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What are the sources and conditions responsible for exceedences of the 24 h PM_{10} limit value ($50\,\mu g\,m^{-3}$) at a heavily trafficked London site?

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Abstract

The European Union has set limit values for PM_{10} to be met in 2005. At Marylebone Road, London, where the traffic is heavy, the daily limit value of $50\,\mu g\,m^{-3}$ is exceeded more than 35 times a year. A total of 185 days with daily PM_{10} concentrations exceeding the limit value of $50\,\mu g\,m^{-3}$ measured between January 2002 and December 2004 (data capture of 89.5%) are discussed in this paper. These exceedences were more frequent in early spring and in autumn. Concentrations have been disaggregated into regional, urban (background) and local (street) contributions. Most of the episodes of gravimetric PM_{10} above the limit value were associated with a high regional background and very often the regional contribution dominated the PM_{10} mass. The secondary aerosol (especially the particulate nitrate) made a major contribution to the PM_{10} load. These situations were frequently observed when air masses came from the European mainland (showing that both emissions from the UK and other EU countries contributed to the exceedences), and less frequently with maritime air masses that have stagnated over the UK (showing that emissions from the UK alone less frequently contributed to the high regional background). However, the higher frequency of episodes breaching the limit value at the roadside site than at the rural site and the higher frequency of PM_{10} concentrations above the limit value on weekdays show that the high regional contributions are additional to local and urban emissions. Local emissions mainly due to traffic were the second important contributor to the exceedences, while the contribution of the urban background of London was less important than the local emissions and the regional background. Applying the pragmatic mass closure model of Harrison et al. [2003. A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites. Atmospheric Environment 37, 4927–4933], revealed that the regional aerosol is comprised very largely of ammonium nitrate and sulphate and secondary organic aerosol. Findings suggest that international abatement of secondary aerosol precursors may be the most effective measure to fulfil the requirements of the European Directive 1999/30/CE by lowering the regional background.

Keywords: PM_{10}; Vehicle emissions; Long-range transport; Meteorology; Secondary aerosol; Nitrate; Sulphate

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1. Introduction

The Air Quality Framework Directive (96/62/EC) and the First Air Quality Daughter Directive (1999/30/EC) set out limit values for PM_{10} in ambient air across Europe which were due to be met in 2005. The limit value of 50 μg m^{-3} over 24 h should not be exceeded more than 35 times a year and the maximum annual average is 40 μg m^{-3}.

The London–Marylebone Road monitoring site is located on the kerbside of a major arterial route in London that is heavily trafficked. The surrounding area is a street canyon frequented by pedestrians because of tourist attractions and shops. High PM_{10} concentrations are measured at Marylebone Road and the permitted number of days with concentrations above the limit value was exceeded in 2005.

At the moment of writing, most of the published studies discussing the difficulty to comply with the new European PM_{10} law focus on Mediterranean locations due to contributions of African dusts and natural dust resuspension (e.g. Chaloulakou et al., 2003; Artiñano et al., 2004; Moreno et al., 2005a). Fewer studies discuss the case of other European locations where such natural contributions are much less significant. A German study (Lenschow et al., 2001) discussed the sources of PM_{10} in Berlin, their trend and possible reduction measures in order to fulfil the future European Directive. Many contributions at the European Aerosol Conference (2005, Ghent, Belgium) showed that the compliance with the European Directive is becoming a wider European concern (e.g. Berghmans et al., 2005; Handler et al., 2005; Moreno et al., 2005b; Wurzler et al., 2005).

In this paper the sources and factors responsible for the exceedences of the 24 h Limit Value at Marylebone Road, London are analysed and discussed.

2. Sampling sites and data for inclusion in the study

The Marylebone Road supersite belongs to the London Air Quality Network. It is located on the kerbside of a major arterial route within the city of Westminster in London. The road is a part of the inner London ring road. The surrounding buildings form an asymmetric street canyon (height-to-width ratio of about 0.8). Traffic flows of over 80,000 vehicles day^{-1} pass the site on six lanes with frequent congestion. Braking is frequent near the measurement site due to the presence of traffic lights 50 m to the west and an intersection to the east. The instruments are in a cabin and sampling inlets are less than 5 m from the road. Local PM_{10} emissions are strongly dominated by the heavy-duty vehicles that represent less than 10% of the traffic (Charron and Harrison, 2005).

Two Partisol Plus Model 2025 are used to sample gravimetric PM_{10} and $PM_{2.5}$. The inlets of the gravimetric PM_{10} and $PM_{2.5}$ instruments are 3.1 m above the ground and the instruments are, respectively, located 4.0 and 4.8 m from the centre of the nearest traffic lane. Both gravimetric PM_{10} and TEOM PM_{10} data are used in this study. Exceedences of the Limit Value are taken to be gravimetric PM_{10} concentrations above 50 μg m^{-3} (since the agreement between gravimetric data and TEOM data at Marylebone Road is poor), while hourly TEOM data were useful to characterize the different episodes. The relationship between gravimetric and TEOM measurements depends on the episode type and is discussed later. Measurements of other particulate matter metrics and components ($PM_{2.5}$, elemental and organic carbon, nitrate, sulphate) and of NO_x (because of its strong relation to particle data at Marylebone Road) are also used in the study. Data and instruments are summarized in Table 1, which includes references to sources of further information.

PM_{10} and $PM_{2.5}$ measured at two reference London urban background sites (Bloomsbury and North Kensington) and two reference rural sites (Harwell and Rochester) are also included in the study in order, respectively, to define London urban background and the regional background. Gravimetric PM_{10} concentrations measured at London North Kensington and Harwell are respectively used for quantification of the London urban background and the regional background.

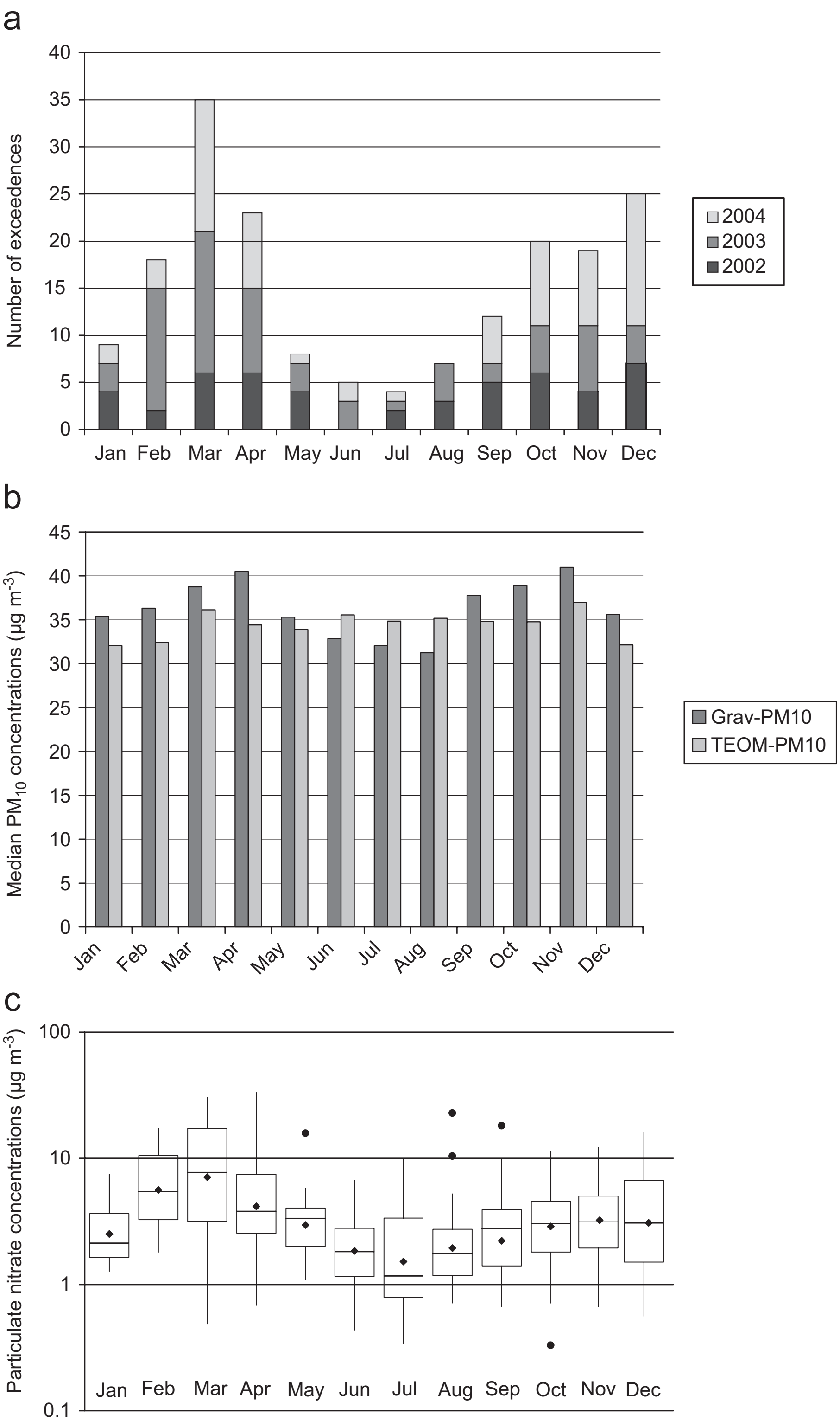
The Bloomsbury site (BB) is located in Russell Square Gardens in the centre of London at about 2 km to the east of Marylebone Road. It is in a garden (grass with many mature trees) and surrounded by a 2/4 lane one-way road system (35,000 vehicles day^{-1}). The nearest road is at a distance of approximately 35 m from the instruments. The North Kensington site (LNK) is in a residential area about 4 km to the west of Marylebone Road. The Harwell site (HW) is located to the west of London (Oxfordshire). It is within the grounds of a research centre and the surrounding area is open with agricultural fields (the nearest road is for access to the research centre only). The

Table 1
Summary of data for inclusion in the study

Data		Instruments and references	Data capture (2002–2004)[a]
London Marylebone Road	Gravimetric PM_{10}	Partisol Plus Model 2025 (R&P)—sharp-cut cyclone inlet for $PM_{2.5}$ measurements	89.5%
	Gravimetric $PM_{2.5}$	Gravimetric weighing after 48 h—equilibration at 20 °C and 50% relative humidity	81.3%
	Gravimetric PM_{coarse}	The coarse fraction is obtained by difference between PM_{10} and $PM_{2.5}$ Detailed in Charron et al. (2004)	68.4%
	Hourly TEOM-PM_{10}	TEOMs (Model 1400AB). Data with default	97.8%
	Hourly TEOM-$PM_{2.5}$	adjustment factor (1.03 'TEOM reading' + 3 μg)	94.7%
	Hourly TEOM-coarse	Detailed in Charron and Harrison (2005)	93.4%
	Hourly NO_x	API (A series) model M200A	96.8%
	3-h elemental and organic carbon (OC&EC)	Ambient carbon particulate monitors series 5400 (R&P) Detailed in Jones and Harrison (2005)	52%
	Daily nitrate and sulphate	Partisol plus model 2025 (R&P) Water extraction/ion chromatography Detailed in Abdalmogith and Harrison (2005)	48.6%
	Hourly vehicle counts	Loop monitoring system Detailed in Charron and Harrison (2005)	Until May 2004 99.1% for 2002–3
London BB	Hourly TEOM-PM_{10}	$PM_{2.5}$ Model 1400AB	63.3%
	HourlyTEOM-$PM_{2.5}$	PM_{10} Model 1400E	93.9%
	Hourly TEOM-coarse		62.4%
	Hourly NO_x		94.4%
London LNK	Gravimetric PM_{10}	Partisol Plus Model 2025 (R&P)—see above	91.1%
	Gravimetric $PM_{2.5}$		89.7%
	Gravimetric PM_{coarse}		82.7%
	Hourly TEOM-PM_{10}	TEOM (model 1400A)	97.6%
	Hourly NO_x		97.1%
Harwell	Gravimetric PM_{10}	Partisol Plus Model 2025 (R&P) Gravimetric weighing after 48 h—equilibration at 20 °C and 50% relative humidity Detailed in Charron et al. (2004)	68.2%
	HourlyTEOM PM_{10}	TEOMs (model 1400A)	98.1%
	HourlyTEOM $PM_{2.5}$		97.6%
Rochester	Hourly TEOM PM_{10}	$PM_{2.5}$ Model 1400AB PM_{10} Model 1400A	78.4%
London	Wind direction		100%
		Met Office data supplied by the BADC Details on www.badc.ac.uk	100%
	Wind speed		
	Mean sea level pressure		100%
	Temperature		100%
	Relative humidity		100%
	Total cloud amount	3D ECMWF trajectories	100%
	Backward trajectories	Details on www.badc.ac.uk	100%

[a]Data capture after checking.

Fig. 1. (a) Number of exceedences of the PM_{10} limit value as a function of the month and year. (b) Median monthly gravimetric and TEOM PM_{10} measured at Marylebone Road (2002–2004); (c) monthly box plots for the particulate nitrate measured at Marylebone Road (June 2002–December 2004). Box plots. Upper part: 75th percentile; lower part: 25th percentile; line inside the box: median; black circle inside the box: arithmetic mean, 50% of the data are included in the box. i.e. between the 25th and the 75th percentiles (= inter quartile range, IQR); the length of the upper whisker is the shorter of these two distances: the distance between the 75th percentile and the maximal value or 1.5 time the IQR and similarly, the length of the lower whisker is the shorter of these two distances: the distance between the minimal value and the 25th percentile or 1.5 time the IQR. When the whisker is 1.5 time the IQR 'outlier values' are drawn outside the box plots as black circles.


a
Number of exceedences
40
35
30
25
20
15
10
5
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
2004
2003
2002
b
Median PM10 concentrations (µg m-3)
45
40
35
30
25
20
15
10
5
0
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec
Grav-PM10
TEOM-PM10
c
Particulate nitrate concentrations (µg m-3)
100
10
1
0.1
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

Rochester site (RO) is located to the east of London (Kent). It is within a rural primary school and the area is open and rural. The nearest road is 80 m away with low traffic volume.

Three-dimensional trajectories supplied by the British Atmospheric Data Centre are used to estimate the pathways followed by air masses arriving at London. Three-days backwards trajectories ending at 925 hPa are computed at an arrival time closest to the high concentrations episode time, either 00, 06, 12 or 18 GMT (hourly TEOM data are then examined).

Synoptic meteorological data from London Samos Weather Centre station (wind speed, wind direction, temperature, relative humidity, total cloud amount) are supplied by the British Atmospheric Data Centre. Wind data measured at the Marylebone Road site are also used in the study.

The different episodes are characterised considering (1) the contribution of the regional background, (2) the contribution of the urban background, (3) the contribution of the local emissions to the exceedences. In practice, the regional background is defined using the PM_{10} concentrations measured at the rural sites; the urban increment is the difference between PM_{10} concentrations measured at the urban background sites and the rural sites; and the local increment due to traffic is the difference between concentrations measured at Marylebone Road and those measured at the urban background sites. An episode is defined as local, urban or regional when the local increment, the urban increment or the regional background are, respectively, larger than the median values (10% larger was arbitrarily chosen). It is concluded that the regional background contributed to the exceedences when high concentrations are measured at both Harwell and Rochester sites and the same approach is used for local and urban contributions (i.e. both North Kensington and Bloomsbury data are used). This excludes any non-representative local influence or the influence of the London conurbation at one of the rural sites. Information from other available data were simultaneously examined (SO_4^{2-}, NO_3^-, EC, OC, NO_x, CO, $PM_{2.5}$). The examination of PM_{10} and $PM_{2.5}$ hourly variations (TEOM data) was also useful for drawing conclusions. Large local contributions result in PM_x that co-varied with traffic data; while the traffic contribution could be hidden by large urban and regional contributions and in this case, PM_x concentrations measured at Marylebone Road are in excellent agreement with those measured at the urban background. In general the results generated by this method showed consistency with particulate sulphate as a tracer of long-range transport and with particulate elemental carbon and NO_x as tracers of vehicle emissions. The relative contributions of local emissions, urban background sources and regional background sources to PM_{10} mass measured at Marylebone Road are also estimated. Because of possible local influences at urban and rural sites and a temporal offset between Harwell data and London data, quantitative estimations have a large associated uncertainty. Episodes are broken down according to their local, urban or regional contributions to the exceedence. Backward trajectories and meteorological data are used for the interpretation, not for the classification.

Particle chemical composition data are available from some or all of the PM_{10} measurement sites (Abdalmogith and Harrison, 2005, 2006; Jones and Harrison, 2005). In interpreting their contribution to measured gravimetric PM_{10} mass, the pragmatic mass closure model of Harrison et al. (2003) has been applied. Differentiation between primary and secondary organic carbon is based on the methods of Castro et al. (1999).

3. Results

3.1. General overview of the episodes

One hundred and eighty-five days with daily gravimetric PM_{10} concentrations exceeding the Limit Value (LV) of $50\,\mu g\,m^{-3}$ were measured between January 2002 and December 2004. Forty-nine occurred in 2002 (data capture of 89.6%); 69 occurred in 2003 (data capture of 94.2%); and 67 occurred in 2004 (data capture of 84.7%). This means that the LV was exceeded on 15% of sampled days in 2002, 20% of sampled days in 2003 and 22% of sampled days in 2004; while the number of exceedences allowed is 35 out of 365 i.e. it shall be less than 10% of sampled days. These exceedences were not evenly distributed over the year (see Fig. 1): they were more frequent in March–April (February is strongly influenced by 2003 data) and from October to December. They coincide with periods of higher gravimetric concentrations: gravimetric PM_{10} concentrations measured at Marylebone Road from 2002 to 2004 showed seasonal variations with early spring/autumn maxima and early summer/winter minima. Similar seasonal variations are observed at London North Kensington and Harwell;

while the 2002, 2003, 2004 spring maxima are not measured by the TEOMs (similarly to 1998–2000 data, see Charron and Harrison, 2005, TEOM data measured at Marylebone Road showed little seasonality). Particulate nitrate data available for the springs of 2003 and 2004 indicate that the ammonium nitrate is lost in the inlet of the TEOM during these episodes. The contribution of the nitrate is discussed within the paper.

PM_{10} concentrations measured at Marylebone Road are high relative to most other UK sites. Gravimetric PM_{10} annual averages were below $40\,\mu g\,m^{-3}$ in 2002 and 2003 (respectively, 36.6 and $37.8\,\mu g\,m^{-3}$) but a little above $40\,\mu g\,m^{-3}$ in 2004 ($41.5\,\mu g\,m^{-3}$). The local increment due to the traffic and the regional background on average contributed respectively 37% and 41% of the PM_{10} concentrations measured from January 2002 to December 2004; while the urban background contribution was lower. However, day to day relative contributions are highly variable. Very similar average contributions were found by Tiitta et al. (2002) for their roadside site in Finland (respectively, 33% and 41%).

PM_{10} concentrations are higher on weekdays than at weekends (Fig. 2(b)). On weekdays, the median gravimetric PM_{10} concentrations are close to $40\,\mu g\,m^{-3}$ (unlike the arithmetic means, medians are not influenced by few high concentrations). As a consequence, exceedences of the daily limit value more often occurred on weekdays than at weekends (Fig. 2(a)) and they were more frequent from Tuesday to Friday inclusive, weekdays with heavier traffic. The weekly pattern of exceedence values has some similarities with the weekly pattern of PM_{10} concentrations; both are related to the weekly pattern of traffic (heavy-duty traffic, Fig. 2(c)).

A regional background contribution higher than usual (relative to median PM_{10} at Harwell and Rochester) is observed for 166 out of the 185 exceedence values. One hundred and twenty out of the 185 exceedence values were associated with air masses coming from the continent, i.e. 64.9% of the episodes (this is a much higher frequency than that of easterly air masses in the UK). For 32 of them, the daily PM_{10} LV was also exceeded at Harwell (140 gravimetric data available out the 185 episodes). This means that transboundary sources frequently contributed to the exceedences as already reported by Abdalmogith and Harrison (2005).

The regional contribution was more than 50% of the PM_{10} load for 70% of the episodes and then, the secondary inorganic particulate matter (sulphate and nitrate) represented a large part of the gravimetric PM_{10} concentrations. The contribution of the regional background was on average 60% of the total PM_{10} load during episodes of exceedence; while it was on average 41% of the total PM_{10} load of all PM_{10} concentrations measured between 2002 and 2004. Similarly, the secondary aerosol was estimated to be on average 56% of the total PM_{10} load during episodes of exceedence; while it was on average 45% of the total PM_{10} load of all PM_{10}

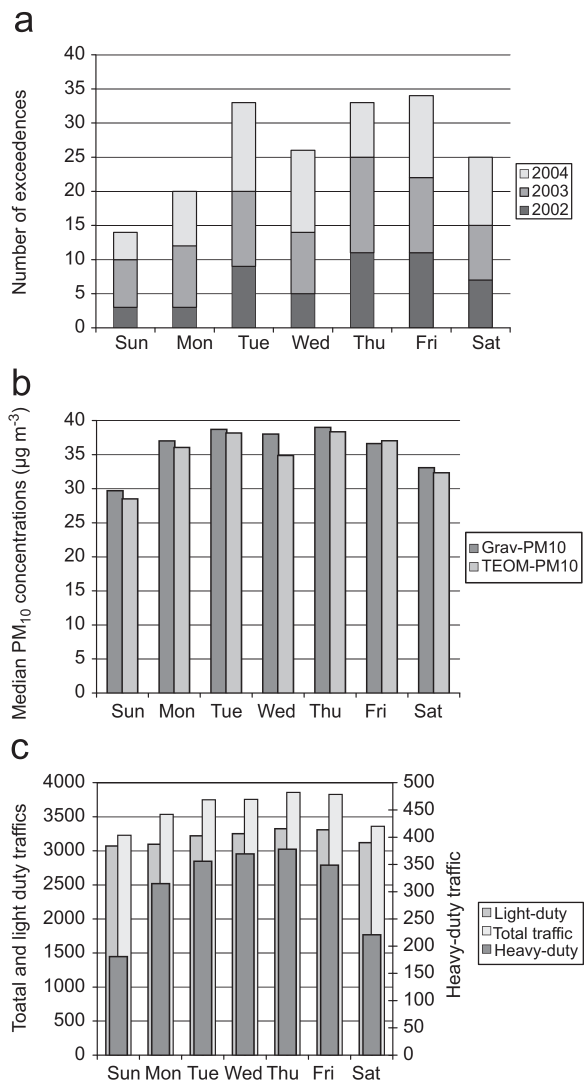


Fig. 2. (a) Number of exceedences of the PM_{10} limit value as a function of the day of the week (2002–2004 data); (b) median daily gravimetric and TEOM PM_{10} measured at Marylebone Road (2002–2004); (c) median numbers of light duty, heavy duty and total vehicles according to day of the week.

concentrations measured between 2002 and 2004 (see later for description, detailed in Table 4). The ammonium nitrate represented on average 54% of the total estimated secondary aerosol mass. The large contribution of the regional secondary aerosol to PM_{10} concentrations and/or episodes of high PM_{10} concentrations have been observed in other European locations (Lenschow et al., 2001; Gehrig and Buchmann, 2003; Tiitta et al., 2002; Memmesheimer et al., 2004; Giugliano et al., 2005; Bessagnet et al., 2005). Lenschow et al. (2001) showed that in Berlin, Germany, 55% of urban background PM_{10} concentrations is caused by long range transport (mainly ammonium nitrate and ammonium sulphate) and natural sources (pollen and wind-borne soil). There were few episodes without a high regional contribution and they occurred more frequently at the end of 2004 (Fig. 3). These episodes are discussed later. A contribution of local sources higher than usual was also frequent and was generally associated with unfavourable local dispersion. The surrounding buildings create a microscale circulation which has been studied for carbon monoxide by Scaperdas and Colvile (1999). When the wind comes from southerly directions (i.e. perpendicular to the street), a re-circulation of air inside the street canyon leads to high concentrations on the southern kerb where the instruments are located. This so-called ''southerly vortex'' situation is responsible for high PM_x concentrations (Charron and Harrison, 2005). However the local increment infrequently made a large contribution to the PM_{10} loading during episodes of exceedence (more than 50% of PM_{10} loading for 13% of the episodes). Note that the local contribution might be underestimated if there are local sources at rural and urban sites.

3.2. Examination of the different types of episodes

Episodes are sub-divided according to local, urban and regional contributions ''higher than usual'' using as reference the median daily data. Six sets have been specified: the ''local episodes'' (high local contribution only, noted ''L''); the ''local and urban episodes'' (high contributions from local emissions and from the urban background, noted ''LU''); the ''regional episodes'' (high regional contribution only, noted ''R''); the ''local and regional episodes'' (high local and regional contributions, noted ''LR''); the ''urban and regional episodes'' (high urban and regional contributions, noted ''UR'') and the ''local, urban and regional episodes'' (all contributions are higher than usual, noted ''LUR''). No ''U'' episode (high urban contribution only) was recorded between 2002 and

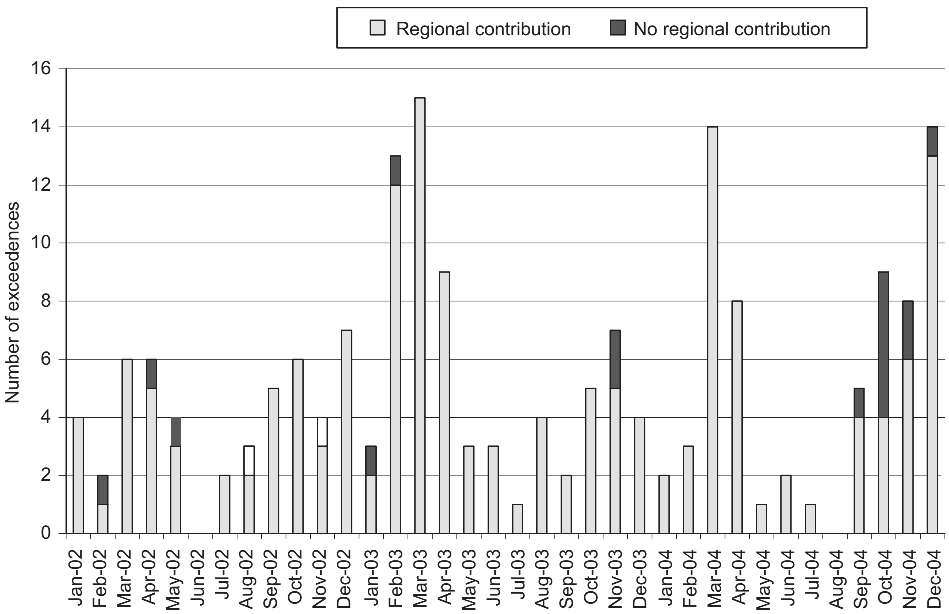


Fig. 3. Monthly number of exceedences of the PM_{10} limit value from January 2002 to December 2004. In grey, the number of exceedences with a contribution from the regional background and in black, the number of exceedences without a contribution from the regional background.

2004. The contribution of local emissions, and of urban and regional backgrounds to the PM_{10} load have also been determined. A dominant contribution means it is more than 40% of the PM_{10} mass; except for "LUR" episodes, where contributions higher than 30% are included. Average concentrations for each type of episode are summarized in Tables 2 and 3 and average local, urban and regional contributions to PM_{10} concentrations measured at Marylebone Road are summarized in Table 4. Table 4 also presents the estimated contributions of the secondary aerosol to the gravimetric PM_{10} mass. For this purpose, the sulphate and nitrate are assumed to exist as ammonium sulphate and ammonium nitrate with their bound water (as in the pragmatic mass closure model of Harrison et al., 2003) and the secondary organic aerosol mass is evaluated using an estimation of the primary OC/EC ratio from measurements at Marylebone Road (around 0.6) (Jones and Harrison, 2005) and the factor 1.4 for the conversion of the carbon mass to the organic compounds mass (see Harrison et al., 2003). Note the excellent agreement between estimations of the secondary aerosol and those of the regional background contribution (Table 4).

3.2.1. The local episodes (L): $N = 12$

Local emissions alone were responsible for PM_{10} concentrations exceeding the daily LV for only 12 episodes. Gravimetric PM_{10} concentrations were below or equal to $60\,\mu g\,m^{-3}$. Most of these episodes were associated with westerly oceanic airmasses (Fig. 4). One episode (21 February 2002) was associated with polar airmasses that had crossed the UK before reaching Harwell. Probably because of the strong wind speed, this episode was not associated with a large regional background. No 'L' episodes occurred on days with a stable anticyclonic situation (pressure >1013 mbars, wind speed <6 knots). The absence of regional and urban contributions is in agreement with the strong wind speed, but the large local increment is more surprising (note that TEOM data, NO_x and elemental carbon concentrations were also high). All these episodes were associated with wind directions leading to the southerly vortex situation (re-circulation of air inside the street). The examination of the few local wind data available (only 2003 and data capture of 76%) showed that the relationship between the local and the synoptic wind speed is poor and that the southerly vortex is associated with a low local wind speed. During these episodes, the local contribution dominates the particle mass and particulate ammonium sulphate and nitrate concentrations (with bound water) on average represented 17% of the PM_{10} particle mass.

Three episodes occurred in February, May and November 2002, while the remaining nine episodes occurred in the end of 2004 (September to December). All these episodes were obviously related to the local traffic. High $PM_{2.5}$ (and for some of them high PM_{coarse}) concentrations co-varied with the simultaneous high NO_x concentrations (that were often above $1000\,\mu g\,m^{-3}$ as NO_2). A contribution of local non-traffic activities (construction and demolition activities; roadworks, etc.) is possible for the three episodes that occurred in 2002 and two episodes of 2004 (17th November and 6th December) since PM_{coarse} concentrations were not correlated with NO_x concentrations and were higher or equal to $PM_{2.5}$ concentrations. However, the PM_{coarse} concentrations measured during these episodes are not as large as the ones measured during the construction and demolition activities that occurred in 1999 and 2000 (Fuller and Green, 2004) and these quite high PM_{coarse} concentrations were clearly not the only contribution to the exceedences.

At the end of 2004, the high concentrations were associated with prevailing winds from the same SE direction (that includes the southerly vortex induced by the surrounding buildings). Except for two episodes, both hourly $PM_{2.5}$ and PM_{coarse} were strongly correlated with NO_x. Episodes of exceedences of the 24 h limit value without any regional contribution (i.e. local or local–urban episodes) were more frequent during this period (see Fig. 4). All this suggests the possible influence of an additional local source (obviously vehicular) at the end of 2004.

3.2.2. The local and urban episodes (LU): $N = 7$

High local and urban contributions were found to be responsible for only seven episodes with gravimetric PM_{10} concentrations above the LV. These episodes were associated with maritime air masses, low synoptic wind speed and sometimes with an anticyclonic situation over London. Southerly vortex situations during rush hour are likely contributors to the high concentrations.

Five of them were winter episodes with similar weather. The weather was very cold (temperature $\leqslant 6\,^{\circ}C$) and the total cloud amount thin. Fast polar

Table 2
Percentiles (25%, 50% (median) and 75%) of concentrations measured at Marylebone Road from January 2002 to December 2004 and the median of concentrations measured during exceedence days, all and classified

	N	Daily grav. PM_{10}	Daily grav. $PM_{2.5}$	Daily grav. coarse	Daily grav. ratio	Daily NO_3^-	Daily SO_4^{2-}	3-h OC	3-h EC	Hourly TEOM PM_{10}	Hourly TEOM $PM_{2.5}$	Hourly TEOM coarse	Hourly TEOM ratio	Ratio TEOM/grav PM_{10}	NO_x	CO
2002–2004																
P0.25		27.6	13.6	7.0	0.45	1.4	1.7	3.1	1.7	23.1	12.0	8.2	0.50	0.80	143	0.70
Median		35.8	21.3	12.4	0.65	2.7	2.6	4.2	2.9	32.3	18.0	13.0	0.59	0.94	264	1.00
P0.75		45.8	29.3	21.6	0.79	4.7	4.1	5.5	4.6	45.4	26.0	19.3	0.67	1.08	426	1.70
Arith. mean		38.6	23.3	15.3	0.62	4.1	3.2	4.5	3.4	35.0	20.0	14.4	0.58	0.96	307	1.27
Exceedences (medians)																
All	185	60.2	39.3	21.2	0.66	7.5	5.3	5.4	3.3	46.2	28.0	17.3	0.61	0.76	361	1.40
L	12	53.8	[a]	[a]	[a]	2.8	2.4	$	$	43.6	25.9	17.8	0.60	0.83	533	1.66
LR	37	56.8	28.7	29.6	0.50	6.6	5.3	6.6	4.3	50.6	30.1	20.2	0.62	0.89	461	1.62
LU	7	56.2	38.2	21.2	0.66	$	$	6.7	6.2	53.8	28.0	26.0	0.51	0.93	633	2.30
LUR	67	66.2	42.9	20.6	0.68	8.6	4.7	6.2	4.5	51.9	31.1	21.7	0.60	0.76	413	1.61
LUR(R)	40	67.7	46.3	18.9	0.71	9.7	5.6	6.1	4.5	51.2	31.1	21.3	0.62	0.76	400	1.44
LUR(o)	27	63.8	33.3	27.7	0.50	7.5	4.4	6.3	4.8	52.8	31.2	23.1	0.56	0.80	471	1.92
R	31	54.0	40.8	12.8	0.77	12.4	5.9	4.3	2.2	39.7	23.1	15.8	0.59	0.72	252	1.11
UR	31	61.2	44.0	18.7	0.68	12.7	7.2	5.5	2.8	45.0	29.7	14.3	0.68	0.63	264	1.26

Concentrations in $\mu g\,m^{-3}$.
[a]Some 2004 $PM_{2.5}$ might not be reliable; $ no or not enough data available.

Table 3
Percentiles (25%, 50% (median) and 75%) of concentrations measured at Harwell (HW) and North Kensington (LNK); numbers of exceedences at HW and LNK (the second figure is the number of days available) and median values of meteorological data measured at London (wind speed in knots, total cloud amount in Oktas, mean sea level pressure in mbar, temperature in °C, relative humidity in %) from January 2002 to December 2004 and medians of concentrations measured during exceedence days, all and classified

	HW Daily grav. PM_{10}	LNK Daily grav. PM_{10}	LNK Daily grav. $PM_{2.5}$	LNK Daily grav. PM_{coarse}	PM_{10} Exc HW	PM_{10} Exc LNK	Wind speed	TCA	MSLP	T	RH
2002–2004											
P0.25	10.0	17.2	11.1	7.9			5.0	4.0	1009	7.7	64.1
Median	15.8	22.4	15.0	12.8			8.0	7.0	1017	11.4	78.3
P0.75	24.7	30.9	22.1	22.0			11.0	7.0	1022	15.9	87.6
Arith. mean	19.7	26.0	18.6	16.3			8.2	5.5	1015	11.8	74.7
Exceedences (medians)											
All	37.5	44.5	34.8	10.5	32/140	61/165	6.3	5.7	1019	10.1	76.3
L	18.9	23.1	16.9	6.4	0/2	0/8	9.0	5.4	1016	12.2	80.2
LR	31.5	35.1	27.9	8.5	3/24	9/37	6.3	6.1	1019	10.6	79.1
LU	14.8	32.6	21.5	9.4	0/5	0/6	5.6	5.3	1019	5.7	82.8
LUR	34.7	47.6	38.1	11.2	8/52	26/55	5.8	5.8	1020	8.2	77.4
LUR(R)	42.6	50.8	41.4	12.5	8/33	17/31	6.7	5.4	1017	8.7	73.3
LUR(o)	22.4	43.4	30.4	10.2	0/19	9/24	4.3	6.3	1023	8.1	80.8
R	42.1	46.3	37.8	11.3	9/29	10/28	7.8	5.1	1020	10.1	68.6
UR	43.9	54.8	50.7	10.5	12/28	16/28	5.3	5.4	1018	10.8	69.6

Concentrations in $\mu g\,m^{-3}$.

Table 4
Percentiles (25%, 50% (median) and 75%) of estimated local emissions, urban background and regional background contributions to PM_{10} measured at Marylebone Road from 2002 to 2004 (in $\mu g\,m^{-3}$) and the medians of the estimated secondary aerosol concentrations; inorganic (ammonium sulphate and nitrate with bound water) and total (inorganic + estimation of the secondary organic aerosol mass) in $\mu g\,m^{-3}$ and median % age

	Gravimetric PM_{10}			Secondary aerosol			
	Local incr.	Urban back.	Regional back.	$(NH_4)_2SO_4+NH_4NO_3$		$(NH_4)_2SO_4+NH_4NO_3+SOA$	
2002–2004							
Units	$\mu g\,m^{-3}$	$\mu g\,m^{-3}$	$\mu g\,m^{-3}$	$\mu g\,m^{-3}$	%	$\mu g\,m^{-3}$	%
P0.25	7	4	10	6	19	10	33
Median	13	8	15	9	29	14	45
P0.75	19	12	23	15	41	20	57
Arith. mean	14	9	18	12	32	17	47
Exceedences (medians)							
All	17	12	36	23	36	34	56
L	31	—	—	9	17	—	—
LR	24	6	29	21	35	24	42
LU	23	23	15	11	19	15	28
LUR	17	15	33	22	35	28	46
LUR(R)	14	14	41	27	42	31	49
LUR(o)	21	19	22	19	28	26	44
R	10	4	41	33	62	38	74
UR	12	13	44	36	61	43	71

The median values of the same estimated concentrations for exceedence days, all and classified, are also presented.

airmasses met another atmospheric system centred over the continent and suffered a change of direction associated with a drop of wind speed. This pattern suggests the presence of a possible polar front and likely temperature inversion over London.

The two other episodes were a spring (20 April 2002) and a summer (29 August 2002) episode associated with warm temperature, high pressure and low wind speed. Fig. 4 shows clearly that slow air masses from the mid Atlantic Ocean have crossed the rural areas of the south-western UK before arriving in London, which probably explains the absence of a regional contribution despite a low synoptic wind speed, as emissions in this region are low.

For most of these episodes, the local contribution dominated the PM_{10} concentrations and both the fine and the coarse fractions contributed to the exceedence. One of these episodes (20 April 2002) occurred a sunday and had a dominant urban background contribution and lower PM_{coarse} concentrations. The secondary aerosol contributed little to gravimetric PM_{10} concentrations measured during these episodes. In particular, low nitrate concentrations were measured and accordingly, the agreement between TEOM and gravimetric data was good; except for the episode with a dominant urban contribution (20 April 2002). The TEOM data were on average 6% lower than the gravimetric data and 3% ($\pm$9%) lower if the data for 20 April 2002 are excluded.

3.2.3. The regional episodes (R): $N = 31$

A high regional background alone was responsible for 31 episodes of exceedence of the LV. 18 of these episodes occurred in 2003. The limit value was simultaneously exceeded 9 times at Harwell (data available for 29/31 days) and the PM_{10} gravimetric concentrations measured at Harwell represented on average 76% of the PM_{10} gravimetric concentrations measured at Marylebone Road. The fine fraction of particulate matter was responsible for the exceedences. These episodes correspond to either cyclonic or anticyclonic situations and very rarely to stable anticyclonic situations (high pressure and low wind speed: two episodes). Airmasses mostly came from European areas with high NO_x or high SO_2 emissions (only two were airmasses that had stagnated over the UK) and not surprisingly, particulate sulphate and nitrate concentrations were high and constituted on average 62% ($\pm$19%) of

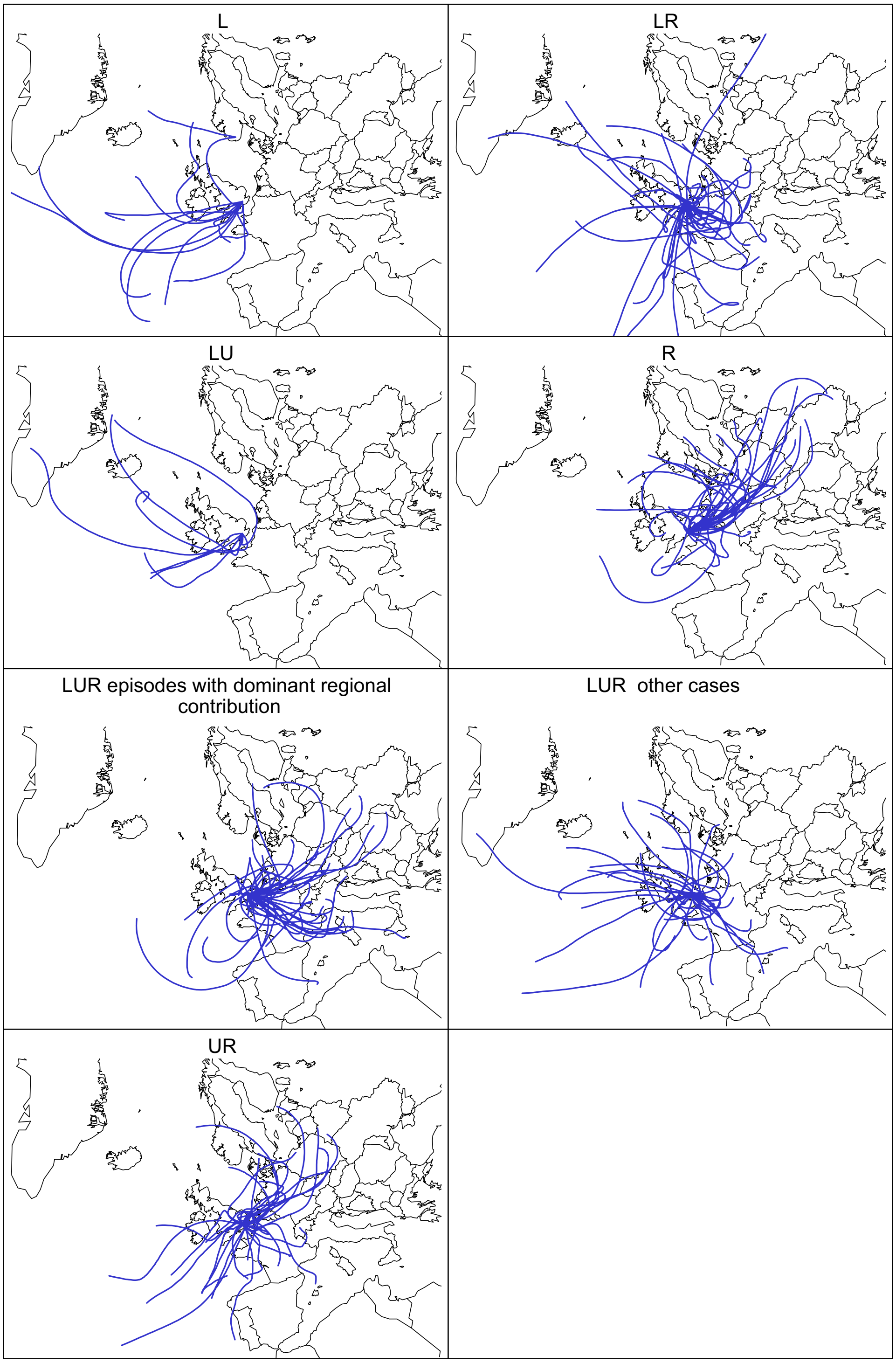


Fig. 4. Backward trajectories associated with each type of exceedence episode.

the particle mass (converted into ammonium salts). On average, 74% of the PM_{10} mass is explained by the secondary aerosol (Table 4, the secondary organic mass is included). The ammonium nitrate contributions ranged from 38% to 75% of the secondary aerosol mass.

During times of heavier traffic, the wind speed was medium or strong, which explains the absence of an urban contribution to the exceedences. Southerly vortex situations were infrequent and generally did not occur during periods with heavy traffic. Easterly winds blowing parallel to the street were more frequently observed but were associated with a strong synoptic wind speed (the wind speed seems less affected by the local topography when it blew from that direction). The agreement between PM_{10} gravimetric and TEOM data was poor showing that volatile material contributed substantially to these episodes.

3.2.4. The local and regional episodes (LR): $N = 37$

Both a high local increment and a high regional contribution were responsible for 37 PM_{10} concentrations exceeding the daily LV. 21 of them occurred in 2004 including 10 from September to December. The agreement between PM_{10} gravimetric and TEOM measurements was variable, either good or poor. Airmasses had various origins and could be classified as continental airmasses (23; mostly from France; two of them have also stagnated over the UK), fast-moving maritime air masses (5) and maritime airmasses that have stagnated before reaching London (9; some of them were associated with strong wind speed over the ocean and low wind speed over land). Similarly, these episodes were associated with various cyclonic or anticyclonic situations and only 14 of the 37 'LR' episodes were associated with stable anticyclonic conditions. While for 14 of these episodes the local and the regional contributions contributed equally to the PM_{10} concentrations, six episodes had a dominant local contribution (mostly oceanic air masses) and 17 had a dominant regional contribution. Wind directions show that a re-circulation of air inside the street (southerly vortex) during periods of heavy traffic probably contributed to the high local increment. For most of these episodes both the fine and the coarse fractions contributed to the exceedences. The coarse fraction was found to be mostly responsible for a high local increment in four episodes spread over 2004 (January, February, March, October). The contribution of ammonium sulphate and nitrate to PM_{10} concentrations was on average 35% and the secondary aerosol is estimated to be on average 46% of the PM_{10} mass.

For about half of the episodes, the high regional and local contributions did not occur simultaneously when hourly TEOM data are examined. High regional concentrations occurred during periods with little traffic (e.g., nights, sunday morning) and were often associated with a low wind speed. During periods with heavy traffic, the wind speed was much stronger and the regional contribution weaker; the enhancement due to local traffic dominated the particle mass.

High regional and local contributions were also observed simultaneously. These episodes were generally associated with strong or medium synoptic wind speed (which probably explains the absence of urban contribution). Only three episodes (end of 2004) were associated with a low synoptic wind speed (it is not clear why these episodes were not associated with a strong urban increment).

3.2.5. The urban and regional episodes (UR): $N = 31$

Thirty-one episodes of PM_{10} concentrations exceeding the daily LV were associated with high urban and regional contributions. Ten out these 31 episodes occurred on weekends. As with the episodes with high regional contribution, there was little correspondence between daily patterns of concentrations (TEOM, gases) and daily pattern of traffic. On the contrary, the agreement between $PM_{2.5}$ measured at Marylebone Road and Bloomsbury was often remarkably good.

Air masses were mostly from the continent (21/31) or were south-westerly or westerly maritime airmasses that had stagnated over the UK before reaching London (9/31). One (6 November 2004) was associated with fast-moving north-westerly airmasses that had crossed Ireland and a large part of the UK before reaching London. Twelve exceedences were measured simultaneously at Harwell.

These episodes were characterised by a low wind speed and an absence of southerly vortex situation during peak traffic times (which likely explains the weak local increment). Surprisingly, only 17 of them were associated with a stable anticyclonic situation over London. In agreement with a weak local contribution, particulate elemental carbon and NO_x concentrations were small.

The agreement between PM_{10} gravimetric and TEOM measurements was poor for all but two episodes (which occurred on 29 and 30 July 2002). PM_{10} concentrations measured by TEOM were on average 37% lower than gravimetric PM_{10} concentrations.

The dominant contribution to PM_{10} was mostly a regional one except for five episodes. Four of them had similar contributions from the urban and regional background (including 29 and 30 July 2002) and one had a dominant contribution from the urban background. Consistent with the large regional contribution, high particulate nitrate and sulphate concentrations were associated with these episodes; together converted into ammonium salts with bound water they represented on average 61% of the PM_{10} particle mass. The 'total' secondary aerosol represented on average 71% of the PM_{10} mass; with again the largest contribution from the particulate ammonium nitrate.

3.2.6. *The mix of local, urban and regional episodes (LUR): $N = 67$*

High local, urban and regional contributions were responsible for 67 exceedences of the limit value. This is the larger sub-set and not surprisingly, it is associated with the largest PM_{10} concentrations at Marylebone Road. This dataset is quite heterogeneous with various contributions from local emissions and from urban and regional backgrounds. The dominant contribution to PM_{10} was mostly regional (37/67), more rarely local or urban (respectively, 4 and 1/67). Fifteen episodes had similar contributions from local emissions and the regional background and 10 had similar contributions from the urban and the regional backgrounds.

Most of these episodes had similar characteristics. Many of them were associated with a low synoptic wind speed and/or a stable anticyclonic situation. Twelve of these episodes were not associated with a low synoptic wind speed and had a dominant contribution from the regional background. During times of heavy traffic, the LUR episodes were mostly associated with a re-circulation of air inside the street canyon (southerly vortex situation) or much less frequently, with winds blowing parallel to the street. Nevertheless, four episodes were not associated with a southerly vortex or wind blowing parallel to the street, and had a dominant contribution from the regional background.

Air masses were mostly continental (47/67 and 4 of them had also stagnated over the UK), or were maritime air masses that either had stagnated over the UK before arriving at London or that had crossed a large part of Great Britain before arriving at London (17/67). Three trajectories do not show a long pathway over land before arriving at London and the high regional background is more difficult to explain. When air masses came from the continent, the regional background often dominated the PM_{10} concentrations (see Fig. 4).

The LUR episodes could be subdivided into two sub-datasets: the LUR episodes with the largest contribution from the regional background (denoted as LUR(R), 40 episodes) and the LUR episodes with similar contributions from local, urban and regional sources (denoted as LUR(O), 27 episodes). While the first group could be characterized by air masses mostly from the continent (Fig. 4); the second group were characterized by stable conditions over London (high pressure system and slow wind speed). The secondary aerosol again contributed very substantially to these episodes: on average 49% of the PM_{10} mass for the LUR(R) episodes and on average 46% of the PM_{10} mass for the LUR(O) episodes.

4. Conclusions

The regional background was the largest contributor to PM_{10} concentrations measured at Marylebone Road between January 2002 and December 2004. Local emissions were on average the second largest contributor; both contribute in quite similar proportions (respectively, 41% and 37 %). The contribution of the regional background was much larger for most of the episodes of PM_{10} concentrations exceeding the 24 h PM_{10} LV. Very often these episodes were associated with air masses coming from mainland Europe which carried large concentrations of secondary aerosol contributing to the exceedence in addition to emissions in the UK. Particulate nitrate constituted the largest part of the secondary aerosol, especially during the spring and December 2004 episodes: some concentrations larger than $20\,\mu g\,m^{-3}$ were measured (which corresponds to a mass of $33\,\mu g\,m^{-3}$ converted into ammonium nitrate with bound water). Because the particulate nitrate is lost in the inlet of the TEOM, these episodes were not seen by the TEOM instrument.

Despite the regional character of most of the episodes, the 24 h PM_{10} LV was less frequently exceeded at urban background and rural sites (see Table 3). However, even when the gravimetric PM_{10} concentrations measured at the urban background were less than $50\,\mu g\,m^{-3}$, many exceeded $45\,\mu g\,m^{-3}$ (see North Kensington median values for LUR, R and UR episodes—i.e. 129 out the 185 episodes, in Table 3). A small contribution of local emissions was then enough to exceed the limit value of $50\,\mu g\,m^{-3}$. Since 75% of local contributions were larger than $7\,\mu g\,m^{-3}$ (see Table 4), these were sufficient to breach the limit value of $50\,\mu g\,m^{-3}$ during regional episodes.

The numerical modelling studies of Abdalmogith et al. (2006) reveal that a substantial proportion of the inorganic secondary aerosol at UK sites derives from precursor emissions in mainland Europe. All these findings suggest that international reduction of emissions responsible for the regional secondary aerosol (SO_2, NO_x, VOCs) will be the most effective path to compliance with the European Directive.

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