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Report

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CPEA 28: Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 2)

Annual Audit Report

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ABSTRACT

This report details the results from the 2006 – 2007 annual audits of field instruments on the Airborne Particulate Concentrations and Numbers Network. The report presents figures that are used for the ratification of Network data and it makes recommendations regarding the future operation of the instruments.

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Approved on behalf of the Managing Director, NPL
by (*Martyn Sené*), Director, *DQL*

Executive Summary

The annual audit round for the Airborne Particulate Network was carried out between June and October 2007. The main purpose is to carry out instrument checks and calibrations so that data ratification can account for instrument drift throughout the year, and, more generally, greater confidence can be placed on the ratified data. The audits also allow for assessment of the site infrastructure and operator competence.

Instrument and site audits were carried out for all instrumentation that had been used to produce data for this network since the last audit in 2006, with the exception of the automatic carbon analysers, which were removed from the sites during May 2007. No major faults were found.

Sample flow rates of all analysers were measured using a Bios DryCal DC-2 volumetric flowmeter. Each analyser also passed a leak test.

An intercomparison of anion analysis methods was undertaken by NPL and King's College London in July 2007, and the results are reported here. They show good agreement between the two laboratories.

The automatic nitrate analysers were tested using a set of gravimetrically prepared aqueous nitrate standards. The responses of the instruments to different masses of nitrate were used to generate linear calibration curves, which are used during the data ratification process to scale the ambient results. The clear practical benefit of using equal volumes of different strength solutions, rather than different volumes of the same strength, as currently used for LSO calibrations, has led to a change in the LSO procedures.

Site safety and infrastructure was found to be good, although opportunities for improvement have been identified and will be actioned before the next audit.

Attention needs to be given to the recommendations of the EUSAAR group for the standardisation of similar measurements around Europe.

CPEA 28: AIRBORNE PARTICULATE CONCENTRATIONS AND NUMBERS IN THE UNITED KINGDOM (PHASE 2)

Annual Audit Report

1 Introduction

The 2007 annual site and equipment audits for the Airborne Particulate Concentrations and Numbers in the UK Network were carried out between June and October 2007.

Annual audits play an important role in the quality procedures of air quality measurements. The audit round has three objectives:

1. To assess the site infrastructure in terms of safety, accessibility and compliance with CEN siting requirements for air quality monitoring.
2. To carry out calibration of the instruments and provide traceability to national standards, and other operational tests. This information is used during the ratification process to apply corrections to the data, ensuring intercomparability of data at each monitoring site and greater overall confidence in the data.

Following the reorganisation of the Network in May 2007, some instruments were switched off and removed from sites. Nevertheless, audits were carried out for every instrument (with the exception of the Automatic Carbon analysers), to ensure proper ratification of data produced during the previous year. At the time of audit, all of the Automatic Carbon analysers had already been removed from the sites and were not available for inspection. The following table details the dates of the audits.

Site	Date of Audit	Comment
Glasgow	27/06/07	
Birmingham	12/07/07	
Port Talbot	26/07/07	Audit of CPC was carried out at NPL.
Manchester	26/07/07	Audit of CPC was carried out at NPL.
North Kensington	14/08/07	Automatic Nitrate audited on 17/10/07
Marylebone Road	15/08/07	
Bloomsbury	23/08/07	Audit of SMPS was carried out at NPL.
Harwell	28/09/07	
Belfast	09/10/07	Automatic Nitrate not available

Table 1. **Audit Dates**

2 Condensation Particle Counters (CPC)

During the annual audit the sample volumetric flow rate of the CPCs (TSI Model 3022A) is measured using a calibrated Bios DryCal DC-2 (Bios International Corporation, NJ, USA). In addition, a HEPA (high efficiency particle attenuator) filter is used to check the analyser zero.

An annual detector calibration is carried out by the manufacturer (TSI Instruments Ltd, UK) but does not form part of this audit round. A full calibration is also performed before and after any maintenance activities. Details of the calibration are given in the NPL Report DQL AS 037 [1]. The results of the audit checks are shown in Table 2. The uncertainty in the high flow measurements, for 95% confidence limits is +/- 3%. The uncertainty in the low flow measurements is estimated to be +/- 5%.

Site	HEPA response (Particles/cm^3)	Sample flow (vl/min) *Set point 0.3*	Diagnostics and Leak Check
Port Talbot	<0.2	0.258	Pass
Belfast	<0.1	0.249	Pass
Birmingham	<0.1	0.232	Pass
Manchester	<0.1	0.253	Pass
Glasgow	<0.6	0.225	Pass
Marylebone Rd	<0.1	0.227	Pass
North Kensington	<0.1	0.251	Pass

Table 2. CPC Audit Results

Ambient air is drawn into the CPC at a high flow rate of 1.5 l/min, to minimise diffusional losses between the inlet and the sensor. Inside the instrument this flow is split and 0.3 l/min are directed to the optical detector. The remaining 1.2 litres bypass the optics and are vented from the instrument.

Sample flow rates are seen to be consistently lower than the 0.3 l/min set point. It is expected that flow rates are highest immediately after a service, and that the flow rate falls roughly linearly over time. At the time of audit, the annual service and calibration round for these instruments was about to begin, so it is not surprising to see these low flow rates and no action was taken.

3 Scanning Mobility Particle Sizers (SMPS)

The three redundant SMPS analysers (TSI Model 3071) at Bloomsbury, Harwell and North Kensington were replaced during March 2007 by a new TSI model 3936/3775. As part of the Network restructuring, the Bloomsbury SMPS was removed from the site and installed at North Kensington in October 2007. For a short period the instrument was in storage at NPL, which is where the audit was carried out. Audit results for the particle sizers are given in Table 3.

Site	HEPA response (Particles/cm^3)	Sample flow (vl/min) *Set point 0.3*	Kr-85 Source Check	Diagnostics and Leak Check
Marylebone Rd	<0.2	0.295	Pass	Pass
North Kensington	<1.0	0.283	In safe storage	Pass
Harwell	<0.1	0.292	Pass	Pass

Table 3. SMPS Audit Results

Unlike the stand-alone CPCs, which mainly operate in the photometric detection mode, no annual calibration is performed on the CPCs used by the particle sizers, as they count individual condensed droplets and the counting process should need no calibration. This assumption will be tested in future as further laboratory facilities at NPL are developed.

4 Partisol 2025

Partisol 2025 samplers, used for the daily PM_{10} measurements of nitrate, sulphate and chloride, automatically change filters every 24 hours. The time and success of these changeovers are remotely monitored by King's College London (Central Management and Control Unit for this network). At the annual audit, the only requirements are to accurately measure analyser flow rates (this is particularly important as the flow rate affects the particle size cut-off), and perform a leak check. The leak test is "passed" if the flow is less than 1.5 l/minute with the sample inlet restricted. Additionally, a record is made of the filter number, noted from the analyser display, in use at each site during the audit. Checks are then made that the reported concentration from that particular filter has been correctly assigned to the date of the audit. The results of these tests on the Partisols are shown in Table 4.

Site	Sample Flow* (vl/min) *Set point 16.67*	Filter in use	Leak test
Harwell	16.73	00406	Pass
Belfast	17.18	Not sampling	Pass
Marylebone Rd	16.83	00252	Pass
North Kensington	16.93	00265	Pass

* The uncertainty in the flow measurements, for 95% confidence limits is +/- 3%.

Table 4. Partisol Audit Results

The chemical analysis for the determination of chloride, nitrate and sulphate deposited on the filters is subject to laboratory QA/QC procedures. These include a daily calibration of the ion chromatograph, analysis of blank filters, routine instrument service and maintenance and repeated extractions of sample filters. A full uncertainty budget [1] has been developed and regular intercomparisons with other measurement laboratories are carried out.

In May 2007 the laboratory responsible for these analyses changed from King's College London to NPL. As part of routine quality procedures, and to confirm there would be no step change in results, an intercomparison was organised which required each laboratory to determine the mass of each anion on half of a bisected filter. The results are shown in Figure 1, and show good agreement at the 10% level.

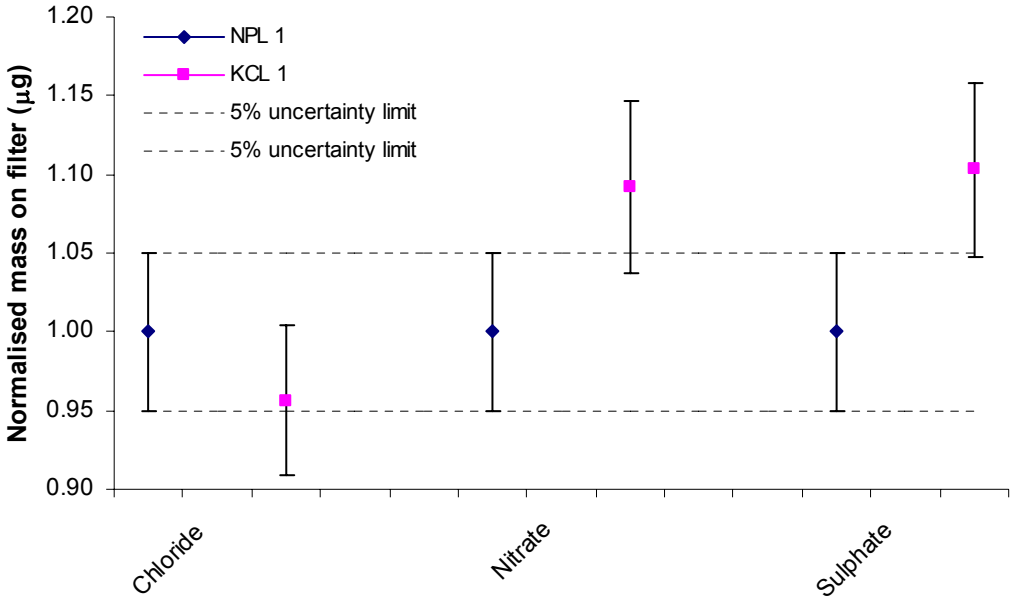

Figure 1. ***Masses of chloride, nitrate and sulphate measured on a sampled filter, July 2007.***

5 Automatic Nitrate Analysers.

Aqueous solutions of KNO_3 were used to test the response of the Thermo 8400N ($PM_{2.5}$) instruments. A known volume of each solution was measured by syringe and deposited onto the flash strip. The zero was also determined, by using deionised water. The instrument then analysed as it would for a normal sample, thus allowing the user to test more of the process than by span gas analysis alone. The instrument response to the known mass of nitrate is used during ratification to correct data.

LSOs carry out this procedure monthly, using a 1μl syringe to deliver different volumes of a 100 ng.μl $^{-1}$ solution of potassium nitrate. During the Marylebone Road audit, this was replicated using a gravimetrically prepared potassium nitrate standard. The responses are shown in Figure 2.

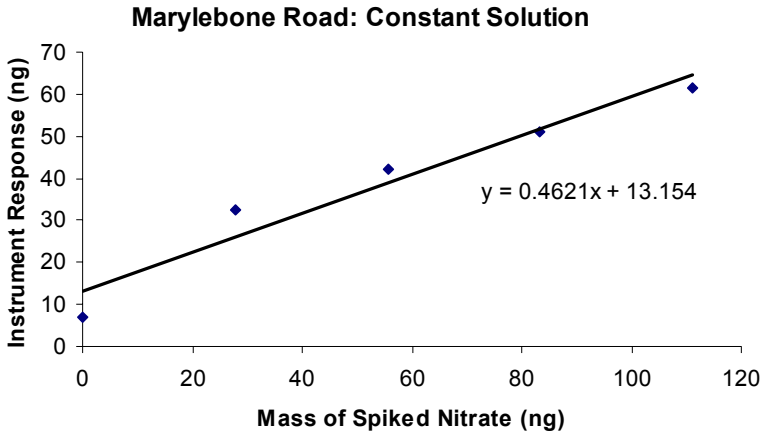

Figure 2. Marylebone Road aqueous calibration with one standard solution

The linearity of this calibration curve is poor. LSOs have reported difficulties depositing 0.2 μl onto the flash strip due to the small size of the droplet. There are also problems at the higher end of the curve, where the instrument response is much lower than expected, most likely due to the large droplet (0.8 μl) running off the flash strip.

To improve the accuracy of the measurement, three further standards were prepared at NPL, in the concentration range 44 ng.μl $^{-1}$ to 184 ng.μl $^{-1}$. These were used to apply different masses of nitrate to the flash strip while keeping the liquid volume constant. The results of these tests at Marylebone Road and Harwell are shown in Figure 3 and Figure 4. The instrument at North Kensington was not operating correctly at the time of audit so an aqueous calibration was not performed.

It was also noted that the analyser was reporting a high zero offset. This is an ongoing issue with the automatic nitrate analysers, but repeated testing showed that, although high, the offset was stable, and therefore this can be used to correct the data during ratification.

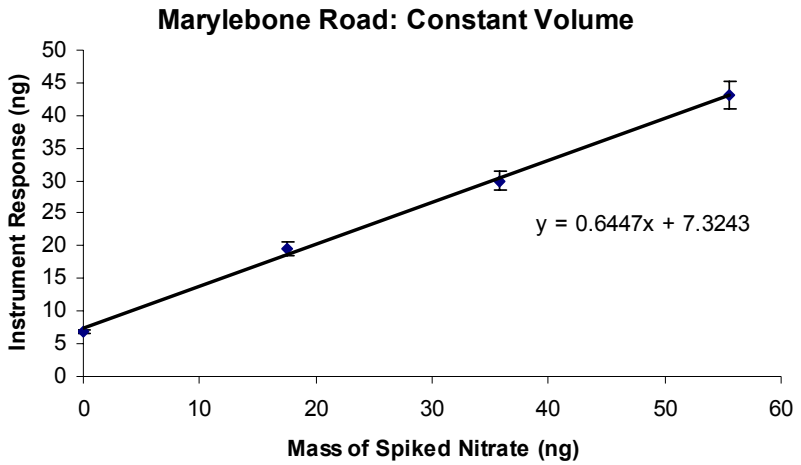

Figure 3. Marylebone Road aqueous calibration with constant volume

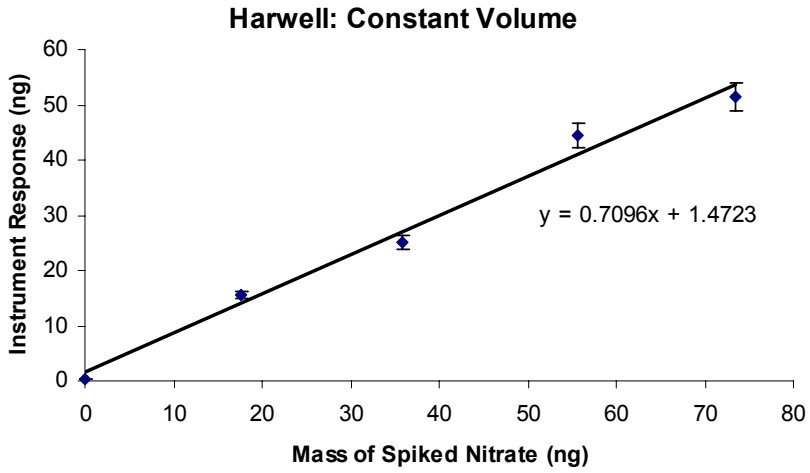

Figure 4. Harwell aqueous calibration with constant volume

In future LSOs will be provided with a range of nitrate solutions of different concentrations, and they will be advised to perform all future calibrations using a constant volume (0.4 μl) to minimise the effect of under- and over-sized droplets described above.

Sample flow rates were measured using the BIOS DryCal flowmeter, and are used to scale the data during ratification. The flow rates are detailed in Table 5:

Site	**Sample Flow* (vl/min)** ***Set point 0.9***
Marylebone Rd	1.034
Harwell	1.028
North Kensington	1.061

* The uncertainty in the flow measurements, for 95% confidence limits is +/- 3%.

Table 5. Automatic Nitrate sample flow rates

6 Automatic Carbon Analysers

Historically, the Thermo 5400 carbon analysers have a poor record of data capture and data quality, due to frequent technical failures and calibration difficulties. The 2005 EPA study [2] showed that these analysers were inconsistent and did not agree well with the manual reference method. The analysers have been discontinued by the manufacturer and ceased operation on this network in May 2007. The four analysers were removed from the sites at Marylebone Road, Harwell, North Kensington and Belfast before this audit round, so have not been included in this report.

Data from the carbon analysers from 2005 and 2006 has been reported as 'validated, but not ratified' due to low confidence in the accuracy of the results, even though audits were performed in those years. Without the correction factors provided by an audit, the 2007 data quality will be somewhat worse than in previous years, and will also be described as validated only.

7 Site Infrastructure and EUSAAR Recommendations

Following the restructuring of the network, the instruments deployed at the time of the writing this report are detailed in Table 6.

	CPC	SMPS	Partisol 2025	Automatic Nitrate
Marylebone Road	x	x	x	x
North Kensington	x	x	x	x
Harwell	x	x	x	x
Birmingham	x			

Table 6. Current Network Structure.

During the annual audits an assessment was made of site safety. All sites in the current network structure have undergone a risk assessment. The radioactive sources in the SMPS analysers are appropriately labelled and routinely checked, either by the LSO or by AEA Energy & Environment. Personal protective equipment is provided as requested. Gas cylinders are secure, roof access has been assessed and electrical safety testing is carried out annually.

Further actions required at each site are given below:

Marylebone Road:
- The SMPS is currently fitted with a PM2.5 sampling inlet. Due to low sample flow and the large diameter of the inlet pipe, residence time of the air in the pipe is too long. It will be replaced with a quarter-inch copper pipe.

North Kensington:
- Due to space restrictions inside the site cabin, the small-form computer installed with the SMPS will be replaced with a new rugged notebook.
- A new telephone line is required to remotely communicate with the SMPS.

Harwell:
- The SMPS is currently fitted with a PM2.5 sampling inlet. Due to low sample flow and the large diameter of the inlet pipe, residence time of the air in the pipe is too long. It will be replaced with a quarter-inch copper pipe.
- A solvent cabinet is required for the butanol stored at this site, to meet local safety requirements.
- A new telephone line is required to allow remote communication with the newly installed CPC.

Birmingham:
- No further actions at this time.

7.1 EUSAAR site recommendations

The EU funded EUSAAR project (European Supersites for Atmospheric Aerosol Research) aims, amongst other things, to improve the harmonisation of the monitoring of many of the pollutants covered by this network. Harwell is a EUSAAR site.

EUSAAR has made various recommendations for SMPS measurements that Harwell, and the other sites, should consider adopting. The inclusion of a drier in the inlet is the most important recommendation. All the recommendations, and the current position (*in italics*), are set out below.

Recommendations for the inlet
(Extract form the WMO/GAW Aerosol Measurement procedures guidelines and recommendations No.153)

The inlet used for aerosol sampling should meet certain design guidelines so that an undisturbed aerosol is delivered to the experimental instrumentation. The purpose of the inlet system is to bring to the aerosol analyzers a sample aerosol representative of the ambient air, at a controlled relative humidity. Humidity control is desirable because of the strong influence of relative humidity on the size of most airborne particles.

To meet those requirements the following actions should be undertaken:

1. The sample air should be brought into the laboratory through a vertical stack. In order to minimize local influences, a minimum height of 2 m above ground level is recommended for the inlet;

This is done.

2. An inlet with omni-directional high efficiency (i.e. a high aerosol transmission efficiency not varying with wind direction or wind speed). This can be achieved with a vertical air duct with a cover that excludes drizzle, rain and snow mounted on top of the inlet duct;

This is done.

3. The inlet should have a particle cut-off diameter of 10 micrometers aerodynamic diameter under ambient conditions;

This is not strictly done. At Harwell we have a $PM_{2.5}$ inlet design operating at low flow, equivalent to around PM_{20}. This would probably have a negligible effect on the results.

4. The sample flow should be laminar in the sample tube in order to avoid additional losses of small particles by diffusion and turbulent inertial deposition. A Reynolds number of about 2000 would be ideal. For example, a Reynolds number of 2000 occurs in a pipe of diameter 10 cm and 20 cm with a flow of 150 l/min and 300 l/min at STP, respectively.

The flow is definitely laminar, but we think the velocity is currently too low. The Re is around 20, but we intend to increase this to around 300 before the end of the year by reducing the diameter of the inlet tubing.

Recommendations for the TSI SMPS systems

In order to meet quality assurance and quality standards within the EUSAAR project the following actions are suggested to be performed:

1. The aerosol size distribution should be measured under dry conditions (<30% Relative Humidity-RH);
2. The aerosol flow should be dried (for example using a naphion drier). Losses in the drier should be calibrated;

While this is desirable in principle, NPL (on Defra's behalf) would like to see data showing actual results of the effect of a suitable drier in practice before implementing a change on the UK network. There may be complex effects relating to drying and diffusion losses, and we also need to consider how a modified system would relate to the collocated unmodified CPC. NPL would therefore like to evaluate other partners' experiences before setting a timescale (with Defra's agreement).

3. The aerosol flow should be monitored e.g. by a calibrated pressure transducer or mass flow meter. The aerosol flow should not fluctuate more than 10% on daily basis. Further it should be checked manually at each service occasion.

With the new TSI 3936L75 SMPS installed at Harwell in April 2007, the closed loop sheath air means that the aerosol flow is well monitored by the system's CPC.

4. The sheath air flow should be dried (for example using a naphion drier or an aerosol diffusion dryer);

We have not experienced operational problems with undried sheath air in this instrument that we have in others. We would like to evaluate the new instrument in the configuration recommended by TSI before making any changes.

5. The RH of the aerosol flow should be monitored by a calibrated humidity sensor (with an accuracy higher than 5% of RH);

Not applicable at the moment.

6. Atmospheric pressure should be monitored;

We believe that atmospheric pressure is monitored at the Harwell site.

7. Condensation Particle Counters (CPCs) should be only used after the calibration of the detection efficiency curve and flow rate.

The CPCs on the network are calibrated for efficiency and for flow rate annually.

References

[1] *CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Estimation of Measurement Uncertainty in Network Data*, NPL Report DQL-AS 037, March 2007

[2] *Comparison of Integrated Filter and Semi-Continuous Measurements of PM2.5 Nitrate, Sulfate, and Carbon Aerosols in the Speciation Trends Network (STN)*, US Environmental Protection Agency, 2005