

## 5.1 INTRODUCTION

Receptor modelling is the term applied to the use of measurements of a pollutant (in this case particles) in the atmosphere (rather than at source) to estimate quantitatively the contributions of different source categories to the mass of particles and of particular chemical constituents. At the simplest level this can involve discrimination between primary and secondary components of particulate matter on the basis of their differing chemical compositions. At a more sophisticated level it can involve detailed statistical analysis of the temporal patterns of individual components of particulate matter with a view to identifying those which are associated in time, and hence which have common sources. Whilst the techniques of receptor modelling are insufficiently precise to allow clear discrimination of all of the primary sources considered in the emissions inventories, or even to provide an exact separation of primary and secondary components, they are capable of identifying and quantifying the contributions of major sources. In the Third Report of the Quality of Urban Air Review Group (QUARG, 1996) major contributions to PM<sub>10</sub> mass were identified as arising from road traffic, secondary inorganic particulate matter and coarse particles, thought to have a primary origin in windblown soil and dust. In this chapter the methodology applied in that report has been extended and refined and new methods developed which have confirmed the basic conclusions of the Third Report of QUARG, and have provided updated and refined estimates of source contributions.

## 5.2 RELATIONSHIPS BETWEEN PM<sub>10</sub> AND CO

Estimates of the road traffic contribution to PM<sub>10</sub> within 10 UK urban areas used carbon monoxide as a tracer of traffic emissions (QUARG, 1996). This receptor modelling had been carried out for the period 1993/4 but since that time additional automatic monitoring sites have been established and the results of an update for the period 1996/7 are presented here which includes 17 urban background sites.

The technique used involves splitting the air monitoring data into four seasons, and within each season extracting data for carbon monoxide and PM<sub>10</sub> for twelve alternate hours of the day. For any given hour, e.g. 12 noon, the paired data for CO and PM<sub>10</sub> for a given site at that time on each day in the appropriate season of the year are pooled and the relationship between the CO and PM<sub>10</sub> concentration calculated using linear regression analysis. In summer and winter particularly, the correlations between the two pollutants were found to be highly significant allowing a relationship to be identified. Although virtually all emissions of carbon monoxide within an urban area arise from road traffic, there is an external contribution to the urban concentration. In the winter, the background has been quantified as 0.14 ppm and in the summer 0.1 ppm from the Northern Hemisphere CO background (Derwent, *et al.*, 1994). The regression equation between CO and PM<sub>10</sub> was used to estimate the PM<sub>10</sub> concentration corresponding to the appropriate seasonal background of CO and hence to a situation with zero influence of motor traffic. The concentration of PM<sub>10</sub> thus arrived at corresponds to the PM<sub>10</sub> in air which does not arise from road traffic. Subtraction of this concentration from the measured average concentration for the site and season gives an estimate of the concentration of PM<sub>10</sub> generated from road traffic.

Figure 5.1 shows the calculated PM<sub>10</sub> arising from traffic, related to the CO estimate due to traffic. There is a point for the summer and winter season data for each of the sites. Thus, as found in 1993/4, the traffic-generated PM<sub>10</sub> is quite strongly correlated with traffic-generated CO. The regression is Traffic PM<sub>10</sub> = 17.69trafficCO, r=0.56. When the concentrations of the two pollutants are converted to the same units, the gradient of the line corresponding with the ratio of CO to PM<sub>10</sub> is equal to 67.6. This compares to 82.8 for the 1993/4 period (QUARG, 1996) and is consistent with a reduction in the CO/PM<sub>10</sub> road traffic emissions ratio which declined from 75.4 in 1993 to 67.7 in 1995 in the national inventory. The urban inventories show ratios of 48 (Greater



Table 5.1 Contribution of PM<sub>10</sub> related to road traffic at 17 U.K. cities in 1996 using CO as a tracer of traffic related emissions.

Winter	% PM <sub>10</sub> related to traffic	Summer	% PM <sub>10</sub> related to traffic	Annual	% PM <sub>10</sub> related to traffic
Wolverhampton	67.9	Southampton	51.6	Wolverhampton	52.1
Leeds	58.8	Liverpool	46.4	Leeds	49.4
Nottingham	54.1	Leeds	40.0	Southampton	40.8
Newcastle	46.5	Wolverhampton	36.2	Liverpool	40.3
Manchester	43.6	Manchester	35.5	Manchester	39.5
Edinburgh	41.4	London Bexley	33.1	Nottingham	38.3
Bristol	37.0	Bristol	29.6	Newcastle	34.4
London Kensington	36.9	London Kensington	28.2	Bristol	33.3
Hull	36.8	Birmingham Centre	26.9	London Kensington	32.6
Birmingham Centre	36.7	Cardiff	23.2	Bexley	32.0
Liverpool	34.2	Nottingham	22.6	Birmingham Centre	31.8
Cardiff	33.7	Newcastle	22.4	Edinburgh	30.9
Birmingham East	30.8	Edinburgh	20.5	Cardiff	28.5
London Bexley	30.8	Birmingham East	20.4	Birmingham East	25.6
Southampton	30.0	Swansea	20.0	Hull	22.3
London Brent	22.7	London Brent	19.0	Brent	20.9
Swansea	14.7	Hull	7.8	Swansea	17.4

Table 5.2 Summary of the fractions of the PM<sub>10</sub> which is 'traffic-related' based on daily linear regression analyses of PM<sub>10</sub> and carbon monoxide during 1993.

Site	No of days with r > 0.5	Fraction of PM <sub>10</sub> which is 'traffic-related'	Fraction 'traffic-related' on days with PM <sub>10</sub> >50 µg m <sup>-3</sup>
Belfast	223	0.75	0.84
Birmingham	175	0.76	0.80
Bristol	181	0.76	0.79
Edinburgh	160	0.66	0.68
Leeds	204	0.74	0.80
Liverpool	133	0.78	0.80
London Bloomsbury	190	0.79	0.83
Newcastle	193	0.69	0.75

monitored simultaneously at the urban background locations (Deacon *et al.*, 1997). Hourly data for PM<sub>10</sub> and NO<sub>x</sub> for each AUN site for 1994 were processed in calendar month subsets containing between 720 and 744 data points, representing >96% data capture. Correlations between the hourly values were found to be significant for most of the sites and months. During the winter months, taken to be from October to March, inclusive, the correlations between PM<sub>10</sub> and NO<sub>x</sub> were highly significant (r > 0.8), the intercepts at zero NO<sub>x</sub> were typically less than one-half of the monthly mean PM<sub>10</sub> concentration and the regression slopes, m, well defined, where:

$$[PM_{10}] = m * [NO_x] + \text{intercept}$$

During the spring and summer months from April to September inclusive, the correlations became somewhat less significant, the correlation coefficients dropped to 0.3-0.5 and the regressions slopes reduced in magnitude. This seasonal behaviour was more marked at some sites while at others it was barely evident.

Table 5.3 summarises the mean and standard deviations of the slopes for all those months which gave correlation coefficients r > 0.5. These generally compare quite favourably with the

Table 5.3 Summary of the linear regression slopes for PM<sub>10</sub> and NO<sub>x</sub>.

Data Type	Site	PM <sub>10</sub> /NO <sub>x</sub> by mass	Source	
Emissions Inventory	National, road transport (1995)	0.056	National Atmospheric Emissions Inventory	
Urban emissions inventory - all sources	London	0.067	London Research Centre	
	Greater Manchester	0.148		
	Merseyside	0.211		
	Bristol	0.114		
	Southampton & Portsmouth	0.093		
	West Midlands	0.089		
	Swansea & Port Talbot	0.147		
	Middlesbrough	0.069		
	Glasgow	0.086		
Urban emissions inventory - all sources excluding industrial processes and combustion	London	0.065	London Research Centre	
	Greater Manchester	0.115		
	Merseyside	0.057		
	Bristol	0.066		
	Southampton & Portsmouth	0.060		
	West Midlands	0.067		
	Swansea & Port Talbot	0.080		
	Middlesbrough	0.053		
	Glasgow	0.078		
Observations	Belfast	0.185±0.038	Deacon <i>et al.</i> , (1997)	
	Bexley	0.078±0.022		
	Birmingham	0.134±0.029		
	Birmingham East, 1993	0.098±0.019		
	Bristol	0.096±0.029		
	Cardiff	0.127±0.046		
	Edinburgh	0.081±0.012		
	Hull	0.100±0.022		
	Leeds	0.113±0.042		
	Leicester	0.103±0.020		
	Liverpool	0.119±0.027		
	London Bloomsbury	0.100±0.024		
	Newcastle	0.106±0.026		
	Southampton	0.093±0.036		
	Hodge Hill- winter	0.065	see Section 3.5	
	Hodge Hill - summer	0.103		
	Marylebone Road - winter	0.052		
	Marylebone Road - summer	0.057		
	London Bloomsbury - winter	0.063		
	London Bloomsbury - summer	0.125		
Rochester - winter	0.089			
Rochester - summer	0.230			
M4 site,	max 1-hr annual	0.082	see Section 3.6	
		0.099		
	max 1-hr annual	0.109		
		0.092		
	M25 site,	max 1-hr annual		0.083
				0.081
max 1-hr annual		0.091		
		0.082		

current ratio by mass for UK urban emissions. The exception is Merseyside, where the Liverpool AUN station is not reflecting the large industrial PM<sub>10</sub> emissions shown in the inventory.

### 5.3 ANALYSIS OF PM<sub>10</sub>/PM<sub>2.5</sub>/NO<sub>x</sub>/ WINDSPEED DATA

In the Third Report of QUARG, relationships between PM<sub>10</sub>, PM<sub>2.5</sub> and NO<sub>x</sub> at the Birmingham Hodge Hill site were analysed in some detail. A larger data set is now available and further results are presented.

Aggregation of the winter data sets from 94/95 and 95/96 from the Hodge Hill site gave the following regression equations:

Hourly data:

$$PM_{2.5} (\mu g m^{-3}) = 0.103 NO_x (ppb) + 8.52 \quad r = 0.78$$

$$PM_{10} (\mu g m^{-3}) = 0.124 NO_x (ppb) + 14.15 \quad r = 0.72$$

$$PM_{coarse} (\mu g m^{-3}) = 0.019 NO_x (ppb) + 5.96 \quad r = 0.29$$

Figure 5.2 Plot of PM<sub>2.5</sub> and NO<sub>x</sub> for hourly winter data at Birmingham, Hodge Hill.

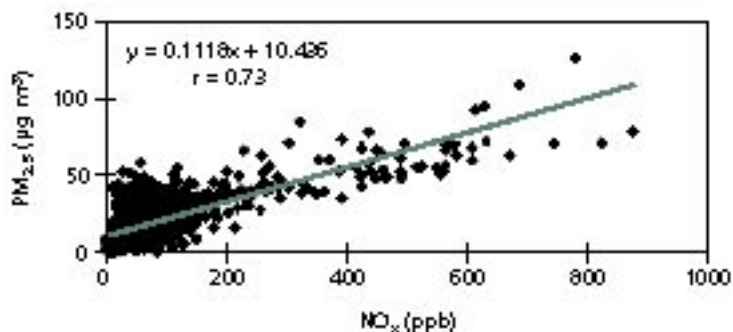
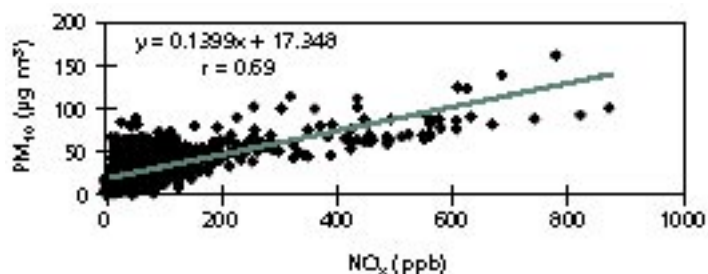


Figure 5.3 Plot of PM<sub>10</sub> and NO<sub>x</sub> for hourly winter data at Birmingham, Hodge Hill.



The results are highly consistent with the earlier analysis of a single winter's data indicating a strong correlation between PM<sub>2.5</sub> and NO<sub>x</sub> consistent with a road traffic source. The gradient is slightly lower than that for the October 1994 to March 1995 data analysed earlier and the intercept, interpreted as primarily due to secondary PM<sub>2.5</sub>, larger at 8.52 µg m<sup>-3</sup> compared to 6.54 µg m<sup>-3</sup> in the earlier data analysis. PM<sub>10</sub> correlates well with NO<sub>x</sub> but, as expected, slightly less strongly than for PM<sub>2.5</sub>, and coarse particles are only rather weakly correlated with NO<sub>x</sub> indicative of a modest traffic-related component. Plots of the relationship between PM<sub>2.5</sub> and NO<sub>x</sub> and PM<sub>10</sub> and NO<sub>x</sub> appear in Figures 5.2 and 5.3 respectively. These give a clear indication that at this site the highest winter PM<sub>2.5</sub> and PM<sub>10</sub> concentrations are associated with high NO<sub>x</sub> and are likely to arise from road traffic emissions, since in the West Midlands conurbation 86% of NO<sub>x</sub> emissions arise from road traffic (Hutchinson and Clewley, 1996).

An analysis of the summer data indicates the following relationships:

Hourly data:

$$PM_{2.5} (\mu g m^{-3}) = 0.114 NO_x (ppb) + 7.66 \quad r = 0.46$$

$$PM_{10} (\mu g m^{-3}) = 0.197 NO_x (ppb) + 14.8 \quad r = 0.42$$

$$PM_{coarse} (\mu g m^{-3}) = 0.065 NO_x (ppb) + 6.15 \quad r = 0.27$$

These data are highly consistent with the winter data but the data plots (Figures 5.4 and 5.5) do not show the very high concentrations of particulate matter and NO<sub>x</sub> present in the winter data. Thus the episodes of primary pollution so evident in the winter data do not appear prevalent in the summer.

#### 5.3.1 AN ESTIMATION OF THE CONTRIBUTION OF WIND BLOWN DUSTS TO COARSE PARTICLE CONCENTRATIONS

There are many sources of coarse particles (PM<sub>10</sub> - PM<sub>2.5</sub>). These include primary emissions from industry and traffic although such emissions are predominantly in the fine particle (PM<sub>2.5</sub>) size range. Additionally activities such as construction work



and quarrying, and natural sources, such as sea spray contribute to coarse particle concentrations. A further contribution arises from surface soils and dusts on paved areas becoming resuspended due to the action of the wind or to turbulence induced by passing road traffic. The elevation of coarse particle concentrations at London Marylebone Road compared to London Bloomsbury is a strong indication that traffic-induced turbulence can lead to a substantial increment in coarse particle concentrations (see section 3.5). Such an effect is likely to be local to the road, whilst suspension of surface dust and soils by the action of the wind is a far more widespread phenomenon.

We have sought to disaggregate the wind driven component of the coarse particle concentration by an analysis of the data collected at sites monitoring  $PM_{2.5}$  and  $PM_{10}$  simultaneously. The method of analysis can be illustrated by data showing the effect of windspeed on fine particle and coarse particle concentrations. Figure 5.6 shows daily  $PM_{2.5}$  concentrations at Birmingham Hodge Hill as a function of average wind speed. The curve is indicative of a dilution process, with  $PM_{2.5}$  concentrations reducing almost with the inverse of windspeed. A plot of the ratio of  $PM_{coarse}/PM_{2.5}$  against wind speed (Figure 5.7) shows a steady increase in this ratio with wind speed and a best fit to the data for  $PM_{coarse}$  alone as a function of wind speed (Figure 5.8) shows a U-shaped relationship. We interpret these data as indicating two components of coarse particles, one of which is diluted with increasing wind speed, as for  $PM_{2.5}$ , the other of which increases with increasing wind speed. The latter component is shown most clearly in the plot of the ratio  $PM_{coarse}/PM_{2.5}$  against wind speed which effectively eliminates the impact of dilution processes.

We have therefore taken a best fit of the relationship of  $PM_{2.5}$  with wind speed to allow for the dilution of coarse particles by windspeed. This curve has been subtracted from the coarse particle versus wind speed data taking an arbitrary lower wind speed assumed to have no wind-blown resuspension component. Figure 5.9 shows the result of this process. By eliminating the impact of

Figure 5.4 Plot of  $PM_{2.5}$  and  $NO_x$  for hourly summer data at Birmingham, Hodge Hill.

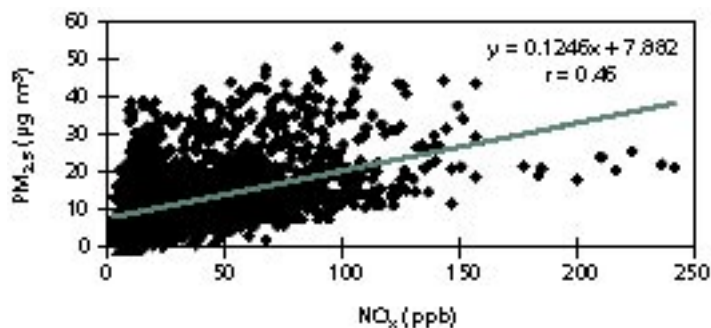


Figure 5.5 Plot of  $PM_{10}$  and  $NO_x$  for hourly summer data at Birmingham, Hodge Hill.

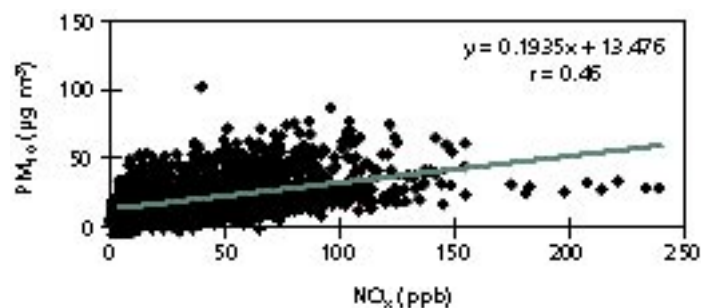
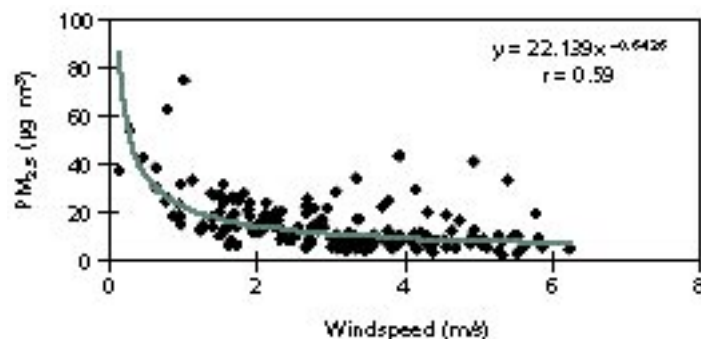


Figure 5.6 Daily average  $PM_{2.5}$  at Birmingham, Hodge Hill as a function of average wind speed, winter data.



dilution on the coarse particle concentrations, the effect of wind speed on particle suspension comes through clearly with concentrations increasing exponentially with wind speed. The selection of a low wind speed at which particle suspension processes are negligible is rather arbitrary, and hence we have carried out sensitivity tests using a range of wind speeds in the range of 0.1 to  $5\text{ m s}^{-1}$ .

Figure 5.7 The ratio of  $PM_{coarse}/PM_{2.5}$  versus wind speed for Birmingham, Hodge Hill, winter data and best-fit line.

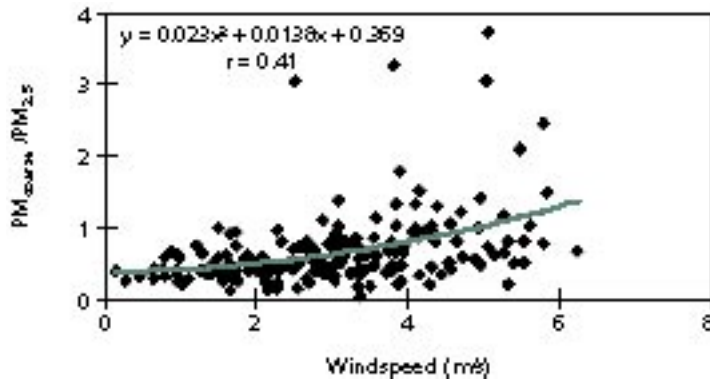


Figure 5.8 The ratio of  $PM_{coarse}$  versus wind speed for Birmingham, Hodge Hill, winter data and best-fit line.

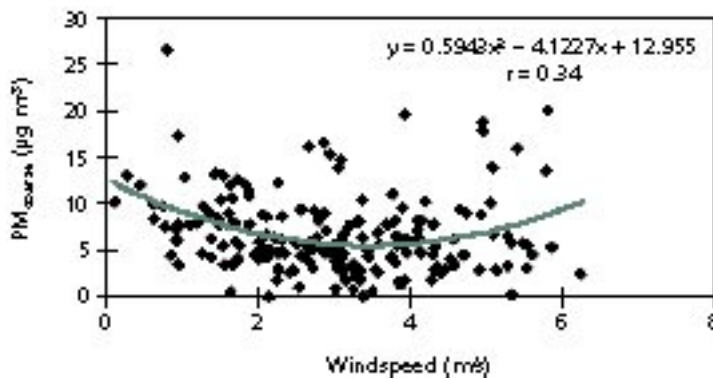
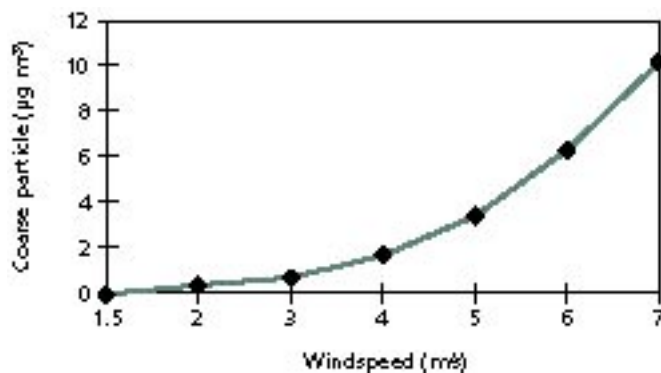


Figure 5.9 Estimated dependence of resuspended concentration upon wind speed at Birmingham, Hodge Hill, winter data.



If a too low wind speed threshold is selected there is a distinct discontinuity in the graph of predicted resuspended particle concentration versus wind

speed as the line approaches the x-axis. We have assumed that the threshold wind speed giving a smooth asymptotic approach of the line to the axis is the true threshold for particle suspension and some support for this method is provided by the fact that the derived thresholds occur at lower wind speeds in dry summer conditions than in the wetter months of the year. Additionally it is found that the curve of suspended coarse particles versus wind speed is steeper and goes to higher concentrations in the dryer summer months. By applying this method, estimates have been derived for the wind suspended component of coarse particulate matter at various sites and seasons shown in Table 5.4 by applying seasonal wind frequency statistics to graphs such as Figure 5.9. The non-wind suspended component of coarse particles is that which is diluted by wind action and presumably corresponds with particle emissions from industry, construction activity, traffic induced resuspension and biological particles. Sea spray would be expected to be in the category of particles increased by increasing wind speed but its contribution to airborne concentrations at inland sites is generally modest. It will be noted that Figure 5.7 and 5.8 show much scatter which does not appear in Figure 5.9, which is derived from best-fit lines. Due to the high degree of scatter in individual data the technique should be seen as most applicable to long-term (e.g. seasonal averages) rather than individual daily data.

A further breakdown of the estimated resuspended and background component of coarse particles at Birmingham Hodge Hill by weekday, weekend, day and night appears in Table 5.5. If resuspension were due solely to the action of the wind, then it would be expected that the resuspended concentration would be the same on weekdays and weekends, but would be greater in the day than the night. In fact, in all seasons there is a substantial weekday to weekend difference, but there is also, except in winter, a very large day-to-night difference. This could be interpreted as due to resuspension requiring two components. The first may well relate to traffic or other activity to suspend the particles from the ground in the first

Table 5.4 Summary of seasonally-averaged estimates of “resuspended” and “background” components of coarse particles.

Site	Season	Threshold wind speed (m/s)	Ct ( $\mu\text{g m}^{-3}$ )	Cr ( $\mu\text{g m}^{-3}$ )	Cb ( $\mu\text{g m}^{-3}$ )
HAR	Summer 97	–	–	–	–
	Autumn 97	3	4.34	0.36	3.98
	Winter 97/98	4	4.54	0.62	3.92
RO	Summer 97	3	8.03	1.09	6.93
	Autumn 97	3	6.64	0.90	5.74
	Winter 97/98	4	5.08	1.21	3.87
LB	Summer 97	2	8.34	0.99	7.35
	Autumn 97	3	10.12	1.23	8.89
	Winter 97/98	4	7.85	1.20	6.65
LM	Summer 97	1	14.30	4.75	9.55
	Autumn 97	1.5	14.30	1.93	12.38
	Winter 97/98	2	13.16	3.19	9.98
HH	Winter 94/95, 95/96 & 96/97	1.5	6.78	1.26	5.51
	Spring 95, 96 & 97	1	9.32	2.74	6.58
	Summer 95, 96 & 97	1	9.38	2.60	6.78
	Autumn 95, 96 & 97	1.5	8.51	0.94	7.58

*Ct* - total coarse particle concentration; *Cr* - resuspended coarse particle concentration;  
*Cb* - background coarse particle concentration.

HAR = Harwell RO = Rochester LB = London Bloomsbury LM = London Marylebone HH = Hodge Hill

Table 5.5 Estimation of “resuspended” and “background” coarse particulate components at Hodge Hill, according to weekday/weekend and day/night.

Season	Period	Threshold wind speed (m/s)	Ct ( $\mu\text{g m}^{-3}$ )	Cr ( $\mu\text{g m}^{-3}$ )	Cb ( $\mu\text{g m}^{-3}$ )	PM <sub>2.5</sub> ( $\mu\text{g m}^{-3}$ )
Winter 94/95, 95/96 & 96/97	Week-day	1.5	7.18	1.74	5.44	15.45
	Weekend	2	5.52	0.69	4.83	12.33
	Day	2	7.63	1.55	6.08	15.04
	Night	2	6.14	1.01	5.13	14.27
Spring 95, 96 & 97	Week-day	1.5	10.15	2.11	8.04	16.40
	Weekend	3	7.30	1.17	6.13	14.62
	Day	1.5	10.60	3.07	7.53	15.77
	Night	3	7.52	0.40	7.13	16.01
Summer 95, 96 & 97	Week-day	1.5	10.40	2.86	7.53	13.59
	Weekend	1.5	6.93	1.29	5.64	11.25
	Day	1.5	10.51	2.78	7.72	13.34
	Night	1.5	6.63	0.30	6.33	11.83
Autumn 95, 96 & 97	Week-day	1.5	8.85	1.24	7.61	14.00
	Weekend	3	7.67	0.43	7.24	13.68
	Day	1.5	9.33	1.07	8.26	13.43
	Night	3	7.71	0.10	7.61	14.38

*Ct* - total coarse particle concentration; *Cr* - resuspended coarse particle concentration;  
*Cb* - background coarse particle concentration.

place; the other factor relating to a need for wind to maintain the particles airborne. This would account for concentrations being higher on weekdays and in the day when both factors would be favourable. Interestingly, very little “resuspended” mass is seen in the nighttime

samples when both traffic is light and wind speeds and air turbulence lower.

The “background” component of coarse particles is also higher on weekdays than at weekends and in the day rather than the night. This component is



Figure 5.10 Daily  $PM_{coarse}$  versus  $PM_{10}$  at London Marylebone Road, (20/6/97 to 30/11/97).

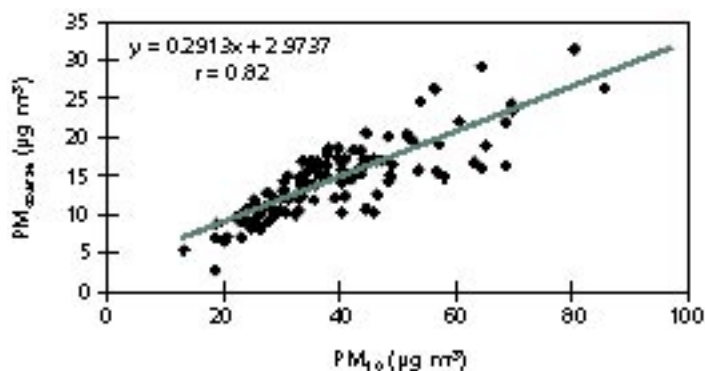
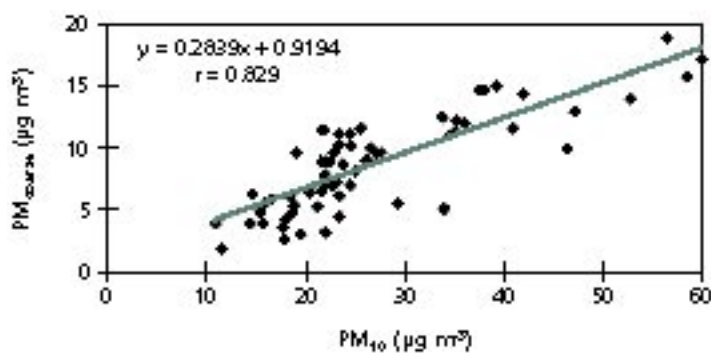


Figure 5.11 Daily  $PM_{coarse}$  versus  $PM_{10}$  at London Bloomsbury, (20/6/97 to 31/8/97).



attributed to emissions (including biological particles, seasalt etc) and hence a greater source strength would be expected on weekdays as opposed to the weekend, as is actually observed. For most the periods this weekday-to-weekend difference rather closely parallels that in the  $PM_{2.5}$  as might be anticipated for an emitted component. The day/night difference also occurs in a similar sense. This component may arise from traffi-generated resuspended dusts, and hence correlates with exhaust emissions (see section 3.5.1). Autumn 1995 has anomalous  $PM_{2.5}$  data trends due to a large “Bonfire Night” influence.

### 5.3.2 EPISODICITY OF COARSE PARTICLE MASS

In order to estimate the episodicity of coarse particles, the percentile distribution of coarse particle concentrations as fixed 24-hour averages at all sites (Table 5.6), and 24-hour running means at the Hodge Hill site (Table 5.7) have been calculated. These data show that it is very unlikely for coarse particles alone to lead to an exceedence of a 24-hour running mean concentration of  $50 \mu g m^{-3}$ . Plots of coarse particle concentration versus  $PM_{10}$

Table 5.6 Percentile distribution of coarse particle concentrations, fixed 24-hour averages ( $\mu g m^{-3}$ ).

Percentile	50%	90%	95%	98%	99%	99.9%
<b>HH</b>						
Winter (94/95 & 95/96)	6.47	12.88	15.59	18.53	19.95	25.78
Spring (95 & 96)	7.69	14.96	18.57	23.15	23.59	33.19
Summer (95 & 96)	9.23	18.38	20.96	24.03	29.02	52.27
Autumn ( 10 & 11/94, 95 & 9/96)	7.89	14.10	15.50	18.03	19.42	23.52
Two years (1/10/94 - 30/9/96)	7.73	15.45	18.40	22.69	23.95	41.89
<b>LM</b>						
17/7/97 - 31/8/97	15.03	20.03	21.35	21.99	22.60	23.15
1/9/97 - 30/11/97	13.89	18.71	25.89	28.40	29.90	31.06
17/7/97 - 30/11/97	14.35	19.94	23.80	26.15	28.87	30.97
<b>LB</b>						
18/6/97 - 31/8/97	8.75	14.27	14.85	16.69	17.74	18.77
1/9/97 - 30/11/97	8.94	15.89	19.66	22.55	28.24	39.74
18/6/97 - 30/11/97	8.79	14.56	17.33	20.73	22.64	38.60
<b>RO</b>						
1/6/97 - 31/8/97	7.18	12.60	14.35	15.12	16.21	19.79
1/9/97 - 30/11/97	5.16	8.85	15.43	17.16	19.44	28.62
1/6/97 - 30/11/97	6.53	11.54	14.64	17.06	18.26	28.05
<b>HAR</b>						
28/9/97 - 30/11/97	3.98	7.10	8.33	9.27	9.37	9.44

HAR = Harwell RO = Rochester LB = London Bloomsbury LM = London Marylebone HH = Hodge Hill

Table 5.7 Percentile distribution of coarse particle concentrations, running 24-hour averages at Hodge Hill, Birmingham ( $\mu\text{g m}^{-3}$ ).

Percentile	50%	90%	95%	98%	99%	99.9%
Winter (94/95 & 95/96)	6.12	12.74	16.08	18.34	20.03	26.79
Spring (95 & 96)	7.80	15.25	19.83	27.92	35.37	64.79
Summer (95 & 96)	9.32	18.47	21.94	25.28	29.66	57.55
Autumn (10 & 11/94, 95 & 9/96)	7.93	14.83	17.58	24.06	27.06	34.30
Two years ( 1/10/94 - 30/9/96)	7.79	15.63	19.01	23.81	28.35	57.59

concentration for fixed 24-hour periods as shown in Figure 5.10 for Marylebone Road and Figure 5.11 for London Bloomsbury data show that, in general, high concentrations of  $\text{PM}_{\text{coarse}}$  correspond to periods of high concentrations of  $\text{PM}_{10}$ , and that  $\text{PM}_{\text{coarse}}$  represents only a modest proportion of  $\text{PM}_{10}$  and that therefore  $\text{PM}_{2.5}$  must be similarly elevated. This gives a clear indication that at the sites examined, coarse particles have a common source with fine particles, and that wind-driven resuspension which would result in high concentrations of coarse particles, but low concentrations of  $\text{PM}_{2.5}$ , is not the process responsible for episodic high concentrations of coarse particles. Rather, it is likely to be a common source in local traffic activity and industrial emissions that is responsible since coarse particles are unlikely to play a major role in long range transport of secondary pollution.

## 5.4 PARTICLE NUMBER AS A TRACER FOR VEHICLE EMISSIONS

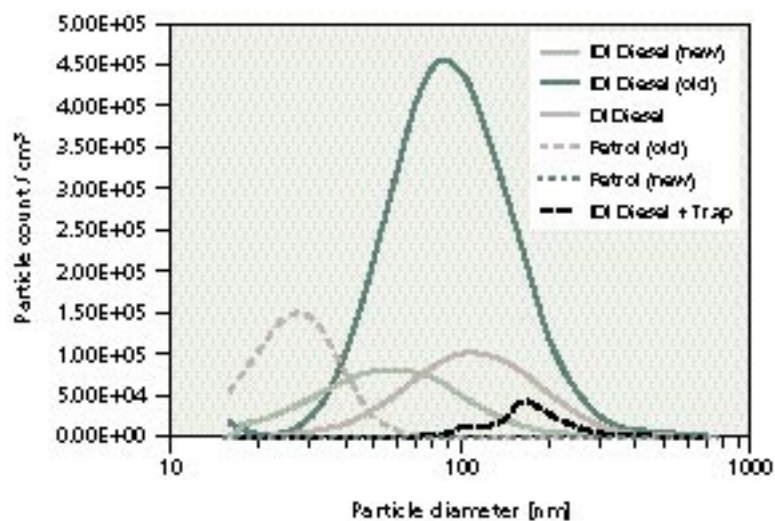
### 5.4.1 PARTICLE SIZE OF VEHICLE EMISSIONS

Existing emission factors and particle measurements of all particles are based on mass metrics. However, the most recent data available suggest that the majority of particles emitted from vehicle exhausts are significantly less than 1  $\mu\text{m}$  diameter, with very high number concentrations (Moon & Donald, 1997), and that this is true for diesel and petrol-based engines (Greenwood *et al*, 1996, Rickeard *et al*, 1996). Examples of the size distribution of exhaust emissions are shown in Figure 5.12 from a range of diesel and gasoline engines at 90 kph (steady state) (from Moon & Donald, 1997). Despite the wide range of engines,

vehicles and fuels tested, the particle size distributions measured are very similar. For number based distributions, most consist of a single peak between 60 nm and 120 nm with a wide log normal distribution. With some engine/fuel combinations, or at certain conditions, a second peak is seen at a much smaller size, from 10 nm to 30 nm. This has been seen by most of the instrument types used, so it is not a characteristic of any measuring technique. Mass based measurements confirm what is seen by the number based instruments, showing a peak from 150 nm to 300 nm. However, for some engines and fuels significant mass based emissions have been seen at higher sizes, up to 10  $\mu\text{m}$ .

Thus monitoring of these distinctive size ranges in urban centres by real-time measurement of particle size distribution, or more simply, by particle counting offers scope to discriminate particles sourced from vehicles.

Figure 5.12 Typical particulate emission profiles from a range of vehicle types.



#### 5.4.2 PARTICLE NUMBER VERSUS $PM_{10}$ DATA FOR HIGH VEHICLE DENSITIES

The usefulness of particle counting is borne out by existing data reported by Harrison *et al.* (1998) and Booker & Earnshaw (1998) for monitoring in Birmingham (A38 roadside) and Oxford (City centre) respectively. In each case, where particle number is monitored at roadside, counts may vary rapidly in the range  $10^3$  -  $10^7$  particles/cm<sup>3</sup>, and are typically more sensitive than equivalent co-located mass measurements. Hourly averaged measurements are of the order of  $5 \times 10^5$  particles/cm<sup>3</sup>. By comparing hourly averaged mass and number data, it is notable that:

- the particles contributing to this number peak are sub-micron, and have little mass associated with them. The data of Booker *et al* in Oxford shows increased particle counts as measured by a Condensation Particle Counter (CPC: 0.005 - 10  $\mu$ m) but not by optical or time-of-flight instruments (0.5 - 10  $\mu$ m) where the lowest size observed is 0.5  $\mu$ m. No elevation of particle mass by the TEOM was observed.
- no significant increase in particle mass was observed in the Oxford study when comparing  $PM_{10}$  at the City Centre with a suburban location with lower traffic densities.

- Figure 5.13 indicates that particle number concentration is heavily influenced by meteorological conditions; on windy days, any traffic plume, as measured by particle counting is rapidly dispersed. However, on still days a clear temporal relationship between traffic flow and particle count is observed.
- on still days, the particle number peak exhibits a strong correlation with traffic density. The use of traffic census data derived from chassis length and height combined with emissions factors relating to different vehicle types indicate that in Oxford, diesel buses are a significant contributor to particle emissions (as shown in Figure 5.14) whilst petrol vehicles make little contribution to particle number.

#### 5.4.3 PARTICLE NUMBER MONITORING OF DIESEL EMISSIONS

In a follow-up study in Oxford City Centre, the samplers were moved from a crossroads split between a through road dominated by petrol-engined vehicles, to an area confined to (principally diesel) bus and taxi traffic moving through the centre, essentially, a 'diesel canyon', less prone to interference from through petrol-engined traffic. This is a common pattern in a number of UK cities.

Figure 5.13 Relationship between hourly average particle number and inbound traffic flow (vehicles per hour).

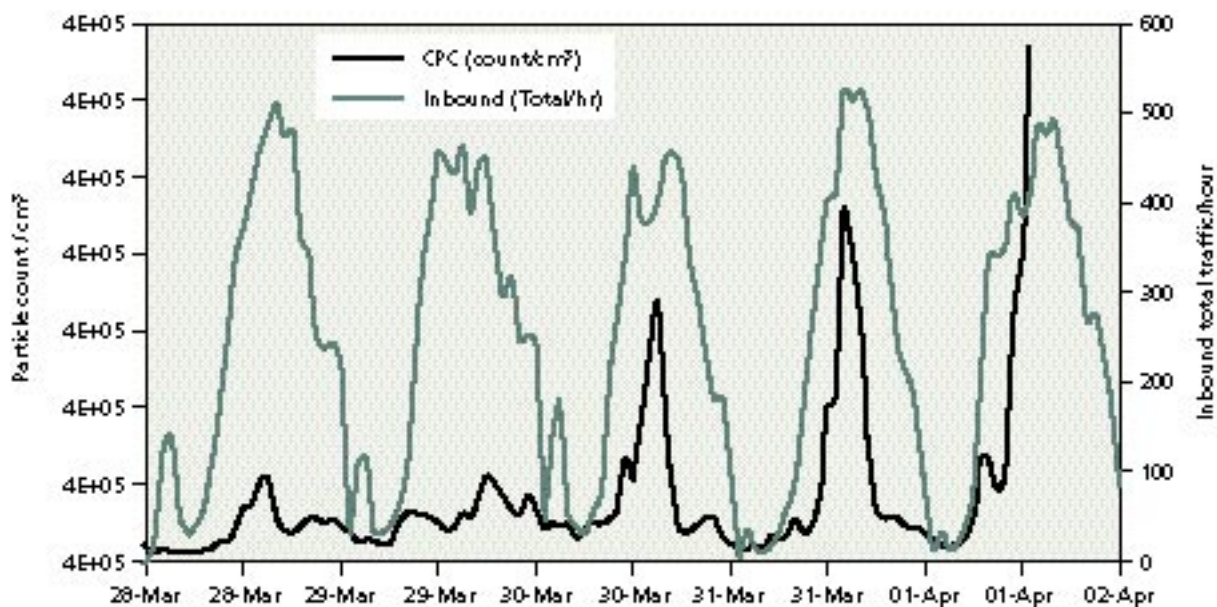
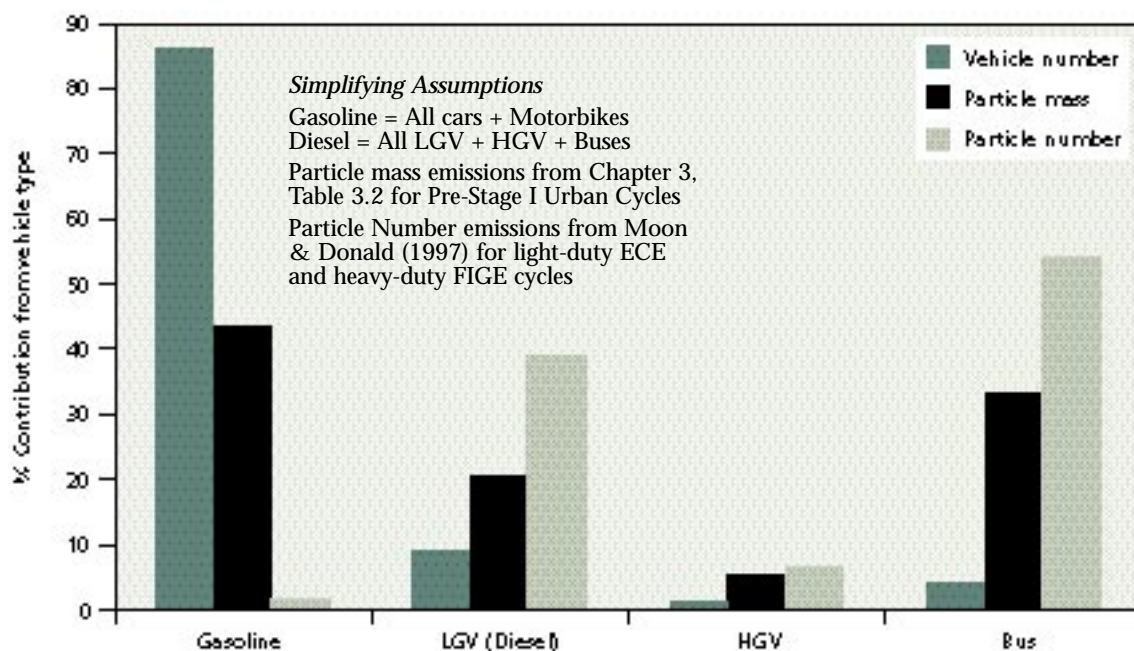


Figure 5.14 Particle mass and particle number by vehicle class (Oxford Carfax).



Thus, there was scope for monitoring to further discriminate between petrol and diesel sources.  $PM_{10}$ , particle number,  $NO_2$  and CO were measured in real-time and preliminary data suggest:

- Figure 5.15 shows a plot of particle number data versus time over an extended period with averaged 30 seconds values shown. A strong relationship is again observed between traffic density and particle number; and in this case rush hour peaks are more clearly discriminated, consistent with peak densities for bus traffic. It is also notable that levels are significantly lower over a weekend, where bus traffic is reduced.
- Figure 5.16 indicates that  $PM_{10}$  data and particle number data show similar patterns. This is consistent with monitoring a dominant single source in the region of the sampler. However, it can be noted that particle number shows a more consistent double rush hour pattern, and falls to very low background levels overnight. In contrast, residual  $PM_{10}$  values are observed overnight consistent with imported secondary aerosol.
- by reducing the time period of measurement to 2 second and 1 minute moving averages, real-time particle number data can be related to individual bus movements, as shown in Figure 5.17. These data suggest there is scope to identify individual 'dirty' vehicles.
- a series of correlations were observed between the gaseous and particle measurements - these offer scope in discriminating diesel ( $NO_2$ ) and petrol (CO) engined emissions, which may in turn improve the validation of the receptor modelling approach. In Figure 5.18, a very strong correlation is observed between particle number and  $NO_2$ , both on an hourly and daily average basis, consistent with the sampling location being dominated by diesel sources. In Figure 5.19, a plot of CO versus particle number shows a reasonable correlation (although not as strong as for  $NO_2$ ). This is consistent with a contribution from petrol-engined vehicles nearby in the City Centre area, which will contribute a similar rush hour pattern as the diesel buses.



Figure 5.15 Particle number concentration (30s average) recorded in Cornmarket Street, Oxford during 15th to 28th February 1998.

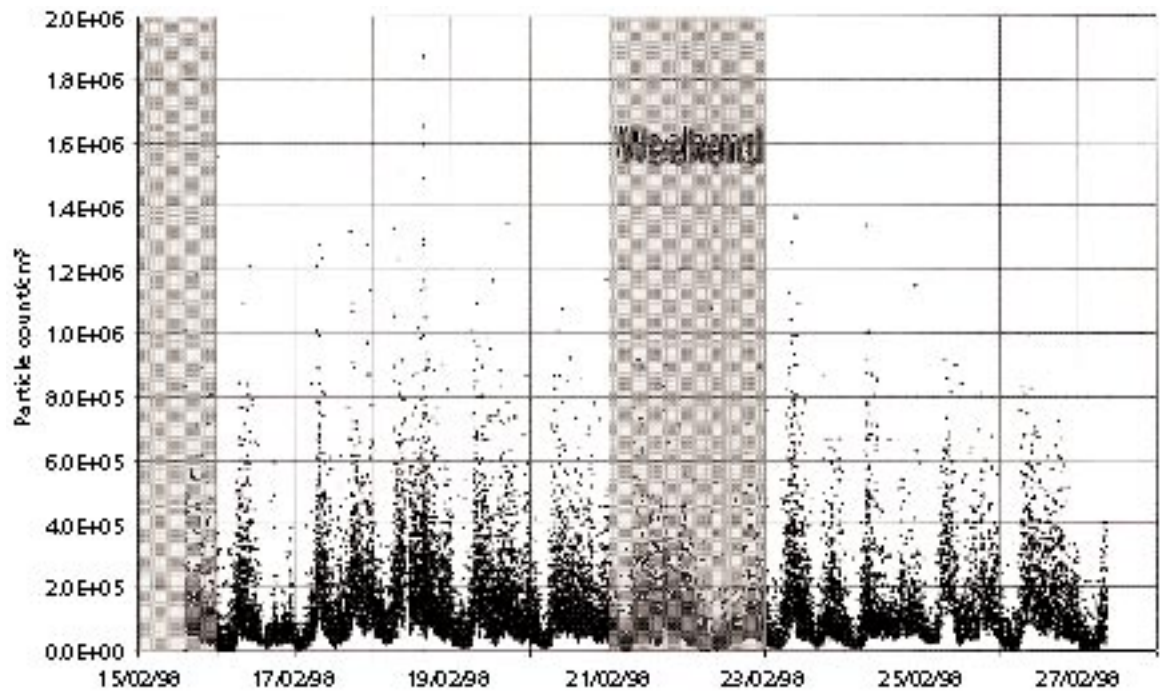
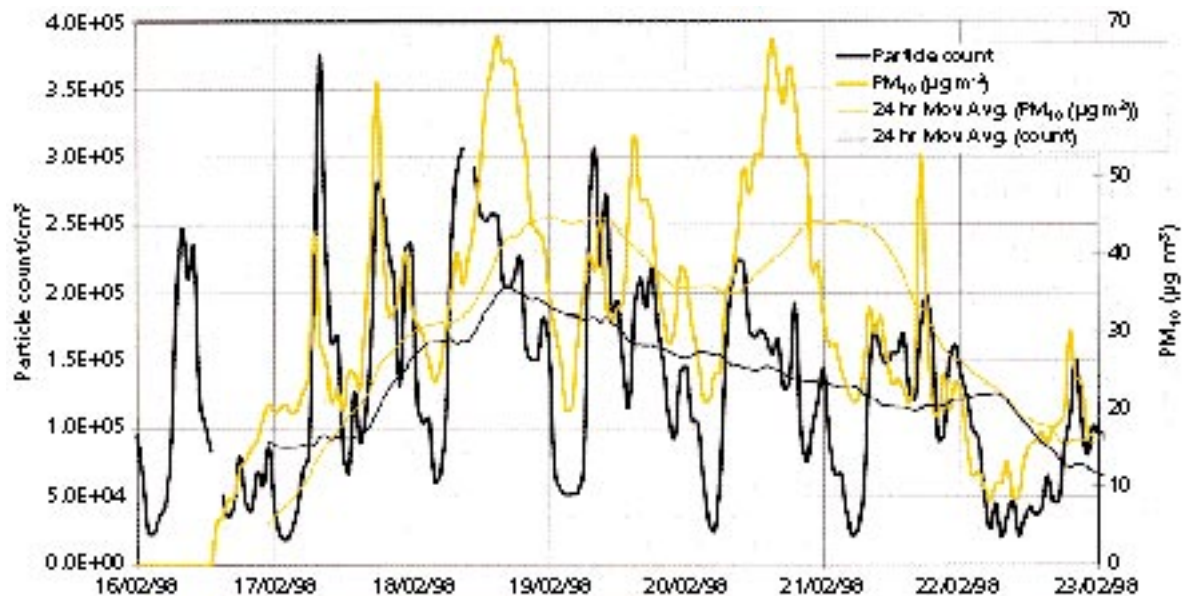


Figure 5.16 Relationship between particle number concentration and PM<sub>10</sub> concentrations ( $\mu\text{g m}^{-3}$ ) recorded in Oxford City Centre (hourly and daily running average data are shown).



In conclusion, these recent data indicate that there is scope for particle number to be used as a real-time metric of local vehicle emissions. Comparison with existing PM<sub>10</sub> data and CO and NO<sub>2</sub> gaseous concentrations may offer a route to further discriminate between diesel and petrol emissions,

as may more accurate particle size distribution data. However, there remains a lack of information on the long-term temporal and spatial distribution of these emissions under varying weather conditions, which requires further investigation.



Figure 5.17 Relationship between particle number concentration and the number of bus movements in Oxford City Centre (two second running average data).

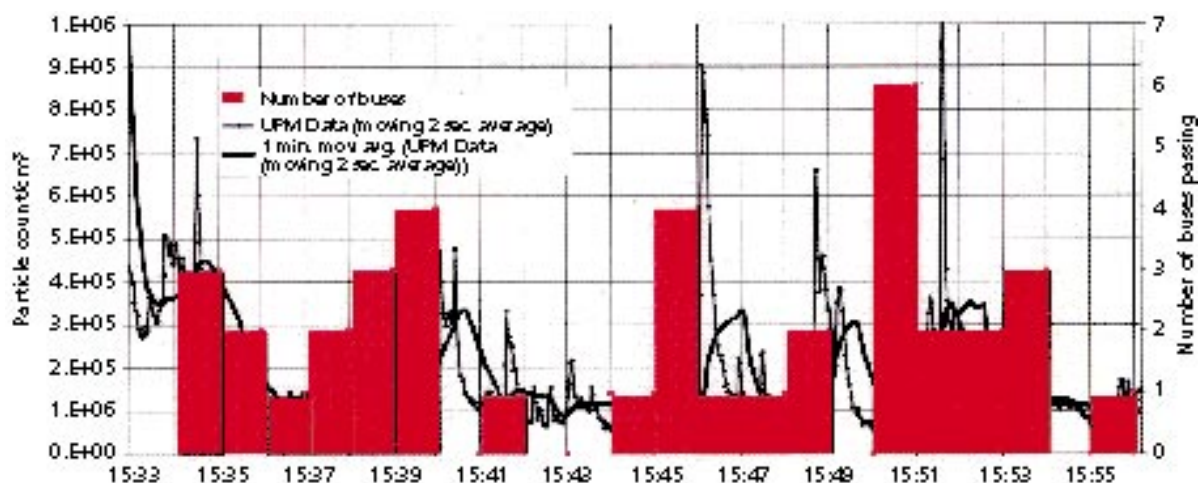
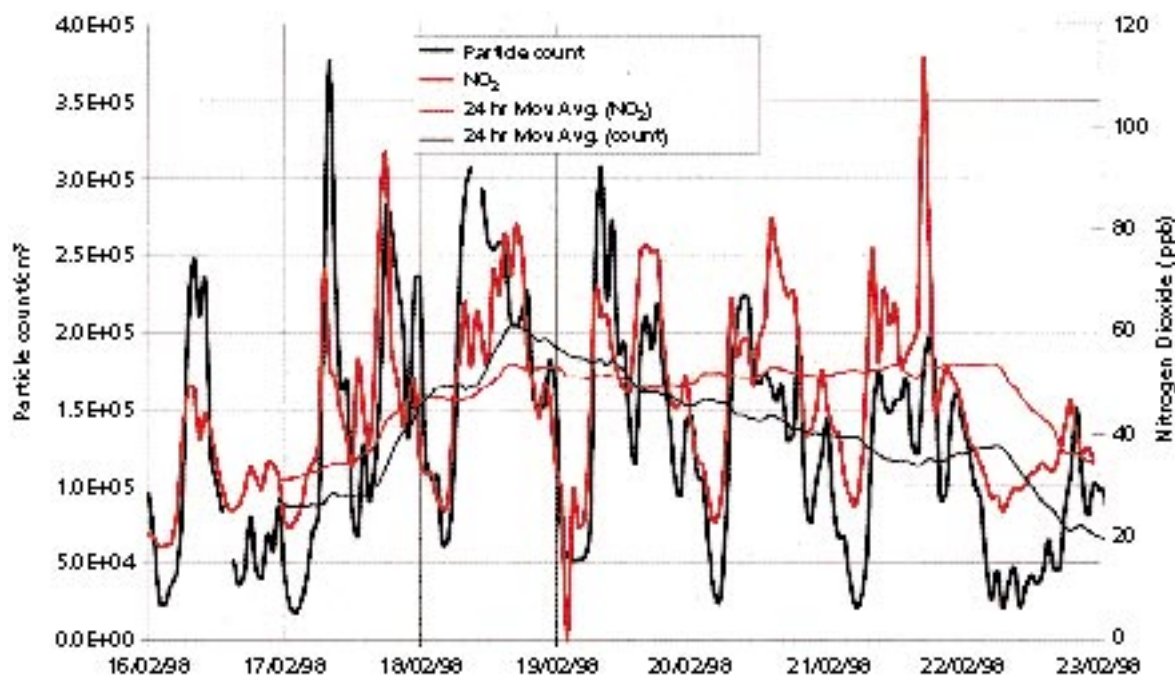


Figure 5.18 Relationship between particle number concentration and NO<sub>2</sub> (ppb) concentrations recorded in Oxford City Centre (hourly and daily running average data shown).



#### 5.4.4 PARTICLE NUMBER MONITORING AT THREE LOCATIONS

In addition to the PM<sub>2.5</sub> and PM<sub>10</sub> measurements at the four additional sites mentioned in Section 3.5, the Department of the Environment, Transport and the Regions is also funding measurements of particle number size distributions at three of the sites: a) the kerbside site on Marylebone Road, London; b) the

central urban background site at London Bloomsbury; and c) the rural background site at Harwell. Number particle size distributions in the particle size range 10 to 450 nm have been measured since the beginning of May 1998 using Scanning Mobility Particle Sizers (SMPS). Problems of inlet blockage by particles of aerodynamic diameter larger than about 1 µm are still being experienced at the Bloomsbury site (possibly associated with pollen from

Figure 5.19 Relationship between particle number concentration and CO (ppm) concentrations recorded in Oxford City Centre (hourly and daily running average data shown).

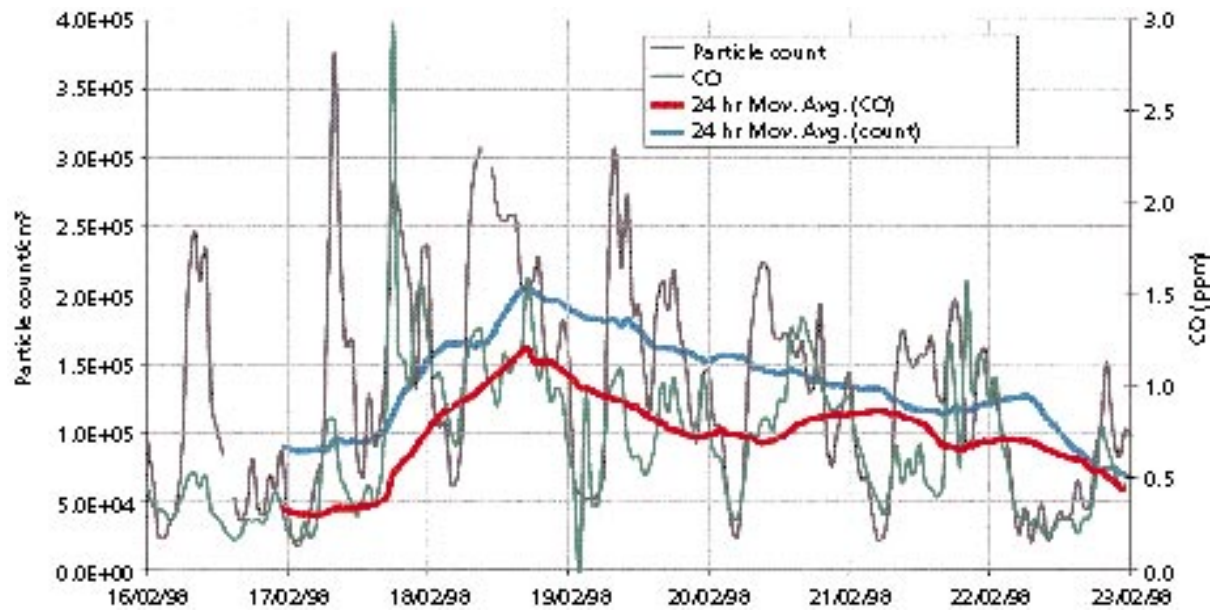
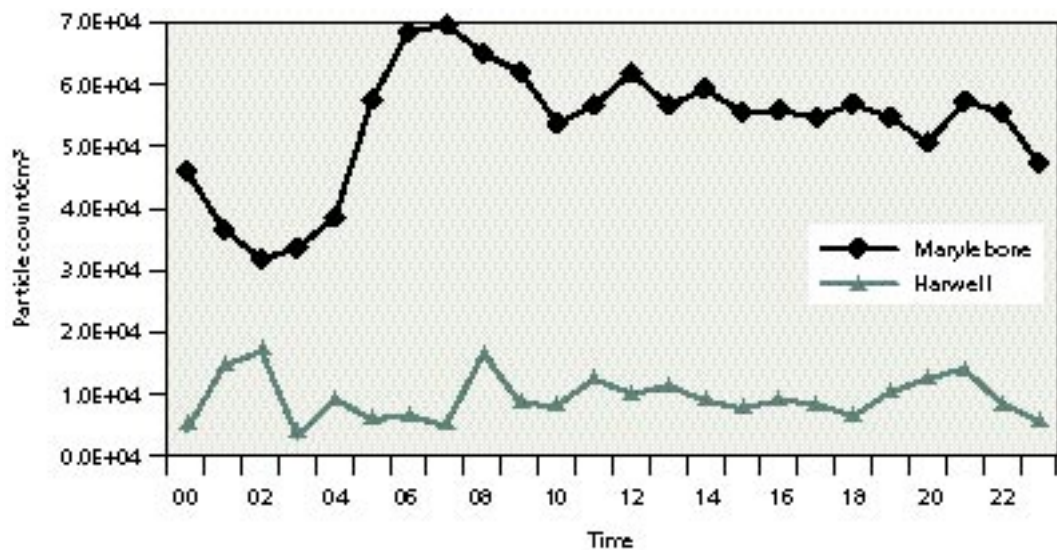


Figure 5.20 A comparison of the diurnal trends of average total particle numbers from Marylebone Road and Harwell for the months of April and May 1998.



the surrounding trees), and so preliminary data from the other two sites are presented (Mark, 1998). A comparison of the diurnal trends of hourly average total particle numbers from Marylebone Road and Harwell for the months of April and May 1998 are given in Figure 5.20. The wide difference in total particle is clearly shown with levels averaging between 30,000 to 70,000 particles/cm<sup>3</sup> at Marylebone Road,

and 3,000 to 18,000 particles/cm<sup>3</sup> at Harwell. In addition, there is a clear difference in diurnal patterns with a rapid rise in number concentration due to the early morning traffic being clearly seen at Marylebone Road, but not at Harwell. The diurnal variation in particle number is similar to that of NO<sub>x</sub> and differs from CO, consistent with a predominantly diesel source at Marylebone Road.

## 5.5 RECEPTOR MODELLING OF SPECIFIC CHEMICAL COMPONENTS

### 5.5.1 SEA-SALT

Atmospheric particles were sampled at five rural acid deposition monitoring sites during the 1980's. Measurements were carried out by Warren Spring Laboratory using Beckman Dichotomous samplers between 1980 and 1986 (Irwin, 1982, Stedman, 1991). Daily samples of fine (<2.5 µm) and coarse (2.5 - 15 µm) particles were collected on Poly-tetra-fluoro-ethylene (PTFE) filters and analysed by ion chromatography. Data capture was variable but data for the long runs of reasonably continuous data listed in Table 5.8 have been analysed.

Table 5.9 lists mean concentrations of these periods for each ion. If we assume that all the Cl present in these samples is of sea salt origin then the corresponding atmospheric concentrations of NaCl shown in Table 5.10 are obtained. The total concentration is consistently about 1.5 µg m<sup>-3</sup> at the three inland sites, higher at Lough Navar (2 µg m<sup>-3</sup>) and much higher at the more marine influenced site at Goonhilly (4 µg m<sup>-3</sup>).

Table 5.9 Mean concentrations at five rural sites (µg m<sup>-3</sup>).

Site	Fine					Coarse				
	SO <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	Na	Cl	SO <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	Na	Cl
Eskdalemuir	3.36	0.18	1.18	0.27	0.24	0.33	0.31	0.06	0.46	0.64
Goonhilly	3.60	0.57	1.38	0.63	0.67	0.45	0.62	0.05	1.20	1.76
Stoke Ferry	4.26	0.88	1.68	0.25	0.19	0.57	0.57	0.12	0.55	0.69
Ludlow	5.28	0.92	2.12	0.27	0.28	0.54	0.53	0.12	0.52	0.68
Lough Navar	2.16	0.22	0.65	0.29	0.32	0.30	0.31	0.04	0.56	0.88

These data should be considered in conjunction with the Leeds measurements of chloride (Section 3.10.2.5). Together they provide a consistent view of the contribution of sea-salt to PM<sub>10</sub> mass.

Table 5.8 Sampling periods.

Site	Start month	End month	Min samples*	Max samples*
Eskdalemuir	8/83	12/85	430	646
Goonhilly	10/84	4/86	158	356
Stoke Ferry	12/84	3/86	244	367
Ludlow	3/83	10/85	366	510
Lough Navar	5/84	3/86	351	614

\* The number of valid samples varies from ion to ion, the highest number of valid samples being for fine SO<sub>4</sub> and the lowest for coarse NH<sub>4</sub>

Table 5.10 Estimated sea salt particle concentrations (µg m<sup>-3</sup>).

Site	Fine NaCl	Coarse NaCl	Total NaCl
Eskdalemuir	0.40	1.05	1.45
Goonhilly	1.11	2.93	4.04
Stoke Ferry	0.32	1.11	1.43
Ludlow	0.46	1.11	1.57
Lough Navar	0.53	1.47	1.99

**5.5.2 ESTIMATED CONTRIBUTION OF SEASALT AND SECONDARY AMMONIUM NITRATE AND AMMONIUM SULPHATE TO PM<sub>10</sub> MASS AT URBAN AND RURAL SITES**

A sampling campaign for PM<sub>10</sub> using High Volume Samplers has been operated through six seasons at four sites. The sites range from The Lizard (rural and coastal) to Pershore and Lichfield (small towns) and suburban Birmingham. Air samples were collected for six-hourly intervals and analysed for chloride, nitrate and sulphate. Table 5.11 presents the results of calculation of the percentage of PM<sub>10</sub> mass comprised by seasalt, secondary ammonium

nitrate and ammonium sulphate, and the sum of the two, if it is assumed that all chloride, nitrate and sulphate are bound as NaCl, NH<sub>4</sub>NO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> respectively. This assumption may over-estimate the secondary component if some acid sulphate is present. The sampling campaign was for one week sequentially at each site during each season. There were therefore changes in weather conditions both between sites within a season as well as between seasons at the same site. The results (Table 5.11) show clearly a major contribution of seasalt at The Lizard during most seasons, and indeed, in autumn 1996 this was far the predominant component. In the autumn, winter and spring periods, seasalt can apparently represent

Table 5.11 Inferred contribution of seasalt and secondary inorganic particles to PM<sub>10</sub> at four UK sites (n=28 for each site and season).

SEASON	SITE	NaCl/PM <sub>10</sub> Mean ± s.d. (%)	[NH <sub>4</sub> NO <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ]/PM <sub>10</sub> Mean ± s.d. (%)	NaCl + NH <sub>4</sub> NO <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> /PM <sub>10</sub> Mean ± s.d. (%)
Summer 95	Lizard	41±20	22±12	63±23
	Birmingham	5±4	29±10	34±12
	Pershore	3±4	39±12	42±12
	Lichfield	2±6	31±7	33±8
Autumn 95	Lizard	16±19	54±23	70±10
	Birmingham	16±14	35±16	51±10
	Pershore	12±7	38±13	50±12
	Lichfield	8±4	37±10	45±9
Winter 95/96	Lizard	5±4	50±15	54±17
	Birmingham	35±14	27±10	60±10
	Pershore	30±21	36±15	66±14
	Lichfield	12±6	40±15	52±15
Spring 96	Lizard	35±28	37±22	71±12
	Birmingham	10±10	49±17	59±15
	Pershore	16±14	51±15	67±14
	Lichfield	11±7	39±12	50±12
Summer 96	Lizard	38±24	27±18	66±10
	Birmingham	6±6	22±5	28±9
	Pershore	1±2	17±9	18±9
	Lichfield	6±6	20±5	26±10
Autumn 96	Lizard	72±14	16±7	88±15
	Birmingham	16±12	58±35	74±39
	Pershore	39±25	23±12	62±20
	Lichfield	30±16	51±19	81±25



a quite significant proportion of particle mass at the other sites, although it is not clear whether resuspension of road salt makes a contribution to this phenomenon. The contribution of secondary ammonium nitrate and ammonium sulphate is much less spatially and seasonally variable. Together, the seasalt and secondary nitrate and sulphate components can comprise as a weekly average anything from 20% of PM<sub>10</sub> mass at Pershore in summer 1996 through to 100% of mass at The Lizard in autumn 1996. The occurrence of totals greater than 100% may be the result of either analytical imprecision or an over-estimation of mass from the conversion of chloride, nitrate and sulphate concentrations to equivalent compounds.

### 5.5.3 SECONDARY ORGANIC CONTRIBUTION OF PARTICLE MASS

Research conducted jointly between the University of Birmingham and University of Aveiro, Portugal (Castro *et al.*, 1998), has measured the ratio of organic carbon to black carbon at a range of sites. Whilst organic carbon comprises both primary and secondary organic compounds, black carbon corresponds to an almost elemental form of carbon, with few other bonded atoms, formed in combustion processes. The research showed that at all sites the minimum value of the organic carbon to black carbon ratio was 1:1. In Birmingham, in the winter, all samples collected with a PM<sub>10</sub> high volume sampler lay at or little above this ratio, which is believed to correspond to that typical of primary organic carbon to black carbon. In the summer samples from Birmingham, the organic carbon to black carbon ratio became relatively elevated and the increase is interpreted as due to secondary organic carbon formed by chemical reactions of volatile organic compounds to form less volatile species. In the winter months, the average concentration of primary organic carbon was 3.95 µgC m<sup>-3</sup>, and the average secondary organic carbon was 0.63 µgC m<sup>-3</sup>, representing 17% of organic carbon. In contrast, in the summer primary organic carbon accounted for 1.65 µgC m<sup>-3</sup> and secondary organic carbon on average for 3.10 µgC m<sup>-3</sup> or 65% of organic carbon. Given that the ratio of mass of

organic carbon compounds to their carbon content is generally assumed to be around 1.2, this implies from this small data set (n=13) that secondary organic carbon compounds in winter and summer accounted respectively for 0.8 and 3.7 µg m<sup>-3</sup> of PM<sub>10</sub> mass. These samples were collected with a High Volume sampler with PM<sub>10</sub> inlet which is expected to retain the major part of the particulate organic carbon. This is in contrast with the TEOM where a major part of secondary organic carbon may be lost during sampling.

## 5.6 ATTRIBUTION OF PM<sub>10</sub> MASS TO COMBUSTION EMISSIONS, SECONDARY COMPONENTS AND 'OTHER' PARTICLES

### 5.6.1 INTRODUCTION

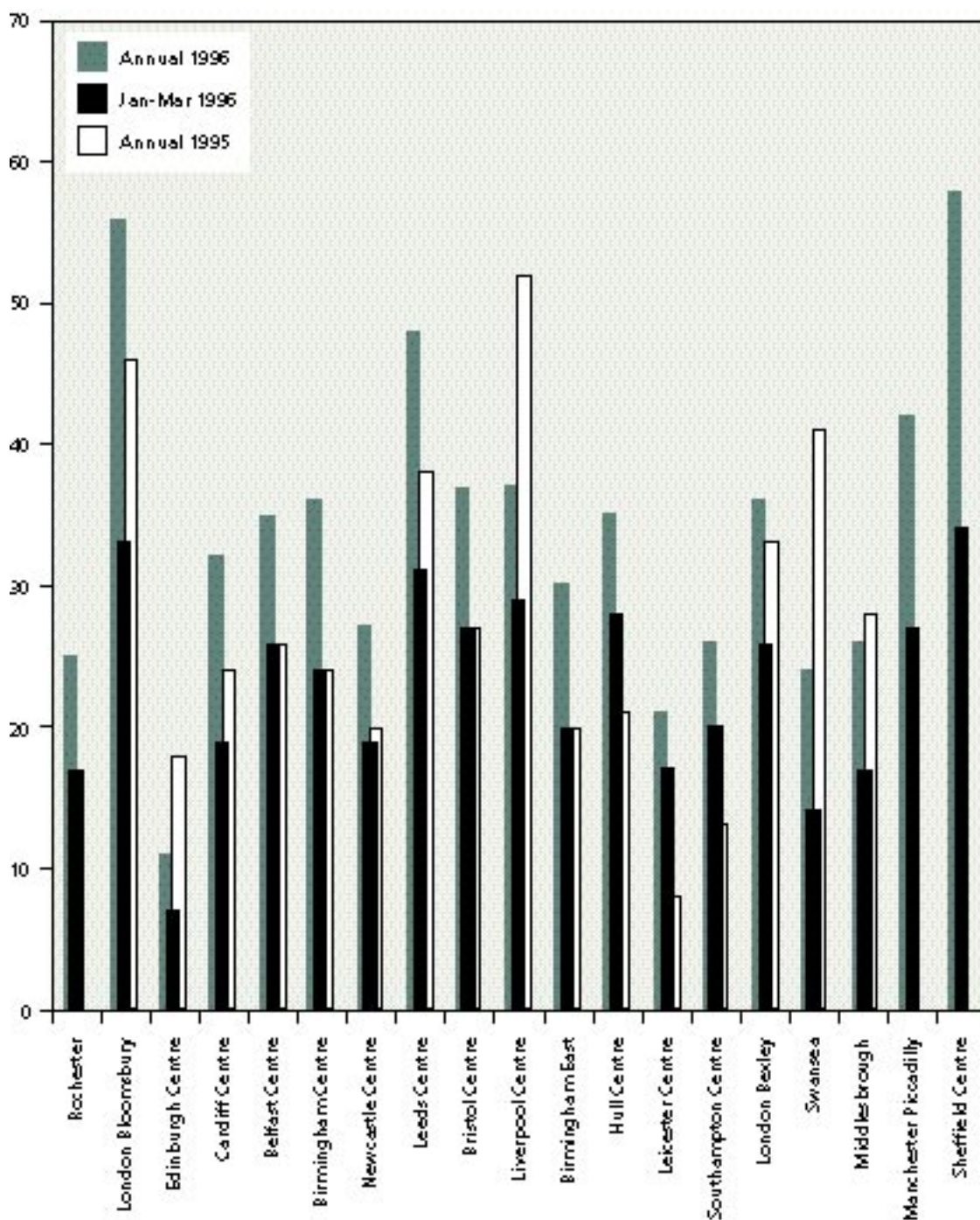
The development of a method for the source attribution of episodes of elevated PM<sub>10</sub> concentrations has been reported by Stedman (1997a,b, 1998) and is summarised here. A combination of measured daily mean PM<sub>10</sub>, black smoke and sulphate concentrations are used to assign contributions to PM<sub>10</sub> from primary, secondary and coarse particles on a daily basis.

As will be seen later, the early part of 1996 provided an unusual period of air pollution with an exceptional prevalence of high concentrations resulting mainly from transport of air pollutants from the European continent. This presented an excellent opportunity to develop a method to discriminate the secondary contribution to airborne particulate matter from particles arising from other sources.

There were two geographically widespread and prolonged episodes of elevated PM<sub>10</sub> concentrations during the period January to March 1996: the first in late January and early February and the second in mid March. Figure 5.21 shows the importance of this period in contributing to the total number of days with concentrations greater than or equal to 50 µg m<sup>-3</sup> during 1996 and also the 1995 period. At many sites more than three



Figure 5.21 Number of days with maximum running mean PM<sub>10</sub> concentrations  $\geq 50\mu\text{g m}^{-3}$  in January-March 1996 and the entire year.

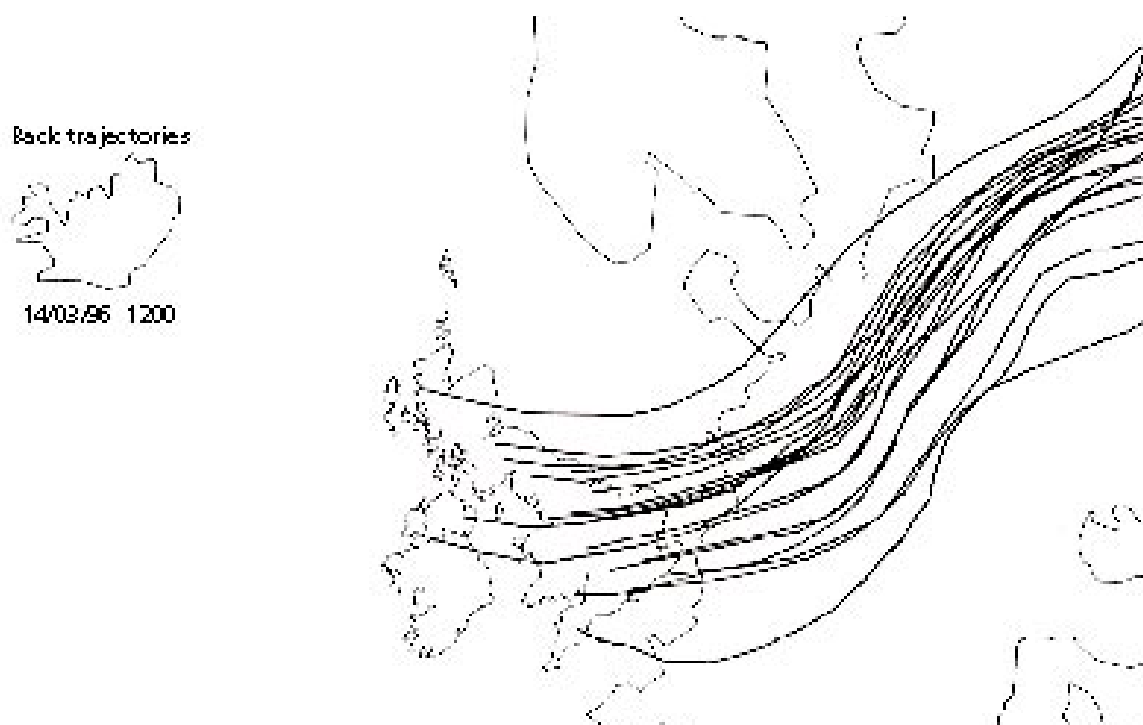


quarters of these days were during these three months and at almost all sites more than half of the episodes were confined to this period.

Secondary particles formed the main contribution to the high concentrations during these episodes. This has been demonstrated by the comparison of

urban concentrations with those in rural areas (King and Dorling, 1997, Stedman, 1997b) showing that urban and rural concentrations were similar during these episodes. In addition, the PM<sub>10</sub> concentrations in urban areas during these episodes did not show the type of strong diurnal variation that would be associated with the poor dispersion

Figure 5.22 Back trajectory analysis for meteorological conditions over UK on 14th March 1996 at 12 noon.



of primary particles from local combustion sources. King and Dorling (1997) and Stedman (1997b, 1998) also pointed out that these episodes were characterised by winds from the east bringing long range transported secondary particles to the UK from the continent. This transport is well illustrated by the 96-hour air mass back trajectories for 14 March 1996 shown in Figure 5.22.

The contributions to ambient  $PM_{10}$  concentrations from primary, secondary and coarse particles can be analysed by comparison of measurements from different national monitoring networks. Daily  $PM_{10}$  measurements are compared with daily black smoke measurements in Figure 5.23. Network daily mean  $PM_{10}$  concentrations over the whole of the UK have been calculated for 20 automatic monitoring sites within the national monitoring networks, which are mostly in urban areas. Network daily mean black smoke concentrations have been calculated from the more than 200 sites within the national Smoke and  $SO_2$  monitoring network (Stevenson *et al.*, 1995), which are also mostly in urban areas. Concentrations of black smoke were determined by reflectance of filter samples and represent fine combustion particles of diameter less than about 4

$\mu m$ . Black smoke measurements therefore provide a good indicator of combustion related primary  $PM_{10}$  concentrations. There will, however, be a small contribution to measured black smoke concentration from dark particles other than soot. The elevated concentrations of  $PM_{10}$  on 15th and 16th January and 28th February 1996 corresponded with elevated black smoke concentrations, indicating that there was a significant contribution to  $PM_{10}$  from combustion related primary particles on these days. Black smoke concentrations during the two prolonged  $PM_{10}$  episodes were, however, low indicating that combustion sources were not making the dominant contribution to these episodes.

Figure 5.24 shows the network mean particulate sulphate concentrations during this period. The daily mean concentration was calculated for the network of eight rural sites shown in Figure 5.25. These sites are equipped with similar monitoring equipment to that deployed at Smoke and  $SO_2$  network monitoring sites (RGAR, 1997). Sulphate concentration on the filters was determined by ion chromatography; these measurements therefore represent sulphate particles of diameter less than about 4  $\mu m$ . It is not possible to assess the detailed

Figure 5.23 Network daily mean PM<sub>10</sub> and black smoke concentrations ( $\mu\text{g m}^{-3}$ ).

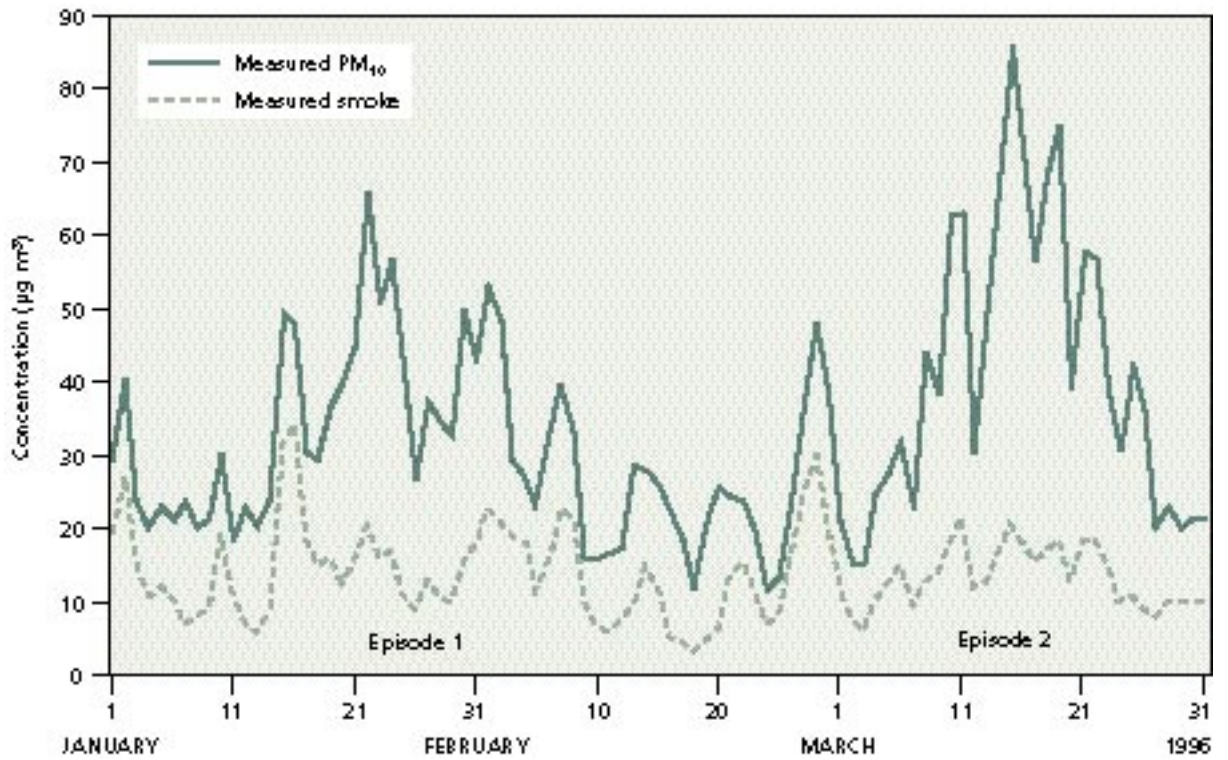


Figure 5.24 Network daily mean particulate sulphate concentration.

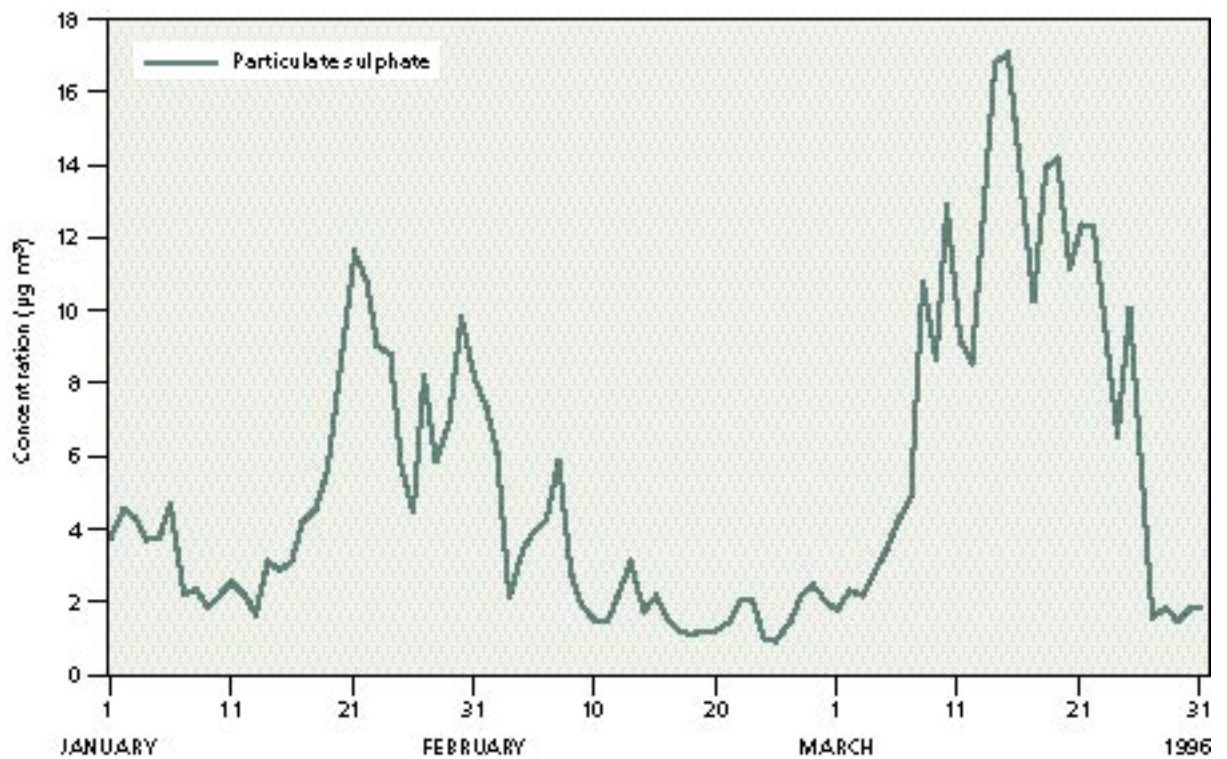
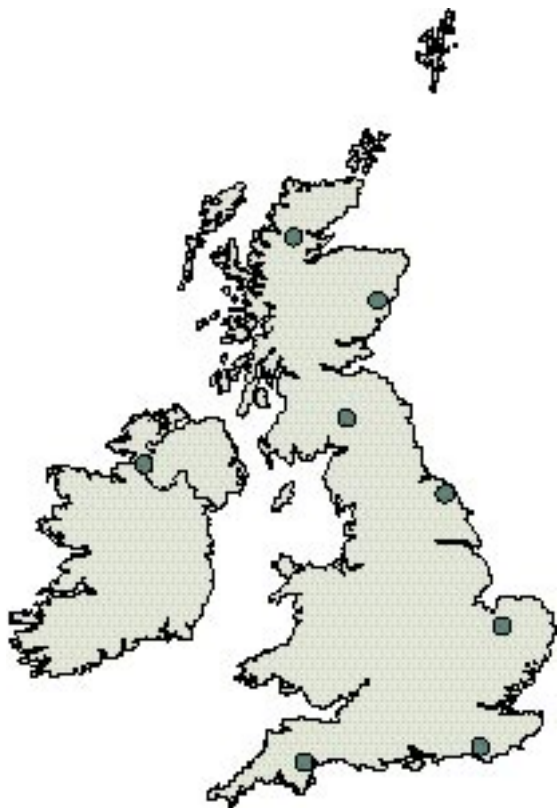




Figure 5.25 UK rural particulate sulphate measurement sites.

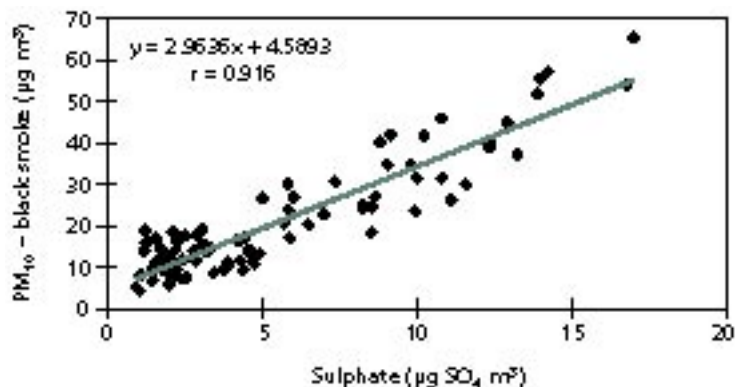


spatial variability of concentrations from measurements at this sparse network of eight sites but the concentrations of secondary particles can be expected to be relatively uniform due to their long atmospheric lifetime. It is clear from a comparison of Figures 5.23 and 5.24 that particulate sulphate measurements provide an excellent indicator of the secondary particle component of  $PM_{10}$ .

If the primary combustion contribution to daily  $PM_{10}$  concentrations is removed from the total  $PM_{10}$  concentration by subtracting the black smoke concentration, then what is left is a non-combustion component: a combination of secondary particles and coarse particles. Figure 5.26 shows a scatter plot of this parameter plotted against the daily sulphate concentrations. This shows the following:

- *There is a clear relationship between the non-combustion component of  $PM_{10}$  and the sulphate concentration. Sulphate is providing a good indicator of the concentration of secondary particles.*

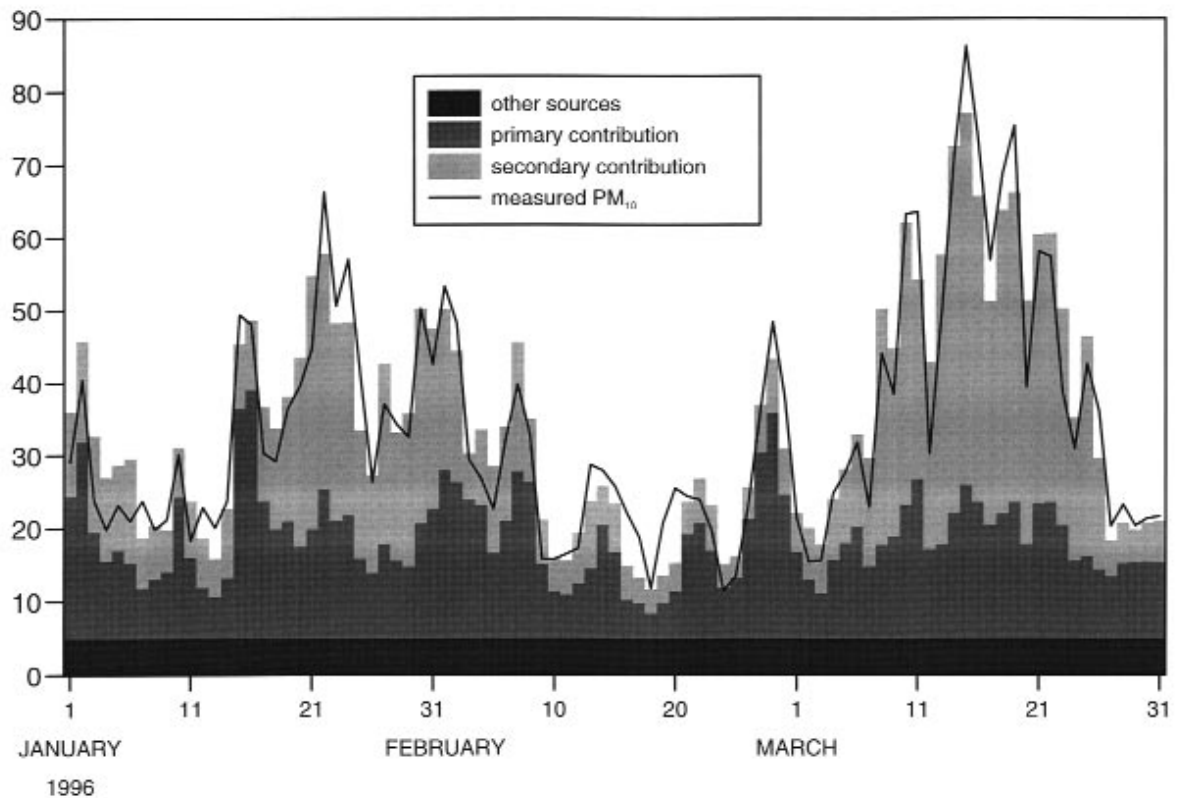
Figure 5.26 The relationship between daily  $PM_{10}$ , black smoke and sulphate concentrations, January to March 1996.



- *The intercept of about  $5 \mu\text{g m}^{-3}$  represents an approximately constant concentration of 'other' particles during this period.*
- *The slope of about 3 shows the scaling factor required to convert sulphate measurements to secondary  $PM_{10}$  on a network mean basis. This factor is required because the measurements are of sulphate only. There will also be a counter ion such as ammonium present in addition to nitrate particles.*

It is important to note that sulphates may not necessarily make a dominant contribution to secondary  $PM_{10}$  in comparison to nitrates. The relative proportions of sulphate and nitrate will depend on the emissions and atmospheric chemistry that takes place in air mass. We are forced to focus on using sulphate as an indicator because of the scarcity of nitrate monitoring sites. The factor of 3 also is partly determined by the relative locations of the  $PM_{10}$ , black smoke and sulphate monitoring sites. While urban areas in England are strongly represented in both the  $PM_{10}$  and black smoke monitoring networks, the sulphate monitoring network sites are more evenly distributed, with several sites in remote areas of Scotland and Northern Ireland. This is important because there is a gradient in particulate sulphate across the country, with concentrations in southern England being more than twice those in northern Scotland (RGAR, 1997). Values in the range 2 to

Figure 5.27 Network daily mean PM<sub>10</sub> concentrations (µg m<sup>-3</sup>), January to March 1996.



2.5 are obtained if this factor is calculated on an individual site, rather than network mean basis.

This relationship therefore provides a method for illustrating the contributions to measured PM<sub>10</sub> concentrations on a daily basis. A constant 'other' particle concentration is assumed for each day; the combustion related primary particle concentration is represented by the concentration of measured black smoke and the secondary particle concentration is estimated by multiplying the measured concentration of sulphate by a factor of three. While the 'other' particle fraction calculated in the model is similar to the coarse fraction, strictly it does not include only coarse particles as the model is based on source rather than size fractions. Figure 5.27 shows this method can be used to illustrate the contributions to the measured PM<sub>10</sub> concentrations during the episode periods. This figure clearly shows the significant secondary particle contributions to the two prolonged episode periods and the primary particle contributions to the shorter episodes. Combustion related particles transported from distant sources will be included

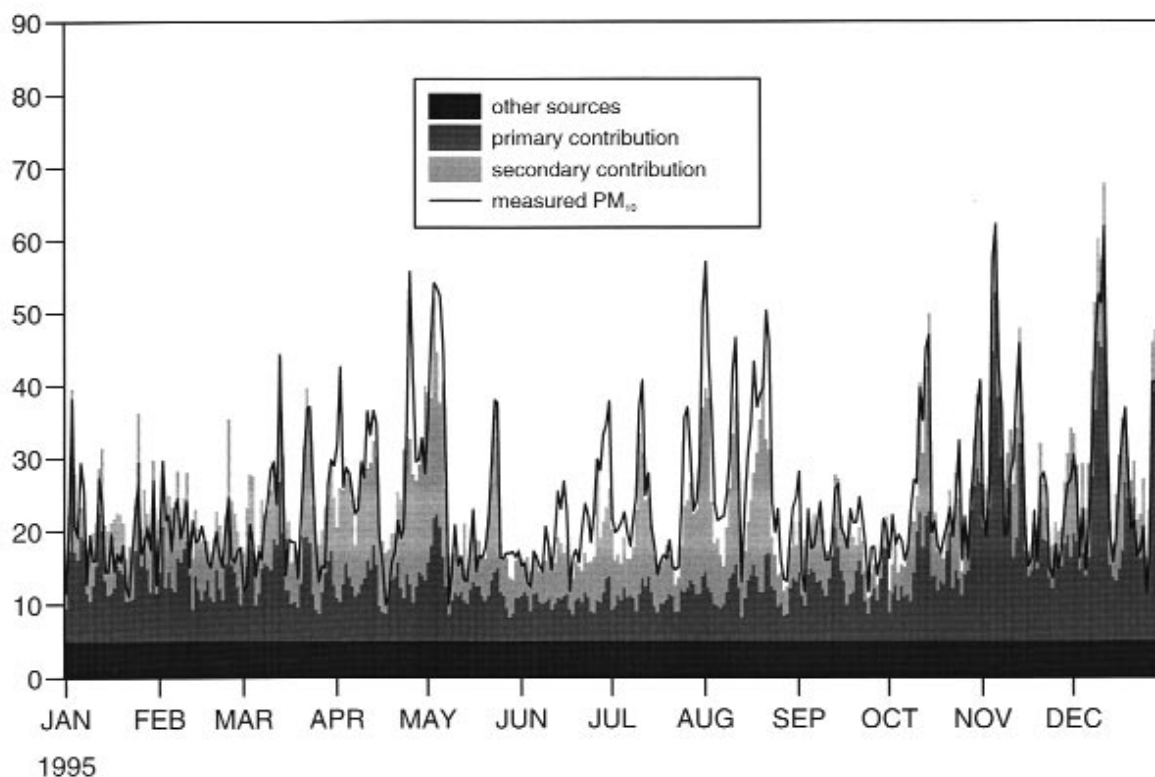
along with locally derived dark particles in the black smoke measurements and not in the sulphate component. It is likely, however, that local sources will tend to dominate the black smoke measurements. If there is a significant contribution to measured PM<sub>10</sub> from European primary PM<sub>10</sub> emissions (see Section 3.4) on episode days with easterly winds then this could contribute to the primary, secondary or coarse contribution defined in this model, depending on the nature of the emissions.

### 5.6.2 THE FREQUENCY OF SECONDARY PARTICLE PM<sub>10</sub> EPISODES

The high concentrations of secondary PM<sub>10</sub> during early 1996 provide an excellent dataset to establish the relationships between PM<sub>10</sub>, black smoke and sulphate concentrations because of the wide range of measured sulphate concentrations. The regression relationships between these contributions to daily PM<sub>10</sub> concentrations are reasonably robust and can be applied to other periods. Figure 5.28 shows the contributions to daily PM<sub>10</sub> for 1995 and



Figure 5.28 Network daily mean PM<sub>10</sub> concentrations (µg m<sup>-3</sup>), 1995.



provides further illustrations of the different types of PM<sub>10</sub> episodes. Elevated PM<sub>10</sub> concentrations with a significant secondary particle component were measured in early May, and again in July and August. These periods were also associated with photochemical ozone episodes in the UK, in contrast with the early 1996 episodes, which were of particles only. The PM<sub>10</sub> episodes in November and December were dominated by combustion sources. The high concentrations in early November were associated with Guy Fawkes Night celebrations (Clark, 1997, Section 3.7).

A constant 'other' particle concentration of 5 µg m<sup>-3</sup> has been assumed for each day during 1995 in this analysis. A comparison of co-located PM<sub>10</sub> and PM<sub>2.5</sub> measurements at an urban background monitoring site in Birmingham (Harrison *et al.*, 1997) has shown that mean concentrations of coarse particles are higher in the summer than during the winter, with seasonal mean concentrations for the period 1994-1995 of 10.9 µg m<sup>-3</sup> and 6.5 µg m<sup>-3</sup> respectively. Harrison *et al.*, (1997) have also found that coarse particle concentrations at this site can be

significantly higher on some summer episode days. It is also evident from Figure 5.28 that particle concentrations on some days during the summer of 1995 were higher than predicted by the model presented here. This additional PM<sub>10</sub> is likely to have been coarse particles. This point is discussed later.

Daily network PM<sub>10</sub> concentrations have been analysed in this way for 1994, 1995 and 1996 and the results are summarised in Table 5.12.

Table 5.12 The contributions to daily network mean PM<sub>10</sub> (µg m<sup>-3</sup>). Calculated using the relationships derived for the period January to March 1996.

Year	Measured	Estimated	Primary	Secondary	'Other'	r*
1994	24.9	24.1	10.3	8.8	5.0	0.88
1995	24.0	23.9	10.0	8.9	5.0	0.85
1996	25.5	24.6	10.2	9.4	5.0	0.90

\* the correlation coefficient between measured and estimated total PM<sub>10</sub>

The early part of 1996 was exceptional in terms of the magnitude and duration of the secondary particle contribution to PM<sub>10</sub> episode concentrations in the UK. Periods with significant

contributions to PM<sub>10</sub> from secondary particles do occur each year however, in both summer and winter, as illustrated in Figure 5.28 for 1995.

An examination of the secondary particle related PM<sub>10</sub> episodes in the years 1994 to 1996 shows that a daily network mean sulphate concentration of about 9 µg m<sup>-3</sup> (corresponding to a secondary PM<sub>10</sub> concentration of 27 µg m<sup>-3</sup>) can lead to a daily PM<sub>10</sub> concentration in excess of 50 µg m<sup>-3</sup>. The average black smoke concentration on days with sulphate concentration above this threshold is about 17 µg m<sup>-3</sup>, leading to a total PM<sub>10</sub> concentration, including 'other' particles of the order of 50 µg m<sup>-3</sup>. Table 5.13 lists the number of days in each year since 1992 that the network mean sulphate concentration was at least 9 µg m<sup>-3</sup>. This confirms that 1996 was the year with the most days with secondary particle related days with PM<sub>10</sub> concentrations in excess of the standard but all years have some of these days.

Table 5.13 The number of days with network mean sulphate concentrations greater than 9 µg m<sup>-3</sup> (corresponding to a network mean PM<sub>10</sub> concentration greater than fixed daily 50 µg m<sup>-3</sup>).

Year	Number of days
1987	14*
1988	8*
1989	6*
1990	16*
1991	13*
1992	5
1993	8
1994	3
1995	3
1996	20

\* Daily concentrations 1987-1991 adjusted to be consistent with 1992-1996 values.

Particulate sulphate measurements at the full network of eight rural sites shown in Figure 5.25 commenced in 1987, five years before PM<sub>10</sub> measurements started. The data for the earlier years does not, however, provide a direct indication of the likely return frequency of the magnitude of secondary particle episodes seen in 1996 because sulphate levels have decreased significantly in the UK since 1987 (RGAR, 1997).

Mean values for the period 1994 - 1996 are typically about 75% of those measured in the period 1987-1989. Annual mean concentrations fell during the period 1987-1991 and then remained roughly constant. The number of sulphate episode days for each year listed in Table 5.13 for these earlier years have therefore been adjusted to take into account the change in concentration up to 1991. This indicates that for current levels of secondary particles, the meteorological conditions leading to episodes of the magnitude of those experienced in 1996 can be expected to occur once every five to ten years.

### 5.6.3 ANALYSIS OF DATA FOR INDIVIDUAL CITIES

The regression analysis has been repeated for six individual monitoring sites within the national Automatic Urban Monitoring Network and data for the years 1995 and 1996 have been analysed. A regression model of the form:

$$[measured\ PM_{10}] = A [measured\ black\ smoke] + B [measured\ sulphate] + C$$

was derived for monitoring sites for the whole of 1996 and the coefficients obtained are shown in Table 5.14. Measurements over the several black smoke monitoring sites in each city were averaged where possible and sulphate concentrations were taken from the nearest rural monitoring sites. The black smoke coefficient varies from 0.6 to 1.0 depending on the site, possibly reflecting the different sources of primary PM<sub>10</sub> in these cities. The sulphate coefficient varies from about 2.25 to 3.1; this may in part be due to the locations of sulphate monitoring sites, often rather far from the cities in question, within this sparse network. These differences may also reflect a variation in the chemical composition of the secondary particles. These 1996 regression models have been applied to measurement data from 1995 (Figures 5.29 and 5.30) and show the estimated split between primary, secondary and 'other' particles.

Table 5.14 Regression coefficients for 1996 PM<sub>10</sub> data.

	Smoke coefficient, A	SO <sub>4</sub> coefficient, B	Intercept, C	r
London Bloomsbury	0.64	2.26	10.96	0.88
Birmingham Centre	0.59	2.41	8.30	0.84
Bristol Centre	1.03	2.35	10.83	0.84
Manchester Piccadilly	0.60	2.46	9.77	0.86
Newcastle Centre	0.66	3.13	7.73	0.92
Belfast Centre	0.71	2.30	9.21	0.89

Focus was given to days with measured fixed daily mean PM<sub>10</sub> concentrations greater than or equal to 50 µg m<sup>-3</sup> in order to attribute individual days with high concentration to particular source types. Tables 5.15 and 5.16 list the episode days (mean concentrations >50 µg m<sup>-3</sup>) at Newcastle Centre. The percentage primary and secondary contributions to measured concentration on these days were calculated by multiplying the measured black smoke and sulphate concentrations by the appropriate regression coefficients. The percentage contribution from 'other' particles was estimated by subtracting the sum of the primary and secondary contributions from the measured PM<sub>10</sub> concentration. The percentages are only shown if the contribution for a single source

exceeds 40%. Source apportionment for the 1995 and 1996 annual periods is given in Table 5.17.

Table 5.15 Episodes of PM<sub>10</sub> in Newcastle in 1995-source apportionment using 1996 regression factors.

Date	PM <sub>10</sub> (µg m <sup>-3</sup> )	% primary	% secondary	% 'other'
2.4.95	60			68
25.4.95	50			61
3.5.95	61		62	
4.5.95	63		49	
22.8.95	60		45	
14.10.95	52		64	
4.11.95	55	55		
12.11.95	54		43	44
13.11.95	71			

Figure 5.29 Daily mean PM<sub>10</sub> concentrations at Birmingham Centre, 1995 (µg m<sup>-3</sup>).

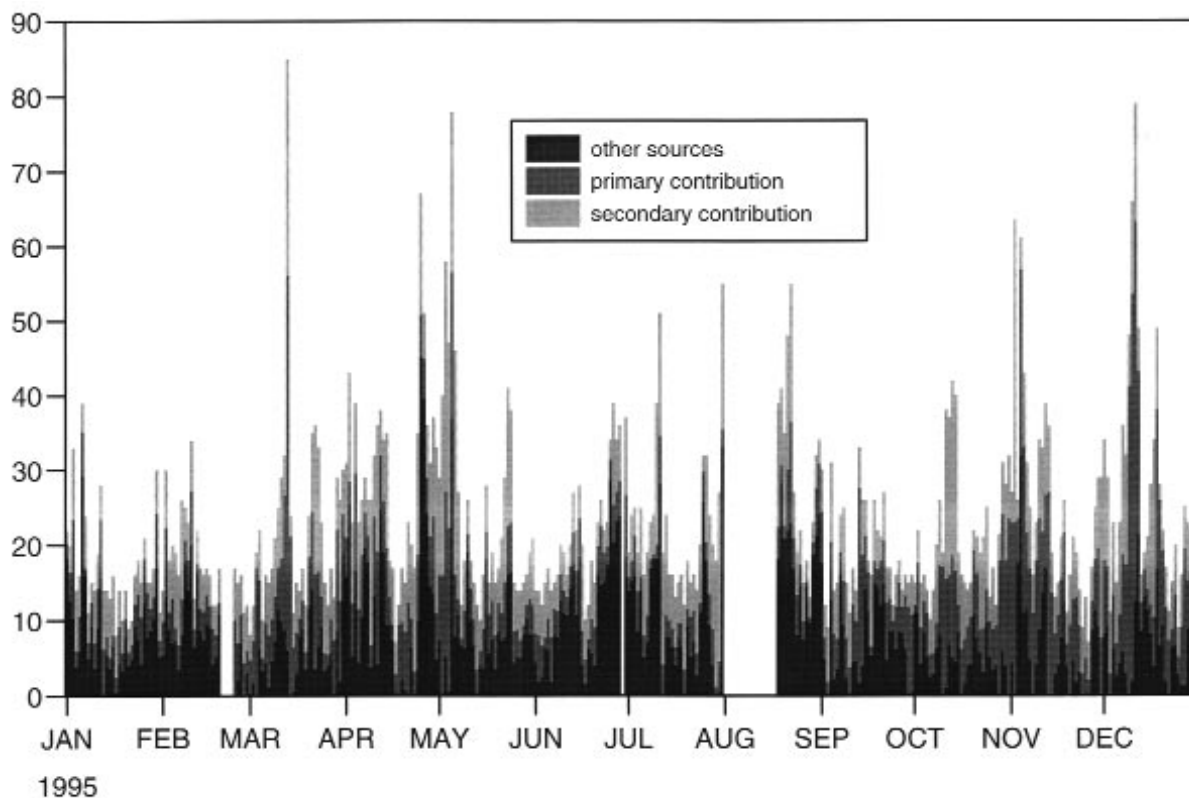


Figure 5.30 Daily mean concentrations at Newcastle Centre, 1995 ( $\mu\text{g m}^{-3}$ ).

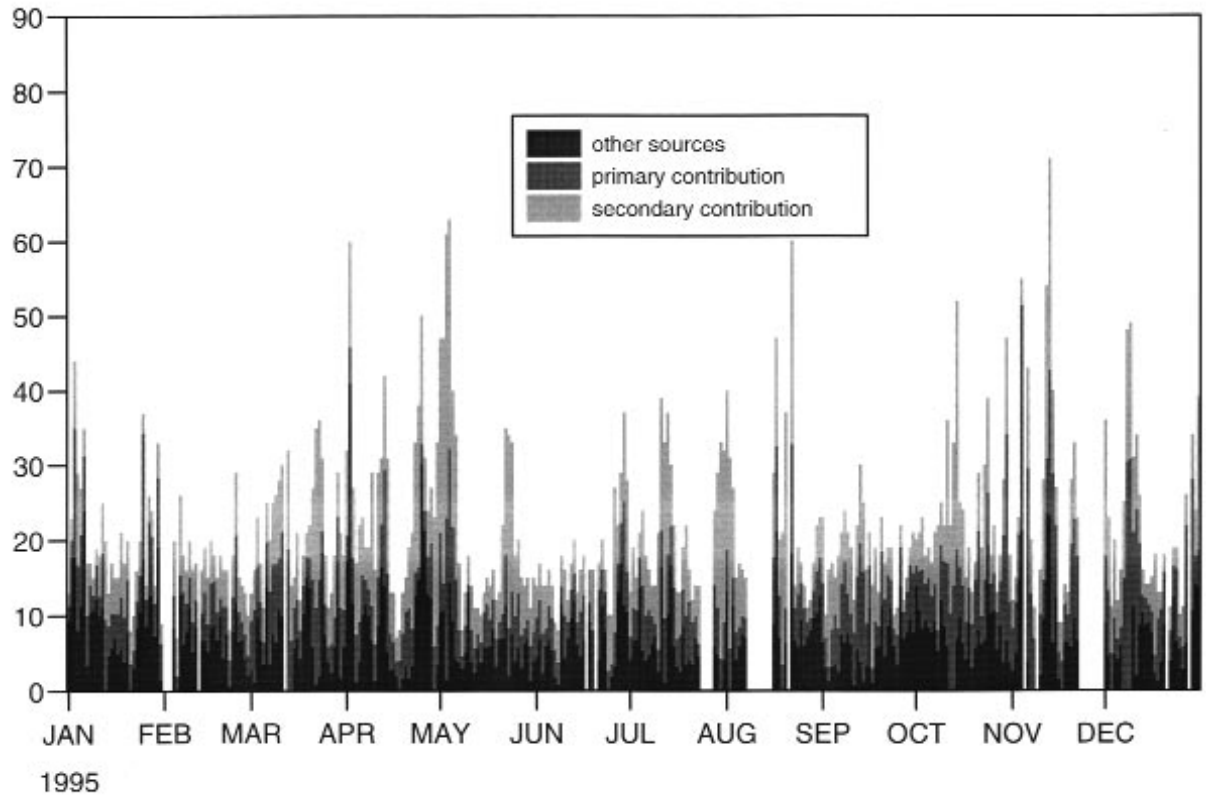


Table 5.16 Episodes of  $\text{PM}_{10}$  in Newcastle in 1996- source apportionment using 1996 regression factors.

Date	$\text{PM}_{10}$ ( $\mu\text{g m}^{-3}$ )	% primary	% secondary	% 'other'
22.1.96	65		66	
9.3.96	59		60	
10.3.96	77		61	
11.3.96	67		49	
14.3.96	55		111	
15.3.96	88		80	
16.3.96	66		77	
17.3.96	52		77	
18.3.96	66		69	
21.3.96	94		63	
22.3.96	86		54	
23.3.96	86		42	49
19.8.96	67		45	
20.8.96	51		55	

Similar analyses were carried out for all of the six sites and the resulting numbers of days with episodes of each type are listed in Table 5.18. If the primary and secondary contributions are both in excess of 40%, then the episode day was assigned

to the primary + secondary (p+s) column. If none of the individual contributions were above 40%, then the day was assigned to the p+s+o category, showing mixed origin. This table shows that:

- episodes of all types are seen
- there were many episodes of secondary type in 1996
- the number of days with daily mean concentrations greater than or equal to  $50 \mu\text{g m}^{-3}$  is lower by a factor of between 1.5 and 2.2 than the number of days with a maximum running 24 hour mean concentration greater than or equal to  $50 \mu\text{g m}^{-3}$ , the column labelled as 'Strategy' in the table.

The daily variation in coarse particle concentration has not been addressed directly in this analysis. The 'other' particle concentration is estimated on a daily basis as the difference between the measured  $\text{PM}_{10}$  concentrations and the estimated total of primary and secondary. Any contribution to measured  $\text{PM}_{10}$  concentrations that does not exhibit a similar temporal variation to either black smoke or sulphate is therefore included as 'other'

Table 5.17 Source apportionment for 1995 and 1996 ( $\mu\text{g m}^{-3}$ ).

Site	mean	1995	mean	mean	1996	mean
	primary contrib.	mean secondary contrib.	'other' contrib.	primary contrib.	mean secondary contrib.	'other' contrib.
London Bloomsbury	9	9	11	9	10	11
Birmingham Centre	7	8	8	7	9	8
Bristol Centre	7	8	11	7	8	11
Manchester Piccadilly	-	-	-	8	8	10
Newcastle Centre	6	8	7	6	10	8
Belfast Centre	9	6	9	9	6	9

particles. It is likely that there is an approximate correspondence between our estimates of 'other' particles and a measurement of coarse particle concentration calculated as the difference between co-located  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  measurements.

The large number of  $\text{PM}_{10}$  episode days dominated by high concentrations of coarse particles is notable in both London and Birmingham. The validity of the high 'other' particle concentrations predicted by the regression model for Birmingham are assessed directly by comparison with the  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  concentrations data from the Hodge Hill site. Figure 5.31 shows the excellent agreement between the measured daily mean  $\text{PM}_{2.5}$  concentrations at Hodge Hill and the sum of the combustion related and secondary particle concentrations for Birmingham predicted by the model. Figure 5.32 shows a comparison of the measured coarse particle

concentration ( $\text{PM}_{10} - \text{PM}_{2.5}$ ) with the predicted concentration. While the model predicts negative 'other' particle concentrations on several days, it very rarely makes significant overpredictions of the 'other' particle concentration.

All of the cities that have been looked at have several days with estimated daily mean other particle concentrations in the range of 25 - 30  $\mu\text{g m}^{-3}$  in both 1995 and 1996. It is impossible to know if these days are coarse particle episodes or are due to an underestimate of the primary or secondary contribution. For projections to 2005 or 2010 these days can have a significant influence on the 99th percentile. This is important because the other particle concentration are assumed to remain unchanged between now and 2005 and 2010, while the contributions from the other sources are expected to reduce.

Table 5.18 Source apportionment of  $\text{PM}_{10}$  episode days (concentration  $\geq 50 \mu\text{g m}^{-3}$ ) at six monitoring sites.

Number of days	Strategy	total	primary	secondary	'other'	p+s	p+o	s+o	p+s+o
<b>1995</b>									
London Bloomsbury	46	26	3	2	18			3	
Birmingham Centre	24	11	3	1	6		1		
Bristol Centre	27	12	3	4	1		2	2	
Manchester Piccadilly		-	-	-	-	-	-	-	-
Newcastle Centre	20	9	1	4	2			1	1
Belfast Centre	25	13	7		4		1	1	
<b>1996</b>									
London Bloomsbury	56	37	5	21	4			2	5
Birmingham Centre	36	20		12	4		2	1	
Bristol Centre	37	18	1	7	5	2		1	
Manchester Piccadilly	42	21	1	14	4				2
Newcastle Centre	27	14		13				1	
Belfast Centre	31	18	8	7	3				



Table 5.19 Maximum and 99th percentile of fixed daily mean 'other' particle concentrations within the model ( $\mu\text{g m}^{-3}$ ).

	London Bloomsbury	Birmingham Centre	Bristol Centre	Manchester Piccadilly	Newcastle Centre	Belfast Centre	Edinburgh Centre	Liverpool Centre
1996 max	47	50	66	54	43	30	36	50
1996 99%ile	28	29	31	26	20	26	21	29
1995 max	44	45	29	-	41	44	44	44
1995 99%ile	37	33	33	-	23	35	34	42

Table 5.20 Maximum and 99th percentile of fixed daily mean coarse particle concentrations from co-located  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  measurements ( $\mu\text{g m}^{-3}$ ).

	London Bloomsbury 19/6/97- 27/8/98	Rochester 21/5/97- 27/8/98	Marylebone Road 17/7/97- 27/8/98	Birmingham Hodge Hill 1/1/95- 31/12/95	Birmingham Hodge Hill 1/1/96- 30/9/96
max	39	44	29	57	20
99%ile	21	20	27	27	19

Figure 5.31 The relationship between measured and modelled fine particulates at Birmingham 1996.

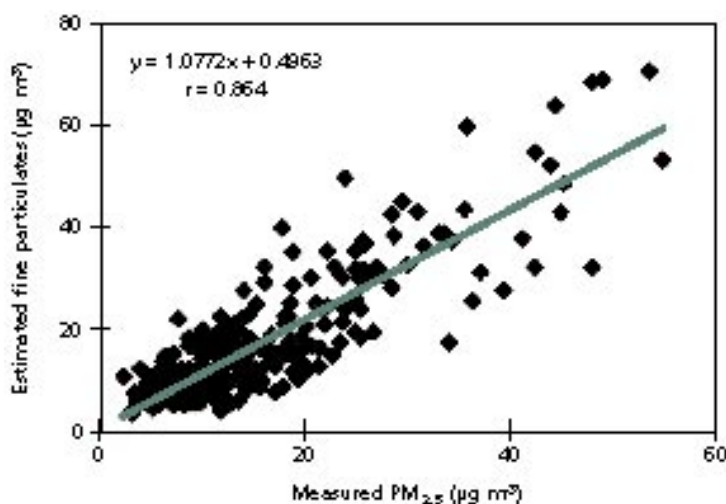


Figure 5.32 The relationship between measured and modelled coarse particles at Birmingham 1996.

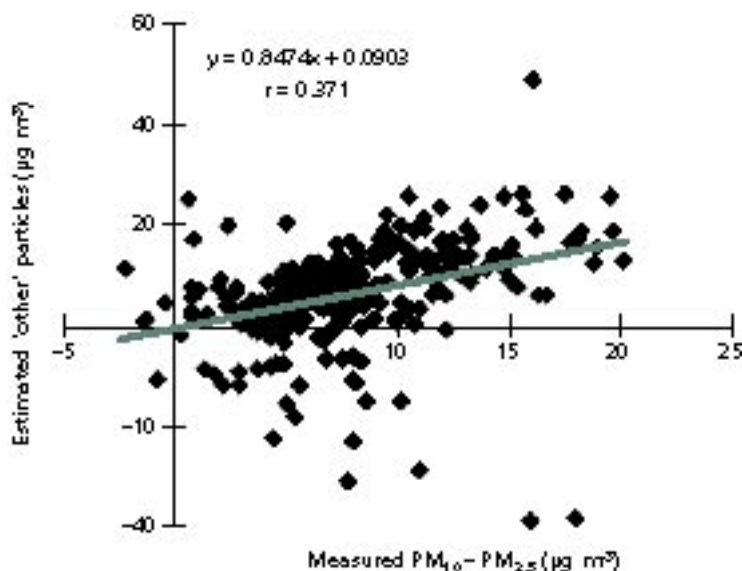


Table 5.19 lists the maximum and 99th percentile of fixed daily mean 'other' particle concentrations within the model.

These can be compared with the coarse particle concentration derived from the difference between co-located  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  measurements (Table 5.20).

The measured coarse particle 99th percentile concentrations look perhaps  $10 \mu\text{g m}^{-3}$  lower than the 99th percentile 'other' particle concentration in the model, although it is not possible to make a direct comparison.

The applicability of black smoke measurements at locations several kms away from the automatic  $\text{PM}_{10}$  measurement sites for the regression modelling technique has been examined for the London Bloomsbury site. The average black smoke concentration at a total of six sites in central London was used in the regression analysis for London Bloomsbury. Figure 5.33 shows a comparison of these London average black smoke concentrations with measurements made at London Bloomsbury during a measurement methods inter-comparison study (Loader, 1997). While black smoke concentrations were consistently slightly higher at Bloomsbury, there is no indication of combustion related particle episodes occurring at either Bloomsbury or other locations in Central London. This increase in

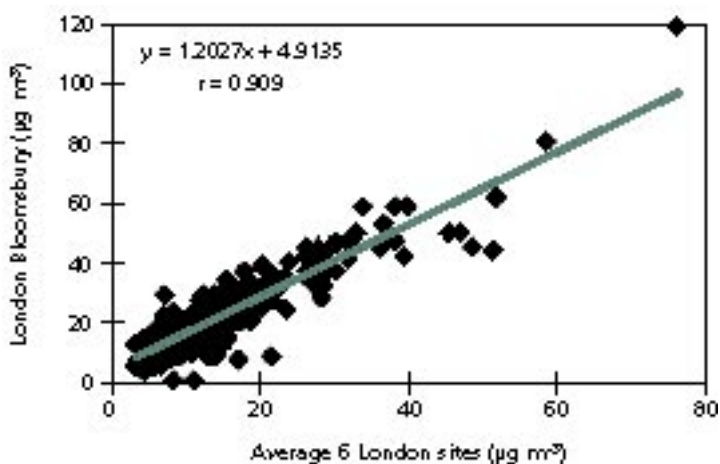
Table 5.21 Estimated annual means and 99th percentiles of PM<sub>10</sub> concentrations at urban background sites, including predictions for 2005 and 2010 (µg m<sup>-3</sup>).

	London Bloomsbury	Birmingham Centre	Bristol Centre	Manchester Piccadilly	Newcastle Centre	Belfast Centre	Edinburgh Centre	Liverpool Centre
<i>Annual mean</i>								
1996	30	25	26	26	23	24	19	25
1995	28	23	24	-	22	24	20	27
<i>NAQS 99th percentile</i>								
1996	100	94	87	85	100	94	62	86
1995	80	77	70	-	71	95	61	72
<i>Fixed daily means above 50 µgm<sup>-3</sup></i>								
1996	37	20	18	21	14	18	6	22
1995	24	11	11	-	9	13	8	28
<i>Annual mean</i>								
2005 estimate based on 1996	25	20	22	22	19	21	17	21
2005 estimate based on 1995	23	19	19	-	18	21	18	22
2010 estimate based on 1996	23	18	20	20	18	20	16	19
2010 estimate based on 1995	21	17	18	-	16	20	17	21
<i>NAQS 99th percentile</i>								
2005 estimate based on 1996	82	76	70	71	82	76	55	70
2005 estimate based on 1995	69	65	57	-	57	82	57	63
2010 estimate based on 1996	76	69	64	65	72	70	53	64
2010 estimate based on 1995	65	58	52	-	52	79	55	61
<i>Fixed daily means above 50 µgm<sup>-3</sup></i>								
2005 estimate based on 1996	11	13	7	8	10	9	4	10
2005 estimate based on 1995	9	6	2	-	2	8	3	9
2010 estimate based on 1996	9	7	6	6	7	6	2	7
2010 estimate based on 1995	9	3	0	-	2	8	2	6

black smoke concentrations at Bloomsbury compared with other central London sites is presumably due to the proximity of the site to heavily trafficked roads, but since the difference is systematic, it is unlikely that the use of non-colocated smoke data in our regression modelling would lead to an overprediction of the coarse particle concentrations.

This technique has now been extended to provide forecasts of PM<sub>10</sub> concentrations in 2005 by the multiplication of the individual contributions by the appropriate reduction factors for the likely change in concentrations of primary, secondary and 'other' particles from current levels. If this analysis is carried out on a daily basis, then predictions of percentiles of concentrations can be calculated in addition to annual means.

Figure 5.33 The relationship between smoke measurements at London Bloomsbury and at 6 other London sites.



#### 5.6.4 PREDICTING $PM_{10}$ CONCENTRATIONS IN 2005 FROM CURRENT MEASUREMENTS

The  $PM_{10}$  model that has been developed enables us to make relatively sophisticated estimates of both annual mean and high percentile  $PM_{10}$  concentrations for future years. The key advantage of this method is that the  $PM_{10}$  concentrations have been separated into their component parts and appropriate reductions can be applied to these components, based on an understanding of the likely impact of current policies on future levels. The estimated  $PM_{10}$  concentrations for 2005 and 2010 have been calculated and are shown in Table 5.21. Values for London Bloomsbury, Birmingham Centre, Bristol Centre, Newcastle Centre, Belfast Centre, Edinburgh Centre and Liverpool Centre were calculated for both 1996 and 1995 meteorology, while calculations for Manchester Piccadilly were only carried out based on 1996 measurements. The predicted annual mean concentrations for 2005 are generally about 80% of the 1996 values. They were calculated based on the following assumptions:

- **Primary combustion  $PM_{10}$ .** *Primary combustion  $PM_{10}$  concentrations are expected to decline substantially between now and 2005, due largely to a reduction in emissions from road transport sources due to the introduction of tighter standards for vehicle emissions. Projected emission inventory estimates of urban road traffic  $PM_{10}$  emissions from the UK National Atmospheric Emissions Inventory have been compared with estimates of current emissions. The emissions in 2005 are expected to reduce to a value of 0.51 times the 1996 levels and in 2010 to a value of 0.37 times the 1996 levels. In Table 5.21 it was assumed that 75% of primary emissions in UK cities were from traffic exhaust and 25% from other local sources and the latter emissions were assumed to remain at current levels in 2005 and 2010. This 75% is an average of the split between traffic and other sources across the major cities in Great Britain. Across all of the urban areas in Great Britain the split is 67% whereas in London 91% of primary*

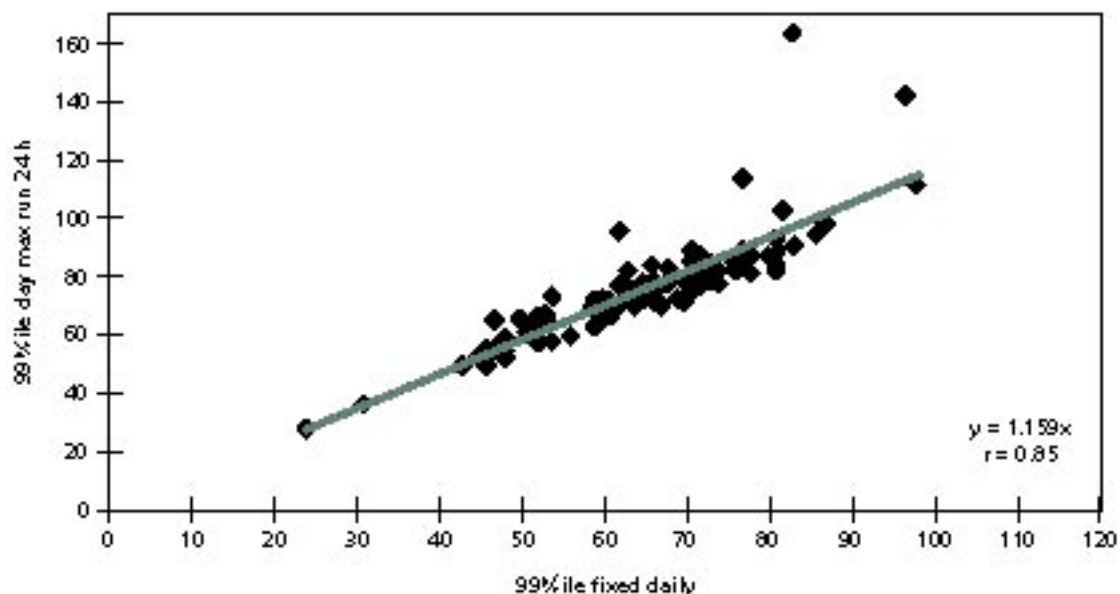
*emissions is from traffic exhausts sources. In Belfast, however, coal use currently contributes substantially to primary particle concentrations in Belfast. The estimated  $PM_{10}$  concentrations for 2005 and 2010 concentrations for Belfast were made using a more pessimistic assumption that domestic coal emissions remain at current levels.*

- **Secondary  $PM_{10}$ .** *The estimates of the secondary particle concentrations in 2005 in the UK have been based on the results of the EMEP model (see section 4.3.2), which showed that levels in 2010 are likely to be about 70% of 1996 levels on the basis of current policies. It has been assumed that this reduction up to 2010 will be linear, leading to an estimate of concentration in 2005 being equal to 0.807 times the current values.*
- **'Other'  $PM_{10}$ .** *It has been assumed that there will be no change in the 'other' particle concentration between 1996, 2005 and 2010.*

The model has also been used to provide estimates of high percentiles, such as the target 99th percentile of the daily maximum of running 24-hour mean  $PM_{10}$  concentrations for 2005, as specified by the UK Air Quality Strategy. One of the particular strengths of the model is that it provides a daily breakdown of the  $PM_{10}$  concentrations. The concentrations on each individual day can therefore be adjusted by the appropriate amount, according to the relative contributions from primary combustion, secondary and 'other' particles, to provide daily estimates of concentrations for a future year. This enables us to predict what the concentrations would be in 2005 if the meteorology were to be an exact repeat of either 1996 or 1995. 1996 provides something of a 'worst case' estimate due to the prevalence of 'other' particle episodes and 1995 was a more typical year. In order to take the episodic nature of the daily 'other' particle contribution into account, this contribution on a daily basis has been calculated to be the difference between the measured  $PM_{10}$  concentration and the sum of the primary combustion and secondary components.

This analysis directly provides an estimate of the 99th percentile of daily mean  $PM_{10}$  concentrations, so one additional step is required to provide an

Figure 5.34 Relationship between 99th percentile of fixed daily means and the 99th percentile of the daily maximum of running 24 hour average concentrations of PM<sub>10</sub>, 1993-1997 ( $\mu\text{g m}^{-3}$ ).



estimate of the value required for comparison with the UK National Air Quality Strategy (DoE, 1997) objective. The 99th percentile of the daily maximum of running 24-hour mean PM<sub>10</sub> concentration ('strategy' 99th percentile) is generally slightly higher than the 99th percentile of daily values, by a factor of about 1.16 (Figure 5.34). This is primarily due to primary particle episodes, which are generally of shorter duration than secondary particle episodes leading to daily maximum 24-hour running mean concentrations higher than fixed daily means. This factor of 1.16 tends to overestimate the 'strategy' 99th percentile in years dominated by secondary particle episodes such as 1996, while underestimating values in years such as 1995, where high percentiles were less dominated by secondary particle episodes.

The estimated 'strategy' 99th percentiles for 2005 based on both 1996 and 1995 meteorology are higher than  $50 \mu\text{g m}^{-3}$  (much higher than  $50 \mu\text{g m}^{-3}$  for 1996 meteorology) indicating that current policies will not deliver compliance with the objective for 2005 at city centre locations during years with significant secondary particle episodes.

Projections of the primary combustion contribution to PM<sub>10</sub> concentrations in 2005 have

been calculated from current PM<sub>10</sub> measurements according to the best estimate of the likely change in UK urban road traffic exhaust emissions. It is clear from section 3.4.2 that contributions to primary combustion PM<sub>10</sub> from long range transport of the order  $15 - 30 \mu\text{g m}^{-3}$  may have occurred on several days during 1996. This contribution has not been treated separately from the local contribution and has been scaled by the likely change in UK urban road traffic exhaust emissions. This clearly increases the uncertainty of the projections because it is possible that emissions reductions of the magnitude of those assumed for local sources reductions may not take place for these more distant sources.

The contribution to primary PM<sub>10</sub> from bonfire night emissions has also not been treated separately from other primary sources in the analysis. It was shown in section 3.7 that bonfire night emissions are currently likely to contribute to up to 4 to 5 additional days with concentrations higher than  $50 \mu\text{g m}^{-3}$ . It is clear that these bonfire night emissions are not going to reduce in line with road traffic emissions and our projections have not included this contribution to the number of days with concentrations greater than  $50 \mu\text{g m}^{-3}$ . The expected reductions in both primary and

Table 5.22 Regression coefficients for NO<sub>x</sub>-based model for 1996 PM<sub>10</sub> data.

	NO <sub>x</sub> coefficient, A	SO <sub>4</sub> coefficient, B	Intercept C	r
London Bloomsbury	0.112	2.55	9.29	0.86
Birmingham Centre	0.207	2.29	6.52	0.85
Bristol Centre	0.145	2.62	7.97	0.87
Manchester Piccadilly	0.160	2.95	7.69	0.86
Newcastle Centre	0.155	3.48	5.66	0.91
Belfast Centre	0.302	2.65	5.91	0.92
Edinburgh Centre	0.122	2.99	6.42	0.82
Liverpool Centre	0.187	2.56	7.57	0.87

Table 5.23 EU 'Daughter Directive' limit values for PM<sub>10</sub>.

	Averaging period	Limit Value	Date by which limit value is to be met
<i>Stage 1</i>			
1. 24 hour limit value for the protection of human health	24 hours	50 µg m <sup>-3</sup> not to be exceeded more than 35 times per year (≅ 90th percentile of 50 µg m <sup>-3</sup> )	1 January 2005
2. Annual limit value for the protection of human health	calendar year	40 µg m <sup>-3</sup> PM <sub>10</sub>	1 January 2005
<i>Stage 2*</i>			
1. 24 hour limit value for the protection of human health	24 hours	50 µg m <sup>-3</sup> not to be exceeded more than 7 times per year (≅ 98th percentile of 50 µg m <sup>-3</sup> )	1 January 2010
2. Annual limit value for the protection of human health	calendar year	20 µg m <sup>-3</sup>	1 January 2010

\* *Indicative limit values to be reviewed in the light of further information on health and environmental effects, technical feasibility, and experience in the application of Stage 1 limit values in the Member States.*

secondary particle concentrations will however reduce the total PM<sub>10</sub> concentrations on bonfire night episode days in the future and it is therefore likely that the number of additional days with concentrations greater than 50 µg m<sup>-3</sup> will not be as many as are seen in current measurements.

The estimated number of days with daily mean PM<sub>10</sub> concentrations greater than or equal to 50 µg m<sup>-3</sup> are listed in Table 5.21. The figures for 1995 and 1996 underestimate the current number of days with a daily maximum of running 24-hour mean PM<sub>10</sub> concentration above this value, as indicated in Table 5.21. This should be borne in mind when considering the predictions for 2005 and 2010.

### 5.6.5 ALTERNATIVE MODEL OF DAILY PM<sub>10</sub> CONCENTRATIONS USING NO<sub>x</sub> MEASUREMENTS

One of the limitations of the method that has been used to assign the contributions to daily PM<sub>10</sub> concentrations from different sources is that the concentration of particles that are neither primary combustion related or secondary has been calculated as the difference between the measured PM<sub>10</sub> concentration and the estimated total of primary and secondary. Any contribution to measured PM<sub>10</sub> concentrations that does not exhibit a similar temporal variation to either black smoke or sulphate is therefore included as other particles.



Table 5.24 PM<sub>10</sub> concentrations 1996 and 1995 (µg m<sup>-3</sup>) at urban background sites for comparison with EU 'Daughter' Directive limit values (µg m<sup>-3</sup>).

	London Bloomsbury	Birmingham Centre	Bristol Centre	Manchester Piccadilly	Newcastle Centre	Belfast Centre	Edinburgh Centre	Liverpool Centre
<i>Annual mean</i>								
1996	39	33	34	34	30	31	25	33
1995	36	30	31	-	29	31	26	35
<i>Stage 1 EU 90th percentile of fixed daily means</i>								
1996	68	52	57	55	51	55	39	55
1995	60	48	55	-	46	50	42	62
<i>Stage 2 EU 98th percentile of fixed daily means</i>								
1996	91	86	81	84	86	81	61	87
1995	83	72	74	-	70	77	67	76
<i>Fixed daily means above 50 µg m<sup>-3</sup></i>								
1996	65	38	40	39	39	44	14	48
1995	58	30	33	-	25	35	19	60

An alternative regression model of daily PM<sub>10</sub> concentrations, which utilises NO<sub>x</sub> measurements instead of black smoke measurements as an indicator for the primary particles has therefore been developed. This has the advantage that the NO<sub>x</sub> measurements are directly co-located with the PM<sub>10</sub> measurements but an implicit assumption in this model is of common sources for NO<sub>x</sub> and primary PM<sub>10</sub>. While the black smoke monitoring method includes greater uncertainties than NO<sub>x</sub> measurements, it has the advantage of more directly sampling the atmospheric particle concentration.

The regression coefficients for this NO<sub>x</sub>-based model are listed in Table 5.22. The correlation coefficients are very similar to those obtained for the black smoke-based model but the intercept, C, is generally several µg m<sup>-3</sup> lower than for the black smoke-based regressions; the difference being that PM<sub>10</sub> has now been assigned to either primary or secondary instead of other. Estimates of PM<sub>10</sub> concentrations for 2005 and 2010 have also been calculated using this NO<sub>x</sub> based model and were found to be very similar to those listed in Table 5.21. The similarity of the predictions based on the black smoke and NO<sub>x</sub> based models increases our confidence in the projections.

#### 5.6.6 PREDICTING PM<sub>10</sub> CONCENTRATIONS FOR COMPARISON WITH EU 'DAUGHTER DIRECTIVE' LIMIT VALUES.

The estimates of PM<sub>10</sub> concentrations presented in Table 5.24 and 5.25 have been multiplied by 1.3 for comparison with the EU limit values (Table 5.23). This is to take into account the difference between TEOM measurements of PM<sub>10</sub> and the EU reference gravimetric method. While there is considerable uncertainty to the exact relationship between TEOM and gravimetric measurements (Section 2.1), we have chosen to use a factor of 1.3 as a conservative approach.

The statistics for comparison to the EU 'Daughter Directive' for 1995 and 1996 are shown in Table 5.24 (limit values are not applicable until 2005 and 2010).

Predictions of PM<sub>10</sub> concentrations for 2005 and 2010 for comparison with the 'Daughter Directive' have been made based on 1995 and 1996 analysis. A "business as usual" primary emissions reduction scenario, blanket reduction of secondary particle concentrations using EMEP coefficients (µg m<sup>-3</sup>) have been used in the calculations. Current

Table 5.25 Predicted PM<sub>10</sub> concentrations at urban background sites for 2005 and 2010 based on 1996 and 1995 analysis (µg m<sup>-3</sup>).

	London Bloomsbury	Birmingham Centre	Bristol Centre	Manchester Piccadilly	Newcastle Centre	Belfast Centre	Edinburgh Centre	Liverpool Centre
<i>Annual mean</i>								
2005 estimate based on 1996	33	26	29	29	25	27	22	27
2005 estimate based on 1995	30	25	25	-	23	27	23	29
2010 estimate based on 1996	30	23	26	26	23	26	21	25
2010 estimate based on 1995	27	22	23	-	21	26	22	27
<i>Stage 1 EU 90th percentile of fixed daily means</i>								
2005 estimate based on 1996	54	42	45	46	42	47	35	45
2005 estimate based on 1995	49	40	43	-	37	44	36	51
2010 estimate based on 1996	50	39	43	42	37	43	33	41
2010 estimate based on 1995	45	38	39	-	34	42	35	46
<i>Stage 2 EU 98th percentile of fixed daily means</i>								
2005 estimate based on 1996	80	72	67	70	69	67	53	69
2005 estimate based on 1995	72	60	59	-	57	70	55	66
2010 estimate based on 1996	73	65	61	61	61	62	50	62
2010 estimate based on 1995	67	56	56	-	51	67	52	62
<i>Fixed daily means above 50 µg m<sup>-3</sup></i>								
2005 estimate based on 1996	42	23	23	23	18	27	8	22
2005 estimate based on 1995	33	14	18	-	12	22	12	34
2010 estimate based on 1996	31	19	15	14	12	19	6	19
2010 estimate based on 1995	27	9	12	-	8	21	9	27

national policies are likely to deliver concentrations at urban background sites lower than the Stage 1 90th percentile limit value except possibly in central London. For Stage 2 the 98th percentile and the annual limit value is likely to be exceeded at all sites (Table 5.25)

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