentration compared with that hydrocarbons. The conclu<br>is several times greater in<br>carbon photo-oxidation.<br>By way of comparison. several times greater in concentration compared with that from aromatic hydro-<br>rbon photo-oxidation.<br>By way of comparison, the above model experiment also generated  $18 \mu g m^{-3}$ <br>particulate sulphate from the oxidation of

carbon photo-oxidation.<br>By way of comparison, the above model experiment also generated  $18 \mu g m^{-3}$ <br>of particulate sulphate from the oxidation of SO<sub>2</sub>. The modelled concentrations of By way of comparison, the above model experiment also generated  $18 \mu g m^{-3}$ <br>of particulate sulphate from the oxidation of  $SO_2$ . The modelled concentrations of<br>5-10  $\mu g m^{-3}$  for SOAs suggest that natural biogenic  $\alpha$ -pi of particulate sulphate from the oxidation of  $SO_2$ . The modelled concentrations of 5–10  $\mu$ g m<sup>-3</sup> for SOAs suggest that natural biogenic  $\alpha$ -pinene may potentially make a significant contribution to the concentration 5–10  $\mu$ g m<sup>-3</sup> for SOAs suggest that natural biogenic  $\alpha$ -pinene may potentially make<br>a significant contribution to the concentration of secondary particulate matter and,<br>hence, total fine particulate matter during sum a significant contribution to the concentration of secondary particulate matter and, hence, total fine particulate matter during summertime regional pollution episodes. However, significant uncertainties remain concerning hence, total fine particulate matter during summertime regional pollution episodes.<br>However, significant uncertainties remain concerning the scavenging of the semi-<br>volatile terpene degradation products by the ambient aero volatile terpene degradation products by the ambient aerosol and the subsequent latile terpene degradation products by the ambient aerosol and the subsequent<br>is of this aerosol.<br>The present study in figure 4 shows that the SOA formed from the photo-oxidation<br>aromatic hydrocarbons produces only  $ca$  10

fate of this aerosol.<br>The present study in figure 4 shows that the SOA formed from the photo-oxidation<br>of aromatic hydrocarbons produces only  $ca$ .  $10-15\%$  of the total yield of SOAs from *Phil. Trans. R. Soc. Lond.* A (2000)

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ral biogenic  $\alpha$ -pinene and man-mad<br>photo-oxidation in the UK PTM.

photo-oxidation in the UK PTM.<br>both natural biogenic and man-made hydrocarbon photo-oxidation across Europe in<br>the UK PTM. Table 2 provides an analysis of the percentage contributions made by the UK PTM. Table 2 provides an analysis of the percentage contributions made by<br>the UK PTM. Table 2 provides an analysis of the percentage contributions made by<br>each aromatic hydrocarbon to the overall SOA vield from arom both natural biogenic and man-made hydrocarbon photo-oxidation across Europe in<br>the UK PTM. Table 2 provides an analysis of the percentage contributions made by<br>each aromatic hydrocarbon to the overall SOA yield from aroma the UK PTM. Table 2 provides an analysis of the percentage contributions made by each aromatic hydrocarbon to the overall SOA yield from aromatic hydrocarbons as a class. These calculated contributions reflect the differen each aromatic hydrocarbon to the overall SOA yield from aromatic hydrocarbons as<br>a class. These calculated contributions reflect the different emissions, OH reactivities<br>and SOA yields for each individual aromatic hydrocar a class. These calculated contributions reflect the different emissions, OH reactivities<br>and SOA yields for each individual aromatic hydrocarbon. Three species—toluene,<br>p-xylene and ethylbenzene—together account for over 8 and SOA yields for each individual aromatic hydrocarbon. Three species-<br> $p$ -xylene and ethylbenzene—together account for over 80% of the overall S<br>from aromatic hydrocarbon photo-oxidation under European conditions. from aromatic hydrocarbon photo-oxidation under European conditions.<br>4. Discussion

Particulate sulphate is generally the major observed component of secondary par-Particulate sulphate is generally the major observed component of secondary particulate matter in urban areas, and the United Kingdom shows no exception in this regard (APEG 1999). A highly sophisticated Lagrangian dispers Particulate sulphate is generally the major observed component of secondary particulate matter in urban areas, and the United Kingdom shows no exception in this regard (APEG 1999). A highly sophisticated Lagrangian dispers ticulate matter in urban areas, and the United Kingdom shows no exception in this<br>regard (APEG 1999). A highly sophisticated Lagrangian dispersion model has been<br>used here to describe the formation of particulate sulphate regard (APEG 1999). A highly sophisticated Lagrangian dispersion model has been<br>used here to describe the formation of particulate sulphate by the photochemical oxi-<br>dation of  $SO_2$ , its sole precursor species. A comparis used here to describe the formation of particulate sulphate by the photochemical oxidation of  $SO_2$ , its sole precursor species. A comparison of model particulate sulphate with observations for five rural monitoring sites dation of  $SO_2$ , its sole precursor species. A comparison of model particulate sulphate<br>with observations for five rural monitoring sites shows good agreement overall, with<br>a close registration of the major pollution epis with observations for five rural monitoring sites shows good agreeme<br>a close registration of the major pollution episodes, though with a t<br>model to underestimate the observations somewhat during winter.<br>The Lagrangian disp a close registration of the major pollution episodes, though with a tendency for the model to underestimate the observations somewhat during winter.<br>The Lagrangian dispersion model has been used to attribute the origins of

particulate sulphate arriving at the measurement sites during two major pollution The Lagrangian dispersion model has been used to attribute the origins of the particulate sulphate arriving at the measurement sites during two major pollution episodes in March 1996 and July 1996. The origins of the parti particulate sulphate arriving at the measurement sites during two major pollution<br>episodes in March 1996 and July 1996. The origins of the particulate sulphate varied<br>markedly between the different sites for the different episodes in March 1996 and July 1996. The origins of the particulate sulphate varied<br>markedly between the different sites for the different episodes. Under some circum-<br>stances, particulate sulphate levels are dominated by markedly between the different sites for the different episodes. Under some circum-<br>stances, particulate sulphate levels are dominated by long-range transport in from<br>the continent of Europe, and this was noticeably the ca other conditions, United Kingdom  $SO<sub>2</sub>$  emissions appear to be the dominant source.

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<sup>2654</sup> *R. G.DerwentandA.L.Malcolm* Downloaded from rsta.royalsocietypublishing.org

2654  $R. G. Derwent and A. L. Malcolm$ <br>In contrast with the case of particulate sulphate, SOA is much less well understood, In contrast with the case of particulate sulphate, SOA is much less well understood, and the questions asked are of a much more rudimentary nature. A highly detailed photochemical model has been assembled inside a highly s In contrast with the case of particulate sulphate, SOA is much less well understood,<br>and the questions asked are of a much more rudimentary nature. A highly detailed<br>photochemical model has been assembled inside a highly s photochemical model has been assembled inside a highly simplistic meteorological model to assess the relative importance of natural biogenic aerosol precursors as photochemical model has been assembled inside a highly simplistic meteorological<br>model to assess the relative importance of natural biogenic aerosol precursors as<br>opposed to man-made precursors. It is concluded that the fo model to assess the relative importance of natural biogenic aerosol precursors as<br>opposed to man-made precursors. It is concluded that the formation of SOAs from<br>the photo-oxidation of terpenes is likely to be several time the photo-oxidation of terpenes is likely to be several times greater in magnitude than that from aromatic hydrocarbon photo-oxidation.

These conclusions from our study necessarily address secondary particles in the than that from aromatic hydrocarbon photo-oxidation.<br>These conclusions from our study necessarily address secondary particles in the<br>fine particle size range as a whole and do not specifically address the very smallest<br>par These conclusions from our study necessarily address secondary particles in the<br>fine particle size range as a whole and do not specifically address the very smallest<br>particles in the ultrafine particle size range. There ar particles in the ultrafine particle size range. There are currently a number of large gaps in understanding which have precluded our focusing on the ultrafine particle particles in the ultrafine particle size range. There are currently a number of large<br>gaps in understanding which have precluded our focusing on the ultrafine particle<br>size range. There is currently no way of knowing how m gaps in understanding which have precluded our focusing on the ultrafine particle<br>size range. There is currently no way of knowing how much of the ultrafine secondary<br>particulate matter in the UK atmosphere has arisen by t size range. There is currently no way of knowing how much of the ultrafine secondary<br>particulate matter in the UK atmosphere has arisen by the homogeneous or hetero-<br>geneous nucleation routes. There are so few measurements particulate matter in the UK atmosphere has arisen by the homogeneous or hetero-<br>geneous nucleation routes. There are so few measurements of ultrafine particles in<br>the United Kingdom that it would be difficult to check mod geneous nucleation routes. There are so few measurements of ultrafine particles in<br>the United Kingdom that it would be difficult to check model performance against<br>observations in any comprehensive manner. Furthermore, the the United Kingdom that it would be difficult to check model performance against observations in any comprehensive manner. Furthermore, there are no internationof ultrafine particle observations.<br>Whether any of our conclusions concerning the source attribution of particulate ally agreed air-quality guidelines with which to assess the public-health significance

of ultrafine particle observations.<br>Whether any of our conclusions concerning the source attribution of particulate<br>sulphate and of SOAs adequately reflect real-world behaviour depends on the ade-<br>quacy and accuracy of the Whether any of our conclusions concerning the source attribution of particulate<br>sulphate and of SOAs adequately reflect real-world behaviour depends on the ade-<br>quacy and accuracy of their input parameters. Without compreh sulphate and of SOAs adequately reflect real-world behaviour depends on the ade-<br>quacy and accuracy of the assumptions and simplifications made in the models and<br>on the accuracy of their input parameters. Without comprehen quacy and accuracy of the assumptions and simplifications made in the models and<br>on the accuracy of their input parameters. Without comprehensive monitoring of<br>aerosol composition across the United Kingdom, it will be diff on the accuracy of their input parameters. Without comprehensive monitoring of aerosol composition across the United Kingdom, it will be difficult to make significant progress. However, we have some confidence that our bas aerosol composition across the United Kingdom, it will be difficult to make significant<br>progress. However, we have some confidence that our basic conclusions concerning<br>the importance of the long-range trans-boundary trans progress. However, we have some confidence that our basic conclusions concerning<br>the importance of the long-range trans-boundary transport of particulate sulphate<br>and the importance of natural biogenic precursors for SOAs

and the importance of natural biogenic precursors for SOAs should be robust.<br>This work was supported as part of the Public Meteorological Service R & D Programme of the Meteorological Office and through the Air Quality Be This work was supported as part of the Public Meteorological Service R & D Programme of the Meteorological Office and through the Air Quality Research Programme of the Department<br>of the Environment. Transport and the Regi Meteorological Office and through the Air Quality Research Programme of the Department of the Environment, Transport and the Regions (contract no. EPG  $1/3/128$ ). The authors Meteorological Office and through the Air Quality Research Programme of the Department<br>of the Environment, Transport and the Regions (contract no. EPG 1/3/128). The authors<br>acknowledge the help and encouragement they have of the Environment, Transport and the Regions (contract no. EPG 1/3/128). The authors<br>acknowledge the help and encouragement they have received from Roy Maryon and Derrick<br>Ryall of the Meteorological Office and from Harvey Ryall of the Meteorological Office and from Harvey Jeffries of the University of North Carolina.<br>The Master Chemical Mechanism was implemented with the assistance of Michael Jenkin, AEA<br>Technology, and Sandra Saunders and The Master Chemical Mechanism was implemented with the assistance of Michael Jenkin, AEA

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*Discussion*

*Discussion*<br>N. ROSE (*ECRC, University College London, UK*). Does the grid used in your SO<sub>2</sub><br>model extend to marine areas, and if so is there a significant contribution, to the  $P$ iscussion<br>
M. ROSE (*ECRC*, *University College London*, *UK*). Does the grid used in your SO<sub>2</sub><br>
model extend to marine areas, and if so is there a significant contribution, to the<br>
UK from shipping sources in the Nor model extend to marine areas, and if so is there a significant contribution, to the UK, from shipping sources in the North Sea and English Channel?

R. G. Derwent. The emission inventories used in our modelling work extend over  $n$ , if om sinpping sources in the North Sea and English Challier.<br>R. G. DERWENT. The emission inventories used in our modelling work extend over<br>marine areas and included substantial emissions of  $SO_2$  from the North Sea R. G. DERWENT. The emission inventories used in our modelling work extend over<br>marine areas and included substantial emissions of  $SO_2$  from the North Sea, English<br>Channel and North Atlantic Ocean shipping as well as natu marine areas and included substantial emissions of  $SO_2$  from the North Sea, English<br>Channel and North Atlantic Ocean shipping as well as natural emissions of DMS.<br>M. WALLIS (*FoE Cymru, Cardiff, UK*). I question the corr

M. WALLIS (*FoE Cymru, Cardiff, UK*). I question the correlation between the data<br>and your sulphate meteorological model. The July 1996 episode for Lough Navar<br>shows 93% from the UK and 7% from European sources, as publis and your sulphate meteorological model. The July 1996 episode for Lough Navar shows 93% from the UK and 7% from European sources, as published in the APEG and your sulphate meteorological model. The July 1996 episode for Lough Navar<br>shows 93% from the UK and 7% from European sources, as published in the APEG<br>report (APEG 1999) and no significance for validation of your model shows 93% from the UK and 7% from European sources, as published in the APEG<br>report (APEG 1999) and no significance for validation of your model. The total year<br>1995 data you presented shows what is well known, that anticy report (APEG 1999) and no significance for validation of your model. The total year<br>1995 data you presented shows what is well known, that anticyclonic conditions with<br>easterly or southeasterly winds allow accumulation of 1995 data you presented shows what is well known, that anticyclonic conditions with easterly or southeasterly winds allow accumulation of locally emitted air pollutants. You cannot distinguish this from your 'European' sou easterly or southeasterly winds allow accumulation of locally emitted air pollutants.<br>You cannot distinguish this from your 'European' source. APEG para. 4.3.1 says,<br>'during the winter time, the model clearly underestimat You cannot distinguish this from your 'European' source. APEG para.<br>
'during the winter time, the model clearly underestimates the observat<br>
the neglect of the ammonic-ozone- $SO_2$  cloud droplet oxidation route'.<br>
The UK g uring the winter time, the model clearly underestimates the observations due to<br>e neglect of the ammonic-ozone- $SO_2$  cloud droplet oxidation route'.<br>The UK government uses your results to say that we cannot meet  $PM_{10}$  s

the neglect of the ammonic-ozone- $SO_2$  cloud droplet oxidation route'.<br>The UK government uses your results to say that we cannot meet  $PM_{10}$  standards<br>by UK traffic and industry controls, so the issue is important for po The UK government uses your results to say that we cannot meet  $PM_{10}$  standards<br>by UK traffic and industry controls, so the issue is important for policy. The APEG<br>Committee was not convinced. Has your new work been vali by UK traffic and industry controls, so the is<br>Committee was not convinced. Has your ne<br>and what confidence can be placed in it? and what confidence can be placed in it?<br>R. G. DERWENT. The modelling work on particulate sulphate has been validated

and what comparison with observations and the results have been published by Malcolm *et*<br>by comparison with observations and the results have been published by Malcolm *et*<br>al. (2000) **R. G. DERV**<br>by comparise<br>al. (2000). by comparison with observations and the results have been published by Malcolm *et*<br>al. (2000).<br>C. N. HEWITT AND H. STEWART (*Institute of Environmental and Natural Sciences*,<br>*Injuencity of Lengaster, HK*). You use the Ma

*ul.* (2000).<br>C. N. HEWITT AND H. STEWART (*Institute of Environmental and Natural Sciences*, *University of Lancaster, UK*). You use the Master Chemical Mechanism to predict the degradation of  $\alpha$ -pinene emitted by veget C. N. HEWITT AND H. STEWART (*Institute of Environmental and Natural Sciences*, *University of Lancaster*, *UK*). You use the Master Chemical Mechanism to predict the degradation of  $\alpha$ -pinene emitted by vegetation in th *University of Lancaster, UK*). You use the Master Chemical Mechanism to predict the degradation of  $\alpha$ -pinene emitted by vegetation in the UK and to describe the formation of semi-volatile organic products that may nucl the degradation of  $\alpha$ -pinene emitted by vegetation in the UK and to describe the formation of semi-volatile organic products that may nucleate or condense onto pre-<br>existing particles. From this, it was shown that bioge formation of semi-volatile organic products that may nucleate or condense onto pre-<br>existing particles. From this, it was shown that biogenic emissions of terpenes have<br>the potential to account for a significant fraction o existing particles. From this, it was shown that biogenic emissions of terpenes have the potential to account for a significant fraction of the secondary organic aerosol in the UK.

In our work on the emissions of volatile organic compounds from the biosphere to the atmosphere, we have shown that relatively few plant species contribute to the In our work on the emissions of volatile organic compounds from the biosphere to<br>the atmosphere, we have shown that relatively few plant species contribute to the<br>emissions of the total flux of VOCs in the UK. In fact, th the atmosphere, we have shown that relatively few plant species contribute to the emissions of the total flux of VOCs in the UK. In fact, three tree species probably contribute more than  $60\%$  of the total biogenic isopr emissions of the total flux of VOCs in the UK. In fact, three tree species probably con-<br>tribute more than 60% of the total biogenic isoprene flux in the UK. These are *Quer-*<br>cus spp (oak, 27%), *Picea sitchensis* (Sitka tribute more than 60% of the total biogenic isoprene flux in the UK. These are *Quercus* spp (oak, 27%), *Picea sitchensis* (Sitka spruce, 27%) and *Populus* spp (poplar, 11%). Our current best estimate of the total isopr cus spp (oak, 27%), *Picea sitchensis* (Sitka spruce, 27%) and *Pop* 11%). Our current best estimate of the total isoprene emission rate temperature of 30 °C and a light intensity of 1000 µmol m<sup>-2</sup> s<sup>-2000</sup>  $s^{-1}$  (S cus spp (oak, 27%), *Picea sitchensis* (Sitka spruce, 27%) and *Populus* spp (poplar, 11%). Our current best estimate of the total isoprene emission rate is  $88 \text{ th}^{-1}$  at a temperature of 30 °C and a light intensity of temperature of 30 °C and a light intensity of 1000  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> (Stewart *et al.* 00).<br>In the case of the C<sub>10</sub> monoterpene family, our work indicates that 10 plant species<br>obably account for more than 85% of the t

2000).<br>In the case of the  $C_{10}$  monoterpene family, our work indicates that 10 plant species<br>probably account for more than 85% of the total monoterpene emission flux in the In the case of the  $C_{10}$  monoterpene family, our work indicates that 10 plant species<br>probably account for more than 85% of the total monoterpene emission flux in the<br>UK. These are *Picea sitchensis* (Sitka spruce, 35%) probably account for more than 85% of the total monoterpene emission flux in the<br>UK. These are *Picea sitchensis* (Sitka spruce, 35%), *Pinus sylvestris* (Scots pine,<br>13%), *Calluna vulgaris* (heather, 9%), *Larix* spp (la UK. These are *Picea sitchensis* (Sitka spruce, 35%), *Pinus sylvestris* (Scots pine, 13%), *Calluna vulgaris* (heather, 9%), *Larix* spp (larch, 7%), *Pinus contorta* (beach pine, 6%), *Cirsium arvense* (creeping thistle, 13%), *Calluna vulgaris* (heather,  $9\%$ ), *Larix* spp (larch,  $7\%$ ), *Pinus contorta* (beach<br>pine,  $6\%$ ), *Cirsium arvense* (creeping thistle,  $6\%$ ), *Picea abies* (Norway spruce,  $5\%$ ),<br>*Hordeum vulgare* (barley,  $2$ pine, 6%), *Cirsium arvense* (creeping thistle, 6%), *Picea abies* (Norway spruce, 5%), *Hordeum vulgare* (barley, 2%), *Pisum sativum* (peas, 2%) and *Taraxacum* agg. (dandelion, 2%). The monoterpene compounds known to b *Hordeum vulgare* (barley, 2%), *Pisum sativum* (peas, 2%) and *Taraxacum* agg. (dandelion, 2%). The monoterpene compounds known to be emitted from these species are  $\alpha$ -pinene,  $\beta$ -pinene, D-limonene, camphene, delta-3  $\alpha$ -pinene,  $\beta$ -pinene, D-limonene, camphene, delta-3 carene, myrcene,  $\beta$ -phellandrene, *Phil. Trans. R. Soc. Lond.* A (2000)

 $s^{-1}$ . T

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Exercise and  $\alpha$ -thujene. Our current best estimate of<br>i.e is 68 t h<sup>-1</sup> at a temperature of 30 °C and a<br>. This is reduced to 11 t h<sup>-1</sup> or 96 kt yr<sup>-1</sup> at an<br>. light intensity of 500 µmol m<sup>-2</sup> s<sup>-1</sup> (Stewart *et* 

s¡<sup>1</sup> (Stewart *et*

erage temperature of 10 °C and a light intensity of 500  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> (Stewart *et* . 2000).<br>Interestingly, the commonly held notion that *brassica napus* (oil seed rape) is a olific emitter of monoternenes is almos al. 2000).<br>Interestingly, the commonly held notion that *brassica napus* (oil seed rape) is a<br>prolific emitter of monoterpenes is almost certainly incorrect. It is known to emit Interestingly, the commonly held notion that *brassica napus* (oil seed rape) is a prolific emitter of monoterpenes is almost certainly incorrect. It is known to emit  $\alpha$ - and  $\beta$ -pinene,  $\delta$ -limonene, sabinene and  $\alpha$ prolific emitter of monoterpenes is almost certainly incorrect. It is known to emit  $\alpha$ - and  $\beta$ -pinene,  $\delta$ -limonene, sabinene and  $\alpha$ -thujene, but at rates at least an order of magnitude lower (on a per dry weight b above. of magnitude lower (on a per dry weight basis) than the emitting tree species listed above.<br>Clearly, a quantitive assessment of the role of emissions of VOCs to secondary

aerosol formation requires an understanding of the species specific flux rates of the compounds from the biosphere to the atmosphere and of their chemistry in the atmosphere.

compounds from the biosphere to the atmosphere and of their chemistry in the<br>atmosphere.<br>R. G. DERWENT. These comments are most helpful, and we will endeavour to use<br>your results in our future work atmosphere.<br>R. G. DERWENT. These commer<br>your results in our future work. *Additional reference*

*Additional reference*<br>Stewart, H., Hewitt, C. N. & Bunce, R. 2000 Emissions of volatile organic compounds from the<br>biosphere to the atmosphere in the United Kingdom, Atmos, Environ (Submitted) biosphere to the atmosphere in the United Kingdom. *Atmos. Environ.* (Submitted.)