EXTERNAL CONTRIBUTION TO URBAN AIR POLLUTION

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Abstract. Elevated particulate matter concentrations in urban locations have normally been associated with local traffic emissions. Recently it has been suggested that such episodes are influenced to a high degree by PM_{10} sources external to urban areas. To further corroborate this hypothesis, linear regression was sought between PM_{10} concentrations measured at eight urban sites in the U.K., with particulate sulphate concentration measured at two rural sites, for the years 1993–1997. Analysis of the slopes, intercepts and correlation coefficients indicate a possible relationship between urban PM_{10} and rural sulphate concentrations. The influences of wind direction and of the distance of the urban from the rural sites on the values of the three statistical parameters are also explored. The value of linear regression as an analysis tool in such cases is discussed and it is shown that an analysis of the sign of the rate of change of the urban PM_{10} and rural sulphate concentrations provides a more realistic method of correlation. The results indicate a major influence on urban PM_{10} concentrations from the eastern side of the United Kingdom. Linear correlation was also sought using PM_{10} data from nine urban sites in London and nearby rural Rochester. Analysis of the magnitude of the gradients and intercepts together with episode correlation analysis between the two sites showed the effect of transported PM_{10} on the local London concentrations. This article also presents methods to estimate the influence of rural and urban PM_{10} sources on urban PM_{10} concentrations and to obtain a rough estimate of the transboundary contribution to urban air pollution from the PM_{10} concentration data of the urban site.

Keywords: airborne particulate matter, regional air pollution, transboundary pollution

1. Introduction

Particulate matter has been the subject of various studies in the past decade due to its relevance as an air pollutant and its possible hazardous effect on health. Health effects strongly depend on the particle size distribution. PM_{10} (i.e. particulate matter which can pass a size selective inlet of 10 μm at 50% efficiency), has been the subject of many studies, since it includes particles which are small enough to enter the alveolar regions of the lung causing a decrease in the efficiency of the clearance mechanism and possibly acting as carriers of toxic substances which may be adsorbed into the inner lining of the respiratory system or absorbed into the blood stream. Besides its negative impact on human health, there are also adverse environmental effects. For example, some of the airborne particles may

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have diameters of the same order of magnitude as the wavelength of visible light, giving rise to visibility reduction by optical scattering (QUARG, 1996).

Particles within the PM_{10} envelope can be either primary or secondary in origin. Primary combustion-related particles are emitted directly into the atmosphere from sources such as road traffic, coal burning and industry while secondary particles are formed within the atmosphere by the oxidation of sulphur dioxide and nitrogen oxides to form sulphate and nitrate particles, respectively. Regression analysis comparing measured PM_{10} concentrations with those of CO have indicated that traffic exhaust-related sources contribute 40 to 50% of the measured winter mean PM_{10} concentrations in U.K. cities (QUARG, 1996).

However King and Dorling (1997), and Stedman (1997) independently showed that episodes of high PM_{10} concentrations in urban areas may be affected by external sources to a higher degree than by local traffic-derived particulate matter. This hypothesis was further strengthened by Micallef and Colls (1998) who sought linear regression between PM_{10} concentration measured at various urban sites, with particulate sulphate concentration measured at two rural sites. Their analysis showed that the slopes, intercepts and correlation coefficients were within narrow ranges for the years of data considered and so pointed to a possible relationship between urban PM_{10} concentrations and rural sulphate concentrations. However, it is not clear whether this relationship is spatially and temporally independent. There is also the need for a reasonable estimate of the extent of the transboundary contribution to the local urban PM_{10} concentrations.

In the present work, PM_{10} and sulphate aerosol concentrations have been used together for various urban and rural sites over the period 1993–1997. The exercise was repeated with several London urban sites and a nearby rural site for which PM_{10} data was available. Methods are also presented by which the extent of transboundary contribution to urban air pollution may be estimated.

2. Site Information

The data used for the analysis were collected at 20 monitoring sites in the United Kingdom, 17 of which are urban and three of which are rural. Of the urban sites, nine are situated in urban London (Bexley, Eltham, Hillingdon, North Kensington, Sutton, Bloomsbury, Camden, Haringey and Brent) and eight are situated in North England and the Midlands (Leeds, Hull, Liverpool, Middlesborough, Birmingham, Sheffield, Manchester and Leicester). Of the rural sites, one is in North East England (High Muffles), one is in the Midlands (Stoke Ferry) and one is in South East England (Rochester), near London. The approximate geographical location of the sites is shown in Figures 1 and 2. The urban site data are comprised of PM_{10} and in some cases Nitrogen Oxides data whereas the rural site data are comprised mainly of sulphate concentrations with one site (Rochester) having PM_{10} data.

Figure 1. Geographical location of the monitoring sites: Middlesborough (1), High Muffles (2), Hull (3), Leeds (4), Sheffield (5), Manchester (6), Liverpool (7), Birmingham (8), Leicester (9), Stoke Ferry (10), London (11), Rochester (12).

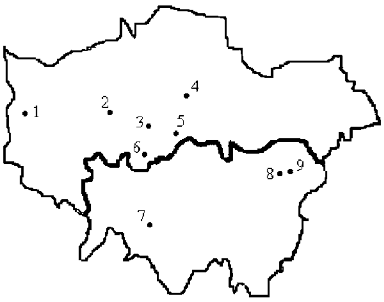

Figure 2. Geographical location of London urban monitoring sites: Hillingdon (1), Brent (2), Camden (3), Haringey (4), Bloomsbury (5), North Kensington (6), Sutton (7), Eltham (8), Bexley (9).

3. Data Analysis and Discussion

PM_{10} concentrations for urban Leeds, Hull, Liverpool, Middlesborough, Birmingham, Sheffield and Manchester were linearly correlated with particulate sulphate concentrations measured at the rural High Muffles site for years 1993–1997 (some of the site monitors were started later than 1993 and so not all sites have data spanning over these years). It should be noted that regression analyses other than linear gave no significantly better fit. The results of this analysis are shown in Tables I to IV.

It may be noted that results for 1993–1995 data are similar for almost all sites, whereas results for 1996–1997 data are significantly different. The calculated correlation coefficients were within the range 0.14–0.66. However the correlation coefficients for 1996 data were all significantly high with a range of 0.48–0.66 and

TABLE I

Results of linear regression (correlation coefficient, slope and intercept from top to bottom in each individual cell) of daily average PM_{10} and particulate sulphate concentrations measured at various Automatic Urban Network monitoring sites in the Midlands and North East England. Bold marked cells contain results of linear regression analysis for cross years.

	Leeds				Hull			
	1993	1994	1996	1997	1994	1995	1996	1997
High Muffles 1993	0.49 12.4 15.0	$\mathbf{2.0 \times 10^{-4}}$ **0.3** **26.2**						
High Muffles 1994		0.48 10.8 14.0			0.40 8.0 16.9	**0.01** **0.9** **23.3**		
High Muffles 1995						0.39 8.3 15.7		
High Muffles 1996			0.61 9.3 15.4			**0.002** **–0.3** **24.6**	0.66 9.3 14.5	
High Muffles 1997			**0.02** **3.1** **23.8**	0.14 9.3 19.7				0.18 6.7 18.0

coefficients for 1997 were all significantly lower with a range of 0.14–0.26. The range for the correlation coefficient for the years 1993–1995 was 0.24–0.49. Although the correlation coefficients are not particularly high (except for 1996), one must bear in mind that these sites are located in very different places and that nitrate aerosol was not taken into account (data were not available). For each particular year or group of years, the range of the correlation coefficient was within narrow limits. This indicates a possible relationship between urban PM_{10} and rural sulphate concentrations, which is further substantiated by the fact that both the gradients and the intercepts fall into the narrow ranges of 5.7–12.4 and 10.5–19.7, respectively. The average and standard deviations of the correlation coefficients, gradients and intercepts were calculated (Table VII). The standard deviation represents only 24% or less of the average (using High Muffles data), for all years considered, which indicates a relationship between urban PM_{10} concentration and High Muffles sulphate concentration. This whole analysis was repeated using Birmingham, Leicester

TABLE II

Results of linear regression (correlation coefficient, slope and intercept from top to bottom in each individual cell) of daily average PM_{10} and particulate sulphate concentrations measured at various Automatic Urban Network monitoring sites in the Midlands and North East England. Bold marked cells contain results of linear regression analysis for cross years

	Liverpool				
	1993	1994	1995	1996	1997
High Muffles 1993	0.34 12.2 17.7		**0.003** **–0.9** **27.8**		
High Muffles 1994		0.24 7.7 16.7			
High Muffles 1995			0.30 8.6 17.7	**0.001** **–0.5** **25.6**	
High Muffles 1996				0.54 8.3 15.1	
High Muffles 1997					0.16 5.9 19.1

and Leeds as urban sites and Stoke Ferry as a corresponding rural site. Conclusions drawn are similar to those for High Muffles (Tables V and VI):

(a) Results using 1993–1995 data were similar whereas for 1996 and 1997 data were significantly different, with correlation coefficients higher for 1996 and lower for 1997.

(b) The gradients and intercepts fall in the narrow ranges of 5.2–8.1 and 11.5–20.0, respectively, which are very similar to the ranges calculated for the High Muffles data.

The latter indicates that the relationship found is not particular to High Muffles and it could be valid throughout the United Kingdom.

TABLE III

Results of linear regression (correlation coefficient, slope and intercept from top to bottom in each individual cell) of daily average PM_{10} and particulate sulphate concentrations measured at various Automatic Urban Network monitoring sites in the Midlands and North East England. Bold marked cells contain results of linear regression analysis for cross years

	Birmingham				
	1993	1994	1995	1996	1997
High Muffles 1993	0.29 8.6 16.5		$\mathbf{9.0 \times 10^{-5}}$ **–0.1** **23.3**		
High Muffles 1994		0.37 8.0 13.8			
High Muffles 1995			0.30 7.9 15.0		
High Muffles 1996		**0.038** **–2.00** **25.3**		0.49 7.6 15.3	
High Muffles 1997					0.16 5.8 16.4

It is expected that the amount of transported sulphate aerosol will generally decrease with the distance of the urban from the rural sites. Linear regression analysis of the 1996 correlation coefficient with the approximate distance of the urban sites from High Muffles gave a negative gradient straight line fit with a correlation coefficient of 0.56 (Figure 3). The value of 0.56 can be considered high when one considers that various other factors such as wind direction, wind speed and urban site location also affect the amount of transported sulphate aerosol. This argument is further strengthened when one considers that the same analysis done for 1997 (for which there was practically no correlation between the urban PM_{10} and the rural sulphate concentrations) gave a correlation coefficient of 0.08.

It is also worth noting that the correlation coefficients for 1996 seem to be direction-dependent. For example, it is to be expected that Leeds and Hull have high values for the correlation coefficient due to their proximity to High Muffles. On the other hand Liverpool and Middlesborough, which are at very different

TABLE IV

Results of linear regression (correlation coefficient, slope and intercept from top to bottom in each individual cell) of daily average PM_{10} and particulate sulphate concentrations measured at various Automatic Urban Network monitoring sites in the Midlands and North East England. Bold marked cells contain results of linear regression analysis for cross years

	Sheffield		Manchester		Middles-borough		
	1996	1997	1996	1997	1995	1996	1997
High Muffles 1995					0.41 9.8 11.2		
High Muffles 1996	0.62 10.6 15.1	**0.02** **1.2** **24.0**	0.48 7.6 17.1		**0.01** **2.3** **20.2**	0.60 8.8 10.5	
High Muffles 1997		0.26 8.3 17.8	**0.02** **2.6** **23.8**	0.15 5.7 18.8		**0.04** **3.7** **17.8**	0.22 8.7 11.6

distances from High Muffles (170 and 43 km, respectively), have very similar correlation coefficients of 0.54 and 0.60. This can only be explained if the winds carrying sulphate aerosol move East to West rather than North (Liverpool is to the West of High Muffles whereas Middlesborough is to its North – See Figure 1). A similar argument follows from an inspection of the correlation coefficients of Middlesborough and Sheffield for 1996. Sheffield has a larger correlation coefficient (0.62) than does Middlesborough (0.60) even though their distances from High Muffles are 105 and 43 km, respectively. This result, combined with the fact that Sheffield is to the South West of High Muffles whereas Middlesborough is to its North, further indicates that an easterly wind is responsible for transporting the sulphate aerosol over the United Kingdom.

There were two geographically widespread and prolonged episodes of elevated PM_{10} concentrations in many United Kingdom cities during March 1996. Concentrations were elevated for much of the United Kingdom from 8 March to 24 March, with concentrations remaining high in some cities for a few days longer. King and Dorling (1997) and Stedman (1997) demonstrated that secondary particles formed the main contribution to the high concentrations during these episodes and also pointed out that these episodes were characterised by winds from the east bringing long range transported secondary particles to the United Kingdom from the Continent. Taking this as the hypothesis for the elevated correlation coefficients for 1996, linear correlation between the urban PM_{10} concentrations of Liverpool, Birming-

TABLE V

Results of linear regression (correlation coefficient, slope and intercept from top to bottom in each individual cell) of daily average PM_{10} and particulate sulphate concentrations measured at various Automatic Urban Network monitoring sites in the Midlands and North East England. Bold marked cells contain results of linear regression analysis for cross years

	Birmingham				
	1993	1994	1995	1996	1997
Stoke Ferry 1993	0.31 5.2 15.5				
Stoke Ferry 1994		0.39 8.0 11.5			
Stoke Ferry 1995	**0.01** **–1.8** **27.9**		0.29 7.8 14.0		
Stoke Ferry 1996		**0.04** **–1.9** **25.7**		0.55 7.4 14.0	
Stoke Ferry 1997					0.27 6.2 14.8

ham and Hull and the sulphate concentration data of High Muffles for 1996, but excluding the data for March 1996, were sought. The results obtained are presented in Table VIII. In all three cases, the new value of the correlation coefficient was significantly lower from those calculated using the whole year of data but similar in magnitude to the correlation coefficients for previous years (1993–1995). However, when the same procedure was repeated using data for the years 1993 and 1994 for the same sites, the newly calculated correlation coefficients were not significantly different from those calculated using the whole data. This shows that the elevated magnitudes of correlation coefficients in 1996 were principally due to prolonged high PM_{10} concentrations in March of that year which was attributed by King and Dorling (1997) and by Stedman (1997) to easterly winds transporting secondary aerosol from the Continent.

TABLE VI

Results of linear regression (correlation coefficient, slope and intercept from top to bottom in each individual cell) of daily average PM_{10} and particulate sulphate concentrations measured at various Automatic Urban Network monitoring sites in the Midlands and North East England. Bold marked cells contain results of linear regression analysis for cross years

	Leeds				Leicester			
	1993	1994	1996	1997	1994	1995	1996	1997
Stoke Ferry 1993	0.24 5.8 19.5	**0.05** **1.7** **20.4**						
Stoke Ferry 1994	**4×10^{-6}** **–0.03** **27.1**	0.26 8.1 15.3			0.35 6.8 12.3			
Stoke Ferry 1995						0.33 6.3 12.4	**0.001** **–0.5** **22.3**	
Stoke Ferry 1996			0.45 7.0 16.3				0.58 6.5 12.5	
Stoke Ferry 1997				0.13 6.3 20.0				0.37 6.8 12.9

Calculated correlation coefficients were relatively low for all sites. This raises the question of whether linear correlation is the appropriate tool to use in such an analysis. Plotting the time series for both urban PM_{10} and rural sulphate concentrations it became clear that the general profiles of the two pollutants correspond to a significant degree but the ratio of the two pollutant concentrations is not a constant but is rather time dependent. The changes in the concentrations of the two pollutants cannot be said to be proportional but the fact that both their peaks and troughs coincide is a clear sign of the effect of rural sulphate concentrations on the local urban PM_{10} concentration. The case of direct proportionality between the concentration of the two pollutants is a highly idealised one since this assumes that transported sulphate aerosol is the only (or at least the main) cause of urban PM_{10} concentrations and that external influences such as atmospheric weather conditions have negligible effect on the urban air quality. A more realistic model assumes that transported sulphate aerosol forms a significant part of the urban PM_{10} fraction

TABLE VII

Results of the calculation of the average, standard deviation and percentage error for each of the correlation coefficients, gradients and intercepts. The first table refers to data from High Muffles, while the second table shows the same analysis for Stoke Ferry. Note that in the latter case, correlation coefficients are for 1993–1997 only

	Average	Standard deviation	Percentage error
High Muffles data			
Correlation Coefficient (1993–1995)	0.36	0.08	22.3
Correlation Coefficient (1996)	0.57	0.07	11.9
Correlation Coefficient (1997)	0.18	0.04	23.4
Intercept	15.8	2.4	14.9
Gradient	8.6	1.7	20.0
Stoke Ferry data			
Correlation Coefficient (1993–1997)	0.35	0.12	35.6
Intercept	14.7	2.7	18.2
Gradient	6.8	0.9	12.8

although other sources (such as traffic-derived particulate matter) may contribute more. This argument points to a method by which the effect of transported sulphate aerosol on urban PM_{10} concentrations may be shown more clearly. By calculating the rate of change over one day for each pollutant, a two-symbol code consisting of ones and/or zeros (one stands for a positive rate of change while zero stands for a negative rate of change) is obtained for each day. The first digit stands for the sign of the rate of change of the urban PM_{10} concentration while the second digit stands for the sign of the rate of change of the rural sulphate concentration. The codes 11 and 00 indicate the same sign for the rate of change of the two pollutants whereas the other two combinations (01 and 10) indicate otherwise. This analysis was performed using urban PM_{10} data from Leeds, Hull, Middlesborough, Liverpool and Birmingham and rural site data from High Muffles. It was repeated for Birmingham and Leicester urban sites with rural site data from Stoke Ferry. The years of data used were 1993–1997 for Liverpool and Birmingham, 1995–1997 for

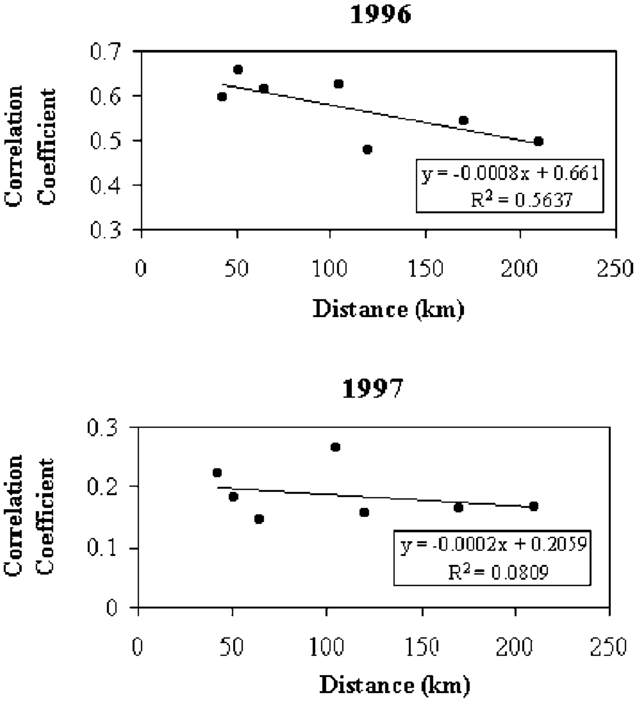

Figure 3. Scatter plot of the correlation coefficient against the distance of the urban site from rural High Muffles for 1996 and 1997 using the data from seven urban sites located in the North of England.

Middlesborough, 1994–1997 for Hull and Leicester and 1993, 1994, 1996, 1997 for Leeds. The results of the analysis using all the data available for the sites are shown in Table IXa. The number of days which had codes 11 and 00 were grouped together, counted and expressed as a percentage of the total number of days (given in the table under the heading of percentage number of correlation) and the number of days having codes 10 and 01 were similarly counted and expressed as a percentage of the total number of days (given in the table under the heading of percentage number of non-correlation). This analytical method is useful as a means of correlating the general profile of the two pollutants but is insensitive to the actual amount of urban PM_{10} which is due to transboundary sources. It can be seen that on average about 63% of the days had similar changes in the rates of change of the urban PM_{10} concentration and the rural sulphate concentration. If there was no relationship between the two concentrations one would expect an equal division between the codes 11 and 00 and the other codes 01 and 10. The 63–37% division amongst the codes is indicative of a relationship for three main reasons.

(1) If the percentages calculated were just due to statistical chance, then it would be expected that the percentage division varies about the 50–50% chance di-

TABLE VIII

Results comparing the correlation coefficient when March data is deleted with the correlation coefficient calculated using a whole year of data. The values from top to bottom in each individual cell are the correlation coefficient using the whole year of data, the correlation coefficient using the whole year data less the March data and the percentage change of the correlation coefficient upon deletion of the March data

	Liverpool	Birmingham	Hull
1994	0.24	0.37	0.41
	0.23	0.36	0.42
	2.60	1.60	3.20
1995	0.30	0.30	0.39
	0.29	0.29	0.40
	3.30	3.00	0.80
1996	0.54	0.49	0.66
	0.32	0.31	0.50
	40.40	38.10	23.70

vision for the various sites. However it can be seen that for all sites, the percentage division is very nearly the same even though they are located at greatly differing distances from the rural site.

(2) Given the large number of days over which the analysis has been performed it is very unlikely that 63–37% division is due to statistical chance. The percentage amount of deviation of the observed number of days from the statistically expected number of days with codes 11 or 00 was calculated for each of the six urban sites. The range of this deviation was 21–36%. It is known that if a system of values is dependant only on chance then the values will tend to the statistical expectation as the amount of data is increased. For such a system with about 1180 values, the percentage deviation from the statistical expectation would be less than five percent. In our case the average total number of days used for each site for this analysis was 1331 and the average percentage deviation was 26%. This shows clearly that the 63–37% division amongst the codes cannot be attributed to statistical chance. This is further supported by the application of the Chi-Squared test to this data, from which it is concluded that at the 99% level of confidence, the observed frequencies are not due to statistical chance.

TABLE IX

Results of the analysis of the sign of the rate of change using all data for (a) corresponding years (b) cross years

(a)	Percentage number of correlations	Percentage number of non-correlations
High Muffles		
Leeds	68	32
Hull	64	36
Middlesborough	62	38
Liverpool	61	39
Birmingham	61	39
Stoke Ferry		
Birmingham	62	38
Leicester	65	35
Total average	63	37

(b)	Percentage number of correlations	Percentage number of non-correlations
Cross years using High Muffles data		
Birmingham	51	49
Hull	53	47

(3) When the same analysis was done for cross years (Table IXb) for Birmingham and Hull (i.e. 1993 sulphate data with 1994 PM_{10} data, etc. for all years of data), the percentage division was 51–49% and 53–47% and the percentage deviation from the statistical expected number of days with these codes was 3.5%. i.e. simply due to statistical chance (as expected). The contrast which the average and the percentage deviation for corresponding years (63–37%, 26%) makes with the average and percentage deviation for cross years (52–48%, 3.5%) is indicative of a relationship.

If the percentages calculated were just due It must be acknowledged however that since this method is an abstraction of the linear correlation method it necessarily returns a better correlation than using the latter technique since the amount of information used in this analysis is less than that used previously for linear regression.

TABLE X

Percentage count of the four codes (11, 00, 01, 10) for all sites for (a) corresponding years (b) cross years. Note that 1 stands for a positive rate of change and 0 stands for a negative rate of change. The first digit in the two digit code represants the rate of change of the urban PM_{10} concentration while the second digit represants the rate of change of the rural sulphate concentration

(a)	U0-R0	U0-R1	U1-R0	U1-R1
High Muffles				
Leeds	34	15	17	34
Hull	32	17	19	32
Middlesborough	30	18	20	31
Liverpool	30	19	21	31
Birmingham	31	19	20	31
Stoke Ferry				
Birmingham	31	18	20	31
Leicester	32	17	18	33
Total average	31	18	19	32

(b)	U0-R0	U0-R1	U1-R0	U1-R1
Cross years using High Muffles data				
Birmingham	27	24	24	26
Hull	26	24	25	25

The number of days having the codes 11, 00, 01 and 10 were counted individually and expressed as a percentage of the total number of days (Table Xa). Statistical chance would attribute a 25% probability for each code. However, it can be seen that codes 11 and 00 were more frequent (about 31% each) and codes 01 and 10 (about 18% each) rather less. This pattern was evident for all urban sites considered and hence cannot be attributed to statistical chance alone. When the same analysis was done for cross years for Birmingham and Hull (Table Xb), all the codes returned a percentage very near 25%. This contrasts greatly with the percentage values obtained using corresponding years and is a further indicator that the percentages obtained are due to a possible relationship between urban and rural concentrations rather than due to statistical chance alone.

TABLE XI

Results of the analysis of the sign of the rate of change using high rate of change data for (a) corresponding years (b) cross years

(a)	Percentage number of correlations	Percentage number of non-correlations
High Muffles		
Leeds	80	20
Hull	78	22
Middlesborough	84	16
Liverpool	69	31
Birmingham	76	24
Stoke Ferry		
Birmingham	82	18
Leicester	74	26
Total average	76	22

(b)	Percentage number of correlations	Percentage number of non-correlations
Cross years using High Muffles data		
Birmingham	46	54
Hull	55	45

Time series for the daily rate of change of the urban PM_{10} concentrations showed that it varied principally between –40 μg m^{-3} and +40 μg m^{-3}. High rates of change (i.e. days for which rate of change $\geq$+20 μg m^{-3} or $\leq$–20 μg m^{-3}) were filtered from the rest of the data and the same analysis was performed as before (Table XIa). The average percentage division for corresponding years was 77–22%, implying a distinctly greater correlation between the urban and rural concentrations than when using all data (63–37%). The contrast was even greater when the analysis was done for cross years using the filtered data (Table XIb) giving 46–54% for Birmingham and 55–45% for Hull. It can be concluded from these results that transported sulphate aerosol from rural sites is contributing somewhat to the urban PM_{10} concentration and that this contribution is especially significant for large changes in the daily urban PM_{10} concentration.

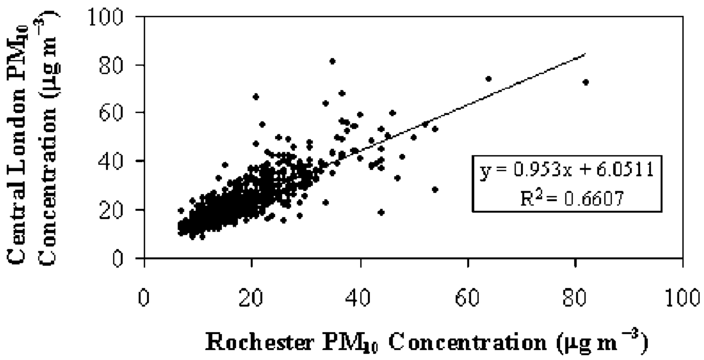

Figure 4. Scatter plot of the average urban London PM_{10} concentration (using Bloomsbury, Brent, Camden and Haringey data) against the rural PM_{10} concentration in Rochester for the period 1996–1999.

One of the problems involved when investigating the external contribution to urban sites is that rural sulphate data is available for few rural sites and only till 1997. This problem was circumvented by filtering low frequency pollution cycles (i.e those most probably due to external or natural sources) from the high frequency cycles which are more typical of traffic and other local urban sources. This was done by passing the PM_{10} concentration data of each urban site through a Butterworth lowpass filter of order one having a cutoff period of 30 days. The resulting data set was then correlated with the original data and the correlation coefficient hence obtained was a measure of the amount of external pollution affecting the site during that particular time period. This was done for Hull (1994–1997), Middlesborough (1995–1997), Birmingham (1993–1997), Manchester (1996–1997), Sheffield (1996–1997) and Liverpool (1993–1997). A correlation coefficient was obtained for each year and it was then compared with the correlation coefficients obtained before by correlating the sulphate concentration of High Muffles with the PM_{10} concentration of the sites. Linear regression of the two coefficients gave a reasonably high degree of correlation of 0.76. This shows that from the PM_{10} data of an urban site, a rough estimate of the amount of external pollution can be obtained, without the need of any sulphate data.

Another plausible explanation for the low value of the correlation coefficients obtained is that only sulphate aerosol data was used for the analysis, whereas it is known that the secondary PM_{10} fraction is affected by other types of particulate matter such as nitrate aerosol. So to overcome this difficulty, PM_{10} data from rural Rochester were correlated with PM_{10} concentrations in nine urban sites in the London area for the years 1996–1999. The results are shown in Table XII and the associated scatter plot in Figure 4. The correlation coefficient range is 0.55–0.79 with an average of 0.65 and a standard deviation of 0.09 which represents 13% of the average. The gradient and intercept ranges are 0.86–1.02 and 1.4–9.8, respectively. In the fitted straight line equation, y represents the urban PM_{10} con-

TABLE XII

Results of linear regression analysis for nine urban sites in London

London urban sites	Correlation coefficient	Gradient	Intercept
Bexley	0.79	1.02	1.42
Eltham	0.73	0.86	3.22
Hillingdon	0.55	0.93	4.76
North Kensington	0.65	0.96	3.59
Sutton	0.58	0.88	5.48
Bloomsbury	0.75	0.99	6.09
Camden	0.56	1.00	9.84
Haringey	0.64	0.99	4.93
Brent	0.64	0.86	3.09

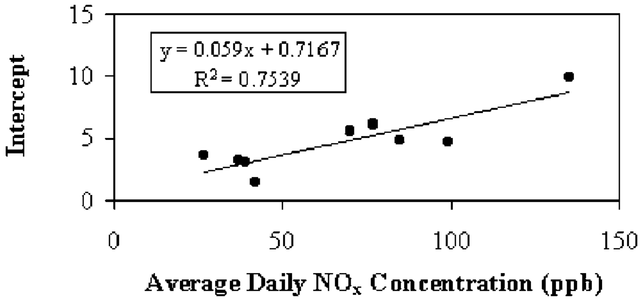

Figure 5. Scatter plot of the urban daily average NO_x concentration in London against the intercept for the period 1996–1999.

centration and x represents the rural PM_{10} concentration. Hence the gradient is taken as a measure of the contribution of transported PM_{10} from the rural area and the intercept as a measure of the local contribution to urban PM_{10}. This is supported by the fact that the gradient is very nearly the same for all sites (the standard deviation is only 7% of the average gradient) showing that it is practically site-independent whereas the large range in the intercepts shows that it is strongly site dependent (the standard deviation is 51% of the average intercept). To further confirm this hypothesis, the daily average Nitrogen Oxides (NO_x) concentration for the period 1996–1999 for all sites was calculated and linearly correlated with the intercepts obtained by the previous analysis (Figure 5). The high value of the correlation coefficient (0.75) combined with the fact that NO_x concentrations are a good indicator of urban activity indicates that the intercept is a measure of the local contribution to urban PM_{10}.

TABLE XIII

Results showing the number of days in various London urban sites in which there was a high (greater than or equal to 40 μg m^{-3}) or low (less than 40 μg m^{-3}) PM$_{10}$ concentration given that in Rochester there was a high PM$_{10}$ concentration

	Number of days in which urban PM$_{10}$ level is low	Number of days in which urban PM$_{10}$ level is high	Percentage number of 'low' days in urban site	Percentage number of 'high' days in urban site
Brent	16	16	50	50
Haringey	8	21	28	72
Camden	4	22	15	85
Bexley	10	40	20	80
Eltham	13	18	42	58
Hillingdon	10	15	40	60
North Kensington	9	22	29	71
Sutton	12	21	36	64
Bloomsbury	6	41	13	87
Average			30	70

King and Dorling (1997) and Stedman (1997) demonstrated that secondary particles formed the main contribution to the high PM$_{10}$ concentrations found across the U.K. in January to March 1996. The remaining question to be answered is whether the high secondary particle contribution to episodes was peculiar only to that period in 1996 or if in general all episodes are significantly affected by transported particulate matter from external sources. An episode correlation analysis was done. Given that the PM$_{10}$ concentration in Rochester was greater than or equal to 40 μg m^{-3}, the number of days in an urban site having a PM$_{10}$ concentration less than 40 μg m^{-3} and the number of days having a PM$_{10}$ concentration greater than or equal to 40 μg m^{-3} were counted. If the number of days for which the urban concentration was high was approximately equal to the number of days for which the urban concentration was low, then one would conclude that there was no relationship between the episodes in Rochester and London whereas if the number of urban high concentration days was significantly greater than that for which the concentration was low, one would conclude that the episodes in Rochester and London were affecting each other. This analysis was done using the nine urban London sites, the results of which are shown in Table XIII. The average number of days for which there were episodes in both sites (rural and urban) were significantly greater than the average number of days for which there were no episode correlation. Results show that, given a high concentration of PM$_{10}$

TABLE XIV

Results showing the number of days in Rochester in which there was a high (greater than or equal to 40 μg m^{-3}) or low (less than 40 μg m^{-3}) PM_{10} concentration given that in various London urban sites there was a high PM_{10} concentration

	Number of days in which Rochester PM_{10} level is low	Number of days in which Rochester PM_{10} level is high	Percentage number of ‘low’ days in Rochester	Percentage number of ‘high’ days in Rochester
Brent	18	16	53	47
Haringey	47	21	69	31
Camden	94	22	81	19
Bexley	29	40	42	58
Eltham	11	18	38	62
Hillingdon	39	15	72	28
North Kensington	31	22	58	42
Sutton	34	21	62	38
Bloomsbury	57	41	58	42
Average			59	41

in Rochester, there was a 70% chance that there was one in London. However it is not clear which was affecting which. To settle this problem, the analysis was repeated with the restriction placed on the urban site data i.e., given that there was a high concentration of PM_{10} in an urban area, what was the number of days in Rochester in which there were high PM_{10} concentrations and what was the number of days in Rochester in which there were low PM_{10} concentrations. The analysis was again performed for all nine urban sites (Table XIV). It can be seen that the average percentage number of days for which there was episode correlation was only 40%, mening that episodes in London were not the main cause of episodes in Rochester. Hence by combining with the previous result (70% episode correlation in London, given there are high concentrations in Rochester), it can be concluded that episodes in Rochester affect episodes in the urban London significantly. It is clear that although high concentrations of PM_{10} in Rochester are the cause of some episodes in the London area, locally-generated particulate matter in London being transported to Rochester cannot be neglected and may well be the cause of the elevated magnitude of the correlation coefficients when compared to those calculated using sulphate aerosol data. There is also the possibility that the high degree of correlation is not due to the pollutant moving from one site to the other. One

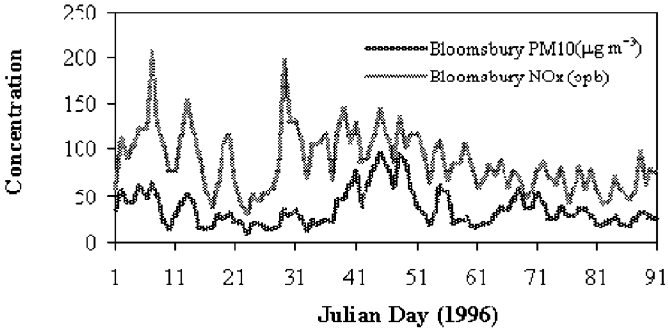

Figure 6. Variation of the London Bloomsbury NO_x and London Bloomsbury PM_{10} concentration over the first 91 days of 1996.

particular case would be that of a single high pressure system causing simultaneous accumulation of emitted pollutants across wide areas of the U.K.

There is the need of a rough estimation of the amount of particulate matter in urban London which is due to transport from rural areas such as Rochester. NO_x emissions are known to be principally due to road traffic, power stations, heating plants and industrial processes. This makes it a good local urban activity indicator. Average London Bloomsbury NO_x concentration data and the average local PM_{10} concentration were plotted for the first 91 days of 1996 (Figure 6). Some peaks occur in the two data sets at the same time. The peaks in NO_x imply an increase in urban activity (especially road traffic) and hence an increase in locally-generated PM_{10} in London, which is then carried over to Rochester. However there are also some large peaks in the London NO_x concentrations which are not followed by a marked increase in local PM_{10} concentrations and some significant increases in local PM_{10} concentrations which are not followed by similar changes in urban NO_x emissions. This shows that a significant amount of urban PM_{10} is due to external influences rather than generated due to various local urban activities. This also hints to a possible method of estimating the influence of these external sources on the local urban PM_{10} concentrations. By subtracting the NO_x and PM_{10} concentrations of each day from the values of the previous day, one gets the rate of change of the concentrations over 24 hr. If the rate of change is positive it indicates an increasing concentration, while if the rate of change is negative it indicates a decreasing concentration. The number 1 denotes a particular day in which the rate of change is positive, and the number 0 indicates one in which the rate of change is negative. This procedure is repeated for the three data sets i.e. for the urban NO_x data, for the urban PM_{10} data and for the rural PM_{10} data. Thus for each day one gets a series of three digits composed of 1's and 0's. There are eight possible combinations each implying a certain cause for the local urban PM_{10}. The causes can be roughly subdivided into three: 100 and 011 imply the influence of rural Rochester on urban London; 111 and 000 imply the influence of urban London on rural Rochester and the rest (101, 010, 110 and 001) imply an indeterminate cause. The latter could imply the influence of other external sources or further contributions to the local urban PM_{10} from urban London and from rural Rochester. The daily rate of change for each of the three data sets for the years 1996–1999 was calculated and each day marked with the appropriate three-digit code according to the signs of the rate of change. The NO_x and local urban PM_{10} data used were obtained by averaging the NO_x and urban PM_{10} concentrations in Bloomsbury, Brent, Camden and Haringey (Central London sites) over the whole period. This ensured that NO_x and PM_{10} data were more representative of the plume over London than of local street levels. The number of days bearing the same three digit code were counted for each of the eight codes and grouped into the larger three subdivisions mentioned before (i.e. 111 and 000 data were grouped together, etc.). There were 229 days having the code 100 or 011, 574 days having the code 000 or 111 and 179 days having any one of the remaining four codes. This means that 23% of all days considered were affected by PM_{10} coming from Rochester, 58% were due to locally generated PM_{10} and 18% had an undetermined cause. The method was further validated by seeking linear correlation between urban PM_{10} and rural PM_{10} concentration and between urban PM_{10} and urban NO_x concentration for each of the three groups of data and comparing these to results obtained using the whole data set. As expected, for those days which the rate of change analysis determined as being mostly influenced by rural PM_{10} concentrations, there was a higher coefficient (0.75 to 0.80) for the urban and rural PM_{10} concentrations but a substantial decrease (0.33 to 0.14) in the correlation coefficient for urban NO_x and urban PM_{10} data. The data implying an urban to rural transport showed an increase in both correlation coefficients (0.75 to 0.78 and 0.33 to 0.35), as expected, whereas linear correlation using the data which implied an indeterminate cause showed that urban NO_x was a prime cause for urban PM_{10} (0.33 to 0.40) and that transport of PM_{10} between London and Rochester was significantly lower than in the other cases (0.75 to 0.53). The fact that about one quarter of urban PM_{10} in London is due to PM_{10} transport from Rochester to London is very significant and makes it clear that air quality considerations have to take account of this transboundary contribution to urban air pollution if the local urban concentrations of particulate matter are to be kept within reasonable safe limits.

Stedman (1997) showed that since black smoke is a good indicator of primary PM_{10}, the concentration of local secondary PM_{10} is approximately proportional to the daily local PM_{10} concentrations minus the daily black smoke concentrations. Secondary PM_{10} can be either locally-generated by the photochemical oxidation of sulphur dioxide and nitrogen dioxide or else it is transported from external sources in the form of an aerosol. Photochemical oxidation takes several hours to complete and thus requires stable air masses of sulphur dioxide and nitrogen dioxide in the local atmosphere. This is not typical of urban areas in the United Kingdom since power stations and other major sources of sulphur dioxide are not usually located in the urban areas and so this implies transported masses of sulphur dioxide to the urban site. However, it is known that in London the major sources of sulphur dioxide are located very near the central urban areas and so it is reasonable to assume that some amount of secondary PM_{10} is due to the local photochemical processes. Linear correlation was sought between the non-combustion component of PM_{10} in London (represented by the average local daily PM_{10} minus the average local daily black smoke concentration) and the local urban sulphur dioxide concentration for the years 1996–1999. The correlation coefficient obtained was 0.21 which is incidentally very near the average correlation coefficient calculated (0.22) for a similar analysis involving the correlation of co-located sulphur dioxide and sulphate data carried out on nine rural sites in the U.K (Micallef and Colls, 1999). This justifies the assumption of stable air masses containing sulphur dioxide over London. The same analysis was repeated using average London Nitrogen Oxides concentration and also using rural Rochester PM_{10} concentration, instead of the sulphur dioxide concentration data. The correlation coefficients were 0.0003 and 0.57, respectively. The low correlation coefficient for NO_x is explained by the fact that NO_x concentrations are continually changing due to the local traffic emissions (hence the process of photochemical reaction is not favoured) and also because ammonia is not present in any great quantities in an urban area (the major sources of ammonia are fertilised fields, which are found in rural areas, and industry). Hence there is little if any nitrate aerosol formation in local urban areas. However one notes that the correlation coefficient using rural PM_{10} data is high when compared to the other two. Combining all these facts the following deductions can be made about the secondary PM_{10} fraction in London:

(1) It is mainly composed of sulphates, not nitrates.
(2) Some secondary PM_{10} is produced locally by photochemical reactions.
(3) The major source of secondary PM_{10} is transported aerosol from rural Rochester, which is most likely influenced by transboundary sources.

The transport of secondary sulphate aerosol from the Continent is also supported by previous studies. Secondary sulphate aerosol belongs to the accumulation mode of the ambient aerosol distribution, and hence has a relatively long lifetime which allows for long-range transport. In 1982/1983 in Leeds, sulphate was found to constitute 8% of the total mass of particulate matter in the coarse fraction and 25% of that for the fine fraction (Clarke, Willison and Zeki, 1984). Hjellbrekke *et al.* (1995) give a map for the concentration of airborne sulphate aerosol over Europe, using data collected from the UNECE European Monitoring and Evaluation Programme (EMEP), which indicates a negative concentration gradient from Eastern Europe towards the United Kingdom. The United Kingdom Review Group on Acid Rain, in their third report (1990), did a sector analysis for data collected over the time period 1986–1988 at seven rural sites. The influence of long-range transport of sulphate aerosol from the Continent became apparent. This influence was further confirmed by Micallef and Colls (1999) who sought linear correlation between co-located concentration data of sulphur dioxide and sulphate aerosol at nine rural monitoring sites in the United Kingdom. Analysis of the gradients and intercepts revealed that a significant portion of sulphate aerosol at these sites is not produced by the local photochemical oxidation of sulphur dioxide but is rather transported from external sites, possibly transboundary ones.

4. Conclusions

Reasonable correlation has been found between rural sulphate aerosol and urban PM_{10} concentrations at several monitoring sites situated in the Midlands and North East England. Interpretation of the associated linear regression analysis together with results of the analysis of the sign of the rate of change of the two concentrations confirms the transboundary contribution of sulphate aerosol to urban PM_{10} concentrations. Good correlation has been found between urban PM_{10} concentration data for nine monitoring sites in London and rural PM_{10} concentrations in Rochester. Episode correlation analysis showed that a significant number of episodes which occur in London are caused by episodes occurring in Rochester, which is known to be influenced by transported secondary PM_{10} from the Continent. Analysis of the sign of the rate of change of urban NO_x, urban PM_{10} and rural PM_{10} concentrations has shown that about one quarter of the ambient urban PM_{10} in London is not produced by local urban activities but rather is transported from transboundary sources.

Acknowledgements

Data used in this work were accessed from the United Kingdom Department of the Environment, Transport and the Regions' National Air Quality Information Archive made available on the World Wide Web at www.aeat.co.uk/netcen/aqarchive. This web page is maintained by AEA Technology's National Environmental Technology Centre (NETCEN).

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