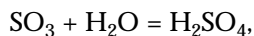
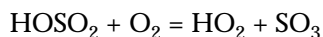
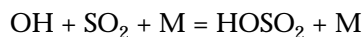


4.1 INTRODUCTION

There are a wide variety of substances which, following their release into the atmosphere in the gaseous phase, form low volatility species through the action of atmospheric chemical reactions. These low volatility species are initially present as gaseous species but ultimately, some distance downwind, become particles or become attached to particles. If they become secondary particles by the nucleation of entirely new particles and grow by coalescence, then the particles are said to have been formed by homogeneous nucleation. However, more often the low volatility species attach themselves to pre-existing aerosol species in which case the process is called heterogeneous nucleation. In both situations, the gaseous emission has led to the increase in the mass of the particles per unit volume, but only in the first case with homogeneous nucleation has there also been an increase in the number of particles per unit volume.

4.1.1 SULPHURIC ACID AND SULPHATE AEROSOL PARTICLES

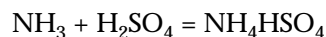
In situations relevant to the United Kingdom, the formation of secondary particulate matter through the generation of entirely new particles by homogeneous nucleation, appears to occur by the photochemical oxidation of sulphur dioxide (SO₂). Sulphur dioxide is a common constituent of ambient air in the United Kingdom mainly through its emission from coal-burning in large electricity-generating stations and from industrial coal- and oil-burning. Photochemical oxidation of sulphur dioxide is initiated through the following sequence of reactions:



where M represents an atmospheric nitrogen or oxygen molecule, and OH is the hydroxyl free radical.

The sulphuric acid, H₂SO₄, vapour then nucleates to form sulphuric acid droplets and by simultaneously condensing water vapour, grows rapidly out of the nanometre size range. These initial nuclei continue growing rapidly by condensing more water vapour, by coalescing with each other by Brownian aggregation and by coagulation with pre-existing aerosol particles. Ultimately the particles increase in size producing a relatively stable distribution of particles sizes in the nucleation and accumulation modes, covering the entire 10 nm to 1 µm size range.

The highly acidic aerosol droplets can also take up ammonia, NH₃, from the gas phase forming droplets of ammonium sulphate, leading also to a growth in aerosol mass per unit volume, through the reactions:



The main sources of NH₃ are agricultural in origin through the storage, disposal and application to soils of animal wastes and industrial fertilisers.

The timescale for the nucleation and accumulation processes involving sulphuric acid are generally rapid compared with the timescale of the SO₂ oxidation processes. The photochemical production of sulphuric acid particles therefore occurs on the spatial scale of the SO₂ oxidation which in turn depends on the hydroxyl radical (OH) concentration. Under typical conditions, the SO₂ oxidation rate by this route occurs at the rate of about a few per cent per hour. This gives a timescale of 30-50 hours and a spatial scale of about 500-750 km which is well into the regional or long-range transport scale.

Photochemical oxidation of SO₂, as its name implies, is driven by sunlight and occurs to a greater or lesser extent at different times of the year. Under photochemical episode conditions during summertime, the chemical reactions which lead to the production of elevated ozone concentrations

also lead to the elevated concentrations of the highly reactive OH radical which oxidises SO₂ to sulphuric acid aerosol. This aerosol will rapidly take up any available ammonia, producing a mixture of sulphuric acid droplets and ammonium sulphate particles. This complex mixture of particles and droplets is a highly efficient light scattering medium and can produce a marked reduction in visual range. This visibility reduction is the origin of characteristic heat hazes often noticed during photochemical pollution episodes (Lovelock, 1972).

During an intense photochemical episode at Harwell, Oxfordshire during 3rd July 1971, hourly mean sulphate aerosol concentrations reached 70 µg SO₄ m⁻³, of which 27 µg SO₄ m⁻³ was measured as sulphuric acid (Atkins *et al.*, 1972). There has been a general decline in sulphate concentrations in the UK since that time.

Photochemical oxidation followed by homogeneous nucleation is an important oxidation route for SO₂

because of its ability to form new particles and also to increase the mass of pre-existing particles. This is not the only SO₂ oxidation route and in wintertime and in the presence of cloud droplets, other oxidation routes come into play involving heterogeneous nucleation. These routes involve the dissolution of SO₂ in cloud droplets and the subsequent oxidation of the dissolved SO₂ by hydrogen peroxide, ozone or oxygen. Because these droplet oxidation routes necessarily involve pre-existing cloud droplets, they do not lead to an increase in the number of particles. They do lead, however, to the increase in mass of the cloud droplets. If the fate of the cloud droplets is to fall as rain then the SO₂ oxidation in droplets will have led to the presence of sulphate in rain. If the cloud droplets subsequently evaporate, then the SO₂ oxidation will have led to an increase in the mass of the original cloud condensation nuclei which had formed the pre-existing cloud droplets.

Photochemical and cloud oxidation of SO₂ occur over similar timescales and spatial scales, though

Figure 4.1 European distribution of particulate sulphate using annual mean data from the EMEP monitoring network.

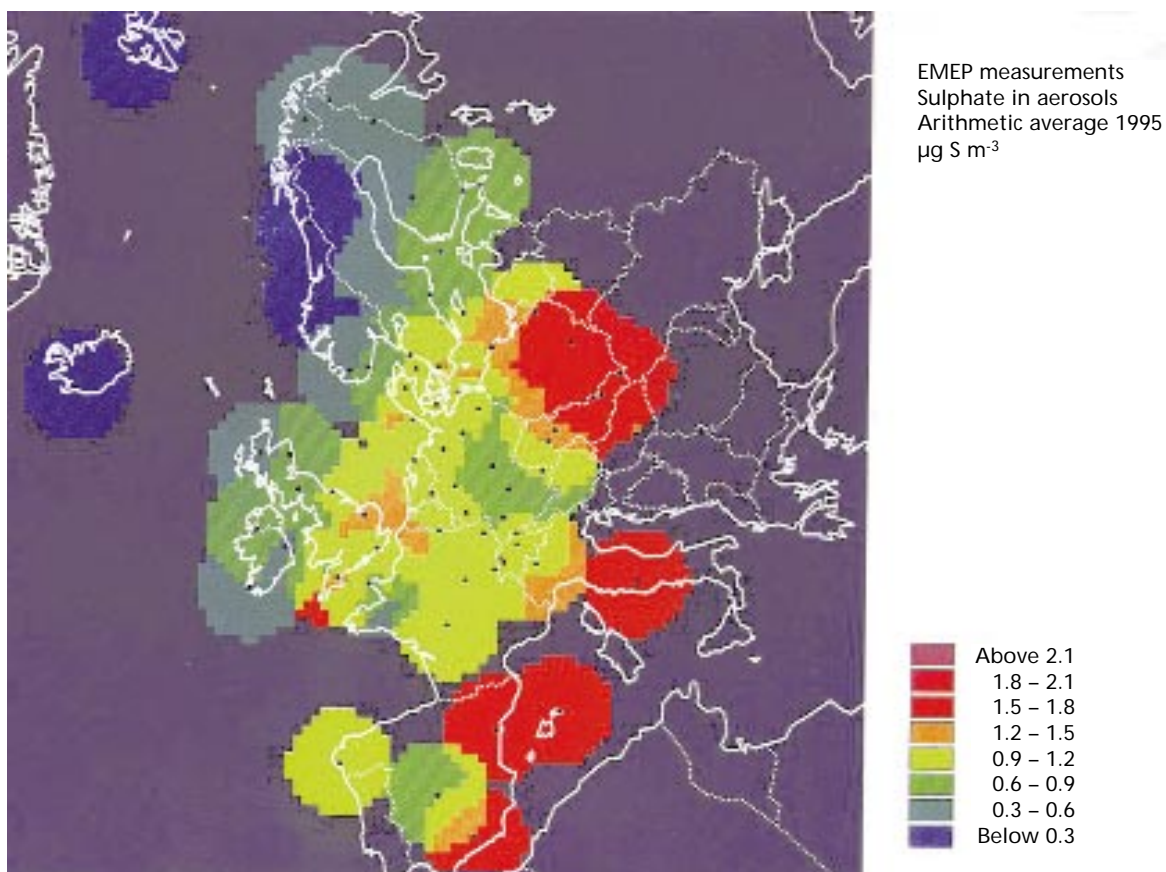
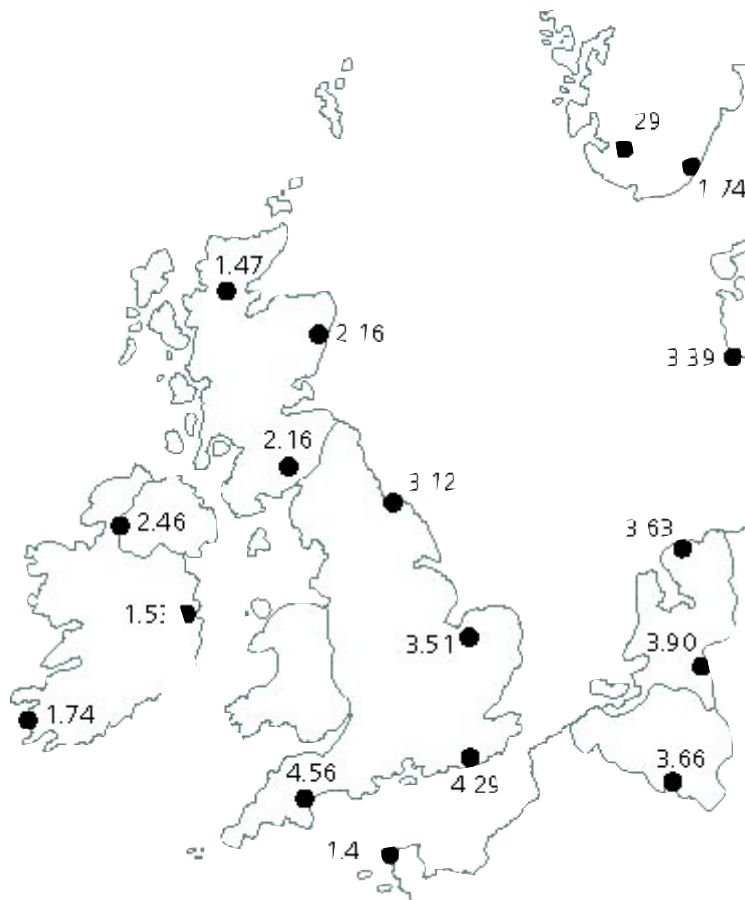


Figure 4.2 The UK distribution of particulate sulphate mapped in its European context using annual mean 1995 data from the UK EMEP monitoring stations, expressed in $\mu\text{g SO}_4 \text{ m}^{-3}$.



not often in the same air masses, and usually with different seasonal intensities. Particulate sulphate from the oxidation of SO_2 by the various routes is therefore present in air over Europe on most days. The daily measurements of particulate sulphate from the EMEP acid rain monitoring network (Hjellbrekke *et al.*, 1997) clearly reveal a systematic pattern across Europe with highest mean concentrations across a wide area from central England through the low countries into central Europe, see Figure 4.1. The UK measurements of particulate sulphate have been recently reviewed by the UK Review Group on Acid Rain (RGAR, 1997). They show an annual mean distribution across the British Isles which reflects the European distribution, with a maximum in the south and east of England and a minimum in the north and west of Scotland and Northern Ireland, see Figure 4.2.

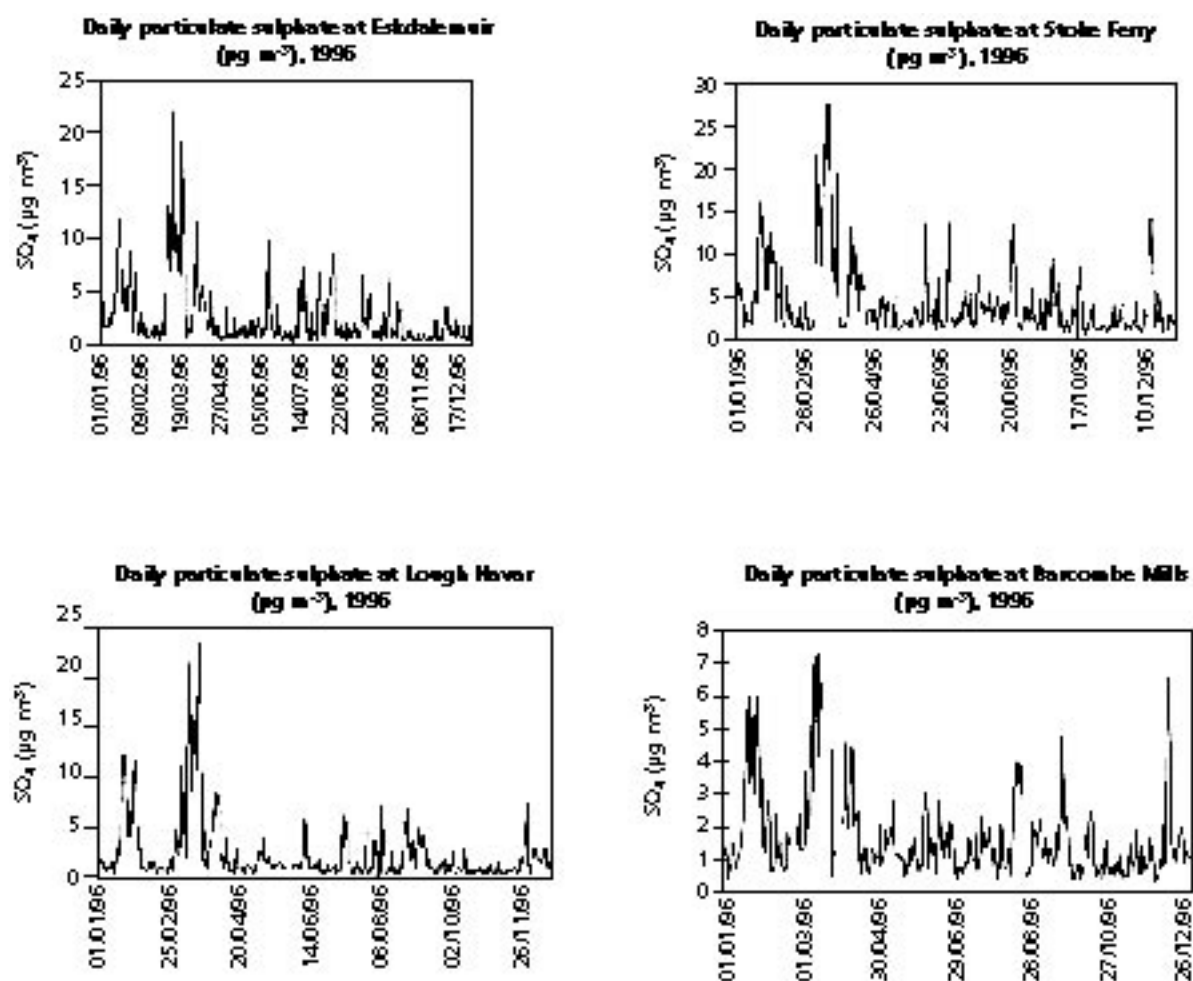
The broad scale nature of the spatial distribution of particulate sulphate is driven by the widely distributed nature of the SO_2 sources from coal and oil burning across Europe and the long lifetime of the aerosol particles once formed. Long range transboundary transport is therefore an important facet of the fate and behaviour of particulate sulphate.

The daily variations in particulate sulphate during 1996 at four of the EMEP sites in the UK are shown in Figure 4.3. This figure shows that there is a baseline level of particulate sulphate which is present during most days at each of these rural sites. This baseline appears to be somewhat higher at the more southerly and easterly sites of Barcombe Mills and Stoke Ferry ($1.2 \mu\text{g S m}^{-3}$) compared with the more westerly sites: Eskdalemuir and Lough Navar ($0.45 \mu\text{g S m}^{-3}$). Lowest baseline values are found in Scotland with levels at about $0.3 \mu\text{g S m}^{-3}$.

Superimposed upon this daily baseline, are pollution episodes which appear to occur at intervals throughout the year. During 1996, a wintertime episode in March dominated the annual time series at all the sites and there was little difference in the daily peak concentrations recorded between the widely spaced sites. Each site registered the highest peak daily mean particulate sulphate concentration for the entire year of 1996 of between 7 and $10 \mu\text{g S m}^{-3}$, equivalent to $21\text{-}30 \mu\text{g SO}_4 \text{ m}^{-3}$. These peak concentrations on their own are about one half of the current national air quality standard ($50 \mu\text{g m}^{-3}$). The possible origins of this particulate sulphate are discussed later in this chapter.

The annual daily time series for particulate sulphate for 1996 in Figure 4.3 shows a number of summertime episodes which produce peak daily mean concentrations in the range $1\text{-}5 \mu\text{g S m}^{-3}$, equivalent to about $3\text{-}15 \mu\text{g SO}_4 \text{ m}^{-3}$. The highest ozone concentrations monitored during the summer of 1996 at most of the rural ozone monitoring sites occurred during the 19th and 20th July and coincided exactly with a peak in the time

Figure 4.3 Daily variations in particulate sulphate concentrations for the UK EMEP monitoring stations during 1996.



series of daily particulate sulphate concentrations for the rural sites. For comparison with the wintertime episode, the origins of this photochemically-generated particulate sulphate are also identified later in this chapter.

4.1.2 PARTICULATE AMMONIUM

The long term trends from 1954 onwards in particulate sulphate, nitrate and ammonium at Harwell, Oxfordshire (Lee *et al.*, 1997) are illustrated in Figure 4.4. The annual mean particulate sulphate concentrations rose from about 4-6 $\mu g\ SO_4\ m^{-3}$ in 1954 to a maximum of about 7-11 $\mu g\ SO_4\ m^{-3}$ in 1976. Subsequently, mean particulate sulphate concentrations have

been significantly lower and have been in the range 3-8 $\mu g\ SO_4\ m^{-3}$ over the period up to 1991. Particulate nitrate, however, shows a steady and approximately linear increase over the entire period. The general shape of the particulate ammonium trend is similar to that of particulate sulphate, but there is little evidence of the downwards trend shown by particulate sulphate after 1976 (Lee *et al.*, 1997).

Measurements of ammonia together with total particulate ammonium are made at 2 sites and the results have recently been compiled by the Review Group on Acid Rain (RGAR, 1997). These observations are difficult to interpret because a range of gaseous and particulate reduced nitrogen

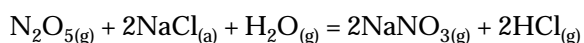
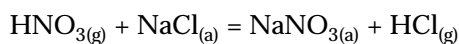
(= NH_x) species are detected. The mean concentrations of total inorganic ammonia over the 1992-4 period are reported as 0.9 and 1.7 µg N m⁻³ at Eskdalemuir and High Muffles, respectively. If it is assumed that about 60% of the total inorganic ammonia is present as NH_x in the aerosol phase (Lee *et al.*, 1997), then particulate ammonium concentrations at High Muffles can be expected to be about 1.5 µg NH₄ m⁻³. This is somewhat smaller than the Harwell levels and may point to a spatial gradient across the UK.

European measurements of particulate ammonium have been reported for 18 sites for 1995 (Hjellbrekke *et al.*, 1997) but they do not provide adequate spatial coverage to allow European scale mapping. The closest site to the UK is at Kollumerwaard, Netherlands, which has reported mean particulate sulphate and ammonium concentrations of 3.6 µg SO₄ m⁻³ and 2.3 µg NH₄ m⁻³ for 1995. These annual mean levels are closely similar to those reported for the Harwell, Oxfordshire site in 1991 (Lee *et al.*, 1997).

4.1.3 PARTICULATE NITRATE

The main fate of the NO_x emissions from motor vehicle exhausts, industrial combustion and power stations, is conversion to nitric acid, ammonium nitrate and nitrogen pentoxide in a relatively rapid series of daytime and night-time reactions. Although nitric acid, ammonium nitrate and nitrogen pentoxide have relatively low volatility compared with the NO_x from which they have been generated, they are all unable to undergo homogeneous nucleation. Instead, they attach themselves to pre-existing particles by heterogeneous nucleation.

If the pre-existing particle was a sea-salt particle, then additional chemical reactions can occur leading to the liberation of gaseous hydrogen chloride by sea-salt displacement:



Sea-salt displacement leads to anomalous Na:Cl ratios compared with those in sea-water and such anomalous ratios have indeed been reported for particles monitored at Harwell, Oxfordshire (Lee *et al.*, 1997). Further information is given on sea-salt in Sections 3.10.2.5, 5.5.1 and 5.5.2.

There is only one measurement station for particulate nitrate in the UK, at Harwell, Oxfordshire. The long term trend in particulate nitrate at this site since 1954 is shown in Figure 4.4. Particulate nitrate shows a roughly linear increase over the entire measurement record since 1954, from 1-2 µg NO₃ m⁻³ in 1954 to 5-7 µg NO₃ m⁻³ in 1991.

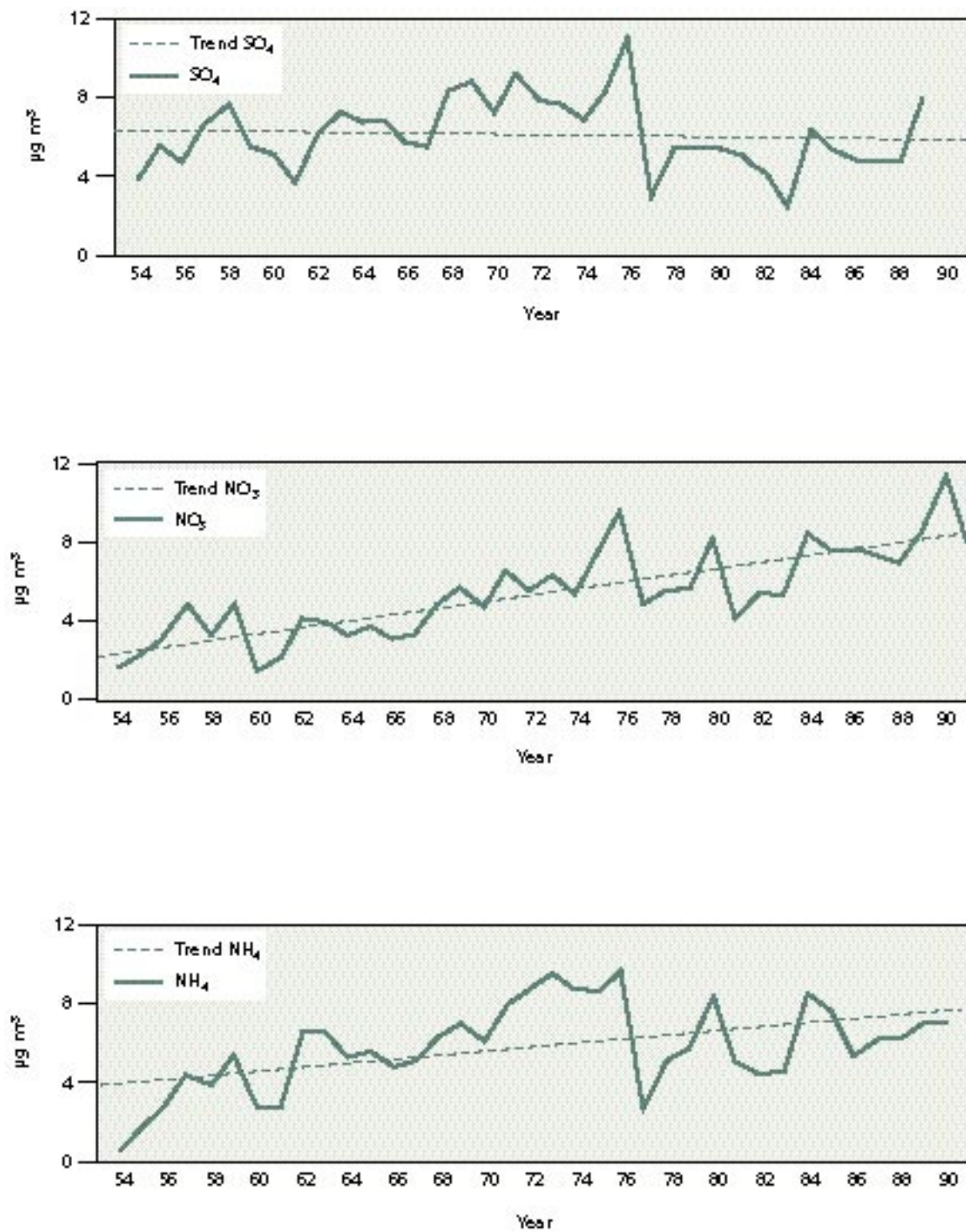
Measurements of nitric acid together with total particulate inorganic nitrate are made at 2 sites and the results have recently been compiled by the Review Group on Acid Rain (RGAR, 1997). These observations are difficult to interpret because a range of gaseous and particulate oxidised nitrogen species are detected. Furthermore, there are no continuous measurements of nitric acid available in the UK from which to separate out the contribution from particulate nitrate.

There is a European network of sites monitoring particulate nitrate operated by EMEP (Hjellbrekke *et al.*, 1997) but not enough measurement stations reported results in 1995 to allow European scale mapping, as has been carried out in Figure 4.2 for particulate sulphate. The closest EMEP site to the UK is at Kollumerwaard, Netherlands, which reported a mean particulate nitrate concentration of 4.6 µg NO₃ m⁻³ for 1995, which is closely similar to that reported in 1991 for Harwell, Oxfordshire (Lee *et al.*, 1997).

4.1.4 ORGANIC AEROSOL FORMATION

There have been no studies into the importance of organic aerosol formation for UK conditions. From our understanding of the published literature, two sources of secondary organic aerosol have been identified as potentially important under UK conditions and these are:

Figure 4.4 Long-term time series observations of annual mean particulate sulphate, nitrate and ammonium at Harwell, Oxfordshire from 1954 onwards.



- the photochemical oxidation of man-made aromatic hydrocarbons to form furandione compounds, (Forstner *et al.*, 1997);
- the ozonolysis and photochemical oxidation of terpenes from natural biogenic sources (Hoffmann *et al.*, 1997).

4.1.5 SECONDARY PARTICULATE MATTER AND THE MEASUREMENTS OF PM₁₀ AND PM_{2.5}

In the national air quality monitoring networks operated on behalf of, or in co-operation with, the Government, the bulk of the PM₁₀ and PM_{2.5} monitoring is carried out with TEOM-based instruments. These particular instruments, process the particulate matter present in the atmosphere before detection, leading to the loss of a considerable mass of the secondary particulate material actually present in the atmosphere. From our understanding of the physical properties of the secondary particulate matter itself, we can divide the secondary particulate matter into three tranches: that which is likely to be quantitatively detected, that which is unlikely to be detected and that for which we are uncertain of the detection.

Of the secondary particulate matter present in the UK environment, it is likely that sulphuric acid and ammonium sulphate are quantitatively detected by the TEOM PM₁₀ and PM_{2.5} monitors.

It is unlikely that any of the ammonium nitrate and secondary organic aerosol species are detected by the TEOM PM₁₀ and PM_{2.5} monitors, based on the experience of the instrument designers under USA conditions (Allen *et al.*, 1997). No analogous studies have been performed under UK conditions.

Because there is no time-resolved information available in the UK on the split between sodium and ammonium nitrate aerosol in the total inorganic nitrate aerosol, we are uncertain of the extent to which particulate nitrate is detected by the TEOM PM₁₀ and PM_{2.5} monitors. They may

monitor only the one fraction of the total inorganic nitrate aerosol associated with sodium nitrate, on a long term basis. During pollution episodes, when the supply of sea-salt aerosol may become exhausted in polluted air masses, we have little idea about the fraction of particulate nitrate that will be detected by the TEOM PM₁₀ and PM_{2.5} monitors.

Many of the secondary particulates are hygroscopic and so their mass concentration and other properties vary with atmospheric humidity and hence time of day. As a result, an uncertain fraction of the accumulated mass of water taken up by the secondary particles will also be lost within the TEOM PM₁₀ and PM_{2.5} monitors.

4.2 MEASUREMENTS OF SECONDARY COMPONENTS

4.2.1 UK MEASUREMENTS AT EMEP SITES

Particulate sulphate is measured on a daily basis at eight rural acid deposition monitoring sites on Whatman 40 filters within 8 port bubbler samplers. Measurements at Eskdalemuir are available from 1978 and the full network was established in 1987.

Table 4.1 lists the annual mean, 99th percentile and maximum daily mean particulate sulphate concentration at the eight acid deposition monitoring sites. Concentrations fell gently from 1987 to 1991 and then remained roughly constant until 1995. Concentrations are generally higher in 1996 than in recent years.

Annual mean sulphate concentrations for Central London have been measured on a daily basis since 1979 using a modified M-type sampler. Annual means for years with at least 150 valid daily means since 1987 are also listed in Table 4.1. Figure 4.5 shows a comparison of annual mean sulphate concentrations from this urban site and rural measurements at three sites. The concentrations measured in Central London are generally slightly higher than at the rural sites, partly because the M-

type sampler will allow more coarse particles to be collected than the bubbler sampler used at the rural sites. Figures 4.6 and 4.7 are scatter plots of daily sulphate concentrations at Stoke Ferry and Central London compared with Barcombe Mills. There is considerable scatter on both plots and there is an indication that the intercept is larger for Central London. This difference is confirmed by the difference in mean values for the data shown in these plots (means for the period April 1995 - March 1996: Barcombe Mills = 1.9 $\mu\text{g m}^{-3}$, Stoke Ferry = 1.7 $\mu\text{g m}^{-3}$ and Central London = 2.7 $\mu\text{g m}^{-3}$).

Particulate concentrations have also been measured at two of the rural acid deposition monitoring sites since 1988, High Muffles and Stoke Ferry. Concentrations of sulphate, nitrate, ammonium, sodium and chloride are determined by ion chromatography following weekly sampling on open faced PTFE filters. Annual mean particulate sulphate concentrations measured on these PTFE filters are generally between 0.1 and 0.3 $\mu\text{g m}^{-3}$ lower than those derived from the daily bubbler measurements (Table 4.2).

4.2.1.1 Secondary PM_{10} mapping.

Figure 4.8 shows a map of estimated secondary PM_{10} concentration for 1996. The same procedure as in QUARG (1996) has been followed, this map has been derived from UK measurements of sulphate particles at 8 rural EMEP sites (see Figure 5.25) and assuming a constant sulphate to nitrate ratio across the country derived from the co-located sulphate and total inorganic nitrate at Eskdalemuir and High Muffles. This is equivalent to using a scaling factor of 2.45 to convert from sulphate concentration (in $\mu\text{g SO}_4 \text{m}^{-3}$) to secondary PM_{10} , as measured by the TEOM instruments. This factor agrees well with the coefficients for this relationship derived from a comparison of daily measurements of PM_{10} , sulphate and black smoke (see Table 5.14 in Section 5.6.3) ranging from 2.26 to 3.13.

Figure 4.5 Annual mean particulate sulphate concentrations ($\mu\text{g SO}_4 \text{m}^{-3}$).

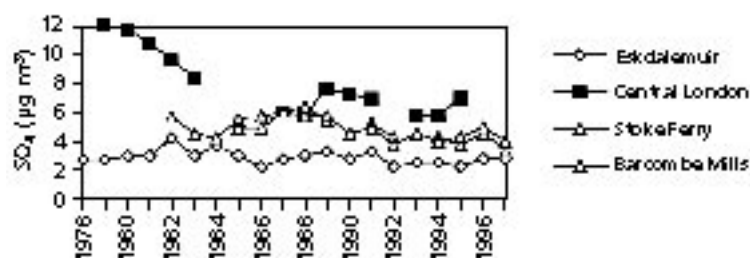


Figure 4.6 Comparison of daily mean sulphate concentrations April 1995 - March 1996 ($\mu\text{g SO}_4 \text{m}^{-3}$).

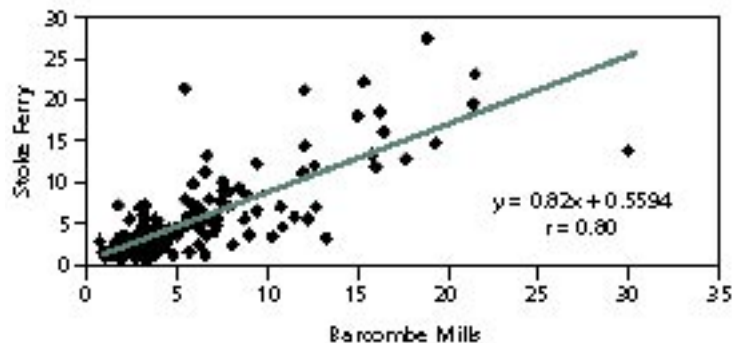
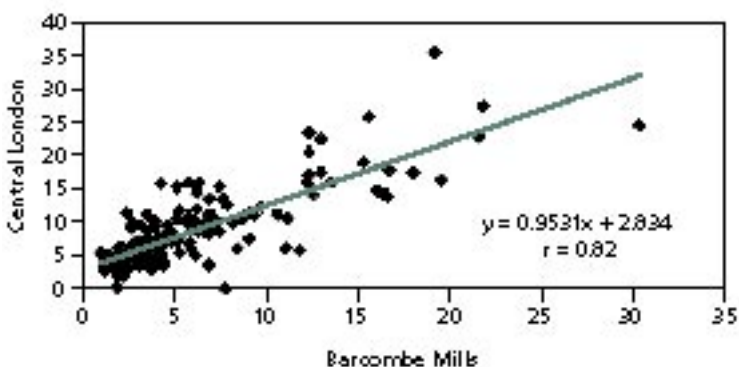


Figure 4.7 Comparison of daily mean sulphate concentrations April 1995 - March 1996 ($\mu\text{g SO}_4 \text{m}^{-3}$).



4.2.2 LEEDS STUDY

4.2.2.1 Mass Concentrations of Sulphate and Nitrate

Details of this study have been given in Section 3.10.2. Table 4.3 shows the urban 3-site average total sulphate and nitrate levels collected by the impactors during 8 separate weeks in Leeds during 1995/6 together with the corresponding rural values for 4 weeks. The averages over all 8 weeks were 4.04 $\mu\text{g m}^{-3}$ of NO_3^- and 5.47 $\mu\text{g m}^{-3}$ of SO_4^{2-} .

Table 4.1 Annual mean, 99th percentile and maximum daily mean particulate sulphate concentration at eight acid deposition monitoring sites ($\mu\text{g SO}_4 \text{ m}^{-3}$), 1987 - 1997.

Year	87	88	89	90	91	92	93	94	95	96	97
<i>Eskdalemuir</i>											
mean	2.7	3.0	3.3	2.7	3.3	2.1	2.4	2.4	2.1	2.7	2.1
99%ile	13.5	11.1	13.8	15.9	14.1	9.3	8.4	9.9	9.6	16.8	9.3
max	24.9	17.4	19.5	25.2	18.3	16.8	16.8	10.8	10.8	21.6	10.5
<i>Stoke Ferry</i>											
mean	6.0	6.3	5.4		5.1	4.2		4.2	3.6	4.5	3.3
99%ile	22.5	22.8	14.1		20.7	21.9		13.5	13.5	21.9	11.4
max	24.9	27.6	18.9		29.7	27.0		14.7	19.2	27.6	22.2
<i>Lough Navar</i>											
mean			2.7	2.4	2.7	1.8	2.4	2.7	2.4	2.4	1.8
99%ile	15.6	14.7	13.5	12.9	14.1	9.6	10.8	10.8	10.5	17.1	9.0
max	22.2	21.9	25.2	17.7	17.4	12.0	11.7	13.5	12.0	23.4	11.4
<i>Barcombe Mills</i>											
mean	6.0	5.7	5.7	4.5	4.8	3.6	4.5	3.9	4.2	4.8	3.9
99%ile	31.2	21.3	16.8	15.0	19.2	10.8	20.4	14.1	12.3	21.6	14.4
max	36.0	64.2	25.8	17.4	21.0	15.3	25.8	17.1	13.5	30.3	21.6
<i>Yarner Wood</i>											
mean	3.9	5.1	5.1	3.6	3.9	2.7	3.3	3.6	4.5	3.3	2.7
99%ile		18.3	17.4	16.8	18.0	10.8	15.3	12.6	18.9	16.5	10.8
max	21.9	25.8	34.2	20.1	25.5	15.6	17.7	15.0	24.6	20.7	13.5
<i>High Muffles</i>											
mean	4.2	5.1	4.8	3.9	4.2	3.3	3.0	3.3	3.0	3.6	2.7
99%ile	15.6	16.8	15.9	16.8	14.4	13.8	11.7	12.3	12.6	19.5	11.4
max	21.0	24.0	21.9	23.7	19.8	15.9	15.6	23.7	14.4	21.9	15.3
<i>Strathvaich Dam</i>											
mean	2.4	2.4	2.1	2.7	3.0	1.5	1.5	1.8	1.5	1.5	1.2
99%ile	9.0	8.7	10.2	21.0	15.0	9.6	6.3	7.8	9.0	9.6	7.5
max	13.8	12.9	12.3	41.7	18.3	41.1	8.7	12.6	10.5	12.9	12.9
<i>Glen Dye</i>											
mean	2.4	2.7	3.3	4.5	3.0	1.2	2.1	2.1	2.1	2.4	2.1
99%ile	11.4	12.3	18.3	25.5	9.9	7.8	10.5	11.4	11.1	15.9	9.9
max	23.4	14.4	32.1	58.8	13.5	11.4	17.1	17.4	12.0	21.6	14.7
mean of means	3.9	4.2	4.2	3.6	3.9	2.7	2.7	3.0	3.0	3.3	2.4
Central London mean	6.0	5.7	7.5	7.2	6.9		5.7	5.7	6.9	6.9	7.2

Assuming all the nitrate and sulphate are ammonium salts the contribution to the total mass concentration of these components is $12.7 \mu\text{g m}^{-3}$. In percentage terms the fraction of the total mass represented by these components ranged from 20-40%, average 29%. However, the impactor over samples relative to the TEOM quite significantly and relative to the Leeds TEOM results for the same weeks the fraction is about 43% (range 39-58%). This must be regarded as an upper limit since the

heated TEOM will not collect any ammonium nitrate whereas the impactor will. In addition, as mentioned in the section on sea-salt (Section 3.10.2), there will be a small amount of secondary ammonium chloride - typically of the order of $0.5 \mu\text{g m}^{-3}$ in winter and virtually zero in summer.

In all of the weeks where comparative data are available the urban sulphate and nitrate levels are higher than the rural levels. However for sulphate

Table 4.2 Annual average particulate concentrations of ionic components from rural weekly measurements ($\mu\text{g m}^{-3}$).

	SO_4^{2-}	NO_3^-	NH_4^+	Na	Cl
<i>High Muffles</i>					
1988	3.3	1.76	1.28	0.7	1.0
1989	3.9	2.2	1.4	0.8	1.1
1990	3.3	1.76	1.4	0.8	1.1
1991	3.9	2.2	1.8	0.8	1.2
1992	3.0	1.76	1.4	0.9	1.2
1993	3.3	1.76	1.1	0.7	0.9
1994					
1995	2.4	1.76	1.0	0.8	1.0
1996	3.0	2.2	1.4	0.8	0.8
1997	2.4	1.76	1.0	0.7	0.8
<i>Stoke Ferry</i>					
1988	4.5	3.52	2.0	0.8	1.2
1989	4.2	3.52	2.0	0.8	1.0
1990					
1991	4.5	3.52	2.7	0.9	1.0
1992	3.3	3.08	1.9	0.8	0.9
1993					
1994					
1995	3.0	3.08	1.7	0.8	1.0
1996	3.6	3.52	2.0	0.8	1.0
1997	2.7	3.52	1.5	0.8	1.0

the differences are very small - the rural sulphate is not less than 0.85 of the urban value. The differences for nitrate are somewhat larger, the rural / urban ratios being from 0.46-0.84. This suggests an additional urban source of nitrate.

The estimated annual mean secondary PM_{10} contribution of nitrate and sulphate for the area of the UK covering Leeds is 8-10 $\mu\text{g m}^{-3}$ as shown in

Figure 4.8 Estimated annual mean secondary inorganic PM_{10} concentration, 1996 ($\mu\text{g m}^{-3}$).

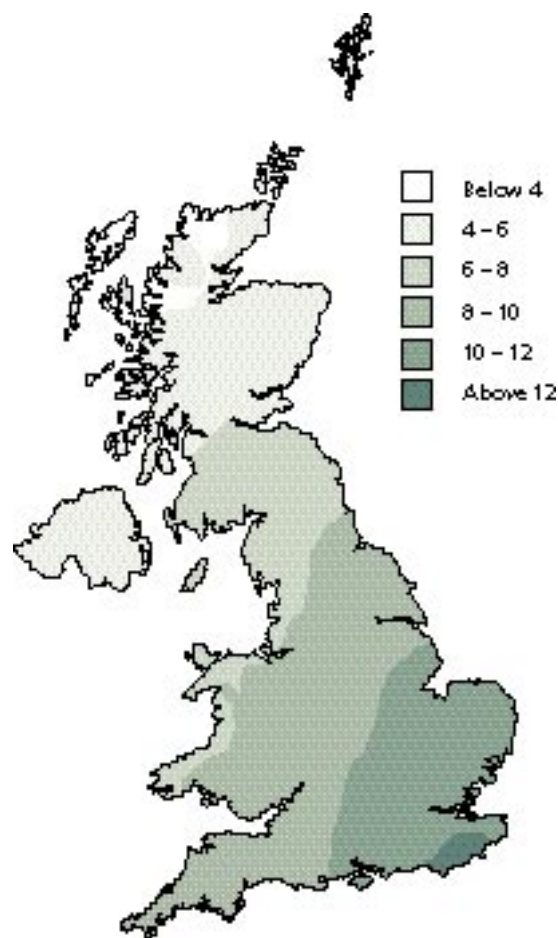


Figure 4.8. Secondary PM_{10} for various rural sites are approximately half the total measured PM_{10} . The Leeds data are consistent with this picture.

Table 4.3 Weekly average mass concentrations of aerosol components at Leeds 1995/6 ($\mu\text{g m}^{-3}$).

Week beg.	Urban NO_3^-	Rural NO_3^-	Urban SO_4^{2-}	Rural SO_4^{2-}	Urban NH_4^+	Rural NH_4^+	Total Mass	Sum of salts*
15-May-95	1.16		2.32				18	4.7
21-Jun-95	4.13		3.73				26	10.5
05-Jul-95	4.53		5.48				54	13.4
26-Jul-95	7.2		6.07				55	17.7
09-Aug-95	2.95	2.42	6.68	5.87	1.18	0.83	42	13.0
18-Oct-95	4.35	2.31	4.34	4.12	0.67	0.36	42	11.6
15-Nov-95	2.77	1.27	3.96	2.80	1.22	0.94	44	9.0
17-Jan-96	5.26	4.43	11.18	9.57	4.89	2.35	69	22.2
Average	4.04	-	5.47	-	-	-	44	12.7

*Sum of ammonium sulphate and nitrate:

$1.29\text{NO}_3 + 1.375\text{SO}_4$ (taking $\text{NH}_4\text{NO}_3 = 1.29 \times \text{NO}_3$ and $(\text{NH}_4)_2\text{SO}_4 = 1.375 \times \text{SO}_4$).

4.2.2.2 Particle size

Particles formed by direct conversion from gaseous species are expected to be in the fine size range whereas those formed from reactions with sea salt or minerals such as CaCO_3 are expected to be coarser. These trends are illustrated by the results from the Leeds particle size survey. The cumulative size distribution curves are shown in Figure 4.9 from which the following conclusions can be drawn for the urban sites:

Table 4.4 Particle size distributions at urban sites.

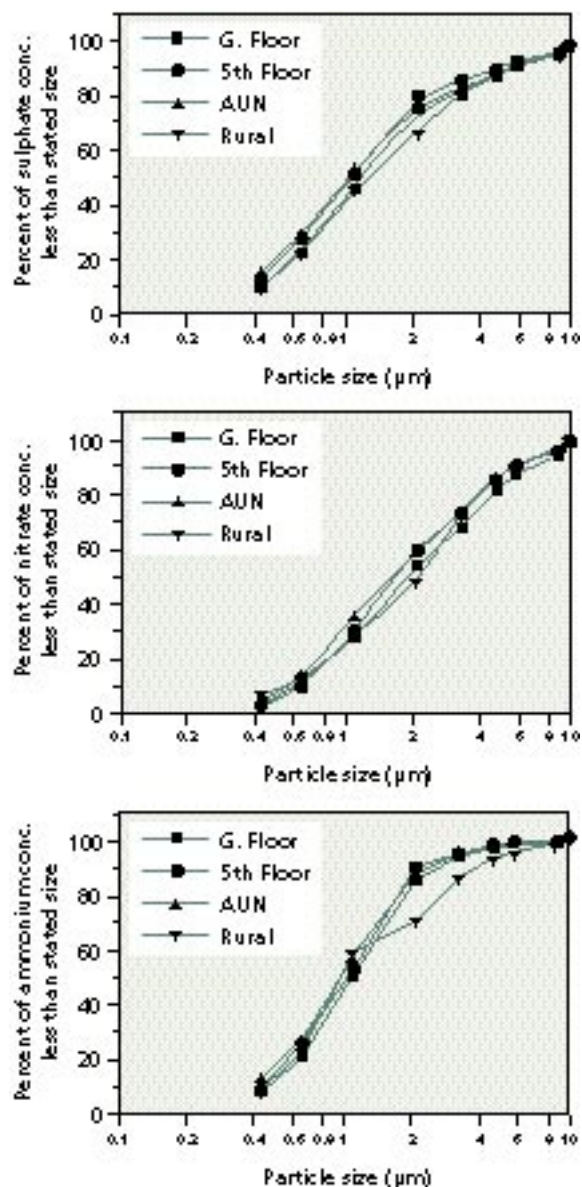
	20% below	50% below	80% below
Sulphate	0.5 μm	1.1 μm	3.0 μm
Nitrate	0.9 μm	1.6 μm	4.5 μm
Ammonium	0.6 μm	1.0 μm	1.8 μm

Note that the sizes recorded could relate to either dry particles or droplets i.e. in whichever state the aerosols exist at the prevailing relative humidity during sampling.

The plots of $\Delta M/\Delta \log D$ (ΔM is the incremental mass concentration and D is the aerodynamic diameter of the particle) are shown in Figures (4.10-4.12), these figures being the averages for 8 sampling weeks. Sulphate appears bimodal with one main peak in the region of $1\mu\text{m}$ and another smaller one between 3 and 6 μm . Nitrate is more uniformly spread over the whole range up to 6 μm .

An attempt has been made to apportion the sulphate and nitrate to the categories of fine and coarse ammonium salt, fine and coarse metallic salt and (in the case of sulphate) fine and coarse acid. Fine in this context refers to impactor stages collecting particles less than 2.1 μm and coarse particles 2.1 to 10 μm . To do this it is necessary to assign the ammonium in each impactor size range to the sulphate and nitrate present. The ammonium is assigned pro-rata to the number of equivalents of SO_4^{2-} and NO_3^- . The fraction of metallic salts is obtained by difference. The results

Figure 4.9 Cumulative size distributions of sulphate, nitrate and ammonium from the Leeds 1995/6 survey.



of this analysis for one summer week and one winter week are shown in Figure 4.13. Significant features include:

- the absence of coarse ammonium in summer;
- the much higher proportions of ammonium salts in winter;
- the dominance of metallic nitrates in summer changing to a balance between ammonium and metallic nitrates in winter.

Figure 4.10 Size distribution of sulphate based on percentage of mass in each size range at four sites in the Leeds 1995/6 survey.

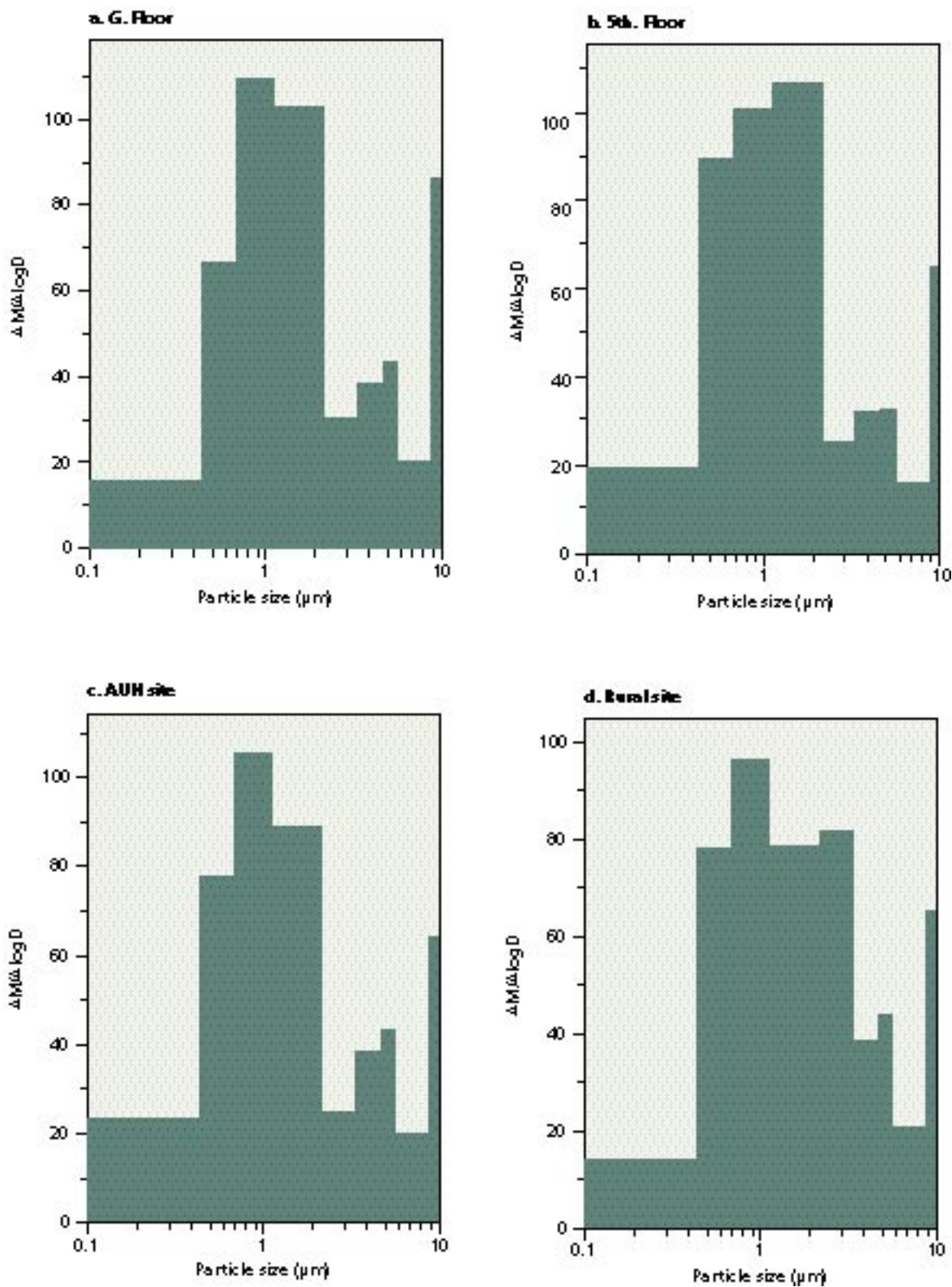


Figure 4.11 Size distribution of nitrate based on percentage of mass in each size range at four sites in the Leeds 1995/6 survey.

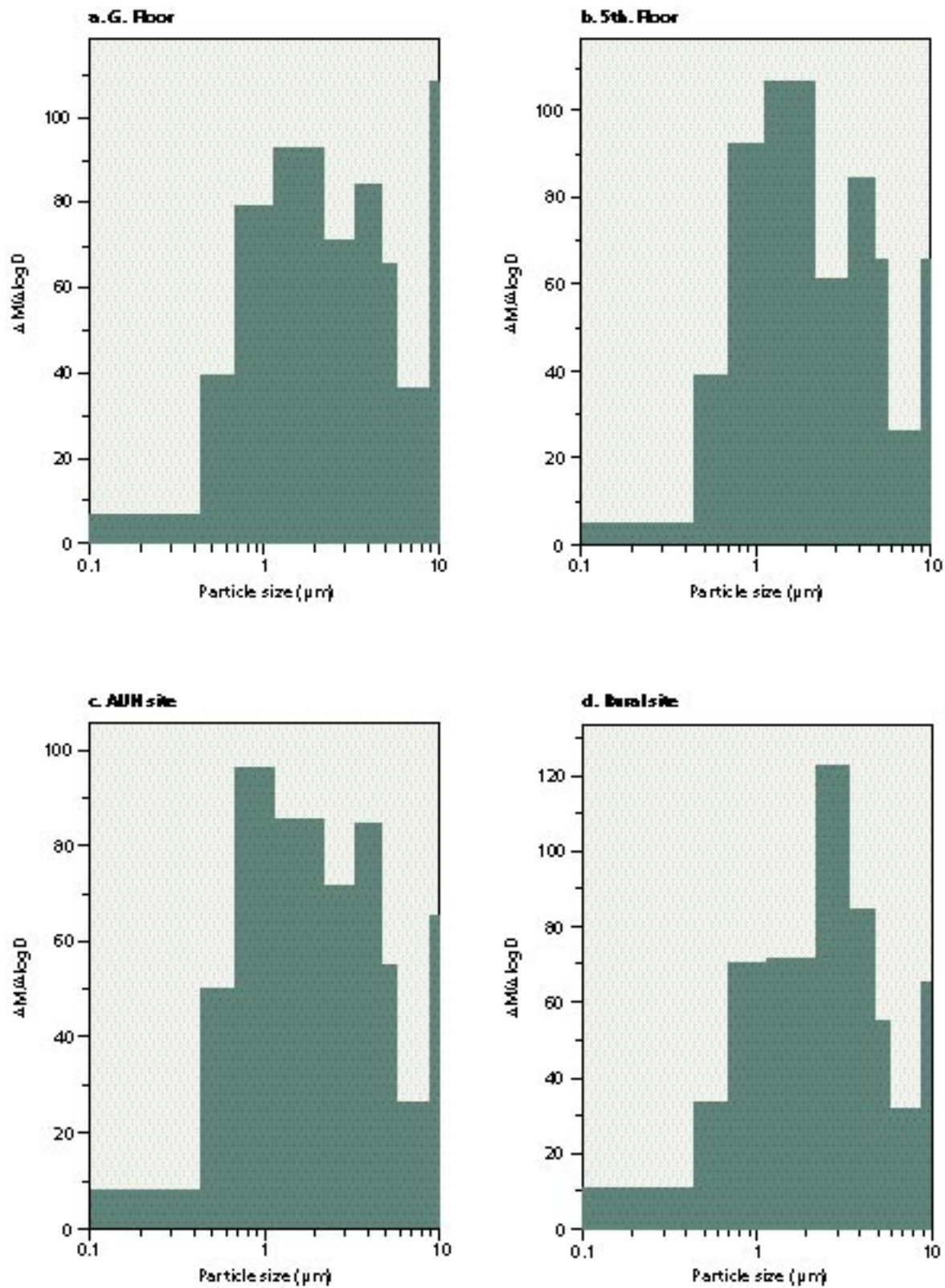


Figure 4.12 Size distribution of ammonium based on percentage of mass in each size range at four sites in the Leeds 1995/6 survey.

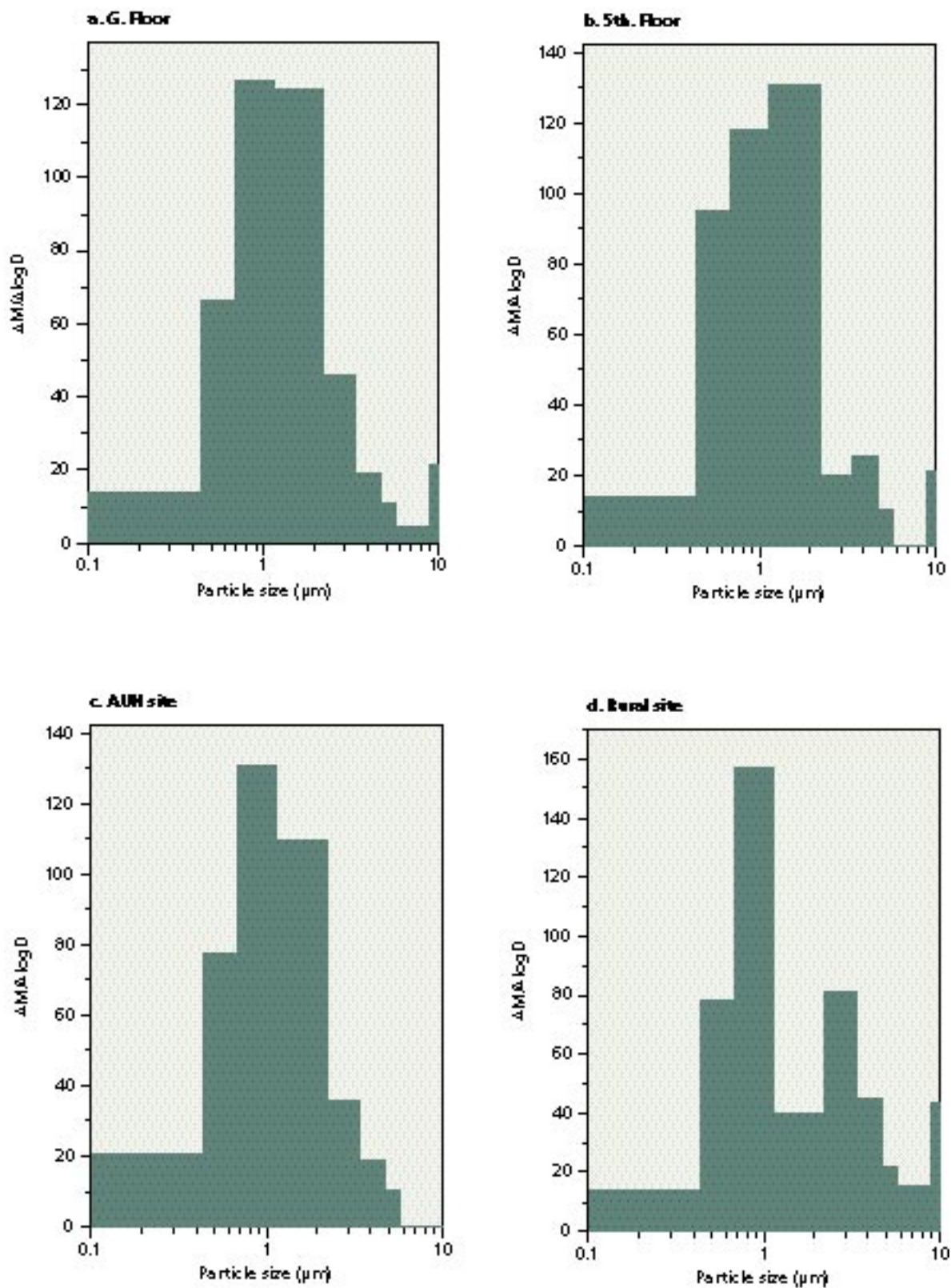
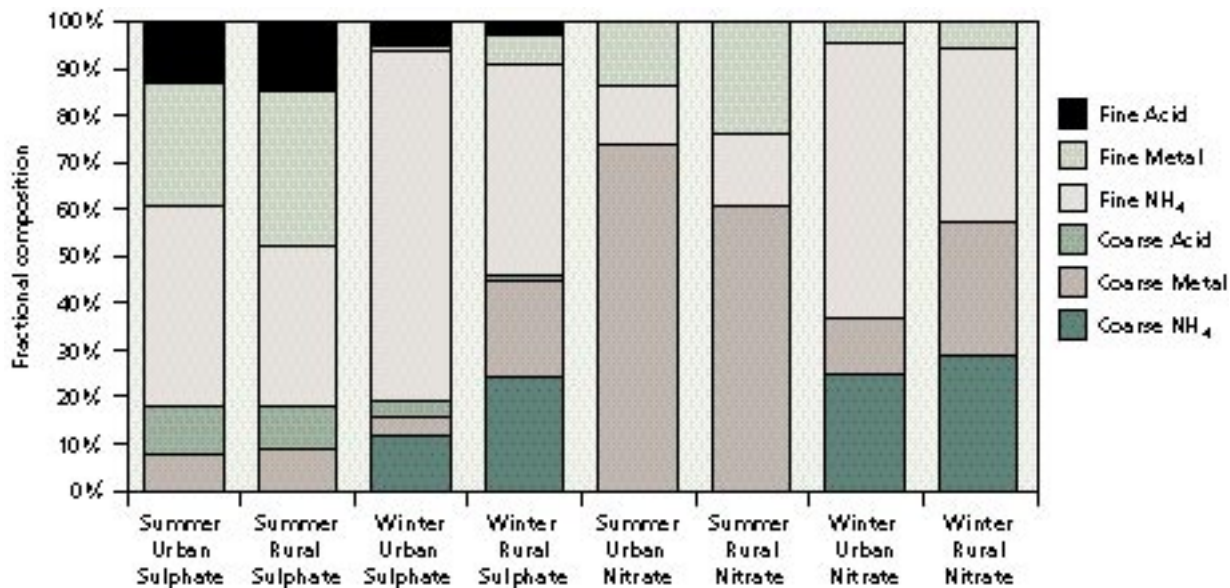


Figure 4.13 Apportionment of sulphate and nitrate to ammonium salts, metallic salts and acidic forms for weeks beginning 9/8/95 (summer) and 17/1/96 (winter) from the Leeds survey. Urban values are 3 site averages, rural values for 1 site.



4.3 MODELLING OF SECONDARY COMPONENTS

4.3.1 ATTRIBUTION OF THE SOURCES OF THE SECONDARY PM₁₀ AND PM_{2.5} OBSERVED IN THE UK MONITORING NETWORKS

The Department of the Environment, Transport and the Regions have commissioned the Meteorological Office to employ its NAME model (Maryon, *et al.*, 1991; Ryall and Maryon, 1996) to provide information, with a high degree of spatial and temporal resolution, on the origins of the secondary sulphur compounds detected by the various monitoring networks. Using a sophisticated Lagrangian dispersion model, the air concentrations of sulphur dioxide and particulate sulphate and precipitation concentrations of sulphur are being modelled with a spatial resolution of 15 km x 15 km and with a 15-minute time resolution.

Figure 4.14 illustrates the NAME model calculated SO₂ concentrations for a range of national AUN sites, together with the observed concentrations during the early months of 1996. For the large part,

the NAME model accurately predicts the occurrence of elevated SO₂ concentrations in the city centres, without obvious bias in terms of over- or under-estimation. There are, however, a number of occasions under which the model is not performing correctly, possibly caused by the inadequate temporal resolution in the annual SO₂ emissions data being used. The NAME model should more properly use 15-minute SO₂ emissions data.

Figure 4.15 illustrates the NAME model calculated particulate sulphate concentrations for the UK EMEP monitoring stations, together with the observed daily mean concentrations. During the summertime, the NAME model is able to predict quantitatively, the occurrence of elevated particulate sulphate concentrations and again there is no obvious bias towards over- or under-estimation. During wintertime, however, the model clearly underestimates the observations due to the neglect of the ammonia-ozone-SO₂ cloud droplet oxidation route.

4.3.1.1 The July 1996 Episode

To provide further information on the source attribution of secondary particulate sulphate,

Figure 4.14 NAME model results and observations for SO₂ at national AUN sites during 1996.

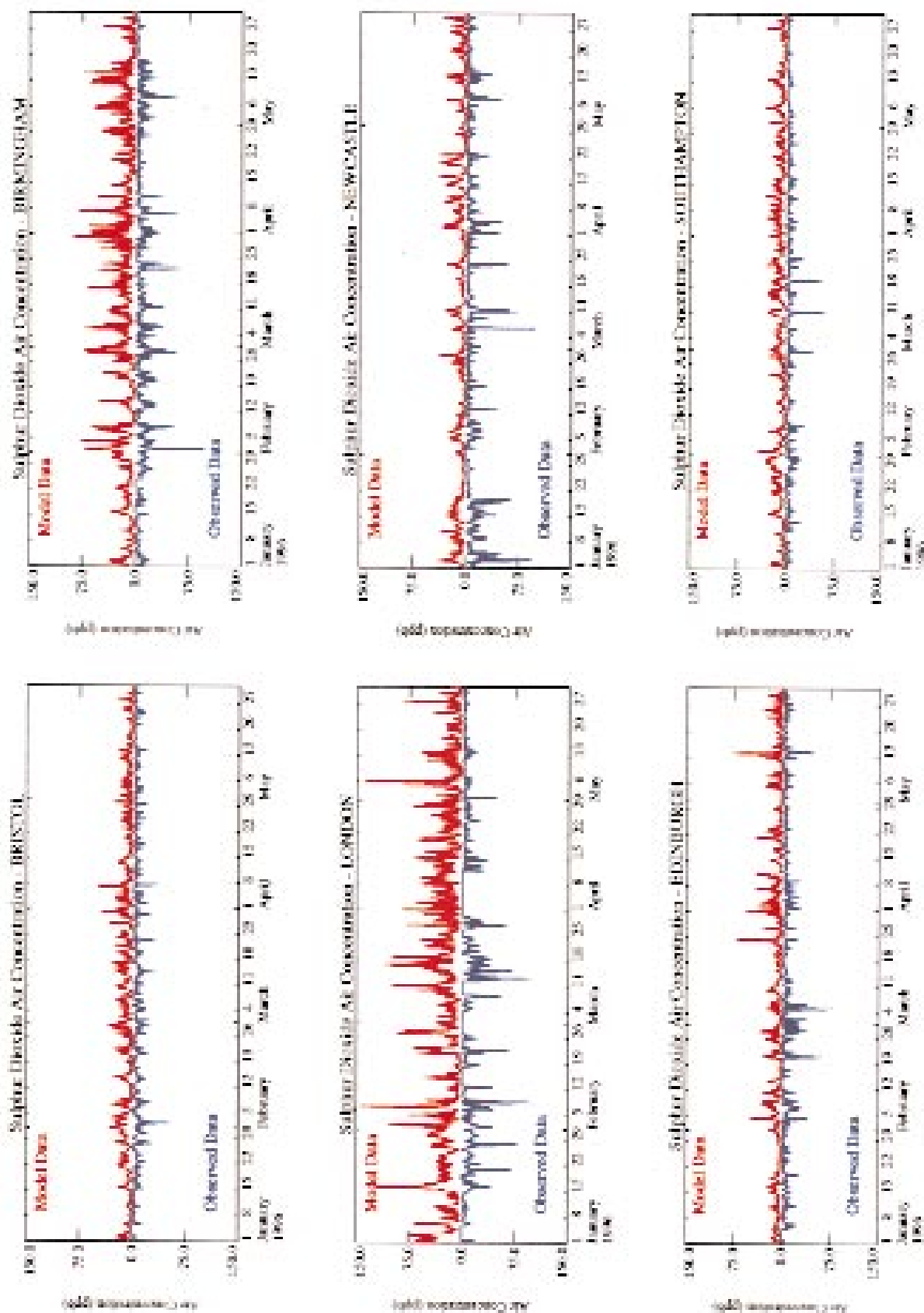


Figure 4.15 NAME model results and observations for particulate sulphate at UK EMEP monitoring sites during 1995.

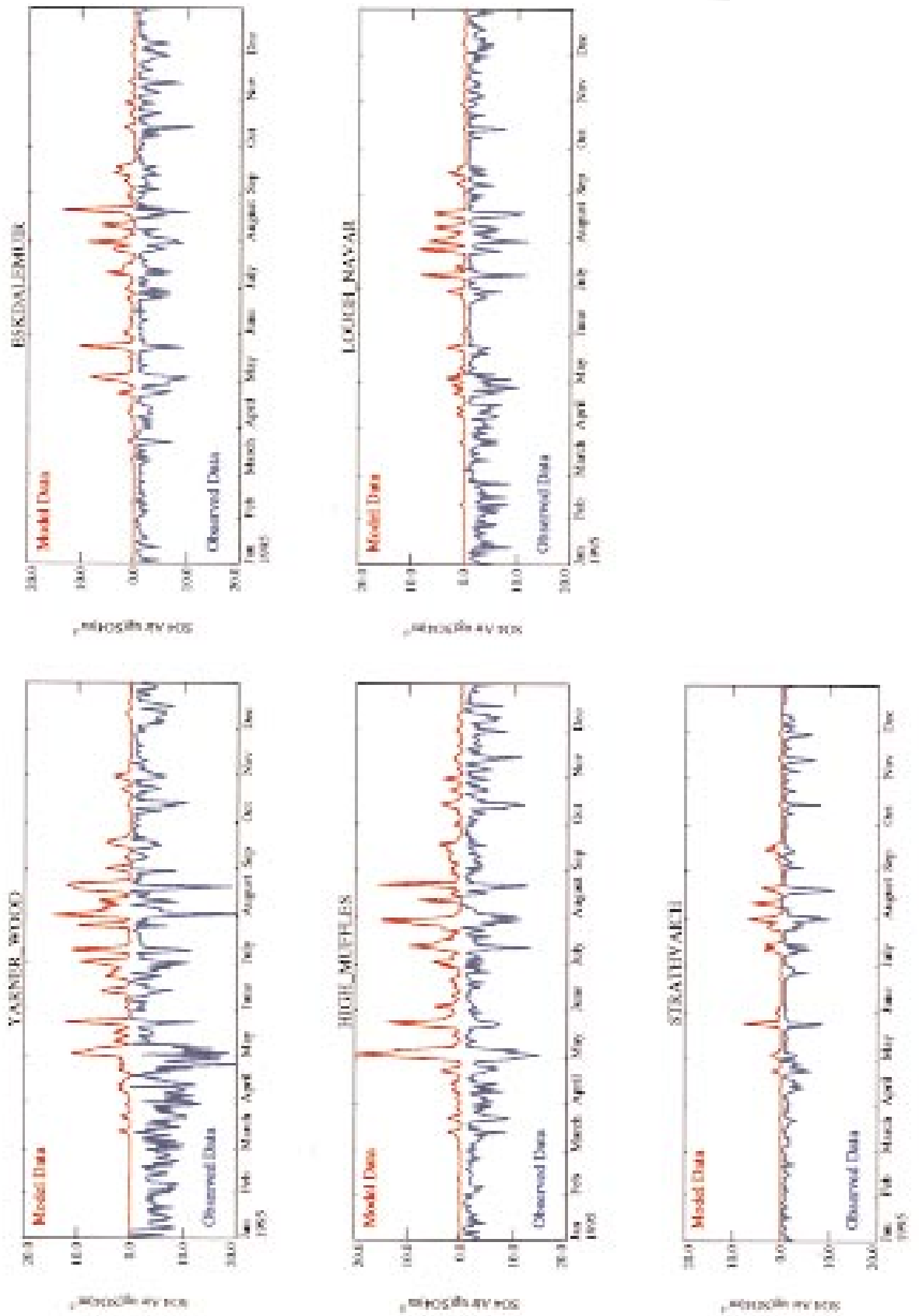
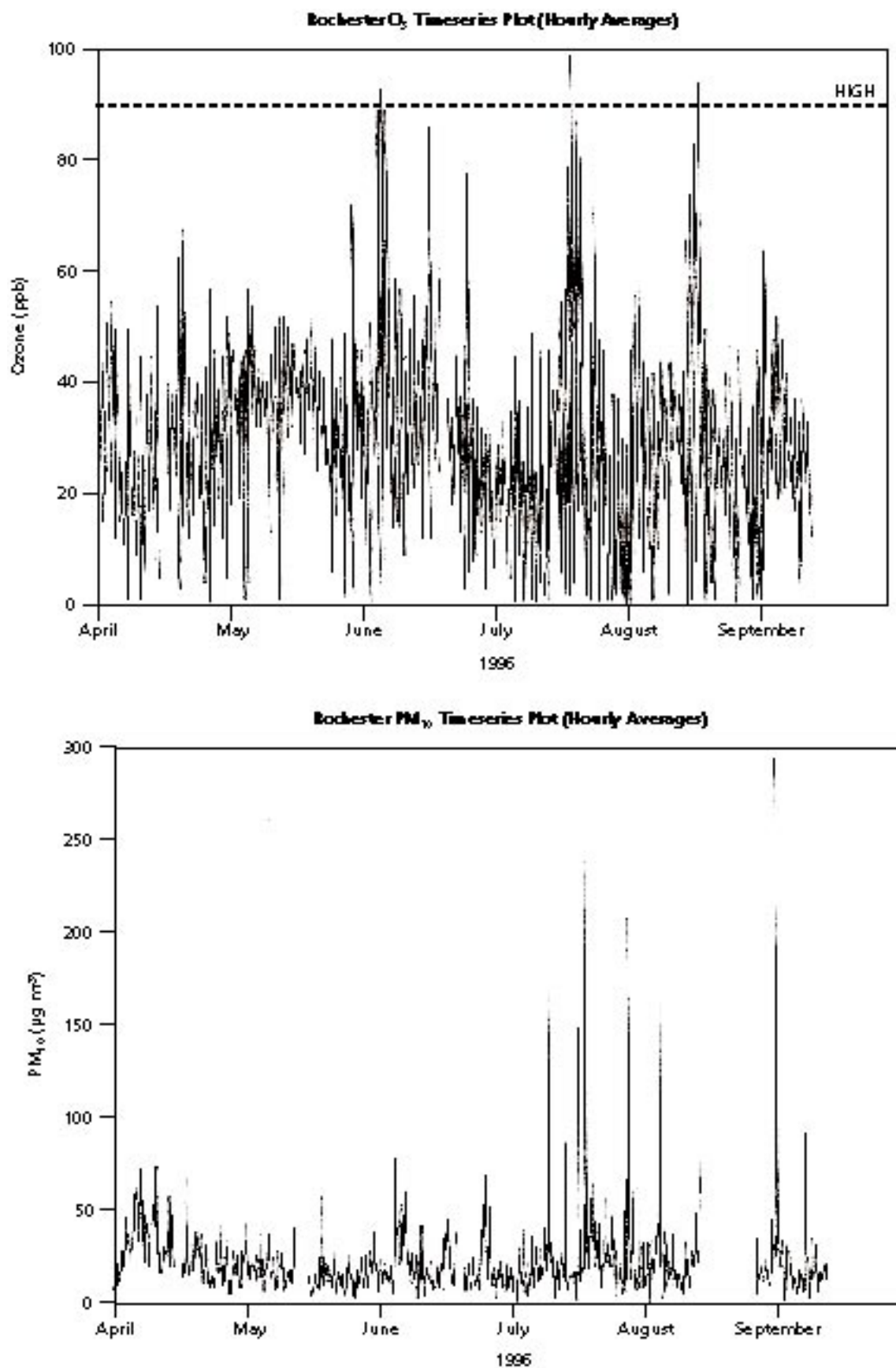


Figure 4.16 Hourly mean observations for ozone and PM_{10} at the Rochester rural monitoring site during the summer of 1996.



attention has been focused on the July 1996 photochemical episode which brought the highest ozone concentrations monitored during 1996 to almost all of the rural ozone monitoring sites in the British Isles. Associated with the peak hourly ozone concentrations were elevated particulate sulphate and PM₁₀ levels (Figure 4.16). The national air quality standard for PM₁₀ (50 µg m⁻³) (DoE, 1997) was exceeded at three London sites during this photochemical pollution episode.

Figure 4.17 shows the NAME model analysis for a PM₁₀ monitoring site in Haringey, London at which there was an exceedance of the national air quality standard for PM₁₀ (50 µg m⁻³ as a 24 hour running mean). The model is able to account for the elevated PM₁₀ levels observed during this episode and shows that the levels were clearly elevated above those estimated for the days on either side of it. The model analysis points to the majority of the secondary particulate sulphate arriving at the selected monitoring site as having been emitted as SO₂ within the UK. Only a small fraction of the secondary particulate sulphate has been formed from SO₂ emitted outside of the UK in the rest of Europe. Figure 4.18 provides the analogous NAME model analysis for the daily particulate sulphate measurements made at Lough Navar. The NAME model provides a realistic account of the occurrence of the episode at this and all of the rural particulate sulphate monitoring sites.

Table 4.5 presents the relative percentages of the secondary particulate sulphate at each monitoring site which has been formed from SO₂ emitted within the UK and in the rest of Europe. During the summertime episode the percentages arising from UK sources fell within the range 43-98% and that from European sources 2-57%. Figure 4.19 plots out the origins of the SO₂ which had been converted to particulate sulphate and undergone long range transport to Middlesbrough. This figure shows the overwhelming importance of SO₂ sources within the UK which had led to the elevated secondary particulate sulphate observed in Middlesbrough on 20th July. During this episode, ozone, PM₁₀ and particulate sulphate levels were elevated at almost all the UK monitoring sites.

Table 4.5 Meteorological Office NAME model source attribution of the SO₂ which had been oxidised to particulate sulphate and reached each monitoring site during the period 1st - 31st July 1996.

Site	Percentage from UK sources, %	Percentage from European sources, %
<i>AUN and London Network PM₁₀ sites</i>		
Southampton	57	43
Bristol	79	21
Cardiff	80	20
Swansea	81	19
Rochester	75	25
Haringey 1	76	24
Tower Hamlets	77	23
Thurrock	76	24
Sutton	76	24
Kensington&Chelsea	78	22
Birmingham	87	13
Birmingham East	87	13
Leicester	89	11
Liverpool	93	7
Leeds	92	8
Hull	89	11
Middlesbrough	91	9
Newcastle	94	6
Edinburgh	98	2
Belfast	92	8
<i>Rural Particulate Sulphate sites</i>		
Yarner Wood	43	57
Barcombe Mills	59	40
Stoke Ferry	82	18
High Muffles	88	11
Eskdalemuir	97	3
Lough Navar	93	7
Strath Vaich	92	8

4.3.1.2 The March 1996 Episode

Attention has been drawn to the March 1996 pollution episode in which TEOM PM₁₀ measurements became elevated over a very large area of the British Isles (Stedman, 1997; King and Dorling, 1997; SEIPH, 1998). Every AUN and SEIPH-operated TEOM PM₁₀ monitoring site registered exceedences of the National Air Quality Standard. This episode occurred in a part of the year when the NAME model is unable to predict quantitatively the sulphate production. However, it gives quantitative attribution of total sulphur (the sum of sulphur dioxide and sulphate) to source regions, and the best estimates of the origins of the sulphur during that episode emitted in the UK and continental Europe are

Figure 4.17 Hourly mean TEOM PM₁₀ data and NAME model results for Haringey, London during the July 1996 episode, showing the contributions from UK and European sources.

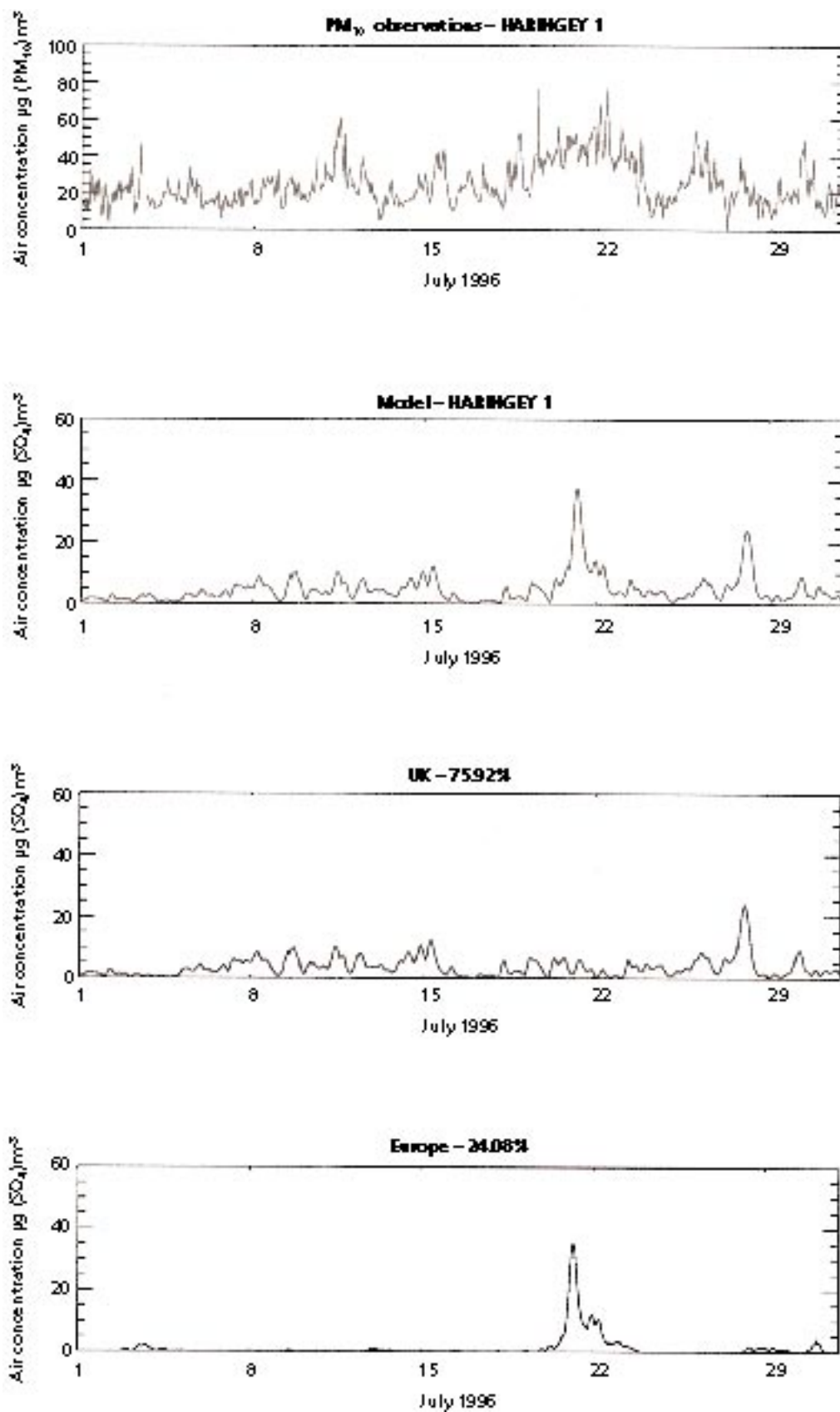
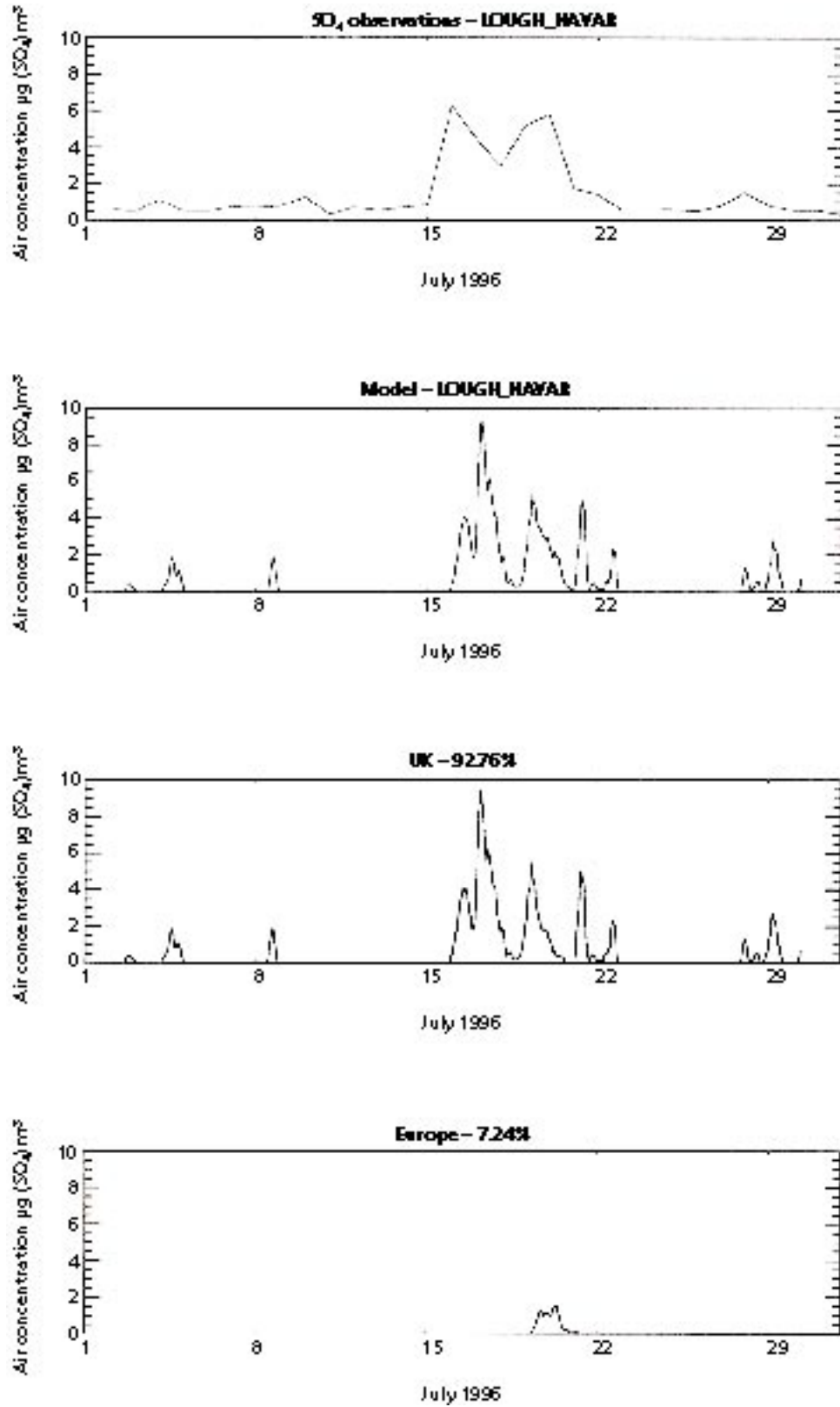


Figure 4.18 Daily mean particulate sulphate data and NAME model results for Lough Navar during the July 1996 episode, showing the contributions from UK and European sources.



presented in Table 4.6. During the period with the highest daily mean PM₁₀ values the percentages from UK and European SO₂ sources were estimated to be 14-46% and 54-86% respectively.

Table 4.6 Meteorological office NAME model source attribution of total sulphur reaching each monitoring site during the period 26th February - 31st March 1996.

Site	Percentage from UK sources, %	Percentage from European sources, %
<i>AUN and London Network PM₁₀ sites</i>		
Southampton	40	62
Bristol	46	54
Cardiff	45	55
Swansea	46	54
Rochester	26	74
Bloomsbury	35	64
Bexley	31	68
Haringey 1	35	65
Tower Hamlets	33	67
Greenwich	34	66
Birmingham	44	55
Birmingham East	44	56
Leicester	38	62
Liverpool	46	54
Leeds	35	65
Hull	14	86
Middlesbrough	16	84
Newcastle	18	82
Edinburgh	25	75
Belfast	42	58

Rural Particulate Sulphate sites

Yarner Wood	34	65
Barcombe Mills	30	70
Stoke Ferry	20	80
High Muffles	11	88
Eskdalemuir	28	72
Lough Navar	43	56
Strath Vaich	20	79

4.3.2 MODELLING OF SECONDARY PARTICULATE MATTER REDUCTIONS BY 2010

The NAME model is able to provide attribution of sulphate to precursor source regions and has been applied to specific episodes. In this section results are presented from the application of two other models for estimation of annual average secondary particulate concentrations over the UK.

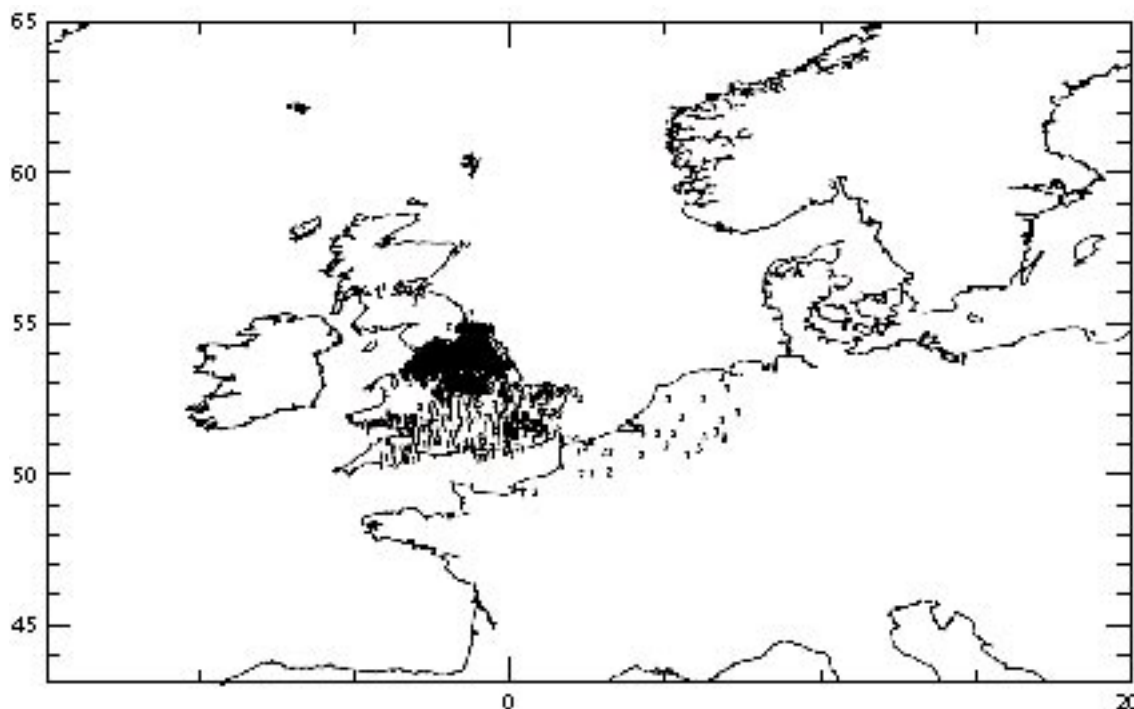
Comparison has been made between secondary particulate concentrations based on two models- the HARM model (for which results were provided by Dr Whyatt and Dr Metcalfe) and the EMEP model (Tarrason and Tsyro, 1998). In each case the models calculated separate contributions from SO₄, NO₃ and NH₄. The HARM model (Metcalfe *et al.*, 1995) is a straight line trajectory model coupled with a wind rose, and incorporates simple chemistry and averaged dry and wet deposition. The EMEP model (Barrett *et al.*, 1996) is a Lagrangian trajectory model, calculating back trajectories terminating at a grid of receptors every 6 hours from meteorological data; again it includes relatively simple chemistry, dry deposition, and wet deposition as and when precipitation occurs. The HARM model is focused on a finer spatial grid spanning the UK, whereas the EMEP grid is pan-European with cells of about 150km across.

Table 4.7 compares concentrations of SO₄, NO₃ and NH₄ from the two models for grid-squares over London and over Edinburgh. Both models have been applied using gridded European emissions in the early to mid 1990s.

Table 4.7 Modelled annual average secondary particulate concentrations for the UK.

LONDON area	Total secondary particulate	SO ₄ µg m ⁻³	NO ₃ µg m ⁻³	NH ₄ µg m ⁻³
HARM ~ early 1990s	8.5	3	4.8	0.7
EMEP:- a) 1996	21	6	13	2
b) In 2010 with Current Reduction Plans	15	4	10	2
EDINBURGH area	Total secondary particulate	SO ₄ µg m ⁻³	NO ₃ µg m ⁻³	NH ₄ µg m ⁻³
HARM Early 1990s	4.5	2	2.2	0.4
EMEP:- a) 1996	7	2	4	1
b) In 2010 with Current Reduction Plans	5	1	3	1

Figure 4.19 NAME model analysis for Middlesbrough for 20th July 1996, showing the origins of the air parcels and their length of travel. Key: 0 means a travel time of between 0 and 23 hours; 1 - 24-47 hours; 2 - 48-71 hours; 3 - 72-95 hours.



It can be seen that the EMEP model gives much higher concentrations than the HARM model, the latter seeming more consistent with measurements over the UK. Inspection of EMEP model results as compared with observations across the EMEP European network indicates that NO_3 concentrations are on average about twice the observed values, although some of this may be due to loss of some NO_3 in the measurement techniques. The modelled and observed SO_4 show no systematic bias overall, but the higher concentrations seem rather large over the major areas of sulphur emission such as the UK. One possible factor may be the assumption that 5% of S emissions are directly as SO_4 , whereas the HARM model assumes they are entirely as SO_2 . Both models appear to underestimate the NH_4 contribution, although in both cases this makes a relatively small contribution in terms of particulate mass.

Using source-receptor matrices provided by EMEP, the UK contribution to the total secondary fine particulate concentration appears to be about half, but this may overestimate local contributions of

sulphate as noted above. In addition the table gives secondary particulate concentrations calculated by EMEP on the basis of countries reported "Current Reduction Plans" for the year 2010. The reductions are consistent with the overall reduction of 30% used subsequently in this report. They reflect compliance with the second sulphur protocol, but do not necessarily include all reductions under legislation currently being implemented or arising under future agreements (such as the new multi-pollutant, multi-effect protocol being negotiated under the CLRTAP of the UN ECE, and the EU strategy to reduce acidification).

Even allowing for over-prediction in the EMEP model, comparison of Table 4.7 with measured data for PM_{10} , shows that the secondary particulate contributions to the annual average PM_{10} are substantial. On an episodic basis they will be an important factor in exceedance of air quality standards in the UK. However, it should be pointed out that neither the HARM or the EMEP model has been explicitly developed to model secondary particulate concentrations, and there are also large

uncertainties in the modelled primary particulate concentrations. Further work is required in this field to assess the imported contributions to particulate burdens over the UK, and to provide statistics on episodic situations within the overall annual average.

4.4 FUTURE CONCENTRATIONS OF SECONDARY PARTICULATE MATTER IN THE UNITED KINGDOM

Because of mounting concerns over the last two decades, the European countries have agreed to make dramatic reductions in their SO₂ emissions with a view to reducing the long range transport of acidic sulphur species to remote and sensitive environments. These SO₂ emission reductions have been negotiated within the aegis of the United Nations Economic Commission for Europe under its international convention on Long Range Transboundary Air Pollution and its Oslo protocol. Within the Oslo protocol, UK SO₂ emissions are set to decline by about 75% on their 1990 values by the year 2010 and the corresponding emissions for Europe, as a whole, by 40% on the same basis.

It is therefore likely that secondary particulate sulphate concentrations will decline dramatically over the period up to 2010 as the European countries fulfil their international treaty obligations. However, because there is a markedly different balance of effort taking place between the different countries of Europe and because of the marked difference in the relative importance of imported and UK particulate sulphates between episodes, it is not straightforward to estimate likely trends in secondary particulate sulphate in different places by the year 2010.

Because of the differing trends in precursor emissions across European countries, estimates of future concentrations of secondary particulate matter must be based upon a pan-European model. Currently, the best estimates are provided by the EMEP model using the "Current Reduction Plans" for emissions for the Year 2010 as described in Section 4.3.2. On the basis of the results presented in Table 4.7 we have used a value of 30% reduction in secondary particulate

matter concentrations in predicting trends in future PM₁₀ concentrations within the UK. It should be noted that the uncertainty in this prediction is substantial and is compounded by the fact that secondary particulate matter includes not only sulphates but nitrates whose behaviour in the TEOM instruments is uncertain.

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