Air Pollution in the UK: 2003

Part 3 - Appendices

1- The Major Air Pollutants measured in the UK

2- Regional Maps of UK Automatic Air Monitoring Sites

3- The UK's Automatic and Sampler-based Air Monitoring Networks

4- Calculation methods, statistical methods and measurement uncertainty

Appendix 1- The Major Air Pollutants measured in the UK

We describe major sources and effects of these pollutants, together with typical UK-wide patterns of exposure.

The principal air pollutants measured in UK National Air Monitoring networks are:

- Nitrogen oxides, and primarily nitrogen dioxide (NO_2)
- Sulphur Dioxide (SO_2)
- Carbon Monoxide (CO)
- Ozone (O_3)
- Particles- primarily measured as PM_{10} at the present time
- Benzene (C_6H_6)
- 1,3-butadiene (C_4H_6)

The first five of these are measured in the AURN, whilst the two volatile organic compounds- benzene and 1,3-butadiene- are measured in the Hydrocarbon network. The various pollutants have different sources and behave very differently once emitted into the atmosphere. As a result, spatial and temporal patterns can differ markedly between the pollutants.

In this appendix, we briefly examine the sources, effects and distributions of these major pollutants. For more detail, please refer to the authoritative series of pollutant-specific analyses and guidelines produced by EPAQS (the UK Expert Panel on Air Quality Standards)[18-25] and World Health Organisation[26].

Oxides of Nitrogen

Nitrogen oxides are formed during high temperature combustion processes from the oxidation of nitrogen in the air or fuel. The principal source of nitrogen oxides - nitric oxide (NO) and nitrogen dioxide (NO_2), collectively known as NO_x - is road traffic. For the UK as a whole, approximately 45% of all oxide of nitrogen emission originates from this source, with most of the remainder arising from power stations and other industrial sources. Since power station and industrial emissions are usually from elevated sources (i.e. high chimneys), motor vehicles represent by far the largest source of low-level NOx emission and therefore make the largest contribution (75% or greater) to long-term ground level concentrations in urban areas.

Nitric oxide is not generally considered to be harmful to health at the concentrations found in the ambient atmosphere. However, nitrogen dioxide has a variety of environmental and health impacts. Its direct health impact as a respiratory irritant may be significant. In the presence of sunlight, it can react with Volatile Organic Compounds (VOCs) to produce photochemical pollutants including ozone. Nitrogen dioxide can also be further oxidised in air to acid gases such as nitric acid, which contribute to the production of acid rain over regional scales.

The highest NOx levels in UK cities are generally observed at kerbside locations. However, since much of the NO_2 is formed from primary emissions of NO by time-dependent oxidation processes in the atmosphere, the relative decline in NO_2 concentration away from the kerbside is slower than for NO.

Modelling and monitoring studies- for example with diffusion tube samplers- have shown that NO_2 concentrations tend to be greatest in central urban areas. However, this cannot always be assumed to be the case, especially where major road systems, industrial areas or other large sources are located away from city centre areas.

Sulphur Dioxide

Sulphur dioxide (SO_2) is an acid gas which acts as an irritant to the respiratory system and may exacerbate or initiate symptoms in asthmatics. It also contributes to acid rain over a regional (for example European) scale.

This pollutant is formed by the oxidation of sulphur impurities in fuels during combustion processes. A very high proportion (approximately 85%) of UK SO_2 emissions originate from power stations and industrial sources. As the use of coal for domestic heating has decreased, its emissions and atmospheric concentrations in urban areas have decreased considerably over the last 20-30 years.

Geographically, SO_2 concentrations in the UK are highest in urban areas such as mining regions in the north of England and in Northern Ireland, where there is still significant use of coal for domestic heating. Modelling studies have indicated that the highest SO_2 concentrations in cities usually occur in the central areas.

Carbon Monoxide

Carbon monoxide is a toxic gas produced by incomplete combustion of fossil fuels. At worst-case ambient levels (in congested streets, car-parks or tunnels), exposure may reduce the oxygen-carrying capacity of the blood and impair oxygen delivery to the brain and other organs, particularly affecting adults with angina and diseases of the coronary arteries.

Carbon monoxide in urban areas results almost entirely from vehicle emissions. The emission rate for individual vehicles depends critically on vehicle speed, being higher at low speeds.

Since CO is a primary pollutant, its ambient concentrations closely follow emissions. In urban areas, concentrations are therefore highest at the kerbside and decrease rapidly with increasing distance from the road. Since traffic is by far the most important source of CO, its spatial distribution will follow that of traffic: this will generally result in the highest levels being observed in the city centre, where most congested areas tend to be found.

Ozone

Ozone is a highly reactive oxidising agent, with a wide range of material, vegetation and human health impacts. Acute health effects of ozone may include eye/nose irritation, respiratory problems and airway inflammation.

A natural background ozone concentration exists in the atmosphere due to mixing of ozone from the stratosphere and its generation in the troposphere. The background concentration depends on latitude and time of year: in the UK, measurements show the resulting annual average background concentration to be about 70 $\mu g/m^3$.

Ozone is not emitted directly into the atmosphere in any significant quantity and its presence in the lower atmosphere at concentrations exceeding background results primarily from a complex series of reactions involving NO_x and hydrocarbon precursors in the presence of sunlight and high temperatures. The reactions producing ozone occur in air containing these precursors as it moves downwind; ozone formation can occur over a timescale of a few hours to several days. As a result, ozone concentrations are decoupled temporally and spatially from precursor sources and ambient concentrations are strongly dependent on meteorological conditions, together with scavenging and deposition rates.

In urban areas, chemical scavenging by NO_x emissions results in ozone concentrations that are generally lower than in rural areas. Moreover, urban ozone concentrations tend to be highly variable over small spatial scales, with concentrations lowest where corresponding levels of other pollutants such as NO are highest. In cities, therefore, ozone concentrations will tend to be lower in central areas and increase in the suburbs, although the spatial variation will be complex and, in open spaces in urban areas, levels of ozone may approach those found in nearby rural areas.

Particulate Matter

Particulate Matter is a generic descriptor covering a wide range of particle size fractions, morphologies and chemical compositions. Although coarse (large) particle size ranges may cause significant local nuisance or soiling impacts, it is the finer (small) fractions that are capable of deep lung/airway penetration. This is why these fractions are measured in UK national monitoring networks.

Particles are produced from a variety of natural and man-made sources. Natural sources include sea salt, soil blowoff, Saharan dust, forest fires and volcanic activity. Man-made sources include incomplete combustion processes (e.g. coal and diesel smoke), industry and construction activity. Particles may be either directly emitted into the atmosphere (primary particles) or formed there by chemical reactions (secondary particles). Both particle size, usually expressed in terms of its aerodynamic diameter, and chemical composition are greatly influenced by its origin.

The principal source of PM_{10} (the mass fraction of particles collected by a sampler with a 50% inlet cut-off at aerodynamic diameter 10µm) in many cities is road traffic emissions, particularly from diesel vehicles. As well as creating dirt, odour and visibility problems, PM_{10} particles are associated with health effects including increased risk of heart and lung disease. In addition, they may carry surface- absorbed carcinogenic compounds into the lungs. Concern about the potential health impacts of fine particulate matter has increased over recent years.

Existing PM_{10} data show that daily average concentrations are usually highest in the winter months and lowest in the summer. During winter episode periods, PM_{10} levels increase together with other traffic-related pollutants such as oxides of nitrogen. During the spring and summer, the photochemical oxidation of sulphur dioxide and oxides of nitrogen to particulate sulphate and nitrate is another important source.

Benzene

Benzene is a fat-soluble volatile toxic organic compound with a range of potential effects. Acute exposure to benzene at occupational levels can cause narcotic, anaesthetic or fatal consequences. Benzene is a proven genotoxic carcinogen, and ambient long-term exposure is implicated in the formation of a range of types of leukaemia in the general population.

Benzene has no significant natural sources, so that ambient exposure results primarily from petrol combustion in road transport emissions or evaporation of petrol (which contains benzene) from filling stations. Benzene is naturally broken down by chemical reactions in the atmosphere, although these reactions can take several days. As a result, outdoor benzene concentrations tend to closely follow road networks and traffic density patterns.

1,3-Butadiene

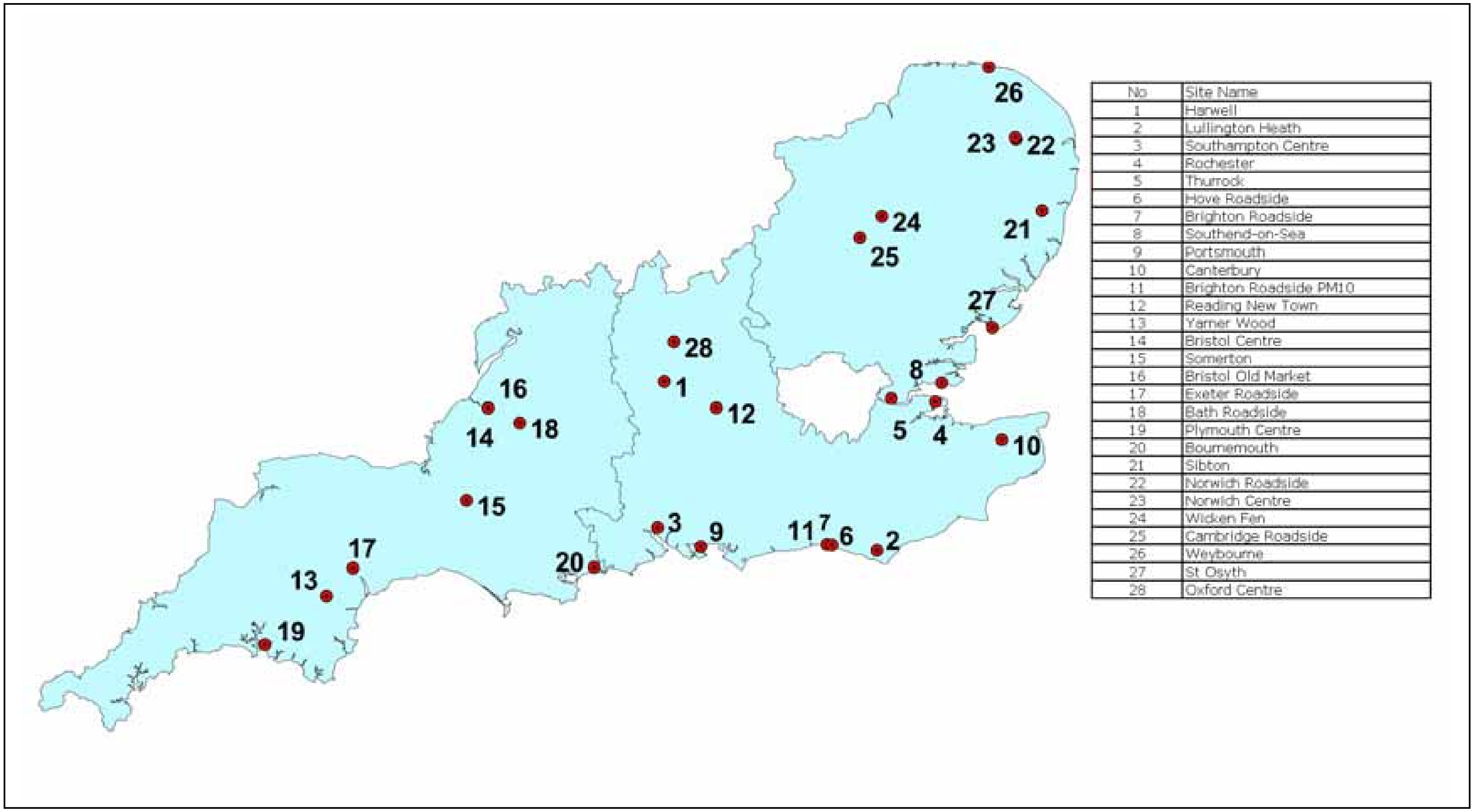
Evidence from occupational human exposure and laboratory studies on animals shows 1,3-butadiene to be a potent carcinogen, exposure to which can cause a range of cancers of the lymphoid system, blood-forming tissues, lymphomas and leukaemias.

This substance is used in some industrial sectors, primarily in the production of synthetic rubber. However, ambient exposure of the general population results primarily from fuel combustion- mainly from petrol-fuelled motor vehicles, but also from other fossil fuels, accidental fires and industrial releases.

Unlike benzene, this is not a constituent of petrol, so evaporative or fugitive emissions are not a significant source. Although 1,3-butadiene is removed by catalytic converters and not produced from diesel engines, spatial and temporal exposure patterns in the UK are dominated by road transport.

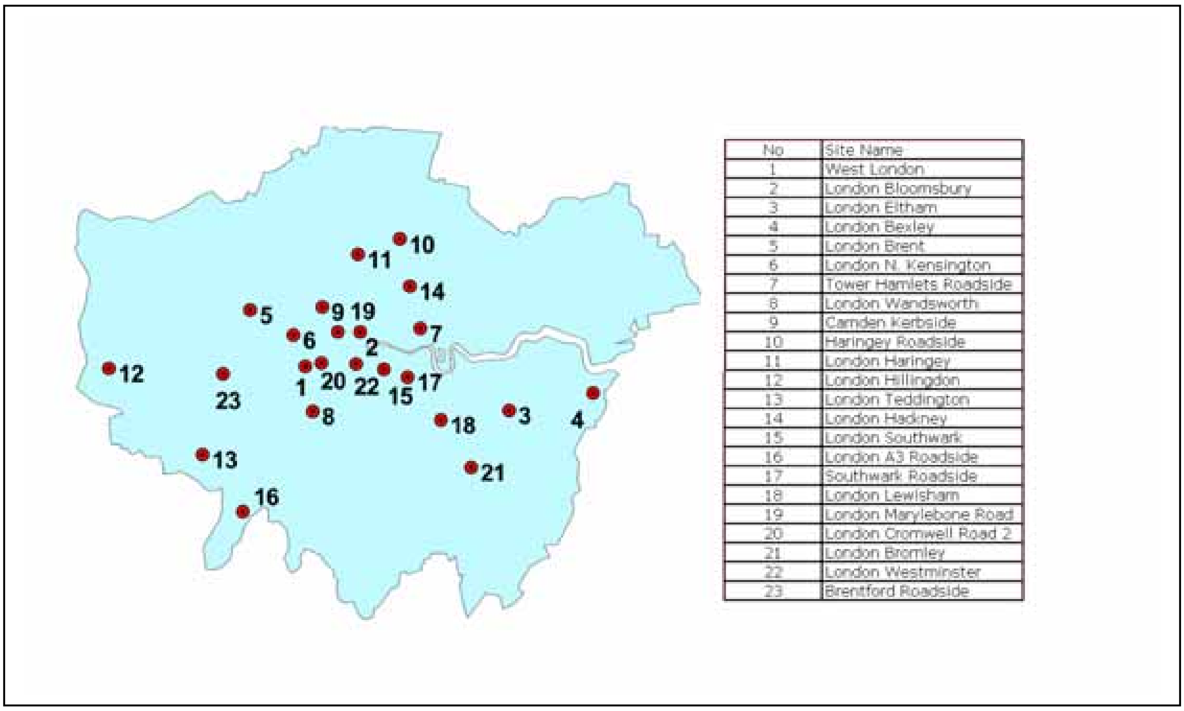
Appendix 2- Regional Maps of UK Automatic Air Monitoring Stations

These maps show Automatic Urban and Rural Network (AURN) and Hydrocarbon air monitoring sites in different parts of the UK.



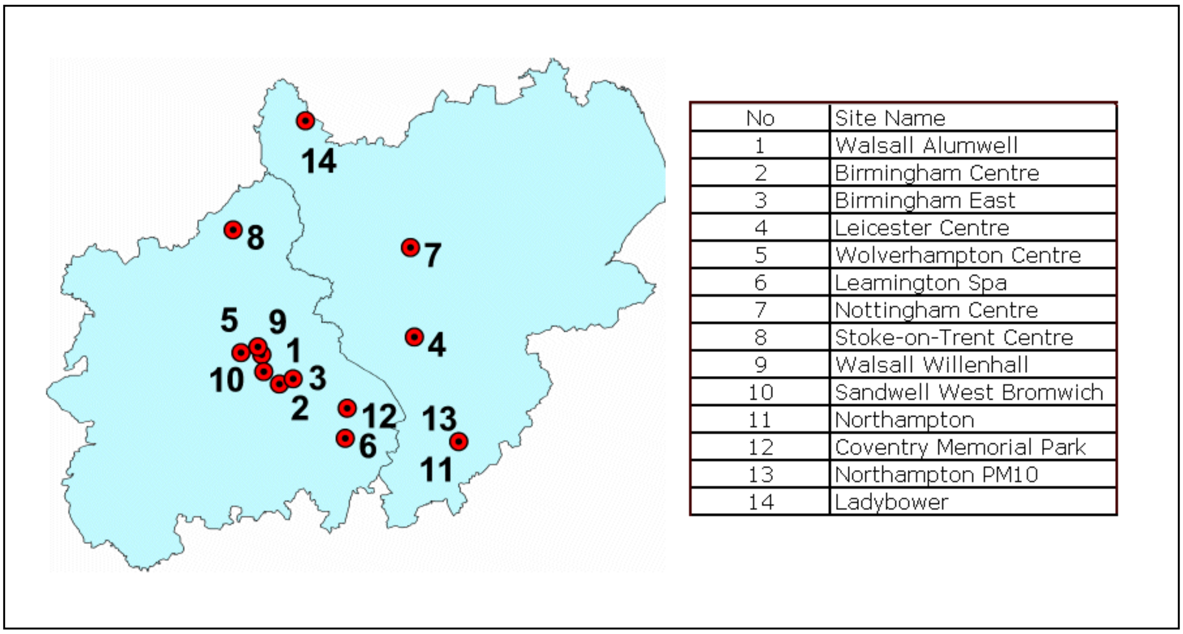
No	Site Name
1	Harwell
2	Lullington Heath
3	Southampton Centre
4	Rochester
5	Thurrock
6	Hove Roadside
7	Brighton Roadside
8	Southend-on-Sea
9	Portsmouth
10	Canterbury
11	Brighton Roadside PM10
12	Reading New Town
13	Yarner Wood
14	Bristol Centre
15	Somerton
16	Bristol Old Market
17	Exeter Roadside
18	Bath Roadside
19	Plymouth Centre
20	Bournemouth
21	Sibton
22	Norwich Roadside
23	Norwich Centre
24	Wicken Fen
25	Cambridge Roadside
26	Weybourne
27	St Osyth
28	Oxford Centre

Figure 2.1 Automatic Sites, Southern England



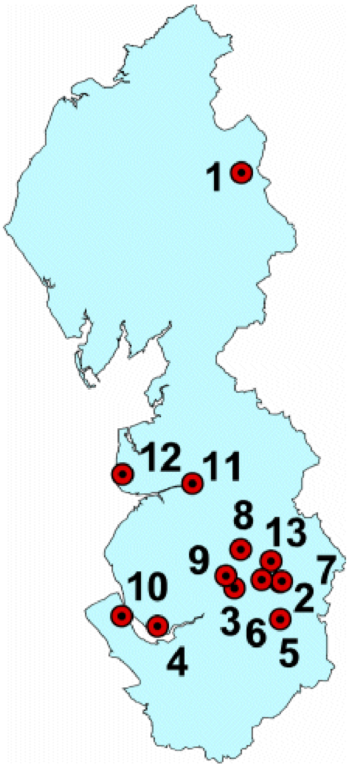
No	Site Name
1	West London
2	London Bloomsbury
3	London Eltham
4	London Bexley
5	London Brent
6	London N. Kensington
7	Tower Hamlets Roadside
8	London Wandsworth
9	Camden Kerbside
10	Haringey Roadside
11	London Haringey
12	London Hillingdon
13	London Teddington
14	London Hackney
15	London Southwark
16	London A3 Roadside
17	Southwark Roadside
18	London Lewisham
19	London Marylebone Road
20	London Cromwell Road 2
21	London Bromley
22	London Westminster
23	Brentford Roadside

Figure 2.2 Automatic Sites, London



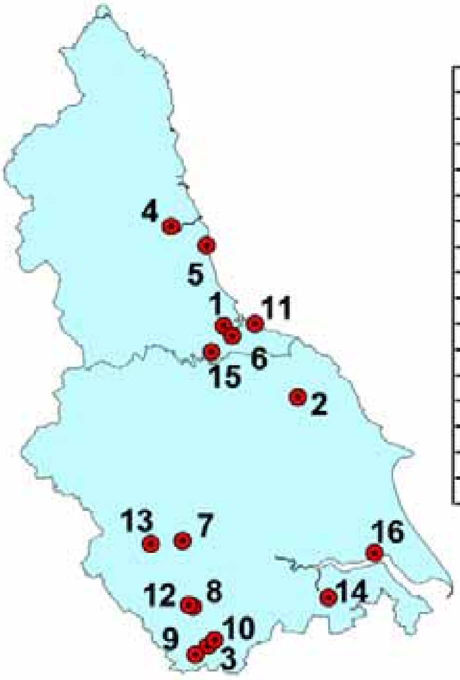
No	Site Name
1	Walsall Alumwell
2	Birmingham Centre
3	Birmingham East
4	Leicester Centre
5	Wolverhampton Centre
6	Leamington Spa
7	Nottingham Centre
8	Stoke-on-Trent Centre
9	Walsall Willenhall
10	Sandwell West Bromwich
11	Northampton
12	Coventry Memorial Park
13	Northampton PM10
14	Ladybower

Figure 2.3 Automatic Sites, Midlands



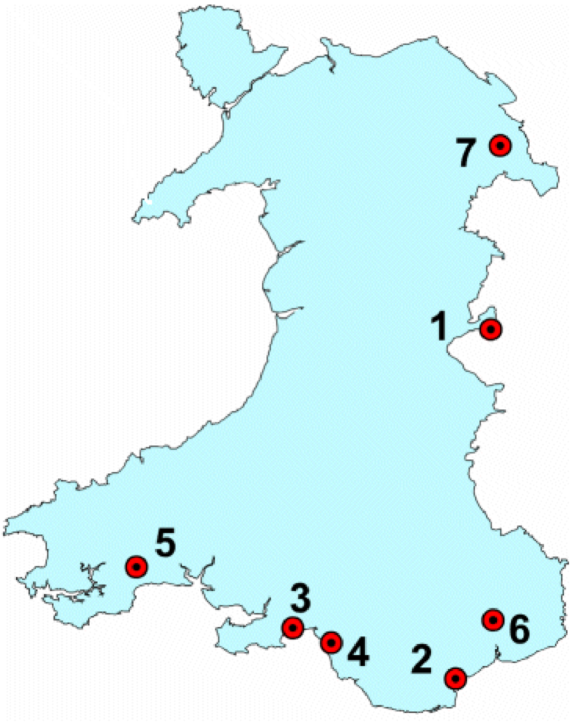
No	Site Name
1	Great Dun Fell
2	Manchester Town Hall
3	Glazebury
4	Liverpool Speke
5	Manchester Piccadilly
6	Manchester South
7	Bury Roadside
8	Bolton
9	Salford Eccles
10	Wirral Tranmere
11	Preston
12	Blackpool
13	Wigan Leigh

Figure 2.4 Automatic Sites, NW England



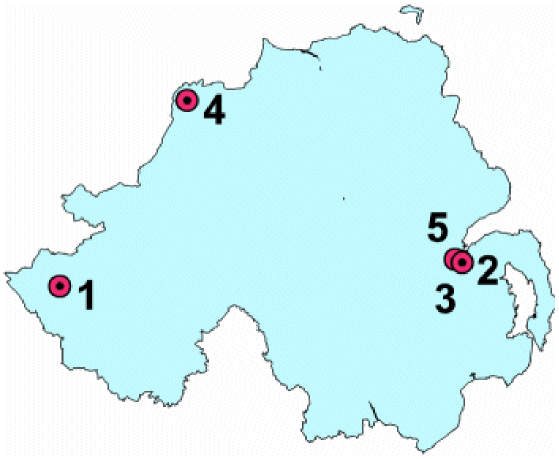
No	Site Name
1	Billingham
2	High Muffles
3	Sheffield Tinsley
4	Newcastle Centre
5	Sunderland
6	Middlesbrough
7	Leeds Centre
8	Barnsley 12
9	Sheffield Centre
10	Rotherham Centre
11	Redcar
12	Barnsley Gawber
13	Bradford Centre
14	Scunthorpe
15	Stockton-on-Tees Yarm
16	Hull Freetown

Figure 2.5 Automatic Sites, NE England



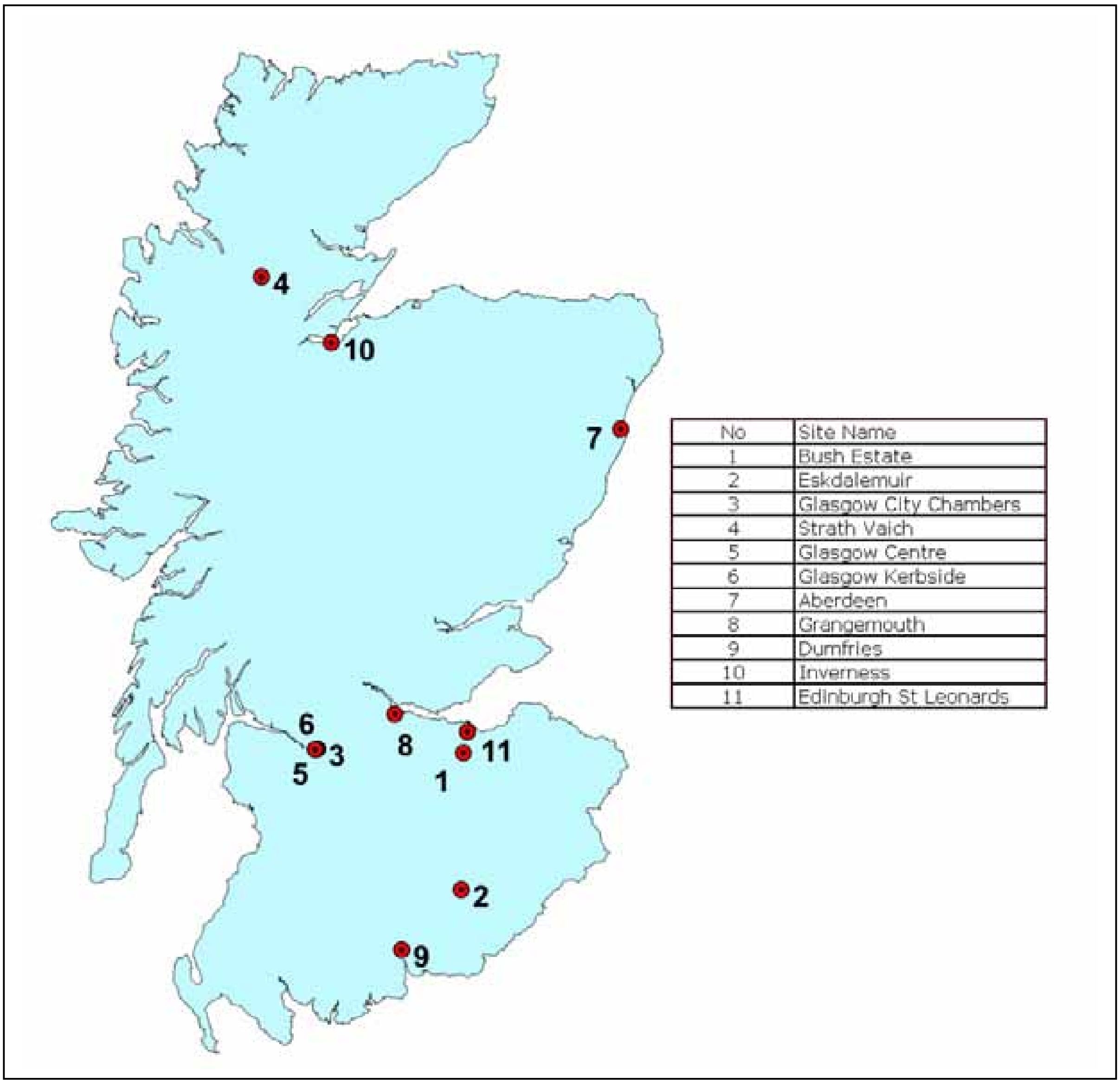
No	Site Name
1	Aston Hill
2	Cardiff Centre
3	Swansea
4	Port Talbot
5	Narberth
6	Cwmbran
7	Wrexham

Figure 2.6 Automatic Sites, Wales



No	Site Name
1	Lough Navar
2	Belfast East
3	Belfast Centre
4	Derry
5	Belfast Clara St

Figure 2.7 Automatic Sites, Northern Ireland



No	Site Name
1	Bush Estate
2	Eskdalemuir
3	Glasgow City Chambers
4	Strath Vaich
5	Glasgow Centre
6	Glasgow Kerbside
7	Aberdeen
8	Grangemouth
9	Dumfries
10	Inverness
11	Edinburgh St Leonards

Figure 2.8 Automatic Sites, Scotland

Appendix 3- The UK's Automatic and Sampler-based Air Monitoring Networks

Here we provide a concise guide to the different UK air monitoring networks, their objectives and methodologies.

A 3.1	**The Smoke and Sulphur Dioxide Sampler Network**
A 3.2	**The Nitrogen Dioxide Diffusion Tube Network**
A 3.3	**The Automatic Urban and Rural Network**
A 3.4	**The Acid Deposition and Rural SO_2 networks**
A 3.5	**The Automatic Hydrocarbon Network**
A 3.6	**The PAH and TMPS Networks**
A 3.7	**The Multi-element and Industrial Metals Network**
A 3.8	**The Non-automatic Hydrocarbon Network**

A 3.1 The Smoke and SO_2 Network

(Network managed and quality assured for Defra by Netcen)

The Smoke and SO_2 Network was set up in 1961, to monitor progress in compliance with the Clean Air Acts, and formed the backbone of the UK's Air Quality monitoring for many years, prior to the widespread implementation of automatic monitoring techniques in the 1990s.

The objectives of the network are as follows:

- To monitor compliance with EC Directives relating to these pollutants
- To provide a representative assessment and analysis covering major population centres throughout the UK, with a wide spatial coverage
- To provide a long-term database, for the purposes for assessing trends and spatial distribution

The network uses well-established and reliable sampler methods to measure daily average concentrations of suspended particulate matter and sulphur dioxide. Suspended particulate matter is measured using the standard black smoke method. Sampled air is drawn through a filter paper, forming a smoke stain. The darkness of the smoke stain is measured using a reflectometer, and the ambient concentration determined from a standard calibration.

Sulphur dioxide is measured indicatively using the net acidity method. The sampled air is bubbled through dilute, acidified hydrogen peroxide solution, for absorption of sulphur dioxide. The ambient concentration is determined by titration of the solution back to its original pH of 4.5.

At the present time (March 2004), there are 118 sites located in urban areas of the UK.

There is a particularly long historical dataset from this network, with some sites operating since the early 1960s. It has provided an invaluable record of pollutant concentrations throughout the UK over four decades. Smoke data, in particular, are still widely used in health effect studies and other scientific work. As a record of the progress of the Clean Air Acts, the Network provides a clear example of how policy can successfully improve air quality nationwide.

A 3.2 The Nitrogen Dioxide Diffusion Tube Network

(Network managed and quality assured for Defra and the DAs by Netcen)

This large-scale sampler network was established in 1993. Its objective is to assess the spatial and temporal distribution of NO_2 concentrations in a variety of urban areas of the UK, ranging from the major cities to smaller towns.

Monthly average measurements are made using simple but cost-effective NO_2 diffusion tubes; these low-cost passive samplers ideal for indicative monitoring.

Diffusion tubes exposed by Local Authorities are analysed by analytical laboratories and the results forwarded to Netcen for central collation and processing. Netcen provides a centrally-managed system for the monitoring of NO_2 on a national scale.

There are currently 1247 sites in the Network, operated by 297 Local Authorities. All are in urban areas. Monthly measurements are routinely performed at four locations within each local authority:

- **Roadside**, 1-5m from the kerb of a busy road (2 sampling locations).

- **Urban Background** (2 sampling locations), >50m from any busy road and typically in a residential area.

The NO_2 Network forms a useful supplement to the AURN, offering excellent spatial coverage of this important traffic-related pollutant throughout the UK. In addition, this technique is useful for 'hot spot' identification; areas of high NO_2 concentration identified by this network may be prioritised for further monitoring, with more sophisticated automatic techniques.

A 3.3 The Automatic Urban and Rural Network

(Network managed by Casella Stanger and quality assured by Netcen)

The AURN is the largest UK automatic monitoring programme. It consists of automatic air quality monitoring stations measuring oxides of nitrogen (NOx), sulphur dioxide (SO_2), ozone (O_3), carbon monoxide (CO) and particles (PM_{10}). These are monitored on an hourly basis at measurement sites throughout the UK.

As of March 2004, the AURN consists of 120 monitoring sites. Of these, 58 are directly funded by Defra and the devolved administrations, and a further 61 affiliated sites are owned and operated by local authorities; 14 of these sites are also in the London Air Quality Network (LAQN). The network has grown dramatically since it was first established in 1992 (see Figure 1)

The major objectives of the network are as follows:

- Checking if statutory air quality standards and targets are met (e.g. EU Directives)
- Informing the public about air quality
- Providing information for local air quality review and assessments within the UK Air Quality Strategy
- Identifying long-term trends in air pollution concentrations
- Assessing the effectiveness of policies to control pollution

A number of organisations are involved in the day-to-day running of the network. Currently, the role of Central Management and Co-ordination Unit (CMCU) for the AURN is contracted to Casella Stanger, whilst the Environmental Research Group (ERG) of King's College London has been appointed as Management Unit for the London Air Quality Network (LAQN). AEA Technology's Netcen undertakes the role of Quality Assurance and Control Unit (QA/QC Unit) for the AURN. The responsibility for operating individual monitoring sites is assigned to local organisations, such as local authority Environmental Health Officers with relevant experience in the field. Calibration gases for the network are supplied by Messer UK Ltd and are provided with a UKAS certificate of calibration by AEA Technology, Netcen.

The techniques used for monitoring within the AURN are summarised overleaf. These techniques represent the current state-of-the-art for automated monitoring networks and, with the exception of the automatic PM_{10} analysers, are the reference methods of measurement defined in the relevant EU Directives.

Additional monitors for NO_2, SO_2 and PM_{10} particulate matter were added to the AURN in 2001 and further monitors for CO were introduced in 2002. Additional monitors for O_3 and rural NOx have recently been installed to comply with the third Daughter Directive on Ozone.

As $PM_{2.5}$ measurements are also required under the first Daughter Directive, 4 automatic analysers for $PM_{2.5}$ monitoring were incorporated into the AURN during 2003. In 2004, further expansion of the network is planned with the addition of five new sites, primarily monitoring O_3 and NO_X.

AURN Measurement Techniques

O_3	UV absorption
NO/NOx	Chemiluminescence
SO_2	UV fluorescence
CO	IR Absorption
PM_{10}	Tapered Element Oscillating Microbalance Beta Attenuation monitor Gravimetric monitor

There have been considerable changes in European air quality legislation in the last few years and the AURN has successfully expanded and evolved to conform to these new requirements.

A 3.4 The Acid Deposition and Rural SO_2 Monitoring Networks

(Managed and operated by a consortium of CEH and Netcen)

These are closely related and share common sites; the two programmes are therefore discussed together here.

The Acid Deposition Monitoring Network

The Acid Deposition Monitoring network (ADMN) was established in 1986 to monitor the composition of precipitation and hence to provide information on deposition of acidifying compounds in the United Kingdom. Its main emphasis has always been the assessment of potential impacts on UK ecosystems. Other measurements are also made within the programme - sulphur dioxide, nitrogen dioxide, particulate sulphate - to provide a more complete understanding of precipitation chemistry in the United Kingdom.

This network has evolved substantially over time. It was originally based on two sub-programmes- a ‘primary’ network providing high quality and high frequency data, which could be used to identify trends over time- and a ‘secondary’ network providing information on the spatial distribution of acid deposition in the UK. Originally, there were 9 primary and 59 secondary sampling sites. Subsequent changes made to the programme, including the incorporation of new measurement techniques for trace rural gases and altered sampling frequencies, have made this distinction less clearcut.

In 1999, 7 new sites were established to monitor rainwater composition in ecologically-sensitive areas and a new denuder-based sampler network of 12 sites was established to monitor nitric acid, other acid gases and aerosol components.

In 2003/4, the network covers the following measurements and sites:

The Acid Deposition Monitoring Network- site numbers and measured parameters

Precipitation Composition	– Rainwater sampling using a bulk collector on a ***fortnightly*** basis at 38 sites – Rainwater sampling using a bulk collector on a ***daily*** basis at one site
Sulphur Dioxide	– Sampled on a ***monthly*** basis at 8 sites
Particulate Sulphate	– Sampled on a ***daily*** basis at 5 sites
Nitrogen Dioxide	– Diffusion tube measurements on a ***monthly*** basis at 32 sites
Nitric Acid and Other Acid Gases	– Denuder measurements on a ***monthly*** basis at 12 sites

The Rural Sulphur Dioxide (SO_2) Network

The Rural Sulphur Dioxide (SO_2) network was established in 1991 to provide additional information on the spatial distribution of SO_2 at rural sites across the UK. The network originally comprised 31 sites at which concentrations of SO_2 were measured on a weekly basis using a hydrogen peroxide bubbler instrument and one site (Bush) at which daily measurements were made. Measurements were also made at a further 8 sites, which form part of the programme of measurements of the Acid Deposition Monitoring Network (see above).

The SO_2 concentrations which were measured in the late 1990s at some of the sites, especially the daily sites in remote areas, were at or below the Limit of Detection (LoD) of the hydrogen peroxide bubbler method. A new sampling method was required with a lower Limits of Detection while retaining data integrity and consistency. Following an intercomparison exercise at the Auchencorth Moss site near Edinburgh between September 1998 and May 1999, the choice of samplers to replace the bubbler method was limited to the denuder or the filter pack methods on the grounds of cost, improved sensitivity, method robustness, ease of operation and the quality of the measurements.

For practical reasons, it was decided to replace the bubbler method with the filter pack method and to make fortnightly measurements. The filter pack method was introduced into the network during 2001. At the end of 2003, the sampling period was changed from fortnightly to monthly at all SO_2 monitoring sites in the Rural SO_2 and Acid Deposition Monitoring Networks.

A 3.5 The Automatic Hydrocarbon monitoring network

(Network managed and quality assured for Defra and the DAs by Netcen)

Automatic hourly measurements of speciated hydrocarbons, made using an advanced automatic gas chromatograph (VOCAIR), started in the UK in 1991. By 1995, monitoring had expanded considerably with the formation of a 13-site dedicated network measuring 26 species continuously at urban, industrial and rural locations. The focus in this measurement programme was two-fold: firstly to assess ambient concentrations of a range of Volatile Organic Compounds (VOCs) with significant photochemical oxidant formation potential, and secondly to measure two known genotoxic carcinogens (benzene and 1,3-butadiene) for comparison against emerging UK Air Quality Objectives. Data on these ‘air toxics’ was also regularly reported to the public.

The automatic hydrocarbon monitoring network, as originally constituted, used state-of-the-art measurement techniques, combined with advanced software techniques for signal processing and validation. It was the first network of its kind in the world. The Automatic Hydrocarbon Network operated successfully for 10 years before the programme was re-focussed, re-designed and simplified in 2002.

The UK Automatic Hydrocarbon Network currently consists of five sites, located at Cardiff, Glasgow, Harwell, London Eltham and London Marylebone Road. Three of these sites – Cardiff, Glasgow and Harwell- utilise an Environnment VOC71M analyser configured to measure and report the concentrations of 1,3-butadiene, benzene, toluene, ethylbenzene, (m+p)-xylene and o-xylene. Benzene data are used for comparison with the UK Air Quality Objectives and are also reported to the European Commission to fulfil requirements of the Benzene Daughter Directive; 1,3-butadiene data are used for comparison with UK Objectives.

The two London sites are fitted with automatic Perkin Elmer gas chromatographs measuring a wider range of VOCs, equivalent to that studied under the original measurement programme. Both instruments are capable of measuring and reporting at least 27 hydrocarbons. Measurements from the Eltham site will be reported to the European Commission, satisfying new requirements under the Ozone Daughter Directive for monitoring photochemical ozone precursors. Corresponding benzene and the 1,3-butadiene data are used for comparison with the UK Air Quality Objectives, whilst benzene data are reported to the European Commission.

Hourly benzene and 1,3-butadiene data from all sites continue to be reported to the public at large through a range of web, electronic, text and broadcast media.

A 3.6 The PAH and TOMPs Networks

(Networks managed and operated for Defra and the DAs by Netcen)

These two programmes are highly integrated, being based on a 24-site sampler network covering a broad range of representative urban, industrial, semi-rural and rural location types; 18 of these are operated wholly within the PAHs programme, whilst a further 6 sites are operated as part of the PAH and TOMPS monitoring networks.

i) PAHs

Polycyclic aromatic hydrocarbons (PAHs) are a large group of persistent bioaccumulative organic compounds with toxic or human carcinogenic effects; they are produced through industrial, chemical and combustion processes.

There are three major policy drivers and data uses for this programme:

- The establishment of a UK Air Quality Objective for PAHs, based in turn on the recommendations of the Expert Panel on Air Quality Standards (EPAQS) for an annual air quality standard of 0.25 ng benzo[a]pyrene /m^3.
- The current development of a fourth European Community Air Quality Daughter Directive, which will cover a range of toxic trace and metallic species including PAHs; it is likely that a target annual average of 1 ng bnzo[a]pyrene /m3 will be established under this emerging Directive.
- The UK's decision to sign, and ratify when possible, the UNECE protocol on Persistent Organic Pollutants (POPs), which includes PAHs. Under the protocol, there is a requirement for signatories to control and assess the long-range transport of specified PAHs.

All these policy imperatives require sound data on ambient concentrations, trends and distributions of PAHs in the environment.

Modified Anderson GP1-S pesticide samplers, capturing both gas and particle-phase PAHs on glass fibre and polyurethane filters, are deployed at all 24 UK network locations. Careful extraction from the filter and foam media and subsequent analysis by Gas Chromatography/Mass Spectroscopy (GC/MS) provides data on 16 PAH species.

ii) TOMPs

Toxic Organic Micropollutants (TOMPs)- conventionally including Polychlorinated Dibenzo-P-Dioxins and Polychlorinated Dibenzofurans (PCDD/Fs) are formed as unwanted by-products during various chemical, industrial and combustion processes. These highly toxic and persistent species are ubiquitous in the environment, but normally at extremely low concentrations.

The TOMPs network provides data to inform the public of air quality and information to support the development of policy to protect the environment. The specific aims of the TOMPs programme are:

- To identify sources of TOMPs in the UK's atmosphere
- To quantify sources that are regarded as potentially significant
- To measure concentrations of TOMPs in ambient air and deposited material in UK cities, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere.

The TOMPS network measures concentrations of these trace organic species at six PAH network sites. The sampling method is again based around the use of a modified Andersen GPS-1 sampler, with subsequent chemical analysis requiring the use of a range of sophisticated techniques including gas chromatography coupled with high-resolution mass spectrometry or electron capture detectors.

A 3.7 The Multi-element and Industrial Metals Network

(Network managed and operated for Defra and the DAs by Casella Stanger)

The UK Government has in the past funded separate long-term monitoring programmes responding to specific needs of EC Directives in relation to toxic and industrial metals. These originally included:

- Five urban multi-element monitoring sites providing measurements of 9 important trace elements (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn and V)
- Eight sites for the monitoring of lead-in-petrol (2 rural, 3 urban and 3 kerbside) and
- Eight sites operating in three industrial areas monitoring lead- Walsall (IMI and Brookside works) and Newcastle (Elswick works).

The EU Framework Directive (96/62/EC)[3] establishes a framework under which, by means of Daughter Directives, the EU can establish limit and target values for concentrations in ambient air of certain pollutants. The First Daughter Directive (99/30/EC)[28] sets a Limit Value for lead in air concentrations at 0.5 µg/m^3, expressed as an annual mean to be achieved by 1st January 2005.

The agreement reached between the European Parliament and the Environment Council on the Directive on the Quality of Petrol and Diesel Fuels led to the ban of sales of leaded petrol in the UK with effect from 1 January 2000. This has, in turn, led to a dramatic decline in ambient lead levels in many UK environments; in consequence, the number of monitoring sites has reduced to two – Manchester and Cardiff – where continued monitoring still takes place.

The proposed Fourth Daughter Directive, which is currently still under discussion, aims to set Target Values for Arsenic, Cadmium and Nickel. In 2000, a year-long monitoring network was established at 30 industrial site locations across the UK in order to establish the UK's position with respect to the requirements of this Daughter Directive. Results of this programme showed that further monitoring at a number of sites was required in order to establish compliance with proposed Target Values. Monitoring continues currently at five sites – Avonmouth, Hallen Village, Swansea, Sheffield and Runcorn.

Rural trace elements have also been monitored at 4 sites (Chilton (Oxon), Styrrup (Notts), Windemere (Cumbria) and Trebanos (Wales)) since 1972 as part of the Rural Trace Element Network. Monitoring at these sites continues to date.

The disparate nature of the historic monitoring networks for heavy metals in the UK, which have individually responded to specific Directive needs, resulted in differences in practice between networks and did not permit UK-wide reporting in a consistent manner. In 2003, all monitoring was rationalised into a single integrated network (with the exception of the Rural Trace Element sites). Sampling is now undertaken for weekly periods at sites on the PM_{10} fraction of particulates using R&P Partisol 2000 samplers.

Analysis of samples occurs with UKAS-accredited ICP-MS analysis, with acid digest techniques consistent with that proposed in the CEN WG14 proposed reference method. Consistency in approach has been achieved with historical data collection and analyses through thorough equivalence exercises.

A 3.8 The Non-Automatic Hydrocarbon Network

(Managed and operated by the National Physical Laboratory)

The UK Non-Automatic Hydrocarbon Network measures ambient benzene concentrations at 35 sites around the United Kingdom, as well as 1,3-butadiene at 10 of these locations. Butadiene is measured at sites expected to have high concentrations of this carcinogenic pollutant, in order to assess compliance with the UK Air Quality Strategy Objective (2.25 µg/m^3 expressed as a running annual mean).

Benzene is also monitored to assess compliance with UK Objectives (between 3.25 and 16.25 µg/m^3 depending on area and compliance date, expressed as a running annual mean), as well as with the corresponding EC Air Quality Directive Limit Value (5 µg/m^3 annual average). Note that both species have Objectives and Limit Values expressed in the form of an annual average concentration, so that high time resolution is not required from the measurements.

Sampling is therefore undertaken for periods of a fortnight onto sorbent tubes containing Carbopack X. For benzene, the air is pumped through the sampling tubes using purpose-built pump units that switch between two tubes to produce two nominally identical samples covering each fortnight. For 1,3-butadiene, pairs of sorbent tubes sample the air passively (by diffusive processes) over the fortnight of sample exposure.

Every fortnight the tubes are changed, and the instruments checked by Local Site Operators, who send the exposed tubes to the network management unit for analysis.

Currently, all samplers are located at monitoring stations operated within the Automatic Urban and Rural Network (AURN)- discussed separately in Section A 3.3. Measurements began over the period December 2001 to August 2002, following the decommissioning of the first generation Automatic Hydrocarbon Network, which provided on-line measurements of hourly data for 26 hydrocarbon species at 13 sites (see A 3.5). The data obtained now provide a useful addition to automatic measurements undertaken in the current 5-site programme.

The fortnightly pumped measurement method for benzene was developed specifically for this network, following the requirement of the EU Directive that, in view of their inherently lower measurement uncertainty, measurements for reporting purposes be made by pumped sampling rather than by diffusive sampling. Previously, pumped sampling for benzene had been geared to short periods of a day or less. The combination of a suitable sorbent material and sound engineering in the pump control box has led to a very successful method.

The EU instructs CEN, the European Committee for Standardisation, to set out standard methods to be used to comply with Directives. The CEN benzene standards are nearing completion, and will include the pumped method used in this network.

Appendix 4- Calculation methods, statistical methods and measurement uncertainty

Here we provide boring but essential information on measurement accuracy, trend calculation and the mathematical methods used to calculate measurement statistics. Why do you think we put this section last…?

A 4.1 Statement on Accuracy of Air Quality Measurements

The EU Air Quality Directives now specify a required level of data accuracy (uncertainty). The accuracy requirements for the various parameters are summarised in Table 1 below. Please note that there is also a requirement for 90% data capture in each year.

A common approach to determining measurement uncertainty for all pollutants is provided by a CEN (The European Centre for Standardisation) report entitled: ‘Air quality – approach to uncertainty estimation for ambient air reference methods’. CEN has produced a series of draft standards setting out how National Networks in Member States should operate analysers in order to meet the required uncertainty of ±15% for NO_2, SO_2, CO and O_3 (at the 95% confidence level).

The report includes a set of performance characteristics against which analysers need to be assessed for official approval, as well as activities required for ongoing Quality Assurance and Control (QA/QC). Although the current situation is not entirely clear (for example, no analysers commonly used in the UK have been put through a complete set of performance tests), it is likely that the great majority of UK National Network measurements will meet the uncertainty requirement.

The situation with particulate measurements is more complicated. This is because of the wide scale use of analysers that do not conform to the EU Reference Method for PM_{10} monitoring. Much work is being undertaken- both within Member States and at the EU level- to assess the performance of the different analysers and techniques used for measurement of PM_{10}.

Table 1 – Measurement uncertainty objectives given in EU Air Quality Directives

Pollutant	**Uncertainty for Continuous Measurement (listed as accuracy in the Directive)**
NO_2, NO_X	15%
SO_2	15%
Particulate Matter	25%
CO	15%
O_3	15%

Note: The percentages given in the table are for individual measurements averaged over the period considered by the limit or target value, at concentrations close to the limit or target value, for a 95% confidence interval.

A 4.2 Calculation Methods

A 4.2.1 Introduction

The intention of this section is to provide all the information required to reproduce the statistics contained in this report from the original hourly dataset. This dataset is now widely available from the UK National Air Quality Archive on the World Wide Web- www.airquality.co.uk.

The definition of standard statistical functions, such as means, percentiles, regressions and standard errors can be obtained from a number of statistical references. A description of log-normal distributions and related statistics has also been provided elsewhere[28].

Various air quality guidelines and statistics are defined in the documentation published by the UK Government[2,10,11], the European Community[3,,29-31], the World Health Organisation[26,32-34] and The Expert Panel on Air Quality Standards (EPAQS) [18-25]. This section describes how these statistics are calculated from the original dataset. All exceedence statistics in this report are calculated using methods that are compliant with the requirements of each air quality standard.

Where the exact method of calculation of a statistic has not been precisely defined by the above bodies, a method has generally been chosen that leads to a more stringent air quality guideline.

These calculation methods have been developed over time and are not necessarily those that were used in previous reports of this series.

A 4.2.2 Definitions

Basic Reporting Unit

The basic reporting unit for the National automatic monitoring networks is the hourly average (the terms "mean" and "average" are taken to be equivalent in this report). All statistics of greater than one hour duration are based on hourly averages. For example, the annual mean is the arithmetic mean of the hourly means during the year. Hourly means that are invalid, for any reason, are ignored.

Hourly averages are derived from:

- At least three 15-minute averages per hour in the AURN
- 30-minutes of sampling in the Hydrocarbon Network

Although 15-minute averages are used in the UK National Air Quality standard for SO_2 and the WHO CO guidelines, 15-minute averages are not the basic reporting unit. Annual means, for example, based on 15-minute average may not be equal to those based on hourly averages since there may be, on occasion, insufficient 15-minute data to make a valid hourly mean. 15-minute data are only used to calculate hourly means and any statistic specifically related to 15-minute means.

Mass Units

The units that used to measure the concentrations are not always the same as those used to calculate and report statistics. For example, ozone is measured by the instrumentation in parts per billion (ppb) and the statistics are reported here in terms of the µg m^{-3} mass units. Particulate matter PM_{10}, on the other hand, is measured and reported in terms of µg m^{-3}.

To calculate statistics, therefore, the measured data are first converted into the reporting units, then the statistics are calculated. Comparison with any limit values are only performed in terms of mass units. This method will give slightly different results, due to rounding errors, to calculations using data in ppb and comparing with limit values converted into ppb.

Dates and Times

All data are recorded as Greenwich Mean Time (GMT). Please note that diurnal variations are calculated in local time.

Daily means are defined as midnight to midnight; 24-hour running means are means over any 24-hour period).

Data Precision

All concentrations are recorded and reported to a number of decimal places that is greater than or equal to the measurement precision of individual hourly means. For example:

- Ozone is measured to 2 ppb and are reported to 1 ppb or 2 µg m^{-3}
- Benzene is measured to 0.1 ppb and are reported to 0.1 ppb or 0.3 µg m^{-3}

Note that 15-minutes means, where available, are also recorded to the same data precision as hourly means.

Percentiles

Percentiles of SO_2 daily means are calculated using the method described in the European Community SO_2 Directive[29]. All other percentiles use the European Community NO_2 Directive[30] method. For example: after sorting the data into ascending numerical order, the 98th percentiles are at the following ranks:

SO_2	0.98 times the number of valid means rounded up to the nearest integer
NO_2	0.98 times the number of valid means rounded to the nearest integer

For example, the 98th percentile of 365 daily means (rank 357.7) is the 8th highest concentration using the SO_2 Directive method and also the 8th highest concentration using the NO_2 Directive method.

Data Capture Threshold

A 75% data capture threshold is set for all short-term averages of up to the duration of a month. For example:

- An hourly mean requires at least three 15-minute means
- A monthly mean requires at least 75% of daily means and each daily mean requires at least 18 hours of data

Note that it is possible to have a month with 75% data capture for hourly means, but with less than 75% daily means.

Annual and seasonal statistics, such as the summer mean and the annual 98th percentile of hourly means, should be interpreted with respect to the quoted data capture. These statistics are generally not shown if the data capture is less than 25%. However, some short-term values such as the date of the annual maximum hourly mean are shown, since these may still be of interest.

Air Quality Standards and Guidelines

Air quality guidelines used in this report are those defined in the documentation published by the UK Government[2,10,11], the European Community[29-31], the World Health Organisation[26].

The following conversion factors from measured units to mass units defined in the EU Decision on Exchange of Information[6].

Conversion Factors Between ppb and $\mu g\ m^{-3}$ and ppm and mgm^{-3}

Pollutant	**WHO** **25°C and 1013mb**	**EC** **20°C and 1013mb**
Ozone	1 ppb = 1.9622 $\mu g\ m^{-3}$	1 ppb = 1.9957 $\mu g\ m^{-3}$
Nitrogen dioxide	1 ppb = 1.8804 $\mu g\ m^{-3}$	1 ppb = 1.9125 $\mu g\ m^{-3}$
Carbon monoxide	1 ppm = 1.1447 mg m^{-3}	1 ppm = 1.1642 mg m^{-3}
Sulphur dioxide	1 ppb = 2.6163 $\mu g\ m^{-3}$	1 ppb = 2.6609 $\mu g\ m^{-3}$
Benzene	1 ppb = 3.189 $\mu g\ m^{-3}$	1 ppb = 3.243 $\mu g\ m^{-3}$
1,3-butadiene	1 ppb = 2.2075 $\mu g\ m^{-3}$	1 ppb = 2.2452 $\mu g\ m^{-3}$

Note that the minimum data period that can be compared to a guideline is fifteen minutes, since this is currently the time resolution of most UK automatic data. The WHO 10-minute SO_2 guideline is not, therefore, reported.

Running Means

Wherever possible, running means, rather than simple means, are used for comparison with air quality standards.

For example: the Air Quality Standard CO 8-hour standard in this report is based on all possible 8-hour means during a year. Calculating all possible means can produce twenty-four possible exceedences every day. This is a more stringent method than taking simple, non-overlapping, means (e.g. three 8-hours means in a day).

Please note that in this report:

- The WHO 30-minute guideline is calculated as a running mean based on 15-minute averages
- The UK National Air Quality standard running annual means for benzene and 1,3-butadiene requires a 75% data capture. Newly established sites cannot, therefore, report the running annual mean.

Exceedence

An exceedence of an air quality guideline is defined in this report as a concentration **greater than** the guideline threshold. This definition was changed from "**greater than or equal"** the guideline threshold, in order to be consistent with EC Directives.

Exceedence Counting

The following method is used where an air quality guideline is based on an average:

1. Calculate the average
2. Apply the 75% data capture threshold
3. Round the average to the data precision
4. Compare with the guideline

For example: at stage 3, an 8-hour average ozone concentration of 100.4999 µg m^{-3} is rounded to 100 µg m^{-3}. This does not exceed the UK National Air Quality standard running 8-hour ozone mean of 100 µg m^{-3}.

However, if no rounding occurs, the concentration would exceed the standard. Also, if this value is the highest running 8-hour during the year, an anomaly would occur in the report since the maximum would be reported as 100 µg m^{-3} yet there would be an exceedence.

To calculate the number of days with an exceedence, the date (in GMT) of the last hour of the running mean is used.

Cumulative Frequency Distributions

Cumulative frequency distributions in this report are graphed on log-normal axes. A reasonably straight line indicates that pollutant concentrations are log-normally distribution and can be predicted from the geometric mean and the standard geometric deviation[29]. The y-axis shows the logarithm to base 10 of the percentile concentrations, while points on the x-axis are normally distributed.

The geometric mean and standard geometric mean are calculated by use of logarithms and, therefore, can only include concentrations greater than zero.

Diurnal Variations

Diurnal variations are the average concentration for each hour of day during the period of interest. Local time is used, rather than GMT, since this will more closely reflect the daily cycle of manmade emissions.

Long-Term Trends

Long-term trends reported here are based a non-parametric linear regression method[29] which has the following stages:

- The gradient is calculated by “Theil’s incomplete” method[37]
- The null hypothesis (i.e. the statistical significance of the trend) is tested by the Spearman’s rank correlation coefficient[38]
- The 95th confidence interval for the gradient is given by Kendall's Tau[39]

Values for the Spearman’s rank correlation coefficient used in this report are as published by Conover[36].

This method does not assume that the errors on the data points are normally distributed and is, therefore, more appropriate than simple linear regression by least squares. However, the results obtained have been demonstrated to be broadly similar[40].

Exponential regressions may be appropriate for some time series, e.g. SO_2 in London, but for the majority of cases a linear trend over recent years is of most interest. Only linear trends are provided in this report.

Trends are reported for sites where there are at least five valid measurements. A valid measurement requires a data capture of at least 50%.

Where a site has a statistically significant trend of more than five years, the five-year trend and the trend over the full monitoring period are reported. Ten-year trends are highlight in the summary table in Appendix 4.

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The Defra air quality information web resource:
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The Scottish Executive Air Quality pages:
www.scotland.gov.uk/about/ERADEN/ACEU-AQT/00016215/homepage.aspx

The Welsh Assembly Government Environment link:
www.wales.gov.uk/subienvironment/index.htm

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