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R. G. Derwent and A. L. Malcolm

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By R. G. Derwent and A. L. Malcolm

Climate Research Division, Meteorological Office,
London Road, Bracknell RG12 2SZ, UK

While much of the suspended particulate matter found in the ambient air in urban areas has been emitted directly into the atmosphere, some has been formed there by photochemical reactions from gaseous precursor species. Two major components of 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 oxidation of terpenes and aromatic hydrocarbons. A Lagrangian dispersion model has been used to describe 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 trajectory model is used to describe the formation of secondary organic aerosols and to assess the relative contributions from natural biogenic and man-made precursor sources during conditions typical of photochemical pollution episodes.

Keywords: suspended particulate matter; particulate sulphate; secondary organic aerosols; terpenes; aromatic hydrocarbons; SO_2

1. Introduction

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 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 particulate pollution in future air-quality policy.

While much of the suspended particulate matter found in urban areas has been 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 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 secondary particulate matter, or secondary particles, to distinguish it from the primary emitted material. In air-quality policy terms, this distinction is paramount. For emission controls to be effective against secondary particles, they have to operate on the sources of the precursor pollutants that drive the atmospheric chemical production of the secondary particles.

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 specific set of clearly defined atmospheric processes. The term describes primarily the processes whereby gas-phase chemical reactions involving specific precursor gases produce low-volatility products which are capable of homogeneous nucleation to form tiny new particles that can then increase in size by coagulation and capture by pre-existing ambient particles. The term also describes the processes whereby the low-volatility gas-phase reaction products condense onto pre-existing ambient 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 in the atmosphere, heterogeneous nucleation can only increase the mass of the aerosol particles per unit volume. Homogeneous nucleation operates in the ultrafine particle size range, and heterogeneous nucleation across the ultrafine and fine particle size ranges.

The main chemical constituents of secondary particulate matter that have been identified generally in urban locations include sulphuric acid and ammonium sulphate, 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 man-made SO_2 and NO_x precursors. In contrast, the organic constituents appear to have been derived from natural biogenic precursors.

This paper focuses on quality policy for the United Kingdom and aims to address the two following questions.

(1) Is it possible to attribute the origins of the secondary particulate sulphate observed in the UK to UK SO_2 sources alone or are European SO_2 sources also making a contribution?

(2) Is it possible to assess the likely contribution from natural biogenic sources to secondary organic aerosol levels in the UK?

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

2. Source attribution of particulate sulphate in the UK

Of all the chemical constituents of secondary suspended particulate matter, easily the best quantified are sulphuric acid and ammonium sulphate aerosols, known collectively as particulate sulphate. This situation holds particularly for the United Kingdom (APEG 1999), the focus of this study. The formation mechanisms for sulphate aerosols have been well characterized (Finlayson-Pitts & Pitts 1986), and particulate sulphate observations are available for the United Kingdom (QUARG 1996; APEG 1999) and Europe (Hjellbrekke 1999; Lazaridis *et al*. 1999).

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 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 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 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 July episode was dominated by UK sources.

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 study and have compared the model results with observations from five rural sulphate measurement sites. Attribution plots during the two episodes are also presented, revealing the likely origins of the observed particulate sulphate.

(*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 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 dispersion simulated by 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 deposition scheme is based on a resistance analogy parametrization to determine the deposition velocity and wet deposition is parametrized by washout and rainout processes using a scavenging coefficient method. Cloud fraction and cloud liquid water output from the UM are used to drive the aqueous phase of the chemistry.

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

(*b*) *Oxidation of sulphur dioxide*

In the atmosphere the gas-phase oxidation of sulphur dioxide (SO_2) is dominated by its reaction with the hydroxyl radical, OH. The hydroxyl radical plays an impor-

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

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

tant part in tropospheric chemistry due to both its high reactivity with trace species such as SO_2 and because of its photochemical regeneration in the atmosphere. In 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 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 SO_2 with O_3 is dependent on the acidity of the cloud droplets and is much more likely to be limited by high acidity (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 of this base species can be included in the calculation of cloud pH.

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 km × 50 km area 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 chemistry model which is driven by global meteorological data from the UM and runs on a much larger scale than NAME (a 5° × 5° grid square is used, which gives a resolution of *ca.* 600 km × 400 km at mid-latitudes), and, hence, is unable to produce the same degree of fine spatial and temporal resolution that can be achieved in NAME. A full description 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 thereafter is modelled in NAME as a three-dimensional field.

(*c*) *NAME results for 1996*

Five rural measurement sites (Yarner Wood, Eskdalemuir, High Muffles, Strathvaich and Lough Navar) produce daily values of ambient particulate sulphate, and 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) on behalf of the Department of the Environment, Transport and the Regions (DETR) at http://www.aeat.co.uk/netcen/airqual/index.html.

The model was run over a domain of longitude 15.0° W to 20.0° E and latitude 43.0° N to 65.0° N. Modelled sulphuric acid has been added to modelled ammonium sulphate to give particulate sulphate in $\mu g\ m^{-3}$ of SO_4. Table 1 shows a set of four

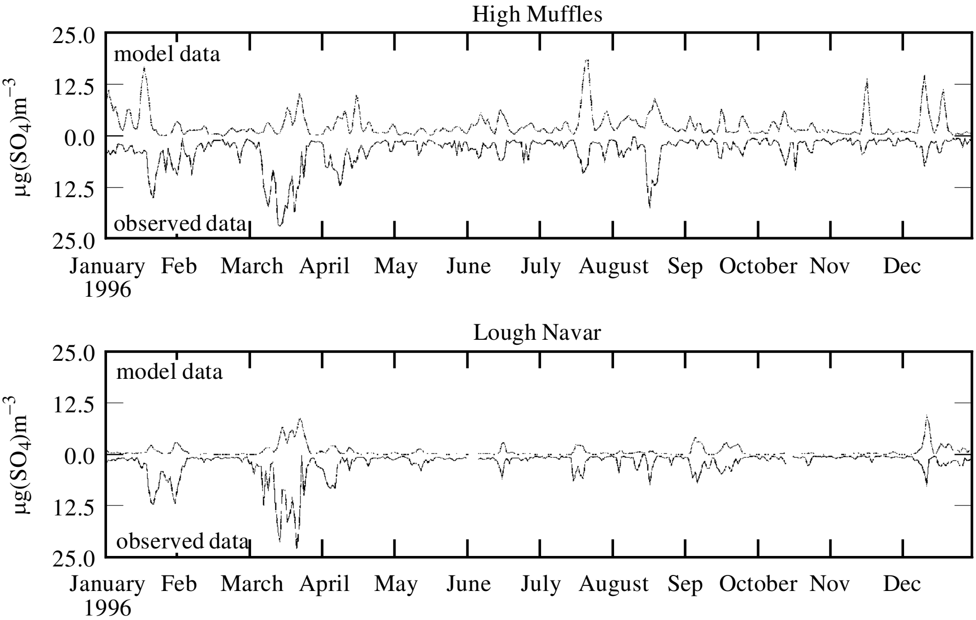


Figure 1. NAME model daily sulphate aerosols plotted against measured sulphate aerosols at Lough Navar and High Muffles for 1996.

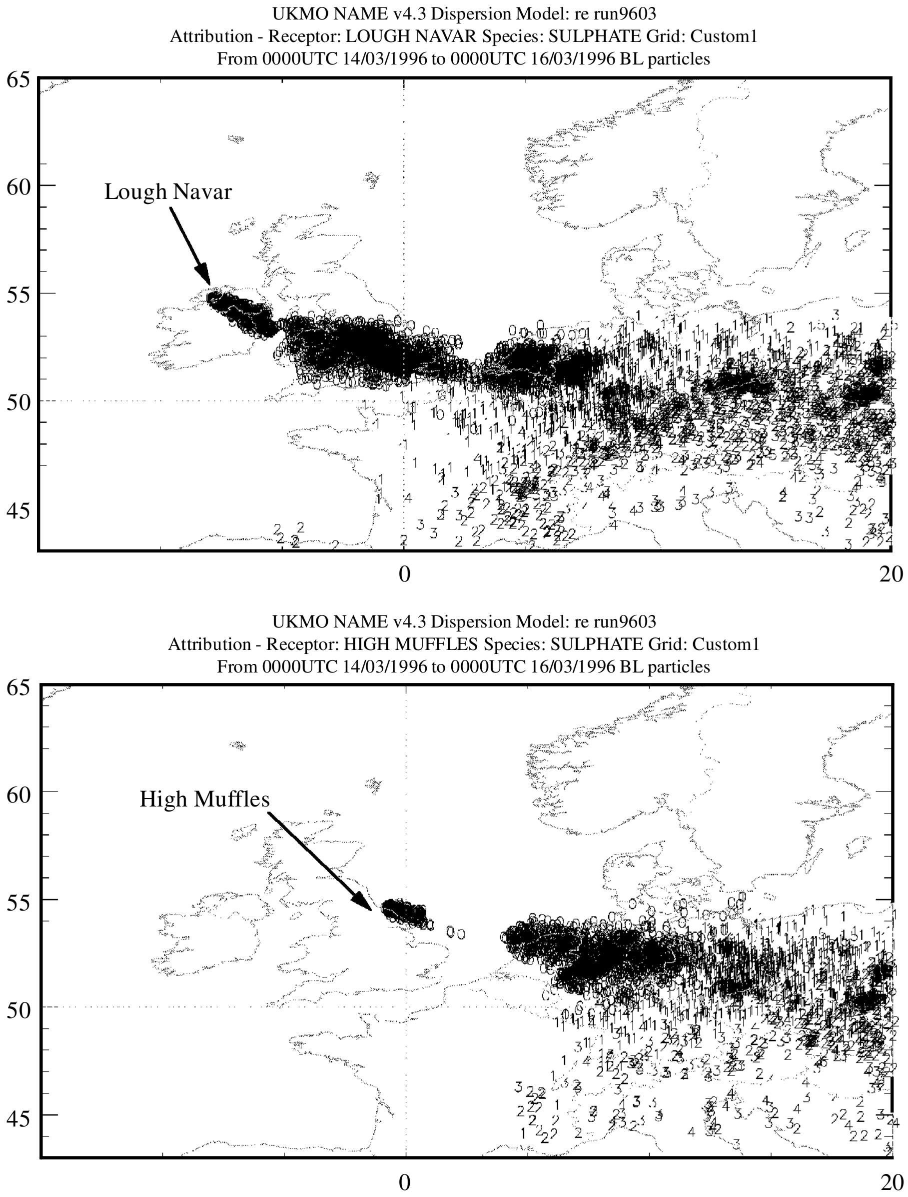
standard statistics (correlation, bias, normalized mean square error (NMSE), and percentage within a factor of two) calculated on daily values for the five sites over 1996.

Comparison with a previous model run for this period (Malcolm *et al.* 2000) shows 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 by 5.41 and the average percentage within a factor of two is increased by 21.6%.

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 episode in March is still 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 transport of particulate sulphate, perhaps that is to be expected. To improve model performance significantly, we would need more detailed resolution SO_2 emissions (both spatially and temporally) and also 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 sub-grid scale meteorological 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 14–16 March 1996 and 19–



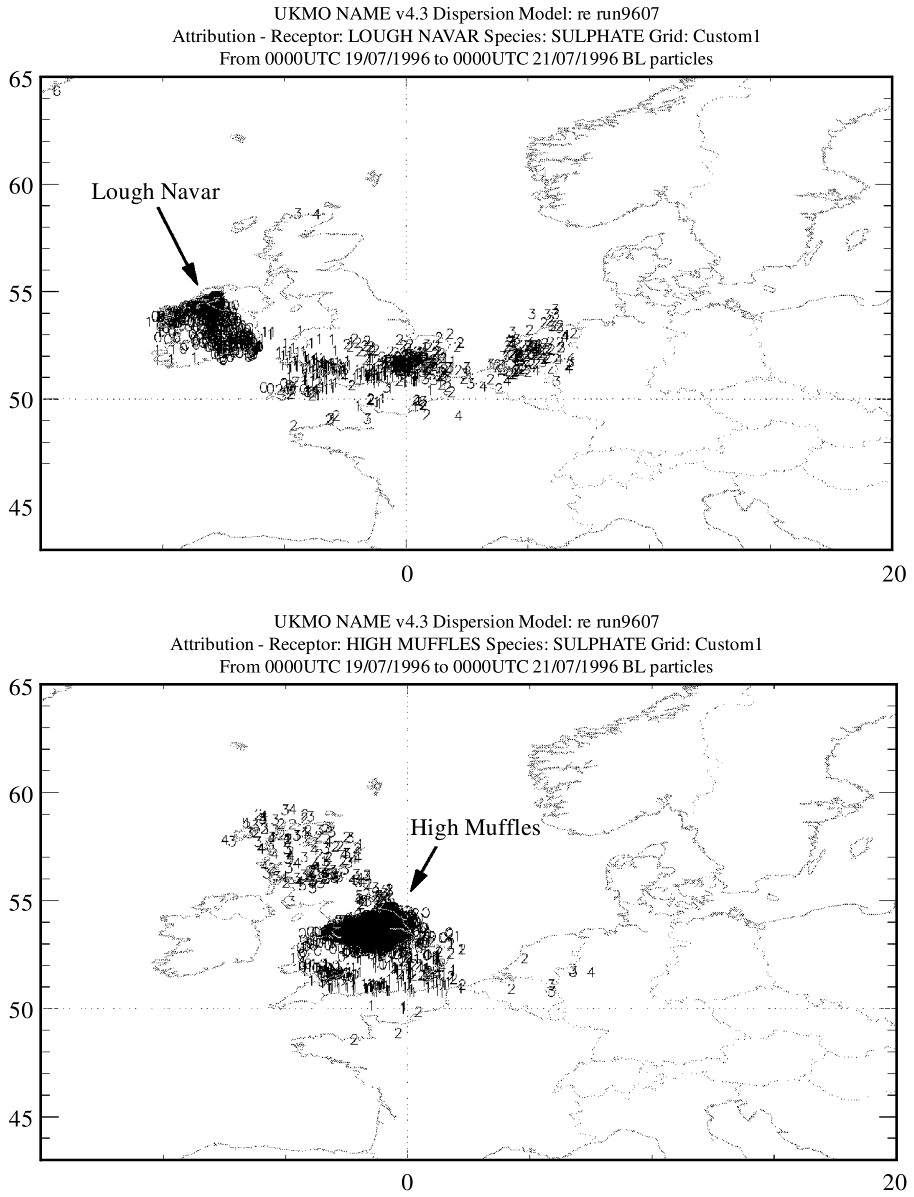
UKMO NAME v4.3 Dispersion Model: re run9603
Attribution - Receptor: LOUGH NAVAR Species: SULPHATE Grid: Custom1
From 0000UTC 14/03/1996 to 0000UTC 16/03/1996 BL particles

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 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 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 High Muffles in these examples).

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 Europe. Some of the SO_2



UKMO NAME v4.3 Dispersion Model: re run9607
Attribution - Receptor: LOUGH NAVAR Species: SULPHATE Grid: Custom1
From 0000UTC 19/07/1996 to 0000UTC 21/07/1996 BL particles

UKMO NAME v4.3 Dispersion Model: re run9607
Attribution - Receptor: HIGH MUFFLES Species: SULPHATE Grid: Custom1
From 0000UTC 19/07/1996 to 0000UTC 21/07/1996 BL particles

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 transport to Northern Ireland. High Muffles is dominated by the European sources during this period, with the only UK contribution being from coastal areas near to the measurement site. Again, travel times of several days are seen.

In figure 3 the particulate sulphate modelled at Lough Navar during this two-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 in the Midlands region. The

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 al*. (2000).

The Lagrangian nature of the NAME model makes it possible to attribute modelled sulphate aerosols to the SO_2 emission from which it was generated. This facility has 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 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 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 an important role in the formation of tropospheric aerosols. The sunlight-driven atmospheric photo-oxidation of high-molecular-weight hydrocarbons has been shown to produce low vapour pressure reaction products that partition between the gas and aerosol phases (Pandis *et al*. 1992). These reaction products are known as semi-volatile organic compounds because of their ability to pass between the gas and aerosol phases (Kamens *et al*. 1999). In the aerosol phase, these reaction products are 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 most important source (Odum *et al*. 1996).

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 trajectory model has been used 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 pollution episode.

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

The formation of SOAs during a summertime regional scale pollution episode has been described using the UK Photochemical Trajectory Model (UK PTM). This model addresses the detailed chemical development in an air parcel as it moves across the European emissions grid following a six-day trajectory from Austria through to 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, humidities, boundary-layer depths, wind speeds and wind directions were all diurnally varying and given values appropriate to the conditions of regional scale pollution episodes.

The UK PTM employs the Master Chemical Mechanism (MCM) to describe the 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 the reactions of the simple atoms and radicals containing oxygen, hydrogen and nitrogen and those of

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/mcmproj.html.

The fast photochemistry and regional photochemical ozone production occurring in the UK PTM are driven by the emissions picked up by the air parcel as it traverses Europe. The emissions of NO_x, CO, SO_2, isoprene and volatile organic compounds (VOCs) were employed at 150 km × 150 km scale across Europe based on EMEP emissions (Mylona 1999), at 50 km × 50 km where available from either EMEP or EC CORINAIR (Bouscaren & Cornaert 1995) and at 10 km × 10 km within the United Kingdom from Salway *et al.* (1996). European emission inventories (Mylona 1999) may be downloaded from the World Wide Web at http://www.emep.int.

The emissions of all VOCs were split into the emissions of individual organic compounds using the detailed speciated emission inventory available for the United Kingdom 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 and the peroxyacylnitrates.

(*b*) *Model treatment of SOAs*

The formation of SOAs in the UK PTM was driven by the emissions of terpenes from natural biogenic emissions and aromatic hydrocarbons as the air parcel traversed Europe. Emissions of terpenes at a spatial resolution of 1° × 1° and for the month of July for Europe were taken from the Global Emission Inventory Activity emissions database (http://blueskies.sprl.umich.edu/geia/).

It was assumed that all the terpene emissions occurred into the UK PTM as α-pinene. No explicit temperature or time dependence was assumed for these emissions, and the emissions from a particular grid square were held constant at the monthly average emission rate. Emissions of each of the aromatic hydrocarbons was taken from the EMEP (Mylona 1999), EC CORINAIR (G. McInnes 1994, personal communication) and UK NAEI inventories using the VOC speciation taken from Derwent *et al*. (1996).

The MCM version 2.0 was used to describe the reactions of α-pinene with OH radicals and ozone during daylight and with NO_3 radicals and ozone during nighttime (Jenkin *et al*. 2000). Altogether the α-pinene degradation scheme contained over 329 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 hydroperoxypinonaldehyde. These semi-volatile organic compounds have been scavenged in the UK PTM by pre-existing aerosol species in competition with their subsequent atmospheric degradation. No loss of semi-volatile organic matter from the aerosol back into the gas phase was allowed in order to simulate the upper limit concentrations of SOAs.

The MCM version 2.0 was also used to describe the reactions of aromatic hydrocarbons with OH radicals which generate SOAs. A small fraction of chemical flux through these reactions was assumed to generate low-volatility reaction products, 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*. 1997), otherwise they have been set to zero. Again, these semi-volatile organic compounds have been scavenged in the

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*

(Mass fractions of SOAs produced from each aromatic hydrocarbon oxidized were taken from 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-dimethylethylbenzene and 3,5-diethyltoluene.)

aromatic hydrocarbon	fraction by mass of SOA to hydrocarbon oxidized	percentage contribution to SOA formation (%)
toluene	0.089	60.0
o-xylene	0.026	4.0
m-xylene	0.038	4.5
p-xylene	0.025	12.8
ethylbenzene	0.086	9.2
1,3,5-trimethylbenzene	0.031	0.4
m-ethyltoluene	0.065	1.9
p-ethyltoluene	0.054	2.2
o-ethyltoluene	0.062	1.9
n-propylbenzene	0.081	3.0

UK PTM by pre-existing aerosol species. No loss of semi-volatile organic matter from 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-furandiones (Forstner *et al.* 1997).

(*c*) *Model results for SOAs*

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-volatile organic matter from the aerosol once scavenged has been allowed, the concentrations of SOAs represent an upper limit to those anticipated in the real atmospheric boundary layer. The figure shows the concentrations of SOAs formed from the photo-oxidation of both natural biogenic hydrocarbons and man-made aromatic hydrocarbons. The conclusion is that the SOA formed from terpene photo-oxidation is several times greater in concentration compared with that from aromatic hydrocarbon photo-oxidation.

By way of comparison, the above model experiment also generated 18 $\mu g\,m^{-3}$ of particulate sulphate from the oxidation of SO_2. The modelled concentrations of 5–10 $\mu g\,m^{-3}$ for SOAs suggest that natural biogenic α-pinene may potentially make 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 the scavenging of the semi-volatile terpene degradation products by the ambient aerosol and the subsequent fate of this aerosol.

The present study in figure 4 shows that the SOA formed from the photo-oxidation of aromatic hydrocarbons produces only *ca.* 10–15% of the total yield of SOAs from

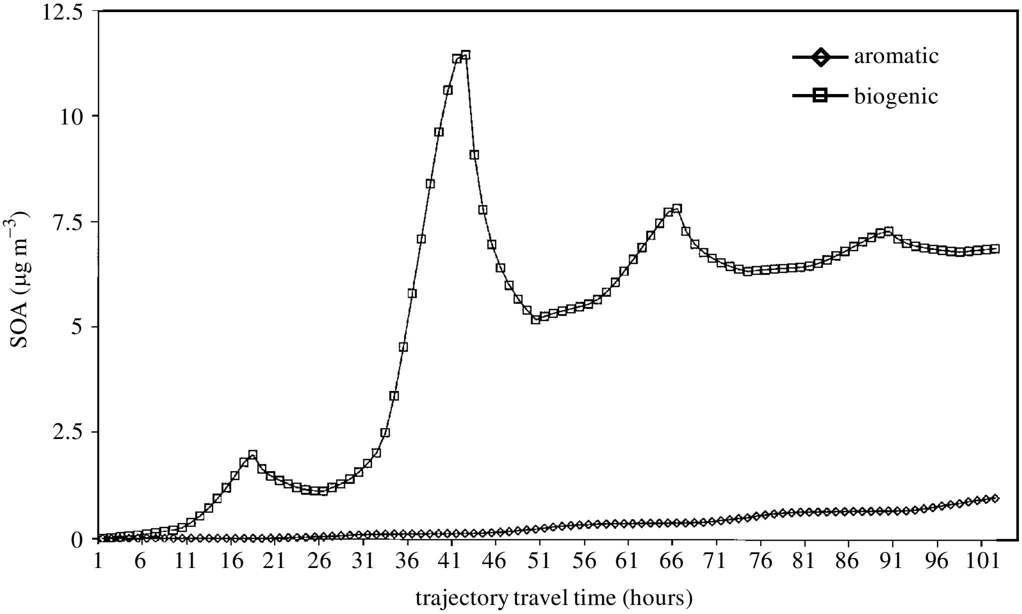


Figure 4. SOAs from natural biogenic α-pinene and man-made aromatic hydrocarbon photo-oxidation in the UK PTM.

both natural biogenic and man-made hydrocarbon photo-oxidation across Europe in 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 different emissions, OH reactivities and SOA yields for each individual aromatic hydrocarbon. Three species—toluene, *p*-xylene and ethylbenzene—together account for over 80% of the overall SOA yield from aromatic hydrocarbon photo-oxidation under European conditions.

4. Discussion

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 dispersion model has been 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 shows good agreement overall, with a close registration of the major pollution episodes, though with a tendency for the model to underestimate the observations somewhat during winter.

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 particulate sulphate varied markedly between the different sites for the different episodes. Under some circumstances, particulate sulphate levels are dominated by long-range transport in from the continent of Europe, and this was noticeably the case during March 1996. Under other conditions, United Kingdom SO_2 emissions appear to be the dominant source.

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 simplistic meteorological model to assess the relative importance of natural biogenic aerosol precursors as opposed to man-made precursors. It is concluded that the formation of SOAs from 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 fine particle size range as a whole and do not specifically address the very smallest 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 size range. There is currently no way of knowing how much of the ultrafine secondary particulate matter in the UK atmosphere has arisen by the homogeneous or heterogeneous nucleation routes. There are so few measurements of ultrafine particles in the United Kingdom that it would be difficult to check model performance against observations in any comprehensive manner. Furthermore, there are no internationally agreed air-quality guidelines with which to assess the public-health significance of ultrafine particle observations.

Whether any of our conclusions concerning the source attribution of particulate sulphate and of SOAs adequately reflect real-world behaviour depends on the adequacy and accuracy of the assumptions and simplifications made in the models and 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 basic conclusions concerning the importance of the long-range trans-boundary transport of particulate sulphate and the importance of natural biogenic precursors for SOAs should be robust.

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Discussion

N. Rose (*ECRC, University College London, UK*). Does the grid used in your SO_2 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 marine areas and included substantial emissions of SO_2 from the North Sea, English Channel and North Atlantic Ocean shipping as well as natural emissions of DMS.

M. Wallis (*FoE Cymru, Cardiff, UK*). I question the correlation between the data 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 report (APEG 1999) and no significance for validation of your model. The total year 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' source. APEG para. 4.3.1 says, 'during the winter time, the model clearly underestimates the observations due to the neglect of the ammonic–ozone–SO_2 cloud droplet oxidation route'.

The UK government uses your results to say that we cannot meet PM_{10} standards by UK traffic and industry controls, so the issue is important for policy. The APEG Committee was not convinced. Has your new work been validated by peer review and what confidence can be placed in it?

R. G. Derwent. The modelling work on particulate sulphate has been validated by comparison with observations and the results have been published by Malcolm *et al*. (2000).

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 α-pinene emitted by vegetation in the UK and to describe the formation of semi-volatile organic products that may nucleate or condense onto pre-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 emissions of the total flux of VOCs in the UK. In fact, three tree species probably contribute 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 isoprene emission rate is 88 $\mathrm{t\,h^{-1}}$ at a temperature of 30 °C and a light intensity of 1000 $\mathrm{\mu mol\,m^{-2}\,s^{-1}}$ (Stewart *et al*. 2000).

In the case of the C_{10} monoterpene family, our work indicates that 10 plant species probably account for more than 85% of the total monoterpene emission flux in the 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, 6%), *Picea abies* (Norway spruce, 5%), *Hordeum vulgare* (barley, 2%), *Pisum sativum* (peas, 2%) and *Taraxacum* agg. (dandelion, 2%). The monoterpene compounds known to be emitted from these species are α-pinene, β-pinene, D-limonene, camphene, delta-3 carene, myrcene, β-phellandrene, sabinene and 1,8-cineole. Additionally, there are suggestions that other compounds may be emitted by these species, including α-, β- and γ-terpinene, cymene, α-phellandrene, β-fenchene, tricyclene and α-thujene. Our current best estimate of the total monoterpene emission rate is 68 t h^{-1} at a temperature of 30 °C and a light intensity of 1000 µmol m^{-2} s^{-1}. This is reduced to 11 t h^{-1} or 96 kt yr^{-1} at an average temperature of 10 °C and a light intensity of 500 µmol m^{-2} s^{-1} (Stewart *et al*. 2000).

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 α- and β-pinene, δ-limonene, sabinene and α-thujene, but at rates at least an order of magnitude lower (on a per dry weight basis) than the emitting tree species listed above.

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.

R. G. DERWENT. These comments are most helpful, and we will endeavour to use your results in our future work.

Additional reference

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