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Quality Assurance and Quality Control (QA/QC) Procedures for UK Air Quality Monitoring under the Air Quality Standards Regulations

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Executive Summary

This report has been prepared for the UK Department of Environment, Food and Rural Affairs (Defra) and the Devolved Administrations of Scotland, Wales and Northern Ireland. It has been commissioned by the Environment Agency who are appointed to manage the UK air quality monitoring contract work on their behalf.

Within the UK, air quality monitoring is undertaken to provide information on air pollutant concentrations. The primary function of the monitoring is to provide data for the purpose of assessing the UK's compliance with the Air Quality Standards Regulations. The data are also used by scientists, policy makers and planners to enable them to make informed decisions on managing and improving air quality for the benefit of health and the natural environment.

The UK's air quality compliance monitoring is divided into several sub-networks for operational and management purposes. The relevant sub-networks are:

- The Automatic Urban and Rural Network (AURN);
- The UK Hydrocarbon Network;
- The UK Heavy Metals Network;
- The Polycyclic Aromatic Hydrocarbons (PAH) Network;
- The UK Urban Nitrogen Dioxide Network (UUNN);
- The UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) network which provides monitoring of a range of chemical species, for input to $PM_{2.5}$ speciation;
- The Particle Numbers and Concentrations network which provides measurement of Elemental Carbon (EC) and Organic Carbon (OC).

To ensure that the data produced are fit for purpose, robust QA/QC procedures are in place for each pollutant. Responsibility for their implementation rests with the relevant management and QA/QC contractors for each sub-network. These ensure the accuracy and precision of the published pollutant concentrations.

This report outlines the UK's data quality requirements and describes how these are addressed for all the relevant pollutants monitored. The report covers:

- Measurement methods
- Type-testing and equivalence of analysers
- Data telemetry, and validation of provisional data
- QA/QC including network inter-comparisons and data ratification
- Traceability of the measurements to national and international standards.
- Calculation of uncertainty for comparison with Data Quality Objectives.

Contents

1 Introduction

1.1 Scope

This document provides information on the quality assurance and quality control (QA/QC) procedures applied to air quality monitoring undertaken within the United Kingdom (UK) to assess compliance the Air Quality Standards Regulations [1] [2] [3] [4] and their amendments.

For operational and management reasons, the UK's air quality compliance monitoring regime is organised into several constituent sub-networks. However, all these networks form part of a single compliance network. The relevant sub-networks are:

- The Automatic Urban and Rural Network (AURN);
- The UK Hydrocarbon Network;
- The UK Heavy Metals Network;
- The Polycyclic Aromatic Hydrocarbons (PAH) Network;
- The UK Urban Nitrogen Dioxide Network (UUNN);
- The UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) network which provides monitoring of a range of chemical species in $PM_{2.5}$ particulate matter;
- The Particle Numbers and Concentrations network which provides measurement of Elemental Carbon (EC) and Organic Carbon (OC) in $PM_{2.5}$.

This document is not intended as an operational reference manual for day-to-day working purposes. Rather, it is intended to satisfy the requirement for a comprehensive record of the QA/QC procedures used for the UK's various types of compliance monitoring, together in one document.

Section 2 of this document lists the relevant legislation and the pollutants it covers, the reference methods, and the Data Quality Objectives (DQOs). Section 3 then provides an overview of the UK's compliance monitoring - the pollutants measured by each sub-network, techniques used, network operation and quality management procedures.

For each sub-network, this document then describes:

- Type testing and equivalence requirements and procedures (section 4).
- How data are collected from the monitoring sites, how they are handled and how the provisional data are disseminated to the public and other stakeholders (section 5).

- QA/QC: how the instruments are calibrated, the precision and accuracy quantified and monitored, and the processes of data validation and ratification (section 6).
- Details of traceability: in particular, how the requirements of the Air Quality Standards Regulations are met, for measurements to be traceable in accordance with ISO/IEC 17025:2017 [5] (section 7).
- Measurement and calculation of uncertainty (section 8).

2 Legislative Background and Requirements

2.1 UK Legislation on Ambient Air Quality

In the UK, ambient (outdoor) air quality is regulated by the Air Quality Standards Regulations. These are as follows:

- The Air Quality Standards Regulations 2010 in England [1], and their December 2016 amendment [6]
- The Air Quality Standards (Scotland) Regulations 2010 in Scotland [2], and their December 2016 amendment [7]
- The Air Quality Standards (Wales) Regulations 2010 in Wales [3]
- The Air Quality Standards Regulations (Northern Ireland) 2010 [4], and their December 2016 amendment [8]
- The Air Quality (Amendment of Domestic Regulations) (EU Exit) Regulations 2019 [9].

2.1.1 Provisions of the Air Quality Standards Regulations

The Air Quality Standards Regulations set ‘limit values’, ‘target values’ and ‘long-term objectives’ for ambient concentrations of pollutants. These are explained below, as well as provisions regarding monitoring and reporting of data.

Limit values are legally binding and must not be exceeded. They are set for individual pollutants and comprise a concentration value, an averaging period for the concentration value, a number of exceedances allowed (per year) and a date by which this must be achieved. Some pollutants have more than one limit value, for example relating to short-term average concentrations (such as the hourly mean) and long-term average concentrations (such as the annual mean).

Target values and **long-term objectives** are set for some pollutants and are configured in the same way as limit values. These are not legally binding, but the UK must take all necessary measures not entailing disproportionate costs to meet the target values and long-term objectives.

The Air Quality Standards Regulations include detailed provisions on the **monitoring and reporting** of air quality, including:

- The division of the UK into zones for the purposes of compliance reporting.
- The location and number of sampling points.
- The measurement methods to be used.
- Data quality objectives (DQOs).
- Siting criteria each monitoring station must meet.
- Provision for reporting compliance.
- Provision of information to the public.

The UK has statutory monitoring networks in place to meet the requirements of the above legislation, with air quality modelling used to supplement the monitored data.

2.1.2 European Background

The UK's Air Quality Standards Regulations have their origins in the following European Union (EU) legislation:

- Directive 2008/50/EC of 21st May 2008, on Ambient Air Quality and Cleaner Air for Europe [10]. This is referred to in this document as 'the Air Quality Directive' and covers the following pollutants: sulphur dioxide, nitrogen oxides, particulate matter (as PM_{10} and $PM_{2.5}$), lead, benzene, carbon monoxide and ozone. It revised and consolidated previously existing EU air quality legislation relating to the above pollutants.

- Directive 2004/107/EC of 15th December 2004 [11], relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. This is referred to as 'the Fourth Daughter Directive' and covers the four elements cadmium, arsenic, nickel and mercury, together with polycyclic aromatic hydrocarbons (PAH).

At the time that these Directives were adopted, the UK was a Member State of the EU, and was therefore legally required to incorporate - or "transpose" - the provisions of EU Directives into UK national law by a specified date. The Air Quality Standards Regulations were the means by which this was done. The full provisions of the above EU Directives have therefore remained part of UK legislation although the UK has now left the EU.

It should be noted that generally, the Air Quality Standards Regulations *refer* to the relevant section of the Air Quality Directive or Fourth Daughter Directive, rather than repeating the provisions in their own text. For this reason, in subsequent sections of this document, there are still many references to EU Directives in addition to the Air Quality Standards Regulations.

2.2 Pollutants Covered

The Air Quality Standards Regulations require assessment of the following pollutants:

- Sulphur dioxide (SO_2)
- Nitrogen dioxide (NO_2) and total oxides of nitrogen (NO_x)
- Carbon monoxide (CO)
- Benzene
- Particulate matter as PM_{10} and $PM_{2.5}$
- Ozone
- Ozone precursor substances *(note – there are no limit or target values, or DQOs, for these.)*
- Lead (Pb)
- Arsenic (As)
- Cadmium (Cd)
- Nickel (Ni)
- Mercury (Hg)
- Benzo[a]pyrene (B[a]P), as an indicator species for the group of compounds known as polycyclic aromatic hydrocarbons or PAH.
- Additional recommended PAH species.
- Deposition of PAH and metallic elements in the particulate phase. *(Note – there are no limit or target values for these.)*

The Air Quality Standards Regulations also require the measurement of the following chemical species in the $PM_{2.5}$ fraction: sulphate (SO_4^{2-}), nitrate (NO_3^-), sodium ion (Na^+), potassium ion (K^+), ammonium ion (NH_4^+), chloride ion (Cl^-), calcium ion (Ca^{2+}), magnesium ion (Mg^{2+}), elemental carbon (EC) and organic carbon (OC). These are to be measured in rural background areas. *(Note – there are no limit or target values, or DQOs, for these.)*

2.3 Data Quality Objectives (DQOs)

The Air Quality Standards Regulations specify that the DQOs provided in Annex I (one) of the Air Quality Directive [10] must be met. These are summarised in Table 2-1 for the pollutants covered by this report. This table shows the objectives for fixed measurements: objectives are also set for indicative measurements and modelling but are not presented here.

Table 2-1 DQOs for ambient air quality assessment, fixed measurements

	SO_2, NO_2, NO_x, CO	**Benzene**	**PM_{10}/$PM_{2.5}$ & Pb**	**O_3 and related NO and NO_2**
Fixed measurements (a) Uncertainty	15%	25%	25%	15%
Minimum data capture	90%	90%	90%	90% during summer, 75% during winter
Minimum time coverage, urban background and urban traffic	-	35%(b)	-	-
Minimum time coverage, industrial sites	-	90%	-	-

(a) The uncertainty (expressed at a 95% confidence level) of the assessment methods will be evaluated in accordance with the principles of the CEN Guide to the Expression of Uncertainty in Measurement (ENV 13005-1999), the methodology of International Organisation for Standardisation ISO 5725:1994 and the guidance provided in the CEN report 'Air Quality – Approach to Uncertainty Estimation for Ambient Air Reference Measurement Methods' (CR 14377:2002E). The percentages for uncertainty in the above table are given for individual measurements averaged over the period considered by the limit value (or target value in the case of ozone), for a 95% confidence interval. The uncertainty for the fixed measurements shall be interpreted as being applicable in the region of the appropriate limit value (or target value in the case of ozone).

(b) Time coverage is distributed over the year to be representative of various conditions for climate and traffic.

Calculation of data coverage and allowance for planned maintenance will be taken into account in determining compliance with the DQOs. The Air Quality Standards Regulations also require that monitoring of As, Cd, Ni, Hg, B[a]P and other PAH is compliant with the DQOs provided in Annex IV of the Fourth Daughter Directive [11]. These are summarised in Table 2-2.

Table 2-2 Data Quality Objectives of 4th Daughter Directive

	B[a]P	**As, Cd and Ni**	**PAH other than B[a]P, and total gaseous Hg**	**Total Deposition**
Uncertainty				
Fixed and indicative measurements	50%	40%	50%	70%
Modelling	60%	60%	60%	60%
Minimum data capture	90%	90%	90%	90%
Minimum time coverage				
Fixed measurements	30%	50%	-	-
Indicative measurements [a]	14%	14%	14%	33%

[a] Indicative measurements being measurements that are performed at a reduced regularity but fulfil the other data quality objectives

Details of how measurement uncertainty is calculated are provided in section 8. The managers of each sub-network are required to report compliance with the above DQOs on an annual basis. Annual reports from the sub-networks are published online via the “Library” section of the Defra UK Air Information Resource, UK-AIR, under the option for “Monitoring Networks”- see http://uk-air.defra.gov.uk/library/reports?section_id=13 .

2.4 Measurement Methods

The Air Quality Standards Regulations’ reference methods of measurement for the various pollutants are as specified for the EU, in Annex VI of the Air Quality Directive. These are the Standard Methods developed by CEN (the European

Committee for Standardisation) and realised in the UK through published CEN Standards as follows:

- EN14211:2012 [12] (NO_x).
- EN14212:2012 [13] (SO_2).
- EN14625:2012 [14] (O_3).
- EN14626:2012 [15](CO).
- EN12341:2014 [16] (PM_{10} and $PM_{2.5}$).
- EN16450: [17] (PM_{10} and $PM_{2.5}$ using automated systems.
- EN14662-1:2005 [18] (non-automatic benzene monitoring, C_6H_6).
- EN14662-3:2015 [19](automatic benzene monitoring, C_6H_6).
- EN14902:2005 [20](Pb, Cd, As, and Ni in the PM_{10} fraction of suspended particulate matter).
- EN15853:2010 [21], (Hg deposition).
- EN15841:2009 [22], (As, Cd, Pb and Ni in atmospheric deposition).
- EN16913:2017 [23], for speciated $PM_{2.5}$: NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}. (Note, this is the European Standard Method for speciated $PM_{2.5}$ monitoring although not yet specified in the legislation.)

UK experts continue to work closely with CEN to develop standards describing how samplers and analysers should be tested, approved for use, calibrated and have their ongoing performance determined. The CEN Standards allow the UK to reliably and consistently quantify the uncertainties associated with their measurements of air pollution. CEN, through the various Working Groups, continues to revise and improve the Standards as new information becomes available. Many of the QA/QC procedures adopted in the UK arise directly from the requirements of the CEN standard methods and are described in later sections of this report.

3 Overview of UK Compliance Monitoring

The pollutants measured in the UK air quality compliance monitoring sub-networks are detailed in Table 3-1.

Table 3-1 The UK's Air Quality Compliance Monitoring in 2022

Sub-Network	**Pollutants**
Automatic Urban and Rural Network (AURN)	Ambient concentrations of CO, NO_x, NO (with NO_2 calculated as NO_x - NO), SO_2, O_3, PM_{10}, $PM_{2.5}$.
UK Hydrocarbon Network	Ambient concentrations of benzene and a range of volatile organic compounds (VOCs)
UK Heavy Metals Network	Ambient concentrations in PM_{10} of arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), vanadium (V), zinc (Zn). Four rural sites: in addition to the above, ambient concentrations in deposition in the particulate phase, of aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), caesium (Cs), copper (Cu), iron (Fe), lead (Pb), lithium (Li), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), rubidium (Rb), selenium (Se), strontium (Sr), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V), zinc (Zn).
PAH Network	Ambient concentrations, and deposition in the particulate phase, of 27 PAH species including benzo[a]pyrene.
Particle Numbers and Concentrations Network	Elemental Carbon (EC) and Organic Carbon (OC) in $PM_{2.5}$.
UKEAP Network	The following cations and anions in the $PM_{2.5}$ fraction, in rural background areas: sulphate (SO_4^{2-}), nitrate (NO_3^-), sodium ion (Na^+), potassium ion (K^+), ammonium ion (NH_4^+), chloride ion (Cl^-), calcium ion (Ca^{2+}), magnesium ion (Mg^{2+}).

UK Urban Nitrogen Dioxide Network	Ambient concentration of nitrogen dioxide (NO_2) using passive samplers.

Other air quality research monitoring is undertaken in further sub-networks in the UK but is not detailed here as it is not used for compliance purposes. For information on these other monitoring programmes, please refer to the following page on Defra's online UK Air Information Resource (UK-AIR): http://uk-air.defra.gov.uk/networks/network-info?view=non-automatic .

3.1 Overview of the AURN

The Automatic Urban and Rural Network (AURN) is the largest automatic monitoring network in the UK and provides a large proportion of the UK's statutory compliance monitoring evidence base. Data from the AURN are available on Defra's online UK Air Information Resource, UK-AIR at http://uk-air.defra.gov.uk/. The AURN aims to:

- Inform the public about air quality in near-real time.
- Provide data for comparison with statutory air quality standards, objectives, target and limit values.
- Assess effects of air pollution on health and the environment
- Inform and support the development of cost-effective planning solutions and identify long-term trends and sources of pollution.
- Inform policy development.
- Provide data for use by the scientific community in research.
- Enhance our understanding of atmospheric chemistry.

3.1.1 Pollutants measured in the AURN

The pollutants measured by the AURN are listed in Table 3-1 above.

3.1.2 Measurement Techniques Used in the AURN

Details of the measuring techniques used in the AURN are provided in Table 3-2. The AURN consists predominantly of automatic monitoring equipment. Gaseous pollutants are monitored with the defined EU reference methods. For particulate matter the AURN is based on methods which have demonstrated equivalence to the reference method, but which (unlike the reference method) allow continuous on-line monitoring. At a small number of sites, gravimetric samplers, which provide daily mean results, are operated alongside the automatic particulate monitoring instruments: this co-location of instruments is done either for a site-specific reason, or as part of an ongoing study of equivalence of methods.

Table 3-2 AURN Measurement Techniques

Pollutant	CEN standard/ref method	Details
O_3	EN 14625:2012 “Ambient air quality – standard method for the measurement of the concentration of ozone by ultraviolet photometry”	**UV absorption:** ozone absorbs UV light. The absorption of UV by sampled air is used to calculate the ozone concentration.
NO_2/NO_x	EN 14211:2012 “Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide [i.e. nitric oxide] by Chemiluminescence”	**Chemiluminescence:** this method measures the energy emitted when nitric oxide (NO) is reacted with ozone (O_3) in an evacuated chamber to form chemiluminescent nitrogen dioxide (NO_2).
SO_2	EN 14212:2012 “Ambient air quality – Standard method for the measurement of the concentration of sulphur dioxide by UV fluorescence”	**UV fluorescence:** SO_2 molecules are excited to higher energy states by UV radiation. These excited molecules then release their energy as fluorescent radiation. The intensity of this is used to measure the concentration of SO_2 in sampled air.
CO	EN 14626:2012 “Ambient air quality - Standard method for the measurement of the concentration of carbon monoxide by non-dispersive infra red spectroscopy”	**IR absorption:** CO strongly absorbs infrared radiation of wavelength 4.5 to 4.9 µm. A reference detection system is used to alternately measure absorption due to CO in the sampled air stream and a high-concentration pure CO signal as a correlated reference. An infrared detector gives a signal proportional to the CO concentration.
PM_{10} and $PM_{2.5}$	EN 12341:2014 “Ambient air quality - Standard gravimetric measurement method for the determination of the PM_{10} or $PM_{2.5}$ mass fraction of suspended particulate matter” *(Note: at the time of writing, a new 2023 version is expected soon).*	The AURN uses three methods which are equivalent for both metrics (PM_{10} and $PM_{2.5}$): The **Fidas 200^{TM}**, an instrument which uses an optical technique to monitor particulate concentration. The **Beta-Attenuation Monitor** (BAM) which measures the attenuation of beta rays passing through a paper filter on which particulate matter from sampled air has been collected. Two types of **gravimetric** sampler that collect daily samples onto a filter for subsequent weighing. Used at a very small number of sites at the time of writing.

In order to be acceptable for use in the AURN, the equivalent methods used for measurement of particulate matter must have demonstrated equivalence with the reference method according to the provisions of the Guide to Demonstration of Equivalence (GDE). The current is GDE supersedes a version previously published in November 2005. A newer (2016) document, BS EN 16450, covers automatic particulate monitoring instruments. BS EN 16450 builds on the procedures documented in GDE 2010, with slightly amended calculation methodologies.

Since the initial assessment of automatic PM analysers in 2004-06, a number of manufacturers have submitted analysers for evaluation against the equivalence criteria. From 2012, the UK has required additional testing to be undertaken in the UK to demonstrate that analysers remained equivalent when operated in the UK climate. Test criteria for UK certification are published at https://uk-air.defra.gov.uk/assets/documents/MCERTS_for%20UK_Particulate_Matter_final.pdf

Details of the analysers tested and their certification is available at: https://www.csagroup.org/en-gb/services/mcerts/mcerts-product-certification/mcerts-certified-products/mcertscertified-productscontinuous-ambient-air-monitoring-system-mcerts-for-uk-particulate-matter/

One of the requirements of EN 16450 is for ongoing Particulate Matter Equivalence Trials to ensure analysers continue to demonstrate comparability to the reference method. As a result, a programme of ongoing equivalence demonstration has been implemented in the AURN. At the time of writing, these are carried out on a permanent basis at two sites: London Teddington Bushy Park and Manchester Piccadilly. At each of these two sites, one of each type of particulate matter monitoring instrument currently used in the AURN (the BAM 1020 and the Fidas 200^{TM}) is operated in co-location with the gravimetric reference method (an SEQ) for PM_{10} and $PM_{2.5}$.

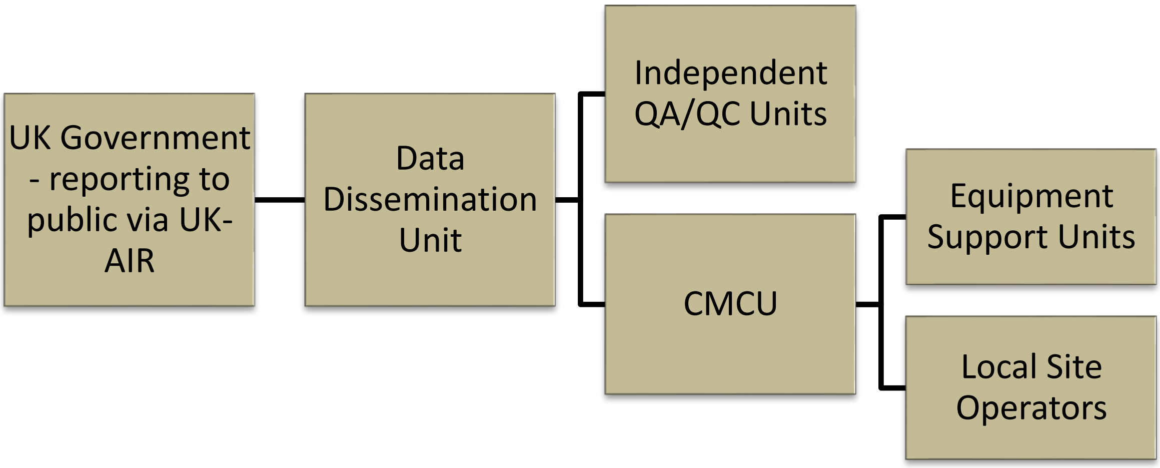
3.1.3 AURN Network Operation and Management

Several organisations are involved in the day-to-day running of the network, under contract to Defra and the DAs. At the time of writing (2022), the role of Central Management and Co-ordination Unit (CMCU) for the AURN is contracted to Bureau Veritas. Ricardo Energy & Environment (‘Ricardo’) currently undertakes the role of Quality Assurance and Control Unit (QA/QC Unit) for the majority of sites within the AURN, with the National Physical Laboratory (NPL) fulfilling this role for the Automatic London Network (ALN) subset, currently comprising 16 sites. The responsibility for operating individual monitoring sites is assigned to local site operators (LSOs) with relevant experience in the field under the direct management of (and under contract to) CMCU. Calibration gases for the network are supplied by BOC Ltd and are provided with a United Kingdom Accreditation Service (UKAS) certificate of calibration by Ricardo. The monitoring equipment is serviced and maintained by a number of Equipment Support Units (ESUs), under contract to the CMCU.

Dissemination of the data from the AURN via the Defra online UK Air Information Resource (UK-AIR) at http://uk-air.defra.gov.uk/ and other media such as free telephone services and Twitter is undertaken by the Data Dissemination Unit (under separate contract). A summary report of the data is also published annually in the "*Air Pollution in the UK*" series of reports, available online via UK-AIR.

Figure 3-1 summarises the structure data flow and operation of the AURN and the major interactions between the participating organisations.

Figure 3-1 Structure of the AURN regarding data flow



Quality control and assurance are managed by the QA/QC Unit, whose primary function is to maintain the data quality and ensure that the EU Directive DQOs are met. In this way this independent unit is able to coordinate the quality efforts of all other AURN stakeholders and approach all QA/QC issues in a focused and structured way.

3.1.4 Role of the AURN and QA/QC Units

The role of the QA/QC Units is to ensure that data produced by the AURN are robust, reliable and of high quality. These data are used to fulfil the reporting requirements of the Air Quality Standards Regulations, so should meet the legal obligations and DQOs of the Regulations. The QA/QC Units interact closely with the AURN CMCU and Gas Provision contractors to ensure that these network objectives are met.

Compliance with the data capture objectives of the Air Quality Standards Regulations, for each pollutant at each site, is currently reported annually in the series of reports entitled "*AURN Annual Technical Report*", available via the Library pages of UK-AIR (see http://uk-air.defra.gov.uk/library/).

3.2 Overview of the Hydrocarbon Network

The Air Quality Standards Regulations (like the Air Quality Directive from which they are derived) requires measurement and reporting of benzene (which is covered by the Air Quality Directive as a pollutant in its own right), and ozone precursor substances. The ozone precursor substances include volatile organic compounds (VOCs): Annex X (ten) of the Directive provides a list of 31 species recommended for measurement. The Hydrocarbon Network includes three components: the Automatic Hydrocarbon Network, European Monitoring and Evaluation Programme (EMEP) supersites and the Non-Automatic Hydrocarbon Network.

Ozone precursor measurement is carried out by the Automatic Hydrocarbon Network. Automatic hourly measurements of a range of hydrocarbon species (including all the ozone precursor species specified in Annex X of the Directive except formaldehyde and total non-methane hydrocarbons), are made using automated pumped sampling with *in-situ* gas chromatography, at four sites in the UK. The VOCs monitored include benzene. Historic VOC emission mitigation strategies have focussed predominantly on the transport sector. In the present day, VOCs emitted from the solvent production and use sector have reduced the least since 1990. Following advice from the UK Air Quality Expert Group (AQEG) [24] Defra requested additional measurements of Oxygenated VOCs (OVOCs), including methanol, ethanol, 2-butanone and acetone in order to gain further understanding of these VOCs and their relative abundance in the UK. Action is being taken to refresh network instrumentation to be able to monitor at least three of these four OVOCs in future years.

Two monitoring sites, at Chilbolton Observatory in Hampshire and Auchencorth Moss in Midlothian, are also part of the European Measurement and Evaluation

Programme (EMEP) [25] and Aerosol, Clouds and Trace Gases Infrastructure (ACTRIS) [26] programmes. EMEP is an international co-operative programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe ACTRIS is a pan-European research infrastructure (RI) producing high-quality data and information on short-lived atmospheric constituents and on the processes leading to the variability of these constituents in natural and controlled atmospheres. Data relevant to NMVOCs has been reported to the World Health Organisation Global Atmosphere Watch programme (GAW) for Auchencorth Moss since 2020. [27]

The four automatic Hydrocarbon Network sites are accompanied by a network of 34 non-automatic sites. These measure ambient concentrations of benzene only, by the CEN standard method [18], which involves pumping air through an adsorption tube to trap the compound, which is later analysed in a laboratory. At each site two tubes sample alternately every eight minutes for a fortnightly exposure period. This network monitors compliance with the Air Quality Directive’s limit value for benzene. All non-automatic sites in the Hydrocarbon Network are co-located with AURN sites.

3.2.1 Pollutants Measured in the Hydrocarbon Network

Table 3-3 shows the compounds measured in the Automatic Hydrocarbons network. Only benzene monitoring is required for compliance with the Air Quality Directive.

Table 3-3 Compounds Measured by the Hydrocarbons Network (including the Automatic Hydrocarbon Network, EMEP supersites and the Non-Automatic Hydrocarbon Network)

Compounds	
Ethane	2-methylpentane
ethene	n-hexane
propane	isoprene
propene	benzene
ethyne	i-octane
i-butane	n-heptane
n-butane	n-octane

Compounds	
trans-2-butene	Toluene
1-butene	ethylbenzene
cis-2-butene	meta- and para-xylene
i-pentane	ortho-xylene
n-pentane	1,3,5-trimethylbenzene
1,3-butadiene	1,2,4-trimethylbenzene
trans-2-pentene	1,2,3-trimethylbenzene
1-pentene	

3.2.2 Techniques used in the Hydrocarbon Network

The automatic hydrocarbon network (for ozone precursor compounds and benzene) uses automated pumped sampling with *in-situ* gas chromatography. The sample is drawn from the ambient atmosphere to the analyser in as short a time as possible. This is achieved by use of a high-volume sample manifold, where ambient air is drawn through the manifold to a point close to the inlet of the analyser. The rate at which the air is drawn through this high-volume inlet is such that the sample remains in the manifold for less than one second, the instrument is positioned as close to the manifold as is possible. It is then sampled from this point at 15 ml/min for 40 minutes of every hour into the analyser.

The analytical system within the automatic hydrocarbon analyser consists of an automatic trapping/thermal desorptioning system (using Peltier cooling) connected to a conventional gas chromatograph (GC). The thermal desorber (TD) collects the sample from ambient air. The TD extracts the analytes from the sample onto a Peltier cooled adsorbent trap. The trapped analytes are thermally desorbed and carried through a heated transfer line by carrier gas into the GC. The GC contains two columns and a heartcut device to separate, by volatility, the analytes into two fractions. The more volatile fraction is separated on a PLOT (Porous Layer Open Tubular) column whereas the less volatile fraction is separated on a methyl silicone column. A flame ionization detector monitors the chromatography on each column. The control and data-handling system are run from a computer. The system is supplied with gases from a hydrogen generator, zero air compressor and a helium carrier gas cylinder.

3.2.3 Hydrocarbon Network Operation and Management

Several organisations are involved in the day-to-day running of the network, under contract to the Environment Agency. At the time of writing (2022), the role of CMCU for the Hydrocarbon Network is contracted to Ricardo, which also undertakes the role of QA/QC Unit. The responsibility for operating individual monitoring sites is assigned to LSOs with relevant experience in the field under the direct management of (and under contract to) the CMCU. Calibration gases for the network are supplied by the National Physical Laboratory (NPL). The monitoring equipment is serviced and maintained by PerkinElmer, under contract to the CMCU.

Key aspects of the operation and management of this network are as follows:

- Maintenance of the monitoring instruments and associated ancillary equipment in the network.
- Provision of on-site consumables.
- Carrying out preliminary validation of the data, for which proprietary artificial intelligence pattern recognition software is used along with bespoke data processing software developed by Ricardo.
- Supplying these data to the Data Dissemination Unit.
- Retaining and maintaining the raw and validated air quality data in a separate archive.
- Taking appropriate actions, in consultation with the QA/QC contractor, to ensure that the network achieves the data quality objectives of the Air Quality Standards Regulations for benzene.

3.2.4 Quality Management in the Hydrocarbon Network

The main aspects of quality management in the hydrocarbon network are:

- Regular visits to network sites (at least once per year) and meetings with the LSOs in order to discuss and review the condition of the site and equipment, data capture and associated issues.
- An annual inter-calibration, with provision of advice, and where necessary, of any service and maintenance requirements arising from the findings.
- Yearly auditing of LSO operations, including the provision of operator training. These audits are timed to coincide with the inter-calibration to ensure cost-efficiency.

- Ratification of validated data provided by the CMCU. The ratified data are transferred to the Defra online air quality information resource (UK-AIR) within three months of receipt of data.
- Quarterly progress reporting to the Environment Agency to cover the operation of the network, data capture performance and trend analysis.
- Annual reports are produced to summarise the data collected. These reports describe the data collected and reported for the calendar year.
- Long term data analysis.
- Attendance at the annual network review meeting with the CMCU, the Environment Agency, LSOs and other stakeholders.
- Provision of policy advice on hydrocarbon monitoring issues and data interpretation to the Environment Agency, LSOs, the Air Quality Expert Group and other review groups as requested.
- Provision of calibration gases for both routine site calibration checks and six-monthly network intercalibrations.
- Attendance at any relevant WHO intercomparisons and meetings. These are usually held at the WHO/EU Joint Research Council, Ispra (Italy) to ensure the standard gas mixture used and the methodology used for quantification is equivalent to other laboratories in Europe.
- Participation in round robin exercises under ACTRIS [26]/EMEP [25]/GAW [27].

An annual report is produced covering both the automatic and non-automatic hydrocarbon monitoring. This includes comparison of the Network's performance with the DQOs. The most recent report can be found at http://uk-air.defra.gov.uk/library/reports?section_id=13.

3.3 Overview of the Heavy Metals Network

The UK Heavy Metals Monitoring Network measures metal concentrations in ambient PM_{10} and deposited metals. As of March 2022, this network comprised 24 monitoring sites around the country (14 in England, six in Wales, two in Scotland and two in Northern Ireland). The network comprises a mix of urban background, urban and suburban industrial, urban traffic, and rural locations.

Twenty-three of the 24 monitoring sites measure metals in ambient PM_{10}. In addition, five of the 24 sites measure deposition of metals, four of which also monitor mercury in deposition. The rural sites were specifically chosen to be representative of rural background areas and are as free from local sources of metal emissions as possible, while still being accessible for site operators.

The contractor responsible for the management of this network is the National Physical Laboratory (NPL), with deposition measurements subcontracted to the UK Centre for Ecology and Hydrology (UKCEH).

The Network has the following objectives:

- To achieve compliance with monitoring requirements set out in the Air Quality Standards Regulations.
- To provide data to the UK Government on the UK's performance against the limit values, target values, and DQOs described in the relevant legislation.
- To assess impacts around 'hot spots' of metallic pollution to air, particularly in industrial areas.
- To produce accurate and reliable data for dissemination to the general public and for use by scientific and medical researchers and the air quality community.

The UK Heavy Metals Monitoring Network is the regulatory air quality monitoring network that fulfils the majority of the UK's obligation under the Air Quality Standards Regulations relating to the monitoring of the mass concentrations of lead, nickel, arsenic and cadmium, in the PM_{10} phase of ambient air, and total gaseous mercury (referred to as: Hg(v)). The Network forms the basis of the UK's compliance monitoring for the Air Quality Standards Regulations, for lead, arsenic, cadmium, nickel and mercury.

3.3.1 Pollutants measured in the Heavy Metals Network

The full suite of metals measured by the Network in ambient PM_{10} is: arsenic, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, selenium, vanadium, and zinc.

The full suite of metals measured in deposition at five rural sites (Auchencorth Moss, Chilbolton Observatory, Heigham Holmes, Lough Navar and Yarner Wood) is Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, U, V, W, Zn. Deposited mercury is also measured at all of these except Lough Navar.

3.3.2 Measurement Techniques used in the Heavy Metals Network

3.3.2.1 Metals in PM_{10}

Ambient concentrations of metals in the PM_{10} phase of ambient air are measured by sampling onto filters. This is done using Digitel^{TM} DPA14 instruments operating at a calibrated flow rate, nominally of 1 m^3 h^{-1}, fitted with PM_{10} selective inlet heads, using 47 mm diameter cellulose membrane filters in filter cassettes. This sampling is carried out in accordance with EN 12341:2014. The air sampling period is one week, with the filter changeover time being set at 06:00 on the morning of the LSO visit. Experience has shown that this approach maximises the chance of detecting and rectifying a sampler fault such as Filter Exchange Error.

Filter cassettes are assembled taking precautions to minimise metal contamination (i.e. using acid washed equipment and clean-room powder-free gloves).

Aerosol sampler deployment and changeover of filter cassettes conform to EMEP standards and aim to prevent contamination by providing a rigorous protocol for filter changeover and laboratory preparation prior to analysis.

The exposed filters are then returned to the contractor’s laboratory where they are analysed to determine the content of various metals in the particulate matter, in order to produce concentration values for these metals in ambient air according to EN 14902:2005.

Weekly concentration data are produced for metals in PM_{10} at five locations. All other stations produce data averaged over four-weekly periods. The production of the data is subject to a number of rigorous QA/QC procedures that are detailed in subsequent sections.

3.3.2.2 Deposition of Metals

(i) Metals in Rainfall

Bulk collectors, bottle and funnel type, are deployed for the collection of bulk precipitation.

The levels of metals found within precipitation are at the µg/l level or lower. It is therefore essential that rigorous protocols are used for cleaning sampling equipment between collector deployments to prevent contamination within the laboratory. Collectors comprising a five-litre polyethylene bottle, 14 cm diameter polyethylene funnel and a debris filter are cleaned by soaking for 24 hours with 0.1 M nitric acid. Bottles, funnels and debris filters are then rinsed with ultra-pure water (> 18 MΩ cm^{-1}, Millipore) and finally dried in a filtered air-drying cabinet. Bulk collectors are assembled in a dedicated laboratory, double bagged, and then sent out to field sites in flight cases along with instructions for collector changeover.

(ii) Mercury in rainfall

An adapted EMEP protocol for sampling mercury in precipitation (EMEP (2002), [28]) is used.

The sampling equipment and cleaning protocols are specific for mercury because of this metal’s special characteristics, i.e. it is present at ng/l levels in precipitation and is prone to background contamination. Briefly, precipitation for the determination of mercury is collected in special precipitation samplers, based on those used within the Swedish National Monitoring Program, the Iverfeldt design.

The collector was designed to prevent the diffusion of gaseous mercury (Hg_0) into the collection vessel by the use of a 0.5m capillary tube between collection funnel and bottle.

Sampling and analysis of bulk precipitation for mercury is particularly prone to contamination and therefore duplicate bulk precipitation samples are collected at each of the four network sites at which mercury is monitored.

The precipitation collector was based on the Iverfeldt design with a long tube to reduce mercury diffusion to and from the atmosphere. A number of modifications have been made in order to reduce possible contamination and improve safety of use:

- The funnel and tube are made of Polytetrafluoroethylene (PTFE) as per the Florida Atmospheric Monitoring Survey.
- The debris filter and capillary components are made of PTFE.
- The joints connecting individual components are close fitting and thus designed to reduce contamination form ingress of gaseous Hg_0.
- To reduce diffusion of gaseous Hg_0 a glass bottle is used for final collection.

Glassware and reagents are rigorously tested in order to identify and reduce sources of contamination. Bottles are cleaned on a monthly basis according to the EMEP protocol by soaking in 1% nitric acid followed by bromate/bromide reagent and a final rinse with ultra-pure water.

Mercury samplers are deployed, in duplicate, at the four main network sites, pre-acidified with hydrochloric acid as a preservative and changed on a monthly basis.

The field protocols are similar to those used for the deployment of bulk precipitation samplers and are designed to prevent sample contamination at the field sites and during transport.

3.3.3 Analytical Techniques used in the Heavy Metals Network

3.3.3.1 Analysis of Metals in PM_{10}

Analysis for particulate-phase metals is carried out by the contractor. This uses Agilent A8800 and A8900 ICP-MS triple quadrupole mass spectrometers, following the contractor’s procedure, accredited by UKAS to ISO 17025:2017, which is fully compliant with the requirements of EN 14902:2005.

Upon arrival at the contractor’s laboratory, the filters are cut accurately in half (for sites where weekly results are produced) and into quarters (where four-weekly results are produced). For the sites producing weekly data, the half portion is digested at temperatures up to 220˚C using an Anton Parr Multiwave 5000 microwave. For the sites producing four-weekly data, one quarter of each of the four filters comprising the four-week period is digested together. The digestion mixture used is 8 ml of nitric acid and 2 ml hydrogen peroxide.

ICP-MS analysis of the digested solutions is carried out using at least four gravimetrically-prepared calibration solutions. A quality assurance (QA) standard is repeatedly analysed (after every two solutions), and the change in response of the QA standard has been mathematically modelled to correct for the long-term drift of the instrument. The short-term drift of the ICP-MS is corrected for by use of an internal standards mixture (containing elements yttrium (Y), indium (In), bismuth (Bi), and scandium (Sc)), continuously added to all the samples via a mixing block. Each sample is analysed in triplicate, each analysis comprising five replicates.

The amount of each metal in solution (and its uncertainty) is then determined by a method of generalised least squares using software developed by the contractor to construct a calibration curve.

3.3.3.2 Analysis of Metals in Deposition

The bulk collectors are weighed to estimate rainfall amounts then acidified with ultra-pure nitric acid (Baker Ultrex II) to a final strength of 1% v/v.

The acidified 5 L bulk precipitation samples are left for 24 hours to allow desorption of metals from the walls of the collector bottle and then a 50 mL sub-sample is transferred to a separate acid washed bottle.

Acidified and preserved samples are stored at 4°C prior to final measurement by ICP-MS (Perkin Elmer Nexion 300D). The ICP-MS measurement uses similar procedures and QA/QC checks outlined above for the measurements of particulate phase digests. However measurements for additional metals are made, resulting in values for Al, Sb, As, Ba, Be, Cd, Cs, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Rb, Se, Sr, Sn, Ti, W, V and Zn being produced. The procedure is in full accordance with EN 15841.

3.3.3.3 Mercury in Rainfall:

For the mercury in deposition samples, the Hg collector bottles are weighed to estimate rainfall amounts and then stored at 4°C prior to analysis.

Mercury in precipitation is determined by Atomic Fluorescence Spectrometry (AFS) using a PS Analytical Galahad analyser with pre-concentration of mercury on a gold trap to increase instrument sensitivity. This method employs a reductive desorption process. During this step, tin chloride is added to the sample being analysed in a gas–liquid separator. This reduces all the collected mercury to elemental mercury and liberates this into the gas phase using a stream of argon bubbling through the gas-liquid separator. This mercury vapour is then collected on the mercury adsorption trap, which was then heated, desorbing the mercury onto a permanent trap. Subsequent heating of this trap then desorbed the mercury onto the detector.

The system is calibrated using gravimetrically prepared mercury in liquid standards. These standards are traceable to NIST mono-elemental reference materials. The procedure is in full accordance with EN 15853 and EN ISO 17852.

3.3.4 Heavy Metals Network Operation and Management

Operation of the network is currently managed by NPL, using Local Site Operators (LSOs) who are responsible for changing samples using NPL protocols. Samples are sent to NPL's laboratory for analysis. All metal concentrations are analysed by the contractor using strict QA/QC protocols and uploaded to the UK-AIR online data repository. Details of data handling for this network are provided in section 5.4.1.

A service and maintenance contract is in operation, with 6-monthly service rounds and calibrations undertaken by an equipment support unit (ESU) under subcontract. The ESU is called out as required to deal with any equipment problems that might occur.

The contractor carries out six-monthly site audit visits to all the Network sites. At these visits the site infrastructure, performance and integrity are assessed. The LSOs are also audited and receive extra training where required.

3.3.5 Quality Management in the Heavy Metals Network

Particulate samples are taken at all sites in the Network using Digitel^{TM} DPA14 instruments (fitted with PM_{10} heads) operating at a calibrated flow rate, nominally of 1 m^3 h^{-1}, in accordance with EN 12341:2014.

Analysis for particulate-phase metals is carried out by the contractor at its laboratory, using Agilent A8800 and A8900 triple quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS QQQ), following the contractor's procedure, accredited by UKAS to International Organisation for Standardisation ISO 17025:2017 [5]. This is fully compliant with the requirements of EN 14902:2005.

The project is managed according to the requirements of the Joint Code of Practice for Research, to which both Defra and the current contractor are signatories. In addition, the chemical analysis performed at the contractor's laboratory are accredited by UKAS to ISO 17025:2017.

Methods for the analysis of trace metals in precipitation are included within the analyst's accreditation scheme (UKAS Testing Laboratory 2506; specific details can be found at http://www.ukas.com/). UKAS accreditation includes an outline of the performance characteristics for the instrumental methods used for the determination of trace metals in precipitation as well as mercury in surface waters. The performance characteristics comprise: validation data obtained during the process of laboratory accreditation by UKAS, ongoing quality control and participation in proficiency testing schemes where applicable (e.g. LGC Standards Aquacheck: http://www.lgcpt.com/Default_eng.aspx).

An annual report is produced. This includes comparison of the Networks' performance with the Directive DQOs. The reports can be found at http://uk-air.defra.gov.uk/library/reports?section_id=13 .

3.4 Overview of the PAH Network

The primary objective of the network is to provide polycyclic aromatic hydrocarbon (PAH) concentration information at the sites in the network. It determines the ambient concentrations of PAH in ambient air in the UK through monitoring and chemical analysis The collection of this data enables the assessment of current concentrations of PAH to:

a) Enable demonstration of the UK's compliance with the Air Quality Standards Regulations [1] [2] [3] [4] (target value of 1 ngm^{-3} for the annual mean concentration of B[a]P) which is not to be exceeded after 31st December 2012,
b) Assess concentrations against the National Air Quality Objective for PAH (annual mean of 0.25 ngm^{-3} benzo(a)pyrene (B[a]P) in ambient air) published in the UK Air Quality Strategy [29].
c) Provide data and metadata under the OSPAR convention and the UNECE Convention on Long Range Transboundary Air Pollutants.

The network also provides data on ambient concentrations in the UK that:

- Enable trends of airborne concentrations of PAH in representative UK industrial, urban and other areas to be assessed, and to compare and contrast them with those in rural locations.
- Allow data to be made available to the wider research community and the public via data submission to the UK-AIR online information resource (http://uk-air.defra.gov.uk).
- Provide ambient concentrations that allow improvement in the understanding of PAH source local to sites. Enabling the examination of their agreement with the National Atmospheric Emissions Inventory (www.naei.org.uk). To input into estimates of atmospheric PAH concentrations, future projections, and the identification of the key areas of uncertainty.
- Provide input to national and local scale modelling of PAH.

At the time of writing (March 2022), the Network comprises 33 stations. Twenty-two of these 33 stations are in England, four in Scotland, four in Wales and three in Northern Ireland.

3.4.1 Pollutants measured in PAH Network

The PAH compounds measured in 2021 are shown in Table 3-4.

Table 3-4 Range of PAH analysed

PAH number	Compound	PAH number	Compound
1	Phenanthrene	15	Benzo[e]pyrene
2	Anthracene	16	Benzo[a]pyrene
3	Fluoranthene	17	Perylene
4	Pyrene	18	Dibenzo[a,c]anthracene
5	Retene	19	Dibenzo[a,h]anthracene
6	Benzo[b]naphtho[2,1-d]thiophene	20	Indeno[1,2,3-cd]pyrene
7	Benzo[c]phenanthrene	21	Benzo[ghi]perylene
8	Benzo[a]anthracene	22	Anthanthrene
9	Cyclopenta[c,d]pyrene	23	Dibenzo[a,l]pyrene
10	Chrysene	24	Dibenzo[a,e]pyrene
11	5-Methylchrysene	25	Coronene
12	Benzo[b]Fluoranthene	26	Dibenzo[a,i]pyrene
13	Benzo[k]Fluoranthene	27	Dibenzo[a,h]pyrene
14	Benzo[j]Fluoranthene	-	-

3.4.2 Measurement Techniques used in the PAH Network

All stations utilise the Digitel^{TM} DHA-80 high volume aerosol sampler. Ambient air is sampled through glass fibre filters, which capture particulate which contains PAH compounds for later analysis in a laboratory. The Network requires the sampling and analysis of the following types of samples:

***'A' (particulate) samples - samples taken from 'A' (Digitel^{TM} filter only) stations*.** Samples of the PM_{10} fraction of ambient air on a filter. 'A' samples are taken daily at all Network stations using Digitel^{TM} DHA-80 samplers with automatic filter changers. The duration of the sampling period is 24 hours, with the sample changeover occurring at midnight. The samples are bulked into groups representing calendar months for analysis. Sampling is in accordance with EN 15549:2008 [30].

***‘B’ (particulate + vapour) samples – samples taken from ‘B’ (Digitel^{TM} filter + PUF) stations have been discontinued since 2014*.**

Between 2010 and 2014 samples of the PM_{10} fraction of ambient air on a filter, plus the vapour phase of ambient air on a PUF cartridge were taken for three (non-consecutive) days per week at two Network stations using Digitel^{TM} samplers with automatic filter and PUF changers. Each sample was collected over a 24-hour period, and samples were taken every 72 hours. The samples were bulked into groups representing calendar months for analysis. Sampling is in accordance with EN 12341:2014. This sampling is no longer undertaken as part of the UK PAH Monitoring Network.

***‘C’ (deposition) samples - samples taken from ‘C’ (deposition) stations*.**

Deposition samples taken fortnightly at two Network stations (Auchencorth Moss & Chilbolton Observatory). Each sample is collected over 14 days, and a sample is taken every 14 days. The samples are bulked into groups representing a four-week time period for analysis. Sampling is in accordance with the funnel bottle bulk collector detailed in EN 15980:2011 [31].

Following sampling, all filters and deposition gauges are returned to the contractor’s laboratory. Analysis takes place according to EN 15549:2008 [30] for particulate samples, for the PAH listed in Table 3-4.

Analyses of ‘A’ (particulate) samples are carried out in accordance with EN 15549:2008 [30]. Samples are bulked into monthly batches and extracted by sonication in an ultrasonic bath using dichloromethane as the extraction solvent. The extracts are cleaned for particulates, reduced in volume to 1 ml, and analysed using gas chromatography – mass spectrometry (GC-MS). The GC-MS is calibrated using a series of calibration standards containing all the PAH reported at a range of concentrations covering the concentrations expected in the samples. The PAH species measured are shown in Table 3-4.

The limits of detection of the GC-MS method are determined by running a series of filter blanks every six months, and a solvent blank with every analytical run. Analysis of ‘C’ (deposition) samples is carried out in accordance with EN 15980:2011 [31]. In summary, the deposition samples collected over a fortnightly period bulked into a four-week period and extracted using liquid-liquid extraction. The resulting extract is dried, reduced to a volume of approximately 1 ml, and analysed using GC-MS as described above.

3.4.3 PAH Network Operation and Management

Operation of the network is currently managed by Ricardo, using LSOs who are responsible for changing samples following Ricardo protocols. An Equipment Support Unit (ESU) contract is in place to provide annual servicing of the Digitel^{TM} DHA-80 samplers and additional sampler support under a subcontract as required. Ricardo or the external ESU resolve equipment problems.

Ricardo carries out annual site audit visits to all the Network sites along non-adjusting flow calibrations on an approximately quarterly basis for which Ricardo holds ISO-17025 accreditation. At these visits the site infrastructure, performance and integrity are assessed. The audits visits to each of the sites also allow LSOs to be observed/audited and receive extra training where necessary.

3.4.4 Quality Management in the PAH Network

QA/QC procedures are in place to cover all aspects of the Network management, from sampler operation to chemical analysis and data processing. Details of these can be found in section 6.

An annual report is produced for the PAH Network. This includes details of data capture achieved by the Network over the year. Information regarding the network and the location of the annuals can be found at:

https://uk-air.defra.gov.uk/networks/network-info?view=pah.

3.5 Overview of UK Urban NO_2 Network (UUNN)

The UK Urban NO_2 Network (UUNN) is the largest diffusion tube monitoring network in the UK. The primary aim of the UUNN is to supplement the current national assessment for air quality (comprising the Automatic Urban and Rural Network (AURN) and Pollution Climate Mapping (PCM) approaches) to provide additional local NO_2 monitoring data for inclusion within the national UK compliance report.

UUNN monitors were sited specifically to target areas where modelling had indicated an exceedance of the annual mean NO_2 limit value, and where concentrations predicted by the PCM model and by local modelling completed by a relevant local authority were not in good agreement.

The UUNN measures concentrations of NO_2 only. Monitoring is currently undertaken at 296 locations. This includes 38 AURN monitoring sites to provide co-location monitoring data for validating monitored NO_2 concentrations. Figure 3-2 provides a map of the UUNN monitoring locations.

Figure 3-2 UUNN Monitoring Locations

3.5.1 Measurement Techniques used in the UUNN

Monitoring is completed using Palmes-type diffusion tubes, a monitoring method widely used for the measurement of NO_2 across the UK. The diffusion tubes utilised on the UUNN are supplied by a UKAS accredited laboratory and have a modification in comparison to standard diffusion tubes, in the form of a wind protection cap. This is intended to reduce the effects of wind turbulence and thereby improve the accuracy of the diffusion tube measurements. UUNN diffusion tubes are also deployed in triplicate at each monitoring location to reduce the level of uncertainty, and therefore increase the level of accuracy, associated with each monitored concentration.

3.5.2 UUNN Operation and Management

Operation of the network is currently managed by Bureau Veritas. Monthly diffusion tube changes are undertaken by a cohort of Local Site Operators (LSOs). Diffusion tubes collect data on a monthly basis; each set of diffusion tubes is changed nominally monthly, adhering to a specific UUNN monitoring calendar.

3.5.3 Quality Management in the UUNN

QA/QC procedures are in place to cover all aspects of the Network management, details of these can be found in section 6.

An annual report is produced for the UUNN. This includes details of data capture achieved by the Network over the year and are available on UK-AIR. At the time of writing (February 2022) the most recent report covers calendar year 2020 [32].

3.6 Other Measurements

3.6.1 Cations and Anions in Rural $PM_{2.5}$

Measurements of particulate-phase cations and anions in $PM_{2.5}$: sulphate (SO_4^{2-}), nitrate (NO_3^-), sodium ion (Na^+), potassium ion (K^+), ammonium ion (NH_4^+), chloride ion (Cl^-), calcium ion (Ca^{2+}), and magnesium ion (Mg^{2+}) are measured at two rural background sites. The two monitoring sites used are Chilbolton Observatory in Hampshire, and Auchencorth Moss in Midlothian. These are both Level II EMEP ‘supersites’ and provide representative measurements of the atmospheric composition in the north and south of the UK. The monitoring is carried out under the UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) network contract: the current contractors are the UK Centre for Ecology and Hydrology (UKCEH) and Ricardo who operate the Auchencorth Moss and Chilbolton Observatory sites respectively.

A MARGA 2S is an online ion chromatography (IC) system used to analyse inorganic cations and anions in rural $PM_{2.5}$ at both sites. The MARGA utilises an automated continuous-flow Wet Rotating Denuder (WRD) coupled to a Steam-Jet Aerosol Collector (SJAC) sampler. It provides hourly measurements of the water-soluble species (listed in the paragraph above) in aerosol $PM_{2.5}$ (and PM_{10}). It also provides a measure of the concentration of water-soluble trace gases (HCl, HONO, HNO_3, NH_3, and SO_2) in the sampled air. The MARGA 2S samples the ambient air through a PM_{10} size-selective inlet head at a nominal flow rate of 2 m^3 hr^{-1}. The $PM_{2.5}$ fraction is separated from the sampled PM_{10} by means of a cyclone separator fitted at the inlet to the $PM_{2.5}$ WRD. The horizontal WRD removes water-soluble gases from the sampled air stream. The sampled particles pass through the denuder unsampled and water soluble particles undergo rapid growth in a steam chamber (~ 120°C) and then are mechanically separated out via a cyclone.

The liquid streams from the WRD and SJAC are continuously degassed and collected using a syringe pump module located in the detector box. There are two sets of syringes to enable tandem sampling and analysis: whilst one set of solutions is drawing liquid from the WRDs and SJACs, another set of syringes are transferring samples to the anion and cation chromatography units for analysis. The samples are continuously calibrated by mixing the with a LiBr internal standard prior to analysis on both anion and cation chromatography systems.

The MARGA 2S used to measure anions and cation in rural $PM_{2.5}$ is a research-grade instrument. In 2019 a new CEN standard was published, EN16913:2017 [23], which is now the standard method for determination of a range of anions and cations (NO_3^-, NH_4^+, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}) in $PM_{2.5}$ on filters. An initial equivalence desk-based study has been undertaken and submitted to the Environment Agency and Defra to compare the automatic methods (ACSM/HR-TOF AMS/MARGA/ AIM) to the filter method in the standard [33]. Data handling procedures are given in section 5.6.1 and QA/QC procedures are summarised in section 6.7.1.

3.6.2 Elemental Carbon (EC) and Organic Carbon (OC)

Annex IV of the Air Quality Directive requires Member States to measure EC and OC in the $PM_{2.5}$ size fraction of particulate matter at rural background locations. This requirement is met by these measurements at Chilbolton (formerly at Harwell) and Auchencorth Moss, made within the research-based Particles Network, which started measurements in late 2011. The parameters EC and OC are effectively defined by the thermo-optical analytical technique used.

Simplistically, the analysis can be considered as having two aspects. Firstly, the measurement of total carbonaceous material (TC) on the filter, by thermal desorption and oxidation followed by carbon detection (usually as methane after the conversion of carbon dioxide and other compounds in a catalytic converter). This aspect can be simply calibrated, and quality controlled using calibration solutions on clean filters.

Secondly, the division of TC into EC and OC. This is based on the carbonaceous material that is released during heating in an inert atmosphere being designated as OC, while material that is released after the addition of oxygen to the atmosphere is designated as EC. A correction needs to be made to account for pyrolysis (charring) of organic material during the inert atmosphere phase, based on an optical measurement of the darkening of the filter throughout the process.

The analytical method is standardised by CEN "*EN 16909:2017 (Ambient air - Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters*." [34]

Sampling is carried out using reference (Digitel^{TM} DPA14 Low Volume Aerosol Sampler (LVS)) $PM_{2.5}$ samplers collecting either daily - at the Chilbolton site - or for 7 days - at the Auchencorth Moss site) onto high purity quartz filters (Pallflex Tissuquartz 2500QAT-UP).

The current contractor at the time of writing (2022) is NPL. This contractor manages the Particles Network, carries out the laboratory analysis and audits the sites. CEH acts as LSO for the Auchencorth Moss monitoring site and Ricardo acts as LSO for the Chilbolton site. Equipment support is currently subcontracted to Enviro Technology Services at the Auchencorth site, and the Environment Agency at the Chilbolton site.

QA/QC consists of checks on the sampling system, such as corrections to the sampled volume after flow calibration, and checks on the laboratory analysis, which are primarily blank analyses, TC calibrations, and checks with internal reference material. The procedure describes a method for the accurate measurement of the collected TC on ambient air monitoring filters in µg cm^{-2} and is accredited by UKAS to ISO 17025:2017. The accuracy of the subdivision into EC and OC is not covered by the accreditation.

4 Type Testing and Equivalence of Analysers

4.1 Requirements of the Air Quality Standards Regulations

The Air Quality Standards Regulations require ambient air quality to be carried out according to the provisions of Annex VI of the Air Quality Directive, 2008/50/EC, which defines the reference methods to be used for compliance monitoring. This Annex also sets out the procedure for demonstration of equivalence with the reference methods, which must be followed if any alternative methods are to be utilised. Annex VI part D requires that all new equipment introduced into the network complies with the reference method or has been demonstrated to be equivalent.

For the gaseous analysers, the relevant Standard Methods include a requirement for type testing and approval. The approach used in the UK to conform to this requirement is described in Section 4.2.

For particle monitoring (PM_{10} and $PM_{2.5}$) compliance is achieved by ensuring that all analysers used in the network have been demonstrated to be equivalent to the reference methods. The mechanism for demonstrating equivalence for particle monitors in the UK is provided in Section 4.3. Subsequent sections describe the requirements for benzene, metals and PAH compounds.

4.2 Type-Approval of Analysers for NOx, SO_2, O_3 and CO

Type-approval tests are used to evaluate a set of performance characteristics for at least two identical analysers in a laboratory and two analysers in the field. The standard specifies a comprehensive and rigorous set of tests and type approval of an analyser is based on conformance of the analyser with all the individual performance criteria. The standards also require the calculation of the overall expanded uncertainty of the measurement result based on the numerical values of all the relevant tested performance characteristics - this is compared with the relevant prescribed maximum uncertainty in the DQOs (e.g. ±15% at 95% confidence level for NO_2 at the relevant hourly limit value). The tests and calculations carried out are:

Laboratory tests:

- Short-term drift tests at zero and span concentrations (12 hours).
- Response times rising and falling.
- Repeatability at zero concentrations and at the relevant limit or target value (where appropriate).
- Lack of fit (residuals from the linear regression function including the zero value).
- Sensitivity to sample gas pressure and sample temperature.
- Sensitivity to electrical voltage.
- Sensitivity to the temperature surrounding the analyser.
- Effects of interferences from other substances present in the atmospheric samples.
- Effect of fluctuating concentrations (averaging test).
- Converter efficiency where applicable (NO_x).
- Differences between sample and span inputs, where applicable.

Field tests (3 months):

- Long-term reproducibility between two analysers during the field measurements.
- Long-term drifts at zero and span levels.
- Period of unattended operation, and fraction of total time the analyser is available for measurements.

Overall uncertainty of measurement results:

- Determined by combining the type approval results obtained from the relevant tests above, expressed at a 95% confidence level. This process of combining uncertainties is covered by the BS EN Standard Methods.

4.2.1 Analyser Type Testing in the UK

For gaseous analysers, the Type Approval testing process is managed in the UK by the Environment Agency under its MCERTS scheme (http://www.environment-agency.gov.uk/business/regulation/31829.aspx).

Certification is provided by the CSA Group https://www.csagroup.org/en-gb, the appointed certification body. The CSA Group is accredited by UKAS to ISO/IEC standard 17065:2012 “Conformity assessment - Requirements for bodies certifying products, processes and services” [35].

The MCERTS Performance Standards mirror the requirements of the CEN Standard Methods referenced in the Directive, and decisions are made by a certification committee. The relevant performance standard for gases is: Continuous Ambient Air Monitoring Systems (CAMS). UK testing against the standards began in 2005, and a number of instrument suppliers have successfully had their gaseous analysers type-approved under these schemes. Further details can be found at:

https://www.csagroup.org/en-gb/services/mcerts/mcerts-product-certification/mcerts-certified-products/mcerts-certified-products-continuous-ambient-air-monitoring-system/

For measurements in the UK national network, the specific conditions and facilities at each site have been used to calculate measurement uncertainties for individual analysers. These results are published every six months in QA/QC Data Ratification Reports for the Automatic Urban and Rural Network and are available at: http://uk-air.defra.gov.uk/library/reports?section_id=13.

4.2.2 Checks Required on Deployment of Automatic Analysers

The CEN Standard Methods set a number of operational condition checks that need to be performed for each site and analyser deployed. These are summarised as follows:

- Estimate of the sample gas pressure and temperature variations.
- Estimate of the air temperature and mains voltage variations.
- Estimate of concentrations of a range of potential interferent species (H_2O, CO_2, O_3, NH_3 and benzene) in the local atmosphere.
- Functional check of the analyser and sampling system.
- Functional check of the data telemetry system.
- Lack of fit (linearity) test.
- Converter efficiency check for NO_x analysers.
- Determination of the required frequency of filter changes and analyser consumables changes.

These parameters need to be reviewed in order to ensure that all the analysers at all the sites are operating within the operating conditions for which they have been “type approved”, and also to determine the required frequency of certain maintenance actions which may depend on the pollutant concentrations at the particular site, or other factors.

These checks are undertaken during type testing of the instrument, and also where required as part of the commissioning audit of new monitoring sites.

4.3 Equivalence Testing for PM_{10} and $PM_{2.5}$

4.3.1 Requirements of the Air Quality Directive

The CEN Standard Method for particulate matter (PM) analysers describes both the design of the analyser (the reference method), and the operating methodology. The reference method is a gravimetric technique: however, due to the time required to weigh exposed filters and process the results, data from gravimetric samplers cannot be used for rapid public information purposes. The Air Quality Standards Regulations therefore allow the UK to use alternative techniques where "equivalence" with the reference method can be proven in accordance with specific requirements. A procedure for demonstration of equivalence has been defined by the EC, primarily to ensure measurements with near real-time analysers fulfil the requirements of the DQOs defined in the Air Quality Directive (and therefore in the Air Quality Standards Regulations). This procedure is defined in the 2010 GDE, which is available online at http://ec.europa.eu/environment/air/quality/legislation/pdf/equivalence.pdf . For PM, GDE 2010 is now superseded, but forms the basis of the procedures for equivalence documented in EN16450:2017.

4.3.2 UK Work Programme on Equivalence

The UK has an extensive database of equivalence study results which provide valuable performance information. The results of these test programmes can be found in the following reports:

- UK Report for On-going Particulate Matter (PM_{10} and $PM_{2.5}$) Equivalence (available online at https://uk-air.defra.gov.uk/library/reports?report_id=1097)
- Demonstration of equivalence for UK PM (available online at: https://www.csagroup.org/en-gb/services/mcerts/mcerts-product-certification/mcerts-certified-products/mcertscertified-productscontinuous-ambient-air-monitoring-system-mcerts-for-uk-particulate-matter/)

Following these studies and tests, instrument manufacturers have continued to submit methods for equivalence tests and declaration of suitability. The current status of measurement methods is set out in table form, at the “Certification: MCERTS for UK Particulate Matter” UK-AIR web page at http://uk-air.defra.gov.uk/networks/monitoring-methods?view=mcerts-scheme .

4.3.3 UK Approval of Equivalence

The responsibility for declaring measurement methods equivalent for use in the UK lies with Defra as the Competent Authority. Many manufacturers have also, but separately, opted to get UK type approval with the “Continuous Ambient Measurement Systems (CAMS)” performance standard (see http://uk-air.defra.gov.uk/networks/monitoring-methods?view=eu-standards) through the MCERTS scheme which mirrors the requirements of the 2010 GDE. Defra has developed in partnership with the Environment Agency a new and additional level of certification through the MCERTS scheme which requires the instruments to demonstrate equivalence in a representative particulate matter pollution climate for the UK. This certification is called "MCERTS for Particulate Matter UK" and details are available at http://uk-air.defra.gov.uk/networks/monitoring-methods?view=mcerts-scheme.

Other methods have been MCERTS certified for the Performance Standard for Indicative Ambient Particulate Matter. This is entirely different to the CAMS standard. Measurements from *indicative* MCERTS analysers carry a higher measure of uncertainty than reference equivalent analysers. Indicative analysers may not fulfil the requirements of the Air Quality Standards Regulations DQOs.

4.4 Equivalence and Type Testing of Benzene Measurement Techniques

Automatic hourly measurements for benzene are made using the Ozone Pre-cursor Analyser (OPA) manufactured by Perkin Elmer. At purchase, this was the best method available for measuring a large suite of VOCs simultaneously. There is no type approved OPA capable of measuring a suite of VOCs. However, many of the key parameters will be available either from literature or from existing test data. There will still be a number of parameters that require additional testing such as non-linearity (“ufit”), reproducibility of the field conditions (“urf”) and uncertainty due to interference with ozone (“uO_3”). Tests are performed to evaluate these. While these tests would not formally constitute type approval, they will provide a strong indication of fitness for purpose. Once these evaluations are complete, the calculations are updated and provide an assessment of CEN compliant results for every analyser used in the network.

The non-automatic system used for non-automatic monitoring of benzene was developed by NPL. This dual sample tube controlled-flow pump unit uses a method described in EN 14662-1:2005, ‘Ambient air quality – Standard method for measurement of benzene concentrations’ [18]. A revised standard is due for completion in 2022. This method has been validated by NPL and is the reference method for measuring benzene.

4.5 Equivalence and Type Testing of Metals Measurement Techniques

4.5.1 Ambient Metals Measurement

In the Heavy Metals Network, gravimetric samplers (Digitel^{TM} DPA14 instruments, fitted with PM_{10} size-selective sampling heads) are used to sample PM_{10} over weekly periods according to EN 12341:2014. The operational performance of the Digitel^{TM} DPA14 particulate samplers is compliant with EN 12341:2014.

The analysis procedure, which is compliant with EN 14902:2005, is accredited to ISO 17025:2017.

In 2012, the current contractor assessed the overall equivalence of the reference method EN 15852:2010 to the manual method used on the Network. This is reported in Brown et al. 2012 [36].

The tests carried out were based on the Guidance for the Demonstration of Equivalence of Ambient Air Monitoring Methods issued by an EC Working Group. This Guidance defines an approach to test whether an instrument complies with the DQO for overall uncertainty as defined within the relevant Air Quality Directive which, for PM_{10}, is 25%.

4.5.2 Rural Measurements of Metals Deposition

As described in section 3.3, the rainfall samples are collected via passive bulk deposition samplers, using separate bottles for the samples to be analysed for mercury, compared to the samples analysed for other metals.

The sample concentrations are determined by Atomic Fluorescence Spectrometry (AFS; Hg only) and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS; all other metals).

Validation and quality control data for the determination of metals by ICPMS concluded that that the instrumental method is suitable for the determination of a wide range trace metals in precipitation. The accuracy and precision for a synthetic rain obtained from Environment Canada are acceptable when compared with certified values. Total uncertainty and limits of detection are also reported.

As part of UKAS accreditation, the laboratory is required to carry out an annual audit of method performance by assessing analytical quality control data. An assessment for the period of operation of the rural metal deposition network operation so far (years 2004 to 2022) shows that the determination of trace metals by ICPMS was, and continues to be, fit for purpose. Accuracy is better than ±5% and precision is, for the majority elements measured, better than ±5% of the nominal QC value.

The performance of the contractor's laboratory (UKCEH Lancaster) in the Aquacheck inter-laboratory proficiency testing scheme (group 5b; low level metals) was undertaken using Cu, Cr, Pb, Ni, Zn, Cd and Hg as examples of typical laboratory performance. The performance of the contractor's laboratory in this scheme is acceptable, with the majority of analyses receiving a z score of better than ±2, indicating excellent agreement between the contractor's laboratory and a wide range of UK and worldwide testing laboratories. The performance of all metals determined for the network is tested within Aquacheck or similar schemes.

The contractor also participated in the EMEP *"Analytical intercomparison of heavy metals in precipitation"* between 2006 and 2011. For all metals reported in 2010 (i.e. As, Cd, Cr, Cu, Pb, Ni and Zn) their laboratory met the required data quality objective (DQO) set within the scheme. These are as follows:

- 25% accuracy or better for Pb, Ni, Cr & As concentrations <1µg/l, Cd concentrations<0.5 µg/l, Zn concentrations <10µg/l and Cu concentrations <2 µg/l
- 15% accuracy or better for Pb, Ni, Cr & As concentrations >1µg/l, Cd concentrations >0.5 µg/l, Zn concentrations >10µg/l and Cu concentrations >2 µg/l.

Further information about the scheme, including detailed reports relating to laboratory performance, can be found on the EMEP website at http://www.nilu.no/projects/ccc/intercomparison.html .

4.6 Equivalence and Type Testing of PAH Measurement Techniques

The Digitel^{TM} DHA-80 samplers now used throughout the PAH Network are considered to be equivalent to the requirements of the European Standard for sampling PM_{10} matter (EN 12341:2014 [16]). These samplers are therefore considered valid for use with the European Standard method for the measurement of benzo[a]pyrene in ambient air (EN 15549:2008 [30]). Samples are taken onto GFA glass fibre filters for a period of 24 h at a flow rate of 30 m^3 h^{-1}.

Deposition sampling using the funnel-bottle bulk collector, is performed as specified in EN 15980:2011 [31] which includes analytical QA/QC. The requirements of EN

12341:2014 [16] do not apply to deposition sampling, only to sampling of PM_{10} suspended particulate matter.

4.7 Equivalence and Type Testing of UUNN Diffusion Tubes

Diffusion tubes are used as an indicative measurement and so are not subject to the same equivalence procedures as other methods. However, the expanded uncertainty on the UUNN has been calculated using Guide to Demonstration of Equivalence (GDE) 2010 [37] Chapter 9, which is written for continuous Particulate Monitors. Whilst GDE 2010 Chapter 7 (which relates to diffusion tubes) might be considered more relevant, the mathematics within this Chapter do not extend as far as correcting the data for slope and/or intercept and would lead to an over reporting of concentrations.

5 Data Telemetry, Validation and Dissemination

In order to provide rapid data on the current air quality situation in the UK, data from the UK’s automatic monitoring sites are collected via telemetry from each monitoring site, every hour, and made available on the UK-AIR website. These data are validated, but not fully ratified, and hence are described as provisional data. The process for collecting, validating and disseminating the provisional data is described below. Data handling and validation are also described for pollutants measured by non-automatic techniques, which are not made available on such a short timescale. The full ratification procedures which the data undergo are set out later, in section 6.

5.1 Data Handling in the AURN

Data from the UK’s automatic monitoring sites are collected via telemetry from each monitoring site, every hour, and made available on UK-AIR. The data are at this stage still provisional, having not yet undergone the ratification process. This section describes the process of collecting, validating and disseminating the provisional data from the AURN.

5.1.1 Collecting the data from AURN sites

The CMCU dials-up via telemetry links (e.g. land-lines, GSM modems, 4G routers and GPRS) to poll data acquired within the hour. Each station is automatically dialled every hour during daytime and alternate hours during the night (1800- 0700). Onboard and external logging systems provide a mechanism of capturing data (either in concentration or raw electronic mV format).

A number of the AURN sites within Greater London are also part of the London Air Quality Network. These sites are also polled hourly, on the same basis as the other AURN sites. Data are collected to two decimal places for CO and to at least one decimal place for other gases and for particles.

5.1.2 Validation of AURN Data

Upon completion of the station poll the fifteen-minute averages (or hourly data in the case of BAM particulate monitors) collected from the site operating system are stored in the data management system database. The collected values are referred to as “raw” since they are not scaled and remain in the data management system “raw” database as a complete record of all values collected from the station. Instrument calibration values derived from site by either LSOs or ESUs are stored in the data management system calibration files and the raw values are automatically scaled by application of the calibration factors present in the system. Automatic screening algorithms (specifically designed macros and a range of tailored scripts for manual data interrogation) are employed to validate the scaled data.

The scaled data are automatically compiled into a prescribed format and emailed to Defra’s Data Dissemination Unit (DDU) by 25 minutes past the hour for upload to the UK-AIR website. Upon completion of any required editing the revised values are automatically re-sent in the next hourly cycle in order to over-write those previously supplied.

5.1.3 Dissemination of Provisional AURN Data

Data from the AURN are marked as ‘provisional’ or ‘ratified’ depending on what stage they are at in the process of ratification. When data are first collected from the analyser on site, they are scaled with calibration data from the last calibration. In many cases, this will produce satisfactory data, with problems only arising if the instrument is unstable or drifting rapidly. The data are then automatically screened using computer algorithms to highlight suspect data, but ***no data are deleted at this stage.***

The data sent to UK-AIR are also available – on an hourly basis - on air quality websites operated by the UK Devolved Administrations, RSS data feeds and Twitter. In addition, daily e-mail bulletins of AURN monitoring data are provided to over 150 media organisations and other network stakeholders - including the BBC and BSkyB, national and regional radio and newspapers and other scientists and journalists.

All of the provisional data, together with all the identified suspect data, undergo full ratification, (as described in section 6.1.8 to 6.1.11) in three-month blocks. As part of the ratification process, any suspect data may be reinstated if deemed to be genuine. Following the ratification process, the fully ratified datasets are re-sent to UK-AIR (in three-monthly blocks, three months in arrears) and the provisional data are overwritten with the ratified data.

However, as the data are improved via the ratification process, they are automatically fed through to UK-AIR. This ensures that the provisional data available on UK-AIR always reflect the most up to date, highest quality data available. Initial polled data are maintained by the CMCU through its initial polling software and are maintained as an historical record of the data collection process.

All fully ratified hourly data from the AURN are formally reported on an annual basis: this is a legal requirement of the Air Quality Standards Regulations. Annual reporting is done via the UK-AIR website and includes the ‘Air Pollution in the UK’ series of annual reports, published by 30th September of the following year.

5.1.4 Data Handling for Gravimetric PM Samplers in the AURN

The AURN currently includes three gravimetric samplers, each of which samples either PM_{10} or $PM_{2.5}$. At present these are as follows: one SEQ sampler for PM_{10} at an urban industrial monitoring site in South Wales, and two Digitel^{TM} samplers, one each for PM_{10} and $PM_{2.5}$ at an urban traffic monitoring site in central London which is part of the ALN subset. The size fraction sampled is determined by a size-selective inlet fitted to the sampler. Sampling is on a daily basis, with automatic filter changeover at midnight. The sampler holds up to 15 filters. Each batch of filters includes a field blank. The CMCU is responsible for conditioning and weighing the filters before and after exposure. Ambient PM concentrations are calculated from the mass of material collected on the filter (determined by weighing before and after exposure) and the volume of air sampled over the 24-hour period.

Ambient concentrations are calculated by the CMCU and supplied to the relevant QA/QC Unit in spreadsheet format. The QA/QC Unit carries out the ratification process, which checks that:

- The correct day’s filter weighing is matched to the correct day’s sampling data.
- There were at least 18 hours' valid sampling for each daily sample.
- The sample volume is at least 75% of the sampler’s nominal daily sampling volume.
- There are no gaps in the dataset.
- There are no values which appear obviously spurious, e.g. unusually low or high, and cannot be accounted for.
- There are no negative values (less than minus the measurement uncertainty).

If both PM_{10} and $PM_{2.5}$ are monitored using gravimetric samplers at the same site, PM_{10} should not usually be greater than $PM_{2.5}$ (allowance is made for the measurement uncertainty.

Data are ratified three-monthly in arrears. The ratified dataset is sent to the Data Dissemination Unit.

5.2 Data Handling for Automatic Hydrocarbon Monitoring

The data management system undertakes preliminary validation of the data using proprietary pattern recognition software, which has been specifically modified to compare the chromatograms with ‘templates’ identifying specific hydrocarbon peaks. This system automatically assigns component labels to peaks within the chromatogram.

The incidence of mis-identification of peaks, and therefore mis-reporting of data, is reduced significantly when compared with use of the peak identification methodology of the instrument system.

The data files are sent every hour to a file transfer protocol (ftp) server, the contents are stored in a processing database, and an interactive app is able to visualise the data. This software is used for QA/QC.

This system provides preliminary screening of hydrocarbon monitoring data to identify suspect data. When the fit of data to the MatchFinder templates becomes poor, it can be due to one of a number of reasons; malfunction of the instrument or an early warning of an unusual event such as a pollution episode, are two examples. By means of further manual checking, a decision to delete or retain such data is made by one of the hydrocarbon network data management team. This includes application of approximate site-specific response factors and daily checks of the templates.

All data are manually checked every working day by a trained member of the network management team. During these manual checks a number of parameters are evaluated and corrected where necessary. System performance is judged on a daily basis and the accuracy of peak integration and identification is monitored, with any necessary actions being taken. The results of the daily checks and any resulting actions are recorded as this will be important information in the data ratification process. The manual checking of the data, rather than basing reliance on the automatic systems, ensures any developing problems are identified quickly and resolved in good time.

Validated data are provided daily to the Data Dissemination Unit for dissemination via UK-AIR.

Data ratification is split into several stages. Initial checks include the identification of additional missed peaks and erroneous peak areas and changes in chromatography parameters over a three-monthly period. Once complete, the data are interrogated as a timeseries and x,y scatter plots to investigate changes in atmospheric mixing ratios between sites of a similar type, and against previous years. Finally blanks and calibrations are used to determine any potentially required blank corrections. The final level of the ratification procedure is the application of final response factors. Calibrations are run once every 14 days, where at least four calibration samples are taken, any erroneous calibration runs are nulled and will not form part of the average used for such response factors. This converts the raw peak areas collected from the chromatograms to concentration units. The results of the analyser calibration checks, together with data from the network intercalibrations, are used to produce the response factors. Response factors for the instruments (PerkinElmer Ozone Precursor Analyser (PE-OPA)) generally tend to be very stable.

During the third level of ratification the results of the network intercalibration and instrument audits are evaluated to determine whether any further action is required with respect to data scaling.

This multi-input approach to data ratification is used to provide the necessary level of information to provide the level of confidence needed for the data to be described as “ratified”.

On completion of this three-level ratification process the data are sent to UK-AIR on a quarterly basis, and also stored within the contractor’s own QA/QC database.

Formal reporting of data to EMEP/ACTRIS/GAW programmes are undertaken annually by 30th April the following year.

5.3 Data Handling for Non-Automatic Benzene Monitoring

The procedures used for non-automatic benzene monitoring are completely different from the automatic monitoring techniques and the data handling procedures reflect these differences.

The project structure requires data to be held and processed by the contractor and by a subcontractor (analytical laboratory).

The primary data handling system (produced by the contractor) is the Sample Registration System (SRS), which has been designed to efficiently and transparently track the progress of a sample (represented by two pumped tubes) throughout the system. The necessary calculation and quality control routines are also built into the system. The SRS is built using a database and an interactive application.

In principle, each sample exposure has a unique identification made up of two parts; the etched identification mark on the thermal desorption tube (tube ID) and the batch number (each fortnight's set forms a complete batch). As there is a limited number of tubes used (~400 stock tubes which are cleaned, re-filled and re-used), the tube ID will occur more than once during the lifetime of the project. Hence, each sample's identification is a composite of the batch number and tube ID.

This also makes it possible to track the use and performance of individual tubes as they are repeatedly cleaned, re-filled and re-used.

5.4 Data Handling for Metals Monitoring

5.4.1 Particulate-phase Metals

Analysis of the Network samples of metals in PM_{10} is described in section 3.3.3. This produces individual concentration values for four-weekly or weekly periods. These individual measurement results each have a stated measurement uncertainty, quoted at the 95% confidence level. Annual means at each site are produced by calculating the means of these values, weighted according to the data capture during each period. Network-wide annual means are then produced by averaging annual means from the individual sites, again using appropriate weighting if a site has been monitoring for less than the full year.

A QA/QC circle meeting (the 'quality circle') ratifies ambient concentration data produced by the Network. Personnel performing the ratification procedure are independent of the Network analysis and management process. It is the aim of the ratification procedure to distinguish between changing ambient concentrations (including long terms trends, seasonal variation and single pollution events), and analytical discrepancies within the large amount of Network data. Ratification takes place in accordance with several guidelines, outlined below:

1. Only data where the valid sampling hours are greater or equal to 75% of the total sampling period will be eligible to produce valid concentration data, and count towards the total data capture percentage.

2. Data not meeting the DQOs for uncertainty or time coverage for the relevant air quality Directive are not eligible to produce concentration data and are

counted as lost data capture.

3. Data excluded following the ratification procedure will also not be eligible to produce valid concentration data or count towards the total data capture percentage.

4. Upon production, data for each element at each site are plotted in a time series or displayed as a continuous list of values which may be easily compared.

5. In the first instance these data are assessed visually for any obvious discrepancies with due regard to long terms trends, short term variability and seasonal variation. Then outlier tests are performed to detect any potentially discrepant data, including the use of powerful chemometric techniques.

6. If valid reasons for obviously discrepant values are found (e.g. incorrect calculation, low exposure time, non-valid exposure volume, analytical error) these values may be either excluded or corrected (depending on the nature of the error).

7. As part of the internal quality and technical auditing procedures, a selection of ambient air concentrations calculated each month are thoroughly audited by a party independent of the analysis procedure. For these samples, the sample number, target analyte, auditor, audit date and status of the data are recorded in a designated spreadsheet after auditing. These audits concentrate most heavily on nickel, arsenic, cadmium, and lead analyses, as these are directly relevant to the Air Quality Strategy Regulations.

The data are then transferred to the contractor’s secure database and processed ready for submission to UK-AIR.

The time resolution of the data provided is weekly at six stations for metals in particulate, weekly at three stations for vapour phase mercury, and four-weekly at all other stations for both particulate-phase metals and vapour phase mercury.

5.4.2 Metals in Deposition

The concentrations of metals in the precipitation samples generated by the laboratory analysis are uploaded to a database as part of the reporting requirements of the contractor’s UKAS-accredited laboratories. This database is stored in a central server within UKCEH and receives daily back-ups. This database also records all of the relevant metadata on each sample, including the start and end date and time of each exposure period, site operator observations and all of the intermediate data produced during the analytical process.

The data are then filtered via database queries, to produce output tables which normally cover, for example, a single calendar years' worth of data. These output tables are copied into Excel for ease of data. There are separate spreadsheets mercury and non-mercury the metals. The spreadsheets have been designed to include a separate worksheet for the raw data from each monitoring site. These sheets are linked to pre-programmed sheets which are used to convert the sample acid digest concentrations to concentrations in precipitation data. The spreadsheets have built-in quality assurance checks where appropriate, such as checking there is no overlap in sampling between individual samples etc. The spreadsheets also have in-built formulae to calculate statistics such as the annual mean, data collection rate, etc. The spreadsheet also identifies samples which are below the limit of detection, and greater than the annual mean plus 2x the standard deviation. It also generates the appropriate EMEP flags to accompany the data.

The spreadsheets are all manually checked (on the basis of expert judgement) before the data are prepared for uploading to the UK-AIR portal. This involves copying the data from each site-based worksheet into a single worksheet, where the data are formatted to match the UK-AIR reporting requirements. This final sheet is then saved in Excel format before being saved as a tab delimited text file and uploaded to the UK-AIR portal.

The ratified dataset is uploaded annually to UK-AIR. Provisional data are not supplied.

The time resolution of the measurements of metals in precipitation is also two-weekly.

5.5 Data Handling for PAH Monitoring

Analytical procedures are given in section 3.4.2. A 'quality circle' approach is used to ratify ambient concentration data produced by the UK PAH Network. Personnel performing the ratification procedure are independent of the Network analysis and management process. It is the aim of the ratification procedure to distinguish between changing ambient concentrations (including long terms trends, seasonal variation and single pollution events), and analytical discrepancies within the large amount of Network data. Ratification takes place as detailed below:

1. Assessment of the flow measurements taken at each of the sites to identify if there are any potential sampling issues that need to be taken into account. These are usually identified and resolved at site or prior to the quality circle however any such issues will be discussed, and impacts reviewed.
2. A series of automated and manual checks are undertaken on each daily filter sample to assess validity of that sample.
3. Filters that don’t meet the required standards are excluded from being included in the monthly bulked submission for that monthly period and will not contribute to the reported concentration for that period or the annual mean and will reduce the data capture accordingly.
4. Once data is available each PAH at each site is plotted in a time series, which may be easily interrogated. These data are assessed visually for any obvious discrepancies with due regard to long term trends, short term variability and abnormalities in seasonal variation.
    - These reviews concentrate most heavily on benzo[a]pyrene (B[a]P) as this is directly relevant to the Air Quality Standards Regulations.
    - Where there are concerns with data calculated investigations are made with local contacts or Environment Agency Inspectors or Industrial contacts to identify if there were local influences.
    - If no reason for the unusual measurements, samples may be resubmitted for analysis
5. If valid reasons for obviously discrepant values were found, then investigations would be undertaken to assess the impact and corrective action taken to prevent repetition.

The data are then transferred to the contractor’s secure database and processed ready for submission to UK-AIR at the appropriate juncture. Data are sent to the Data Dissemination contractor for upload to UK-AIR.

5.6 Data Handling in the UUNN

The procedures used for non-automatic monitoring are different from the automatic monitoring techniques and the data handling procedures reflect these differences. The project structure requires data to be held and processed by the network manager and by a subcontractor (analytical laboratory).

The analytical laboratory prepares and sends new diffusion tubes to each LSO a few days before the specified changeover date. In addition to the diffusion tubes themselves, the package to each LSO contains:

- An exposure sheet, for recording details of exposure: site name, tube ID number, date and time that exposure started and ended.
- Sticky labels bearing a QR code and a tube ID number (assigned by the laboratory). There will be two identical sets of labels: one of the pair to be stuck on the tube, and the other on the form.

Once the diffusion tubes have been exposed during the 4/5 week period, as specified by the UUNN calendar, they are collected and sent back to the laboratory for analysis, bearing the QR code (used for identification) and the exposure sheet.

On receipt of the analysis reports from the analytical laboratory, the network manager collates all data using a consolidation tool built using Microsoft Excel. The necessary calculation and quality control routines are also built into the tool. The outputs of the Excel tool are then reconciled against an online data handling system built specifically for the UUNN.

5.7 Data Handling for Other Measurements

5.7.1 Cations and Anions in Rural $PM_{2.5}$

The MARGA 2S provides on-line analysis of cations and anions in near real-time by means of Ion Chromatography (IC). The presence and concentration of the cation and anion species in the sampled $PM_{2.5}$ and PM_{10}: sulphate (SO_4^{2-}), nitrate (NO_3^-), sodium ion (Na^+), potassium ion (K^+), ammonium ion (NH_4^+), chloride ion (Cl^-), calcium ion (Ca^{2+}), and magnesium ion (Mg^{2+}) are determined from the resultant chromatograms. Detection of the individual species is based primarily on:

- Peak retention time, and
- Integrated peak area.

The concentrations of the species of interest in the sample solution (termed the “liquid concentration”) is determined by the specific conductivity of each species relative to the internal standard (Li^+ and Br^-). The mass concentrations of the species of interest (termed the “air concentration”) are subsequently determined from the liquid concentration by accounting for the:

- Liquid flow rate (nominally 0.417 ml min^{-1}) and
- Air flow rate (nominally 1 m^3 hr^{-1}).

The liquid and air concentrations are written to file to provide an hourly measure of the composition of PM_{10} and $PM_{2.5}$.

When commissioned, default retention times of the cations and anions species of interest are entered into the instrument by the instrument manufacturer (Metrohm-Applikon BV, Schiedam, The Netherlands). Over time peak retention times may change due to instrumental factors, e.g. column ageing. In order to account for this, the peak retention times are checked regularly and adjusted accordingly by the LSO. Peaks are identified if they fall within a window of ±5% of the operator defined peak retention time. The MARGA 2S system parameters are logged by the instrument and are optimised by the MARGA 2S operating software to ensure good resolution of the peaks in the ion chromatographs.

Samples from the WRD or SJAC are injected into the anion and cation IC columns at 15-minute intervals. The resultant anion and cation chromatograms are written to file for later re-analysis, if required. For a volume of ambient air sampled during hour “H” of the day, the liquid samples from the WRD and SJAC are analysed in the order described in Table 5-1.

Table 5-1 MARGA 2S sampling times, particle size fractions and source

Time	**Size fraction**	**Source**
17 minutes past hour “H+1”	$PM_{2.5}$	WRD (gas-phase)
32 minutes past hour “H+1”	$PM_{2.5}$	SJAC (particle-phase)
47 minutes past hour “H+1”	PM_{10}	WRD (gas-phase)
02 minutes past hour “H+2”	PM_{10}	SJAC (particle-phase)

Provisional data are reported on UK-Air on a quarterly basis. On an annual basis the data are ratified, with changes as appropriate, including applying the calculated detection limit. The ratified data are then submitted to UK-AIR annually.

The MARGA 2S used to measure anions and cations in rural $PM_{2.5}$ is a research-grade instrument. In 2019 a new CEN standard was published, EN16913:2017 [23], which is now the standard method for determination of a range of anions and cations (NO_3^-, NH_4^+, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}) in $PM_{2.5}$ on filters. An initial equivalence desk-based study [33] has been undertaken and submitted to the Environment Agency and Defra to compare the automatic methods (Aerosol Chemical Speciation Monitor (ACSM) / High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-TOF AMS) / Monitor for Aerosols and Gases in Ambient Air (MARGA) / Aerosol

Instrument Monitor (AIM)) to the filter method in the standard. QA/QC procedures for the MARGA 2S measurements are summarised in section 6.7.1.

5.7.2 Elemental Carbon (EC) and Organic Carbon (OC)

No live data are generated at the monitoring site. A 1.5 cm^2 sample is taken from a loaded quartz filter and analysed on a Sunset Laboratories instrument at the laboratory. The analysis uses a thermal-optical protocol specified in BS EN 16909:2017, termed EUSAAR2. The charring correction is made using an optical transmittance signal which is generated during analysis.

The values of TC, EC and OC obtained by the instrument, in µg (of carbon) per cm^2, are converted to µg m^{-3} using a well-characterised value for the sampled area of the filter, and the sampled volume of air (at ambient conditions), using data downloaded from the samplers, and results from the field flow audits.

Provisional data are ratified, with changes as appropriate, at a quality circle. Ratified data are then released annually via UK-AIR.

6 Quality Assurance and Quality Control

In order to produce data that are correct, meaningful and useful, the measurement techniques utilised and data handling must have a sound scientific basis. The data must be both accurate and precise.

Accuracy refers to the agreement between a measurement and the true value. It allows us to have confidence that the concentration measured is correct. In turn, this allows us to compare data over time, at different UK locations, or internationally.

Precision refers to the repeatability of measurement. A precise instrument will always give the same result if the same measurement is repeated. An imprecise instrument will show some variability in the same situation.

This section describes the QA/QC procedures employed by each network to ensure that the DQOs of the Air Quality Standards Regulations are achieved.

6.1 QA/QC in the AURN

The AURN's QA/QC Units use a variety of quality procedures, described in more detail in this section.

The purpose of the QA/QC Units is to ensure that the AURN data are:

- Genuinely representative of ambient pollutant concentrations in the areas under investigation.
- Comparable and reproducible. Results must be internally consistent and comparable with international or other accepted standards, where these exist.
- Consistent over time. This is particularly important if long-term trend analysis of the data is to be undertaken.
- Representative over the period of measurement; for most purposes, a yearly data capture rate of at least 90% is required for determining compliance with the limit values of the Air Quality Standards Regulations, although 85% is permitted due to an allowance of 5% for routine servicing and maintenance.
- Consistent with the DQOs and methodology guidance defined in Regulations for relevant pollutants and measurement techniques.

6.1.1 Local Site Operator (LSO) calibrations

LSOs are employed in the UK to undertake routine tasks at AURN monitoring stations to ensure that the data output is uninterrupted and of the highest possible quality. The actions of the LSOs therefore affect both data quality and data capture.

For this reason, LSOs are carefully selected by an evaluation board through a round of competitive tendering undertaken by the CMCU based on their expertise, experience and understanding of the AURN and the importance of data quality. Training, and regular assessment, of the LSOs is carried out at scheduled site audits (by the QA/QC Units).

The key responsibilities of the LSOs are to:

- Carry out routine operation and calibration procedures for the equipment at the site, in conformance with the LSO manual.
- Identify and report potential problems and changes to the site and surrounding area.
- Identify and report potential safety issues at the site.
- Undertake simple tests and repairs to the site and/or equipment as directed by the CMCU.
- Attend training (both formal and informal) as requested by the CMCU and/or QA/QA Unit
- Attend QA/QC site audits as requested.
- Liaise with other AURN stakeholders as requested by the CMCU.
- Carry out all activities with regard to relevant health and safety standards.
- Complete the electronic calibration sheets, checklists and site servicing records in full and email these to the CMCU and QA/QC Unit within 24 hours of each site visit.
- For sites with gravimetric particulate monitors, return exposed filter magazines to the CMCU within 48 hours of each site visit where appropriate.
- Undertake other reasonable requests as directed by the CMCU during a pollution episode or other emergency.
- Use their experience of air pollution monitoring to identify and report any faults or potential faults as soon as possible.
- Provide information on local activities that may affect the pollution climate or site suitability at the monitoring station.
- Change calibration gas cylinders

These responsibilities are carried out during routine visits (every two weeks at urban traffic sites, four-weekly at urban background sites and quarterly at all rural background sites) and additional emergency call outs.

6.1.2 LSO Manual

A comprehensive operations manual for the AURN has been produced and disseminated to all site operators. This is a key QA/QC tool, serving to harmonise field procedures and improve the quality of the data produced by the monitoring equipment through accurate calibration and optimised operation. The LSO manual is available electronically via the “AURN Hub” - a website which provides useful information and contact details for LSOs. The most recent update was in October 2021.

Training is also provided to any new LSOs and training updates are available to all LSOs during at the twice-yearly site visits by the QA/QC Unit.

6.1.3 LSO Support

Both the CMCU and QA/QC Units have dedicated telephone lines and email addresses, for LSOs to access specialist knowledge and advice regarding the AURN sites and equipment.

6.1.4 Equipment Support Units (ESU) for Service and Repair

ESUs are responsible for the routine and emergency maintenance and repair of the monitoring and ancillary equipment at each AURN site. They are directly appointed by the CMCU by competitive tender. The ESUs role is key to achieving the 90% data capture target for all sites and pollutants.

Routine servicing is carried out on a 6-monthly basis and is coordinated with the audit visits of the QA/QC Unit (see Section 6.1.5) to ensure that the necessary instrument parameters and calibrations are recorded to allow full data ratification. Minimum requirements for routine instrument maintenance, testing and calibration are provided to ESUs. All routine service visits are fully documented and completed in accordance with procedures provided by the QA/QC Unit.

In the event of an instrument malfunction, the ESU attends the site to carry out emergency repairs within 72 hours of notification of the problem as highlighted by the CMCU, and expected resolution within ten working days.

Telemetry facilities and automated data checking now also allow for rapid recognition of possible instrument malfunctions and the CMCU typically uses this information to inform the relevant ESU of the likely cause of malfunction.

6.1.5 AURN inter-calibration and site audits

Within the UK, there has been a system of routine site audit and network inter-calibration, involving all network sites, for many years. The primary aims and objectives of the site audit and network inter-comparison exercise can be summarised as follows:

- Check and evaluate a wide range of analyser key functions via a comprehensive set of tests and calibrations - well beyond those that can be checked by routine LSO calibrations.
- Check all on-site calibration standards against common transfer standards that are directly traceable to the gas standards calibration contractor’s laboratory (currently Ricardo) and national metrology standards.

This network inter-calibration is undertaken by the QA/QC Unit at six-monthly intervals and includes every site and every analyser in the network. The inter-calibration therefore provides detailed and quantified information on overall network performance.

Many of the site audit and network inter-calibration procedures used in the UK have now been incorporated into the ongoing QA/QC procedures detailed in the Standard Methods. However, in some cases the standard methods differ in detail or are even more exacting than previous requirements. Procedures used in the UK are routinely adapted to be fully compliant with the British Standard and CEN requirements.

Ozone analysers are audited on a three-monthly basis: because of a requirement to calibrate with a traceable standard every three months, a separate ozone inter-calibration is carried out for this purpose between six-monthly inter-calibrations.

6.1.6 AURN inter-calibration procedures

These exercises provide the following information:

- Evaluation of the concentrations of site calibration cylinders, using a set of certified cylinders (transfer standards) that are taken to all the sites. The concentrations of the site cylinders are used to scale pollution datasets, so it is important to check that the concentration of gases in the cylinders remain stable over time.
- Analyser accuracy and precision, using a series of calibrated gas standards, to ensure reliable datasets from the analysers.
- Calibration of ozone analysers with an ISO17025 certified ozone photometer.
- Instrument linearity, to check that doubling a concentration of gas to the analyser results in a doubling of the analyser signal response. If an analyser is not linear, data cannot be reliably scaled into concentrations.
- Instrument signal noise, to check for a stable analyser response to calibration gases.
- Analyser response time, to check that the analyser responds quickly to a change in gas concentrations.

- Leak and flow checks, to ensure that ambient air reaches the analysers, without being compromised in any way.
- NO_x analyser converter efficiency, to ensure reliable operation. This is the device that allows the measurement of NO_2 to be undertaken, so it must work correctly.
- Particulate analyser flow rate checks, to ensure that the flow rates through critical parts of the analyser are within specified limits.
- Zero baseline checks on automatic particulate analysers. In the case of the BAM, this entails using in-line high-efficiency particulate absorbing (HEPA) filters or equivalent to ensure that the instrument measures zero for particle-free air for a period of several days. The zero test procedure for the Fidas 200^{TM} is different and can be carried out during a routine audit.
- Site infrastructure and environment checks to ensure that metadata on the station remain accurate and up to date and that any site safety issues are noted for action***.***

As noted above, these tests performed on site are now undertaken to the exacting requirements of Standard Methods and hence are fully compliant with the Air Quality Standards Regulations. The gas calibration contractor is accredited (Calibration Laboratory Number 0401) under ISO 17025:2017 to perform these tests.

Accreditation to ISO 17025:2017 requires:

1. Documented procedures to calibrate analysers
2. Demonstration of competence of operators in performing calibrations
3. Demonstration of traceability of measurements to metrology standards
4. Calculation of uncertainty budgets for measurements reported on Calibration Certificates.

6.1.7 Use of Information from the Site Audit and Network Inter-calibration

The site audit and inter-calibration results provide vital information for the data ratification process. For example, if calibration cylinder concentrations or ozone monitor calibration concentrations are identified to have changed at any site then the information from the audit and inter-calibration is used to ensure that the data are correctly rescaled during the ratification process. Also, if faults such as poor converter efficiencies for NO_x analysers are identified then the data are corrected or deleted in line with the CEN requirements.

6.1.8 AURN Data Ratification (Gas Analysers)

Data validation is followed by more thorough checking at three-month intervals to ensure that the data are reliable and consistent. This latter process is called data “verification” or “ratification”. The latter is the term more usually used in the AURN.

The first step is to go back to the “raw” unvalidated data from the analyser - this allows traceability of all operations on the data within the ratification process to be maintained. The data have already been scaled in near real-time by the CMCU in order to provide the validated provisional data. However, for validation only the latest calibration results are available for data scaling. Re-scaling the data at the start of the ratification process allows any new information gathered over the full 3-month period to be incorporated right at the start of the process.

The “raw” data are scaled into ambient concentrations by removing any baseline zero and multiplying by the scaling factor (sensitivity). This can be expressed mathematically as follows.

$$\mathbf{c = F \times (V - Z)}$$

where:

c = the ambient concentration (ppb)

F = the instrument sensitivity (ppb / mV)

V = the instrument measurement (mV)

Z = the instrument zero baseline (mV)

The instrument sensitivity (F) is calculated during calibrations as follows:

$$\mathbf{F = C / (S - Z)}$$

where:

F = the instrument sensitivity (ppb / mV)

C = the concentration of the calibration standard (ppb)

S = the instrument response to the calibration standard (mV)

Z = the instrument response to the calibration zero standard (mV)

Identical formulae are used where the ambient measurements are expressed in ppm units and where the instrument records data in units other than mV: e.g. V or nominal ppb.

These scaling values (Z and F) are derived from a range of instrument calibrations:

- Routine manual LSO calibrations
- Automatic analyser calibrations
- ESU calibrations at services or repair visits
- QA/QC Unit inter-calibrations.

6.1.8.1 Analyser Zero Baseline

For gas analysers the instrument zero baseline is generally measured every night during the auto-calibration cycle. However, as this auto calibration only checks analyser performance, it is not an absolute calibration. Often, the scrubbing material within the auto-calibration system is spent and hence this estimate becomes unreliable, or the relevant equipment may not be present on-site. However, this auto-calibration zero is just one estimate of the baseline.

LSOs and ESUs also perform zero baseline measurements, and these may also be used to estimate the measurement zero point. However, these can occasionally be unreliable for various reasons. The QA/QC Unit also provides a zero baseline measurement during the inter-calibration.

If necessary, a zero baseline can also be estimated from the lowest ambient measurement, since concentration levels are often very low for some pollutants at certain times during a month.

Deciding on the most appropriate zero baseline must account for all these sources of information and is a difficult yet vital task since the choice will affect the reported concentrations. The baseline finally applied to the data is based on the real measurements (auto-calibration, LSO, ESU and QA/QC) and the judgement of the data ratifier using software algorithms developed over many years of experience.

Isolated or occasional negative values are permitted to remain in the dataset so long as they are not less than minus the limit of detection of the method. However, any values less than the negative LoD are rejected.

6.1.8.2 Instrument Sensitivity

A similar decision is required for the instrument sensitivity. This is estimated from calibrations by certified calibration gas sources such as the SO_2 cylinders used by the LSOs and ESUs. The overnight auto-calibration equipment may produce a sensitivity based on SO_2 permeation tubes or uncertified SO_2 cylinders. There will also be span calibrations made by the QA/QC Unit during the network inter-calibration. Some of these estimates may be unreliable due to equipment failure or the use of non-certified gases. The judgement of the Data Ratifier, aided by the software algorithms, is therefore required to decide what sensitivity should be applied.

6.1.8.3 Instrument Drift

Besides deciding the best zero baseline and instrument sensitivity, the data ratification must also take account of any analyser drift in either zero or sensitivity. Zero and sensitivity may vary day-by-day but a rapid drift may be the sign of an instrument malfunction. Data ratification must evaluate where data can be accepted, accepted with modification or has to be deleted.

6.1.8.4 Instrument failure

Instruments may fail for numerous reasons. The equipment is serviced at the regular six-monthly ESU visits but malfunctions can arise between services. Some faults are minor, such as sample flows just below optimum but flow blockages can prevent the instrument from sampling ambient air. Ratification uses all available information: raw measurements, calibrations, alarms, engineer reports etc., to decide if the data can be corrected or needs to be rejected. The commencement of any fault must be determined. This is often a matter of judgement based on experience.

6.1.8.5 NOx data processing

The approach to ratifying NO_x data is slightly different to that for the other gaseous AURN pollutants.

NO_x instruments use the chemiluminescent technique to measure NO gas by reaction with an internally generated ozone source. In order to report NO_x, NO and NO_2 concentrations the instrument has to split the ambient sample into two. NO is measured directly in the first stream. The second stream passes through a catalyst that converts any NO_2 into NO. This stream, known as NO_x, is then measured. NO_2 is calculated by the difference between the NO_x from the second stream and the NO from the first.

The efficiency of the converter is crucial to correct determination of NO_2 using the chemiluminescent technique. The converted efficiency is determined at each inter-calibration visit and where this is less than the required 95%, data are rejected as they are likely to fall below the required DQO. CEN standard 14211:2012 permits scaling at lower efficiencies provided the DQO is still fulfilled.

When the CEN procedures are fully implemented, there will be a requirement to correct data for converters with efficiency between 95% and 98% (note, this requirement is specific to the chemiluminescent technique: should other types of analyser be used in future, this may not be applicable).

To achieve reliable NO_2 concentrations, the NO and NO_x channels are ratified separately and then NO_2 calculated by subtraction. This is a more reliable and flexible system than relying on the internal calculation of NO_2 within the analyser.

Calculations must be undertaken in mole fraction units (ppb) and the conversion to mass concentration units (to four decimal places) undertaken separately. This allows NO_x concentrations to be reported correctly in the units required by the Air Quality Standards Regulations (μgm^{-3} as NO_2).

Review of the NO_x/NO_2 ratio over an extended period is a useful tool to assist in data ratification. Seasonal patterns should be reasonably consistent at each monitoring station. Any sudden change in the ratio requires investigation, and unless linked to a change in the local pollutant emissions around the site it will probably result in rejection of data.

6.1.9 AURN Data Ratification (Particle Analysers)

Ratification of data from particle analysers is generally simpler than for gaseous analysers since there are fewer calibrations and checks which can be carried out in the field.

In most cases day-to-day scaling factors do not need to be adjusted and ratification consists primarily of deciding on the validity (or otherwise) of the measurements. This decision in will be based on instrument diagnostics, comparison with co-located measurements and other nearby stations, assessment of prevailing pollution sources, and results of instrument and infrastructure checks carried out at QA/QC audits.

For all types of instruments flow rate and leak checks are carried out during 6-monthly audit visits and services. A ramped correction may be applied to sampled volumes, where flow rates are found to be more than ±3% out from the flow rate recorded by the instrument. However, if the flow rate differs by more than ±10% the data are rejected.

For high-resolution 15-minute or hourly measurements it is sometimes apparent that there is a high degree of random instrument instability or “noise” not linked to changes in ambient pollutant concentrations. If this is the case, then these data will be rejected.

As part of the routine QA/QC audits, BAM particulate analysers have zero checks carried out every six months. This involves placing a HEPA filter on the inlet for a few days, to identify analysers which have high baseline responses to air containing no particulate matter. The CEN standard method for ambient particulate matter EN16450 states that action must be taken when baseline response is higher than three µg m^{-3} but does not state what the action should be. Originally, the only agreed action was to delete the data. However, as part of ongoing improvement activities a protocol was agreed in 2015 to enable baselines to be corrected where baseline responses exceed three µg m^{-3}. A zero baseline correction may therefore be applied to BAM particulate data where the zero test result indicates this is appropriate.

The zero baseline check for the Fidas instrument is carried out using a different testing procedure: zero baseline correction is not applicable to the Fidas.

Further ratification checks for all analysers include:

- That there are no negative values (less than minus the limit of detection).
- That PM_{10} is greater than $PM_{2.5}$, in cases where both parameters are monitored using the same method at the same site (allowing for the measurement uncertainty, particularly at rural sites where both PM_{10} and $PM_{2.5}$ are often low).

Additional data ratification considerations for two specific types of AURN particle analysers are discussed in the following sections: the Beta Attenuation Monitor (BAM) and the Fidas 200^{TM}.

6.1.9.1 Beta Attenuation Monitor

The BAM records several diagnostic parameters which are also used to identify potentially suspect data. Having carried out the checks above, and rejected any suspect data thus identified, the diagnostics are plotted, and examined for either long-term changes (that could indicate the pump is slowly failing or tape debris is building up on the nozzle), or short-term spikes:

- QTot, the hourly sampled total volume: this should be around 0.83 m^3 for PM_{10}, 0.7 m^3 for $PM_{2.5}$, and steady.
- ‘Ref’ – the reference measurement made using a calibration foil – should be steady.

- The stability parameter should be within ±5 (outside ±10 usually indicates a problem)

6.1.9.2 The Fidas 200^{TM}

Having undertaken the checks above, Fidas diagnostic parameters are also reviewed as follows:

- The flowrate should be steady at around 4.8 litres per minute, and within the range 4.65 – 4.95 li/min.
- The sample flow velocity should be between 7-11 ms^{-1}.
- The particle coincidence parameter should be in the range 0-10% and ideally well below 5%.
- Pump suction should be in the range 35-95% with no drift.
- The TIDF diagnostic should be within ±3.5 channels
- The IADS heater temperature should be in the range 23-65 °C, and the LED lamp temperature in the range 20-50 °C.

6.1.9.3 Non-Automatic Particle Monitors

Non-automatic PM_{10} and $PM_{2.5}$ daily mean measurements are collected manually by the CMCU and emailed monthly to the relevant QA/QC Unit in spreadsheets.

Instrument alarms and warnings (due to instrument flow outliers for example) are examined by the data ratifier to decide if the daily mean is valid or not. In addition, the QA/QC Unit uses spreadsheets to check that:

- Minimum sampling time (18 hours) and minimum sample volume (75% of nominal daily sample volume) are achieved for each daily sample.
- There are no gaps in the dataset which cannot be explained by power or filter exchange failures.
- Any unusually low, high, or otherwise anomalous values are explained, or else rejected as spurious.

A field blank correction, based on an unexposed filter which remains in the filter canister while the other filters in the batch are exposed, may be applied to the results. (Field blank correction is permitted for equivalent gravimetric methods such as the Partisol 2025, though not for reference method samplers such as the SEQ.) This takes account of any zero baseline artefacts which may occur during the exposure and measurement process. Choice of filter substrate will depend on requirements for any subsequent analysis of the particles collected. However for mass measurements PTFE coated “Emfab” filters are generally preferred to Quartz in order to avoid problems associated with moisture absorption. The issue of field blank correction, and how this process can improve quality control and reduce measurement uncertainty, are set out in a 2009 report by Bureau Veritas [38].

As with other pollutants, account is taken of any measurements at nearby sites or from other instruments at the site in question in order to determine if there are any anomalies with the dataset. Each non-automatic PM sampler is compared with the nearest comparable automatic BAM or Fidas. (At present, all AURN gravimetric samplers are co-located with BAMs).

6.1.10 Factors to Consider in Data Ratification

Data ratification procedures involve a critical review of all available information relating to a particular data set, in order to verify, amend or reject the data. A wide range of inputs need to be considered in the ratification process, as shown inTable 6-1. The overall aim of the ratification process is to ensure that:

- the final ratified dataset contains only valid data
- in the period between site audits, these data remain with the uncertainty level determined at the audit.

The close examination of analyser calibration service history, along with the overview procedures described above ensure that only valid data are retained.

Table 6-1 Factors to Consider in Data Ratification

Factor	**Relevant Questions**
Instrument history and characteristics.	Has the equipment malfunctioned in this way before?
Calibration factors and drift.	Rapid or excessive response drift can make data questionable.
Negative or out of-range data.	Are the data correctly scaled?
Rapid excursions or “spikes”.	Are such sudden changes in pollution concentrations likely?
Characteristics of the monitoring site.	Is the station near a local pollution sink or source which could give rise to these results?
Effects of meteorology.	Are such measurements likely under these weather conditions?

Time of day and year.	Are such readings likely at this time of day/week/year?
The relationship between different pollutants.	Some pollutant concentrations may be expected to rise and fall together.
Results from other sites in the network.	These may indicate whether observations made at a particular site are exceptional or questionable. Data from other sites in the area can be compared for a given period to determine if measurements from a particular station are consistent with general pollution concentrations.
QA Audit and Service reports	These will highlight any instrumental problems and determine if any correction of the data is necessary for long-term drift etc.

The actual data uncertainty can only be determined at the 6-monthly site audits when all of the required parameters are measured and can be combined with analyser type testing and calibration cylinder uncertainties. The careful application of zero and span calibration data, and careful application of any corrections required as a result of the sites audit (e.g. to account for changing calibration cylinder concentrations) are designed to ensure that the data remain within the uncertainty level determined at the audit.

6.1.11 Quality Circle

The QA/QC Units use a Quality Circle approach for final review of the data. The Quality Circle is a meeting involving representation from all disciplines of the QA/QC Unit: quality standards, inter-calibration team and data ratification. The meeting reviews any significant problems and decides on the appropriate actions by consensus. Data issues that are not clear to the ratification team may, for instance, be resolved by the inter-calibration manager’s better understanding of the instrument detection principle. The meeting also discusses the results of the QA/QC inter-calibration. The meeting then needs to decide if, and how, any problems observed at the inter-calibration affect the measured data.

The Quality Circle always needs to review data in the light of new information, whether this comes from the inter-calibration exercise or from other sources. Ratified data only rarely need to be revised and re-issued, though this does happen very occasionally. Where a possible fault is suspected but the results of the inter-calibration or other detailed investigations are still awaited then the data may remain as provisional on the Archive until these investigations are completed. Again, this only happens infrequently.

A key role of the Quality Circle is to identify where improvements in the overall quality system can be devised. This may be through improved equipment, improved procedures, improved software or software algorithms etc. When such points are identified they are actioned by the QA/QC Unit to ensure continuous improvement in the quality system.

6.1.12 UKAS Accreditation (ISO/IEC 17025:2017)

In any monitoring network where traceability of measurements and compliance with DQOs are critical, it is essential that the QA/QC procedures are accredited to recognised, traceable standards. By accrediting key processes in the QA/QC programme, it is possible to demonstrate compliance of the monitoring network to the requirements of the Air Quality Directive. For network inter-calibration procedures, the QA/QC Units are required to hold UKAS accreditation to ISO 17025:2017 for the on-site calibration of gaseous analysers and flow measurement of particulate analysers.

Accreditation to ISO 17025:2017 requires an organisation to:

- Document the procedures used to calibrate analysers
- Demonstrate competence of operators in performing calibrations
- Demonstrate traceability of measurements to metrology standards
- Calculate uncertainty budgets for measurements reported on Calibration Certificates.

UKAS is the recognised accreditation body in the UK and performs annual surveillance visits to the QA/QC Units to assess competence and compliance with all the requirements of ISO 17025:2017.

The Air Quality Standards Regulations require that the measurements are traceable in accordance with ISO 17025:2017. Section 8 of this report describes the traceability of the UK measurements within the AURN, in compliance with this requirement.

In addition, the Directive requires that any laboratory taking part in Community-wide inter-comparisons covering pollutants regulated in the Directive is accredited according to ISO 17025:2017 for the reference methods referred to in Annex VI of the Directive. The accreditation held by the QA/QC units ensures compliance with this requirement.

The Gas Standards Calibration Laboratory (currently Ricardo) is also accredited to ISO 17025:2017 (the current contractor is UKAS Calibration Laboratory No 0401), and UKAS accreditation conforms to the requirements of ISO 17025:2017 for the certification of gas calibration standards for a range of pollutants within a specified concentration range. This includes the gases and concentrations appropriate to the AURN.

The schedule of UKAS accreditation for the current contractor is available at https://www.ukas.com/wp-content/uploads/schedule_uploads/00001/0401Calibration-Multiple.pdf

(Please note, the contractor's name is given in the schedule as 'Ricardo-AEA': Ricardo Energy & Environment is a business name of Ricardo-AEA.)

6.2 QA/QC of Automatic Hydrocarbon Measurements

The Air Quality Directive requires benzene data to be reported with an uncertainty of ±25%. The Directive does not specify a DQO (uncertainty of measurement) for the measurement of the remainder of the hydrocarbon species referred to as ozone precursors.

Type approval, operational methodologies, mechanisms for QA/QC and calculation of measurement uncertainty budgets are clearly prescribed in EN 14662-3:2005. All of these areas need to be completely satisfied before an absolute calculation of measurement uncertainty can be undertaken.

The UK automatic hydrocarbon network is already operated to a high standard and will only need minor adjustment to be fully compliant with section 9 of EN 14662-3:2015. These adjustments centre on annual linearity evaluations, better quantification of calibration measurements and evaluation of site specific variables.

Robust, traceable, documented methodologies are implemented for calibration, data transmission and ratification, providing rigorous QA/QC for the automatic VOC analysers together with regularly undertaken European international intercomparisons at the EC Joint Research Centre (JRC), Ispra (Italy) and participation in European round-robin exercises under EMEP, ACTRIS and GAW.

Routine network operation is carried out as follows:

- Daily checks performed daily by network manager or network management team member.
- Fortnightly LSO visits.

- Fortnightly quantification calibrations using a certified reference gas maintained at a stable temperature (i.e. must be kept in a temperature controlled location within a monitoring station).
- Data ratification is carried out quarterly. The ratification process includes:
    - Data reviewed and checked for erroneous data and scaled or removed if necessary
    - Re-assignment of mis-identified peaks
    - The final data is reviewed at a quarterly quality circle meeting with all members of the project team
    - Any outstanding corrections following the quality circle meeting are made by the network manager before dissemination

6.3 QA/QC of Non-Automatic Benzene Measurements

Bi-annual service and maintenance visits are carried out at all measurement sites. Portable appliance Testing (PAT) is performed every other visit (annually). Sampling tubes are sent out to LSOs fortnightly in advance for exposure the following week. Each site receives a travel blank tube at least once per quarter. Samples are analysed at a sub-contractor's laboratory, conditioned and returned to the contractor for re-use.

Data ratification is carried out quarterly. The ratification process is as follows:

- Check blank is <2 ng.
- Check audit dates, time and flow rates have been entered correctly.
- Check sampling time is the same for both date/time and counter, investigate erroneous data.
- Check difference between the two tubes comprising each sample, investigate suspected erroneous data or mark as not for dissemination.
- Review site operator comments.
- Plot time series for the year to date to identify anomalous data points.
- Compare concentrations with same period in previous year.
- Data are compared against other species that might well have a close relationship in ambient air, such as NOx and CO data, where available.
- Data are compared against other local sites.
- Apply data flags (manually).
- Upload ratified (or provisional if applicable) data to UK-AIR.

6.4 QA/QC of Heavy Metals Measurements

The QA/QC measures employed by the Network to ensure robust sampling are as follows:

- The contractor visits all the Network sites to perform six-monthly site audits.
- At these visits the site infrastructure, performance and integrity are assessed.
- The LSOs are also audited and receive extra training where required.

6.4.1 Metals Network Site Audits

During each Network site audit visit the contractor:

- Audits the procedures of the LSO on-site, giving introductory training where necessary, and encouraged LSOs to feed-back into the running of the Network
- Assesses the current condition of all on-site equipment, including the condition of the PM_{10} sampling head and impactor plate
- Calibrates the flows of both the particulate (for volumetric and standard flow), and gaseous phase (volumetric flow), monitoring equipment
- Leak tests both the particulate and gaseous phase monitoring equipment
- Calibrates the site rotameter (used by the LSOs for determining the flow rate through the total gaseous mercury sampling line).

6.4.2 Metals Network Servicing

The ESU performs preventative maintenance on the samplers twice a year.

The flow rate of the samplers is calibrated at each ESU visit, at the site audits, yielding overall, quarterly flow calibrations.

6.4.3 Additional Sampling and Analysis QA/QC Procedures

A sub-set of the QA/QC procedures employed during Network operation to ensure the quality of the data produced is listed below:

6.4.3.1 Sampling

- Despatch and analysis of one field-blank filter per site per quarter.
- Thorough checks of the returned filters to check for damage during transport. Rejection of damaged filters.
- Logging of all samples on the contractor’s Network database. Rejection of any unidentifiable samples and full investigation of any discrepancies.

- Continued training of, and regular communication with, the LSOs. This includes assessment of performance during site audits.

6.4.3.2 Particulate phase metals (ICP-MS analysis)

- Optimisation of the ICP-MS prior to each set of analysis. Comparison of the optimised parameters with pre-defined criteria.
- Regular extraction of an appropriate certified reference material (e.g. NIST SRM 1648a or NIES No.8) to check the recovery of the digestion method. Recoveries must be within the limits specified by EN 14902:2005.
- Regular measurement of laboratory filter blanks to ensure appropriate blank subtractions are made from measured values.
- Maximum levels for the standard deviation of the five internal standard-corrected measured intensities of each analysis of each sample.
- The maximum absolute weighted residual for all calibration curves (as calculated using the contractor’s data processing software) must be less than one.
- Ratification of all data by a Quality Circle of senior scientific experts within the contractor’s organisation but independent of the analytical team.

6.4.4 QA/QC of Metals in Deposition Measurements

Each deposition monitoring site is serviced and audited every 6 months to maintain the site infrastructure, performance and integrity.

The analytical processes are subject to the QA/QC requirements of UKAS accreditation for ISO 17025:2017, which includes regular inter-laboratory comparisons of data. The accreditation is held by the contractor’s laboratories (CEH Lancaster) for the required analyses. Please note the accreditation is held for surface water samples, rather than specifically for deposition samples. UKCEH Lancaster regularly participates in the yearly EMEP intercomparison of analytical methods for heavy metals in precipitation run by the Norwegian Institute of Air Analysis (NILU).

The databases are subject to rigorous checks and, in addition, the concentrations in each sample are reviewed by the project manager at least quarterly before being uploaded to UK-AIR. Individual samples which are deemed too high (usually more than 2 x Standard Deviations from that year’s annual mean) are flagged as potential outliers that may not be representative of background concentrations.

6.5 QA/QC of PAH Measurements

In order to assure robust sampling procedures, the following QA/QC measures are undertaken:

- Routine servicing of the Digitel^{TM} samplers is carried out at all Network stations at least once a year by the ESU.
- Routine calibration of the Digitel^{TM} samplers is carried out at all Network stations at least once a year by the ESU or Ricardo.
- Yearly audits are carried out at all Network stations by the contractor. As part of these visits, the flow is measured using a calibrated and traceable flowmeter (according to EN 12341:2014 [16] and EN 15549:2008 [30]),
- As specified in EN 15549:2008 [30] the leak test and flow rate of the samplers are checked. These are undertaken on approximately a quarterly basis by Ricardo who in late 2021 became ISO-17025 accredited to undertake the non-adjusting flow calibrations on the DHA-80 samplers using manufacture recommended flow calibration devises that are traceable to National Standards.
- LSOs are audited and where considered necessary they are retrained. In addition, an updated LSO site operation procedure manual is re-issued when necessary.
- Portable appliance testing, periodic (five-year) electrical testing and the updating of risk assessments is also performed at the stations as necessary.
- Analysis of sample blanks and filter blanks is performed.
- Despatch and analysis of field blanks is performed.
- Inspection of all sampling media prior to despatch to stations in accordance with the specifications in EN 15549:2008 [30] and EN 15980:2011 [31]. For example, filters are inspected for pinholes, loose material and non-uniformity.
- Inspection of all filters when returned from stations. Samples that are damaged (e.g. torn or wet filters) or returned un-sampled are rejected and the details of these samples are noted in the contractor’s Network database.
- Rejection of any unidentifiable samples returned from stations.
- Full investigation of any discrepant or unexpected sampling data (e.g. abnormal sample volumes or motor loads).

In order to ensure the quality of the analytical data, the following QA and QC measures are undertaken:

- Regular assessment of the limit of detection of the GC-MS method.
- Regular extraction and analysis of an appropriate certified reference material (NIST SRM 1649b) in order to check the recovery of the extraction methods. Recoveries must be within the limits specified by EN 15549:2008 [30].

- Use of a range of deuterated PAH analogue species in order to assess (and correct for) the recovery of each sample. Following the criterion in EN 15549:2008 [30], if the analytical recovery of d B[a]P for any sample is determined to be less than 50 %, the result is highlighted as not being valid for inclusion in the calculation of the annual mean concentration.
- The Environment Agency's National Monitoring Laboratory (NML) undertake the extract and analysis of the environmental samples from the PAH network and the NML is currently waiting for feedback on the extension of their ISO 17025:2017 scope.

Deposition sampling and analytical QA/QC is performed as specified in EN 15980:2011 [31]rather than EN 15549:2008 [30]. All other aspects of the analysis post extraction are the same.

6.6 QA/QC for the UUNN

All data received from the UKAS accredited laboratory are subject to internal QA/QC review before being published to ensure that, following the calculation of results, there are no errors present in either the analysis process or the results presentation. These are completed both on a monthly basis; to check the exposure information provided by each LSO in terms of the monitoring period (time and date) and identification of any significant outliers or erroneous results, and also on a quarterly basis; to identify any instances where the coefficient of variance between each set of triplicate diffusion tubes is greater than 10%.

Travel blanks are used as a 'control' for possible contamination of the diffusion tubes, either during storage or during transport. Travel blank results should usually be less than the limit of detection. In the event that a travel blank returns a relevant concentration, the batch of diffusion tubes associated to with the travel blank are checked in terms of validity and possible contamination.

6.7 QA/QC for Other Measurements

6.7.1 Cations and Anions in Rural $PM_{2.5}$

The MARGA 2S used to measure anions and cation in rural $PM_{2.5}$ uses an internal standard of lithium bromide (LiBr) for on-going calibration purposes. The LiBr solution is manufactured by the LSO. The internal standards (both stock and working solutions) are analysed by an UKAS accredited laboratory. Measurements are invalidated if the measured Li^+ and Br^- ion concentrations deviate by more than

±20% of the known concentration. Currently the concentrations of Li^+ and Br^- ion in the internal standard are 320 and 3680 µg L^{-1}, respectively, in the MARGA 2S based at the Chilbolton Observatory, whereas at Auchencorth Moss it is 70 µg L^{-1} of Li^+ and 800 µg L^{-1} of Br^-, due to the lower observed concentrations.

As noted in section 5.7.1, peak retention times may change over time due to instrumental factors, e.g. column ageing. In order to account for this, the peak retention times are checked on a regular basis and adjusted accordingly by the LSO. Peaks are identified by the system software if they fall within a window of ±5% of the operator defined peak retention time. Occasionally, measurements may be made where the peak retention time has shifted considerably within a short period of time, e.g. over a period of a couple of hours. This may mean that a peak is missed or misidentified by the system software. In such instances, the resultant anion and cation chromatograms, which are written to file, can be re-analysed and use to verify the presence of species of interest. Once a peak associated with species of interest has been identified the mass concentration of the species can be determined. The retrospective re-analysis of chromatograms is undertaken using proprietary software supplied by the instrument manufacturer (Metrohm-Applikon BV, Schiedam, The Netherlands).

The manufacturer’s quoted detection limits for hourly sampling using the MARGA 2S are given in Table 6-2.

Table 6-2 Manufacturer’s quoted detection limits for the MARGA 2S

Species	**Fixed Loop as used at Chilbolton Observatory (µg m^{-3})**	**Pre-concentration as used at Auchencorth Moss (µg m^{-3})**
NH_4^+	0.05	0.005
Na^+	0.05	0.005
K^+	0.09	0.009
Ca^{2+}	0.09	0.009
Mg^{2+}	0.06	0.006
Cl^-	0.01	0.001
NO_3^-	0.05	0.005
SO_4^{2-}	0.04	0.004
NH_3	0.05	0.005
HCl	0.01	0.001
HONO	0.02	0.002
HNO_3	0.05	0.005
SO_2	0.03	0.003

Due to the slight changes in peak retention over time, small perturbations in the instrument detection limits have been noted due to changes in the IC columns, which are typically replaced every two to three months. For this reason, the limits of detection (LoDs) for each species of interest are determined from the measurements annually, rather than using the manufacturer quoted values. Measurements that report zero values are replaced with ½ LoD, whereas values reported below the LoD are reported but are flagged using EMEP flags. A site log book is maintained by the LSO. This is used to record:

- All operational checks undertaken, including instrument checks undertaken, e.g. replacement of instrument components, connective tubing, inlet cleaning
- Problems with the equipment
- Factors which may have a bearing on the $PM_{2.5}$ measurements (e.g. pump failure, power cuts, burning or nearby construction work).

The following QA/QC measures are undertaken at both sites for the MARGA 2S:

- Portable appliance testing, periodic electrical testing and the updating of risk assessments is also performed at the stations as necessary.
- The sample flow is measured and calibrated using a traceable flowmeter. The audit sheet is retained by the LSO. This is currently undertaken once a month.
- System blank checks are performed once a month to identify contamination or when required.
- Daily measurements (chromatograms and instrument parameter log files) from the instrument are backed-up routinely. At Chilbolton Observatory this is via an FTP connection on a daily basis (at 02:00) to the contractor's internal server. At Auchencorth Moss data are backed up onto a local server. This ensures good data integrity and to limit data loss in the event of the irrevocable failure of the instrument PC.
- System parameters and peak retention times are monitored on a daily basis and adjusted accordingly.
- Instrument working solutions are manufactured according to the manufacturer's guidelines. Working solutions are replenished on a routine basis.
- Variations in system parameters and instrument failures are investigated in a timely manner.
- Annual servicing is carried out by UKCEH staff at Auchencorth Moss and Ricardo staff at the Chilbolton Observatory with support from the manufacturer where considered necessary.

As part of the ratification process:

- Internal standard capture is assessed
- Measurements of the $PM_{2.5}$ from MARGA 2S is compared to PM_{10} reported by the instrument
- Ion balance of both $PM_{2.5}$ and PM_{10} is reviewed to identify any invalid data
- The instruments operational parameters are also used validate/invalidate data.

The ratified measurements are then reported and disseminated via UK-AIR.

6.7.2 Elemental Carbon (EC) and Organic Carbon (OC)

In order to assure robust sampling procedures for EC and OC the following QA/QC measures are undertaken:

- Routine servicing/calibration of the Digitel^{TM} samplers is carried out at both Network stations twice a year by the ESU.
- Yearly audits are carried out at both Network stations by the contractor. As part of these visits, the flow is measured using a calibrated and traceable flowmeter (according to EN 12341:2014), and the LSOs are audited (and, where necessary, retrained). In addition, an updated LSO site operation procedure manual is re-issued when necessary.
- Portable appliance testing, periodic (three-year) electrical testing and the updating of risk assessments is also performed at the stations as necessary.
- Analysis of sample blanks and filter blanks is performed.
- Despatch and analysis of field blanks is performed.
- Inspection of all sampling media prior to despatch to stations. For example, filters are inspected for pinholes, loose material and non-uniformity.
- Inspection of all filters when returned from stations. Samples that are damaged (e.g. torn or wet filters) or returned un-sampled are rejected and the details of these samples are noted in the contractor’s Network database.
- Rejection of any unidentifiable samples returned from stations.
- Full investigation of any discrepant or unexpected sampling data (e.g. unexpectedly high or low sample volumes).

In order to ensure the quality of the analytical data, the following QA and QC measures are undertaken:

- Daily machine zero checks and Potassium phthalate monobasic (KHP) solution checks. These must be within specified limits.
- Regular analysis of an internal reference material.
- Regular calibration of the sample temperatures using the manufacturer’s temperature calibration device.
- TC analysis is covered by accreditation to ISO17025:2017 – the accuracy of the subdivision into EC and OC is not covered by the accreditation.

7 Traceability of Measurements

Traceability requires an unbroken chain of measurements all with stated uncertainties - from a primary international or national standard, through the calibration standards used in the network, to the final measurement result.

Calibration standards are a key link in the traceability chain. The methods by which calibration standards are developed and maintained at a national level fall into a number of different categories. These cover calibration standards that are:

1. Prepared in a manner that is traceable directly to SI units though mass, volume (length), flow (mass and time) etc. These apply to calibration standards for the pollutant gases measured within the AURN (NO_x, SO_2, CO, O_3), although there are different means of realising and disseminating these, in particular between ozone and the other gases.
2. Not able to be produced in a manner that is directly traceable to SI units but traceability can be achieved by means of the realization of a potentially ‘absolute’ method such as optical photometry, when implemented under controlled conditions. This method applies for the measurement of metals and PAH, for example.
3. Not able to be realised in a traceable manner or as a ‘primary’ or ‘absolute’ method, but realised instead *by convention or by definition as the reference method*, preferably having the smallest measurement uncertainties achievable using that method. This method applies for PM_{10} and $PM_{2.5}$ measurements.

This section explains how traceability is achieved for gaseous pollutants, PM_{10}, $PM_{2.5}$, benzene, metals and PAH. It does not cover measurement of deposited metals, deposited PAH, rural cations and anions, EC and OC, because the relevant Directives do not contain any DQOs for these parameters.

7.1 Traceability for NOx, SO_2, CO and Zero Air

7.1.1 Overview

The traceability chain for the gaseous pollutants in the AURN is indicated in Figure 7-1. The “chain” is shown in red – from international standards to individual measurement sites. The check procedures adopted in the UK are also highlighted – and shown in green.

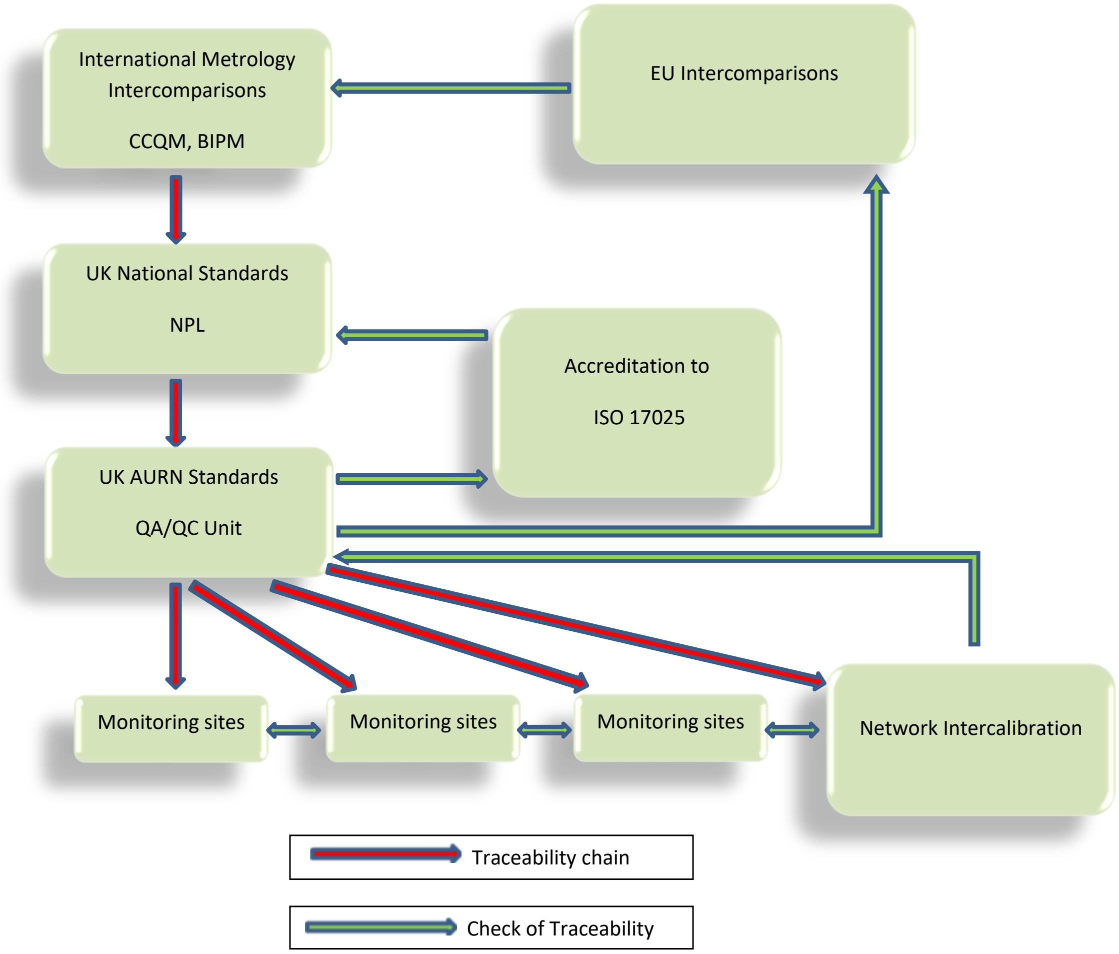


Figure 7-1 Traceability chain and traceability checks for UK AURN gaseous measurements

7.1.2 UK primary gas standards

UK Primary Gaseous Calibration standards are prepared or certified by NPL. For NO, this uses gravimetry to weigh specific pollutant gases together with relevant matrix/diluent gases into high-pressure cylinders and then to dilute these gas mixtures to the required low concentrations for ambient air concentration calibrations, as required. This method of preparation of gas standards is directly traceable to the SI mass unit, via a number of accurate weighings (gravimetry). For SO_2 and CO, commercially available gas mixtures are calibrated by comparison with NPL’s high accuracy primary standards. Typical uncertainties of the UK primary gas calibration standards are as follows:

- NO_x 1%.
- SO_2 3%.
- CO 2%.

These UK standards are cross-referenced with standards prepared by other national institutes through international inter-calibration exercises coordinated by organisations such as EUROMET.

7.1.3 Provision of traceable gas calibration standards to AURN monitoring sites

All AURN sites have calibration gas cylinders for NO, CO, and SO_2, as appropriate, which remain at the site. These cylinders are prepared and supplied by the Gas Supplier but prior to delivery to site they are calibrated at the Gas Standards Calibration Laboratory and provided with a UKAS accredited certificate of calibration. The current contractor, Ricardo-AEA (Ricardo), is UKAS Calibration Laboratory No 0401; UKAS accreditation conforms to the requirements of ISO 17025:2017.

The Gas Standards Calibration Laboratory has a suite of UK primary gas calibration standards purchased from NPL. The calibration cylinders used at every AURN site are certified against these and given an ISO 17025:2017 accredited certificate of calibration. Traceability of the calibration gas used at every AURN site is thus linked in an unbroken chain to national and international gas standards. The uncertainty of calibration gas standards provided to the monitoring sites is typically:

- NO 3-3.5%
- SO_2 2.5%
- CO 2%.

All cylinders used for the AURN network inter-calibration are certified by the Gas Standards Calibration Laboratory. The Gas Standards Calibration Laboratory also participates in recognised international inter-comparisons to ensure the integrity of the gas standards used in the AURN. As noted in section 6, this is a requirement of both ISO 17025:2017 and the Air Quality Standards Regulations in order to demonstrate comparability and traceability.

7.1.4 Zero air calibration standards

As ambient concentrations decrease, the importance of the accuracy of the zero calibration increases. Zero air cylinders are used at some AURN sites, and internal chemical scrubbers at others. These are traceable to a certified NPL zero air standard with the following specifications:

- NO <1 nmol/mol
- SO_2 <1 nmol/mol
- CO <20 nmol/mol

7.1.5 Site calibration and inter-calibration

The final link in the traceability chain from international gas standards to measurements of air quality at individual measurement sites is provided through the periodic calibration of the analysers with the certified cylinders at each site. At some sites automatic systems provide for daily or three-daily calibrations. At other sites two-weekly or monthly manual calibrations are performed.

In order to check the stability of the gas cylinders on site over a period of time, the concentrations of the gases they contain are checked against recently certified cylinders as part of the 6-monthly site inter-calibration exercise. The procedure is analogous to that used in the Gas Standards Calibration Laboratory, but the procedures in this case are not accredited. This is because the conditions for the calibration cannot be reliably controlled at a remote measurement site in the way that they are in the calibration laboratory.

The procedure is therefore to check the site cylinder concentration and if this is shown to have deviated significantly from the certified value the cylinder is replaced. The drift in the concentration is taken into account during data ratification.

7.2 Traceability for Ozone

Unlike stable gases such as CO, NO etc., ozone is too reactive to be prepared in gas cylinders. However, the UV absorption ozone photometer is an absolute method of monitoring, governed by the Beer-Lambert law. Calibration of ozone analysers in the UK are performed using reference ozone photometers, which are themselves calibrated against an ozone standard reference photometer (SRP).

NPL maintains a NIST SRP in the UK (there are others elsewhere in Europe). These are used as ozone reference standards to underpin its international comparison programme. The Bureau International des Poids et Mesures (BIPM) and NIST are cooperating to transfer the international responsibility for the comparison of ozone standards to the BIPM.

7.2.1 Provision of traceable O_3 calibration standards to all AURN ozone monitoring sites

Transfer reference photometers are used for calibration of ozone analysers. These are calibrated every six months by NPL against their SRP, providing UKAS accredited calibrations in the range 0 to 400 nmol/mol with a ±3.0% relative uncertainty (at the 95% confidence level).

The QA/QC Units' transfer reference photometers are commercial photometers certified to UK standard. These photometers are used to calibrate the ozone analysers at all AURN sites every three months. The uncertainty of the calibration of on-site analysers is typically 3-4%. Hence, there is an unbroken chain of traceability to national and international ozone standards.

As an independent check, the QA/QC Units also participate in international intercomparisons for ozone. In addition, the QA/QC Units also provide UKAS accredited calibrations of photometers used by the network's service engineers, enabling them to provide a traceable ozone analyser calibration as part of their routine service and maintenance.

7.3 Traceability for PM_{10} and $PM_{2.5}$

Manual gravimetric methods for particulate monitoring of PM_{10} and $PM_{2.5}$, as specified in the European standards EN 12341:2014 is defined as the European Reference method for particle monitoring in the Air Quality Directive and therefore the Air Quality Standards Regulations. These two standards specify methods that cannot be considered as traceable to the SI system of units in a rigorous manner. The sampling is by a method defined by convention, and the mass measurement can clearly be defined as traceable to SI units. However, the main problem is that the measurement itself is not well defined, as the particles comprising the material sampled will have different shapes, sizes and compositions.

As noted earlier (section 5.1), UK measurements of PM_{10} and $PM_{2.5}$ are largely undertaken with automatic measurement techniques, in order to fulfil the rapid dissemination requirements of the Air Quality Standards Regulations (drawn from the Air Quality Directive, 2008/50/EC). The manual sampling methods are therefore to be used as references against which other measurement techniques used for monitoring PM_{10} and $PM_{2.5}$ for regulatory purposes, may be compared. As a result of such comparisons, other methods of measurement may be demonstrated to be "equivalent" and accepted for the purposes of formal compliance reporting. This concept of the demonstration of "equivalence" is specified in a document prepared by the EU and involves comparisons in the field of any other method for monitoring PM_{10} or $PM_{2.5}$ with the relevant reference method.

The above standards therefore represent reference methods that are specified by definition and with no real traceability to the SI system of units (with the exception of a requirement to determine the mass flow of air through the monitor). This inability to achieve traceability is partially as a result of the complex variable and ill-defined size, shape and composition, of the particulate matter being monitored.

The UK has conducted a detailed and comprehensive equivalence testing programme for PM_{10} and $PM_{2.5}$. Latest results can be found on UK-AIR and the SIRA MCERTS websites.

7.3.1 On-site checks

During the network 6-monthly inter-calibration exercise the flow rates of all network analysers are calibrated by UKAS accredited procedures. This checks the most basic parameters of the measurement – flow and mass – and ensures correct operation of the analysers.

In addition, ongoing QA/QC equivalence checks are incorporated into the network via long-term co-located sampling of PM_{10} and $PM_{2.5}$ with Fidas, BAM and gravimetric samplers at several sites in the network.

7.4 Traceability of Automatic Hydrocarbon Measurements

The uncertainty of NPL VOC gas standards is stated on the certificate as an expanded uncertainty with a coverage factor of approximately 95% in the units of the gravimetric amount fraction. This uncertainty is a combination of the gravimetric uncertainty in the preparation of the mixtures and an allowance for drift over the five-year period the certificate is valid for. NPL carries out continuous stability checks on the VOC standards.

7.5 Traceability of Non-Automatic Benzene Measurements

UKAS accredited flow checks are carried out on a six-monthly basis at audit/service visits by the contractor. Certificates are provided for each audit period. UKAS accredited measurements by GC-MS for benzene from Carbopak X sorbent material is carried out by a subcontracted analytical laboratory.

7.6 Traceability of Metals Measurements

7.6.1 Particulate-phase Metals

As explained above, metrological traceability ensures that any result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty. Here, a ‘reference’ can be a definition of a measurement unit through its practical realisation, or a measurement procedure including the measurement unit for a non-ordinal quantity, or a measurement standard. The measurement results obtained by this network are therefore calibrations and fully traceable to national standards and to primary realisations of the relevant SI units.

Each site is flow checked on a quarterly basis with flow calibrators traceable to national standards. Both the ESU and the contractor use the same ISO 17025:2017 accredited calibration service to calibrate their flow meters. Analysis in the laboratory is traceable to the NIST series of mono-elemental standards which realise the mole, and to the definition of the kilogram through the gravimetric preparation of standard solutions.

Where traceability to SI base units is not possible because the measurement is defined by the procedure – here, PM_{10} sampling – the relevant documentary standard is followed (EN 12341:2014).

Whilst not ensuring traceability *per se,* analytical results for metals are validated by the regular measurement of relevant certified reference materials: NIST SRM 1648a, ERM-CZ120 or NIES No.8.

7.6.2 Metals in Deposition

The analytical laboratory used is accredited to ISO 17025: 2005 by UKAS. In compliance with section 5.6 (clauses 5.6.2.1.1 and 5.6.2.2.1) of ISO 17025:2017, the laboratory maintains a system whereby all analyses are traceable to SI units by means of an unbroken chain of calibrations and comparisons linking them to relevant primary standards of the SI units of measurement. This applies to both measurement equipment used (e.g. balances) and analytical reference materials.

The Tekran instrument (used for TGM and speciated mercury measurement) is a mercury mass measurement method. It is auto calibrated using an internal permeation source. This source is externally verified / calibrated with a with a primary reference standard of saturated mercury at a known temperature with a volumetric syringe to introduce a known mass of mercury. This is carried out using the Tekran 2505 mercury vapour calibration unit, which meets the requirements of BS EN 15852. Field trials and inter-comparison between methods for measuring atmospheric mercury found good agreement between sampling methods including the Tekran analyser [39] [40].

7.7 Traceability of PAH Measurements

The measurement results obtained by this network are calibrations and fully traceable to national standards and to primary realisations of the relevant SI units.

The sampler flow rate is checked on a quarterly basis: from late 2021 this has been done to an ISO-17025 accredited method by the Ricardo team, as it is now part of the scope of their accreditation. These flow calibrations are undertaken on an approximately a quarterly basis. The flow meter used for the PAH Network is as specified by the Digitel^{TM} DHA-80 manufacturers and calibrated traceable to national standards using an ISO 17025 accredited service.

Analysis in the laboratory is traceable to the custom 27 PAH compound ISO 17034 certified reference standards which realise the mole, and to the definition of the kilogram through the gravimetric preparation of standard solutions.

Where traceability to SI base units is not possible because the measurement is defined by the procedure – here, PM_{10} sampling – the relevant documentary standard is followed (EN 12341:2014 [16] and EN 15549:2008 [30]).

Whilst not ensuring traceability per se, analytical results are validated by the regular measurement of relevant certified reference materials, NIST SRM 1649b.The above applies to measurements of PAH concentrations of samples collected as particulate from the air and deposited PAH.

8 Uncertainty of the Measurements

This section sets out the uncertainty calculation philosophy and the typical uncertainty values for measurements of ambient concentrations of gaseous pollutants, PM_{10}, $PM_{2.5}$, benzene, metals and PAH. It does not cover measurement uncertainty of rural cations and anions, EC and OC, because the relevant Directives do not contain any DQOs for these parameters.

In general, all measurement uncertainties are calculated using very similar methodologies. The first stage of the process is set by the Air Quality Standards Regulations which, based on health impact information, specify a Limit or Target Value for a pollutant, together with a DQO for that value. For example, the annual mean Limit Value for NO_2 is 40 µg m^{-3}, with a DQO of ±15% for fixed measurements. Therefore, an annual mean measurement reported at 40 µg m^{-3} must have an associated uncertainty of no more than ±6 µg m^{-3} (i.e. 15% of 40 µg m^{-3}).

The next stage in the process is determined by critical assessment of the performance of the analyser making the measurement. Using principles from the Guide to the Uncertainty of Measurement (GUM) [41], all of the possible components associated with making a measurement are identified, their effects on the measurement quantified and then combined to provide a total uncertainty for the measurement.

For example, the uncertainty associated with making a fixed measurement of carbon monoxide will be influenced by the uncertainty of a number of factors, for example:

- The concentration of calibration gases (zero and span).
- The noise associated with the analyser signal (to zero and span gases).
- The response of the analyser to any interfering gases.
- The response of the analyser to other interferences (temperature, electricity supply, etc.).
- Any lack of linear response of the analyser.

Once all of the possible contributions are identified and evaluated, the results are combined in a “root-sum-square” calculation to arrive at the total measurement uncertainty at the Limit or Target Value.

For all pollutants regulated by the Air Quality Standards Regulations, standard methods have been published that describe exactly how to perform the evaluations and calculations, together with minimum requirements for ongoing Quality Control procedures.

The UK is required to use instrumentation that have been tested against these standard methods and fulfil the requirements of the DQO. Ongoing QC obligations must be fulfilled to ensure that the instruments and associated infrastructure continue to produce data that are compliant with the DQO.

8.1 Uncertainty in the AURN

As a result of all of the QA/QC operations undertaken within the AURN and described in this report, the uncertainty of the measurements can be reliably determined using the methodology defined in the BS EN Standard Methods. This determination of uncertainty is required to demonstrate compliance of the measurements made within the AURN with the DQOs of the Air Quality Standards Regulations.

Analysers used in the AURN have been fully tested against the performance requirements of the BS EN standard methods. The results obtained vary not only by pollutant type but also by manufacturer. Following verification of the performance test results, minor variations to the uncertainty calculations are made to account for analyser and specific field operation functions e.g. NO_x converter efficiency tests and cylinder uncertainties. The results of these calculations are summarised in Table 8-1.

Table 8-1 Calculated Best Measurement Uncertainty of AURN Data using BS EN methodology

Instrument	**NO_x**	**CO**	**SO_2**	**O_3**
API A + E series Analysers (at Limit Value)	14%	10%	13%	12%
Horiba 370 series Analysers (at Limit Value)	12%	11%	12%	9%
Thermo I series Analysers (at Limit Value)	10%	10%	13%	11%
ME 9800(UK) series Analysers (at Limit Value)	11%	14%	11%	12%
Ecotech Serinus (at Limit Value)	15%	10%	14%	12%
AQ Standards Regs DQO (at Limit or Target Value)	15%	15%	15%	15%

Table 8-1 shows that the data obtained from the analysers tested to date fulfil the requirements of the DQOs. The calculations at this stage necessarily contain a number of assumptions about aspects of analyser field performance that will need to be regularly evaluated on site.

The instruments referred to in the table are NOx analysers, but the quoted uncertainties apply to measurements of NO_2, this being the only one of the NOx species for which the BS EN standard provides an uncertainty budget calculation.

For PM_{10} and $PM_{2.5}$, a similar process is employed, but because performance tests using certified calibration standards is not possible, demonstration of equivalence is conducted using a series of comparison tests against a reference sampling device. The UK equivalence trials have demonstrated that data derived from all analysers that meet the equivalence criteria conform to the DQOs for PM_{10} and $PM_{2.5}$ i.e. 25% at the limit value (Table 8-2). (For $PM_{2.5}$, a daily mean of 30 µg m^{-3} is used as a 'pseudo-daily limit value' in this process, because there is currently no actual limit value for daily mean $PM_{2.5}$.)

Table 8-2 Calculated Best Measurement Uncertainty of AURN PM Data using EN methodology

Instrument	**PM_{10}**	**$PM_{2.5}$**
Fidas 200™	7.5%	9.3%
BAM 1020	9.3%	12.6%
Partisol 2025	8%	11%
SEQ	9%	14.8%

8.2 Uncertainty of Automatic Hydrocarbon Measurements

A statement of measurement uncertainty is only required for benzene. All other pollutants are excluded from this requirement.

As noted earlier, the Perkin Elmer™ analyser used in the UK network has not been type approved for the automatic measurement of benzene as specified in EN14662-3:2015. Measurement of the ozone pre-cursor pollutants is not currently regulated by a standard method, and there are no type-approved analysers available that measure both benzene and the precursors. From a monitoring perspective, this makes cost-effective automatic monitoring of benzene and ozone precursors challenging.

The UK has a staged approach to fulfilling the requirements:

- The four automatic analysers in the network are calibrated with certified gas mixtures.
- The four automatic analysers have been regularly intercompared against co-located samples collected using the pumped sampler methodology. Results of these comparisons show that the difference between the techniques is less than 10%.
- The UK regularly participates in round robin calibration exercises, where the concentrations of known gas mixtures are evaluated with a calibrated analyser. In the most recent exercise, the maximum deviation of reported benzene concentrations from the reference value was 7.0%.
- The UK also participates in international intercomparison exercises, where test gases are generated and sampled simultaneously by a number of different analysers owned by Member States.

In addition, calculation of the uncertainty of the calibration factor of an analyser is routinely undertaken, using the principles of the Guide to Expression of Uncertainty in Measurement (GUM) [41]to define the inputs into the calculations. These tests demonstrate that the uncertainty of the calibration factors is routinely better than 25%.

These approaches provide confidence that the calibration and monitoring methodologies used by the UK are sufficiently robust to fulfil the requirements of the benzene DQO (25%).

Hourly uncertainty concentrations according to the ACTRIS standard operating procedures [42] are reported to EMEP/ACTRIS and GAW. This information is held in the NILU database “EBAS” [43].

8.3 Uncertainty of Non-Automatic Benzene Measurements

Flow checks are carried out on a six-monthly basis at audit/service visits. The calculated uncertainty for the Non-Automatic Hydrocarbon sites is typically 15%, expressed at a 95% level of confidence. This includes contributions from the contractor’s UKAS accredited low flow measurements, desorption efficiency and analysis uncertainty.

8.4 Uncertainty of Metals Measurements

8.4.1 Particulate-phase Metals

The range of uncertainties covering the majority of analyses of single filters are shown in Table 8-3 below. All figures are a combination of the analytical and sampling uncertainties and have been derived using full ISO GUM compliant uncertainty budgets developed from measurement equations which describe the entire measurement process. All values are stated to a coverage factor of $k = 2$, providing a level of confidence of approximately 95%.

The measurement uncertainties displayed in Table 8-3 are representative of the range of uncertainties covering the majority of individual measurements over a typical sampling period (here, one week), as required by the Air Quality Directives. The vast majority of the measurements used to compile the data above were of ambient concentrations well below the relevant target values. It is calculated that in the region of the appropriate target value – where the Air Quality Directive’s uncertainty DQOs apply – these relative uncertainties will be significantly lower.

8.4.1.1 Measurement of uncertainty of the annual average

ISO 11222:2002 [44] “Air quality - Determination of the uncertainty of the time average of air quality measurements” is used to determine the uncertainty in the annual mean for each element at each sampling location. This is easily done since the contractor produces a statement of uncertainty with each measurement result.

Data capture across the Network remains high (and any gaps in coverage have generally occurred evenly throughout the year). The uncertainty in the annual mean values are dominated by analytical and sampling uncertainty, with only small uncertainty contributions arising from time coverage below 100%. The effect of these contributions is calculated using the method described in ISO 11222:2002 “Air quality - Determination of the uncertainty of the time average of air quality measurements”. In all cases annual mean uncertainties are compliant with the DQOs for uncertainty in the Air Quality Directives.

Table 8-3 Expanded Relative Uncertainties over a typical sampling period of 1 week

Analyte	***Expanded Relative Uncertainties***	
	Single measurement range[(a)]	***EC Directive maximum[(b)]***
As	10 - 16%	40 %
Cd	9 - 15%	40 %
Co	9 - 25%	-
Cr	10 - 35%	-
Cu	9 - 14%	-
Fe	10 - 13%	-
Mn	9 - 16%	-
Ni	10 - 20%	40 %
Pb	10 - 16%	25 %
Se	11 - 32%	-
V	9 - 16%	-
Zn	9 - 14%	-

(a) ‘Single measurement range’ shows the range of uncertainties covering the majority of analyses of single filters and tubes by the current contractor during 2021.

(b) ‘EC Directive maximum’ shows the maximum permissible uncertainty at the target value allowed by the relevant EU Air Quality Directive.

Expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Air Quality Directives metals are given in Table 8-4 below. These apply at the relevant limit value or target value.

Table 8-4 Annual Mean Uncertainties

Analyte	***Relative Expanded Uncertainties[(a)]***	
	Annual Mean	***EC Directive maximum***
As	25 %	40 %
Cd	14 %	40 %
Ni	16 %	40 %
Pb	14 %	25 %

(a) Relative expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Daughter Directive metals, averaged across the Network.

8.4.2 Metals in Deposition

For the measurement of trace metals by ICP-MS the total expanded uncertainties measured at 5 µg l^{-1} shows a coefficient of variation better than 5% for all elements except Li, Be, Zn and Sn. The coefficients of variation for Li, Be, Zn and Sn are 10.5%, 9.3%, 23.4% and 10.3% respectively. The total expanded uncertainty for the determination of mercury by the AFS method is 25% at 10 ng l^{-1}.

For the metals monitored for compliance with the Air Quality Standards Regulations, samples are checked for an expanded uncertainty of 10% (equivalent to two times the standard deviation of that year's annual mean). The concentrations are checked against the limit value / target value concentrations but are always well below these values.

In the case of metals deposition measurements, concentrations in rainwater are also checked for an expanded uncertainty of 10% (equivalent to two times the standard deviation of that year's annual mean).

8.5 Uncertainty of PAH Measurements

The range of uncertainties covering the analyses of ambient PAH by the current contractor is shown in Table 8-5 below. All figures are a combination of the analytical and sampling uncertainties. Where expanded uncertainties are quoted these have had a coverage factor of k = 2, providing a level of confidence of approximately 95%.

These uncertainties only apply to *ambient* PAH measurement of particulate samples.

The relative expanded uncertainty in a typical analytical result for B[a]P collected from particulate in ambient air from a Network sample was estimated to be ~38% - well within the DQO of an expanded uncertainty of 50% at the target value.

The expanded measurement uncertainty of the deposition measurement of the PAH detailed in BS EN 15980:2011 [31] are considered to be ~57-66% which is within the DQO of an expanded uncertainty of 70% for fixed deposition detailed in the measurement of the PAH detailed in the standard.

Table 8-5 Range of PAHs analysed, with best estimate of the respective expanded uncertainties of particulate measurement.

PAH number	Compound	Expanded Uncertainty	PAH number	Compound	Expanded Uncertainty
1.	Phenanthrene	23%	15.	Benzo[e]pyrene	25%
2.	Anthracene	32%	16.	Benzo[a]pyrene	38%
3.	Fluoranthene	44%	17.	Perylene	25%
4.	Pyrene	31%	18.	Dibenzo[a,c]anthracene	20%
5.	Retene	32%	19.	Dibenzo[a,h]anthracene	18%
6.	Benzo[b]naphtho[2,1-d]thiophene	23%	20.	Indeno[1,2,3-cd]pyrene	21%
7.	Benzo[c]phenanthrene	24%	21.	Benzo[ghi]perylene	31%
8.	Benzo[a]anthracene	29%	22.	Anthanthrene	46%
9.	Cyclopenta[c,d]pyrene	64%	23.	Dibenzo[a,l]pyrene	52%
10.	Chrysene	23%	24.	Dibenzo[a,e]pyrene	34%
11.	5-Methylchrysene	22%	25.	Coronene	14%
12.	Benzo[b]Fluoranthene	32%	26.	Dibenzo[a,i]pyrene	23%
13.	Benzo[k]Fluoranthene	18%	27.	Dibenzo[a,h]pyrene	47%
14.	Benzo[j]Fluoranthene	24%			

8.6 Uncertainty of UUNN Measurements

Monitoring is undertaken at 38 existing AURN monitoring stations to provide data for validating all UUNN monitored NO2 concentrations. At these 38 sites the UUNN diffusion tubes are co-located with reference method chemiluminescent analysers. Data from these 38 sites allow for the calculation of correction factors and uncertainties that can be applied to all sites in the UUNN.

Correction factors and the overall uncertainty have both been calculated in line with the Guide to Demonstration of Equivalence 2010 (GDE 2010) [37]. Annual averages of the 38 co-location sites have been used to plot an x/y scatter graph with the reference method on the x axis and the average of the three co-located diffusion tubes on the y axis. In line with the GDE, the line of best fit has been calculated using orthogonal regression, allowing the intercept to be non-zero.

In the following respects, the data from the co-location sites has been treated in an identical fashion to that of the non-co-located sites:

- All data have been corrected to use an uptake rate at the ambient temperature observed at each site during each month, but are then reported to 293 K in accordance with Annex VI Part C1 of the Air Quality Directive [10];
- Where the Coefficient of Variation (a measure of the repeatability of triplicate tubes, with the lower the percentage indicating the greater repeatability) was greater than 20% then this month has not been used in the calculations for that particular site; and
- Where there is only one diffusion tube result for any given month, then data for this month has not been used in the calculations for that particular site.

For all calculations of the expanded uncertainty, the limit value has been set at 40 μgm^{-3}. Further, the random term of the reference method has been set to zero as it can be assumed to be for an annual average. Annual averages have been calculated as time weighted averages of the monthly data (i.e. accounting for different sampling times).

9 References

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