

# A large reduction in airborne particle number concentrations at the time of the introduction of “sulphur free” diesel and the London Low Emission Zone

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## ABSTRACT

Hourly measurements of airborne particle number concentration (a metric dominated by ultrafine particles) at two sites in London and a site in Birmingham show that over a period of a few months in late 2007 concentrations were reduced by between 30 and 59%. At the London kerbside site particle number emissions from vehicles were reduced by 65% compared to emissions of NO<sub>x</sub>. These reductions occurred at the same time as the introduction of “sulphur free” diesel fuel and the London Low Emission Zone for heavy goods vehicles, and in view of the reduction in Birmingham and the limited change in vehicle technologies at that time, is probably primarily due to the change in fuel sulphur. There is an absence of any similar reduction in the concentration of the regulated air quality mass metrics which may provide an opportunity for further evaluating the effects of ultrafine particle concentrations on human health.

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## 1. Introduction

Although the mass of airborne particulate matter in the ambient atmosphere is subject to regulation, there continues to be debate about which constituents, or which size fractions, of the particulate matter have the most significant effect on human health. In common with other countries, the particulate metrics regulated in the United Kingdom (UK) are PM<sub>10</sub> and PM<sub>2.5</sub> - the masses of particles per unit volume of air with aerodynamic diameters respectively less than 10 μm and 2.5 μm (SI, 2010). It has frequently been proposed (e.g. Seaton et al., 1995; Delfino et al., 2005) that ultrafine particles have a more significant effect on human health per unit mass of similar chemical composition than larger particles, and that the number of particles in the atmosphere, which is dominated by these smaller particles, is therefore a better measure of particulate pollution than PM<sub>10</sub> or PM<sub>2.5</sub>. Several different mechanisms by which ultrafine particles may affect human health have been proposed, with a wide consensus that these particles may cause respiratory inflammation with subsequent thrombotic effects (Knol et al., 2009).

In the UK, the Department for Environment, Food and Rural Affairs (DEFRA) has sponsored the monitoring of the ambient

airborne particle number concentration on an hourly basis by the Airborne Particulate Concentrations and Numbers Network (APCNN) at a small number of sites since 2001. Particle number concentration data from the network during the earlier period of its operation were reported previously (Harrison and Jones, 2005). Improvements in operational practice were introduced in 2005, and a rationalisation of the network took place in 2007 (NPL, 2008), resulting in consistently measured data being available from kerbside and urban background sites in London from mid 2005, and from an urban centre site in Birmingham between mid 2005 and early 2009.

During the period since 2005 there are two known changes to road transport operations which may have resulted in changes to particulate emissions from vehicles.

(i) Legislation enacted in June 2007 (SI, 2007) required that diesel and super-unleaded petrol sold by retailers in the UK for use in highway vehicles from sites selling in excess of  $3 \times 10^6$  L yr<sup>-1</sup> should be “sulphur free” (less than 10 ppm sulphur) (TRL, 2009) from 4 December 2007, with all UK highway vehicle fuel being “sulphur free” by 1 January 2009. Previously the use of “ultra-low sulphur” (less than 50 ppm sulphur) diesel and petrol was required for highway vehicles in the United Kingdom, since 1999 and 2001 respectively for the two fuels. Annual fuel sales figures show that no diesel fuel sold in the UK was “sulphur free” in 2006 (AEA, 2008), while in 2007 59.7% of diesel sold was “sulphur free” (AEA, 2009, p. 166). In a review of tests on the effects of fuel properties on road vehicle emissions (TRL, 2009) it was suggested that there was

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unlikely to be a substantial reduction in particulate emissions for Euro III and Euro IV vehicles as a result of reducing the sulphur content of fuel from 50 ppm to less than 10 ppm, but that there may be a reduction of particulate mass emissions from older petrol vehicles. In measurements of particle number concentrations at a kerbside site in Copenhagen, Wahlin (2009) found the numbers of particles in the 6–700 nm size range were reduced by 27% when “sulphur free” diesel was rapidly introduced in Denmark in 2005, predominantly affecting particles with diameters around 15 nm, but with no significant change in particle mass. This reduction in particle number concentration was in addition to that previously noted in Denmark after a reduction in the sulphur content of diesel fuel from approximately 500 ppm to less than 50 ppm (Wahlin et al., 2001). In the United States, Johnson et al. (2009) observed a reduction by a factor of three in the particle number emissions per mass of fuel burned by free flowing traffic ( $85\text{--}96\text{ km h}^{-1}$ ) when the sulphur content of the diesel fuel was reduced from 33 ppm to 8 ppm Wang et al. (2011) have recently reported a decrease in number concentrations of particles in the 10–50 nm and 50–100 nm diameter size ranges between 2007 and 2009 in Rochester, New York, attributable in part to a reduction of the sulphur content of highway diesel fuel.

Maricq (2007) reviewed the emission of particulate matter from diesel engines, including the effects of differing fuel sulphur contents, noting that in the case of heavy duty diesel engines the fine particulate matter emitted was dominated by unburnt lubrication oil, which while it may contain sulphur, was generally organic, and the sulphur content of the fuel had little effect on the particle number concentration. In the case of light duty diesel engines, two aspects of the operation of a catalyst can affect sulphate emissions (Du and Yu, 2008). The presence of sulphur in the fuel will give rise to the production of sulphur dioxide ( $\text{SO}_2$ ) during combustion, which is then oxidised to  $\text{SO}_3$  by the catalyst, eventually forming particulate sulphate (Maricq et al., 2002a; Maricq, 2007; Zhao et al., 2010; Du and Yu, 2008). Significant concentrations of particulate sulphate are not observed if no catalyst is present, or if the sulphur content of the fuel is less than 15 ppm (Du and Yu, 2008). The effectiveness of the process is dependent upon the operating conditions of the catalyst, with higher concentrations of sulphate being produced at higher catalyst operating temperatures, when the engine is operating at high speed or under load (Zhao et al., 2010). Sulphate emissions may also be affected by the deposition of sulphur within the exhaust system when the engine is running cold which may be released at a later time when the system is hotter (Du and Yu, 2008). In the case of gasoline engines there is little change in particle number concentration due to changes in sulphur content because there is very little oxygen in the exhaust and  $\text{SO}_2$  is therefore not oxidised to  $\text{SO}_3$  by any catalyst present (Maricq et al., 2002b).

(ii) The London Low Emission Zone (LEZ), which covers the area of Greater London, was confirmed in May 2007 (GLA, 2007), and was enforced for heavy goods vehicles (HGVs) greater than 12 tonnes from February 2008, and for other goods vehicles, buses and coaches greater than 3.5 tonnes from July 2008. The London LEZ applies to vehicles using diesel and biodiesel fuels, and requires HGVs to comply with EURO III emission standard for particulate matter, or better. The EURO III standard for HGVs does not require the fitting of a particle trap. However, for pre-EURO III vehicles, the most cost-effective form of compliance is likely to have been the retro-fitting of a particle trap.

Compliance rate data indicate that for HGVs greater than 12 tonnes, between February 2007 and August 2009 around 23% of these vehicles changed from non-compliance to EURO IV compliant. For HGVs of 3.5–12 tonnes, the approximately 39% non-compliant vehicles in February 2007 had mostly (35%)

become EURO III or EURO IV compliant by August 2009. In the case of buses, most vehicles (mainly operated on behalf of London Buses) complied with EURO IV in February 2007, with non-compliant vehicles converting to EURO III or EURO IV by March 2009. About 1% of the entire vehicle fleet changed due to the introduction of the LEZ over the analysis period (2007–2009), amounting to approximately 600 HGVs per day. Traffic volumes did not change significantly over the period.

Heavy duty diesel vehicles are generally found to emit about 20 times more particles per vehicle mile than light duty vehicles (Wang et al., 2010), with emissions dominated by unburnt lubrication oil (Maricq, 2007). Earlier measurements made at the London kerbside site used in this paper showed average particle number emissions per vehicle to be 10 times greater for heavy duty diesel vehicles than diesel and gasoline powered light duty vehicles (Jones and Harrison, 2006).

This paper examines the changes in particle number concentration at three sites in the UK over the period of the introduction of “sulphur free” diesel and the enforcement of the London LEZ in comparison with the concentrations of other air quality metrics.

### 1.1. Sites and instrumentation

The sites used in the APCNN for the measurement of particle number concentration were collocated with a number of UK Automated Urban and Rural Network (AURN) sites at which the regulated air pollution metrics are monitored. Particle number concentrations were measured by TSI Type 3022A Condensation Particle Counters which detect all particles with diameters greater than 15 nm, with a minimum detectable particle diameter of 3 nm. Detection efficiency is 50% at 7 nm diameter. The instrument can record particle concentrations of up to  $10^7\text{ cm}^{-3}$  with an accuracy of 20%. At higher number concentrations, vapour depletion can lead to an increase in the lower cut-point size (Harrison and Jones, 2005). The instruments were serviced and calibrated annually. Minor changes in operational practice were made in 2005 to allow for any drift in instrument sensitivity between calibrations to be accounted for, and the entry flow rate of the instruments was increased to reduce possible entry losses. Data is verified and released annually (e.g. NPL, 2010).

A review of sites resulted in the discontinuation of measurements at the original urban and industrial sites at Glasgow, Belfast, Manchester and Port Talbot in 2007, and the commencement of measurements at the rural site at Harwell. An urban centre site at Birmingham was closed in January 2009, due to urban redevelopment. Taking account of the changes in the network, consistently monitored particle number concentrations are available from the Marylebone Road (roadside) and North Kensington (urban background) sites in London since the summer of 2005, and from the Birmingham Centre (urban centre) site between September 2005 and January 2009.

The Marylebone Road monitoring site is located on the south side of a major highway in a street canyon in central London, where traffic volumes are typically around 80,000 vehicles per day. A light controlled pedestrian crossing some 70 m to the west, and a signal controlled junction some 200 m to the west (Fig. 1a), can result in queues of west bound traffic alongside the sampling position, particularly in the late afternoon and evening. The North Kensington monitoring site is within the grounds of a school in a residential suburb of London approximately 4 km west of the Marylebone Road site. There is a lightly trafficked residential road immediately to the east (Fig. 1b). The Birmingham Centre monitoring site was located adjacent to a car park and pedestrianised plaza (Fig. 1c). The main highway route through central Birmingham enters a naturally ventilated tunnel 200 m to the south east of

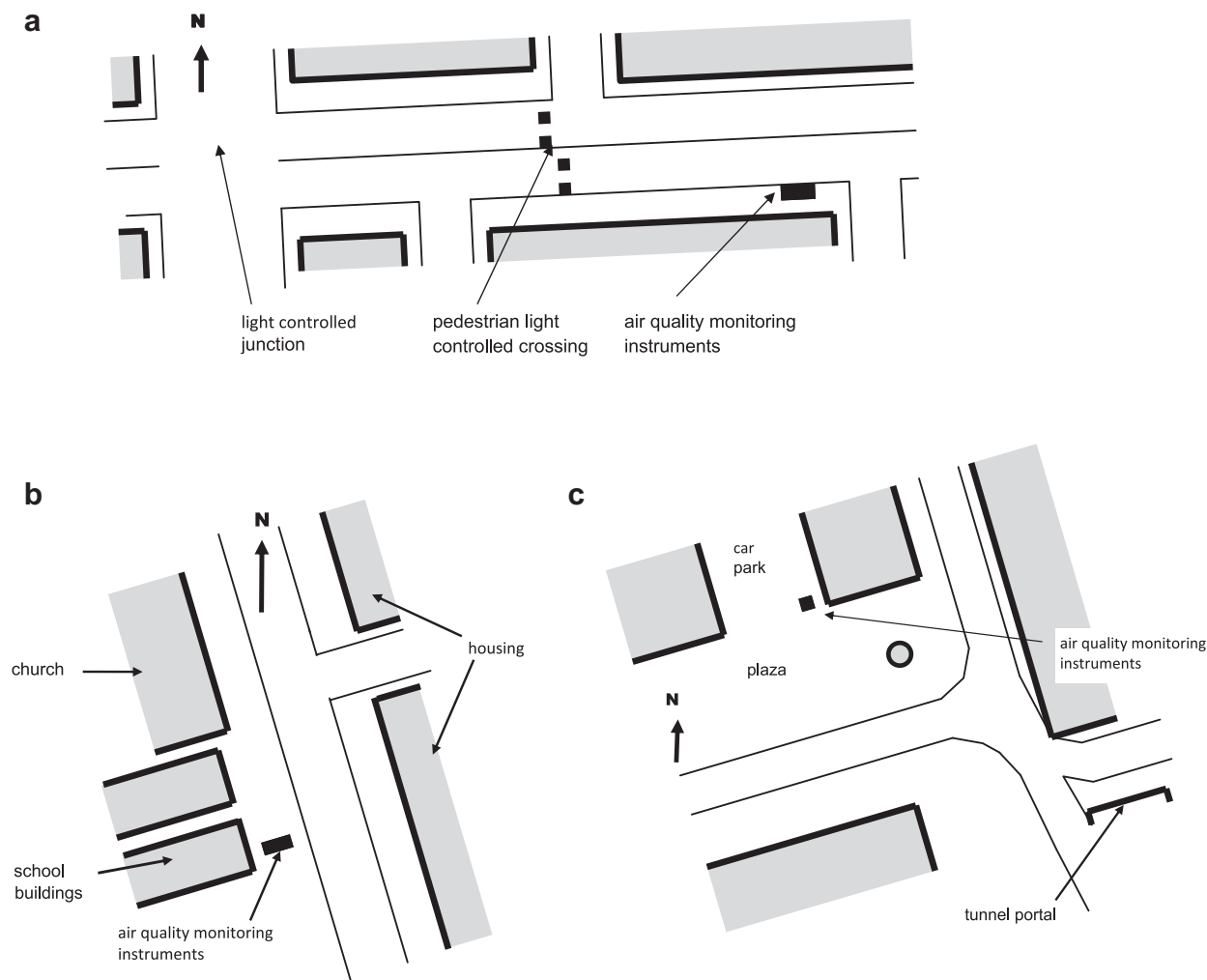


Fig. 1. Site location: (a) Marylebone Road; (b) North Kensington; (c) Birmingham Centre.

the site, where there is also a road junction above the tunnel portal, while the main railway station in Birmingham is located some 400 m to the east south east. The locations of all sites are listed in Table 1.

At the co-located AURN sites hourly values of the concentrations of oxides of nitrogen ( $\text{NO}_x$ ) are measured by chemiluminescent methods, while sulphur dioxide ( $\text{SO}_2$ ) measured by UV fluorescence and carbon monoxide (CO) measured by IR absorption are available throughout the period at Marylebone Road and North Kensington. During the period of measurement the method of  $\text{PM}_{10}$  monitoring was changed within the AURN with FDMS-TEOM instruments being installed at Birmingham in March 2007, and at Marylebone Road and North Kensington in March 2009, following an earlier change to the method of adjusting data for volatile losses. These operational changes make it more difficult to identify actual

changes in airborne particulate matter mass in the AURN data. However, consistent non-volatile  $\text{PM}_{10}$  data measured by Type 1400 TEOMs, operated in accordance with the supplier's original calibration with Arizona Road Dust (ARD) (Patashnick and Rupprecht, 1991), were available throughout the period from the London Air Quality Network for both the Marylebone Road and North Kensington sites.

Particle size spectra data measured by scanning mobility particle sizer (SMPS) are available for the sites at Marylebone Road and North Kensington. Up until March 2006 measurements in the APCNN were made by TSI Model 3071 instruments which were developing serious problems and would no longer be supported by the supplier (NPL, 2007). These instruments were replaced in March 2007 by TSI Model 3936L75 instruments. Operational problems were experienced with the new instrument at Marylebone Road during 2008 with higher than expected concentrations of small particles being measured after the instrument had been serviced by the supplier (NPL, 2009), after which operational changes were made to improve the reliability of SMPS data (NPL, 2010). As a result of the operational difficulties consistent size spectra data is not available over the 2005 to 2010 period, although the monthly mean size spectra in late 2007 do provide useful qualitative information.

Daily sulphate ion concentration data (measured by ion chromatography on daily filters) are available from the APCNN for the

**Table 1**  
Sites - Descriptions and locations.

Site name	Site type	Longitude (degrees)	Latitude (degrees)
Marylebone Road	kerbside	-0.1548	51.5227
North Kensington	urban background	-0.2129	51.5215
Birmingham Centre	urban centre	-1.9078	52.4789
Heathrow	meteorological	-0.4490	51.4787
Colehill	meteorological	-1.6892	52.4798

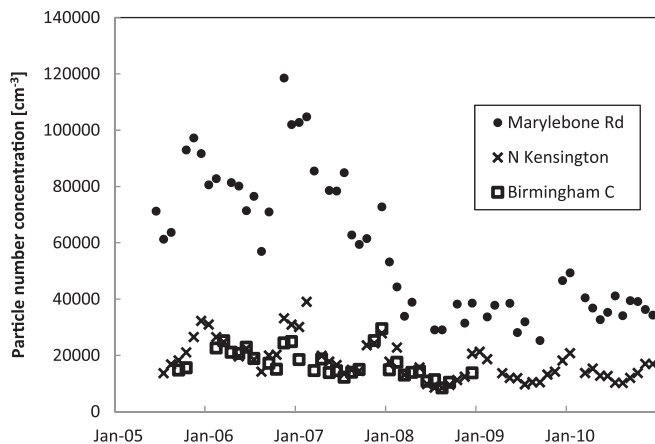


Fig. 2. Monthly mean particle number concentration at three sites.

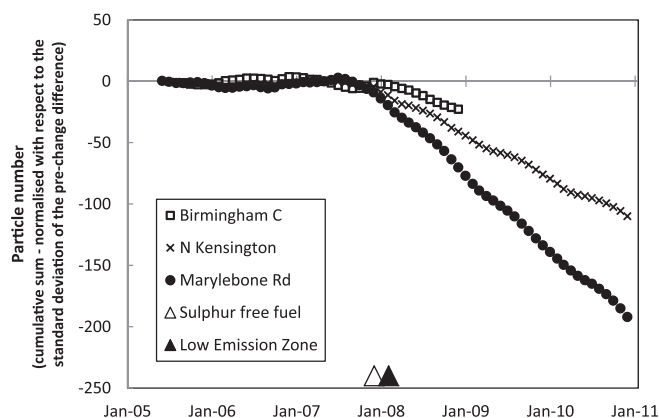


Fig. 3. Normalised monthly cumulative sums of particle number concentration difference. Triangles indicate the introduction of sulphur-free diesel and the LEZ respectively.

Marylebone Road and North Kensington sites. Daily black smoke data are available for the Marylebone Road site from January 2006 to December 2009.

Analysis of data from the London sites was carried out using meteorological data from Heathrow, while meteorological data from Colleshill was used in relation to the Birmingham sites. Manning et al. (2000) found that wind direction data measured within 40 km from a sampling site (as is the case here) was generally representative of wind directions at the sampling site. The locations of the meteorological sites are also given in Table 1.

## 2. Results

### 2.1. Change in particle number concentrations with time

The hourly values of particle number concentration were used to calculate daily mean values of concentration at the Marylebone Road, North Kensington and Birmingham Centre sites for all days

where there were more than 12 h of data between June 2005 and December 2010. These daily mean values were then used to calculate monthly means for those months where there were more than 15 days of data. The monthly mean concentrations for each of the sites are shown in Fig. 2. A large reduction in particle number concentrations is apparent at the Marylebone Road site over the 2007 – early 2008 period. A reduction is also seen in the data for North Kensington, and may occur in the Birmingham data, although the latter is not so apparent due to the early termination of data from this site, and the seasonal variability of the data, which is apparent at all three sites.

The cumulative sum technique has been used by others (Carslaw et al., 2006; Barratt et al., 2007) to identify change points in ambient air pollution concentrations. This technique enables the occurrence of a stepped change in concentration to be identified by assessing the accumulated sum of the monthly differences between the post-change values and the mean pre-change value, or values predicted from the pre-change values. In this work, missing monthly mean concentration values were first derived by linear interpolation between the mean concentrations of the preceding and subsequent months. The cumulative sums of the differences between the monthly mean concentrations and a predicted concentration were calculated for particle number concentration at the Marylebone Road, North Kensington and Birmingham sites. These were normalised by the standard deviation of these differences during the June 2005 to May 2007 period.

The predicted concentrations were obtained by fitting a sinusoidal curve to the June 2005 to May 2007 data where there was a clear seasonal cycle of concentration (Marylebone Road and North Kensington sites), or taking the mean concentration of the June 2005 to May 2007 data where there was no clear seasonal cycle (Birmingham Centre site), and extrapolating over the whole period. The failure to fit a sinusoidal curve to the Birmingham data may in part be a result of the interpolation technique failing to represent the maxima in concentrations apparent at the other sites in the period of missing data between November 2005 and January 2006. The cumulative sums are plotted against time in Fig. 3. A major change point in the normalised cumulative sum plot for particle number concentration at Marylebone Road is notable in the latter part of 2007, with similarly timed, although smaller, changes in the North Kensington and Birmingham Centre data. The change is not associated with a particular month, but instead appears to occur over a number of months in late 2007. The difference between the slopes of the North Kensington and Birmingham Centre data after the change point in Fig. 3 is not significant, and is the effect of calculating the cumulative sum of the difference from a sinusoidally fitted curve for the North Kensington data, rather than from the mean of the concentration in the pre-change period as was done for the Birmingham Centre data.

### 2.2. Difference in the mean concentrations over multiple twelve month periods before and after late 2007

From examination of Fig. 3, the period October 2005 to September 2007 was taken as being representative of an integral

Table 2  
Particle number concentrations in the periods before and after the rapid change in concentration in late 2007.

Site	Before: Oct 2005–Sep 2007			After: Feb 2008–Jan 2009			Ratio After/Before
	Mean (cm <sup>-3</sup> )	Std err (cm <sup>-3</sup> )	% data	Mean (cm <sup>-3</sup> )	Std err (cm <sup>-3</sup> )	% data	
Marylebone Road	83,400	404	80.6	34,400	266	59.2	0.41
North Kensington	23,400	109	89.3	14,300	102	87.9	0.61
Birmingham Centre	18,600	121	78.5	12,900	105	71.8	0.70

number of years immediately before the change. The period February 2008 to January 2009 was taken as being representative of an integral number of years after the change, which is after the dates of enforcement of the sale of “sulphur free” diesel from all but the smallest retailers and the London LEZ on HGVs over 12 tonnes gross weight, and includes the maximum amount of data available before the closure of the Birmingham Centre site. The means of all available hourly particle number concentrations measured at each of the sites during these periods are presented in Table 2. Significant reductions of between 30% and 59% are apparent in the mean particle number concentrations between both periods. The ranking of sites in terms of particle number concentration is the same in both periods. While there is a considerable loss of data at Marylebone Road during the second period, the occasions of data loss are spread throughout the year, and the reduction in the mean is not likely to be due to seasonal effects.

### 3. Discussion

#### 3.1. Comparison with other air quality metrics – normalised cumulative sums

Normalised cumulative sum of difference charts of non-volatile  $PM_{10}$  measured with TEOM (ARD) monitors at Marylebone Road and North Kensington;  $NO_x$  at Marylebone Road, North Kensington and Birmingham Centre;  $SO_2$  and black smoke measured at Marylebone Road; and particulate sulphate measured at Marylebone Road and North Kensington, are shown in Fig. 4(a–c). In the case of non-volatile  $PM_{10}$ , which did not have any significant seasonal trend, and  $SO_2$ , black smoke and particulate sulphate, the difference is calculated from the mean value during the June 2005 to May 2007 period.  $NO_x$  concentrations varied seasonally at all three sites and the difference was calculated from the seasonal trend fitted over the June 2005 to May 2007 period. The plots for non-volatile  $PM_{10}$  (Fig. 4a) show a change at North Kensington from late 2007, and a change at Marylebone Road from late 2009. Changes in the data for  $NO_x$  are small, although there is some evidence of a small reduction in  $NO_x$  concentration at North Kensington from 2008 onwards (Fig. 4b).  $NO_x$  concentrations show no significant change at the same time as the change seen in the particle number concentrations at the Marylebone Road and Birmingham sites. Similarly, there were only small changes in  $SO_2$  and black smoke concentrations at Marylebone Road (Fig. 4c). There was a substantial progressive change in sulphate concentration, commencing in mid 2008, at the three sites at which it was measured, which is similar to the timing of the change in non-volatile  $PM_{10}$  at North Kensington.

#### 3.2. Comparison with other air quality metrics – mean concentrations

The mean values of the other air quality metrics measured over the periods before (October 2005 to September 2007), and after (February 2008 to January 2009), the change in particle number concentration are presented in Table 3. In a number of cases the difference is greater than 10% and more than twice the sum of the standard errors (e.g.  $NO_x$ ,  $SO_2$  and sulphate at North Kensington, CO at Marylebone Road), but the reduction is smaller than that seen in the particle number concentration. The change in CO at Marylebone Road appears to occur around a three month period in 2006 when data was not available due to a logger fault (AEA, 2007), after which a change of equipment may have resulted in a difference in the noise levels of the CO measurements.

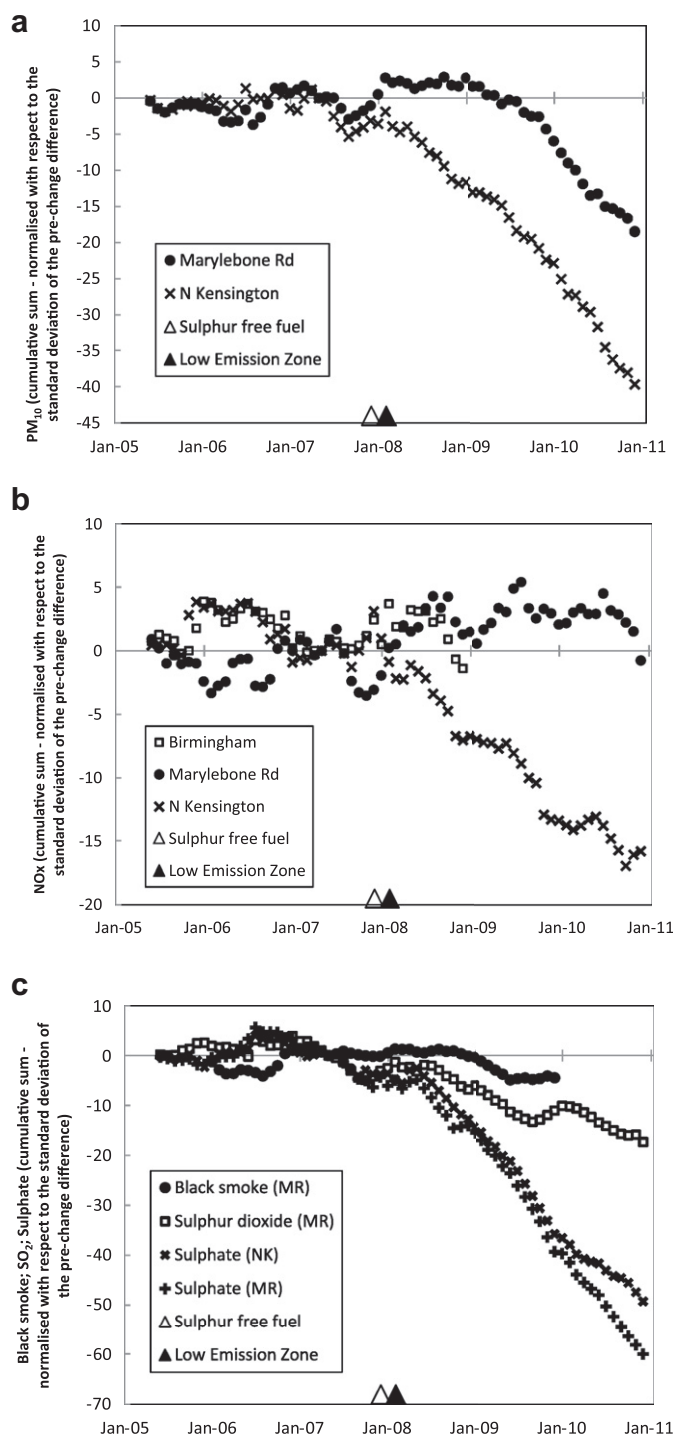


Fig. 4. Normalised monthly cumulative sums of the concentration difference of other metrics: (a) non-volatile  $PM_{10}$  (ARD); (b)  $NO_x$ ; (c)  $SO_2$ , black smoke and sulphate. Triangles indicate the introduction of sulphur-free diesel and the LEZ respectively.

#### 3.3. Ratios of the concentrations of different metrics to $NO_x$ at various wind directions

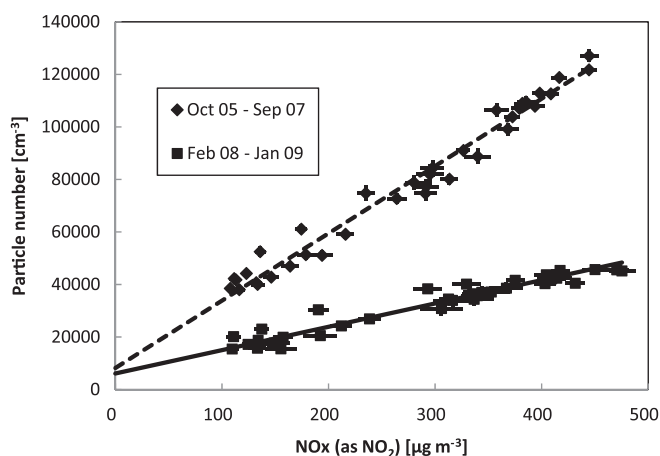
##### 3.3.1. Marylebone Road

At the Marylebone Road site the concentrations of air quality metrics associated with vehicle exhaust are highly non-isotropic, with the highest concentrations occurring when the wind is from the west and concentrations are influenced by traffic at the nearby

**Table 3**

The concentrations of other metrics in the periods before and after the rapid change in particle number concentration in late 2007.

Metric	Site	Before: Oct 2005–Sep 2007			After: Feb 2008–Jan 2009			Ratio After/Before
		Mean	Std err	% data	Mean	Std err	% data	
NO <sub>x</sub> (μg m <sup>-3</sup> )	Marylebone Road	291.1	1.6	97.9	309.3	2.3	99.0	1.06
	North Kensington	61.9	0.6	99.3	53.2	0.6	90.3	0.86
	Birmingham Centre	54.4	0.5	94.3	52.4	0.7	91.5	0.96
PM <sub>10</sub> (ARD) (μg m <sup>-3</sup> )	Marylebone Road	34.8	0.1	97.4	35.8	0.2	95.4	1.03
	North Kensington	19.4	0.1	98.9	18.1	0.1	98.7	0.93
CO (mg m <sup>-3</sup> )	Marylebone Road	0.91	0.004	81.2	0.71	0.004	97.9	0.78
	North Kensington	0.30	0.002	97.3	0.30	0.002	98.1	0.0
	Birmingham Centre	0.35	0.002	93.8	not available			
SO <sub>2</sub> (μg m <sup>-3</sup> )	Marylebone Road	7.23	0.05	94.7	6.93	0.07	93.3	0.96
	North Kensington	3.29	0.04	97.6	2.81	0.04	97.8	0.85
	Birmingham Centre	3.50	0.03	90.5	not available			
Black smoke (μg m <sup>-3</sup> )	Marylebone Road	40.9	1.0	74.7	38.7	1.01	99.2	0.95
Sulphate (μg m <sup>-3</sup> )	Marylebone Road	3.51	0.11	89.3	3.03	0.14	85.2	0.86
	North Kensington	3.09	0.09	96.0	2.51	0.11	95.4	0.81

**Fig. 5.** Marylebone Road - particle number v NO<sub>x</sub> at 10<sup>0</sup> wind sectors.

Heathrow airport site are not likely to be affected by local buildings, and as Marylebone Road and Heathrow are no more than 22 km apart, the wind direction at Heathrow is likely to be representative of the wind direction at Marylebone Road at heights above the influence of local buildings.

The mean values of particle number concentration are plotted against NO<sub>x</sub> concentration for each 10<sup>0</sup> degree wind sector at Marylebone Road for the before and after periods in Fig. 5. Error bars show the standard error of the mean value for each 10<sup>0</sup> wind sector. As there is uncertainty in both variables lines are fitted according to the standardised (or reduced) major axis convention (Ayers, 2001; Warton et al., 2006). The coefficients of the fitted lines are presented in Table 4.

A large and significant difference is apparent (Fig. 5) at Marylebone Road in the relationship between particle number and NO<sub>x</sub> concentrations for the two periods. The predicted values of particle number concentration at zero NO<sub>x</sub> are not significantly different as the sum of the standard errors in the intercepts are small compared to the difference of the intercepts (Table 4). Conversely, the difference in gradients is significant with a large difference compared to the sum of the standard errors. As the effect of sorting the data by wind direction at the kerbside site is to select data by differing degrees of vehicle influence, the difference in gradient between the two periods can be ascribed to a change in the relationship between particle number concentration and NO<sub>x</sub> in vehicle exhaust between the two periods. The intercept indicates the particle number concentration that would be measured in the absence of any particulate matter associated with the emission of NO<sub>x</sub>.

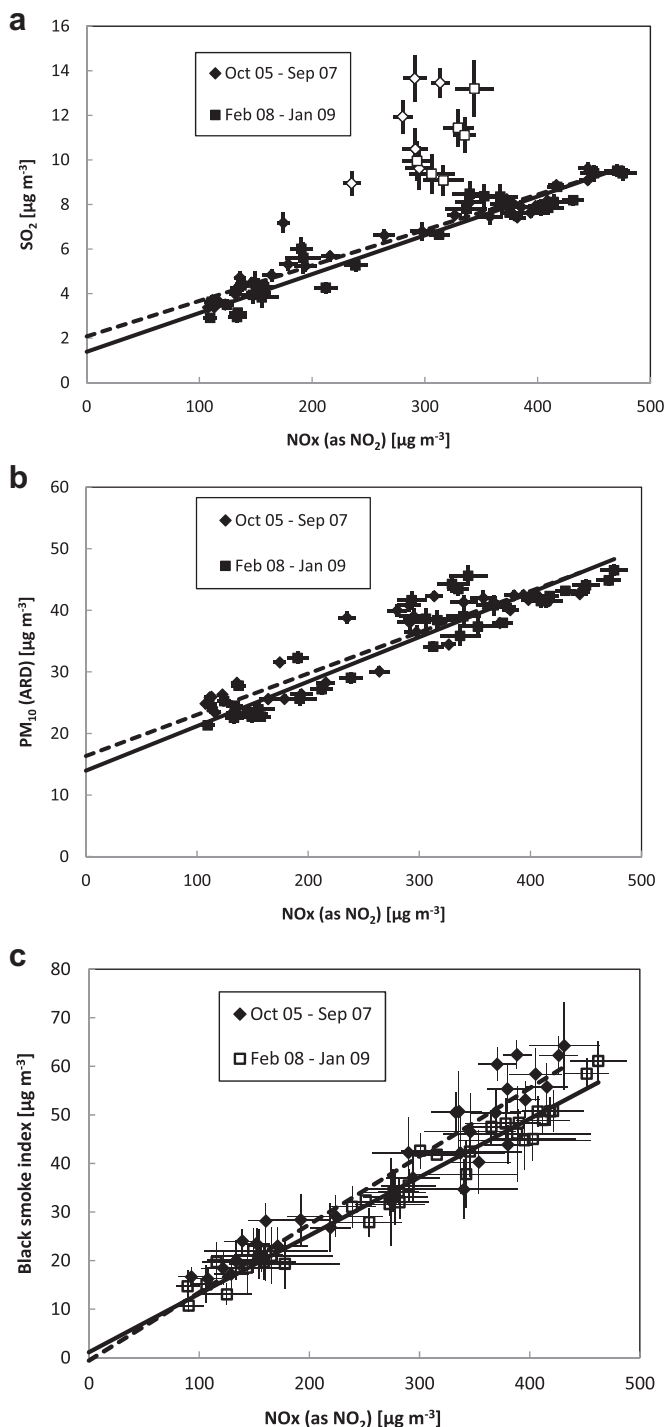
Similar graphs of wind direction-sorted sulphur dioxide, non-volatile PM<sub>10</sub> (ARD), and daily black smoke index, plotted against oxides of nitrogen, are shown in Fig. 6a–c. The coefficients of the fitted lines for these and CO are also presented in Table 4. As

road junction, or from the south and concentrations are influenced by emissions carried from the adjacent road by the airflow rotating in the street canyon (Jones and Harrison, 2005). Elevated concentrations also occur at both the Marylebone Road and North Kensington sites when the wind is from the east, and wind speeds are generally lower, the atmosphere is more stable, and air pollution may be advected from continental sources. Sorting the Marylebone Road data by wind direction has the effect of separating the data into sets with a range of differing relative traffic influences.

Hourly NO<sub>x</sub> and particle number concentration data were sorted into 10<sup>0</sup> sectors by the hourly wind direction data from Heathrow for the periods before and after the change in particle number concentrations. Wind direction measurements made at the

**Table 4**Coefficients of the lines fitted to the relationships between the concentrations of various metrics and NO<sub>x</sub> at Marylebone Road in the periods before and after the rapid change in particle number concentration in late 2007.

Metric	Period	r <sup>2</sup>	Gradient	Std err gradient	Intercept	Std err intercept	Ratio of gradients
Particle number (cm <sup>-3</sup> )	Oct 05–Sep 07	0.98	256.2	6.9	8236	2020	2.89
	Feb 08–Jan 09	0.94	88.8	3.9	6124	1188	
CO (mg m <sup>-3</sup> )	Oct 05–Sep 07	0.96	0.00185	0.00006	0.378	0.018	1.13
	Feb 08–Jan 09	0.98	0.00163	0.00004	0.208	0.012	
SO <sub>2</sub> (μg m <sup>-3</sup> )	Oct 05–Sep 07	0.92	0.0159	0.0009	2.078	0.259	0.91
	Feb 08–Jan 09	0.93	0.0174	0.0009	1.391	0.260	
PM <sub>10</sub> (ARD) (μg m <sup>-3</sup> )	Oct 05–Sep 07	0.86	0.0669	0.0045	16.34	1.30	0.92
	Feb 08–Jan 09	0.88	0.0723	0.0043	13.96	1.30	
Black smoke (μg m <sup>-3</sup> )	Oct 05–Sep 07	0.90	0.1402	0.0076	-0.582	2.224	1.17
	Feb 08–Jan 09	0.97	0.1202	0.0039	1.134	1.164	



**Fig. 6.** Marylebone Road - other metrics v  $\text{NO}_x$  at  $10^\circ$  wind sectors: (a)  $\text{SO}_2$ ; (b) non-volatile  $\text{PM}_{10}$  (ARD); (c) black smoke.

can be seen from the values of the standard errors of the coefficients in Table 4, only the relationship between CO and  $\text{NO}_x$  differs significantly between the two periods. This difference is constant across all wind directions and is therefore not related to the differing traffic influence at different wind directions. As noted above, the major change in CO concentrations occurred over a three month period in 2006 when the instrument was non-operational, and the similarity of the effect at all wind directions may indicate that this difference in concentration is probably due to an instrumentation effect. In the case of  $\text{SO}_2$ , data relating to wind directions

between  $65^\circ$  and  $125^\circ$  which are higher than the general trend in  $\text{SO}_2$  concentrations (shown by open symbols in Fig. 6a), were excluded as these directions are likely to be affected by electricity generating plants around the Thames Estuary. The non-volatile  $\text{PM}_{10}$  (Fig. 6b) shows some evidence of a dependence of ratio upon wind direction with relatively higher  $\text{PM}_{10}$  compared to  $\text{NO}_x$  at wind directions between  $20^\circ$  and  $120^\circ$ . While the difference between the gradients (Fig. 6c) of the black smoke to  $\text{NO}_x$  relationship during the two periods is greater than for other metrics (other than particle number) the significance of the difference is small (Table 4). The standard errors are larger due to the smaller quantity of daily data. No relationship was found between the concentration of particulate sulphate when sorted by wind direction and  $\text{NO}_x$  concentration. Particulate sulphate is dominated by higher concentrations when the wind direction was from the east, and unlike the metrics associated with traffic exhaust, concentrations at Marylebone Road are not higher in southerly and westerly wind directions.

### 3.3.2. North Kensington

The relationships between particle number concentration and  $\text{NO}_x$  concentration at North Kensington, sorted by wind direction, for the before and after periods were calculated according to the standardised (or reduced) major axis convention and the coefficients are presented in Table 5 (see also supplementary information, Fig. S1a). In contrast to Marylebone Road, at North Kensington there is no significant difference in the gradient of the particle number versus  $\text{NO}_x$  relationship between the two periods, but the difference between the intercepts is significant. This can be ascribed to the North Kensington site having no nearby major traffic movements, with traffic emissions being dominated by a more isotropic array of distant sources. However, why the change in traffic particle number: $\text{NO}_x$  ratio is manifest as a change in intercept, rather than gradient at this site is a matter of conjecture.

The equivalent relationships between wind direction-sorted carbon monoxide, sulphur dioxide, and non-volatile  $\text{PM}_{10}$  (ARD) with regard to  $\text{NO}_x$  were examined and the coefficients of the fitted lines are also presented in Table 5 (see also Fig. S1b–d). Less than one year of black smoke data was available at North Kensington during the period prior to the change in particle number concentration so no comparison of black smoke data is made here as it is not possible to account for any seasonal effects. Unlike the Marylebone Road data, there is no significant difference in the intercept of the CO to  $\text{NO}_x$  relationship supporting the conclusion that the result at Marylebone Road is an instrumental effect, rather than a change in the background concentrations of CO across London in general. The  $\text{SO}_2$  data relating to wind directions between  $65^\circ$  and  $125^\circ$  is again influenced by the Thames Estuary electricity generating stations, and as at Marylebone Road, this data was excluded from the analysis. The absolute enhancement in the  $\text{SO}_2$  concentration at these wind directions above the general relationship with  $\text{NO}_x$  is similar at North Kensington to that at Marylebone Road. There is no significant difference between the relationships of non-volatile  $\text{PM}_{10}$  and  $\text{NO}_x$  for the two periods. Both periods show a bifurcated relationship with  $\text{PM}_{10}$  concentrations being relatively greater compared to  $\text{NO}_x$  in easterly winds (Fig. S1d). Correlations are generally poorer than at Marylebone Road for all these additional metrics.

### 3.3.3. Birmingham Centre

The coefficients of the relationships between particle number concentration and  $\text{NO}_x$  concentration for each  $10^\circ$  degree wind sector (measured at Colleshill) at Birmingham Centre for the before and after periods were calculated according to the standardised (or reduced) major axis convention and are presented in Table 6. As in

**Table 5**  
Coefficients of the lines fitted to the relationships between the concentrations of various metrics and NO<sub>x</sub> at North Kensington in the periods before and after the rapid change in particle number concentration in late 2007.

Metric	Period	r <sup>2</sup>	Gradient	Std err gradient	Intercept	Std err intercept	Ratio of gradients
Particle number (cm <sup>-3</sup> )	Oct 05–Sep 07	0.53	188.2	23.8	11,964	1645	1.08
	Feb 08–Jan 09	0.66	174.9	18.3	4640	1101	
CO (mg m <sup>-3</sup> )	Oct 05–Sep 07	0.76	0.00235	0.00020	0.156	0.014	0.91
	Feb 08–Jan 09	0.65	0.00257	0.00028	0.165	0.014	
SO <sub>2</sub> (μg m <sup>-3</sup> )	Oct 05–Sep 07	0.64	0.0298	0.0035	1.19	0.23	0.88
	Feb 08–Jan 09	0.19	0.0338	0.0067	0.73	0.38	
PM <sub>10</sub> (ARD) (μg m <sup>-3</sup> )	Oct 05–Sep 07	0.42	0.166	0.024	9.50	1.65	0.72
	Feb 08–Jan 09	0.57	0.230	0.027	5.48	1.66	

the case of Marylebone Road, there is a significant difference in the gradients of the relationship between particle number and NO<sub>x</sub> concentrations between the two periods, but no significant difference between the intercepts, which are similar to those measured at Marylebone Road, demonstrating that Birmingham Centre is a traffic influenced site. The ratio between the gradients is approximately half of that at Marylebone Road. Higher concentrations of both particle number and NO<sub>x</sub> at Birmingham Centre occur when the wind is from the east to east south east – the direction of the southern tunnel portal and associated junction of the major road through central Birmingham and the railway station. There are no consistent measurements of the other metrics considered above during both before and after periods at Birmingham Centre.

### 3.4. Timing of the reduction in particle number concentrations

The reduction in particle number concentration occurred during a period of a few months in late 2007 (Figs. 2 and 3). This is one year before the recent reduction in economic activity in the UK, which was greatest in late 2008 to early 2009 (ONS, 2010), and the reduction in particle number concentration therefore cannot be due to the effect of changes in economic activity on traffic flow. Late 2007 is however the period between the announcement and enforcement of both the application of the London LEZ to goods vehicles over 12 tonnes gross weight, a class of vehicles which make a disproportionately large contribution to particle number concentrations (Morawska et al., 2008) due to the combustion of lubricating oils, and the sale of “sulphur free” diesel, the fuel most likely to result in the emission of sulphate particulate from vehicles fitted with oxidative catalysts (Maricq et al., 2002a,b). The cumulative sum of the differences of particle number concentration (Fig. 2) does not indicate any other change points that might be associated with vehicle fleet operators bringing goods vehicles between 3.5 and 12 tonnes gross weight and buses into compliance, prior to enforcement of the London LEZ with respect to these vehicles from July 2008, or with the requirement of gasoline fuel for road vehicles to be “sulphur free” by 1 January 2009.

The simultaneous reduction in particle number concentrations at Birmingham Centre (Fig. 3), demonstrates a national, rather than a local London cause for the change, although it should be noted that the ratio of the gradients in the particle number to NO<sub>x</sub> relationship is smaller at Birmingham Centre (Table 6) than at Marylebone Road (Table 4). A small reduction of limited significance

occurred in black smoke concentration (Table 3) and in the black smoke to NO<sub>x</sub> relationship (Table 4) at Marylebone Road between the two periods. This may indicate a small contribution to the reduced particulate number concentration due to the introduction of the London LEZ.

A turning point is apparent in the cumulative sum plots of sulphate at both Marylebone Road and North Kensington in mid 2008 which may be associated with the later introduction of “sulphur free” gasoline.

The period of the reduction in particle number concentrations coincided with a change in the monthly mean particle number spectra measured at Marylebone Road by SMPS (plotted bi-monthly in Fig. 7) during 2007. The monthly mean spectra show the disappearance of a mode at 15–20 nm after October 2007, similar to the results of Wahlin (2009) and Johnson et al. (2009), when “sulphur free” fuel was introduced in Denmark and Minneapolis/St Paul, respectively. Unfortunately, measurements with the current SMPS at Marylebone Road do not predate June 2007, and it is not possible to establish the change in particle size spectra over a longer period of time. The previous SMPS results from Marylebone Road, measured prior to January 2006 with a different instrument type (TSI Model 3071) measuring an extended range of smaller particle diameters, do not indicate such a significant mode around 15–20 nm, and are similar to the post November 2007 results. Application of Positive Matrix Factorization (PMF) to wide range particle size spectra, measured on Marylebone Road in 2007 has identified two sub-100 nm modes in the number size distributions, with that at smaller diameter, ca 20 nm, attributed to the semi-volatile particles formed during diesel exhaust dilution (Harrison et al., 2011). The spectra obtained between August and December 2008, show high concentrations at low particle diameters which are attributed to an instrumentation problem (NPL, 2009), and are notably different from the pre October 2007 spectra in that they have no distinct nanoparticle mode.

The geographically widespread reduction in particle number concentration, its timing, and the similarity of the change in the particle size spectra with the results of Wahlin (2009) and Johnson et al. (2009), tends to indicate that the reduction in particle number concentrations in late 2007 is due to the introduction of “sulphur free” fuel, although the relatively greater change in the particle number to NO<sub>x</sub> relationship at Marylebone Road may indicate that the introduction of the London LEZ brought about an additional reduction.

**Table 6**  
Coefficients of the lines fitted to the relationships between the concentrations of various metrics and NO<sub>x</sub> at Birmingham Centre in the periods before and after the rapid change in particle number concentration in late 2007.

Metric	Period	r <sup>2</sup>	Gradient	Std err gradient	Intercept	Std err intercept	Ratio of gradients
Particle number (cm <sup>-3</sup> )	Oct 05–Sep 07	0.74	190.3	17.3	8539	1073	1.49
	Feb 08–Jan 09	0.89	127.9	7.5	6184	467	



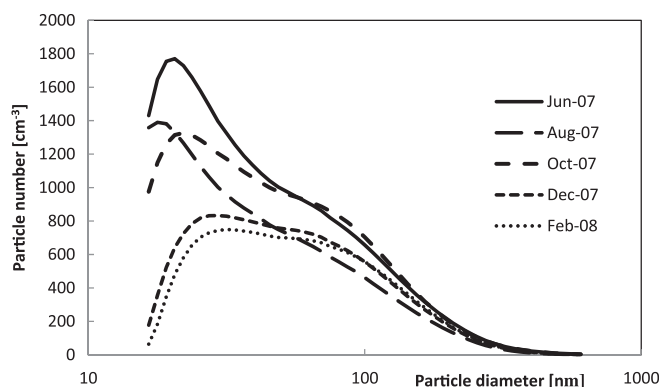


Fig. 7. Marylebone Road - monthly mean particle number size spectra.

#### 4. Conclusions

Using the particle number/ $\text{NO}_x$  gradients in Tables 4 and 6, it can be inferred that during the latter part of 2007 large reductions occurred in the emissions of fine particles relative to  $\text{NO}_x$ , from vehicles at Marylebone Road (65% reduction) and at Birmingham Centre (33% reduction). This fall in emissions resulted in reductions of 59% and 30% respectively in ambient particle number concentrations at these two sites, and a reduction of 39% in the ambient particle number concentration at the North Kensington urban background site.

Apart from a change in carbon monoxide concentrations at Marylebone Road which may be due to an instrumentation problem, significant changes in the concentrations of  $\text{NO}_x$ , carbon monoxide and non-volatile particle mass concentrations were not observed during the latter part of 2007. Reductions in particulate sulphate concentrations occurred in mid 2008.

The reduction in particle number concentration occurred immediately prior to the requirement for all diesel fuel for use in highway vehicles to be “sulphur free” and the commencement of enforcement of the London LEZ for heavy goods vehicles. No similar change was seen in the particle number concentration associated with the later removal of “sulphur free” gasoline from sale, or with the enforcement of the London LEZ on lighter goods vehicles. On the basis of the geographically widespread reduction in particle number concentration, and the effects of the introduction of “sulphur free” diesel reported in other countries, it is probable that the reduction in particle number concentration is primarily due to the introduction of “sulphur free” diesel. However, the greater reduction in particle number concentration in comparison to  $\text{NO}_x$  at Marylebone Road than at Birmingham Centre, and the small reduction of black smoke concentration compared to  $\text{NO}_x$  at Marylebone Road, means that it is not possible to exclude a possible minor influence on particle number concentration at the London sites due to the introduction of the London LEZ in relation to heavy diesel vehicles.

Whatever the cause of the reduction in ambient particle number concentrations in late 2007, it provides an opportunity to examine whether there were any concurrent changes in human health outcomes during a period when the concentrations of ultrafine particles were greatly reduced while those of the regulated air quality metrics did not significantly change.

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#### Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2011.12.050.

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