

# **Air Pollution in the UK: 2004**

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## **Part 3 - Appendices**

- 1- The Major Air Pollutants measured in the UK**
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# 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.

## Measured Pollutants

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

- Nitrogen oxides, and primarily nitrogen dioxide (NO<sub>2</sub>)
- Sulphur Dioxide (SO<sub>2</sub>)
- Carbon Monoxide (CO)
- Ozone (O<sub>3</sub>)
- Particles- primarily measured as PM<sub>10</sub> at the present time
- Benzene (C<sub>6</sub>H<sub>6</sub>)
- 1,3-butadiene (C<sub>4</sub>H<sub>6</sub>)

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 automatic 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)<sup>18-25</sup> and World Health Organisation<sup>26</sup>.

## Nitrogen Oxides

Nitrogen oxides (NO<sub>x</sub>) 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<sub>2</sub>), collectively known as NO<sub>x</sub> - 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 NO<sub>x</sub> 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 NO<sub>x</sub> levels in UK cities are generally observed at kerbside locations. However, since much of the NO<sub>2</sub> is formed from primary emissions of NO by time-dependent oxidation processes in the atmosphere, the relative decline in NO<sub>2</sub> concentration away from the kerbside is slower than for NO.

Modelling and monitoring studies- for example with diffusion tube samplers- have shown that NO<sub>2</sub> 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<sub>2</sub>) 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> concentrations in cities usually occur in the central areas.

## Carbon Monoxide

Carbon monoxide (CO) 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 (O<sub>3</sub>) 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 µg/m<sup>3</sup>.

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<sub>x</sub> 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<sub>x</sub> 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 (PM) 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 such as PM<sub>10</sub> and PM<sub>2.5</sub> 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<sub>10</sub> (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<sub>10</sub> 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<sub>10</sub> data show that daily average concentrations are usually highest in the winter months and lowest in the summer. During winter episode periods, PM<sub>10</sub> 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 (C<sub>6</sub>H<sub>6</sub>) 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 ( $C_4H_6$ ) to be a 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.

<b>Figure 2.1</b>	<b>Southern England</b>
<b>Figure 2.2</b>	<b>London</b>
<b>Figure 2.3</b>	<b>Midlands</b>
<b>Figure 2.4</b>	<b>NE England</b>
<b>Figure 2.5</b>	<b>NW England</b>
<b>Figure 2.6</b>	<b>Wales</b>
<b>Figure 2.7</b>	<b>N. Ireland</b>
<b>Figure 2.8</b>	<b>Scotland</b>

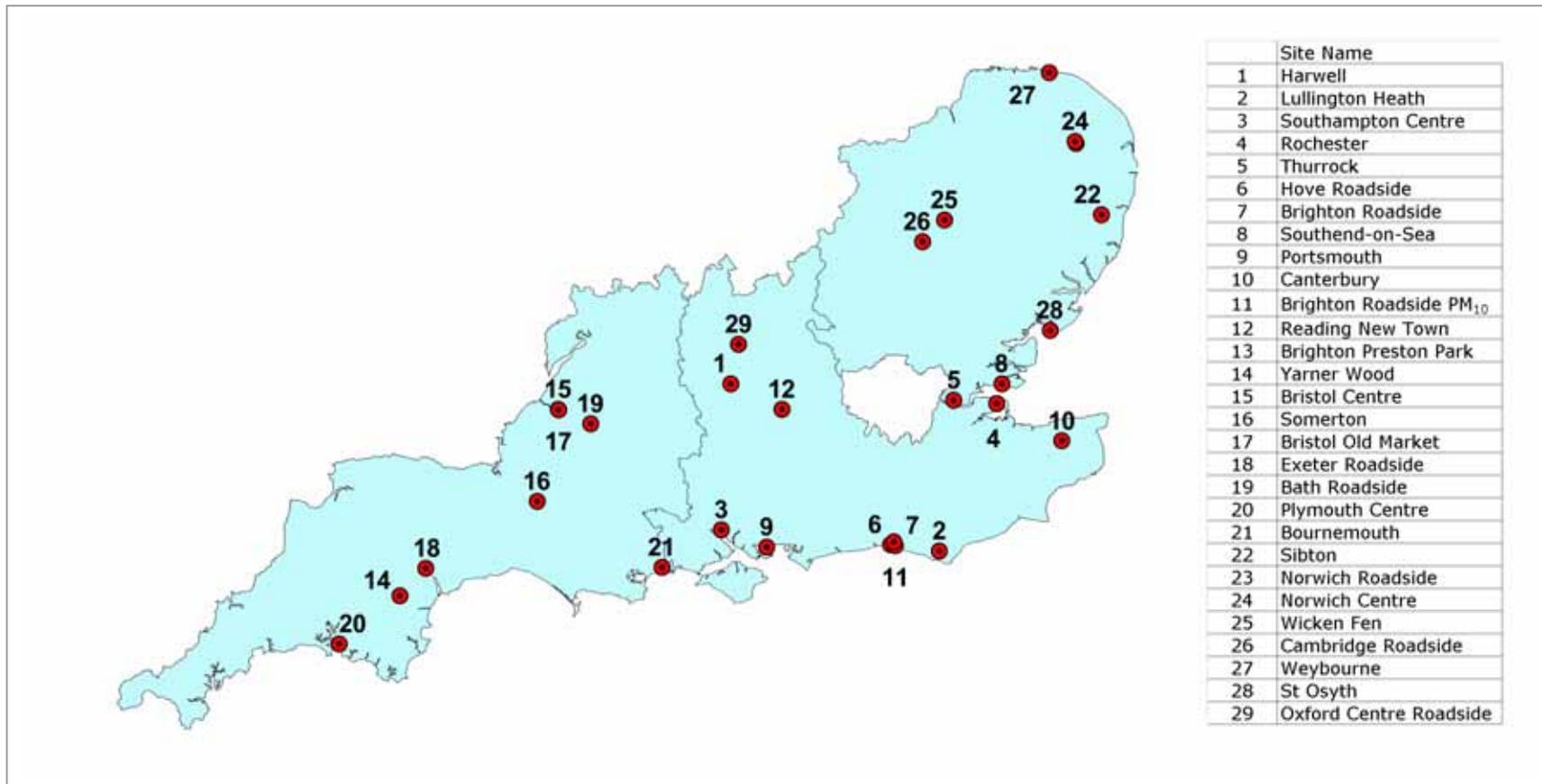


Figure 2.1 Automatic Sites, Southern England

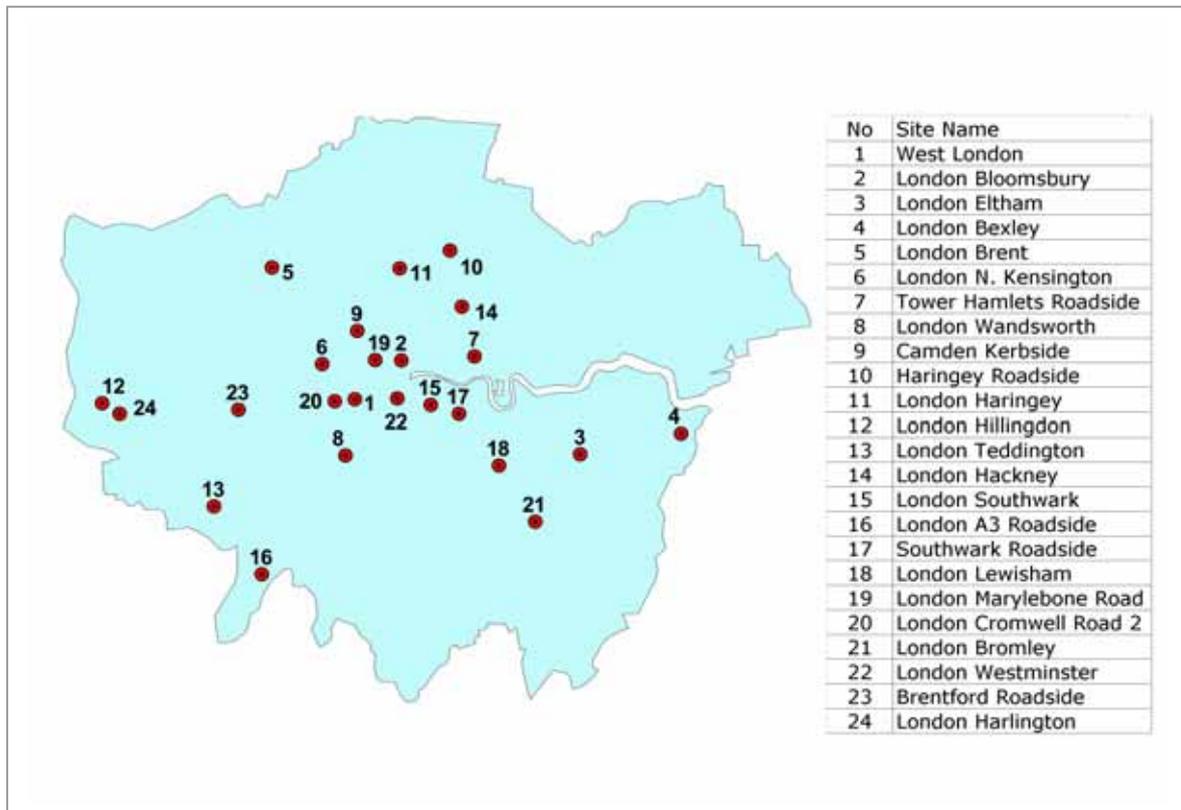


Figure 2.2 Automatic Sites, London

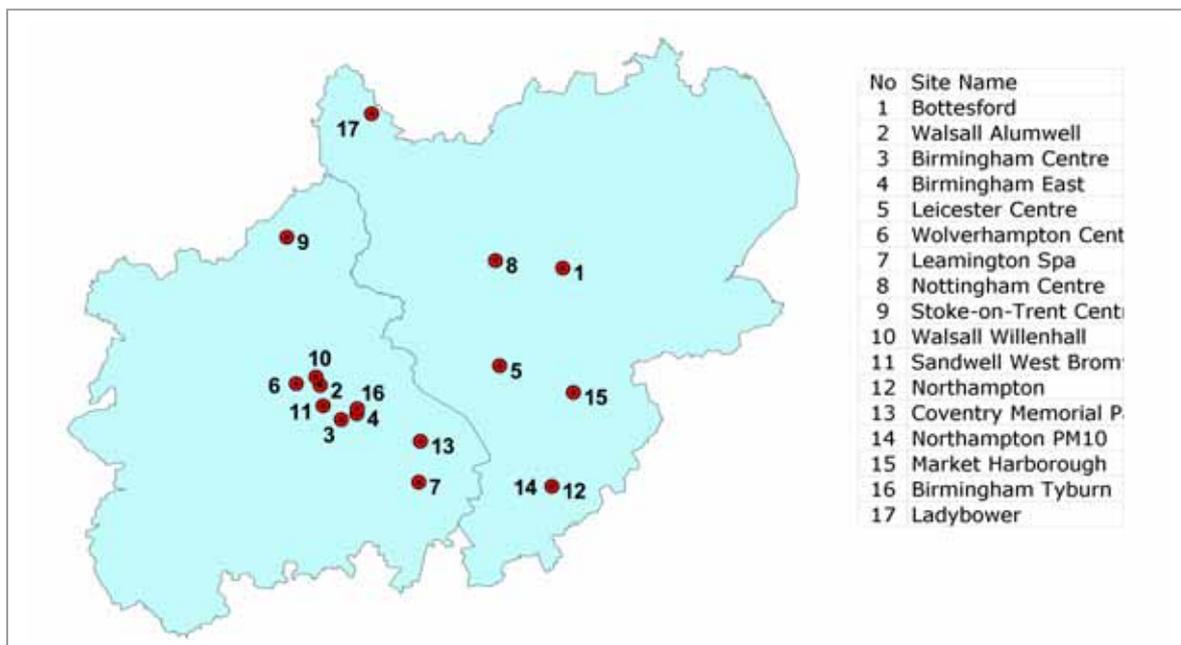


Figure 2.3 Automatic Sites, Midlands

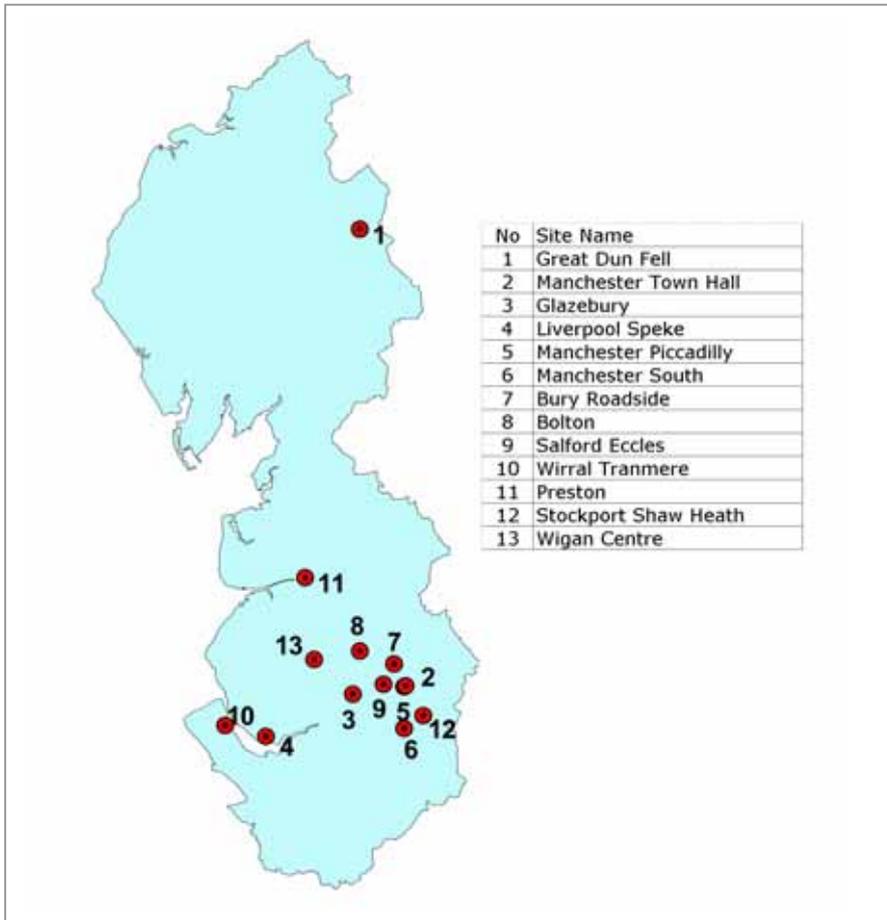


Figure 2.4 Automatic Sites, NW England

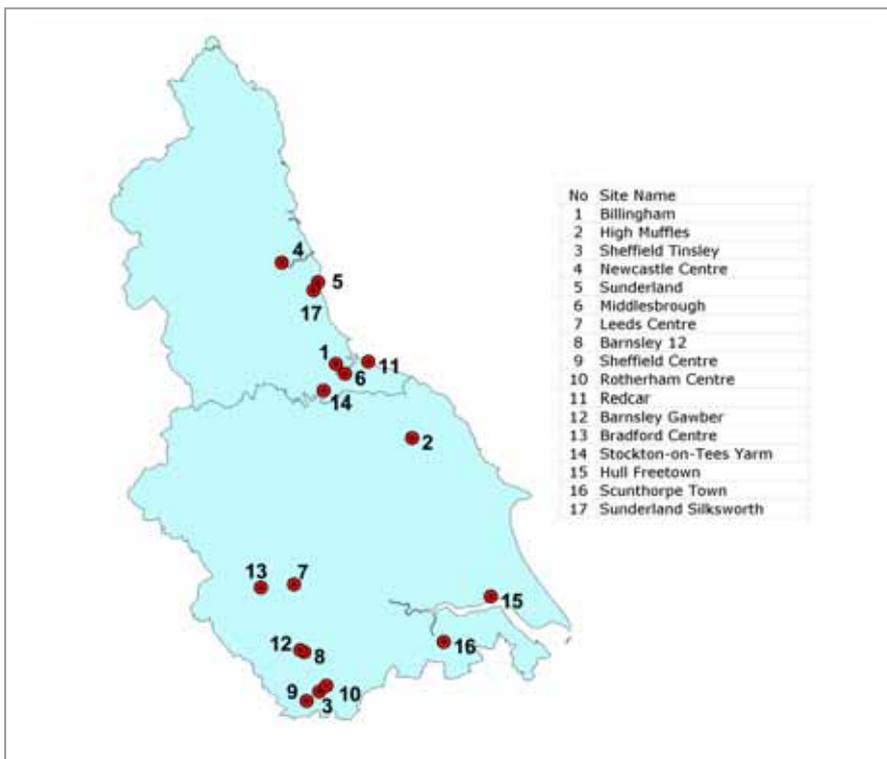


Figure 2.5 Automatic Sites, NE England

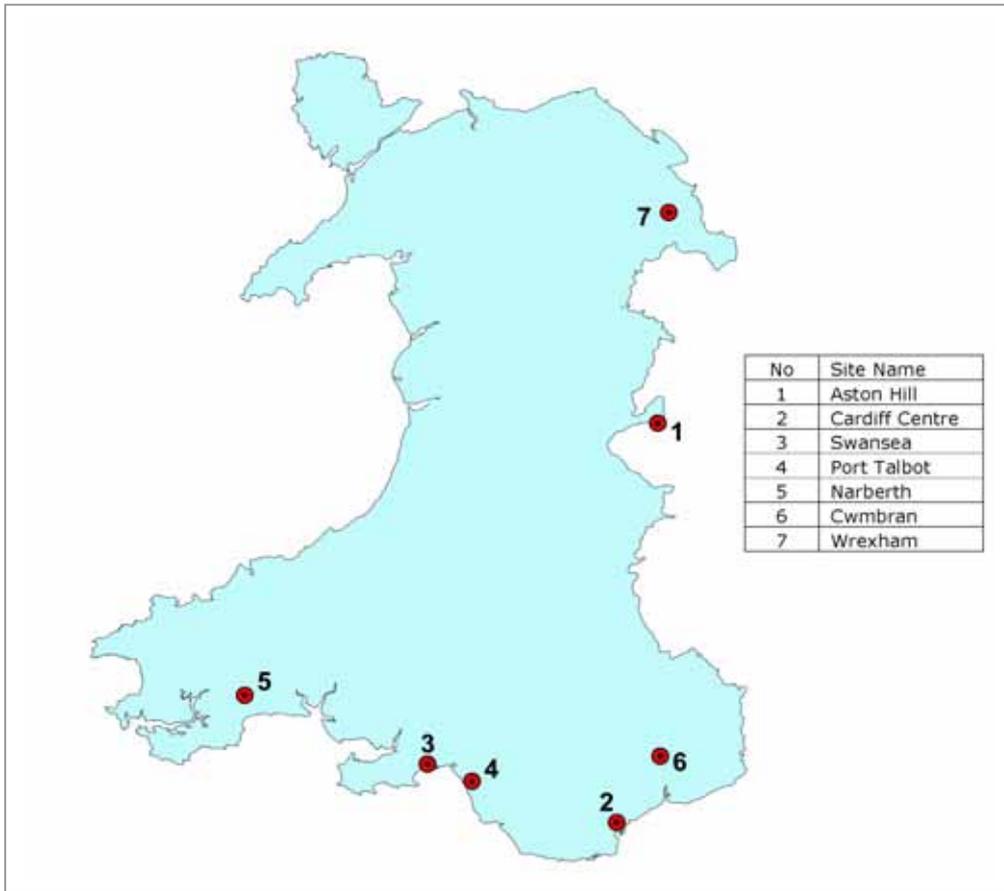


Figure 2.6 Automatic Sites, Wales

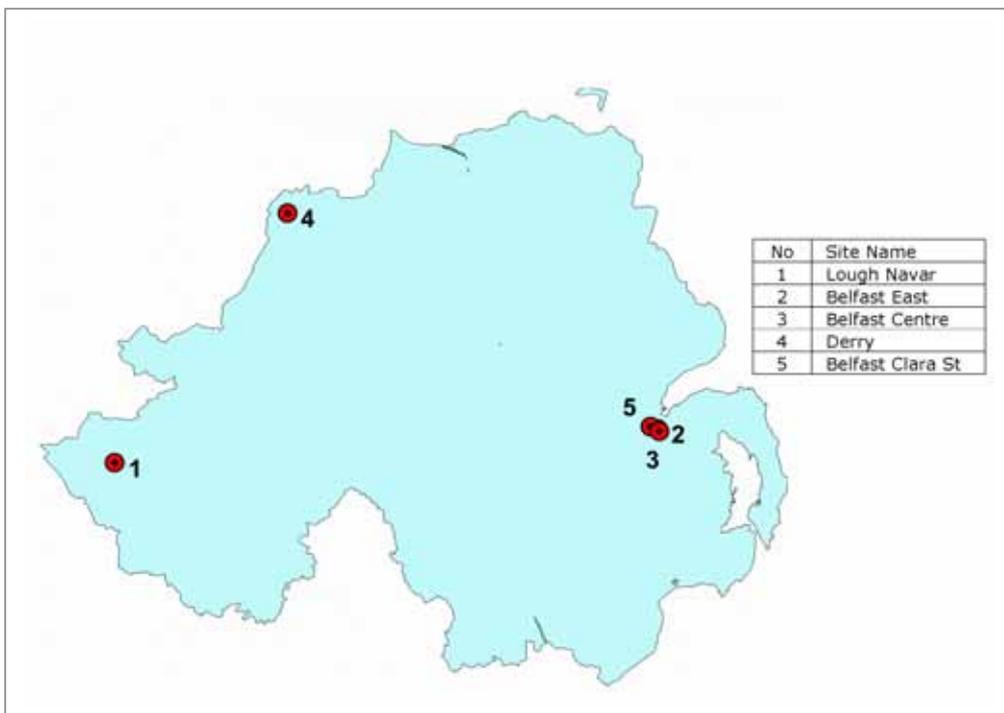


Figure 2.7 Automatic Sites, Northern Ireland

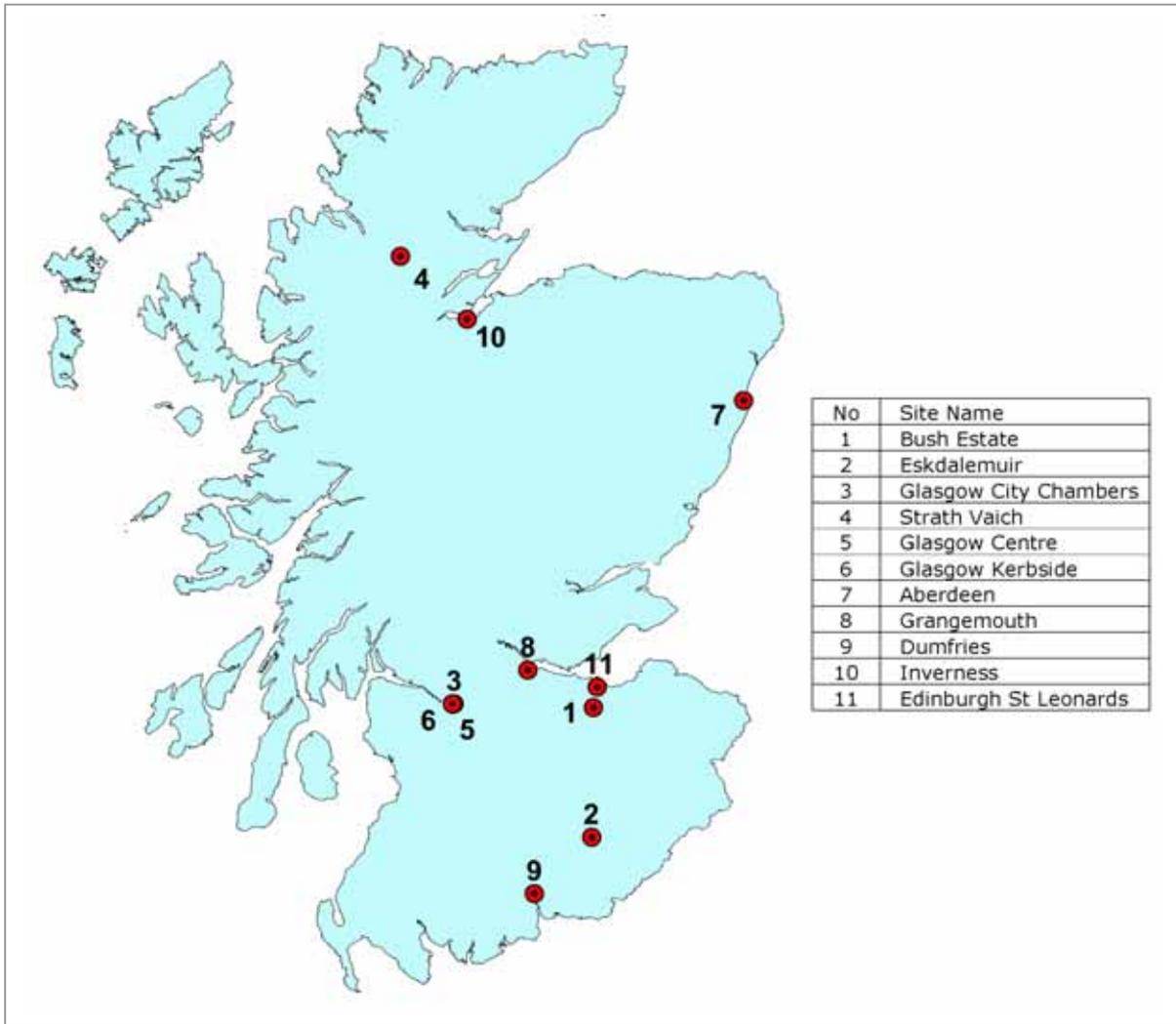


Figure 2.8 Automatic Sites, Scotland

# 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.

<b>A 3.1</b>	<b>The Smoke and Sulphur Dioxide Sampler Network</b>
<b>A 3.2</b>	<b>The Nitrogen Dioxide Diffusion Tube Network</b>
<b>A 3.3</b>	<b>The Automatic Urban and Rural Network</b>
<b>A 3.4</b>	<b>The Acid Deposition and Rural SO<sub>2</sub> networks</b>
<b>A 3.5</b>	<b>The Hydrocarbon Monitoring Networks</b>
<b>A 3.6</b>	<b>The PAH and TOMPS Networks</b>
<b>A 3.7</b>	<b>The Heavy Metals Networks</b>
<b>A 3.8</b>	<b>The National Ammonia Monitoring Network (NAMN)</b>

## A 3.1 The Smoke and SO<sub>2</sub> Network

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

The Smoke and SO<sub>2</sub> 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 (June 2005), there are 101 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> on a national scale.

There are currently 1213 sites in the Network, operated by 324 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<sub>2</sub> 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<sub>2</sub> 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 (AURN)

*(Network managed for Defra and the DAs 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 (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>), ozone (O<sub>3</sub>), carbon monoxide (CO) and particles (PM<sub>10</sub>). These are monitored on an hourly basis at measurement sites throughout the UK.

As of August 2005, the AURN consists of 123 monitoring sites. Of these, 60 are directly funded by Defra and the devolved administrations, and a further 63 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 Air Liquide 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<sub>10</sub> analysers, are the reference methods of measurement defined in the relevant EU Directives.

Additional monitors for NO<sub>2</sub>, SO<sub>2</sub> and PM<sub>10</sub> particulate matter were added to the AURN in 2001 and further monitors for CO were introduced in 2002. Additional monitors for O<sub>3</sub> and rural NO<sub>x</sub> have recently been installed to comply with the third Daughter Directive on Ozone. As PM<sub>2.5</sub> measurements are also required under the first Daughter Directive, 4 automatic analysers for PM<sub>2.5</sub> monitoring were incorporated into the AURN during 2003.

**AURN Measurement Techniques (considered in greater detail in Part 2)**

<b>O<sub>3</sub></b>	UV absorption
<b>NO/NO<sub>x</sub></b>	Chemiluminescence
<b>SO<sub>2</sub></b>	UV fluorescence
<b>CO</b>	IR Absorption
<b>PM<sub>10</sub></b>	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<sub>2</sub> Monitoring Networks

*(Managed and operated for Defra and the DAs by a consortium of CEH and Netcen)*

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

### (i) 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***

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

## **(ii) The Rural Sulphur Dioxide (SO<sub>2</sub>) Network**

The Rural Sulphur Dioxide (SO<sub>2</sub>) network was established in 1991 to provide additional information on the spatial distribution of SO<sub>2</sub> at rural sites across the UK. The network originally comprised 31 sites at which concentrations of SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> monitoring sites in the Rural SO<sub>2</sub> and Acid Deposition Monitoring Networks.

## **A 3.5 The Hydrocarbon monitoring networks**

### **i) The Automatic Hydrocarbon 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-focused, 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 Environment 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 all five sites 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.

## ii) The Non-Automatic Hydrocarbon Network

### *(Managed and operated for Defra and the DAs 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. 1,3-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 ( $2.25 \mu\text{g}/\text{m}^3$  expressed as a running annual mean).

Benzene is also monitored to assess compliance with UK Objectives (between  $3.25$  and  $16.25 \mu\text{g}/\text{m}^3$  depending on area and compliance date, expressed as a running annual mean), as well as with the corresponding EC Air Quality Directive Limit Value ( $5 \mu\text{g}/\text{m}^3$  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 Carboxpack 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 (prEN 14662, 5 parts) are nearing publication, and will include the pumped method used in this network.

## A 3.6 The PAH and TOMPs Networks

*(Networks managed and operated for Defra and the DAs by Netcen and Lancaster University respectively since March 2004)*

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<sup>3</sup>.
- The European Community's fourth Air Quality Daughter Directive (2005/107/EC), which includes a target value for benzo[a]pyrene as a representative PAH as an annual average of 1 ng /m<sup>3</sup>.
- 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 18 UK network locations. Careful extraction of 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 Dibenzop-Dioxins, Polychlorinated Dibenzofurans (PCDD/Fs), PAHs as above, and Polychlorinated Biphenyls (PCBs). PCDD/Fs and PAHs are formed as unwanted by-products during various chemical, industrial and combustion processes. The PCBs were previously manufactured for use in a wide range of electrical and other products until the mid 1980s. 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 in UK cities, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere.
- 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

- The network is also used to investigate the behaviour of newly identified persistent organic pollutants such as brominated flame retardants and other industrial chemicals.

The TOMPS network measures concentrations of these trace organic species at six sites. Samples from these sites are then analysed for PAHs as part of the PAH network. 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 chemical analysis techniques including gas chromatography coupled with high-resolution mass spectrometry.

## A 3.7 UK Heavy Metals Monitoring Networks

### (i) UK urban/industrial network (previously the Lead, Multi-element and Industrial Metals Networks)

*(Network managed and operated for Defra and the DAs by the National Physical Laboratory)*

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)<sup>3</sup> 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)<sup>28</sup> sets a Limit Value for lead in air concentrations at  $0.5 \mu\text{g}/\text{m}^3$ , expressed as an annual mean to be achieved by 1<sup>st</sup> 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. As a consequence, some monitoring sites, which only measured lead concentrations, have since been closed.

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 the 4th Daughter Directive which was then being drafted with the aim of setting limit values for arsenic, cadmium, nickel and mercury. Results of this programme showed that further monitoring at a number of sites was required in order to establish compliance with the proposed Target Values. Monitoring continues currently at five of these sites – Avonmouth, Hallen Village, Swansea, Sheffield and Runcorn.

The 4<sup>th</sup> Daughter Directive (2004/107/EC) was published in the Official Journal of the European Commission on 26<sup>th</sup> January 2005. The 4<sup>th</sup> Daughter Directive sets 'target values' for arsenic, cadmium, nickel (and polycyclic aromatic hydrocarbons) in the  $\text{PM}_{10}$  particulate fraction of ambient air.

Member States must transpose the 4<sup>th</sup> Daughter Directive into national law by 15<sup>th</sup> February 2007. The European Commission will report on its implementation by 31<sup>st</sup> December 2010. Governments must report to the Commission on zones and agglomerations where the target values are exceeded with the first such reports being required by 30<sup>th</sup> September 2008. The 4<sup>th</sup> Daughter Directive also requires monitoring of mercury although no limit or target values have been set.

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), referred to as the UK Heavy Metals Monitoring Network. Sampling is now undertaken for weekly periods at sites on the PM<sub>10</sub> 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 the draft CEN WG14 reference method, which has now been sent out to Member States for final vote. Consistency in approach has been achieved with historical data collection and analyses through thorough equivalence exercises.

Since September 2004, the number of elements measured at the old Industrial Metals sites has been increased to ensure there is consistency across the Network. All 17 sites now monitor for As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Pt, V and Zn. Additionally, measurements are made for ambient vapour phase mercury concentrations at 13 sites.

## **(ii) The Rural Heavy Metals and Mercury Network**

*(Network managed and operated for Defra and the DAs by Centre for Ecology and Hydrology)*

The Rural Trace Element monitoring has been expanded to 10 sites where the PM<sub>10</sub> fraction of particulates have been collected weekly using Thermo FH95 single or FH95SEQ sequential samplers, together with monthly collections of precipitation for accredited ICP-MS analysis. In addition a further three sites collect precipitation samples only and two more sites collect precipitation and cloud water samples.

At the 10 primary sites, newly designed samplers have also been set up to collect Mercury in air and in Mercury in precipitation. The Mercury in air samples are analysed using a TEKRAN system that is also continuously operating at the Auchencorth site to provide speciation data for the different forms of Mercury in the atmosphere. The Mercury in precipitation is analysed using a Cold Vapour Atomic Fluorescence Spectrometer (PSA Ltd) with a Analytical detection limit = 0.8ng l<sup>-1</sup> (99% confidence)

## **A 3.8 The National Ammonia Monitoring Network**

*(Managed and operated for Defra and the DAs by CEH- Centre for Ecology and Hydrology)*

The National Ammonia Monitoring Network (NAMN) was established with approximately 70 sites in 1996. Its objective is to provide long-term estimates of the spatial distribution of ammonia concentrations across the UK, which may be used for:

- Estimating dry deposition fluxes of ammonia, and
- Assessment of models.

A 2-tiered approach was used, which consisted of a baseline network of around 50 sites sampling ammonia using the active DELTA (DENuder for Long-Term Atmospheric sampling) system (where power is available), while a secondary network of passive diffusion tubes explored air concentration variability in high concentration areas, with the

method calibrated at 10 sites against the DELTA approach. In both cases, sampling is performed on a monthly basis.

Further methodological improvements were introduced over time. In 1999, the DELTA method was extended to allow sampling of ammonium aerosol at all active sites. This was followed by the establishment of the Nitric Acid Monitoring Network at 12 of the active sites, using an extension of the DELTA method to additionally sample gaseous  $\text{HNO}_3/\text{SO}_2/\text{HCl}$ , aerosol  $\text{NO}_3^-/\text{SO}_4^{2-}/\text{Cl}^-$  and the base cations  $\text{Ca}^{2+}/\text{Mg}^{2+}/\text{Na}^+$ , also on a monthly basis.

In 2000, a new improved passive sampling method was developed and introduced; the Adapted Low-cost, Passive High Absorption (ALPHA) sampler (LOD =  $0.02 \mu\text{g NH}_3 \text{ m}^{-3}$ ) replaced the less sensitive diffusion tube (LOD =  $1 \mu\text{g NH}_3 \text{ m}^{-3}$ ) in the network.

Accompanying these changes has been an increase in the number of monitoring sites to 94 - to improve the interpolated concentration field for  $\text{NH}_3$  - and a reduction in the number of sites monitoring  $\text{NH}_4^+$ , as this is a secondary pollutant with less spatial variability than  $\text{NH}_3$ .

Overall, the network structure currently consists of:

Site type	Number
DELTA Sites	57
Sampling aerosol $\text{NH}_4^+$	43
ALPHA sites	49
Intercomparison sites with both DELTA & ALPHA samplers	12
Total number of sites	94

# Appendix 4- Analysis of statistically significant trends in UK air pollution levels

Here we summarise those measurement sites with over five years of measurements having statistically significant trends; long-running sites with trends extending over a period of 10 years or more are highlighted.

Pollutant	Site	Type	Parameter	Start Year	End Year	Slope	Low Range	High Range	No. Years
<b>1,3-Butadiene <math>\mu\text{g m}^{-3}</math> / yr</b>									
No trends									
<b>Benzene <math>\mu\text{g m}^{-3}</math> / yr</b>									
	Harwell	Rural	Annual mean	1995	2004	-0.11	-0.13	-0.07	10
	Harwell	Rural	98 %ile	1995	2004	-0.4	-0.58	-0.3	10
<b>Carbon Monoxide <math>\text{mg m}^{-3}</math> / yr</b>									
	Belfast Centre	Urban Centre	Annual mean	1992	2004	-0.1	-0.1	-0.1	13
	Belfast Centre	Urban Centre	98 %ile	1992	2004	-0.3	-0.3	-0.2	13
	Birmingham Centre	Urban Centre	Annual mean	1992	2004	0	-0.1	0	13
	Birmingham Centre	Urban Centre	98 %ile	1992	2004	-0.2	-0.2	-0.1	13
	Birmingham East	Urban Backgr.	Annual mean	1994	2004	0	-0.1	0	11
	Birmingham East	Urban Backgr.	98 %ile	1994	2004	-0.2	-0.2	-0.1	11
	Bristol Centre	Urban Centre	Annual mean	1993	2004	0	-0.1	0	12
	Bristol Centre	Urban Centre	98 %ile	1993	2004	-0.2	-0.2	-0.1	12
	Cardiff Centre	Urban Centre	Annual mean	1992	2004	0	-0.1	0	13
	Cardiff Centre	Urban Centre	98 %ile	1992	2004	-0.2	-0.2	-0.1	13
	Glasgow City Chambers	Urban Backgr.	Annual mean	1990	2004	-0.1	-0.1	0	15
	Glasgow City Chambers	Urban Backgr.	98 %ile	1990	2004	-0.3	-0.4	-0.2	15
	Leeds Centre	Urban Centre	Annual mean	1993	2004	0	-0.1	0	12
	Leeds Centre	Urban Centre	98 %ile	1993	2004	-0.2	-0.2	-0.1	12
	Leicester Centre	Urban Centre	98 %ile	1994	2004	-0.1	-0.2	-0.1	11
	London Bexley	Suburban	Annual mean	1994	2004	0	0	0	11
	London Bexley	Suburban	98 %ile	1994	2004	-0.2	-0.2	-0.1	11
	London Bloomsbury	Urban Centre	Annual mean	1992	2004	0	-0.1	0	13
	London Bloomsbury	Urban Centre	98 %ile	1992	2004	-0.2	-0.2	-0.1	13
	Manchester Town Hall	Urban Backgr.	Annual mean	1992	2004	0	-0.1	0	12
	Manchester Town Hall	Urban Backgr.	98 %ile	1992	2004	-0.1	-0.3	-0.1	12
	Middlesbrough	Urban Backgr.	98 %ile	1995	2004	-0.1	-0.1	0	10
	Newcastle Centre	Urban Centre	Annual mean	1992	2004	-0.1	-0.1	0	13
	Newcastle Centre	Urban Centre	98 %ile	1992	2004	-0.2	-0.2	-0.1	13
	Sheffield Tinsley	Urban Ind.	98 %ile	1992	2004	-0.2	-0.2	-0.1	13
	Southampton Centre	Urban Centre	Annual mean	1994	2004	-0.1	-0.1	0	11
	Southampton Centre	Urban Centre	98 %ile	1994	2004	-0.2	-0.3	-0.2	11
	Swansea	Urban Centre	Annual mean	1995	2004	0	-0.1	0	10
	Swansea	Urban Centre	98 %ile	1995	2004	-0.2	-0.2	-0.1	10
	West London	Urban Backgr.	Annual mean	1990	2004	-0.1	-0.1	-0.1	15
	West London	Urban Backgr.	98 %ile	1990	2004	-0.3	-0.4	-0.2	15
<b>Nitrogen Dioxide <math>\mu\text{g m}^{-3}</math> / yr</b>									
	Belfast Centre	Urban Centre	Annual mean	1992	2004	-1.2	-1.5	-1	13
	Belfast Centre	Urban Centre	98 %ile	1992	2004	-2.5	-3.5	-1.3	13
	Billingham	Urban Ind.	Annual mean	1987	2004	-0.6	-0.9	-0.4	18
	Billingham	Urban Ind.	98 %ile	1987	2004	-0.2	-2	-0.1	18
	Birmingham Centre	Urban Centre	Annual mean	1993	2004	-1.8	-2	-1	12
	Birmingham Centre	Urban Centre	98 %ile	1993	2004	-3.5	-4.5	-2	12
	Birmingham East	Urban Backgr.	98 %ile	1994	2004	-2.7	-5	0	11
	Bristol Centre	Urban Centre	Annual mean	1993	2004	-1.5	-1.6	-1	12
	Bristol Centre	Urban Centre	98 %ile	1993	2004	-3	-3.6	-1.9	12
	Cardiff Centre	Urban Centre	Annual mean	1992	2004	-1.3	-1.6	-1	13
	Cardiff Centre	Urban Centre	98 %ile	1992	2004	-2.4	-2.9	-1.2	13
	Glasgow City Chambers	Urban Backgr.	Annual mean	1987	2004	-0.1	-0.6	0	18
	Ladybower	Rural	Annual mean	1991	2004	-0.8	-1.1	-0.4	14
	Ladybower	Rural	98 %ile	1991	2004	-2	-3	-0.5	14
	Leeds Centre	Urban Centre	Annual mean	1993	2004	-2.3	-2.6	-1.2	12
	Leeds Centre	Urban Centre	98 %ile	1993	2004	-2.4	-3.5	0	12
	Leicester Centre	Urban Centre	Annual mean	1994	2004	-1.2	-1.4	-0.5	11
	Leicester Centre	Urban Centre	98 %ile	1994	2004	-2.3	-2.8	-0.5	11
	London Bexley	Suburban	Annual mean	1994	2004	-1	-1.6	-0.4	11
	London Bexley	Suburban	98 %ile	1994	2004	-2.2	-4	0	11
	London Bloomsbury	Urban Centre	98 %ile	1992	2004	-3.2	-5.7	-0.5	12
	Lullington Heath	Rural	Annual mean	1991	2004	-0.5	-0.7	-0.2	14
	Lullington Heath	Rural	98 %ile	1991	2004	-1.8	-2.5	-1.1	14
	Manchester Town Hall	Urban Backgr.	Annual mean	1987	2004	-0.7	-1.2	-0.5	18
	Manchester Town Hall	Urban Backgr.	98 %ile	1987	2004	-3.3	-4	-1.5	18

Pollutant	Site	Type	Parameter	Start Year	End Year	Slope	Low Range	High Range	No. Years
	Middlesbrough	Urban Ind.	Annual mean	1995	2004	-1	-1.5	-0.3	10
	Middlesbrough	Urban Ind.	98 %ile	1995	2004	-2.2	-2.7	-0.3	10
	Newcastle Centre	Urban Centre	Annual mean	1992	2004	-1.9	-2.8	-1.3	13
	Newcastle Centre	Urban Centre	98 %ile	1992	2004	-3.3	-6.5	-1.6	13
	Sheffield Tinsley	Urban Ind.	Annual mean	1991	2004	-1.3	-1.6	-0.8	14
	Sheffield Tinsley	Urban Ind.	98 %ile	1991	2004	-3	-5.1	-1.9	14
	Southampton Centre	Urban Centre	Annual mean	1994	2004	-1.2	-1.8	-0.7	11
	Southampton Centre	Urban Centre	98 %ile	1994	2004	-2.8	-4.2	-2	11
	Walsall Alumwell	Urban Backgr.	Annual mean	1987	2004	-1	-1.3	-0.6	18
	Walsall Alumwell	Urban Backgr.	98 %ile	1987	2004	-2.3	-2.6	-0.8	18
	West London	Urban Backgr.	Annual mean	1987	2004	-1.4	-1.8	-1	18
	West London	Urban Backgr.	98 %ile	1987	2004	-4.2	-5.6	-3	18
<b>Nitrogen Oxides <math>\mu\text{g m}^{-3}</math> / yr</b>									
	Belfast Centre	Urban Centre	Annual mean	1992	2004	-3.2	-4.4	-2	13
	Belfast Centre	Urban Centre	98 %ile	1992	2004	-14.5	-27.8	-7.5	13
	Billingham	Urban Ind.	Annual mean	1987	2004	-2	-2.3	-1.1	18
	Billingham	Urban Ind.	98 %ile	1987	2004	-7.4	-12	-3.9	18
	Birmingham Centre	Urban Centre	Annual mean	1993	2004	-4	-4.5	-3	12
	Birmingham Centre	Urban Centre	98 %ile	1993	2004	-16.7	-18	-8.8	12
	Birmingham East	Urban Backgr.	Annual mean	1994	2004	-3.3	-4.7	-1	11
	Birmingham East	Urban Backgr.	98 %ile	1994	2004	-22.3	-31.3	-7.7	11
	Bristol Centre	Urban Centre	Annual mean	1993	2004	-4	-6.8	-1.7	12
	Bristol Centre	Urban Centre	98 %ile	1993	2004	-14.7	-31.5	-3.8	12
	Cardiff Centre	Urban Centre	Annual mean	1992	2004	-4.1	-5.1	-2.5	13
	Cardiff Centre	Urban Centre	98 %ile	1992	2004	-19.3	-23	-12	13
	Glasgow City Chambers	Urban Backgr.	Annual mean	1987	2004	-5.3	-5.3	-3.4	18
	Glasgow City Chambers	Urban Backgr.	98 %ile	1987	2004	-26.1	-36	-17	18
	Ladybower	Rural	Annual mean	1991	2004	-1	-1.5	-0.5	14
	Ladybower	Rural	98 %ile	1991	2004	-4.7	-6.4	-1.8	14
	Leeds Centre	Urban Centre	Annual mean	1993	2004	-6.6	-8.4	-4.3	12
	Leeds Centre	Urban Centre	98 %ile	1993	2004	-24.3	-32	-6.8	12
	Leicester Centre	Urban Centre	Annual mean	1994	2004	-2.8	-3.7	-1	11
	Leicester Centre	Urban Centre	98 %ile	1994	2004	-12.7	-23.3	-4.1	11
	London Bexley	Suburban	Annual mean	1994	2004	-4.5	-5.5	-2	11
	London Bexley	Suburban	98 %ile	1994	2004	-26.7	-36.5	-6.8	11
	London Bloomsbury	Urban Centre	Annual mean	1992	2004	-5.4	-6.7	-2.3	13
	London Bloomsbury	Urban Centre	98 %ile	1992	2004	-16.6	-21.3	-10	13
	Lullington Heath	Rural	Annual mean	1991	2004	-0.6	-0.8	-0.3	14
	Lullington Heath	Rural	98 %ile	1991	2004	-3.5	-4	-2	14
	Manchester Town Hall	Urban Backgr.	Annual mean	1987	2004	-5	-5	-3.1	18
	Manchester Town Hall	Urban Backgr.	98 %ile	1987	2004	-23.8	-30	-15.2	18
	Newcastle Centre	Urban Centre	Annual mean	1992	2004	-5.6	-8	-4.4	13
	Newcastle Centre	Urban Centre	98 %ile	1992	2004	-22.4	-34.4	-15.6	13
	Sheffield Tinsley	Urban Ind.	Annual mean	1991	2004	-7.1	-9	-5.7	14
	Sheffield Tinsley	Urban Ind.	98 %ile	1991	2004	-27.4	-42	-12.9	14
	Southampton Centre	Urban Centre	Annual mean	1994	2004	-5	-6	-3	11
	Southampton Centre	Urban Centre	98 %ile	1994	2004	-23.3	-31.4	-12.2	11
	Walsall Alumwell	Urban Backgr.	Annual mean	1987	2004	-5.3	-6.3	-4	18
	Walsall Alumwell	Urban Backgr.	98 %ile	1987	2004	-25.9	-31.8	-16.3	18
	West London	Urban Backgr.	Annual mean	1987	2004	-6.8	-8.3	-5.6	18
	West London	Urban Backgr.	98 %ile	1987	2004	-25.4	-42.1	-20	18
<b>Ozone <math>\mu\text{g m}^{-3}</math> / yr</b>									
	Belfast Centre	Urban Centre	Annual mean	1992	2004	1.1	0	1.1	13
	Birmingham Centre	Urban Centre	Annual mean	1992	2004	1.2	0.6	1.3	13
	Birmingham East	Urban Backgr.	Annual mean	1994	2004	1	0	1.2	11
	Bottesford	Suburban	Annual mean	1981	2004	0.5	0	0.7	24
	Bristol Centre	Urban Centre	Annual mean	1993	2004	0.5	0	1	12
	Bush Estate	Rural	Annual mean	1986	2004	0.3	0	0.6	19
	Cardiff Centre	Urban Centre	Annual mean	1992	2004	1.2	0.7	1.5	13
	Great Dun Fell	Rural	Annual mean	1987	2004	0.4	0.1	0.6	14
	High Muffles	Rural	98 %ile	1988	2004	-1.4	-2.3	-0.2	17
	Leeds Centre	Urban Centre	Annual mean	1993	2004	1	0.5	1.5	12
	Leeds Centre	Urban Centre	98 %ile	1993	2004	1.2	0	2	12
	Leicester Centre	Urban Centre	Annual mean	1994	2004	0.3	0	1	11
	London Bexley	Suburban	Annual mean	1995	2004	0.8	0.3	1.3	10
	London Bloomsbury	Urban Centre	Annual mean	1992	2004	0.6	0.3	1	13
	Lough Navar	Remote	98 %ile	1987	2004	-0.9	-0.9	0	18
	Newcastle Centre	Urban Centre	Annual mean	1992	2004	0.9	0.7	1.3	11
	Newcastle Centre	Urban Centre	98 %ile	1992	2004	1.3	0	2.3	11
	Sibton	Rural	98 %ile	1977	2004	-0.9	-2	-0.2	26
	Southampton Centre	Urban Centre	Annual mean	1994	2004	0.5	0	1.2	11
	Strath Vaich	Remote	Annual mean	1987	2004	0.1	0.1	0.8	18

Pollutant	Site	Type	Parameter	Start Year	End Year	Slope	Low Range	High Range	No. Years
<b>PM10 Particulate Matter <math>\mu\text{g m}^{-3}</math> / yr</b>									
	Belfast Centre	Urban Centre	Annual mean	1992	2004	-1	-1.3	-0.8	13
	Belfast Centre	Urban Centre	98 %ile	1992	2004	-3.6	-7	-2.7	13
	Birmingham Centre	Urban Centre	Annual mean	1992	2004	-0.9	-1	-0.5	13
	Birmingham Centre	Urban Centre	98 %ile	1992	2004	-3.1	-4.4	-2	13
	Birmingham East	Urban Backgr.	Annual mean	1994	2004	-0.8	-1.2	0	10
	Birmingham East	Urban Backgr.	98 %ile	1994	2004	-3.6	-4.8	-0.8	10
	Bristol Centre	Urban Centre	Annual mean	1993	2004	-0.8	-1	-0.3	12
	Bristol Centre	Urban Centre	98 %ile	1993	2004	-2.3	-3.9	-1.3	12
	Cardiff Centre	Urban Centre	Annual mean	1993	2004	-0.8	-1.5	-0.2	12
	Cardiff Centre	Urban Centre	98 %ile	1993	2004	-2.6	-5.7	-0.8	12
	Leeds Centre	Urban Centre	Annual mean	1993	2004	-1.2	-1.3	-0.5	12
	Leeds Centre	Urban Centre	98 %ile	1993	2004	-4.1	-5.5	-2	12
	Leicester Centre	Urban Centre	Annual mean	1994	2004	-0.5	-1.2	-0.1	11
	Leicester Centre	Urban Centre	98 %ile	1994	2004	-1.7	-4.2	-0.3	11
	London Bexley	Suburban	Annual mean	1994	2004	-0.8	-1	0	11
	London Bexley	Suburban	98 %ile	1994	2004	-2.7	-3.9	-0.5	11
	London Bloomsbury	Urban Centre	Annual mean	1992	2004	-1	-1.2	-0.5	12
	London Bloomsbury	Urban Centre	98 %ile	1992	2004	-3.8	-4.6	-2	12
	Newcastle Centre	Urban Centre	Annual mean	1992	2004	-1.4	-2	-1	13
	Newcastle Centre	Urban Centre	98 %ile	1992	2004	-4.9	-6.4	-3	13
	Southampton Centre	Urban Centre	Annual mean	1994	2004	-0.5	-0.8	0	11
	Southampton Centre	Urban Centre	98 %ile	1994	2004	-2	-3	-0.3	11
<b>PM2.5 Particulate Matter <math>\mu\text{g m}^{-3}</math> / yr</b>									
No trends									
<b>Sulphur Dioxide <math>\mu\text{g m}^{-3}</math> / yr</b>									
	Barnsley 12	Urban Backgr.	Annual mean	1994	2004	-1.7	-2.9	-1	11
	Barnsley 12	Urban Backgr.	98 %ile	1994	2004	-7.8	-10.6	-2.5	11
	Belfast Centre	Urban Centre	Annual mean	1992	2004	-4.3	-4.7	-3	13
	Belfast Centre	Urban Centre	98 %ile	1992	2004	-19.7	-20.6	-12.2	13
	Belfast East	Urban Backgr.	Annual mean	1990	2004	-5.5	-6	-4.9	15
	Belfast East	Urban Backgr.	98 %ile	1990	2004	-25.6	-31.7	-20.3	15
	Birmingham Centre	Urban Centre	Annual mean	1992	2004	-1.8	-2.5	-1.3	13
	Birmingham Centre	Urban Centre	98 %ile	1992	2004	-8.6	-11.2	-6.8	13
	Birmingham East	Urban Backgr.	Annual mean	1994	2004	-1.2	-1.5	-0.6	11
	Birmingham East	Urban Backgr.	98 %ile	1994	2004	-5.7	-7.9	-3.4	11
	Bristol Centre	Urban Centre	Annual mean	1993	2004	-1.2	-1.7	-1	12
	Bristol Centre	Urban Centre	98 %ile	1993	2004	-3.8	-6.8	-2.5	12
	Cardiff Centre	Urban Centre	Annual mean	1992	2004	-1.2	-1.3	-1	13
	Cardiff Centre	Urban Centre	98 %ile	1992	2004	-4.8	-5.5	-4	13
	Ladybower	Rural	Annual mean	1989	2004	-1.4	-1.8	-1	16
	Ladybower	Rural	98 %ile	1989	2004	-6.7	-9.4	-5.7	16
	Leeds Centre	Urban Centre	Annual mean	1993	2004	-1.6	-2.4	-1.2	12
	Leeds Centre	Urban Centre	98 %ile	1993	2004	-7.5	-12.3	-5	12
	Leicester Centre	Urban Centre	Annual mean	1994	2004	-1	-2	-0.8	11
	Leicester Centre	Urban Centre	98 %ile	1994	2004	-5.8	-6.9	-4.3	11
	London Bexley	Suburban	Annual mean	1994	2004	-1.5	-2.3	-0.7	11
	London Bexley	Suburban	98 %ile	1994	2004	-10.2	-11.2	-1.7	11
	London Bloomsbury	Urban Centre	Annual mean	1992	2004	-2.2	-2.5	-2	13
	London Bloomsbury	Urban Centre	98 %ile	1992	2004	-9.7	-10.8	-9	13
	Lullington Heath	Rural	Annual mean	1988	2004	-0.4	-0.6	-0.2	14
	Lullington Heath	Rural	98 %ile	1988	2004	-2.3	-3.3	-1.3	14
	Middlesbrough	Urban Ind.	Annual mean	1995	2004	-1.2	-1.5	-1	10
	Middlesbrough	Urban Ind.	98 %ile	1995	2004	-4.4	-7.3	-3.8	10
	Newcastle Centre	Urban Centre	Annual mean	1992	2004	-1.6	-1.8	-1	13
	Newcastle Centre	Urban Centre	98 %ile	1992	2004	-8.9	-9.3	-5.5	13
	Southampton Centre	Urban Centre	Annual mean	1994	2004	-0.7	-1	-0.2	11
	Southampton Centre	Urban Centre	98 %ile	1994	2004	-3.5	-4	-0.7	11
	Sunderland	Urban Backgr.	Annual mean	1993	2004	-1	-1.3	-0.7	11
	Sunderland	Urban Backgr.	98 %ile	1993	2004	-5.4	-8	-3.9	11
	Swansea	Urban Centre	Annual mean	1995	2004	-2	-2.2	-1	10
	Swansea	Urban Centre	98 %ile	1995	2004	-7.6	-10	-4.3	10

# Appendix 5- Listing of current UK, European and WHO Air Quality Criteria

Here we summarise the UK Air Quality Strategy Standards and Objectives, together with corresponding European Community Directive Limit and Target Values and World Health Organisation advisory Guidelines for the major pollutants.

## Nitrogen Dioxide

Guideline Set By	Description	Criteria Based On	Value <sup>(1)</sup> / $\mu\text{g m}^{-3}$ (ppb)	
<b>UK Government Air Pollution Index</b>	LOW	1	1-hour mean	0-95 (0-49)
		2		96-190 (50-99)
		3		191-286 (100-149)
	MODERATE	4	1-hour mean	287-381 (150-199)
		5		382-477 (200-249)
		6		478-572 (250-299)
	HIGH	7	1-hour mean	573-635 (300-332)
		8		636-700 (333-366)
		9		701-763 (367-399)
	VERY HIGH	10	1-hour mean	$\geq 764$ ( $\geq 400$ )
<b>The Air Quality Strategy<sup>(2)</sup></b>  <i>Set in regulations<sup>(3)</sup> for all UK: Not intended to be set in regulations:</i>	Objective for Dec. 31 <sup>st</sup> 2005, for protection of human health	1-hour mean	200 (105) Not to be exceeded more than 18 times per calendar year.	
	Objective for Dec. 31 <sup>st</sup> 2005, for protection of human health	Annual mean	40 (21)	
	Objective for Dec. 31 <sup>st</sup> 2000, for protection of vegetation.	Annual mean NO <sub>x</sub> (NO <sub>x</sub> as NO <sub>2</sub> )	30 (16)	
<b>European Community 1985 NO<sub>2</sub> Directive<sup>(4)</sup></b> <i>Limit remains in force until fully repealed 01/01/2010.</i>	Limit Value	Calendar year of data: 98 <sup>th</sup> ile of hourly means.	200 (105)	
<b>1<sup>st</sup> Daughter Directive<sup>(5)</sup></b>	Limit Value for protection of human health. To be achieved by Jan. 1 <sup>st</sup> 2010	1-hour mean	200 (105) not to be exceeded more than 18 times per calendar year	
	Limit Value for protection of human health. To be achieved by Jan. 1 <sup>st</sup> 2010	Calendar year mean	40 (21)	
	Limit Value (total NO <sub>x</sub> ) for protection of vegetation. To be achieved by Jul. 19 <sup>th</sup> 2001	Calendar year mean	30 (16)	
<b>World Health Organisation<sup>(6)</sup></b> <i>(Non-Mandatory Guidelines)</i>	Health Guideline	1-hour mean	200	
	Health Guideline	Annual mean	40	

(1) Conversions between  $\mu\text{g m}^{-3}$  and ppb are as used by the EC, i.e. 1ppb NO<sub>2</sub> = 1.91  $\mu\text{g m}^{-3}$  at 20°C and 1013 mB.

(2) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1 & Addendum 2003.

(3) Air Quality (England) Regulations 2000 (SI 2000/928), Air Quality (Scotland) Regulations 2000 (SSI 2000/97), Air Quality (Wales) Regulations 2000 (SI 2000/1940 (W138)).

(4) Council Directive 85/203/EEC.

(5) Council Directive 1999/30/EC. Transposed into UK Air Quality Regulations in England by SI 2001/2315, in Scotland by SSI 2001/224, in Wales by SI 2001/2683 (W224), and by Statutory Rule 2002 (94) in Northern Ireland.

(6) WHO Guidelines for Air Quality WHO/SDE/OEH/00.02 (2000).

## Sulphur Dioxide

Guideline Set By	Description		Criteria Based On	Value <sup>(1)</sup> / $\mu\text{g m}^{-3}$ (ppb)
<b>UK Government Air Pollution Index</b>	LOW	1	15-minute mean	0-88 (0-32)
		2		89-176 (33-66)
		3		177-265 (67-99)
	MODERATE	4	15-minute mean	266-354 (100-132)
		5		355-442 (133-166)
		6		443-531 (167-199)
	HIGH	7	15-minute mean	532-708 (200-266)
		8		709-886 (267-332)
		9		887-1063 (333-399)
	VERY HIGH	10	15-minute mean	$\geq 1064$ ( $\geq 400$ )
<b>The Air Quality Strategy<sup>(2)</sup></b>  <i>Set in regulations<sup>(3)</sup> for all UK.</i>  <i>Not intended to be set in regulations.</i>	Objective for Dec. 31 <sup>st</sup> 2005, for protection of human health.		15-minute mean	266 (100) Not to be exceeded > 35 times per calendar year.
	Objective for Dec. 31 <sup>st</sup> 2004, for protection of human health		1-hour mean	350 (132) Not to be exceeded > 24 times per calendar year.
	Objective for Dec. 31 <sup>st</sup> 2004, for protection of human health		24-hour mean	125 (47) Not to be exceeded > 3 times per calendar year.
	Objective for Dec. 31 <sup>st</sup> 2000, for protection of vegetation.		Annual mean & winter (1 <sup>st</sup> October – 31 <sup>st</sup> March) mean	20 (8)
<b>1<sup>st</sup> Daughter Directive<sup>(4)</sup></b>	Objective for Jan 1 <sup>st</sup> 2005, for protection of human health		1-hour mean	350 (132) Not to be exceeded more than 24 times per calendar year.
	Objective for Jan 1 <sup>st</sup> 2005, for protection of human health		Daily 24-hour mean	125 (47) Not to be exceeded more than 3 times per calendar year.
	Objective for Jul 19 <sup>th</sup> 2001, for protection of vegetation.		Annual mean & winter (1 <sup>st</sup> October – 31 <sup>st</sup> March) mean	20 (8)
<b>World Health Organisation<sup>(5)</sup></b>  <i>(Non-Mandatory Guidelines)</i>	Health Guideline		10-minute mean	500
	Health Guideline		24-hour mean	125
	Health Guideline		Annual mean	50

(1) Conversions between  $\mu\text{g m}^{-3}$  and ppb are as used by the EC, i.e. 1ppb  $\text{SO}_2 = 2.66 \mu\text{g m}^{-3}$  at 20°C and 1013 mB.

(2) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1 & Addendum 2003.

(3) Air Quality (England) Regulations 2000 (SI 2000/928), Air Quality (Scotland) Regulations 2000 (SSI 2000/97), Air Quality (Wales) Regulations 2000 (SI 2000/1940 (W138)).

(4) Council Directive 1999/30/EC. Transposed into UK Air Quality Regulations in England by SI 2001/2315, in Scotland by SSI 2001/224, in Wales by SI 2001/2683 (W224), and by Statutory Rule 2002 (94) in Northern Ireland.

(5) WHO Guidelines for Air Quality WHO/SDE/OEH/00.02 (2000).

## Ozone

Guideline Set By	Description		Criteria Based On	Value <sup>(1)</sup> / $\mu\text{g m}^{-3}$ (ppb)
<b>UK Government Air Pollution Index</b>	LOW	1	Max 1-hour and 8-hour mean	0-32 (0-16)
		2		33-66 (17-32)
		3		67-99 (33-49)
	MODERATE	4	Max 1-hour and 8-hour mean	100-126 (50-62)
		5		127-152 (63-76)
		6		153-179 (77-89)
	HIGH	7	Max 1-hour and 8-hour mean	180-239 (90-119)
		8		240-299 (120-149)
		9		300-359 (150-179)
	VERY HIGH	10	Max 1-hour and 8-hour mean	$\geq 360$ ( $\geq 180$ )
<b>The Air Quality Strategy<sup>(2)</sup> All UK.</b> <i>Not currently set in regulations.</i>	Objective for Dec. 31 <sup>st</sup> 2005		Daily max. running 8-hour mean	100 (50) Not to be exceeded more than 10 times per calendar year.
<b>European Community 3<sup>rd</sup> Daughter Directive<sup>(4)</sup></b>	Target Value To be achieved by 3-year period beginning 2010.		Max. daily 8-hour mean.	$120 \mu\text{g m}^{-3}$ Not to be exceeded on more than 25 days per year, averaged over 3 years.
	Target Value for protection of vegetation. To be achieved by 5 years, beginning 2010		AOT40 <sup>(5)</sup> calculated from 1h values May-July.	$18,000 \mu\text{g m}^{-3} \text{ h}$ averaged over 5 years.
	Information threshold		1-hour mean	180
	Alert threshold		1-hour mean	240
<b>World Health Organisation<sup>(6)</sup></b> <i>(Non-Mandatory Guidelines)</i>	Health Guideline		8-hour mean	120

(1) Conversions between  $\mu\text{g m}^{-3}$  and ppb are as used by the EC, i.e.  $1 \text{ ppb O}_3 = 2.00 \mu\text{g m}^{-3}$  at  $20^\circ\text{C}$  and 1013 mB.

(2) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1 & Addendum 2003.

(3) Directive 92/72/EEC. To be repealed 9 Sep 2003.

(4) Directive (2002/3/EC)

(5) AOT40 statistic is the sum of the differences between hourly concentrations greater than  $80 \mu\text{g m}^{-3}$  ( $=40 \text{ ppb}$ ) and  $80 \mu\text{g m}^{-3}$ , over a given period using only the 1-hour averages measured between 0800 and 2000.

(6) WHO Guidelines for Air Quality WHO/SDE/OEH/00.02 (2000).

(7) Growing season is defined as April to September for WHO guidelines, but is daytime (0900-1500) April to September for UNECE guidelines.

## Carbon Monoxide

Guideline Set By	Description		Criteria Based On	Value <sup>(1)</sup> / mg m <sup>-3</sup> (ppm)
<b>UK Government Air Pollution Index</b>	LOW	1	8-hour mean	0-3.8 (0-3.2)
		2		3.9-7.6 (3.3-6.6)
		3		7.7-11.5 (6.7-9.9)
	MODERATE	4	8-hour mean	11.6-13.4 (10.0-11.5)
		5		13.5-15.4 (11.6-13.2)
		6		15.5-17.3 (13.3-14.9)
	HIGH	7	8-hour mean	17.4-19.2 (15.0-16.5)
		8		19.3-21.2 (16.6-18.2)
		9		21.3-23.1 (18.3-19.9)
	VERY HIGH	10	8-hour mean	≥ 23.2 (≥ 20)
<b>The Air Quality Strategy<sup>(2,3)</sup> (Except Scotland)</b>	Objective for Dec. 31 <sup>st</sup> 2003		Max. Daily Running 8-hour mean	10 (8.6)
	Objective for Dec. 31 <sup>st</sup> 2003		Running 8-hour mean	10 (8.6)
<b>Scotland only<sup>4</sup>:</b>	Objective for Dec. 31 <sup>st</sup> 2003		Running 8-hour mean	10 (8.6)
<b>European Community 2<sup>nd</sup> Daughter Directive<sup>(5)</sup></b>	Limit Value. To be achieved by Jan 1 <sup>st</sup> 2005		Max. daily 8-hour mean	10 (8.6)
<b>World Health Organisation<sup>(6)</sup></b> <i>(Non-Mandatory Guidelines)</i>	Health Guideline		15-minute mean	100
	Health Guideline		30-minute mean	60
	Health Guideline		1-hour mean	30
	Health Guideline		8-hour mean	10

(1) Conversions between  $\mu\text{g m}^{-3}$  and ppb are those used by the EC, i.e. 1ppm CO = 1.16 mg m<sup>-3</sup> at 20°C and 1013 mB, except where specified.

(2) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1 & Addendum 2003.

(3) Air Quality (England) Regulations 2000 (SI 2000/928), Air Quality (Scotland) Regulations 2000 (SSI 2000/97), Air Quality (Wales) Regulations 2000 (SI 2000/1940 (W138)).

(4) Air Quality (Scotland) Amendment Regulations 2002 (SSI 2002/297).

(5) Council Directive 2000/69/EC. Transposed into UK Air Quality Regulations in England by SI 2002/3117, in Scotland by SSI 2002/556, in Wales by SI 2002/3183 (W299), and by Statutory Rule 2002 (357) in Northern Ireland.

(6) WHO Guidelines for Air Quality WHO/SDE/OEH/00.02 (2000).

## Benzene

Guideline Set By	Description	Criteria Based On	Value <sup>(1)</sup> / $\mu\text{g m}^{-3}$ (ppb)
<b>The Air Quality Strategy<sup>(2,3)</sup></b> <b>All UK</b> <b>England<sup>(4)</sup> &amp; Wales<sup>(5)</sup> only:</b> <b>Scotland<sup>(6)</sup> &amp; Northern Ireland</b>	Objective for Dec. 31 <sup>st</sup> 2003	Running annual mean	16.25 (5)
	Objective for Dec. 31 <sup>st</sup> 2010	Annual mean	5 (1.54)
	Objective for Dec. 31 <sup>st</sup> 2010	Running annual mean	3.25 (1.0)
<b>European Community 2<sup>nd</sup> Daughter Directive<sup>(8)</sup></b>	Limit Value. To be achieved by Jan 1 <sup>st</sup> 2010	Annual calendar year mean	5 (1.5)

(1) Conversions between  $\mu\text{g m}^{-3}$  and ppb are those used by the EC, i.e. 1ppb benzene = 3.25  $\mu\text{g m}^{-3}$  at 20°C and 1013 mB.

(2) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1 & Addendum 2003.

(3) Air Quality (England) Regulations 2000 (SI 2000/928), Air Quality (Scotland) Regulations 2000 (SSI 2000/97), Air Quality (Wales) Regulations 2000 (SI 2000/1940 (W138)).

(4) Air Quality (Amendment) (England) Regulations 2002 (SI 2002/3043)

(5) Air Quality (Amendment) (Wales) Regulations 2002 (SI 2002/3182 (W298))

(6) Air Quality (Amendment) (Scotland) Regulations 2002 (SI 2002/297)

(7) Council Directive 2000/69/EC. Transposed into UK Air Quality Regulations in England by SI 2002/3117, in Scotland by SSI 2002/556, in Wales by SI 2002/3183 (W299), and by Statutory Rule 2002 (357) in Northern Ireland.

## 1,3 Butadiene

Guideline Set By	Description	Criteria Based On	Value <sup>(1)</sup> / $\mu\text{g m}^{-3}$ (ppb)
<b>The Air Quality Strategy<sup>(2,3)</sup></b> <b>All UK</b>	Objective for Dec. 31 <sup>st</sup> 2003	Running annual mean	2.25 (1)

(1) Conversions between  $\mu\text{g m}^{-3}$  and ppb are those used by the EC, i.e. 1ppb benzene = 2.25  $\mu\text{g m}^{-3}$  at 20°C and 1013 mB.

(2) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1. & Addendum 2003.

(3) Air Quality (England) Regulations 2000 (SI 2000/928), Air Quality (Scotland) Regulations 2000 (SSI 2000/97), Air Quality (Wales) Regulations 2000 (SI 2000/1940 (W138)).

## Polycyclic Aromatic Hydrocarbons (PAH)

Guideline Set By	Description	Criteria Based On	Value / $\text{ng m}^{-3}$
<b>The Air Quality Strategy<sup>(1)</sup></b> <b>England, Wales, Scotland and Northern Ireland.</b> <i>Not set in regulations.</i>	Objective for Dec. 31 <sup>st</sup> 2010	Annual mean ( <i>using B(a)P as an indicator</i> )	0.25

(1) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1 & Addendum 2003.

Particulate Matter as PM<sub>10</sub>

Guideline Set By	Description		Criteria Based On	Value / $\mu\text{g m}^{-3}$
<b>UK Government Air Pollution Index</b>	LOW	1	24-hour mean	0-16
		2		17-32
		3		33-49
	MODERATE	4	24-hour mean	50-57
		5		58-66
		6		67-74
	HIGH	7	24-hour mean	75-82
		8		83-91
		9		92-99
	V. HIGH	10	24-hour mean	$\geq 100$
<b>The Air Quality Strategy<sup>(1)</sup></b> <b>Set in regulations for all UK<sup>(2)</sup>.</b>	Objective for Dec. 31 <sup>st</sup> 2004		24-hour mean	50 Not to be exceeded more than 35 times per calendar year.
	Objective for Dec. 31 <sup>st</sup> 2004		Annual mean	40
<i>Set in regulations Scotland only<sup>(3)</sup></i>	Objective for Dec. 31 <sup>st</sup> 2010		24-hour mean	50 Not to be exceeded more than 7 times per calendar year.
	Objective for Dec. 31 <sup>st</sup> 2010		Annual mean	18
<b>The Air Quality Strategy<sup>(1)</sup></b> <i>Not set in regulations: London only</i>	Objective for Dec. 31 <sup>st</sup> 2010		24-hour mean	50 Not to be exceeded more than 10 times per calendar year.
	Objective for Dec. 31 <sup>st</sup> 2010		Annual mean	23
<b>The Air Quality Strategy<sup>(1)</sup></b> <i>Not set in regulations: Rest of England, Wales, &amp; Northern Ireland.</i>	Objective for Dec. 31 <sup>st</sup> 2010		24-hour mean	50 Not to be exceeded more than 7 times per calendar year.
	Objective for Dec. 31 <sup>st</sup> 2010		Annual mean	20
<b>1<sup>st</sup> Daughter Directive<sup>(4)</sup></b> <b>STAGE 1 – Confirmed.</b>	Limit Value to be achieved by Jan 1 <sup>st</sup> 2005		24-hour mean	50 Not to be exceeded more than 35 times per calendar year.
	Limit Value to be achieved by Jan 1 <sup>st</sup> 2005		Annual mean	40
<b>1<sup>st</sup> Daughter Directive<sup>(4)</sup></b> <b>STAGE 2 – To be confirmed.</b>	Limit Value to be achieved by Jan 1 <sup>st</sup> 2010		24-hour mean	50 Not to be exceeded more than 7 times per calendar year.
	Limit Value to be achieved by Jan 1 <sup>st</sup> 2010		Annual mean	20

(1) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1 & Addendum 2003.

(2) Air Quality (England) Regulations 2000 (SI 2000/928), Air Quality (Scotland) Regulations 2000 (SSI 2000/97), Air Quality (Wales) Regulations 2000 (SI 2000/1940 (W138)).

(3) Air Quality (Amendment) (Scotland) Regulations 2002 (SI 2002/297)

(4) Council Directive 1999/30/EC. Transposed into UK Air Quality Regulations in England by SI 2001/2315, in Scotland by SSI 2001/224, in Wales by SI 2001/2683 (W224), and by Statutory Rule 2002 (94) in Northern Ireland.

**Lead (Pb)**

<b>Guideline Set By</b>	<b>Description</b>	<b>Criteria Based On</b>	<b>Value / <math>\mu\text{gm}^{-3}</math></b>
<b>The Air Quality Strategy<sup>(1)</sup></b>  <b>Set in regulations for all UK.</b>	Objective for Dec. 31 <sup>st</sup> 2004	Annual mean	0.5 (= 500 ng m <sup>-3</sup> )
	Objective for Dec. 31 <sup>st</sup> 2008	Annual mean	0.25 (= 250 ng m <sup>-3</sup> )
<b>1<sup>st</sup> Daughter Directive (1999/30/EEC)<sup>(2)</sup></b>	Limit Value to be achieved by Jan 1 <sup>st</sup> 2005	Annual mean	0.5 (= 500 ng m <sup>-3</sup> )
	Limit Value to be achieved by Jan 1 <sup>st</sup> 2010 in the immediate vicinity of industrial sources	Annual mean	0.5 (= 500 ng m <sup>-3</sup> )
<b>World Health Organisation<sup>(3)</sup></b>  <i>(Non-Mandatory Guidelines)</i>	Health-Based Guideline	Annual Mean	0.5 (= 500 ng m <sup>-3</sup> )

(1) The Air Quality Strategy for England, Scotland, Wales and Northern Ireland. January 2000. ISBN 0-10-145482-1 & Addendum 2003.

(2) Council Directive 1999/30/EC

(3) WHO Guidelines for Air Quality WHO/SDE/OEH/00.02 (2000).

**Metallic Elements Arsenic (As), Cadmium (Cd), Mercury (Hg) and Nickel (Ni), and hydrocarbon Benzo (a) Pyrene**

<b>Guideline Set By</b>	<b>Description</b>	<b>Criteria Based On</b>	<b>Value / ng m<sup>-3</sup></b>
<b>Daughter Directive (205/107/EC)</b>	Target Value for As	Calendar year mean	6
	Target Value for Cd	Calendar year mean	5
	Target Value for Hg	Calendar year mean	Not set
	Target Value for Ni	Calendar year mean	20
	Target Value for B(a)P	Calendar year mean	1

Target values to be non-mandatory.

## Description of UK Government Pollution Indices

Old "Band"	New Index	Health Descriptor
<b>LOW</b>	<b>1</b>	Effects are unlikely to be noticed even by individuals who know they are sensitive to air pollutants.
	<b>2</b>	
	<b>3</b>	
<b>MODERATE</b>	<b>4</b>	Mild effects unlikely to require action may be noticed amongst sensitive individuals.
	<b>5</b>	
	<b>6</b>	
<b>HIGH</b>	<b>7</b>	Significant effects may be noticed by sensitive individuals and action to avoid or reduce these effects may be needed (e.g. reducing exposure by spending less time in polluted areas outdoors). Asthmatics will find that their "reliever" inhaler is likely to reverse the effects on the lung.
	<b>8</b>	
	<b>9</b>	
<b>VERY HIGH</b>	<b>10</b>	The effects on sensitive individuals described for "High" levels of pollution may worsen.

## Air Quality Regulations: Statutory Instruments

Date	Country	S.I. No.	Purpose
30/03/2000	England	SI 2000 No. 928	Inclusion of original Air Quality Strategy Objectives into regulations in England
19/07/2000	Wales	SI 2000 No. 1940 (W138)	Inclusion of original Air Quality Strategy Objectives into regulations in Wales
31/03/2000	Scotland	SSI 2000 No. 97	Inclusion of original Air Quality Strategy Objectives into regulations in Scotland
09/06/2001	Scotland	SSI 2001 No. 224	Transposition of 1 <sup>st</sup> Daughter Directive into Air Quality Limit Values Regulations for Scotland.
25/06/2001	UK	SI 2001 No. 2315	Transposition of 1 <sup>st</sup> Daughter Directive into Air Quality Limit Values Regulations for England.
17/07/2001	Wales	SI 2001 No. 2683 (W224)	Transposition of 1 <sup>st</sup> Daughter Directive into Air Quality Limit Values Regulations for Wales.
08/03/2002	Northern Ireland	Statutory Rule 2002 (94)	Implementation of 1 <sup>st</sup> Daughter Directive in NI.
11/06/2002	Scotland	SSI 2002 297	Amendment of Air Quality Regulations to include more stringent objectives for PM <sub>10</sub> , CO and benzene, specifically for Scotland.
21/11/2002	Northern Ireland	Statutory Rule 2002 (357)	Transposition of 2 <sup>nd</sup> Daughter Directive into Air Quality Limit Values Regulations for Scotland
11/12/2002	England	SI 2002 No 3043	Amendment of Air Quality Regulations to include more stringent objectives for CO and benzene, in England.
16/12/2002	England	SI 2002 No 3117	Transposition of 2 <sup>nd</sup> Daughter Directive into Air Quality Limit Values Regulations for England
17/12/2002	Scotland	SSI 2002 556	Transposition of 2 <sup>nd</sup> Daughter Directive into Air Quality Limit Values Regulations for Scotland
17/12/2002	Wales	Welsh SI 2002 3182 (W298)	Amendment of Air Quality Regulations to include more stringent objectives for CO and benzene, in Wales
17/12/2002	Wales	Welsh SI 2002 3183 (W299)	Transposition of 1 <sup>st</sup> and 2 <sup>nd</sup> Daughter Directives into Air Quality Limit Values Regulations for Wales.

# Appendix 6- 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.

## A 6.1 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 standards setting out how National Networks in Member States should operate analysers in order to meet the required uncertainty of  $\pm 15\%$  for NO<sub>2</sub>, SO<sub>2</sub>, CO and O<sub>3</sub> and  $\pm 25\%$  for benzene (at the 95% confidence level).

The standards include 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 widescale use of analysers that do not conform to the EU Reference Method for PM<sub>10</sub> 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<sub>10</sub>.

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

Pollutant	Uncertainty for Continuous Measurement (listed as accuracy in the Directive)
NO <sub>2</sub> , NO <sub>x</sub>	15%
SO <sub>2</sub>	15%
Particulate Matter	25%
CO	15%
Benzene	25%
O <sub>3</sub>	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 6.2 Calculation Methods

### A 6.2.1 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](http://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<sup>28</sup>.

Various air quality guidelines and statistics are defined in the documentation published by the UK Government<sup>2,10,11</sup>, the European Community<sup>3,29-31</sup>, the World Health Organisation<sup>26,32-34</sup> and The Expert Panel on Air Quality Standards (EPAQS)<sup>18-25</sup>. 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 6.2.2 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<sub>2</sub> 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  $\mu\text{g m}^{-3}$  mass units. Particulate matter PM<sub>10</sub>, on the other hand, is measured and reported in terms of  $\mu\text{g m}^{-3}$ .

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, for example 0800 to 0759.

### ***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  $2 \mu\text{g m}^{-3}$
- Benzene is measured to 0.1 ppb and are reported to 0.1 ppb or  $0.3 \mu\text{g m}^{-3}$

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

### ***Percentiles***

Percentiles of SO<sub>2</sub> daily means are calculated using the method described in the European Community SO<sub>2</sub> Directive<sup>29</sup>. All other percentiles use the European Community NO<sub>2</sub> Directive<sup>30</sup> method. For example: after sorting the data into ascending numerical order, the 98<sup>th</sup> percentiles are at the following ranks:

<b>SO<sub>2</sub></b>	0.98 times the number of valid means rounded up to the nearest integer
<b>NO<sub>2</sub></b>	0.98 times the number of valid means rounded to the nearest integer

For example, the 98<sup>th</sup> percentile of 365 daily means (rank 357.7) is the 8<sup>th</sup> highest concentration using the SO<sub>2</sub> Directive method and also the 8<sup>th</sup> highest concentration using the NO<sub>2</sub> 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 98<sup>th</sup> 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<sup>2,10,11</sup>, the European Community<sup>29-31</sup>, the World Health Organisation<sup>26</sup>.

The following conversion factors from measured units to mass units defined in the EU Decision on Exchange of Information<sup>6</sup>.

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

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

Additional conversion factors used in the UK are as follows:

- $\text{NO}_x$  in  $\mu\text{g m}^{-3}$  is expressed as  $\text{NO}_2$ , i.e.  $(\text{NO ppb} + \text{NO}_2 \text{ ppb}) * 1.91 = \text{NO}_x \mu\text{g m}^{-3}$
- In the UK, gravimetric equivalent  $\text{PM}_{10}$  data are calculated from TEOM monitoring data by applying a conversion factor of 1.3

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  $\text{SO}_2$  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  $100.4999 \mu\text{g m}^{-3}$  is rounded to  $100 \mu\text{g m}^{-3}$ . This does not exceed the UK National Air Quality standard running 8-hour ozone mean of  $100 \mu\text{g m}^{-3}$ .

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  $100 \mu\text{g m}^{-3}$  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 distributed and can be predicted from the geometric mean and the standard geometric deviation<sup>29</sup>. 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<sup>29</sup> which has the following stages:

- The gradient is calculated by "Theil's incomplete" method<sup>37</sup>
- The null hypothesis (i.e. the statistical significance of the trend) is tested by the Spearman's rank correlation coefficient<sup>38</sup>
- The 95th confidence interval for the gradient is given by Kendall's Tau<sup>39</sup>

Values for the Spearman's rank correlation coefficient used in this report are as published by Conover<sup>36</sup>.

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<sup>40</sup>.

Exponential regressions may be appropriate for some time series, e.g.  $\text{SO}_2$  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 highlighted in the summary table in Appendix 4.

### ***Particulate measurements and conversion factors used in this report***

With gaseous pollutants, it is possible to express concentrations as an amount fraction – the ratio of pollutant molecules to the total number of air molecules – for example, parts per billion (ppb). This is not possible for PM, and measurements are always given in units of particulate mass per unit volume of air (typically  $\mu\text{g m}^{-3}$ ). When these units are used without specifying the temperature and pressure of the air, the same 'packet' of air will have a different concentration as these properties of the air change. The European legislation for PM measurement therefore requires that the air volume used must be at the same ambient air temperature and pressure as at the time of sampling. In practice, this means that appropriate corrections need to be made if the flow rate used to calculate the sampled volume is not based on the actual volume of sampled air.

Different measurement techniques, although nominally measuring the same PM, may treat the airstream in different ways, leading to significantly different results. For clarity, all mass measurements of PM<sub>10</sub> and PM<sub>2.5</sub> in this report are expressed as  $\mu\text{g m}^{-3}$  for both gravimetric and TEOM analysers.

The EU First Air Quality Daughter Directive (1999/30/EC) specifies that measurements of PM<sub>10</sub> should be carried out using the reference method, as defined in European Standard EN12341. This standard refers to three sampling devices that may be used:

- Superhigh volume sampler – the WRAC (Wide Range Aerosol Classifier);
- High-volume sampler – the HVS PM10 sampler ( $68 \text{ m}^3 \text{ h}^{-1}$ );
- Low-volume sampler – the LVS PM10 sampler ( $2.3 \text{ m}^3 \text{ h}^{-1}$ ).

None of these instruments can provide real-time (continuous hourly) measurements. As a result, the TEOM analyser is widely used in both the UK and throughout the rest of the world for measuring continuous concentrations of PM. The instrument is based on the principle that the frequency of oscillation of a glass, tapered tube (element) changes by an amount that is directly proportional to the mass of the tube. Therefore, any change in mass of the tube, due to the deposition of particles onto a small filter affixed to one end, will result in a change in the resonant frequency that is proportional to the additional mass.

In order for the TEOM to be used as a USEPA-equivalent method for PM<sub>10</sub> measurement, a default adjustment factor ( $1.03 * \text{TEOM reading} + 3 \mu\text{g m}^{-3}$ ) must be applied to the raw data. This adjustment factor was derived to account for moisture equilibration differences between the TEOM and the HI-vol sample media. The adjustment factor was determined at sites where non-volatile PM dominated and is intended to reflect the filter character more than the PM. It is understood that USEPA has no general policy on the use of this empirical adjustment factor for PM<sub>2.5</sub> measurements. All TEOM analysers in the UK measuring both PM<sub>10</sub> and PM<sub>2.5</sub> are currently set up with this default adjustment factor included. In addition, TEOM analysers within the UK networks are set to report concentrations corrected to 293K and 101.3 kPa.

Due to the need to eliminate the effect of changing humidity on the mass measurement, the TEOM is required to maintain the sample filter at an elevated temperature. This has led to reported differences in concentrations of PM between the TEOM and the European reference sampler (Allen *et al.*, 1997; APEG, 1999; Ayers *et al.*, 1999; Soutar *et al.*, 1999; Salter and Parsons, 1999; Cyrus *et al.*, 2001; Williams and Bruckmann, 2001). This is largely attributed to the loss of volatile species such as ammonium nitrate. As an interim measure, a default 'scaling factor' (also known as correction factor) of 1.3 has been applied to all TEOM PM<sub>10</sub> data reported here, as recommended by the EC Working Group on Particulate Matter (2001).

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