1. Introduction

This is the first report to DEFRA and indicates the progress made to date, covering the period October to December 2001. It details the types of measurements made and provides summary statistics and data capture rates. Where significant amounts of data are missing the reasons for these are given together with details of any remedial action taken.

It is intended that future reports will include rolling averages to lessen the impact of instrument down time during routine servicing which, in the case of particle counting instruments, can be considerable.

2. Sampling Locations and Details

Instruments are located at 11 established sites, ten of which form part of DEFRA's Automatic Urban and Rural Monitoring Network either directly or through affiliation, and one (Harwell Organic) which is part of the Automatic Hydrocarbon Monitoring Network. The sites are:

- Belfast Centre (Urban Centre, O.S Grid ref J339744)
- Birmingham Centre (Urban Centre, O.S Grid ref SP064868)
- Glasgow Centre (Urban Centre, O.S Grid ref NS589650)
- Harwell Inorganic (Rural, O.S Grid ref SU474863)
- Harwell Organic (Rural, O.S Grid ref SU 474863)
- London Bloomsbury (Urban Centre, O.S Grid ref TQ302820)
- London Kensington (Urban Centre, O.S Grid ref TQ240817)
- London Marylebone Rd (Urban Kerbside, O.S Grid ref TQ281820)
- Manchester Piccadilly (Urban Centre, O.S Grid ref SJ843983)
- Port Talbot (Urban Centre, O.S Grid ref SS780882)
- Rochester (rural, O.S Grid ref TQ831762)

3. Monitoring Methodologies

Of the ten monitoring sites, nine are equipped with continuous monitors recording either size fractionated particle concentrations or total number concentrations, together with particle mass concentrations. At two sites, Harwell and Rochester, wind speed and direction are also recorded. A number of the sites also have Partisol gravimetric samplers which serve to compliment the information obtained from the TEOM instruments, although these are operated under a separate contract and are not included in the summary statistics for this report.

3.1 *Particle Mass Concentrations*

Tapered Element Oscillating Microbalances (TEOM) are used to monitor particle mass concentrations. In order to measure both PM_{10} and $PM_{2.5}$ at each site two TEOM's were installed, one fitted with a standard 16.7 l min^{-1} PM_{10} impactor inlet validated according to the US EPA Federal Register requirements, whilst the other was fitted with a 16.7 l min^{-1} cyclone manufactured by URG Inc, USA and reported by them to have a 50% cut-point at 2.5 μm. At the exit of the sample head the flow is isokinetically split into a 3 l min^{-1} sample stream, sent to the instrument's mass transducer, and a 13.7 l min^{-1} exhaust stream. The main flow of 3 l min^{-1} enters the sensor unit through a small Teflon-coated borosilicate glass filter held at the tip of an oscillating tapered glass tube and free to vibrate at its natural frequency. As the filter mass increases so the oscillation frequency changes, and the instrument monitors this change every 2 seconds to determine the mass of particles collected. This information is then used by the instrument to compute updated 15-minute average mass concentration values.

At 6-monthly intervals the TEOM units were serviced in accordance with the manufacturer's recommendations. Critical flows and the calibration constant for each instrument were checked using references traceable to national metrology standards.

3.2 *Particle Number Concentrations*

Total particle number concentrations in the size range 7.5-1000 nm diameter are made using Condensation Particle Counters (CPC) sampling at a flow rate of 300 cc min^{-1} through a 1.5 m length of 1/4" o.d. copper tube.

Although such small particles cannot be directly detected by conventional light scattering techniques, in the CPC the monodispersed aerosol first passes through a chamber which is saturated with n-butyl alcohol vapour and then to a cooled condenser where the alcohol condenses onto the particles. The resulting droplets grow to a diameter of about 10 μm and are counted as a result of light scattered onto a photodetector as they pass through a light beam. The CPC is linked to a microcomputer which is used to control its operation via dedicated software and to store the particle count data.

Size fractionated particle counts are made using Scanning Mobility Particle Sizers (SMPS) which use the electrical mobility detection technique to measure the size distribution. The SMPS system comprises an Electrostatic Classifier (EC) which separates the particles into known size fractions, and a CPC which measures their concentration. The sample inlet is taken from the output flow of a 16.7 l min^{-1} cyclone having a 50% cut-point at 1.0 μm, thus removing most of the large particles which can cause blockages in the system.

Particles entering the system which are larger than the measurement range are removed by inertial impaction. A bipolar charger in the EC is used to charge the particles in the incoming polydispersed aerosol to a known charge distribution, which are then classified according to their ability to traverse an electric field. The EC was configured to allow particles in the range 11-450 μm diameter to be counted.

The SMPS system is linked to a microcomputer and controlled using dedicated software. Particle count and size distribution data are stored on the computer in both graphical and statistical forms.

On an annual basis both the CPC and SMPS systems were removed from site for servicing, and the CPC's calibrated against an Aerosol Electrometer using a monodisperse aerosol of 50 nm diameter sodium chloride particles.

3.3 *Particulate Carbon Concentrations*

Measurements of ambient carbon particulate concentrations (PM_{10}) will be made using the Rupprecht and Patashnick series 5400 monitor which automatically determines the level of carbon particulate using a thermal CO2 analysis technique. The unit differentiates between organic and elemental carbon by burning off the collected particulate at an intermediate temperature of before conducting a full burn at 750 ^{o}C.

3.4 *Particulate Nitrate Concentrations*

The mass concentration of ambient particulate nitrate contained in fine particulate matter ($PM_{2.5}$) will be made using the Rupprecht and Patashnick Series 8400N monitor. It employs a flash volatalisation technique by passing a high current through a nichrome collection strip, and measures the resulting NOx concentration using a specially configured pulse analyser.

3.5 *Particulate Sulphate Concentrations*

Determinations of daily particulate sulphate are undertaken by sampling onto Teflon filters using a Rupprecht and Patashnick Partisol 2025 automatic sampler. Filters are subsequently analysed using extraction and ion chromatography techniques.

Table 1 details the location of the monitoring equipment.

Table 1 Location of monitoring equipment

Site	$PM_{2.5}$ Partisol	$PM_{2.5}$ TEOM	PM_{10} Partisol	PM_{10} TEOM	PM_{10} Sulphate	PM_{10} Carbon	$PM_{2.5}$ Nitrate	SMPS	CPC	Met Sensor
Belfast Centre	*			*	√	√	√		√	
Birmingham Centre	*			*					√	
Glasgow Centre	*		*	*					√	
Harwell (Inorganic)		√		√				√		√
Harwell (organic)					√	√	√			
London Bloomsbury		√		*				√		
London Kensington	*			*	√	√			√	
London Marylebone Rd		√		*	√	√		√	√	
Manchester Piccadilly	*		*	*					√	
Port Talbot	*			*					√	
Rochester		√		*						√ [1]

* Monitoring equipment operating under AURN contract

[1] Local authority owned equipment

4. Data Collection and Validation

4.1 *Tapered Element Oscillating Microbalance (TEOM)*

Fifteen minute PM_{10} and $PM_{2.5}$ averages are downloaded automatically via telemetric links and stored on the central AURN database. Data are validated using built in algorithms and human judgement to provide provisional data sets for the DEFRA's Air quality Information Archive and, in the case of PM_{10}, for the Air Quality Bulletins. PM_{10} data from London Bloomsbury, London Marylebone Rd, and Rochester are subject to further ratification by the QA/QC Unit of DEFRA's AURN. PM_{10} data from Harwell and all $PM_{2.5}$ data are ratified by Casella Stanger.

TEOM instruments are subject to the same QA/QC protocols as used in the AURN. These are generally reliable instruments and therefore the validated data capture is normally high. As shown in Table 1.2, this was generally the case under this project. In addition to regular on site checks, the data were scrutinised to identify any periods where the data were erroneous or otherwise unacceptable. Invalid data can occur following filter changes and when occasional extreme positive or negative data are recorded. Coarse fraction particle concentrations were obtained from the difference between PM_{10} and $PM_{2.5}$ measurements. These can occasionally be negative due to noise on one or more of the instruments. If calculated course particle fractions were lower than –10 ug m^{-3} the data were deleted.

4.2 Scanning Mobility Particle Sizer (SMPS) and Condensation Particle Counter (CPC)

The SMPS system is configured to perform a scan every 2.5 minutes and to compute 15 minute averages from this data. This is considered to be the optimum scan period, taking account of both system response speed and the representative nature of the sample at the beginning and end of each scan.

Main faults resulting in lost or invalid data continue to be related to inlet impactor blockages, pump failures and the inherent limitations of the operating software. Data are examined with reference to the routine instrument check sheets to identify periods of obvious malfunction, and screened for erroneous spikes using an in-house developed validation program that scans the data, applying a number of criteria to determine the validity of very high or low counts.

The CPC takes a reading every 2-3 seconds, and 15-minute averages, are stored in a “long time data” file. Both raw and averaged data are retained enabling detailed examination of any historical periods of special interest.

The CPC is a much simpler instrument than the SMPS, and less prone to mechanical breakdowns and hence loss of data. However, there still exists the problem of software instability and errors, which are responsible for the majority of data losses. In addition, there are periods when particle counts are very low, due to problems with the butanol supply to the CPC, and these data have been removed.

5. Equipment Performance

5.1 *Particle Mass Measurements*

The TEOM has been used in the UK’s AURN since it’s inception in 1991, and the operational experience gained over this period has contributed to the relatively high data capture. Most data losses are caused by power supply problems or vandalism to the sampling head, rather than instrument faults.

5.2 *Particle Counts*

The SMPS is the state of the art method for sizing and counting ultrafine particles but, outside of this project there are no published data to suggest that it has been used as a continuous monitor at remote locations. In this respect, the use of the SMPS has been innovative and has required some development in order to obtain consistent and reliable data.

The CPC is a far simpler instrument and fewer problems are to be expected. However, there were significant data losses, predominantly due to operator error, pump failures, software and electrical supply problems. Operator performance has improved significantly as familiarity with the equipment has improved.

5.4 *Particulate Sulphate Measurements*

The Partisol 2025 is one of the accepted methods for gravimetric particulate determination and is utilised extensively for this purpose. The main failure of the instrument is due to the highly mechanical nature of the filter exchange mechanism and inherent reliability problems this causes.

5.5 Carbon and Nitrate Analysers

It was initially anticipated that the R&P 5400 Carbon and 8400N Nitrate analysers would be operational by the beginning of October 2001, but continued reliability problems have prevented the collection of any valid data during this reporting period.

Since purchasing this equipment there have been a number of issues relating to the design of these systems which, together with the limited operational experience available in the UK, has contributed to this situation. Some of the major problems encountered have included:

- instruments delivered with missing parts (Carbon, Nitrate)
- no instruction manuals for 4 months (Carbon, Nitrate)
- instruction manuals out of date (Carbon)
- operational fault with trumpet valves (Carbon)
- design fault with phase control module (Carbon)
- main pump failure (Nitrate)
- flash strip failure necessitating design modification (Nitrate)
- air temperature probe failure (Nitrate)
- communications software incompatibility (Carbon, Nitrate)
- ingress of rain water through sample inlet (Marylebone Road Carbon)

Rectification of these problems has required a considerable resource input from both Casella Stanger and EMC Environmental Engineering. Supply of spare parts was often a protracted process since these were not always readily available and had to be obtained directly from R&P. This situation is currently being addressed by EMC who are building a comprehensive stock of spare parts.

Some faults, in particular those relating to the phase control modules and flash-strips, were common to all units and therefore prevented monitoring from being undertaken while R&P investigated the fault and provided the necessary design modifications. During this time Casella Stanger took the opportunity to become more familiar with the instruments and to seek further help regarding their operation from other users. It subsequently became clear that the instruments were likely to need considerably more attention, certainly in the early stages while procedures were being developed, than was initially envisaged. It has to be appreciated, however, that these are essentially research instruments, and data capture in the short term is unlikely to be as high as for conventional AURN monitoring equipment.

By early December 2001 all instruments had been modified to the latest design specification and monitoring commenced at all sites. A commissioning programme was scheduled starting at Harwell but this had to be aborted due to the failure of the air conditioning system at the Hydrocarbon site. The Carbon analyser could not be switched on as the extra heat generated by this instrument would have compromised the hydrocarbon data. Furthermore it was discovered that the Carbon unit at Marylebone Road had taken in a significant amount of rain water and had to be returned to EMC for a complete strip-down and service.

The current equipment status is that three of the Carbon units and both Nitrate units are working and are expected to be producing valid data by early March. The fourth Carbon unit will be returned to Marylebone Road as soon as its service has been completed and when the problem with water ingress has been resolved.

It is also anticipated that the remote communications facility will be restored by R&P during early March, but until then data will be collected using a direct link to a laptop during the routine service visits.

6. Data Capture

6.1 *TEOM*

Annual data capture statistics for PM_{10} and $PM_{2.5}$ mass concentrations are presented in Table 2 for each of the monitoring sites.

Table 2 Monthly particle mass data capture (%)
October - December 2001

	PM_{10}				$PM_{2.5}$			
	LM[(1)]	LB[(2)]	RO[(2)]	HAR	LM	LB	RO	HAR
Oct	90	99	99	97	100	99	100	98
Nov	73	100	100	100	100	99	99	100
Dec	79	100	100	95	100	99	100	96
Quarter	81	99	99	97	100	99	99	98

(1) PM_{10} data from Marylebone Rd is available as part of the London Network, which is operated by SEIPH. Casella Stanger do not report these data directly.

(2) London Bloomsbury PM_{10}, Rochester PM_{10} and Harwell PM_{10} are operated under DEFRA's AURN contract.

6.2 *SMPS*

Table 3 SMPS particle count data capture (%) at London Bloomsbury, Marylebone Rd and Harwell, October - December 2001

	Bloomsbury	**Marylebone Rd**	**Harwell**
Oct	7	36	63
Nov	66	0	88
Dec	-	49	86
Quarter	24	29	76

(-) used where no data available due to routine instrument servicing This data not included in data capture statistics.

Problems due to lack of access to Bloomsbury while construction work was being undertaken at the site meant that there were a number of occasions when the SMPS software had stopped monitoring and could not be reset. In addition there were also occasions when the computer controlling the equipment had “crashed” between site visits.

Marylebone figures include the instrument down-time after having been removed for its annual service from 15th November until Early January 2002. Additionally, the time taken to replace a seized external pump resulted in the loss of 29 days data at the start of the quarter.

6.3 *CPC*

Table 4 CPC particle count data capture (%) at the seven monitoring sites, October - December 2001

	CPC						
	LM	**Belf**	**Man Pic**	**Birm**	**Port Talbot**	**Glasgow**	**N Kens**
Oct	100	97	100*	100	92	45	100
Nov	60	-	100	100	91	90	100
Dec	-	100	100	100	66	40	100
Quarter	87	98	100	100	83	58	100

Data capture is generally good across the network. Figures for Belfast are amended to take account of “down time” due to routine servicing of the instruments.

Data for Manchester began on the 16th October when the replacement CPC was installed. Data capture rate has been calculated from this date.

Glasgow Centre has slightly lower data capture due to the software stopping between site visits and the deletion of some invalid data recorded when the butanol reservoir had emptied.

6.4 *Sulphate Partisol*

Table 5 Particulate sulphate data capture (%)
October - December 2001

	Data capture	Total days sampling	Total period
North Kensington	63.8	37	4/11/01-31/12/2001 (58)
Marlyebone Road	90.32	56	30/10/2001-31/12/2001 (62)
Belfast	98.3	60	1/11/2001-31/12/2001 (61)
Harwell	-	-	-

Most data losses occurred due to the failure of the filter exchange mechanism which is prone to jam during filter changeover.

Data at Marylebone Rd was lost due to software problems which took some time to resolve.

7. Summary Data and Statistics

Table 6 Average particle mass concentration ($\mu g\ m^{-1}$), October - December 2001

	PM_{10}	**$PM_{2.5}$**	**PM_{coarse}**
Harwell	13.1	10.9	2.2
London Bloomsbury	22.1	11.2	10.9
Marylebone Road	37.9	28.5	9.4
Rochester	15.3	10.7	4.6

- PM_{coarse} is defined as $PM_{10} – PM_{2.5}$

No sulphate data have been presented in this report as this work requires wet chemical determinations to be made, and there has been insufficient time to perform these analyses and carry out the necessary data validation procedures. These data will be presented in the next report.

8 Recommendations

7.1 CPC vs SMPS measurements

The data collected at the Marylebone road site where CPC and SMPS instruments are co-located show that the total particle counts differ by a factor of approximately 2. The reasons for this lie in the size ranges of the instruments, the CPC and SMPS sampling between 7.5 – 1000nm and 11.5 – 450nm respectively. The SMPS may also undergo particle losses in the classifier, which although corrected for in the software by in built algorithms, may not account for all the losses observed.

It is proposed that the Marylebone Road CPC instrument is moved around the other two sites, to gain data on the comparison between CPC and SMPS equipped sites. Having just returned from it's annual service, the instrument is believed to be in good working order and will be moved after 3 months of good data has been achieved at each site. Provisionally, for the first quarter, the CPC will remain in its present location until the end of March, when it will be relocated to Bloomsbury until the end of June. Following this, the CPC will be installed at the final site, Harwell. This program is of course subject to reasonable data capture from both instruments, during the period.