School of Health and Life Sciences

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**University of London** 

# Marylebone Road ('Supersite') Annual Report 2000

Prepared by David Green Environmental Research Group

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# **Executive Summary**

The Marylebone Road monitoring site continues to supply valuable data for DEFRA's Automatic Urban and Rural Network, the London Air Quality Network and the Hydrocarbons Monitoring Networks. It is also the focus of a range of research work for DEFRA, NERC and other projects.

This report details the analysis of the relationships between monitoring methods and pollutants using the methods laid down in previous annual reports in the light of a larger data set. The report also details the results of the monitoring and examines them in relation to the relevant air quality standards and objectives.

Results from the newly monitored pollutants, including the lead, arsenic, nickel, cadmium and mercury in  $PM_{10}$ , have been detailed in full. The data is examined alongside the national monitoring network data and compared to previous monitoring at this location.

As the site has now been in operation for several years, the longer-term trends in pollutant concentrations have been analysed and compared to local background monitoring sites.

## 1.1 Introduction

The Marylebone Road monitoring site, commissioned by the London local authorities and the Department for Environment, Food and Rural Affairs (DEFRA). The site was installed by Environmental Research Group (ERG), King's College London (KCL) in June 1997.

Marylebone Road is a major route in and out of Central London, running north-east to south-west and carrying approximately 90,000 vehicles per day. The tall buildings on either side form a broad street canyon approximately 40 metres across. The monitoring cabin is located one metre from the kerb on the southern side of the road. Further details of the site and the monitoring methods used are laid out in the Appendix. The site is operated as part of the London Air Quality Network (LAQN) and the Automatic Urban and Rural Network (AURN) for the inorganic analysers and as part of the Hydrocarbon Network (Automatic) for the gas chromatograph.

Between 1997 and 2000 a wide range of non-continuous monitoring techniques were employed and the results compared to those produced by the continuous techniques. These comparisons are examined in detail in previous reports (Green D., 1999, Green D., 2000). At the end of 1999 most of the non-continuous monitoring was decommissioned as many firm relationships between these techniques had been established over the preceding years. Since January 2000 the range of monitoring equipment has expanded to include that used in other DEFRA Urban Air Quality projects including 'Monitoring of Airborne Particulate Concentrations and Numbers in the United Kingdom', 'Hydrocarbon Network (Non-Automatic)' and 'Specification for the Influence of Airborne Particulate Composition and Size on In Vitro and In Vivo Biological Models'.

This report will examine the data produced by the AURN and National Hydrocarbon Monitoring equipment, the non-continuous monitoring and data from the other DEFRA projects where applicable. Data for 2000 has also been examined using the relevant UK and EU standards and objectives.

# 2 Results and Discussion

The Automatic Urban and Rural Network (AURN) QA/QC Unit has ratified all data from the continuous analysers; this data is available from <u>http://www.aeat.co.uk/netcen/airqual</u>.

## 2.1 Particulate Matter

Particulate matter is monitored at Marylebone Road using a wide range of techniques. These examine different fractions of the aerosol ranging from the ultrafine fraction up to  $PM_{10}$  as well as different physical properties and chemical constituents. Much of this monitoring is undertaken under DEFRA's 'Monitoring of Airborne Particulate Concentrations and Numbers in the Untied Kingdom' research program.

This report details measurements made using the TEOM, both  $PM_{10}$  and  $PM_{2.5}$ , the British Standard Black Smoke monitor as well as the chemical analysis of heavy metals in  $PM_{10}$ .

### 2.1.1 Comparison of Black Smoke and TEOM PM<sub>10</sub>

Black smoke analysis uses the optical properties of the particulate collected to assess mass concentration. The black smoke method has been shown to approximate  $PM_{3,2}$  and is essentially a measurement of diesel emissions (Reponen A. *et al*, 1996).



Figure 1: Black Smoke and TEOM PM<sub>10</sub> Measurements

Figure 1 shows the time series of daily measurements of  $PM_{10}$  using a TEOM and measurements of Black Smoke during 2000. The data in Figure 1 shows that the relationship between TEOM  $PM_{10}$  and Black Smoke measurements is not consistent. An examination of this relationship over the previous years is shown in Table 2. The effect of the building works at the adjacent University of Westminster during 1999 had a significant effect on the relationship between the two types of measurements. This is due to the changes in colour and size fractions and is discussed in the previous annual report (Green D., 2000).

	Slope	Intercept	$R^2$
1998	1.2	-1.9	0.3
1999	0.7	17.1	0.3
2000	1.5	-0.9	0.3

Table 1:	Regression	analysis of	Black Smoke	and TEOM PM10	Measurements
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The low value for the regression coefficient ( $R^2$ ) shows that Black Smoke measurements are not a good predictor of  $PM_{10}$  at this location.

### 2.1.2 Comparison of TEOM PM<sub>10</sub> and TEOM PM<sub>2.5</sub>

The TEOM PM<sub>2.5</sub> analyser is installed at Marylebone Road as part of the DETR's 'Airborne Particulate Concentrations and Numbers in the United Kingdom' project.



Figure 2: Regression Analysis of TEOM  $PM_{10}$  and TEOM  $PM_{2.5}$  1998-2000

The regression analysis in Figure 3 shows that the relationship between the two fractions over each of the last three years. It should be noted that this relationship changed during 1999, this was due to the building works at the neighboring University. These would have emitted mechanically generated dust that would have contained a larger portion of  $PM_{10}$  in the coarse fraction; this can be clearly seen on Figure 3. 59% of  $PM_{10}$  is comprised of  $PM_{2.5}$  in 1999, compared to 64% in 1998 and 69% in 2000.

### 2.2 Heavy Metals in PM<sub>10</sub>

Heavy metal emissions arise from the trace concentrations in fuels through combustion and certain industrial processes that can emit metals as vapour, particulate or both. The Marylebone Road cabin has no local industrial sources of heavy metals and thus the measurements at this site will be dominated by background sources and road traffic.

Between July 1997 and January 2000 heavy metal measurements at Marylebone Road were confined to lead. Filters were exposed in an M-type sampler over 7 day periods, laboratory analysis by atomic absorption spectroscopy was carried out to determine the lead concentration. The M-type sampler has been designed to measure airborne particulate matter in a size range that is representative of respirable material.

From January 2000 onwards the range of heavy metals analysis has been extended to include nickel, arsenic, cadmium and mercury. Sampling has been carried out using a Rupprecht and Patashnick Partisol 2000 equipment fitted with a  $PM_{10}$  size-selective inlet with a flow rate of 16.7 l/min. Sampling was undertaken for 7 day periods. Particulate  $PM_{10}$  is collected onto Gelman GN-4 Metricel membrane filters. Analysis was undertaken using UKAS accredited ICP-MS procedures following microwave digestion of the filter samples. Analytical uncertainty for filter samples is estimated to be ±20% for nickel, arsenic, cadmium and lead and ±30% for mercury.

The sampling and analysis methodology are identical to those used in the rest of DEFRA's 'Monitoring of Lead, Arsenic, Nickel and Cadmium around Industrial Sites' program.



The weekly means of lead, arsenic, nickel and cadmium are illustrated in Figures 3 to 7.

Figure 3: Lead Measurements from Marylebone Road



Figure 4: Mercury Measurements from Marylebone Road



Figure 5: Cadmium Measurements from Marylebone Road



Figure 6: Arsenic Measurements from Marylebone Road





When compared to DEFRA's 'Monitoring of Lead, Arsenic, Nickel and Cadmium around Industrial Sites' program, the Marylebone Road site measures concentrations close to the mean of all the other sites. Marylebone Road is the only site in the network located away from the influences of an industrial process. More detail is shown in Table 2.

	Cadmium	Nickel	Lead	Mercury	Arsenic
Network Mean (ngm <sup>-3</sup> )	1.08	3.38	48.04	0.14	1.87
Network Median (ngm <sup>-3</sup> )	0.43	1.99	30.67	0.09	1.30
Marylebone Road (ngm <sup>-3</sup> )	0.39	3.80	38.24	0.06	1.36

Table 2: Lead and Heavy Metal Annual Means compared to Marylebone Road

Further illustrations of the comparison between Marylebone Road and the other sites on the network can be found in Figures 8 and 9. These figures show that concentrations of both lead and the (sum of) other heavy metals at Marylebone Road lies close to the median.









The concentrations of heavy metals stay relatively constant during the year, however, some peaks in lead, cadmium and arsenic are noticeable around Guy Fawkes Night and the Christmas/New Year period. A Swedish study (Alenfelt P., 2000) has found that the emissions of arsenic, cadmium and mercury from fireworks make an insignificant contribution to the total emission and deposition of these elements in Sweden. Lead is a principal constituent of crackling fireworks. It is estimated that fireworks are responsible for 0.8% of total emission and deposition in Sweden.

Figure 10 shows the weekly concentrations of lead at Marylebone Road since sampling started in June 1997. It is clear that many of the highest concentrations were recorded in the weeks around the start of November. The mean lead concentrations during November (1997 and 2000) are 34% higher than for the other 11 months. This suggests that elevated lead concentrations are a result of Guy Fawkes Night.

Figure 10 also shows the rolling annual mean concentration allowing an annual trend to be assessed. Despite the removal of lead from petrol since the start of 2000 there has been no decline in the rolling annual lead concentrations. Annual mean lead concentrations are shown in Table 3, the National Air Quality Strategy Objective for lead is  $0.5\mu gm^{-3}$  by 2004 and  $0.25\mu gm^{-3}$  by 2008.

Year	Lead Concentration (µgm <sup>-3</sup> )	
1997 (June – Dec)	0.046	
1998	0.035	
1999	0.033	
2000	0.038	



Table 3: Annual Mean Lead Concentrations at Marylebone Road 1997 to 2000

Figure 10: Lead concentrations at Marylebone Road since June 1997

### 2.3 Trends

The Marylebone Road monitoring site was established in June 1997, an indication of the trends in pollution concentration can be assessed by examining the rolling annual means. Rolling annual means from June 1998 have been calculated in an attempt to eliminate seasonal effects. These means are have been normalised to 1, relative to June 1998 (or one year from the date of equipment installation) to show relative change.

For comparison, data from Bloomsbury AURN site has been used for the inorganic gases and particulate matter. This is a central London background site close to Marylebone Road.

Data from University College London (UCL) Hydrocarbon Network Monitoring Site has been used as a comparison for benzene and 1, 3 butadiene concentrations. This site is also a central London background site close to Marylebone Road.

To give an indication of the differences in pollutant concentration between the sites used for this comparison the annual means for 2000 are shown in Table 4.

Pollutant	Marylebone Road	Bloomsbury	UCL
NO <sub>2</sub> (ppb)	48.7	30.9	
NO <sub>X</sub> (ppb)	219.0	58.9	
CO (ppb)	2.0	0.6	
O <sub>3</sub> (ppb)	6.6	10.9	
SO <sub>2</sub> (ppb)	5.5	3.9	
PM₁₀ (µgm⁻³)	36.9	21.3	
PM <sub>2.5</sub> (μgm <sup>-3</sup> )	25.9	9.8	
PM <sub>coarse</sub> (µgm⁻³)	11.5	11.0	
Benzene (ppb)	6.4		2.1
1, 3 Butadiene (ppb)	1.6		0.4

#### **Table 4: Annual Mean Concentrations 2000**

Figure 11 shows the relative rolling annual means for both Marylebone Road and Bloomsbury. Marylebone Road  $NO_X$  and  $NO_2$  concentrations are relatively stable but have risen slightly since installation, the  $NO_X$  by 2% and the  $NO_2$  by 8%. The concentrations of both species at Bloomsbury have dropped, the  $NO_X$  by 27% and the  $NO_2$  by 17%.

The relationship between  $NO_X$  and  $NO_2$  at Marylebone Road has changed little although the two traces have diverged slightly. The downward trend of the Bloomsbury  $NO_X$  and  $NO_2$  is considerable and it shows a degree of variation in this trend, the  $NO_2$  rolling annual mean approached the same value as June 1998 in March 2000. This indicates that this background site is strongly influenced by seasonal or annual variations in meteorological conditions, assuming no significant local traffic changes have occurred. This level of  $NO_X$  and  $NO_2$  reduction does not appear to be reflected in other London monitoring sites.

The reduction in  $NO_X$  concentrations of 27% at Bloomsbury is substantial, especially considering Marylebone Road has shown an increase of 8%. Traffic counts at Marylebone Road have shown that the number of vehicles passing the monitoring site has dropped by less than 1%.



Figure 11: Nitrogen Oxides Rolling Annual Means



Figure 12: Particulate Matter Rolling Annual Means

The concentration of  $PM_{10}$  has risen by 4% since monitoring started at Marylebone Road, whereas the  $PM_{10}$  concentration at Bloomsbury has fallen by 17%. These reflect the concentration changes seen in NO<sub>2</sub> in Figure 11.

The change in  $PM_{2.5}$  concentrations has been more dramatic. The  $PM_{2.5}$  concentration at Marylebone Road has risen by 27%, whereas the Bloomsbury  $PM_{2.5}$  concentration has dropped by 6%. As traffic flows along Marylebone Road are constant over this period, the rise in  $PM_{2.5}$  concentrations suggests that emissions from the vehicles have increased. This may be due to changes in the vehicle mix (more heavy goods vehicles and buses) or a change in the fuel used in the existing vehicles (cars and light goods vehicles switching to diesel).

The effect of the building works at the University of Westminster is visible on the Marylebone Road  $PM_{10}$  rolling means between August 1999 and August 2000. This is even more noticeable in Figure 13 that compares the  $PM_{Coarse}$  ( $PM_{10} - PM_{2.5}$ ) from the two sites. Both sites show a similar reduction of around 10% in the annual mean. However, the building works increased the annual mean coarse fraction of  $PM_{10}$  by up to 26%.



Figure 13: Coarse Particulate Matter Rolling Annual Means



Figure 14: Sulphur Dioxide Rolling Annual Means

A sustained downward trend can be seen at both locations for  $SO_2$ . The rolling annual mean for  $SO_2$  fell by 35% at Marylebone Road and 45% at Bloomsbury. This reflects the reduction of sulphur in fuel.





A downward trend is also clearly visible at both sites for CO. The rolling annual mean has fallen by approximately 15% at both locations. This reflects the increased use of catalytic converters.





Although concentrations of  $O_3$  are much lower at Marylebone Road compared to Bloomsbury due to scavenging by NO, overall both sites saw an increase in the annual mean in the order of 10%. This reflects the regional nature of this pollutant. The increased  $O_3$  may be due to two factors; decreased  $NO_X$  scavenging and regional increases in  $O_3$  as measured at rural sites in south east England (Barrat B., 2001).



#### Figure 17: Benzene Rolling Annual Means

A steep downward trend can be seen in the benzene levels at both Marylebone Road and UCL, both sites have seen annual means drop by around 60%. This is likely to be due to changes in fuel and vehicle technology as well as changes to the fuel distribution regulations.



### Figure 18: 1, 3 Butadiene Rolling Annual Means

1, 3 Butadiene has also seen a reduction in the annual mean. Both Marylebone Road and UCL recorded a 40% drop in annual mean concentration. The reasons for this concentration reduction are similar to those for benzene.



#### Figure 19: Rolling Annual and Daily Traffic Counts

Traffic is, of course, the major contributor to pollution concentrations in London, especially at Marylebone Road where vehicle counts average 90,000 per day. Figure 19 shows that there is some day-to-day variation in traffic density, weekend vehicles counts are obviously lower than weekdays. Also periods of low vehicle counts can be clearly seen during the Christmas period, Easter and Bank Holidays. However, the long-term averages have not changed since this monitoring began in June 1998. Changes in pollutant concentration at Marylebone Road are therefore not due to changes in vehicle number but changes in fuel / vehicle technology, vehicle mix or local interferences such as the local building works.

# 3 References

Airborne Particles Expert Group (1999) Source Apportionment of Airborne Particulate Matter in The United Kingdom, DETR.

Alenfelt, P., (2000) Chemical Analysis of Consumer Fireworks. Journal of Pyrotechnics, vol 11.

Allen G. and Reiss R. (1997) Evaluation of the TEOM Method for Measurement of Ambient Particulate Mass in Urban Areas. Journal of Air and Waste Management Association, vol. 47, 682-689.

Barrat B.,(2001) The Kent Air Quality Monitoring Report 2000. King's College London Environmental Research Group

Green D., Fuller G.,(1999) Marylebone Road ('Supersite') Annual Report 1998. King's College London Environmental Research Group

Green D., Fuller G.,(2000) Marylebone Road ('Supersite') Annual Report 1999. King's College London Environmental Research Group

Reponen A. et al (1996) Comparison of Five Methods for Measuring Particulate Matter Concentrations in Cold Winter Climate. Atmospheric Environment, vol. 30, no.22, pp. 3873-3879.

# 4 Appendix

# 4.1 Air Quality Standards

### 4.1.1 UK National Air Quality Standards and Objectives for 2000

Pollutant	Pollutant Objective		Date to be	2000 Booult	
Pollulani	Concentration	Measured as	achieved by	2000 Result	
Benzene	5ppb	Running annual	31 December	10.9ppb	
Benzene		mean	2003		
1,3-	1ppb	Running annual	31 December	1.9ppb	
Butadiene		mean	2003		
Carbon	10ppm	Running 8 hour mean	31 December	No Exceedences	
monoxide	0.5	A	2003 24 December	0.04	
	0.5µgm	Annual mean	31 December 2004	0.04µgm	
Lead	0.25µgm <sup>-3</sup>	Annual mean	31 December	0.04ugm <sup>-3</sup>	
	0.20µg///		2008	0.0 1µg111	
	105ppb not to be	1 hour mean	31 December	100hours	
	exceeded more		2005		
Nitrogen	than 18 times a				
Dioxide	year				
	21ppb	Annual mean	31 December	48ppb	
	-33		2005	4.50.1	
	50µgm <sup>°</sup> not to be	24 hour mean	31 December	159days	
Particles*	than 25 days a year		2004		
(PM <sub>10</sub> )	40ugm <sup>-3</sup>		31 December	18.10m <sup>-3</sup>	
	40µ911	Annual mean	2004	40µgili	
	132ppb not to be	1 hour mean	31 December	No Exceedences	
	exceeded more		2004		
	than 24 times a				
	year				
Sulphur	47ppb not to be	24 hour mean	31 December	No Exceedences	
Dioxide	exceeded more		2004		
	than 3 times a year		04 December	No Essentianes	
	100ppb not to be	15 minute mean	31 December	No Exceedences	
	than 25 times a		2005		
	vear				
	Objectives for the Protection of Human Health				
	50ppb not to be	Daily Maximum of	31 December	No Exceedences	
	exceeded more	running 8 hour mean	2005		
Uzone	than 10 times a				
	year				

\*Particles (PM<sub>10</sub>) relates to gravimetric or gravimetric equivalent, in this case TEOM multiplied by 1.3

Table 5: National Air Quality Strategy Objectives

### 4.1.2 EC Directive 80/779: Smoke and SO<sub>2</sub> Directive

OECD smoke concentrations have been calculated from the British Standard Smoke concentrations using the following equation:

OECD concentration = BS concentration divided by 0.85

EC Directive Limit Values for Smoke in µgm <sup>-3</sup>				
Reference Period	Limit Value	2000 Value		
Year (median)	68	57		
Winter (median)	111	61		
Year (98th percentile)	213	207		
EC Directive Guide Values for Smoke in µgm <sup>-3</sup>				
Reference Period	Guide Value	2000 Value		
Year (mean)	34 to 51	63		
24 hours (mean)	85 to 128	233		

### Table 6: OECD Smoke Concentration 2000

The applicability of the British Standard Smoke method at this location is questionable. This method was designed to measure ambient conditions where the major pollution source was coal burning, both domestic and industrial. Whether this method and the and indeed the relationship between smoke stain and mass is valid in these conditions would need further investigation. Results from this study would indicate that the relationship between PM<sub>10</sub> and black smoke is weak. APEG (1999) also found large differences between TEOM PM<sub>10</sub> measurements and black smoke monitors.

### 4.2 Site Map



# 4.3 Monitoring Methodologies

Species	Method
PM10 (continuous)	TEOM
Black Smoke	British smoke stain method
Nitrogen Oxides	Ozone chemiluminescence
Carbon Monoxide	Infra-red absorption
Sulphur Dioxide	UV fluorescence
Sulphur Dioxide	Bubbler method
Ozone	UV absorption
27 Hydrocarbons	Automatic gas chromatography
Lead, Arsenic, Nickel, Cadmium and Mercury	Filter collection, ICP/MS determination

Table 7: Monitoring Methods