



**Technical Guidance Note
(Monitoring)**

M8

Monitoring Ambient Air

**Environment Agency
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Feedback

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Status of this document

This TGN may be subject to review and amendment following publication. The latest version is available on our website at: www.mcerts.net

Contents

1.	Introduction	1
2.	General purposes of ambient air quality monitoring	1
3.	The need for a monitoring strategy	1
4.	Survey objectives and monitoring strategy	2
5.	Review of existing information	4
5.1	Existing monitoring data and ancillary information	4
5.2	UK automatic monitoring networks	5
5.3	UK non-automatic monitoring networks	5
5.4	UK review groups	6
6.	Which species to measure	7
6.1	Targeting the pollutant	7
6.2	Different phases	7
6.3	Total and speciated measurements	7
6.4	Further chemical or physical characterisation	7
6.5	Media other than air	8
7.	When to sample, how long for, and how many samples to take	8
7.1	General considerations	8
7.2	Continuous or intermittent sampling	9
7.3	The averaging period	9
7.4	Duration of the sampling programme	11
8.	How to measure	12
8.1	Sampling approach	12
8.1.1	Omnidirectional sampling or directional sampling	12
8.1.2	Fixed-point sampling or open path methods	13
8.2	Choice of measuring method	14
8.2.1	Method performance	14
8.2.2	Other considerations	16
9.	Accompanying measurements and Supplementary Data	17
9.1	Meteorological data	17
9.2	Other information	18
10.	Where to sample	18
11.	Data handling	21
12.	Analysis of results and reporting	21
12.1	Presenting the raw data	21
12.2	Assessment against air quality standards	22
12.3	Source apportionment	22
12.3.1	Directional analysis	22
12.3.2	Temporal	23
12.3.3	Concurrence	24
12.4	Air Quality Data Analysis Software	24
12.5	Report content and structure	25
13.	Quality control and quality assurance	25
13.1	Measurement uncertainties	25
13.2	Sampling systems	26
13.3	Sample volumes & flow rates	26
13.4	Sample storage, transit and audit trail	26
13.5	Calibration and validation	27
13.5.1	Continuous gas analysers	27
13.5.2	Automatic particulate analysers	27
13.5.3	Non-continuous methods	28
13.6	Maintenance procedures	28
13.7	Data communication systems	28
13.8	Quality assurance	28

14. Index of Monitoring Methods	30
Table 14.1: Suspended particulate	31
Table 14.2: Suspended particles	34
Table 14.3: Nuisance dust (dustfall)	35
Table 14.4: Nuisance dust flux	37
Table 14.5: Odour	38
Table 14.6: Ozone	42
Table 14.7: Nitrogen oxides	44
Table 14.8: Sulphur dioxide	46
Table 14.9: Carbon monoxide	48
Table 14.10: Heavy metals	49
Table 14.11: Ammonia and NH _x	51
Table 14.12: Inorganic acids	53
Table 14.13: Hydrogen sulphide	55
Table 14.14: Volatile organic sulphurs	58
Table 14.15: Speciated hydrocarbons	59
Table 14.16: Halogenated VOCs	62
Table 14.17: Formaldehyde/aldehydes	63
Table 14.18: PAHs	64
Table 14.19: Dioxins & furans, PCBs	66
15. References for Sections 1 to 13	67
Annex A: Acronyms	68
Annex B: Data Analysis Techniques	70

1. Introduction

This Technical Guidance Note (TGN) is issued by the Environment Agency. It is one of a series providing guidance to our staff, monitoring contractors, industry and other parties interested in environmental monitoring. It combines and replaces TGN **M8** (Version 1) and TGN **M9** (Version 1).

Part 1 of the TGN provides guidance on developing monitoring strategies for assessing levels of pollutants in the ambient atmosphere. Initial consideration is given to identifying the aims and objectives of an ambient air quality monitoring study and the importance of developing a monitoring strategy to ensure these objectives are met. Existing UK air quality monitoring networks are summarised and the separate factors that need to be considered when developing the monitoring strategy are discussed, with some suggested approaches to specific types of study. Guidance on the handling, analysis, interpretation and reporting of air quality monitoring data is given.

Part 2, the index of monitoring methods, provides tabulated guidance on the monitoring methods available for assessing levels of different pollutants in the ambient atmosphere. It has been structured to enable the user to determine an appropriate monitoring method or technique.

This TGN does not attempt to state definitive best available techniques, as the most suitable strategies will depend on the particular circumstances. It is intended that the information provided should be used to aid selection of a suitable strategy for a given application.

2. General purposes of ambient air quality monitoring

Air quality monitoring may be carried out:

- for investigative or research purposes
- for compliance with legislation that encompasses monitoring of the ambient atmosphere e.g. EC Air Quality Directives
- as a requirement of a permit issued under the Environmental Permitting Regulations (EPR)
- by local authorities reviewing air quality in their area
- with emissions inventories and modelling, as part of the Local Air Quality Management system required under The Environment Act 1995,
- for inclusion in environmental statements under the Planning Regulations.

The monitoring of common ambient pollutants is well established, with a range of sophisticated automatic instrumental methods and simpler manual methods available. However, the range of pollutants possibly requiring measurement is wide, and includes many species where the measurement methodology is not so well advanced. Selection of suitable sampling methods requires careful consideration. A number of air quality monitoring techniques and methodology are referred to in this Note.

3. The need for a monitoring strategy

Air quality monitoring programmes need to be designed to provide the most appropriate data to fulfil the aims and objectives of a particular study. Even the most sophisticated monitoring programme can provide unsuitable data if sufficient care is not taken to define the sampling strategy. Designing a monitoring strategy requires decisions to be made on:

- objectives of acquiring the data
- what, where and when to sample
- how long to sample for
- how many samples to take and by what method
- an effective quality assurance/quality control system to ensure high-quality results and to eliminate invalid data.

There are numerous factors that have an important bearing on the way in which an ambient air quality survey is carried out, and these are considered in detail in this TGN. In some cases the survey will form part of a wider monitoring programme that may include measurements of pollutants in water, soil, vegetation or animal tissue. Although many of the same considerations apply to the design of monitoring surveys for these other media, this TGN is restricted to detailed advice on monitoring strategies for ambient air.

4. Survey objectives and monitoring strategy

There is a wide range of possible objectives for carrying out an ambient air quality survey, and a variety of sampling schemes may be adopted for monitoring the pollutants. For example, the monitoring of traffic pollution may be focused towards roadside air sampling, whereas the monitoring of ozone is often carried out at rural sites. There are also different scales to the monitoring survey: the scheme may be a national network of air quality monitoring stations; it may be a smaller network designed to monitor regional or local air quality; or the monitoring may be conducted to assess air quality around a specific site or source. In order to ensure the sampling programme is both technically valid and cost-effective, the objectives of the proposed study should be clearly defined at the design stage. The aims of different studies may vary considerably but often include one or more of those listed in Table 4.1.

Table 4.1: Possible aims of ambient air quality monitoring programmes

<ul style="list-style-type: none"> • Comparison of ambient air-quality levels with standards, objectives or EALs • Establishment of baseline levels before development, or after commissioning of a new pollution source • Site-boundary monitoring for compliance with EPR permit conditions • Monitoring of nuisance effects, e.g. odour, dust • Resolving the contribution of one plant/emission source to the background • Assessment of ambient air quality as part of the Local Air Quality Management system or to aid spatial planning • Assessing the effectiveness of any abatement measures or control measures • Verification of predicted ambient air quality levels e.g. from modelling or chimney height calculations • Monitoring for research purposes, such as investigation of health effects, atmospheric chemistry or atmospheric pollution dispersion • For reconnaissance purposes, using simple methods, in order to decide if the cost of installing automatic monitors is warranted, and if so where they should be placed
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The precise aims of the study will determine the monitoring strategy that needs to be adopted. The main stages in developing the monitoring strategy are shown as a flow diagram in Figure 4.1.

The many factors that need to be considered in forming the strategy are introduced and summarised in Table 4.2.

Figure 4.1: Simplified decision flow chart for determining monitoring strategy

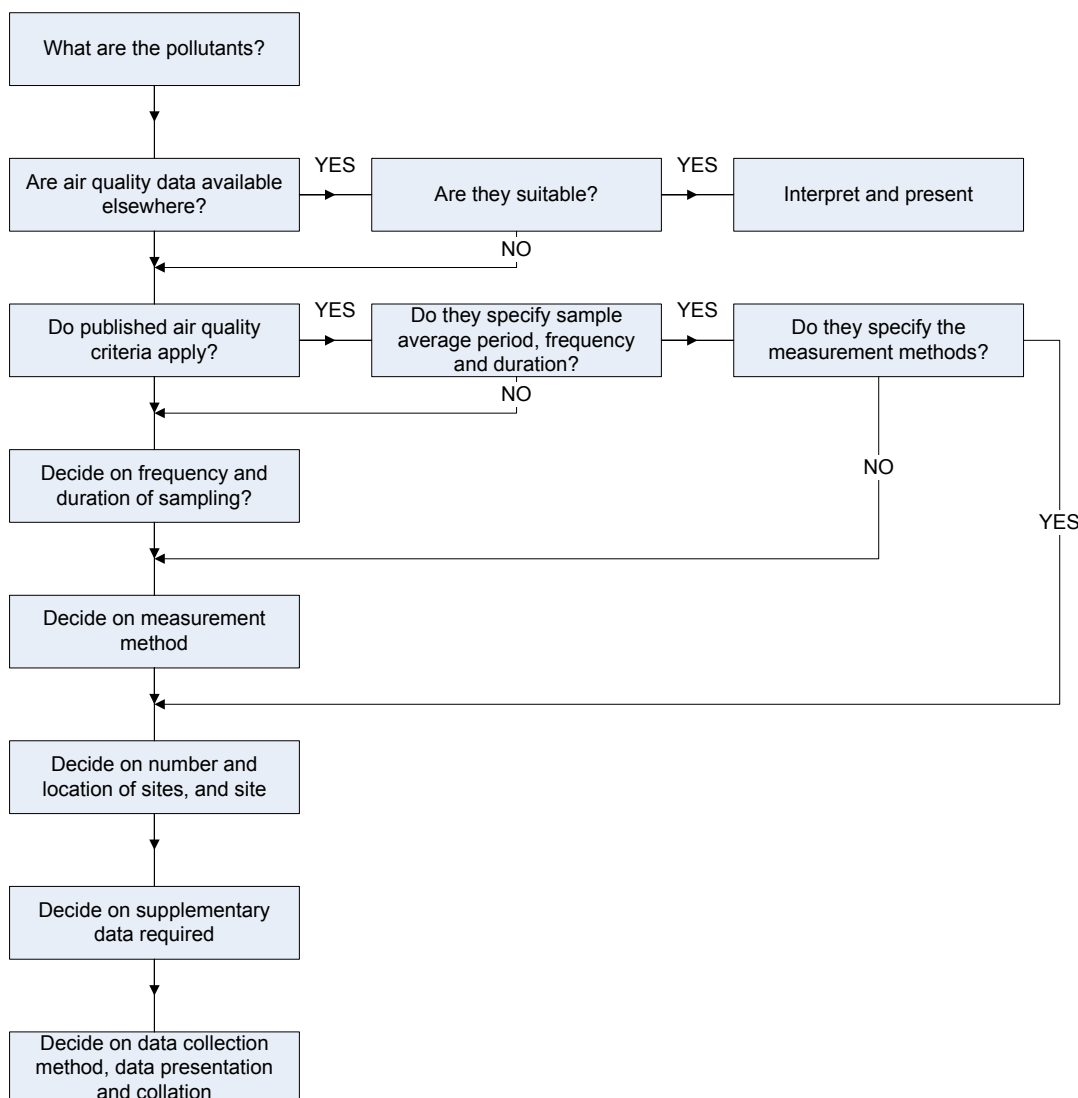


Table 4.2 : Summary of fundamental monitoring strategy considerations

Which species to monitor?	In many cases this may be obvious, but in others it merits careful consideration. Once the target pollutant has been identified, in what form should it be monitored? For example, total hydrocarbons or individual (speciated) hydrocarbons? Total particulate matter or a specific size fraction? Is further analysis required?
When to sample and for how long?	Should sampling be continuous or intermittent? Consider the averaging period of the relevant air quality standard or objective with which the data will be compared; or whether the impact is acute or chronic and the temporal resolution required, e.g. short peaks averaged over three minutes, one-hour averages, daily averages, etc. Short sampling programmes are unlikely to give data representative of general conditions as meteorological conditions and source variations have significant effects on pollutant concentrations.

	Also, where short-term peaks are of interest, these may be unusual events occurring for only a few days each year. Hence short-term monitoring campaigns are of very limited value for characterising air pollution episodes, except for perimeter-fence monitoring of fugitive releases. Consider both the source and receptor when determining when to sample, e.g. during growing season for pollutant-affected crops; during summer for photochemical episodes; during high-wind-speed events for wind-raised dusts.
How to sample?	Both the type of sampling and analytical end method need to be considered. Sampling may be unidirectional or omnidirectional; <i>in-situ</i> , mobile or open path. Method selection involves an appraisal of cost versus performance; the latter including limits of detection, sensitivity, speed of instrument response, susceptibility to interfering species and the overall uncertainty of the measurement.
Supplementary data collection	Other information may be relevant to the study, for example meteorological conditions, process data and traffic flows. Meteorological conditions are obviously important in assessing the impact of a source on its surroundings since they dictate the transport and dispersion of pollutants in ambient air. Many chemical transformations between reactive species in the atmosphere are also influenced by different conditions.
Where to sample?	Spatial considerations encompass both the location of monitoring positions relative to study area or emission source, and individual sampling site criteria, e.g. position relative to local emission sources and any interfering effects. Sampling can be close to source (e.g. fence line) or distant (e.g. for estimating background)
Data handling and data analysis	Is the speed of results generation important? For example, results may be required in real time for public health warnings, whereas several weeks turnaround may be adequate for supplying routine results for EPR permit compliance monitoring.

5. Review of existing information

5.1 Existing monitoring data and ancillary information

Before embarking on an ambient air quality monitoring survey, a review should be made of:

- other relevant monitoring programmes. Both central and local government and a number of other organisations undertake routine monitoring programmes. Consideration of these programmes at an early stage may avoid unnecessary replication of data, and also provide a useful body of data with which comparisons can be made.
- ancillary information such as regional or national emissions inventories providing information on source strengths and their geographical distribution; and supplementary data on, for example, population and traffic movement (Section 9).

Air quality monitoring is overseen at a national level by the Department for Food, Environment and Rural Affairs (Defra) and the Devolved Administrations, within a programme of automatic and non-automatic networks. These networks provide a valuable database on air quality levels within the UK, and can be used to support and supplement data obtained from local monitoring initiatives.

5.2 UK automatic monitoring networks

The Automatic Urban and Rural Network (AURN) is the largest automatic monitoring network in the UK, with over 100 monitoring sites currently in operation. Approximately half of these sites are funded directly by Defra and the Devolved Administrations, while the others are affiliated to Local Authorities across England, Wales, Scotland and Northern Ireland. The monitoring locations range from roadside sites in London to background sites as remote as the Shetland Islands. The locations of all monitoring stations can be found at <http://aurn.defra.gov.uk>. Data from the AURN Network is collected from each site every hour by telemetry. This data, along with archived data from current and defunct monitoring sites, is then made directly available via the Internet (<http://uk-air.defra.gov.uk/>). In addition, annual reports are published by Defra, and provide detailed descriptions of the site locations and monitoring methods, together with a summary of measured data against the relevant air quality standards and objectives.

The London Air Quality Network (LAQN) collates data from over 30 London Borough Councils, in addition to the London AURN stations, to provide a detailed picture of air quality in London. Data is archived and updated hourly at <http://www.londonair.org.uk>. Other examples of local air quality networks include the Herts & Beds Air Quality Network, the Kent & Medway AQ Monitoring Network, Great Air Manchester and the Welsh Air Quality Forum.

The Automatic Hydrocarbon Network uses automatic gas chromatographs to provide hourly concentrations of speciated VOCs at 5 UK locations. This is complemented by the Non-Automatic Hydrocarbon Network (see Section 5.3).

Table 5.1: Summary of UK automatic networks

Network	Description	Pollutants	No. of Sites*
Automatic Urban & Rural Network (AURN)	Located throughout UK ranging from major urban centres, industrial and roadside locations to suburban, rural and remote locations	NO _x NO ₂ SO ₂ CO O ₃ PM ₁₀ PM _{2.5}	132
Hydrocarbon Network	Located in the major urban centres of Glasgow and London and the rural locations Harwell and Auchencorth Moss.	26 hydrocarbon species	5
London Air Quality Network (LAQN)	Local Authority monitoring stations across London, managed by Kings College London	NO _x NO ₂ SO ₂ CO O ₃ PM ₁₀ & PM _{2.5}	14

*Number of sites correct as at January 2011. Not all sites are equipped to monitor all pollutants.

5.3 UK non-automatic monitoring networks

Automatic monitoring is supplemented by a number of non-automatic sampling networks. These networks tend to be based on simpler monitoring methods such as diffusion tubes and often monitor similar pollutants to those in the automatic networks, but at a greater number of sites e.g. hydrocarbon networks. In addition, some of the networks monitor less frequently measured trace pollutants (e.g. TOMPs), but at a limited number of sites. A

summary of the networks is provided in Table 5.2. The data are made available by Defra in the form of an annual report. Results are also reported periodically on the Internet (<http://uk-air.defra.gov.uk/>) after lab analysis.

Table 5.2: Summary of UK non-automatic networks*

Network	Description	Pollutants	No. of sites
The UK Black Smoke Network	The network comprises 10 AURN locations and 11 locations from the former Smoke and SO ₂ Network. Uses 8-port sampler method, which exposes a sample filter for 24 hours midnight to midnight. Filter then analysed with reflectometer.	Smoke	21
Toxic Organic Micro pollutants (TOMPS) Network	Network established to determine environmental levels of suspended and deposited toxic organic micropollutants, using modified Andersen GPS-1 Pesticide samplers. Site locations include two urban centres, one coastal site and three rural background sites.	PCDDs PCDFs PCBs	6
PAH Network	Close links with the TOMPS network. Uses Digitel DHA-80 high volume PM ₁₀ aerosol samplers to provide data on up to 39 polycyclic aromatic hydrocarbons.	PAHs	31
Acid Deposition Network	Monitors composition of precipitation across UK. Incorporates Nitric Acid Monitoring Network	Conductivity pH NH ₄ ⁺ , Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻	38
National Ammonia Monitoring Network	Denuders and diffusion tubes used to make monthly measurements across UK.	NH ₃	95
Heavy Metals Monitoring Networks	Comprises Urban/Industrial Network (which was previously the Lead & Multi Elements Network) and Rural Heavy Metals and Mercury Network.	As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Pt, V and Zn Precipitation & Cloud Water	39
Non-Automatic Hydrocarbon Network	Measures ambient benzene levels using pumped sample tubes exposed for fortnightly sample periods. Samplers located at AURN stations.	Benzene	35

*Correct as at January 2011

5.4 UK review groups

In order to provide a forum for the review of current knowledge on air quality issues and its effects, and to provide recommendations to Government, a number of working groups of experts have been established by Defra including:

AQEG: Air Quality Expert Group
 COMEAP: Committee on the Medical Aspects of Air Pollution

Each of these review groups has prepared a number of detailed reports that summarise air quality information, monitoring techniques, trends in pollutant concentrations, and effects upon human health and the environment.

6. Which species to measure

6.1 Targeting the pollutant

For a single local source, emitting non-reactive pollutants, the monitoring of the concentration of one pollutant may be sufficient to quantify the behaviour of others from the same source, if their ratios in the source emission are known. However, this situation is rarely encountered in practice and it is usually necessary to consider monitoring for a number of pollutants. Usually, the target pollutants will be those strongly associated with the suspected emission source, e.g. nitrogen oxides from road traffic, fluoride from brickworks, or dust from a mineral extraction process. However, there are some instances where the pollutant must first be identified before thought can be given to quantifying it, e.g. when nuisance odours are investigated. In the case of emissions from EPR permitted installations, the list of prescribed substances for release to air provides potential targets. It may be appropriate to prioritise the species emitted by comparing expected ground-level concentrations with accepted air quality standards or objectives.

For many air quality monitoring surveys, the aims and objectives will effectively define the pollutants that need to be measured: examples are monitoring for comparison with published air quality criteria, or monitoring of the impact of releases under EPR. However, even when the pollutant species have been specified, it may still be necessary to consider what precise form of the pollutant should be measured.

6.2 Different Phases

Some pollutants are partitioned between gaseous and particulate phases. There are examples of both organic pollutants, e.g. PAHs, and inorganic pollutants, e.g. mercury. The monitoring method needs to be able to sample the selected phase or both phases, as appropriate.

6.3 Total and speciated measurements

For certain pollutants it is common to express the concentration as the sum total of the individual species present, e.g. routine monitoring of total hydrocarbons. Alternatively, some members of a group of pollutants may be of special importance and may require specific determination. An example is the speciated measurements of benzene, toluene and xylenes. Analogous to this concept is sampling for a particular physical fraction. For example sampling for total suspended particulate matter, or alternatively for particles of diameter $<10\ \mu\text{m}$ (PM_{10}) or diameter $<2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$).

6.4 Further chemical or physical characterisation

Pollutant sources can sometimes be identified by chemical analysis of the samples, based on the fact that the presence of, or ratios of, certain elements are characteristic to one of the sources. For example historically, the ratio of bromine to lead could discriminate between lead-in-air contributions from a smelter and from traffic. Further characterisation may be of the whole sample or it may be more appropriate to analyse individual particles by, for example, scanning electron microscope (SEM) coupled with energy dispersive analysis by

X-rays (EDAX). Physical characterisation by the visual appearance and morphology of particles can also be a powerful tool in identifying the source of the emissions.

6.5 Media other than air

Sampling from media other than air, e.g. soil, herbage or water sampling, is most commonly carried out when an objective of the study includes the impact of the pollutants on human or animal health, crops or fauna and flora. In such cases, the pathways by which the pollutants enter the end receptor must be considered and could include ingestion as well as inhalation of the pollutants. An example would be where the objective of the study was to assess the effect on cattle of fluoride emissions around an aluminium smelter. Ambient air quality monitoring in isolation would not provide an adequate assessment and it would be necessary to sample from the medium that forms the most appropriate receptor: in this case, the pasture that the cattle feed on. Since grass absorbs most fluoride directly from the air rather than from the soil, the sampling strategy should include grass sampling and air sampling as part of the overall survey. Measurement of the amounts and rates of pollutant deposition are important where contamination of vegetation and soil is an issue. Other examples are human exposures to dioxins via cows' milk; and exposure to lead, where inhalation of dust and consumption of lead-contaminated garden produce are major routes. In the latter case it would be appropriate to include both air and herbage sampling in the monitoring strategy.

Herbage sampling needs to take account of seasonal factors: the levels of contamination in vegetation can depend strongly on meteorological factors and growth rates, hence sampling in and out of the growing seasons needs to be considered.

7. When to sample, how long to sample for, and how many samples to take

7.1 General considerations

Three separate issues need to be considered:

- the duration of the whole sampling programme
- whether continuous monitoring is required or intermittent sampling can be carried out
- what the averaging period will be over which an individual measurement is made (for intermittent sampling) or the data are to be expressed (continuous or intermittent sampling).

When monitoring is for comparison with certain air quality standards or objectives, these parameters may already be specified. In other cases the decisions will need to be based on how the pollutant concentration is expected to vary with time, the nature of the effects of the pollutant and the characteristics of the monitoring methods available.

7.2 Continuous or intermittent sampling

The expected short-term variability in pollutant concentrations determines whether it is necessary to sample continuously to accurately characterise air quality, or whether it is possible to sample intermittently. If pollutant levels vary so frequently and significantly that intermittent sampling periods are not likely to be representative of the study period as a whole, then sampling must be carried out continuously. Continuous sampling does not necessarily mean using direct-reading real-time analysers; it is possible to sample continuously using non-direct-reading manual sampling methods with longer sample averaging periods. For example, continuous daily-average concentrations of black smoke and sulphur dioxide were measured for many years using eight-port bubbler sampling apparatus with a subsequent laboratory analysis stage.

If intermittent sampling is carried out then one must consider how long it is necessary to sample for and how many samples to take. This is linked to the averaging period over which the measurements are eventually to be reported (see Section 7.3). If measurements are being made for comparison with a particular air quality standard then it is necessary to take into account the averaging time of that standard. Ideally the duration of each sample should not be greater than the averaging period over which it is expected to be expressed. The duration of individual samples forming part of a continuous measurement may be considerably smaller than the averaging time required for the results, and this may be because the measurement method has performance limits (e.g. sample saturation, sample breakthrough) that make this necessary, or because the air quality standard has been defined in this way. For example an air quality standard may be expressed as an annual-average concentration calculated from daily (24-hour) samples.

Two approaches to scheduling intermittent sampling have been described¹. The modified random system commonly used in air sampling networks, calls for sampling intervals of fixed length, e.g. weekly. During this sampling interval, one day is randomly chosen for sampling. The alternative approach, the systematic approach, calls for starting the sampling programme on a day picked at random, followed by sampling at fixed intervals, other than seven days, from that day onward. The systematic approach appeared to display a better relative precision.

For soil or herbage measurements, individual samples are of course obtained virtually instantaneously, rather than over a distinct averaging period. Nevertheless, many pollutants are accumulated by vegetation over periods of days or weeks, and the sampling frequency of herbage should take into account the expected accumulation time. To characterise large temporal variations it is necessary to carry out frequent sampling, to enable both the peak concentrations and longer-term concentrations to be defined.

7.3 The averaging period

The wide choice of monitoring methods available is accompanied by a similarly wide choice of time periods that can be used for measurements. The aims or objectives of the study may in some circumstances unambiguously define the averaging time. This is the case for monitoring to assess compliance with EU Directive Limit Values, since the averaging time is specified along with the limit concentration. Examples of National Air Quality Standards published in the UK National Air Quality Strategy, and their associated averaging times, are shown in Table 7.1.

Table 7.1: Examples of National Air Quality Standards for England & Wales

<i>Pollutant</i>	<i>Standard Concentration</i>	<i>Measured as</i>
Benzene	5 µg/m ³	annual mean
1,3-butadiene	2.25 µg/m ³	running annual mean
Carbon monoxide	10 µg/m ³	max daily running 8-hour mean
Lead	0.25 µg/m ³	annual mean
Nitrogen dioxide	200 µg/m ³	1 hour mean
	40 µg/m ³	annual mean
Particulates PM ₁₀	50 µg/m ³	running 24-hour mean
Particulates PM _{2.5}	25 µg/m ³	annual mean
Sulphur dioxide	266 µg/m ³	15-minute mean

When the averaging period has not already been fixed, it must be decided upon by taking into account the expected short-term variability in pollutant concentrations and whether such peaks are of importance. Consider the receptor of concern and how long that receptor needs to be exposed for in order to experience possible harm. Pollutants having acute health effects are generally measured over short averaging periods. For example, sulphur dioxide has a major impact on receptor organisms over short-term high-concentration episodes and hence mainly short-period, high-frequency information is relevant. An example at the other end of the scale is lead, which has a long-term cumulative effect making short-term peaks much less important. This is reflected in the long averaging period that applies to the air quality standards for lead. Some pollutants have more than one averaging time of interest because they adversely affect more than one type of receptor and these different adverse effects occur over different periods of time. For example, nitrogen dioxide has a 1-hour standard to protect human health and an annual standard to protect ecosystems. Table 7.2 gives some recommended² averaging times for selected applications.

Table 7.2: Suggested averaging times for different studies

<i>Order of minimum averaging period</i>	<i>Type of survey</i>
10 s	Odour assessment; mobile sensors; acute respiratory effects; studies of puffs
3 min	Useful for studying odours and acute health effects if faster response not available
1 h	Time average concentrations; dispersion studies; diurnal changes; discrete source studies; damage to plants
24 h	Chronic health effects; area source studies; effects of weather systems; effects on different days of the week
1 month	Seasonal and annual variation; long-term effects from global source

Sampling for odours is a special case. Odours resulting from factory stack emissions are often perceived for only a few seconds at a time, when atmospheric turbulence causes the undulating plume to reach ground level. Sampling to assess odours must be carried out over similarly short averaging periods if these intermittent peaks are to be resolved.

If the objective of the study is to verify or support predicted ground-level concentrations made by computer dispersion modelling, then the latter concentration predictions should themselves have been made using an appropriate averaging time and of course the same averaging time should be used in the follow-up monitoring survey.

The chosen averaging period may limit the choice of measuring techniques and vice versa, as some methods may only be capable of operating within a finite range of sampling averaging times. This is particularly true for non-continuous methods having an associated analytical end-method stage, for which a sufficient mass of pollutant must be sampled to achieve an adequate lower detection limit. The mass sampled is dependent on the pollutant flux to the sampler. The determining factor becomes the sampling time, not only for diffusive sampling, but also for active sampling since the sampling flow rate is usually constant. The response time or sampling time of the method should be considered in relation to the required averaging period. Very often the choice will be between a direct-reading continuous method providing a vast quantity of data with a very fine time resolution, and less expensive, indirect manual methods. The latter may be used to sample virtually continuously and are perfectly adequate for many applications. A notable example is the widespread use of NO₂ diffusion tubes, which are usually exposed for about two weeks, but application of an empirical factor to the results enables an estimate of the 98th percentile of hourly means to be obtained³.

When logging data from a continuous method, it should be noted that the shorter the averaging period, the greater the volume of data collected i.e. an averaging period of one minute will produce 60 data points per hour, compared with 12 data points per hour if 5 minute averages are logged. This means that the data storage capacity of the logger is reached over a much shorter monitoring period. It is also difficult to look at very large datasets e.g. a year's data in one minute resolution, and some spreadsheet functions cannot cope with this volume of data.

7.4 Duration of the sampling programme

Pollutant concentrations are significantly affected by temporal variability, such as: seasonal variations and diurnal cycles in meteorological conditions and emission patterns; weekday/weekend differences; and longer-term variations in, for example, production/manufacturing, fuel usage, etc. Therefore, short-duration sampling programmes are unlikely to give data that cover these different variations, so that they may be unrepresentative. Short-term peaks may be unusual events occurring on only a few days in each year (Figure 7.1) and if these episodes are of interest, an extended monitoring period may be required to capture them. Short-duration programmes aimed at episode identification (particularly from elevated point sources) rely on an element of luck and often large expenditure can result in meagre success.

It follows that a monitoring survey of a full year or more is ideally required to take account of the full range of the above variables, although a shorter survey that aims to include an equal number of summer and winter months can sometimes provide a reasonable and more cost-effective estimate. What constitutes a suitable survey duration will also depend on the measurement method used, particularly the sampling duration and frequency. It has been suggested⁴ that if intermittent sampling is conducted weekly, it will be necessary to sample over a period of not less than three months to obtain a representative annual average concentration

In general, long sampling programmes are preferable when comparisons are being made with long-term air quality standards. Figure 7.2 shows the relationship between mean NO₂ calculated from monthly data compared to the mean value obtained from annual data.

Figure 7.1: Number of days of poor air quality (NO₂ exceeding 100 ppb) at AURN sites in 2009

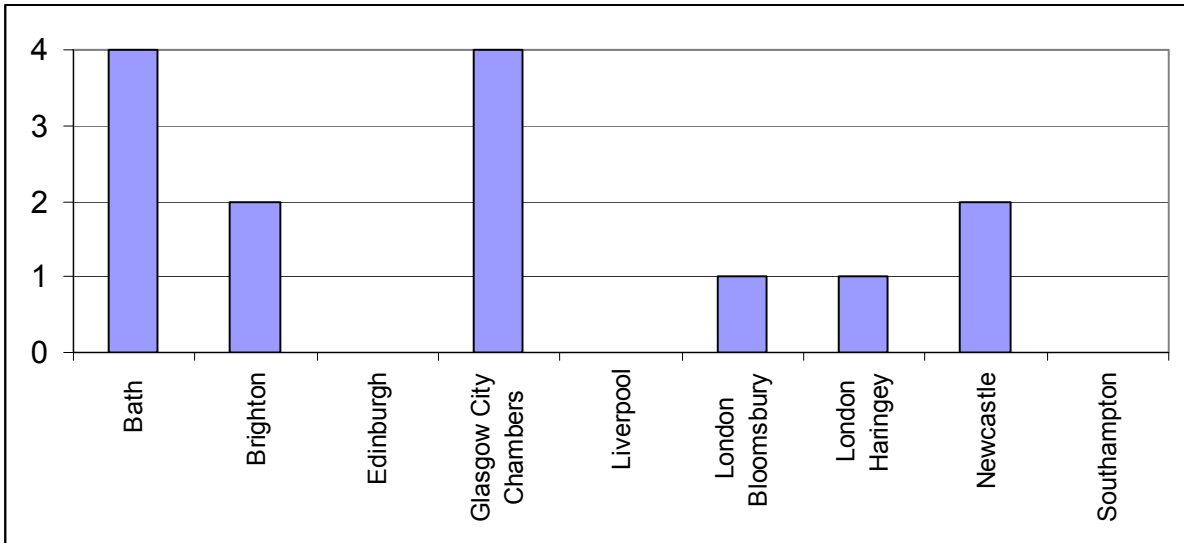
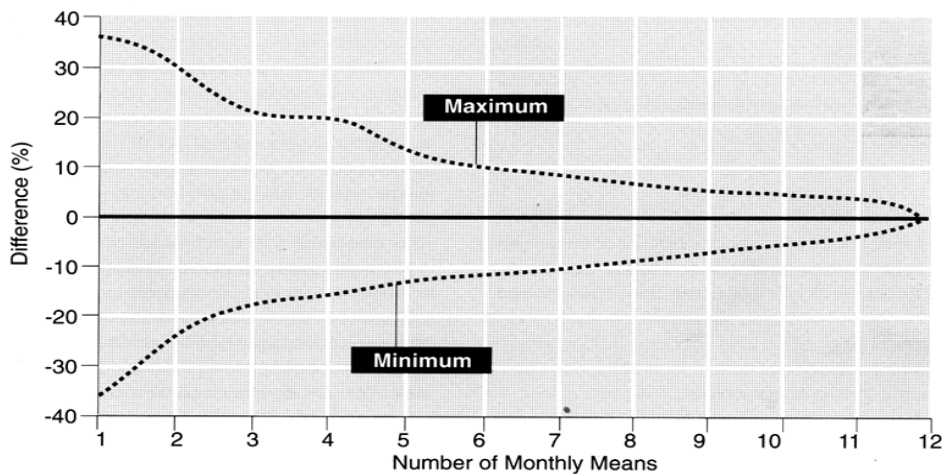


Figure 7.2: True NO₂ annual mean compared to averages over different monthly means⁵



8. How to measure

8.1 Sampling approach

8.1.1 Omnidirectional sampling or directional sampling

Very often, ambient air quality surveys are designed to assess the impact of a particular process, works or site. If sampling is carried out from all directions or under all wind directions (omnidirectional sampling), then the direction of the wind must be taken into account when the data are assessed. Alternatively the sampling itself may be designed to be directional: gases or suspended particulates would then usually be collected by an active sampling system linked to a wind vane and anemometer. Sampling only occurs when the wind is blowing from a specified direction and is above a minimum wind speed.

Directional samplers are most useful when there is a clearly defined suspected source of the pollutant and the background air concentration is expected to be low in comparison. In such cases a single directional sampler, located downwind of the source for an appropriate duration, would be expected to give a good estimate of that source's contribution. It can be an advantage to use a directional sampler with two wind-vane-operated sampling receptors, one receiving sample when the wind arrives from the narrow direction of the source, and the other receiving sample all the remaining times.

Most active directional apparatus samples from a pre-selected wind direction arc of say 30 to 70 degrees that has the axis of interest as its centre line. The distance from the source should be chosen to allow an acceptance arc in this range to be used, whilst at the same time taking account of the type of source: for example, the plume from an elevated source (stack) is expected to reach ground level after a downwind distance equivalent to between 10 and 20 times the stack height (although a more accurate estimation can be obtained from atmospheric dispersion modelling studies). Emissions from any other interfering pollution sources within the acceptance arc will lead to an overestimation of the contribution of the targeted source of interest. On the other hand, if there are other sources that lie outside the acceptance arc then their contribution will be considered part of the background concentration. These situations can be minimised by carefully choosing the most suitable sampling distance from the suspected source in conjunction with an appropriate acceptance arc. If this is not sufficient, several directional samplers can be positioned in different directions around the works to obtain an integrated value of the contribution of the targeted source relative to that of other sources and the general background⁶⁻⁸. Alternatively, directionally-resolving equipment such as the Rupprecht & Patashnick ACCU System can be set up to sample from three or more wind sectors.

8.1.2 Fixed-point sampling or open path methods

The most common sampling system is that of a network of sites at fixed locations, each providing instantaneous spot-concentration values or time-averaged concentrations from a fixed point in space. The success of a fixed network of *in-situ* samplers will be largely dependent on the care with which the sites are chosen in regard to the survey objectives. The principles applying to the location of fixed monitoring sites are covered in detail in Section 10.

Open path measurement techniques allow measurements to be made directly in the atmosphere without obtaining samples. The average concentration of a specifically targeted pollutant is determined over an extended measurement path, rather than at a localised point. Some methods allow the concentration to be spatially resolved. Others give the average concentration over the whole path length, which finds application in assessing the transfer of pollutants across site boundaries and along roads and runways, but the difficulty of interpreting integrated-path data should be recognised. Differential optical absorption spectroscopy (DOAS) instruments such as OPSIS use a double-ended system which measures the average concentration between the instrument and a reflector up to hundreds of metres away. The system is able to measure many common pollutants including SO₂, NO, NO₂, H₂S, O₃, benzene, toluene, xylenes and formaldehyde. Laser interferometry detection and ranging (LIDAR) can measure aerosol particles, and differential absorption LIDAR (DIAL) is able to carry out range-resolved measurements of specific pollutants (e.g. SO₂, NO₂, O₃) over several kilometres by analysing backscattered laser radiation. LIDAR and DIAL are particularly suitable for producing two-dimensional or three-dimensional maps of pollutant concentrations over large areas such as industrial complexes. Measurement by open path techniques tends to be expensive because of the complexity and sophistication of the equipment and data handling facilities.

Open path methods lend themselves to mobile sampling: this may be vehicle-mounted instruments for carrying out measurements at a large number of locations, or for measuring the pollution concentration profile along a given route. Systematic traversing of a plume emitted from an elevated point source is an application well suited to mobile monitoring systems but, because meandering of the plume tends to distort the pattern, each traverse gives only an approximation to the instantaneous cross-wind spread of the plume and several hours of sampling are required to define the plume envelope in a way that could be related to patterns observed from fixed networks. Airborne systems using *in-situ* continuous analysers have been used for some specialist applications, such as tracking power station plumes across the North Sea. Such systems have the advantage of greater freedom of movement, three-dimensional capability and higher speed of traverse, but are of course so expensive as to be only justified for specialist investigations.

8.2 Choice of measuring method

For many pollutants, a reference method will have been stipulated which must be used in order to comply with standards, thus reducing or eliminating any choice of measuring method. However, where no stipulated or best practice method is applicable, the general principles to consider are outlined in the following sections.

8.2.1 Method Performance

Wherever possible, MCERTS certified instruments should be chosen. MCERTS is the Environment Agency's Monitoring Certification Scheme. The MCERTS performance standards⁹ for continuous ambient air-quality monitoring systems (CAMS) have been defined so that MCERTS-certified CAMS will be capable of meeting the requirements of Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. The pollutants covered include nitrogen monoxide (NO), nitrogen dioxide (NO₂), sulphur dioxide (SO₂), carbon monoxide (CO), ozone (O₃), particulate matter (PM₁₀ and PM_{2.5}), benzene and benzene-like VOCs.

If an MCERTS-certified CAM cannot be used for the study, the following method performance characteristics should be considered when determining how well a method is suited to a particular application:

- **Method sensitivity.** This is the amount of indication (the response) produced per amount of air pollutant sampled. For a direct-reading continuous analyser this may be the signal output in millivolts per unit concentration air pollutant. For an integrating wet method, this may be the amount of titrant needed per unit concentration air pollutant to indicate the end-point in an absorbent solution. A highly sensitive method is needed if it is required to measure small changes in air pollutant concentrations. Note that these small changes may be at low or at high concentration levels.
- **Limits of detection and measurement range.** For a method of a given sensitivity, there will be a minimum air pollutant concentration that will produce a measurable response. This is the lower detection limit (LDL) and is influenced by the level of background noise signal or the magnitude and variability of blank values. The method should also produce a linear or other known response to the air pollutant concentration over a particular range. For an instrumental method, there is often one measuring range or it may be possible to switch between a number of alternative measuring ranges. For indirect methods, sufficient sample is collected to enable the analytical end method to be used in its measurement range. The range is effectively altered by varying the amount of air sampled (by altering the sampling flow rate or by altering the duration of sampling) and hence the amount of pollutant collected. However, consideration must also be given to the measurement average time required.

- **Speed of response.** This is most relevant for direct-reading instrumental methods, especially when measurements over short averaging periods are required. The instrument must be capable of responding to the pollutant with sufficient speed to enable the pollutant concentration peaks and troughs of interest to be resolved.
- **Selectivity and specificity.** The measurement method should be specific for the pollutant of interest, or be selective enough to distinguish and quantify the pollutants of interest from unwanted species. At times it may be desirable to monitor with a non-specific method that measures a group of compounds that have similar chemical properties, e.g. the acidimetric method of measuring net gaseous acidity in air samples, which is expressed as the equivalent concentration of SO₂.
- **Susceptibility to interferences.** There are species other than those of interest that could potentially affect the measurement result, giving either a positive or a negative interference. Examples are the presence of water vapour in many infrared analyses, and the presence of organic acids when analysing fluoride by ion chromatography. For samples collected for later analysis, the stability of the sample is important.
- **Accuracy and precision.** Many of the previously mentioned method characteristics have an influence on either the precision or the accuracy, or both. The *overall uncertainty* U (or, as it is more properly known, the *combined uncertainty*) of the result given by an apparatus or a measuring procedure is the estimate of the range of values that the 'true' value can be expected to fall within. It combines in a single value both the *precision* – the degree of agreement between the successive measurements – and *accuracy* – how close the measurement is to the "true" value. The combined uncertainty is conventionally expressed at a confidence level of 95% in the form:

$$\text{(Result): } X \pm U \text{ (units)}$$

For example: nitrogen oxides concentration = 500 ± 35 ppm.

The *repeatability* (r) for any single result is given by the standard deviation (s) multiplied by the value of the mathematical function known as Student's t (obtained from t -tables) appropriate for that (large) number (n) of repeats at 95% confidence limits:

$$r = t \cdot s$$

The *bias* (d) is the difference between the mean (x) of the results and the accepted "true" value (μ) of the reference gas:

$$d = x - \mu$$

The *uncertainty* (U) is the combination of the random and systematic errors:

$$U = d + r$$

General guidance¹⁰ has been published by the International Standards Organisation (ISO), as well as guidance^{11, 12} on estimation of uncertainty for analytical measurements and specific guidance¹³ on certain aspects of air quality measurements.

- **Reliability and unattended operation.** Methods vary in the degree of manual operation and continuing attention they require. For example, direct-reading continuous analysers can require frequent calibration; indirect methods may require renewal of reagents.

These considerations, and the overall reliability of the method, can be more or less important depending on the type of monitoring programme. Long-term reliability and unattended operation would be of crucial importance in a network of monitoring sites at remote locations, but may be less important for a short-term survey close to the laboratory.

8.2.2 Other Considerations

Table 8.1 outlines other factors which may influence the choice of monitoring method.

Table 8.1 : Other influences on choice of monitoring method

Method cost	One factor in the choice of measurement method to be used is the resources available, both financial and human. There are wide variations in the capital costs and running costs of different measurement methods. Some simple, inexpensive apparatus can be labour-intensive when used for extended durations and may incur additional analysis costs. Automated monitoring equipment is available for unattended operation but the capital costs are usually higher and ongoing running and maintenance costs must be met.
Method complexity	The availability of technical staff who have the necessary experience, or who could be trained, is a factor to be considered when selecting an appropriate method. Manual methods, for example diffusion tube sampling are less complex than direct reading continuous analysers, which can require a higher degree of ability in the event of operational failure. However, even with simpler methods it is important that adequate training and instruction is given.
Manufacturer support	This is especially relevant for instrumental techniques. Important considerations here are: the extent of back-up available from manufacturers in the event of equipment malfunction; the availability and delivery of consumable items and spares; the turn-around time for servicing and repairs; and the provision of replacement instruments if some have to be taken out of service.
Portability and size	Generally, the simpler, cheaper methods tend to be more portable than the more expensive, complex methods and can be very useful for obtaining a large number of samples in a short time. Continuous analysers in particular can be quite heavy and bulky and may also require a warm-up time of several hours before monitoring can start. The exceptions are some remote methods, which tend to be very expensive but are designed to be mobile.
Practical requirements	Some monitoring apparatus is designed to be operated in the open air. However, many instruments require some sort of housing to provide shelter, weatherproofing and security. Some apparatus need very few facilities, if any at all, e.g. deposit gauges, dust slides, diffusion tubes. Other apparatus need much more, and a site containing a number of direct-reading continuous analysers will require a secure housing, air conditioning and an electricity supply.

9. Accompanying measurements and supplementary data

9.1 Meteorological data

Meteorological factors are important because they determine the transport and dilution of pollutants in the atmosphere, influence chemical transformations of species in the air, and affect the mechanisms and rates of removal of pollutants from the atmosphere. Knowledge of wind direction and wind speed is essential for attributing pollution episodes to individual point sources. Meteorological conditions will be subject to diurnal and seasonal variations which can superimpose an effect on those due to variations in the pollutant emission source strength. For these reasons, due regard needs to be given to assessing, and possibly measuring, meteorological conditions and emission source details.

Very often, emissions from sources are diluted and transported within a relatively shallow boundary layer adjacent to the Earth's surface, typically no higher than 100–1300 m. Within this layer, turbulence, created by the roughness of the terrain, the strength of the wind and by rising parcels of warmer air, causes progressive dilution of the pollutants with cleaner air as the pollutants are transported away from the source by the wind. Meteorological parameters that are often considered in an air quality monitoring strategy are outlined in Table 9.1.

Table 9.1 Meteorological parameters monitored alongside air quality

Wind speed and direction.	These are often measured at one or more of the monitoring sites to indicate which direction the sampled air emanates from. Ambient pollution levels are often inversely proportional to wind speed.
Temperature and solar radiation	These are measured less often, but can be useful for estimating the likely atmospheric stability conditions and may be used to interpret measurements of photochemically reactive chemicals, e.g. ozone, and the generation of secondary pollutants, e.g. nitrogen dioxide. Vertical probing of the atmosphere by Doppler-SODAR, instrumented towers or radio-sonde balloons provide accurate determinations of atmospheric stabilities and mixing heights, but are outside the scope of most ambient air quality monitoring surveys. Such data are usually sought from the Met Office.
Rainfall, mist, cloud, humidity and surface wetness.	These provide information on the mechanisms for removal of atmospheric pollutants and are particularly important for studies of the corrosive effects of air pollutants on materials. These parameters are also very important for interpreting the results of dust surveys, since dryness and low humidity can result in increased suspended particulate concentrations due to suspension of surface dust. Cloud cover can also be used to infer solar radiation.

Meteorological parameters are measured at a large number of locations across the UK by the Met Office and some other organisations. In some cases it can be appropriate to make use of these data. In other situations, the highly localised nature of meteorological conditions makes it necessary to carry out measurements of meteorological conditions at the point of sampling.

9.2 Other information

Information on the source of pollution is obviously important. Some industrial processes may be cyclic, over periods of hours or days. Other works may shut down overnight or during certain times of the year. Interpretation of ambient data can be helped by having information on activity patterns and fuelling practices e.g. position on growth curve of intensively-farmed poultry or details of fuel switching by power stations. In some cases it may be necessary to take account of time lags between changes at a source and changes at an ambient monitor, due to the time required for dispersion through the atmosphere from source to monitor. Whether one is measuring traffic pollution as a specific aim, or the measurements happen to be subject to interference because the monitoring site is close to a busy road, the daily patterns of traffic flow will be important in interpreting the data.

10. Where to sample

When choosing a monitoring location for a study there are a number of factors that must be considered. It is rare to find a perfect monitoring location, as the choice of location is usually a compromise between competing considerations. Table 10.1 outlines a number of the main issues that should be considered when assessing a potential location. These include a number of technical points that should be taken into account so that the aims and objectives of the monitoring study can be addressed. They also include practical considerations, which must be met so that the equipment can be safely and successfully deployed.

Further information on the requirements for monitoring locations can be found in the Air Quality Standards Regulations 2010¹⁴.

Table 10.1: Influences on choice of monitoring location

Sensitive receptors	Commonly, a monitoring study will be concerned with the impact at a sensitive receptor. A sensitive receptor is a point of particular vulnerability within the local community, for example a nursing home or school within a village or town, or a residence affected by the source. Location of equipment at the sensitive receptor most likely to receive the greatest impact from the pollution source is therefore often the most suitable monitoring location.
Multiple monitoring locations	When using more than one monitoring location to assess the impact from a source it is important to consider the location of the monitors with respect to each other. By locating the monitors at different bearings from the source and collecting meteorological data concurrently with real-time data, the combined directional information can aid in locating the point of emission (see Section 12, Triangulation) By placing the monitors or samplers at the same bearing from a source, but at different distances, information about the impingement and drop-off of pollution from the source can be gained.
Prevailing wind	When positioning monitors or samplers it is important to consider the prevailing wind conditions of the area. In the UK, the predominant wind direction will generally be from between the South and the West. Some areas may experience an unusual prevailing wind if the topography plays a significant role in directing the local air movement. An example of this is a valley where the wind tends to be directed up or down the valley. Significantly altered air flows occur at water-land boundaries

	due to the relatively large differences in temperature that can occur between the two surfaces.
Distance from source	<p>The distance at which a monitor or sampler is positioned relative to the source of concern will have an enormous effect on the concentrations measured. Plumes from sources that are released at ground level, and are not buoyant, will tend to disperse as they move away from the release point. The amount of dispersion will depend on the nature of the pollution, the wind speed, atmospheric mixing, ground roughness and other factors. Such sources will, in nearly all cases, see a reduction in concentration as distance from the source increases. By contrast, a hot, buoyant plume e.g. from a fire, or a plume emitted at some height above the ground e.g. a stack emission, will take time to ground as it moves away from the release point. Therefore, the point of maximum impact from this type of plume may be some distance away. It is sometimes convenient to approximate the maximum impact distance from a stack in terms of the effective height of the stack (the height to which the plume rises, taking into account plume velocity and buoyancy). Some estimates put the maximum concentration distance at 10 x effective stack height, others at 15 or even 25. This is a very rough rule of thumb and does not offer a precise prediction. The physical characteristics of the pollutants should always be borne in mind; larger particulate matter is subject to gravitational settling and may be deposited much closer to the emission source than gaseous pollutants.</p> <p>The use of a modelling study can be informative and useful when choosing monitoring locations. However, the model will commonly produce two different outputs. (1) The point of maximum impact in terms of maximum hourly averages over the modelling period (the period of the meteorological data used will customarily be between one to ten years). It is likely that if a monitoring location was chosen that corresponded to this maximum prediction that the location would be so close to the stack that only on very rare occasions would the monitor measure releases coming from the stack. (2) The point of greatest average concentration over the modelling period i.e. if the modelling period is five years then the average impact over those five years is calculated at points over the modelled area. The point of greatest average concentration as predicted in (2) will almost certainly be at a greater distance from the stack than the predicted maximum hourly average given by (1). The maximum point from (2) is possibly the better monitoring location because the plume will impact here more frequently and the resultant measurements will provide more information about the nature of the source. This is particularly true if the monitoring study is over a relatively short period compared to the modelling period.</p>
Upwind–downwind comparisons	To assess the contribution from a specific source, a common approach is to place two monitors in a line either side of the source at the same time collecting representative meteorological measurements that can be collated with the pollution concentrations. Over a suitable period of time, the average upwind concentrations can be subtracted from the downwind concentrations and the source contribution determined.

Interfering sources	When monitoring to establish the impact from a specific source, the location should not be subject to interfering influences or sources not encompassed by the survey objective e.g. nearby rooftop vents, chimney stacks, multi-storey car parks. Where this is not possible, it may be necessary to use directional sampling apparatus or to collect concurrent meteorological data to enable the emissions from the source of interest to be clearly distinguished.
Background	Most sampling or monitoring surveys require one or more sites at background locations for comparative purposes. These should be located away from the influence of major sources and be representative of the wider region.
Topographical effects	Individual topographic features in an area may cause localised patterns of air flows, affecting the distribution of air pollutants over the area for example bringing the plume to the ground nearer to the source than would otherwise be expected. Sampling sites should not be located in areas where unusual topographic effects are expected unless their investigation forms part of the aims and objectives of the study.
Sampling height	<p>As the concentration of a pollutant will vary considerably with height above ground it is important to choose a monitoring height that fits in with the aims of the study. In most situations the monitoring height will be between one and two metres from the ground. This is a suitable height for assessing the impact on humans as this is the general height at which people breath. However, it is worth noting that for emissions released from ground level the difference of only one metre in monitoring height can result in noticeably different results.</p> <p>There are occasions where monitoring appreciably above ground level makes sense. An example of this is where there is need to remove the dominance of ground level emissions in order to assess the impact of elevated releases. This approach has been used on steelworks looking at the relative contributions to PM₁₀ from fugitive emissions coming from the ground and process emissions coming from a high stack. By placing the monitor 20 metres above ground level, the data was dominated by the stack emissions, the approach effectively removing the influence of the fugitive, ground emissions.</p>
Obstructions	<p>Sampling and monitoring sites should be located, where possible, away from obstructions that will affect air flow. Buildings, walls, trees and other obstructions can cause wind shadows and eddies that effect the distribution of pollution. Monitoring close to obstructions can mean that both the fluctuations of pollution and the overall average concentration will not be representative of the area. It is therefore preferable to monitor at a location that has an open aspect as possible, allowing air movement with the minimum of disturbance.</p> <p>Occasionally, it may be appropriate to monitor in an area known to be affected by obstructions if the objective of the study is to assess the impact at a particular sensitive receptor.</p>
Overhang	Sampling sites should be open to the sky, with no overhanging trees or structures. Trees can act as very efficient pollutant sinks.

Accessibility	Sampling sites must be accessible for servicing, calibration or data collection, but should be secure and in a location where the risks of vandalism or accidental damage (e.g. by wildlife) are minimised.
Services	Where required, adequate services should be available to the monitoring site, namely electrical supply for sampling equipment and air conditioning. Where data will be polled remotely from the site, communications should also be considered e.g. 3G coverage.
Pollution source	Roadside pollution, for instance, should be measured close to the kerbside. Fugitive emissions are usually emitted relatively close to the ground level, and are often monitored adjacent to the site boundary. This is known as 'perimeter-fence monitoring'. Open path monitoring methods are well suited for this because they give a distance-averaged concentration over a long path length such as a boundary.
Pilot study	Short-duration preliminary surveys are often undertaken to provide cost-effective information to enable the design of the main survey to be optimised.

11. Data handling

The means by which data are acquired from the monitoring site depends very much on the type of equipment involved and the type of survey being undertaken. Many of the indirect monitoring techniques have an analytical end-method stage that is quite separate from the sampling stage. In such cases some of the raw data will come from the on-site sampling (e.g. flowrate, volume) but the analytical results will be provided by a laboratory.

In contrast, direct-reading continuous analysers provide streams of data stored on-site using automatic data-loggers able to communicate via telemetry links to a remote central processing unit. Most data-loggers will sample the instrument output at frequent intervals and then compress these data into more manageable time-averaged periods. Both the sampling interval and the averaging time can be specified by the operator and considerable thought must be given to choosing times that are appropriate to the storage capacity of the logger, the response time of the instrument, the temporal variability in pollutant concentrations and regulatory requirements as discussed in Section 7.

Systems are able to collect the data and then transmit the information at predetermined intervals by telemetry. This allows for virtually real-time presentation of the results after they have been inspected to ensure their validity. Telemetric links with the site also allow diagnostic tests to be carried out on instruments to check for correct operation, and enable instrument span and zero checks to be initiated. Telemetric transmission of data is especially important when there are a large number of sites in a network, or where a site is not easily accessible.

12. Analysis of results and reporting

12.1 Presenting the raw data

Analysing collected data is an essential part of ambient air monitoring, as it is only through analysis of the data that the information contained within the data can be revealed. When

considering how to analyse data it is worth bearing in mind the original aims and objectives of the monitoring programme, for example:

- Are levels acceptable?
- Where is the pollution coming from?
- What are the overall trends (are things improving)?
- What conditions give rise to elevated levels of pollution?
- What activities give rise to elevated levels of pollution? Is mitigation working?
- What is the impact of a specific plant?
- Assess against predicted levels, i.e. verification of a model
- Can the data be used to estimate source emission rates?

12.2 Assessment against air quality standards

One of the main reasons that air quality monitoring is carried out and subsequent analysis of the data is required is to establish whether the monitoring location is compliant with air quality standards. There are generally two types of air quality standard, short term - where a pollutant must not exceed a set concentration limit on more than the specified number of occasions during a year, and long term – where an annual average must not be exceeded. As previously discussed, short term or long term standards reflect the nature of the pollutant and whether its effect on human health or other receptors is acute or chronic.

Continuous monitoring data is usually collected as either 15-minute or hourly averaged data. However, many of the standards require the data to be converted to different averaging periods prior to comparison. For example, SO₂ has standards for 15-minute, hourly and 24-hour (midnight – midnight) averaged data, while the standard for CO is an 8-hour rolling average. Rolling averages or moving averages tend to smooth out short term fluctuations and highlight longer term trends and cycles. Each new data point must be the average of at least 75% data, e.g. at least three 15-minute averages to make up an hourly average.

Once the data has been converted to the required resolution the number of exceedances of a particular standard can be determined. If the monitoring period is shorter than a year, the number of exceedances during the monitoring period must be extrapolated to produce the number of exceedances over one year. Therefore, if the monitoring period is shorter than a year consideration must be given as to how representative the period was, i.e. wind direction, source activity, rain fall, season, etc. For example, monitoring around a waste transfer site would be expected to show a greater number of PM₁₀ exceedances in the dry summer months than during the wetter winter months. Caution should be taken when the number of exceedances of a standard are only just within the permitted allowance as under different meteorological conditions that standard may be exceeded. In such situations further monitoring may be warranted.

12.3 Source apportionment

There are a number of different types of analysis that can be used to try and extract further information from the monitoring data. They include directional, temporal and concurrence analysis techniques. These techniques are outlined below and are described in greater detail in Annex B.

12.3.1 Directional analysis

Directional analysis techniques provide an insight into the direction and nature of pollution sources relative to the position of the monitoring location (see Table 12.1). These

techniques assume that the wind direction recorded at the monitoring site is representative of the local wind trajectory.

Table 12.1: Directional analysis techniques

Pollution rose	Charts using polar co-ordinates that show the average concentration of a pollutant in different wind sectors, effectively showing the direction contributing to the highest levels at the monitoring site and therefore the relative position of the dominant source(s) of that particular pollutant.
Triangulation	Triangulation plots can be produced if data is available from more than one monitoring site during a study. By overlaying the pollution roses produced from each data set on a map it is possible to triangulate the biases in the roses, where areas of overlap indicate a common source that is influencing both data sets.
Percentile rose	By calculating the concentration of a pollutant at different percentiles for different wind sectors, it is possible to visually examine the distribution of pollutant concentrations at a particular monitoring site. This may provide information on the nature of the source influencing levels at the site.
Frequency rose	This type of analysis sorts the data into user defined categories (less than or greater than) and can indicate a source's potential for exceeding a given limit.

12.3.2 Temporal analysis

All temporal analysis of air quality data takes advantage of cycles in the production and dispersion of pollutants. Each of the techniques listed in Table 12.2 can be enhanced by first dividing the data into the relevant wind direction sectors (see Annex B). This allows the signal from a particular source to be isolated from the rest of the data and allows closer examination of the particular characteristics of the source(s) of interest.

Table 12.2: Temporal analysis techniques

Diurnal	Temporal distribution of averaged pollutant concentrations for each hour of the day. Traffic generated pollutants often show a diurnal profile that matches the traffic flow levels. This generally takes the form of a double peak pattern, which correspond to the morning and afternoon/evening rush hours. Industrial emissions are usually characterised by more elevated concentrations during the hours with the greatest amount of solar heating of the ground, due to increased convective mixing bringing stack emissions to ground level.
Weekly	Temporal distribution of averaged pollutant concentrations for each day of the week. This can provide useful information about the working practices of individual process activities within the sector of interest.
Seasonal	Temporal distribution of averaged pollutant concentrations for each month of the year. Many pollutants monitored exhibit seasonal cycles.
Trend	By performing a regression analysis on statistics such as annual mean and 98th percentile concentrations, it is possible to assess how air quality compares to previous years and identify whether pollution concentrations are changing over time. Statistically significant trends, or even a reasonable overview of how concentrations are changing, usually only become meaningful when complete data records extend over five years or more ¹⁵ .
Cumulative sum (Cusum)	Cusum was originally developed by E.S. Page as a technique for determining deviations away from set values. Kings

	College London (KCL) have improved the sensitivity of this statistical technique in order to identify change points in ambient pollution levels ¹⁶ .
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12.3.3 Concurrence

Concurrence analysis techniques look at the relationship between the pollutant of interest and other data collected at the same time in order to look for patterns and trends that can help identify possible sources (see Table 12.3). Concurrence methods can focus on two variables (e.g. concentration & wind speed) or more than two (e.g. concentration, wind speed & wind direction). If a particular source impacts distinctly for a particular range of concurrent variables, this range can be used to define a 'conditional window' – in which concentrations can be successively tracked in order to determine trends in that source's emission.

Table 12.3: Concurrence analysis techniques

Wind speed vs pollutant concentration	This type of analysis sorts the data with respect to wind speed and looks at the resultant profile in an effort to establish the nature of the pollutant emission, in particular the height of the release.
Pollution ratio	KCL have developed a model that looks at both NO _x and particulate concentrations in an effort to establish the amount of particulate coming from traffic sources ¹⁷ .
Episode/event analysis	By examining in greater detail the periods of highest concentration of a given pollutant and comparing these to other pollutants and meteorological data collected over the same periods, it is possible to establish whether there is a particular meteorological condition that gives rise high levels and whether other pollutants are also affected. For example, by looking at both CH ₄ concentration and met data collected near a landfill site it is possible to ascertain that most pollution events occur during the evening or early morning when wind speed and temperature drops, indicating relatively stable conditions such as inversion conditions leading to poor dispersion.

12.4 Air quality data analysis software

In an effort to improve efficiency and to ensure consistent handling of the data our Ambient Air Monitoring Team has written a piece of software called 'the toolbox macro'¹⁸. This software was written specifically to analyse ambient air monitoring data and will allow the user to conveniently carry out the majority of the analysis techniques mentioned above. It is written in Visual Basic for Applications (VBA) and runs in Microsoft Excel.

Another software package that has been recently developed specifically for analysing air quality data is Openair. It was developed by David Carslaw and Karl Ropkins in an effort to 'develop and make available a consistent set of tools for analysing and understanding air pollution data in a free, open-source environment'. Openair is a 'package' developed to run in a programming language called 'R'. R is a freeware version of the commercially available S-Plus statistical programming language. R was chosen as it is free, works on several platforms, was designed with data analysis in mind, and has excellent graphics output¹⁹.

12.5 Report content and structure

The exact style and content of an air quality monitoring report will depend upon the expected readership and the original aims and objectives of the survey. However, the basic structure of the report should usually include the following:

- Non-technical summary
- Statement of aims and objectives
- Description of the strategy adopted to fulfil the aims and objectives
- Details of the sampling sites, the sampling methods, analytical methods and QA/QC
- Summary of the results and a statement of uncertainty on the results
- Discussion and interpretation of the results, including comparisons with air quality standards or EALs
- Conclusions
- Recommendations, if relevant
- Appendices containing raw data, supplementary data, or further details of methods used.

13. Quality control and quality assurance

13.1 Measurement uncertainties

All measurement results have an associated 'degree of uncertainty' which defines the limits within which the true value lies to a specified level of confidence. This is evaluated by combining a number of uncertainty components and is expressed as a \pm quantity, i.e. an interval about the result. Quality control procedures are designed to reduce uncertainties to a minimum and to quantify the overall uncertainties that remain.

Measurements are subject to random and systematic uncertainties. Random uncertainties are those which can be related to a statistical probability function, such as the Gaussian distribution, and give rise to a variation about the mean in which there is a greater probability that the value lies closer to the mean than to the extremes. The more measurements that are made the greater the confidence that the mean is close to the true value. Random uncertainties may be due to short-term fluctuations in temperature or air pressure, or are introduced as a result of small variations in the performance of the measurer or in the procedure used. They are controlled by ensuring that all procedures are correctly specified and are followed exactly by all operators. Training should be given to ensure that this is the case.

Systematic uncertainties are not related to any recognised probability function, and are built-in bias which may be present in the measurement equipment or inherent in the procedure. They have the effect of displacing the results from the true value. The bias remains unchanged when a measurement is repeated under the same conditions and, no matter how many measurements are made, the mean result will not represent the true value of the parameter being measured, although it may have a fixed relationship with it. Examples of systematic uncertainties are: an offset in the measuring system, drift in its response between calibrations, personal bias in the interpretation of an analogue scale, or the uncertainty of the value of the reference standard. They are reduced by making sure that all the items of equipment used meet their specification, that primary standards are properly certified and that secondary standards, such as flow measurement devices or transfer gas standards, are properly calibrated. Maintenance and calibration schedules serve to keep systematic uncertainties under control.

13.2 Sampling systems

Where collection or measurement systems involve the use of a sample line, there is the potential for sample loss due to adsorption, diffusion, deposition or reaction. Consideration must be given to the composition and length of the sample line to ensure that any losses are kept to an acceptable limit. For reactive species the sample line material must be chemically inert, such as PTFE or stainless steel, and long lengths should be avoided. Instantaneous grab sampling systems must be tested to ensure that, under the conditions of storage, the integrity of the sample is maintained.

13.3 Sample volumes and flow rates

With the notable exception of diffusive (passive) monitors, most techniques rely on active sampling of the pollutant into the collection or measurement system using a pump. Of these, many give a response that is directly proportional to the sample volume, where the accurate quantification of sample volume is a crucial step towards determining the overall limits of uncertainty of the measurement.

Other techniques, typically continuous real-time monitors, may control the sample flow using physical methods, such as critical orifices or mass-flow controllers, thus maintaining a constant flow to the detector. Measurement of sample flow rate in these systems is not normally checked since the response of the instrument would routinely be determined using certified calibration standards. Some continuous methods, such as those using infrared or ultraviolet absorption detectors, are independent of flow and it is only necessary to check that the sample flow rate remains within defined limits.

Where active sampling by adsorption or absorption is used the collection efficiency will depend upon the flow rate used, and an excessive flow rate may result in lower efficiencies due to sample breakthrough. This can be caused by:

- adsorption/desorption effects
- insufficient residence time between the sample and collection medium preventing physical or chemical combination or
- overloading of collecting medium.

Validation checks should be carried out to ensure that the sample flow rate used does not lead to significant losses.

13.4 Sample storage, transit and audit trail

Where samples are taken for subsequent analysis, it is essential that procedures are in hand which ensure that the sample is identifiable throughout the sampling, sample preparation and analysis route and that the sample integrity is maintained. Each sample should be given a reference number which identifies it throughout the system and sample containers should be marked in such a way that it is difficult for the reference marks to be removed accidentally. The reference number should be noted in a log which is specifically designed for the purpose. The log should also provide details of where the sample was taken, date, time, the purpose of the sample and any other relevant information such as the method by which the sample was obtained, and the method of sample treatment. If the sample is to be analysed by another organisation the date on which the sample was passed to the second organisation should also be noted in the log. A system whereby the detailed history of a sample can be traced is known as an audit trail.

Preservation of sample integrity depends on the type of sample. Particulate samples collected onto filter media should be stored individually in sealed containers in such a way

that losses from the filter surface are minimised. For most other samples, it is best to store them under cool conditions in the dark. Bubblers and impingers should either be sealed, or washed out into suitable bottles marked with the appropriate reference number, and stored in cool boxes for transport back to the laboratory for analysis. All samples should be stored under conditions where there is no risk of contamination, and should be subject to as little handling as possible.

13.5 Calibration and validation

The calibration of an instrument or method determines the relationship between the result of the measurement and the actual concentration of the pollutant of interest and is an essential component of the quality control procedure. It provides the link between the measurements which are being carried out and the significance of the results when assessed against air quality standards and objectives.

13.5.1 Continuous gas analysers

The calibration of continuous gas analysers should be carried out at three levels:

- a functional zero and span check
- routine two point (zero and span) calibration using certified standards
- full validation.

Zero and span checks, often using sources within the instrument, provide a useful guide as to the performance of the instrument. These sources are not usually traceable to National Standards and the instrument responses are not used for data scaling. The routine two-point calibration of a continuous gas analyser is made using a suitable zero source and calibration gas of a concentration within the measurement range. The zero source may be a certified 'zero grade' air or generated in-situ using suitable scrubbers. The calibration gas should be of a certified grade to ensure traceability to National Standards. It is recommended that this calibration be carried out at least every two weeks. Results of the instrument validation are then used in the data ratification process.

Full-scale validation is necessary to demonstrate the instrument's response over its full working range and should be carried out when the instrument is first installed and whenever it undergoes major maintenance or is moved. A full validation exercise should also be carried out every six months. The purpose of validation is to relate the response of the instrument to a range of standards which are traceable to National Standards, and should also include validation of the standards used for the routine calibrations. These exercises are costly and time consuming, since sufficient data are necessary for statistical analysis to provide a calibration function, regression line and confidence limits.

13.5.2 Automatic particulate monitors

Calibration of automatic particulate monitors should be carried out every six months. The procedures for calibration will vary considerably depending upon the type of monitor and the principle of measurement, and it will be necessary to refer to the manufacturer's recommended procedures. There is no simple method of generating standard particulate atmospheres, and calibration will necessarily be limited to checking other parameters such as flow or mass measurement. If the monitor derives its result from particle sizing and counting then calibration will need to be performed by a recognised laboratory.

13.5.3 Non-continuous methods

Calibration of non-continuous methods may not be possible via a direct route, especially if samples are to be analysed by a separate laboratory. Detector responses should be determined by the laboratory at the time of the analysis using certified or reference material. As a check on the analytical procedure, 'spiked' samples should be provided wherever possible together with sample blanks. Occasional replicate samples should be taken to check for variability in the results. Flowmeters should be checked against laboratory reference standards, traceable to National Standards, and flow rates and sample volumes of sampling systems verified and adjusted if necessary.

13.6 Maintenance procedures

The majority of continuous analysers are sophisticated systems requiring trained personnel to operate and maintain them. Major service and maintenance operations are generally beyond the scope of the user and best left to the equipment supplier who will have access to the necessary test equipment and spare parts. For most instruments, maintenance operations will consist of routine preventative maintenance and instrument service or repair. A record should be kept of all maintenance work.

In addition, the following should be carried out as part of the normal operating routine:

- examination or replacement of sample filters;
- examination of the sampling system
- check of sample flow rates
- zero and span check using certified standards (continuous monitors)
- check of data acquisition/recording system.

13.7 Data communication systems

For pollutant monitoring instruments that provide an electrical output, data is handled by automatic data loggers able to communicate via telemetry links to a remote central processing unit. Data-communications systems using telemetry links also allow some basic quality control checks (e.g. span check, zero check, functional check) to be carried out remotely or automatically on instruments installed at monitoring sites. This can allow problems to be spotted at an early stage.

13.8 Quality assurance

Quality assurance (QA) is the effective management of the quality control tasks. Where an organisation uses more than one independent sampling team to carry out the same type of measurement, it is important that a QA programme is set up to ensure that all the measurements are carried out to the same standard and give comparable results. If different sampling/analytical methods are employed, QA is even more important. The QA procedure should ensure that:

- measurements are made in accordance with an agreed protocol
- the correct quality control procedures are in place
- the quality control procedures are being adhered to
- sample identification and routing procedure is well documented
- the correct reporting procedures are used.

The QA programme should also make provision for the audit and inspection of measurement procedures as they are being carried out. This can be achieved by either straightforward

observation of the sampling and analysis teams at work, by parallel measurements by a third party, or by third party accreditation by, for example, the United Kingdom Accreditation Services (UKAS).

14. Index of Monitoring Methods

14.1 Structure

Part 2 of this TGN, the index of monitoring methods, has been structured to enable a user to determine an appropriate monitoring method or technique. Typically the user will be aware of what substance requires sampling, but will need guidance on the technique, equipment and method to use.

The index is classified by substance as follows:

- Table 14.1: Suspended particulate matter as PM₁₀ / PM_{2.5}
- Table 14.2: Suspended particles as black smoke / black carbon
- Table 14.3: Nuisance dust (dustfall)
- Table 14.4: Nuisance dust flux
- Table 14.5: Odour
- Table 14.6: Ozone
- Table 14.7: Nitrogen oxides
- Table 14.8: Sulphur dioxide
- Table 14.9: Carbon monoxide
- Table 14.10: Heavy metals (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Pt, V and Zn)
- Table 14.11: Ammonia and ammonium aerosol (NH_x)
- Table 14.12: Inorganic acids (HNO₃, HCl, HF, HBr, H₃PO₃)
- Table 14.13: Hydrogen sulphide and inorganic reduced sulphur compounds
- Table 14.14: Volatile organic sulphur compounds (including mercaptans, carbon disulphide)
- Table 14.15: Benzene, 1,3-butadiene and other speciated hydrocarbons/VOCs
- Table 14.16: Halogenated volatile organic compounds
- Table 14.17: Formaldehyde and other aldehydes
- Table 14.18: Polycyclic aromatic hydrocarbons (PAHs)
- Table 14.19: Dioxins & furans (PCCDs & PCDFs) and polychlorinated biphenyls (PCBs)

Table 14.1: Suspended particulate matter as PM₁₀ / PM_{2.5}

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Pumped (active) sampling of PM ₁₀ onto filter paper; Gravimetric analysis.	<i>BS EN 12341:1999 Air quality. Determination of the PM₁₀ fraction of suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods.</i>	This is the European reference monitoring method for demonstrating compliance with the EU Directive Limit Values. It is a gravimetric method, in which the mass of particles collected is determined after sampling a known volume of air. The standard refers to three sampling devices that may be used: <ol style="list-style-type: none"> 1. Superhigh volume sampler the Wide Range Aerosol Classifier (WRAC) 2. High-volume sampler – the HVS PM₁₀ sampler (68 m³ hr⁻¹) 3. Low volume sampler – the LVS PM₁₀ sampler (2.3 m³ hr⁻¹) A small number of AURN sites have monitored PM ₁₀ according to the reference method using the BS EN 12341-compliant Klein Filtergerat* (KFG) low-volume sampler with Whatman QMA quartz filters; however, the UK equivalence studies used 8-head samplers (allowing 1 week collection of daily-average samples), operating at 2.3 m ³ hr ⁻¹ and loaded with Enfab (Teflon coated glass fibre) filters.	Gravimetric determination on a 0.1 µg resolution balance with a sample flow of 2.3 m ³ hr ⁻¹ gives a theoretical LoD of 0.002 µg.m ⁻³ for a 24-hr sample.	Measurements made to the European reference method using these instruments will have an expanded uncertainty at the Limit Value that does not exceed Data Quality Objective (DQO) of 25% for PM ₁₀ .
Period-averaged sampling	Pumped (active) sampling of PM _{2.5} onto filter paper, Gravimetric analysis	<i>BS EN 14907:2005 Ambient air quality. Standard gravimetric measurement method for the determination of the PM_{2.5} mass fraction of suspended particulate matter.</i>	This is the European reference monitoring method for demonstrating compliance with the EU Directive concentration caps and exposure reduction targets for PM _{2.5} . The UK equivalence studies used the BS EN 14907-equivalent Leckel sampler (single head), operating at 2.3 m ³ hr ⁻¹ and loaded with Enfab filters.	Gravimetric determination on a 0.1 µg resolution balance with a sample flow of 2.3 m ³ hr ⁻¹ gives a theoretical LoD of 0.002 µg.m ⁻³ for a 24-hr sample.	Measurements made to the European reference method using compliant/ equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO of 25% for PM _{2.5} .
Period-averaged sampling	Partisol 2025 Sequential Sampler - Pumped (active) sampling of PM ₁₀ onto filter paper; Gravimetric analysis.	The Partisol 2025 Sequential Sampler was shown to be equivalent to EN12341 for PM ₁₀ without the need for correction factors; Not equivalent to EN14907 for PM _{2.5} .	Suitable technique for demonstrating compliance with EU Directive Limit Value for PM ₁₀ . Not suitable for demonstrating compliance with EU Directive Limit Value for PM _{2.5} , but may provide useful data for other applications. Up to 16 filters can be loaded into the sequential sampler, allowing up to 2-weekly collection of daily-average samples. Recently, problems have emerged with data from filter-based gravimetric samplers in the national network due to filters gaining moisture in the field and Defra has switched to Enfab filters to eliminate the problem. These also have advantages in robustness and	Gravimetric determination on a 0.1 µg resolution balance with a sample flow of 16.67 l min ⁻¹ gives a theoretical LoD of 0.004 µg.m ⁻³ for a 24-hr sample.	Measurements made to the European reference method using compliant/ equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO of 25% for PM ₁₀ .

* Here and elsewhere in this document, reference to commercial names of equipment or products does not constitute a recommendation or endorsement by Defra, the Devolved Administrations of Scotland, Wales & Northern Ireland, or the Environment Agency

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
			inertness over the other more commonly used media allowed in EN14907 such as Teflon, quartz, and glass-fibre filters.		
Period-averaged sampling	OPSIS SM200 (mass configuration) sampler - Pumped (active) sampling of PM ₁₀ onto filter paper; Gravimetric analysis.	The OPSIS SM200 in mass configuration was shown to be equivalent to EN12341 for PM ₁₀ but only after application of correction factors for slope/intercept; not equivalent to EN14907 for PM _{2.5} .	Suitable technique for demonstrating compliance with EU Directive Limit Value for PM ₁₀ . The UK equivalence studies used the BS EN 14907-equivalent SM200 (mass configuration) sampler, operating at 16.67 l min ⁻¹ and loaded with Teflon membrane filters.	Gravimetric determination on a 0.1 µg resolution balance with a sample flow of 16.67 l min ⁻¹ gives a theoretical LoD of 0.004 µg.m ⁻³ for a 24-hr sample.	Measurements made to the European reference method using ccompliant/ equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO of 25% for PM ₁₀ .
Real-time monitoring	Sampling and analysis using Tapering element oscillating microbalance (TEOM).	The standard TEOM fails to meet the criteria for equivalence to the EU reference method for PM ₁₀ (EN12341) or for PM _{2.5} (EN14907).	Not suitable for demonstrating compliance with EU Directive Limit Values for PM ₁₀ and PM _{2.5} , but may provide useful data for other applications. The TEOM system measures the mass of particles by a fundamental physical law, which states that the mass of PM collected on the tuning fork-like element, oscillating at a known frequency, is directly proportional to the change in frequency. This allows continuous, almost instantaneous measurement of PM ₁₀ (sampling average period of about 15 minutes), which has led to this technique's widespread adoption in UK monitoring networks, where a correction factor of 1.3 has historically been used to take account of loss of volatiles (such as ammonium nitrate and organic carbon aerosols) in the heated (50 °C) inlet of the TEOM. However, the proportion of particles that are volatile varies in a non-linear fashion and this technique fails to meet the equivalence criteria even with the application of a wide range of correction factors. TG(09) ¹ advises local authorities still using TEOMs for LAQM purposes to use the Kings College London VCM model ² to correct data so that it can be expressed in gravimetric terms.	Measurement range: 0 to 5000 mg.m ⁻³ . Typical 1-hr LoD of 0.06 µg.m ⁻³ .	Non-equivalent instrument: expanded uncertainty at the Limit Value for PM ₁₀ and PM _{2.5} exceeds 25%.
Real-time monitoring	Sampling and analysis of PM ₁₀ and PM _{2.5} using TEOM type B retrofitted with Filter Dynamics Measurement System (FDMS).	Shown to be equivalent to the EU reference method (EN12341) for PM ₁₀ and PM _{2.5} (EN14907) without the need for correction factors.	Suitable technique for demonstrating compliance with EU Directive Limit Values for PM ₁₀ and PM _{2.5} . This instrument has been chosen by Defra to expand/ upgrade the national AURN network. (Data from the limited number of PM _{2.5} sites in the AURN had previously been obtained from Partisol 2025 units, TEOM instruments and TEOM-FDMS instruments.)	Measurement range: 0 to 5000 mg.m ⁻³ . Typical 1-hr LoD of 0.06 µg.m ⁻³ .	Measurements made to the European reference method using ccompliant/ equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does

¹ Local Air Quality Management – Technical Guidance TG(09), Defra, 2009.

² Volatile Correction Model (VCM) for PM10 Application to Hourly Time Resolution and AURN FDMS Purge Measurements, ERG Kings College London, available at www.airquality.co.uk

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
					not exceed the DQO of 25% for PM ₁₀ and PM _{2.5} .
Real-time monitoring	Beta Attenuation Monitor (BAM) for PM ₁₀ determination: sampling by pumped (active) sampling onto a filter; Analysis by Beta-ray absorption.	The OPSIS SM200 (in Beta configuration) was shown to be equivalent to EN12341 for PM ₁₀ without the need for correction factors; the Met-One BAM was shown to be equivalent to EN12341 for PM ₁₀ but only after application of correction factors for slope/intercept. Neither are equivalent to EN14907 for PM _{2.5} . (N.B. An international standard also exists: ISO 10473:2000 <i>Ambient air -- Measurement of the mass of particulate matter on a filter medium -- Beta-ray absorption method</i>)	Suitable technique for demonstrating compliance with EU Directive Limit Value for PM ₁₀ . Not suitable for demonstrating compliance with EU Directive Limit Values PM _{2.5} , but may provide useful data for other applications. BAMs estimate the mass of PM collected on a filter tape from the attenuation of beta radiation as it passes through, based on a calibration factor that describes the absorption-to-mass relationship. This technique can be accurate for known compositions of PM. Measurements are quasi-continuous, providing typically one result per hour, rather than instantaneous.	Standard measurement range: 0 to 1000 µg.m ⁻³ . Typical 1-hr LoD 4 µg.m ⁻³ . Typical 24-hr LoD 4 µg.m ⁻³ .	Measurements made to the European reference method using compliant/equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO of 25% for PM ₁₀ .
Real-time monitoring	Light-scattering optical particle counter (nephelometer).	Several instruments available in the UK. There is currently no CEN, ISO or BS standard method covering this technique.	Popular automated method for screening surveys (not suitable for demonstrating compliance), giving continuous real-time results. The number of particles present in different size ranges is measured and mass concentrations are mathematically derived from this using a density factor. Can be set-up to measure PM ₁₀ , PM _{2.5} and PM ₁ . Fixed and portable versions available. The photomultiplier tube (PMT) output from scattered light (often infrared light or laser) is proportional to the size of the particle, but also affected by the shape, colour and refractive index. Results obtained relate only to equivalent polystyrene spheres (used for factory default calibration) giving the same magnitude of light pulses and should be referred to as equivalent optical particle sizes rather than true particle sizes. Most have the facility for retrospective calibration with the PM collected in the field.	Typical measurement range: 0 to 6000 µg.m ⁻³ . Reported performance specifications vary between manufacturers, but typical LoD 0.01-1 µg.m ⁻³ .	Non-equivalent instrument: expanded uncertainty at the Limit Value for PM ₁₀ and PM _{2.5} assumed to exceed 25%.

Notes:

European Reference Methods - Compliance with EU Directive Limit Values is demonstrated using European reference monitoring methods, which allow the inherent measurement uncertainty to be taken into account.

Equivalent methods - Member States are not obliged to employ the reference method as standard across their networks and can use other methods shown to be 'equivalent' with the reference method and pass the test criteria set out in the EC Guidance for the Demonstration of Equivalence of Ambient Air Monitoring Methods. The 2006 *UK Equivalence Programme for Monitoring of Particulate Matter* study http://www.airquality.co.uk/archive/reports/cat05/0606130952_UKPMEquivalence.pdf showed which PM₁₀ instruments/techniques commercially available in the UK were equivalent to the EU reference method (EN12341), allowing them to be used for reporting against Limit Values. Further intercomparison studies will be carried out under the Environment Agency's MCERTS programme for Continuous Ambient Monitoring Systems (CAMS) and the certification will incorporate requirements to show equivalence with the European reference methods for PM₁₀ and PM_{2.5}.

Range, Limit of Detection (LoD), Uncertainty, Response Time – for an explanation of terms, see BS ISO 6879:1995 - *Performance Characteristics and related concepts to measuring methods*.

Table 14.2: Suspended particles as black smoke / black carbon

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Pumped sampling of black smoke onto filter paper; optical analysis (reflectance).	BS1747-2:1969 <i>Methods for the measurement of air pollution. Determination of concentration of suspended matter</i> , BS1747-11:1993 <i>Methods for measurement of air pollution. Determination of a black smoke index in ambient air</i> , ISO 9835:1993 <i>Ambient air -- Determination of a black smoke index</i> .	Black smoke was sampled at the same time as SO ₂ , using a common automated sampler (eight-port bubbler), as part of the UK National Survey since the 1960s. The Network's role in monitoring compliance with the original European Council Directive on Sulphur Dioxide and Suspended Particles (0/779/EEC) ended in 2005 with the repeal of the latter and from 2006 Defra the original network was replaced with a smaller network monitoring black smoke. Daily-average samples are collected on Whatman No.1 cellulose filter papers. The darkness of stain produced by collected particulates is measured by reflectometer. The reflectance value is converted to International Equivalent Standard Smoke (µg.m ⁻³) using a calibration curve. Although the method gives a realistic measurement of black smoke itself, there is no robust relationship with the total suspended particulates (TSP) concentration due to reduction in (black) carbon particle levels in the atmosphere over the years and any TSP estimate could be underestimated by a factor between 2 and 6 on a mass basis. The sample inlet, an upturned funnel, is not specifically designed to be size selective, although one study has shown that the approximate size fraction PM _{4.5} is collected ³ .	The maximum measurable reflectance is between 99% and 99.9%, giving a lower detection limit of between 0.1 and 0.9 µg.m ⁻³ .	At the low average concentrations at the majority of sites the provisional uncertainty is around 30%, dominated by the repeatability of the reflectance measurement on real filter samples. At higher black smoke concentrations, the provisional uncertainty is estimated ⁴ to be around 14%
Real-time monitoring	Aethalometers, measuring black carbon using a real-time optical transmission technique.	There is currently no CEN, ISO or BS standard method covering this technique.	Four different instruments were trialed in a comparative study at the London Marylebone Road AURN site ⁵ . Because of the relationship between Black Smoke Index and black-carbon concentration, Defra has from 2008 replaced the 8-port samplers with Magee Scientific AE-22 automatic aethalometers in the new, smaller national Black Smoke Network. These instruments measure optical absorption at 880 nm (for black/ elemental carbon, 'EC'), and 370 nm (designated as 'UVPM', interpreted as an indicator of aromatic organic compounds such as are found in tobacco smoke, PAH mixtures, wood and biomass burning, smoke, etc.) through a quartz-fibre filter tape on which the sample is collected. Automatic advancement of the filter tape allows continuous, almost instantaneous measurement of PM ₁₀ (sampling average period of between 15 seconds and 1 hour).	LoD is proportional to flow rate (hence inversely proportional to time-resolution) and is approximately 0.1 µg.m ⁻³ at 1-minute resolution at 3 l min ⁻¹ . High specificity: no other aerosol species has optical absorption even 0.001 times that of Elemental Carbon in the visible range ⁶ .	No data available.

³ *Air Pollution in the UK: 2007*, AEA report for Defra and the Devolved Administrations, available at www.airquality.co.uk

⁴ 2007 Annual Report for the UK Black Smoke Network, available at www.airquality.co.uk

⁵ Marylebone Road Aethalometer Trial Report, available at www.airquality.co.uk/archive/reports/cat13/0711261353_Marylebone_Road_Aethalometer_Trial.pdf

⁶ Manufacturer's data sheet, AE22 Aethalometer, available at http://www.mageesci.com/products/spec-sheets/2009/AE22_specsheet_feb09_00_a.pdf

Table 14.3: Nuisance dust (dustfall⁷)

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Measurement of deposition rate ($\text{mg m}^{-2} \text{day}^{-1}$): sampling by passive collection of dust into a Frisbee deposit gauge; gravimetric analysis.	Although there is currently no CEN, ISO or BS standard method covering this technique, a custom and practice method exists: the Stockholm Environment Institute at York (SEI-Y) method (Vallack, H.W. (1995), <i>A Field Evaluation of Frisbee-Type Dust Deposit Gauges</i> , Atmospheric Environment, 29. 1465-1469).	Preferred method for measurement of dustfall by gravimetric means. Great improvement in performance over BS gauge and ISO gauge. A polyester foam dust trap can be used to reduce contamination from falling leaves, etc. Inverted Frisbee mounted horizontally on a pole 1.75 m above the ground. Deposited matter on the collection surface, and the insoluble matter in the rainwater collection are quantitatively removed and separated by gentle vacuum filtration. Insoluble matter dried and determined gravimetrically. Expressed as $\text{mg m}^{-2} \text{day}^{-1}$. Shape has superior collecting efficiency and aerodynamic characteristics that make it suitable for short-term sampling periods of about a week, but usually exposed for longer as custom and practice default nuisance limits are based on monthly exposures. Measurement of deposition rate from a particular direction can be carried out using a directional Frisbee gauge, where the collection surface is exposed only when the associated meteorological equipment indicates that wind is from a defined direction arc. However, the need for meteorological equipment and power limits application for routine monitoring	Gravimetric determination on a 0.1 mg resolution balance with a one-month sampling period gives a theoretical LoD of $0.07 \text{ mg m}^{-2} \text{day}^{-1}$.	No details on uncertainty available. Improvement in performance over BS and ISO gauges.
Period-averaged sampling	Measurement of deposition rate ($\text{mg m}^{-2} \text{day}^{-1}$): sampling by passive collection of dust into ISO deposit gauge; gravimetric analysis.	ISO/DIS 4222: 1975, <i>Measurement of Particulate Fallout by a Horizontal Deposit Gauge</i> , ISO/TC 146/ET4 (Paris 75-2) 69E Discussion Document.	Upward facing polythene cylindrical container with the top edge bevelled at 45° . Top of the cylinder is approximately 1.7 m above the ground. The sampling programme should be long duration, e.g. 1 year, with individual exposure periods of up to 1 month After sampling the collector is removed to the laboratory and the insoluble deposited matter is separated by vacuum filtration and gravimetrically determined after drying. Deposition is expressed as $\text{mg m}^{-2} \text{day}^{-1}$. Applications limited to providing long-term data for comparative purposes.	Gravimetric determination on a 0.1 mg resolution balance with a one-month sampling period gives a theoretical LoD of $0.1 \text{ mg m}^{-2} \text{day}^{-1}$.	No details on uncertainty available. Improvement in performance over BS gauge, but still bulky, limited collection efficiencies, dependent on wind speed, and subject to aerodynamic effects.
Period-averaged sampling	Measurement of deposition rate ($\text{mg m}^{-2} \text{day}^{-1}$): sampling by passive collection of dust into British Standard deposit gauge; gravimetric analysis.	BS 1747-1:1969 - <i>Deposit Gauges</i> .	Apparatus consists of a metal stand supporting an upward facing collecting bowl, 1.2 m above the ground. The sampling programme should be of a long duration, e.g. 1 year, with individual exposure periods of up to 1 month. Insoluble deposited material is separated from the liquid by gentle vacuum filtration, dried and determined gravimetrically. The results are expressed as $\text{mg m}^{-2} \text{day}^{-1}$.	Gravimetric determination on a 0.1 mg resolution balance with a one-month sampling period gives a theoretical LoD of $0.05 \text{ mg m}^{-2} \text{day}^{-1}$.	No details on uncertainty available. The shallow collector bowl is susceptible to sample losses during high winds; hence, the use of this type of gauge is no longer widespread
Period-averaged	Measurement of soiling rate, as Soiling Units (SU)	Although there is currently no CEN, ISO or BS	Developed for assessing the annoyance effect of deposited dust on glossy surfaces, e.g. window cills or	Lower detection limit is 2 SU.	Overall accuracy better than 2 SU, or

⁷ Dustfall is nuisance dust falling out of the air in a nominally vertical direction and depositing onto a horizontal surface.

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
sampling	per week: sampling by passive collection of dust onto a horizontally positioned microscope slide; analysis by measuring the change in specular reflectance.	standard method covering this technique, a custom and practice method exists: Schwar MJR, <i>A Dust Meter for Measuring Dust Deposition and Soiling of Glossy Surfaces</i> , Clean air, Vol. 24, No.4, pp 164-169, 1994.	motor vehicles. A clean microscope slide is exposed for, typically, one week. The slide is positioned horizontally on a surface between 1 m and 2 m above the ground. The dustiness of the exposed slide is quantified by measuring the reduction in specular reflectance relative to a clean unexposed slide using a reflectometer instrument. A measurement in Soiling Units (SU) is obtained by subtracting the reflectance value from 100. The soiling level can be related to perceived annoyance. Inexpensive microscope slide samplers allow large or detailed surveys to be carried out at modest cost.		2%.
Period-averaged sampling	Measurement of soiling rate, as % Effective Area Coverage (EAC) per week: sampling by passive collection of dust onto a horizontally positioned white sticky Fablon pad; analysis by measuring the change in reflectance.	Although there is currently no CEN, ISO or BS standard method covering this technique, a custom and practice method exists: Bearman & Kingsbury, <i>Assessment of Nuisance from Deposited Particulates Using a Simple and Inexpensive Measuring System</i> , Clean Air, Vol.11, No.2, pp77-81, 1981.	Developed for assessing the annoyance from soiling of surfaces, e.g. window cills or motor vehicles. Similar application to the dust slide method. Inexpensive Fablon samplers allow large or detailed surveys to be carried out at modest cost. Standard sampling exposure period is 7 days. The soiling of the exposed sticky pad is measured using a reflectance meter, and expressed as the percentage effective area coverage (%EAC) per day, which can be related to complaint levels.	No data available.	No data available.

Table 14.4: Nuisance dust flux⁸

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Measurement of dust flux rate ($\text{mg m}^{-2} \text{ day}^{-1}$): sampling by passive collection of dust into BS/CERL-type directional dust gauge; analysis by optical (obscuration) end-method (although popular variation from standard is gravimetric analysis).	BS 1747-5:1972 - <i>Directional dust gauges</i> .	<p>Dust flux gauges have a collection device positioned in the vertical plane to intercept dust as it travels parallel to the ground. This approach is best suited for monitoring dust releases across the site boundary, i.e. what is entering and leaving the site.</p> <p>The BS (also known as CERL-type) directional dust gauge has four slotted sampling tubes with collection pots set at right angles to each other, to be positioned with either the sampling slot of each tube lined up with the four ordinate points of the compass, or one slot towards the pollution source. An aqueous suspension of the dust collected in each pot is placed in a water-filled glass cell, and dust loading is estimated by the amount of obscuration of a beam of light passing through the cell. (This end method can only be used where a very large percentage of the total dust is from one source and the dust has approx. reproducible composition and density). The custom and practice variation from the standard is insoluble deposited material filtered, dried and determined gravimetrically. Although the results are expressed in units of $\text{mg m}^{-2} \text{ day}^{-1}$ (for each direction), this is the mass flux rate, not the deposition rate, and so the results are not comparable with those of a deposition gauge.</p> <p>Sampling periods of about 10 days to 1 month are usual and long sampling programmes of about one year are necessary.</p>	Gravimetric determination on a 0.1 mg resolution balance with a one-month sampling period gives a theoretical LoD of $6.5 \text{ mg m}^{-2} \text{ day}^{-1}$ for each of the four directions.	No details on uncertainty available. Known limitations on capture efficiency and results affected by same factors as BS deposit gauge, (although their results are not comparable).
Period-averaged sampling	Measurement of soiling rate, as % Effective Area Coverage (EAC) per week: sampling by passive collection of dust onto a vertically positioned white sticky Fablon sheet (which can be wrapped around a cylinder to form a directional gauge); analysis by measuring the change in reflectance.	Although there is currently no CEN, ISO or BS standard method covering this technique, a custom and practice method exists: Bearman & Kingsbury, <i>Assessment of Nuisance from Deposited Particulates Using a Simple and Inexpensive Measuring System</i> , Clean Air, Vol.11, No.2, pp77-81, 1981.	<p>Standard sampling exposure period is 7 days. The soiling of the exposed sticky pad is measured using a reflectance meter, and expressed as the percentage effective area coverage (%EAC) per day, which can be related to complaint levels.</p> <p>The commercially-available sampling and analysis system allows the direction of dust flux to be summarised (as pollution roses) in, typically, 15 degree arcs about the monitoring point⁹.</p>	No data available.	No data available.

⁸ Dust flux is nuisance dust in transit, travelling in a direction approximately parallel to the ground, or depositing out of the air onto a nominally vertical surface, e.g. building facade.

⁹ *Low Cost Directional Monitoring of Nuisance Dust Around Mineral Workings*, funded by the Mineral Industry Sustainable Technology (MIST) programme and available from DustScan Ltd.

Table 14.5: Odour

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Sensory testing ¹⁰ by the "Sniff Test"	There is currently no CEN ¹¹ , ISO or BS standard method covering this technique. However, a German national standard exists: VDI 3940: 1993, <i>Determination of Odorants in Ambient Air by Field Inspection</i> .	<p>With the "Sniff Test" variant of sensory testing, the field operative measures the odour magnitude as odour intensity. There are two main variants:</p> <p>The US "objective" approach, documented in ASTM E544-99, where the assessor allocates the intensity of the environmental odour against a numerical scale based on a series of standard "sniffing sticks" containing different concentrations of 1-butanol.</p> <p>In Europe, Australia and New Zealand the "subjective" Sniff Test is used more, where the assessor allocates the intensity of the environmental odour against a numerical scale linked to qualitative descriptions such as "not perceptible", "weak", "strong", etc. German national standard VDI method 3940 is very comprehensive but requires a full year's worth of measurements and can require multi-person "sniffing squads". As yet there is no national standard in the UK, but the Environment Agency outlines its own brief and straightforward procedure in an appendix to its draft H4 guidance.</p>	VDI standard intensity (I) scale range 1 (slight/ very weak) to 6 (extremely strong)	No data available.
Period-averaged sampling / Real-time monitoring	Monitoring of specific odorous compounds.	Refer to the relevant standard for the compound in question (e.g. hydrogen sulphide, organic sulphides, ammonia, etc).	<p>A variety of techniques, using either automatic instruments or manual samplers combined with laboratory analysis, can be used to monitor specific odorous compounds in ambient air. Monitoring of odour exposure by determination of individual compounds is only valid in those circumstances where:</p> <ol style="list-style-type: none"> 1) the specific compound(s) in question are responsible for the vast majority of the odour in the emissions, or at least can be considered as an empirical surrogate for the odour; and 2) there is a monitoring technique available that has: <ul style="list-style-type: none"> o sufficient sensitivity - concentrations will probably be very low; and o suitably fine time resolution - odours may be perceived over a few seconds at a time, interspersed by longer periods of no odour. <p>This restricts the type of monitoring technique to either: suitable automatic analysers (e.g. determination of H₂S in air by gold-film resistance monitor); or manual grab samples collected onto (typically) Tenax solid sorbent</p>	Refer to the relevant standard for the compound in question.	Refer to the relevant standard for the compound in question.

¹⁰ Sensory testing techniques use the human nose as the analytical sensor to enable the FIDOL factors (frequency, intensity, duration, offensiveness, location) of the odour to be recorded, a sound approach considering that (currently at least) no analytical instrument can give a unified measure of a complex mixture of compounds that quantifies it as a unified whole in the same way that a human experiences odour.

¹¹ At the time of writing, the International Standards Organisation (ISO) has established a working group (WG27) under technical committee TC264 to look at sensory tests in the field.

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
			followed by (typically) GC-MS analysis in the laboratory.		
Real-time monitoring	Sensory testing by portable field olfactometer	There are no UK protocols for the use of field olfactometers. In the US, state regulations often require boundary odour concentrations to be measured using this technique and McGinley & McGinley ¹² describe the protocols that can be adopted.	Field Olfactometry measures the ambient odour <u>concentration</u> . Laboratory-based dynamic dilution olfactometry (DDO) should not normally be used for ambient odour measurements ¹³ , the only type of instrumental olfactometry suitable for ambient measurements is portable field olfactometry: this technique incorporates the dilution device within a portable device, allowing direct measurements of odour concentration to be carried in real time in the field, without the need for separate sampling and laboratory dilution stages. One portable hand-held instruments in common use in the United States, is the NasalRanger® device.	The NasalRanger® instrument has a lower detection limit of 2 dilutions-to-threshold (2 D/T) ¹⁴ .	No data available.
Real-time monitoring	Electronic noses.	There is currently no CEN, ISO or BS standard method covering this technique.	Electronic noses use a solid-state sensor array. Sensor selection is important and is made on the basis of the general type of odour to be monitored. The matrix may include specific sensors (only react with a very specific compound); and/or non-specific sensors (such as metal-oxide semiconductors), which allow a wider range of responses ¹⁵ . Calibration of electronic noses is performed using known concentrations of source-samples of the actual odour to be monitored (having been determined by laboratory dynamic dilution olfactometry by the source emission standard method BS EN 13725: 2003). Mathematical and statistical models are used to provide a global response from the outputs from the array of sensors that can be used to recognise and quantify the "learned" odour types ¹⁶ . Continuous odour monitoring systems have been developed that make use of an automated system of electronic noses across a site (either at source or on the site boundary), together with meteorological data from an on-site weather tower and atmospheric dispersion modelling, to allow the display of both the current and forecast odour plumes ¹⁷ . The system can	The response of the electronic nose (and therefore its LoD and range) and its specificity depends on the selection of sensors in the array. Many sensors react to a variety of chemicals (odorous and non-odorous) and correct sensor selection is crucial.	No data available.

¹² McGinley M.A. and McGinley C.M., *Developing a Credible Odour Program*, Proceedings of International Conference on Environmental Odour Management, Cologne, 17-19 November 2004, pp271-280, Publ. VDI Verlag GmbH, 2004, ISBN 3-18-091850-0.

¹³ Although lung-sampling followed by laboratory-based dynamic dilution olfactometry (DDO) is the standard method (BS EN 13725: 2003, *Air Quality - Determination of Odour Concentration by Dynamic Olfactometry*) for measuring the odour concentration of source emissions, such as stacks, the lower detection limit of that method (about 50 ou_E m⁻³) is not low enough for measuring typical odour concentration in the ambient environment. So DDO should not normally be used for ambient odour measurements.

¹⁴ The Dilution-to-Threshold ratio is a measure of the number of dilutions (with carbon-filtered air) needed to make the odorous ambient air non-detectable. D/T is similar to the units of ou m⁻³ used in DDO, although the two are not interchangeable or directly comparable because the former is based on the odour detection threshold of one individual and the latter on a panel of typically 6 people.

¹⁵ Guy C., Gaisson F. and Purenne P., *Automated Electronic Nose Network for Measuring Industrial Odours*, Environmental Odour Management International Conference, Cologne, 17-19 November 2004, VDI Report 1850, pp431-451, ISBN 3-18-091850-0.

¹⁶ Nicolas J., Romain A.C. and Kurske M., *The Electronic Nose: a Tool for Controlling the Industrial Odour Emissions*, Environmental Odour Management International Conference, Cologne, 17-19 November 2004, VDI Report 1850, pp1113-125, ISBN 3-18-091850-0.

¹⁷ Pagé T et al, *Monitoring of Waste Water Treatment Odours by Means of OdoWatch™ Electronic Noses*, Paper at 4th Annual CIWEM Conference, Newcastle, Sept 2006.

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
			be set to issue alerts when preset thresholds are exceeded.		
Real-time monitoring	Community techniques ¹⁸ - Community surveys.	There are currently no CEN, ISO or BS standards method covering community surveys or odour panels. However, national methods do exist in those other countries of Europe (e.g. the Netherlands and Germany) and New Zealand that have advanced odour regulation and management systems, for example German national standard VDI 3883: Part 1: 1997, <i>Effects and Assessment of Odours - Psychometric Assessment of Odour Annoyance</i> and Part 2, <i>Determination of Annoyance Parameters by Questioning</i> .	The only direct way of measuring annoyance/nuisance; the community technique of choice where practicable/applicable. The "% annoyed" persons are measured by hidden questions. There is no UK limit; in other countries guidelines are between 10% and 20%. Gives a snapshot of cumulative response (though can be repeated), so will not pick out episodes or distinguish between multiple sources. Restricted to urban or semi-urban areas with substantial population size.	German national standard VDI 3883 gives an effective LoD for measurement of "strongly annoyed persons" of 10%.	No data available.
Real-time monitoring	Community techniques - Odour panels.		When low population size/density makes Community Survey technique unsuitable, Odour Panels (or alternatively, Odour Diaries, can be used). Smaller number of people selected and trained as "field judges" record standard details at set time each day or day each week. German VDI method gives single Annoyance Index value, but <i>not</i> equivalent to % annoyed; and currently no experience in UK of significance. Able to resolve short-term odour episodes, show changes and trends in odour impact, and distinguish between sources	No data available.	No data available.
Real-time monitoring	Community techniques - Odour diaries.	There is currently no CEN, ISO or BS standard method covering this technique. However, a New Zealand MfE protocol exists ¹⁹ .	Used when low population size/density makes Community Survey technique unsuitable. Large number of volunteers record details to a standard format whenever odour occurs. Typical statistic generated is the percentage of days on which odour is detected at a particular intensity and above. Able to resolve short-term odour episodes, show changes and trends in odour impact, and distinguish between sources.	No data available.	No data available.
Real-time	Community techniques -	There is currently no CEN,	Complaints Monitoring is a methodical way of	No data available.	No data available.

¹⁸ The underlying premise of community techniques (community surveys, odour diaries and odour panels) is that the people affected by offensive or objectionable odours are the best source of information on the annoyance or nuisance impacts of those odours. The use of sociological and associated methods is therefore highly appropriate for evaluating this aspect of the odour problem

¹⁹ Ministry for the Environment New Zealand, *Review of Odour Management in New Zealand: Technical Report*. Air quality technical report No. 24. Ministry for the Environment, Wellington, 2002.

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
monitoring	Complaints monitoring.	ISO or BS standard method covering this technique. However, a New Zealand MfE protocol exists ²⁰ .	harnessing the response of the community. Complaints (and absence of them) are considered as a form of monitoring data. Requires an effective system for collecting and evaluating data. Caution is needed in interpretation - there are many reasons why complaint levels will not be an exact indicator of annoyance or nuisance; absence of complaints does not necessarily indicate no annoyance/nuisance. Best data are from dense urban/semi-urban populations, but must be accompanied by contemporaneous wind direction information. In other situations suitable only as a trigger for more rigorous assessment using other assessment tools.		

²⁰ Ministry for the Environment New Zealand, *Review of Odour Management in New Zealand: Technical Report*. Air quality technical report No. 24. Ministry for the Environment, Wellington, 2002.

Table 14.6: Ozone

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Sampling by diffusive (passive) samplers; analysis by ion chromatography (IC).	There is currently no CEN, ISO or BS standard method covering this application of the technique (see Note on passive sampling).	Ozone can be determined manually by sampling (typically over a 2-week period) using acrylic passive diffusion samplers (sodium nitrite absorbent). The ingress of nitrite-containing particles (which potentially interfere) is prevented by a 1 micron filter. Exposed samples are extracted into deionised water and analysed for nitrate by ion chromatography ²¹ or alternatively by colorimeter or spectrophotometer. Recommended exposure period between 2 and 4 weeks, so not suitable for short-term episodes. The usual applications, benefits and limitations of diffusive sampling apply.	The LoD for the Gradko diffusion tubes analysed by IC is stated as approx 1.4 ppb for a 2-week exposure period and a corresponding working range of 6.8 - 200 µg m ⁻³ or more.	The expanded uncertainty of the analytical determination of Gradko diffusion tubes by IC is stated as ±7%. No data on sampling uncertainty.
Period-averaged sampling	Sampling by diffusive (passive) samplers; analysis by IC.	Fully validated CEN-equivalent method.	A passive sampler (the 8-h ozone radial diffusive sampler) has been fully validated (according to the CEN protocol for the validation of diffusive samplers) for monitoring 8-h ozone concentrations in ambient air ²² . All the parameters regarding the sampler characteristics were found to be consistent with the requirements of this protocol apart from the blank value, which must be evaluated and subtracted at each sampling. Using an empirical model to allow for temperature and humidity effects on the uptake rate, the Data Quality Objective for ozone was easily attained. Therefore, the sampler represents an appropriate indicative method.	Standard sampling period for a single exposure is 2 weeks, at which the lower detection limit is 2 ppb.	Equivalent methods have an expanded uncertainty at the Limit Value that does not exceed the DQO of 15% for ozone.
Real-time monitoring	Measurement by continuous direct-reading ultraviolet photometric analyser.	BS EN 14625:2005: <i>Ambient air quality. Standard method for the measurement of the concentration of ozone by ultraviolet photometry.</i> (N.B. Supersedes BS ISO 13964)	This is the European reference monitoring method for demonstrating compliance with the EU Directive Limit Values. Continuous ambient monitoring systems used to report results for this purpose must be product-certified or covered by type approval: CAMSs certified under MCERTS meet the performance criteria in the CEN standards and the relevant Directive Data Quality Objective (DQO). The measurement is based on the absorption of ultra violet light by ozone. The absorption by an air path with no ozone present is measured to give a reference intensity. The absorption of the ozone-containing sample is then measured. The ozone concentration is calculated using the Beer-Lambert absorption equation. The instrument measures over an averaging period of about 30 seconds. The instrument types	Instruments are required by the type-approval test for this standard to have a concentration range covering is 0-500 µg m ⁻³ , a repeatability at zero of ≤1.0 ppb and a response time of ≤180 sec.	Measurements made to the European reference method using compliant/ equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO of 15% for Ozone.

²¹ Gradko Technical Data Sheet TDS6, available from http://www.gradko.co.uk/outdoor_ambient_air.shtml

²² Plaisance et al, *Radial diffusive sampler for the determination of 8-h ambient ozone concentrations*, Environmental Pollution, Vol.148., Issue 1, July 2007, pp1-9.

²³ *Air Pollution in the UK: 2007*, AEA report for Defra and the Devolved Administrations, available at www.airquality.co.uk

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
			currently deployed in the AURN are given in the <i>Air Pollution in the UK</i> series of publications ²³ and the instruments currently certified under the MCERTS scheme are listed at http://www.sira.co.uk/mcerts_prodregister.html		
Real-time monitoring	Measurement by continuous direct-reading chemiluminescence analyser.	BS 1747-12:1993, ISO 10313:1993 <i>Methods for measurement of air pollution. Determination of the mass concentration of ozone in ambient air: chemiluminescence method.</i>	Ozone can also be measured continuously by direct-reading chemiluminescence analyser, utilising the gas-phase chemiluminescent reaction between ozone and ethylene.	Range 2 µg m ⁻³ to 10 mg m ⁻³ . Response time about 3 seconds.	No details available.

Notes:

Passive diffusion samplers - the general performance requirements for all diffusive samplers used for the determination of the concentration of gases and vapours in ambient air, irrespective of the nature of the sorption process and the analytical determination, are covered by BS EN 13528:2002: *Ambient air quality. Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods.* Part 1 - *General requirements*; Part 2 - *Specific requirements and test methods*; Part 3 - *Guide to selection, use and maintenance.*

Table 14.7: Nitrogen oxides

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Diffusions tube (passive) sampling; analysis by Griess-Saltzman method.	No CEN, ISO or BS standard method currently ²⁴ exists for NO ₂ diffusion tube preparation, sampling or analysis. Until such time as a formal standard method is published Defra and the DAs expect application of this technique for LAQM to follow the diffusion tube <i>Practical Guidance</i> ²⁵ .	<p>Palmer-type diffusion tubes are widely used in the UK for indicative measurements of ambient NO₂ for the purposes of LAQM.</p> <p>The diffusion-tube grid is coated with either 50% TEA in acetone, or 20% TEA in water. Individual exposure periods for the tubes should ideally be 2-4 weeks (no longer than 5 weeks and no shorter than 1 week). It is recommend that the survey includes co-location of sample tubes with an automatic NO₂ analyser to allow a bias-adjustment factor to be calculated, and the exposure periods for the co-located tubes should be the same as the other tubes used in the survey.</p> <p>Analysis is (usually) by colorimetry, using Griess-Saltzman developing reagent (a mixture of sulphanilamide solution, phosphoric acid and N-(1-naphthyl)ethylenediamine dihydrochloride solution) added directly to the tube. After the colour has developed, the solution is transferred to a spectrophotometer cell and the absorbance measured at 540 nm. A calibration curve is constructed from sodium nitrite standard solutions mixed with the developing reagent.</p> <p>The usual applications, benefits and limitations of diffusive sampling apply.</p>	The lower detection limit is better than 0.5 ppb for 2-week exposures.	Measurement uncertainty quoted as ±25%.
Period-averaged sampling	Pumped (active) sampling through a fritted bubbler. Analysis by colorimetry using the Griess-Saltzman method.	BS ISO 6768:1998: <i>Ambient air. Determination of mass concentration of nitrogen dioxide. Modified Griess-Saltzman method.</i> (Replaced BS 1747 Part 9)	<p>Air is sampled for about 30 minutes through a fritted bubbler containing Saltzman reagent, where NO₂ reacts to produce a pink coloured azo dye that is quantified spectrophotometrically at 550 nm using standard solutions of sodium nitrite to construct a calibration curve.</p> <p>No longer widely used now that passive diffusion-tube sampling and continuous monitoring for NO₂ are commonplace. The main drawback is that samples cannot be stored for longer than one day.</p>	The method has an upper concentration range of 5 ppm (9400 µg NO ₂ m ⁻³). Sulphur dioxide, ozone and PAN interfere to varying degrees.	No data available.
Real-time monitoring	Measurement by continuous direct-reading chemiluminescence analyser.	BS EN 14211:2005: <i>Ambient air quality. Standard method for the measurement of the concentration of nitrogen</i>	This is the European reference monitoring method for demonstrating compliance with the EU Directive Limit Values. Continuous ambient monitoring systems used to report results for this purpose must be product-certified or covered by type approval: CAMSs certified	The concentration range covered by type-approval test certification is 0-500 µg.m ⁻³ for NO ₂ and 0-200 µg.m ⁻³ for NO.	Measurements made to the European reference method using compliant/ equivalent (e.g.

²⁴ Since the publication of the Practical Guidance, the Directorate General Environment (DG-ENV) of the European Commission has announced its decision to develop a CEN standard method for NO₂ monitoring in ambient air using diffusive samplers. However, it is likely to be several years before the CEN standard method is finalised.

²⁵ *Diffusion Tubes for Ambient NO₂ Monitoring: Practical Guidance*, AEA Report to Defra and the Devolved Administrations, 2008, available at www.airquality.co.uk

²⁶ *Air Pollution in the UK: 2007*, AEA report for Defra and the Devolved Administrations, available at www.airquality.co.uk

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
		<i>dioxide and nitrogen monoxide by chemiluminescence</i>	under MCERTS meet the performance criteria in the CEN standards and the relevant Directive Data Quality Objective (DQO). The determination of oxides of nitrogen is based on the chemiluminescent energy emitted when nitric oxide (NO) is reacted with ozone (O ₃) in an evacuated chamber to form chemiluminescent nitrogen dioxide (NO ₂). The instrument types currently deployed in the AURN are given in the <i>Air Pollution in the UK</i> series of publications ²⁶ and the instruments currently certified under the MCERTS scheme are listed at http://www.sira.co.uk/mcerts_prodregister.html		MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO of 15% for NO ₂ or NO _x .
Real-time monitoring	Measurement by continuous direct-reading chemiluminescence analyser.	BS 1747-9:1987, ISO 7996:1985: <i>Methods for measurement of air pollution. Determination of the mass concentration of nitrogen oxides in ambient air: chemiluminescence method</i>	Technique as above. Interferents - at high temperatures, the converter will also convert nitrogen compounds other than nitrogen dioxide to nitrogen monoxide partially or completely, depending on converter type and temperature. The most important of these are ammonia, amines, nitric acid, some organic and inorganic nitrites and nitrates, and peroxyacetylnitrate (PAN). The determination may be affected by variations of quenching effects originating from either pressure variation or water vapour in the reaction chamber. Generally the reaction takes place under reduced pressure to minimize these effects.	LoD is 10 µg m ⁻³ for NO, 15 µg m ⁻³ for NO ₂ . Measurement range Up to 12,000 µg.m ⁻³ for NO and 18,000 µg.m ⁻³ for NO ₂ . Response times short (a few seconds).	Precision ± 1% (at 20% full scale) or ± 2% (at 80% full scale). Accuracy at 1000 µg m ⁻³ is ±1% of full scale.
Real-time monitoring	Measurement by continuous direct-reading electrochemical analyser.	There is currently no CEN, ISO or BS standard method covering this technique.	Sampled gas passed through electrochemical cells where currents produced are proportional to the concentrations of NO and NO ₂ . Electrochemical analysers usually have a poorer analytical performance than chemiluminescence analysers, but are usually more portable (sometimes battery powered) and considerably cheaper.	Typical ²⁷ range 0-10 ppm NO ₂ , 0-100 ppm NO; and LODs 20 ppb NO ₂ , 500 ppb NO. Response time (T ₉₀) <40 sec.	Typical repeatability ± 1% of signal.

²⁷ Manufacturer's data sheet, StreetBox Urban Pollution Monitor, Signal Ambitech, Signal Group Ltd.

Table 14.8: Sulphur dioxide

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Pumped (active) sampling through a Dreschel bottle with absorption in hydrogen peroxide solution; analysis by acidimetric titration.	BS1747-3:1969 (1986), <i>Methods for measurement of air pollution. Determination of sulphur dioxide.</i>	This routine method was in widespread use since the 1960s in the old UK National Survey of smoke and sulphur dioxide and, since the early 1980s, was used for monitoring compliance with the relevant EU Directive (80/779/EEC) on smoke and SO ₂ . Apparatus consists of pre-filters (to remove particulate matter and simultaneously sample Black Smoke), Dreschel bottles containing dilute hydrogen peroxide, a dry gas meter to record the sampled volume, and a pump (sample flow rate 1.4 l min). An 8-valve 24-hour timer, allows separate daily samples over a full week to be collected between changeover visits. Exposed solutions titrated with standard sodium tetraborate (0.004 N) using BDH 4.5 indicator solution. The method determines total atmospheric acidity; other acid or alkaline gases present in air will interfere. Normally the total acidity titration result may be taken as a good approximation of the SO ₂ concentration. At concentration less than 100 µg SO ₂ m ⁻³ , ammonia interference can be appreciable, but correction can be made after titration with Nessler's reagent. The method can be modified to make it more specific by using ion chromatography (IC) for the analytical end-method.	The LoD of the method is of the order of 10 µg per 50 ml absorbing solution: for 24-hour samples at 1.4 l min ⁻¹ , this is equivalent to a LoD of 5 µg m ⁻³ .	Standard deviation of the analytical method is 16 µg: for 24-hour samples at 1.4 l min ⁻¹ , this is equivalent to a standard deviation of 8 µg m ⁻³ .
Period-averaged sampling	Sampling by diffusive (passive) samplers; analysis by ion chromatography (IC).	There is currently no CEN, ISO or BS standard method covering this application of the technique (see Note on passive sampling)	Diffusion tube with potassium hydroxide absorbent. The ingress of sulphur-containing particles (e.g. diesel fume) is prevented by a 1 micron filter. Exposed samples are extracted into deionised water and analysed for sulphate by ion chromatography ²⁸ . Recommended exposure period between 1 and 4 weeks, so not suitable for short-term episodes. The usual applications, benefits and limitations of diffusive sampling apply.	The LoD for the Gradko diffusion tubes analysed by IC is stated as approx 0.5 ppb for a 2-week exposure period and a corresponding working range of 4 - 200 µg m ⁻³ .	The expanded uncertainty of the analytical determination of Gradko diffusion tubes by IC is stated as ±7%. No data on sampling uncertainty.
Real-time monitoring	Measurement by continuous direct-reading UV fluorescence analyser.	BS EN 14212:2005 <i>Ambient air quality. Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence.</i> (N.B. Supersedes ISO 10498:2004 UV fluorescence method.)	This is the European reference monitoring method for demonstrating compliance with the EU Directive Limit Values. Continuous ambient monitoring systems used to report results for this purpose must be product-certified or covered by type approval: CAMSs certified under MCERTS meet the performance criteria in the CEN standards and the relevant Directive Data Quality Objective (DQO). The analyser works on the principle of UV fluorescence, whereby SO ₂ molecules are excited to higher energy states by UV radiation. As they return to	Instruments are required by the type approval test for this standard to have a concentration range covering is 0-400 ppb (rural applications or 0-2000 ppb (urban), a repeatability at zero of ≤1.0 ppb and a response time of ≤180 sec.	Measurements made to the European reference method using compliant/ equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO

²⁸ Gradko Technical Data Sheet TDS5, available from http://www.gradko.co.uk/outdoor_ambient_air.shtml

²⁹ *Air Pollution in the UK: 2007*, AEA report for Defra and the Devolved Administrations, available at www.airquality.co.uk

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
			<p>their ground state, secondary fluorescent radiation is emitted with intensity proportional to the concentration of SO₂ in the sample. Aromatic Hydrocarbons, H₂O, NH₃, NO, NO₂ and <i>m</i>-xylene are examples of interfering gases, and one or more selective traps should be used to remove interfering gases.</p> <p>The instrument types currently deployed in the AURN are given in the <i>Air Pollution in the UK</i> series of publications²⁹ and the instruments currently certified under the MCERTS scheme are listed at http://www.sira.co.uk/mcerts_prodregister.html</p>		of 15% for SO ₂ .
Real-time monitoring	Measurement by continuous direct-reading electrochemical analyser.	There is currently no CEN, ISO or BS standard method covering this technique.	Sampled gas passed through electrochemical cells where the current produced is proportional to the concentrations. Electrochemical analysers usually have a poorer analytical performance than UV fluorescence analysers, but are usually more portable (sometimes battery powered) and considerably cheaper.	Typical ³⁰ range 0-40 ppm, LoD 25 ppb, response time (T ₉₀) <40 sec.	Typical repeatability ± 1% of signal.

Notes:

Passive diffusion samplers - the general performance requirements for all diffusive samplers used for the determination of the concentration of gases and vapours in ambient air, irrespective of the nature of the sorption process and the analytical determination, are covered by BS EN 13528:2002: *Ambient air quality. Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods. Part 1 - General requirements; Part 2 - Specific requirements and test methods; Part 3 - Guide to selection, use and maintenance.*

³⁰ Manufacturer's data sheet, StreetBox Urban Pollution Monitor, Signal Ambitech, Signal Group Ltd.

Table 14.9: Carbon monoxide

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Real-time monitoring	Measurement by continuous direct-reading non-dispersive infrared (NDIR) analyser.	BS EN 14626:2005 <i>Ambient air quality. Standard method for the measurement of the concentration of carbon monoxide by non-dispersive infrared spectroscopy.</i> (N.B. Supersedes ISO 4424 NDIR method.)	This is the European reference monitoring method for demonstrating compliance with the EU Directive Limit Value. Continuous ambient monitoring systems used to report results for this purpose must be product-certified or covered by type approval: CAMSs certified under MCERTS meet the performance criteria in the CEN standards and the relevant Directive Data Quality Objective (DQO). CO concentrations in ambient air are measured by the absorption of infrared radiation at 4500-4900 nm wavelength. However, other gases with overlapping absorption bands will interfere (e.g. water, carbon dioxide and to a lesser extent methane and ethane) so a reference detection system is used to alternately measure absorption due to CO in the sampled air stream and absorption by interfering specie. An infrared detector and amplification system produces output voltages proportional to the CO concentration. The instrument types currently deployed in the AURN are given in the <i>Air Pollution in the UK</i> series of publications ³¹ and the instruments currently certified under the MCERTS scheme are listed at http://www.sira.co.uk/mcerts_proregister.html .	Range covered by the standard is 0-100 mg m ⁻³ . Instruments are required by the type-approval test for this standard to have a concentration range covering is 0-10 ppb (rural applications or 0-50 ppb (urban), a repeatability at zero of ≤1.0 ppm and a response time of ≤180 sec.	Measurements made to the European reference method using compliant/ equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO of 15% for CO.
Real-time monitoring	Measurement by continuous direct-reading electrochemical analyser.	There is currently no CEN, ISO or BS standard method covering this technique.	Sampled gas passed through electrochemical cells where current is produced by the oxidation of CO, which is proportional to the concentration. Electrochemical analysers usually have a poorer analytical performance than NDIR instruments and the cells have limited lifetimes and require periodic replacement. However, electrochemical instruments are usually more portable (sometimes battery powered) and usually considerably cheaper than NDIR instruments.	Typical ³² range 0-40 ppm, LoD 25 ppb, response time (T ₉₀) <40 sec.	Typical repeatability ± 1% of signal.
Real-time monitoring	Measurement by continuous sampling with batch analysis by gas chromatography (GC).	ISO 8186:1989 <i>Ambient air - Determination of the mass concentration of carbon monoxide - Gas chromatographic method</i>	Carbon monoxide may also be determined semi-continuously by GC with FID detector, using the principle of catalytic reduction of CO to methane. Measurements are made on a cyclic basis by flushing the contents of a sample loop into the instrument.	LoD of about 10 ppb is achieved.	No data available.

³¹ *Air Pollution in the UK: 2007*, AEA report for Defra and the Devolved Administrations, available at www.airquality.co.uk

³² Manufacturer's data sheet, StreetBox Urban Pollution Monitor, Signal Ambitech, Signal Group Ltd.

Table 14.10: Heavy metals (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Pt, V and Zn)

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Pumped (active) sampling of particulate metals onto filters; analysis by graphite furnace atomic absorption spectrophotometry (GF-AAS) or inductively coupled plasma with mass spectrometry (ICP-MS).	<i>BS EN 14902:2005 Ambient air quality. Standard method for the measurement of Pb, Cd, As, and Ni in the PM₁₀ fraction of suspended particulate matter.</i>	This is the European reference monitoring method for demonstrating compliance with the EU Directive Limit Value for lead and the 4th Daughter Directive Target Values for As, Cd, Ni in the PM ₁₀ particulate fraction of ambient air. The UK Urban/Industrial Network (which, together with the Rural Heavy Metals and Mercury Network, make up the UK Heavy Metals Monitoring Network) monitors a range of metallic elements at urban and industrial sites. All sites monitor As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Pt, V and Zn. Separate measurements of vapour phase mercury are made at some sites (see below). Historically, this network grew out of several separate long-term monitoring programmes, with differences in methods and practices. Monitoring has now been rationalised into a single integrated network. Weekly duration samples of PM ₁₀ fraction particulates are obtained using R&P Partisol 2000 samplers operating at 1 m ³ hr ⁻¹ , in accordance with BS EN 12341: 1998, using 47 mm diameter GN Metricel membrane filters. (In the Rural Heavy Metals and Mercury Network the PM ₁₀ fraction of particulates is collected weekly using Thermo FH95 single or FH95SEQ sequential samplers.) Analysis of samples is by microwave acid digestion followed by ICP-MS, in accordance with European Standard EN 14902:2005.	Range ng.m ⁻³ ; covered by the standard is: Pb from 1 to 4000 ng.m ⁻³ ; Cd from 0.1 to 50 ng.m ⁻³ ; As from 0.5 to 350 ng.m ⁻³ ; Ni from 2 to 100 ng.m ⁻³ . The actual lower limits to the above ranges (i.e. the LoD) are required by the standard to be ≤10% of the EU Limit/Target Values. The LoDs (in ng.m ⁻³) achieved in practice ³³ in The UK Urban/Industrial Network are: As 0.03; Cd 0.001; Cr 0.02; Cu 0.02; Fe 0.3; Mn 0.003; Ni 0.01; Pb 0.01; Pt 0.001; V 0.002; Zn 0.06; Hg 0.01.	Measurements made to the European reference method using compliant/ equivalent instruments will have an expanded uncertainty at the Limit Value that does not exceed the Data Quality Objective (DQO) of 25% for Pb and 40% each for As, Cd and Ni. The annual-mean expanded relative uncertainties achieved in practice in The UK Urban/Industrial Network are 18% for Pb, 32% for As, 25% for Cd and 18% for Ni.
Period-averaged sampling	Sampling of lead by pumped (active) sampling onto filters. Analysis by AAS.	BS 1747-13:1994, ISO 9855:1993 <i>Methods for measurement of air pollution. Determination of the particulate lead content of aerosols collected on filters: atomic absorption spectrometric method.</i>	General method for the analysis of particulate Pb in ambient air samples. This standard contains little detail on the sampling aspect. Air samples are collected onto membrane filters or glass-fibre filters and determined by AAS. High levels of antimony interfere.	LoD of 1 µg Pb per sample	No details available.
Period-averaged sampling	Total gaseous mercury - pumped (active) sampling onto sorbent tubes; analysis by mercury analyser with fluorescence detector.	EN 15852:2010 <i>Ambient air quality - Standard method for the determination of total gaseous mercury</i>	The EU 4th Daughter Directive also requires monitoring of mercury, although no Limit or Target Value is set. The UK Urban/Industrial Network samples total gaseous mercury by collection on Amasil (gold-coated silica) tubes using low-flow pumps at a rate of 100 ml min ⁻¹ for either 1 week or 4 weeks (depending on expected concentrations). Analysis is carried out using a PS Analytical Sir Galahad II analyser with a	LoD is 0.02 ng per tube, equivalent to approximately 0.02 ng m ⁻³ for sampling at 100 ml min ⁻¹ for 1 week ³⁴ .	Measurements made under the Directive must have an expanded uncertainty at the Limit Value that does not exceed the DQO of 50% for total gaseous Hg. The annual-mean

³³ Annual Report for 2007 on the UK Heavy Metals Network, NPL report to Defra, March 2008.

³⁴ Annual Report for 2007 on the UK Heavy Metals Network, NPL report to Defra, March 2008.

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
			fluorescence detector, with calibration by injection of known amounts of mercury vapour, based on the draft standard method currently being developed by CEN TC264 WG25 "Mercury".		expanded relative uncertainty achieved in practice in The UK Urban/Industrial Network is 19% for total gaseous Hg.
	Speciated mercury - pumped (active) sampling onto denuder tube and trap; analysis by cold-vapour atomic fluorescence spectrophotometry (CV-AFS).	There is currently no CEN, ISO or BS standard method covering this technique.	Elemental mercury (Hg^0) makes up over 97% of the total atmospheric mercury burden. The remaining amount consists of reactive gaseous mercury (RGM) and particulate mercury (Hg^P). Speciated measurements of mercury are made at one of the Rural Heavy Metals and Mercury Network sites using a state-of-the-art Tekran mercury speciation system ³⁵ , which measures RGM, Hg^P and Hg^0 . The detector in the Tekran 2537A analyser employs Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS). Elemental mercury is sampled and analysed for one hour, whilst RGM and Hg^P are collected on a KCl-coated denuder and particulate trap, respectively. During the following hour, the collected RGM and Hg^P are desorbed and analysed.	The technique is very sensitive, with LoD of the order of $ng\ m^{-3}$ for Hg^0 and $pg\ m^{-3}$ for RGM and Hg^P , which is necessary to measure the very low concentrations of these species in ambient air. Using this method, Hg^0 is analysed with a temporal resolution of 5 minutes every other hour and hourly averages of RGM and Hg^P concentrations are obtained every other hour.	The measurement reproducibility under laboratory conditions has been shown to be about 5-10%. In the field, the system can under-measure these very low concentrations unless the sampler is carefully sited to avoid surface effects ³⁶ .

³⁵ *Air Pollution in the UK: 2007*, AEA report for Defra and the Devolved Administrations, available at www.airquality.co.uk

³⁶ Private communication, CEH Edinburgh.

Table 14.11: Ammonia and ammonium aerosol (NH_x)

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Active sampling of gaseous ammonia by denuder tubes with subsequent collection of particulate ammonium on back-up filter; analysis by Ammonium Flow Injection Analysis (AMFIA).	There is currently no CEN, ISO or BS standard method covering this technique.	<p>The Defra-funded National Ammonia Monitoring Network (NAMN)³⁷ uses two techniques - active denuders and diffusion tubes - to measure ammonia and the ammonium ion on a monthly basis across the UK, in order to quantify temporal and spatial changes in air concentrations and deposition in reduced nitrogen (NH_x) species (gaseous NH₃ and aerosol NH₄⁺) on a long-term basis to examine responses to changes in the agricultural sector (including IPPC-driven abatement of intensive pig and poultry sectors), to verify compliance with international targets (e.g. the UNECE Gothenburg Protocol and the EU National Emissions Ceilings Directive), to test the performance of an atmospheric chemistry models and to contribute to national nitrogen deposition estimates³⁸.</p> <p>Sites with power available use an active diffusion denuder technique for NH₃, using the Centre for Ecology and Hydrology (CEH) Lancaster DELTA (Denuder for Long-Term Atmospheric Sampling) system. Aerosol NH₄⁺ is monitored at a subset of DELTA sites³⁹. Typically 15 m³ air per month is sampled through two glass denuder tubes (coated internally with citric acid) in series, which selectively collects gaseous ammonia. Particulate ammonium is subsequently collected on a downstream, acid-impregnated, filter pack. Exposed denuders and filters are extracted with deionised water and analysed for ammonium using a high sensitivity Ammonium Flow Injection Analysis (AMFIA) system⁴⁰.</p>	The LoD for the DELTA denuder system is about 0.01 µg m ⁻³ for ammonia or for ammonium aerosol.	Replicated sampling has shown the precision of the DELTA technique to be better than 10 % for individual monthly values, with an annual average difference within ± 2 %.
Period-averaged sampling	Sampling of gaseous ammonia by diffusive (passive) samplers; analysis by Ammonium Flow Injection Analysis (AMFIA).	There is currently no CEN, ISO or BS standard method covering this application of the technique (see Note on passive sampling).	NAMN sites where no power is available measured NH ₃ initially using an improved version of the Gradko 35 mm path-length membrane diffusion tubes ⁴¹ . Exposed samples are extracted into deionised water and analysed for ammonium using an AMFIA system.	The LoD for the improved Gradko diffusion tube technique is stated as 1 µg m ⁻³ .	No data available

³⁷ Details given at www.uk-pollutantdeposition.ceh.ac.uk/networks

³⁸ *Air Pollution in the UK: 2007*, AEA report for Defra and the Devolved Administrations, available at www.airquality.co.uk

³⁹ The DELTA system also allows monitoring of other atmospheric components at these sites, including monthly measurements of gaseous HNO₃, SO₂, HCl and aerosol NO₃⁻, SO₄²⁻, Cl⁻, plus base cations Na⁺, Ca²⁺ and Mg²⁺, as part of the UK Nitric Acid Monitoring Network.

⁴⁰ *Analysis of temporal and spatial patterns of NH₃ and NH₄⁺ over the UK – 2007*, Annual report to DEFRA, Centre for Ecology and Hydrology, August 2008

⁴¹ Sutton M.A., Miners B., Tang Y.S., Milford C., Wyers G.P., Duyzer J.H. and Fowler D. (2001b), *Comparison of low-cost measurement techniques for long-term monitoring of atmospheric ammonia*. *J. Env. Monit.*, **3**, 446-453.

Period-averaged sampling	Sampling of gaseous ammonia by diffusive (passive) samplers; analysis by Ammonium Flow Injection Analysis (AMFIA).	There is currently no CEN, ISO or BS standard method covering this application of the technique (see Note on passive sampling).	NAMN sites where no power is available have since moved to the more sensitive CEH ALPHA (Adapted Low-Cost Passive High Absorption) passive diffusion sampler ⁴² that was designed and developed specifically for monitoring ambient levels of NH ₃ . The passive sampling system consists of three replicate ALPHA samplers attached by the use of Velcro to an aerodynamically shaped support (upturned Frisbee or plant saucer) on a pole about 1.5 m height above ground. Triplicate samplers are implemented at each site in order to give a more reliable estimation of the air concentration of ammonia. Exposed samples are extracted into deionised water and analysed for ammonium using an AMFIA system.	The LoD for the ALPHA passive diffusion sampler is stated as approx 0.02 µg m ⁻³ .	Intercomparison with DELTA samplers suggests an annual average precision of 10-13%.
Period-averaged sampling	Sampling of gaseous ammonia by diffusive (passive) samplers; analysis by ion chromatography (IC)	There is currently no CEN, ISO or BS standard method covering this application of the technique (see Note on passive sampling).	35 mm path-length membrane diffusion tube with oxalic acid absorbent. The ingress of ammonium particles is prevented by a 1 micron filter. Recommended exposure period between 1 and 4 weeks. Exposed samples are extracted into deionised water and analysed for ammonium by ion chromatography.	The LoD for the Gradko diffusion tubes analysed by IC is stated as approx 0.95 µg m ⁻³ (1.34 ppb) for a 2-week exposure period.	The expanded uncertainty of the analytical determination of Gradko diffusion tubes by IC is stated ⁴³ as ±7%. No data on sampling uncertainty.
Real-time monitoring	Measurement by continuous direct-reading chemiluminescence NO _x analyser in conjunction with an ammonia converter unit.	There is currently no CEN, ISO or BS standard method covering this technique.	For continuous ammonia measurements in the ppb range, a chemiluminescence NO _x analyser can be used in conjunction with an ammonia converter unit: a twin channel analyser reading NO _x , and NO _x plus ammonia converted to NO _x by the catalyst, allows ammonia concentration to be calculated from the difference.	Instruments typically ⁴⁴ have multiple pre-set ranges, up to 30 mg m ⁻³ (20 ppm). LoD typically 1 ppb Response time (T ₉₀) 120 sec	Precision better than 1 ppb on 500 ppb range.

Notes:

Passive diffusion samplers - the general performance requirements for all diffusive samplers used for the determination of the concentration of gases and vapours in ambient air, irrespective of the nature of the sorption process and the analytical determination, are covered by BS EN 13528:2002: *Ambient air quality. Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods. Part 1 - General requirements; Part 2 - Specific requirements and test methods; Part 3 - Guide to selection, use and maintenance.*

⁴² Tang, Y.S., Cape, J.N. and Sutton, M.A. (2001b), *Development and types of passive samplers for NH₃ and NO_x*. In Proceedings of the International Symposium on Passive Sampling of Gaseous Pollutants in Ecological Research. *TheScientific World*, 1, 513-529

⁴³ Gradko Technical Data Sheet TDS7, available from http://www.gradko.co.uk/outdoor_ambient_air.shtml

⁴⁴ Manufacturer's data, Thermo Scientific.

Table 14.12: Inorganic acids (HNO₃, HCl, HF, HBr, H₃PO₃)

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Determination of total atmospheric acidity by pumped (active) sampling through a Dreschel bottle with absorption in hydrogen peroxide solution; analysis by acidimetric titration.	BS1747-3:1969 (1986), <i>Methods for measurement of air pollution. Determination of sulphur dioxide.</i>	Although most commonly applied to the determination of SO ₂ , the method actually determines total atmospheric acidity. Alkaline gases (e.g. ammonia) present in air will interfere. The method can be modified to make it more specific by using ion chromatography (IC) for the analytical end-method.	The LoD of the method is of the order of 10 µg per 50 ml absorbing solution. For 24-hour samples at 1.4 l min ⁻¹ , this is equivalent to a LoD of 5 µg m ⁻³ .	Standard deviation of the analytical method is 16 µg; For 24-hour samples at 1.4 l min ⁻¹ , this is equivalent to a standard deviation of 8 µg m ⁻³ .
Period-averaged sampling	Pumped (active) sampling of HCl or HF through a Dreschel bottle with alkaline absorbent solution; analysis by acidimetric titration or other end-methods (e.g. ion chromatography).	There is currently no CEN, ISO or BS standard method covering this application of the technique.	For wet absorption sampling, hydrogen chloride is usually bubbled through a fritted glass or a midget impinger. The absorbing medium may be distilled water (HCl is highly soluble in water) but dilute NaOH (0.01 or 0.001 M) gives >99% recovery. All glassware needs to be thoroughly cleaned in distilled water or dilute nitric acid, and blank determinations are essential. Because ambient levels of HCl are usually low, extended sampling times are necessary: sampling at 1 l min ⁻¹ over 24 h is suitable in most cases. Particulate chloride interferes, hence the necessity to remove it by a membrane filter upstream of the bubbler (unless a determination of total chlorine is required in which case the filter is omitted) ^{45,46} . The technique can also be used for determining hydrogen fluoride ⁴⁷ .	No data available	No data available
Period-averaged sampling	Active sampling of gaseous HNO ₃ , HCl and HF by denuder tubes; analysis by ion chromatography.	There is currently no CEN, ISO or BS standard method covering this technique.	Because of the problems of artifact formation, denuder tube methods have been developed which remove all significant interferents. A commercially available annular denuder sampling system ⁴⁸ can measure HCl by sampling air at 15 l min ⁻¹ for 1-24 h through two denuder tubes coated with NaF. The denuders are extracted with deionised water and HCl is determined as chloride by ion chromatography. Particulate chloride collected on a Nylon backup filter can be analysed separately. A similar system for HF uses denuder tubes coated with sodium carbonate-glycerol and a PTFE backup filter. The UK Nitric Acid Monitoring Network provides data on nitric acid, hydrochloric acid, particulate nitrate and other species as part of the UK Acid Deposition Monitoring Network ⁴⁹ . An extension of the DELTA system at the National Ammonia Monitoring Network	The lower detection limits for the method are between 0.1 µg HCl m ⁻³ (1-h sample) and 0.005 µg HCl m ⁻³ (24-h sample) and the denuder collection efficiency is reported to be >99%. Similar performance for determination of HF.	No data available

⁴⁵ Clayton & Davis, *HMIP Manual on Environmental Sampling and Analysis*, WSL report LR680/LR756 (PA), 1989.

⁴⁶ Kirk PWW & Lester JN, *Handbook of Air Pollution Analysis*, 2nd Edn., Ed. Harrison & Perry, Publ. Chapman & Hall, London, p425, 1986

⁴⁷ Katz M, (ed), American Public Health Assoc., *Methods of Air Sampling & Analysis*, 2nd Ed., Washington DC, 1977

⁴⁸ Manufacturer's literature, Rupprecht & Patashnick Co

⁴⁹ *Air Pollution in the UK: 2007*, AEA report for Defra and the Devolved Administrations, available at www.airquality.co.uk

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
			(NAMN) sites is used to obtain monthly measurements of gaseous HNO ₃ , HCl, SO ₂ and aerosol NO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , plus base cations Na ⁺ , Ca ²⁺ and Mg ²⁺ .		
Period-averaged sampling	Active sampling of non-volatile acids (sulphuric acid and phosphoric acid) onto filters; analysis by ion chromatography.	BS ISO 21438-1:2007 <i>Workplace atmospheres. Determination of inorganic acids by ion chromatography. Non-volatile acids (sulphuric acid and phosphoric acid).</i>	This workplace standard method is for the determination of the concentrations of sulphuric acid and phosphoric acid and can be easily modified for ambient applications. The inhalable fraction of airborne particles is collected on filters, extracted and analysed by ion chromatography. The procedure does not allow differentiation between the acids and their corresponding salts if both are present in the air; or between phosphoric acid and diphosphorus pentoxide (phosphoric anhydride) if both are present in the air.	The concentration range is determined by the volume of air sampled. For a volume 1 m ³ , the working range is approximately 5 µg m ⁻³ to 2,000 mg m ⁻³ of sulfuric acid or phosphoric acid.	No data available
Period-averaged sampling	Active sampling of volatile acids except hydrofluoric acid (hydrochloric acid, hydrobromic acid and nitric acid) onto impregnated filters; analysis by ion chromatography.	ISO/DIS 21438-2: <i>Workplace atmospheres - - Determination of inorganic acids by ion chromatography -- Part 2: Volatile acids, except hydrofluoric acid (hydrochloric acid, hydrobromic acid and nitric acid)</i>	This discussion draft International Standard is for the determination of the concentrations of hydrogen chloride (HCl) gas and hydrochloric acid mist, hydrogen bromide (HBr) vapour and hydrobromic acid mist and nitric acid (HNO ₃) vapour and mist in workplace air. It can be easily modified for ambient applications. Samples are collected on an alkali impregnated quartz-fibre filter and analysis by ion chromatography.	Similar to above	No data available

Table 14.13: Hydrogen sulphide and inorganic reduced sulphur compounds

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Sampling of hydrogen sulphide by diffusive (passive) samplers; analysis by ion chromatography (IC).	There is currently no CEN, ISO or BS standard method covering this application of the technique (see Note on passive sampling).	71 mm path-length membrane diffusion tube with zinc acetate absorbent. The ingress of particles is prevented by a 1 micron filter. Adsorbed hydrogen sulphide is converted to stable zinc sulphide, which is extracted in the laboratory and determined quantitatively by visible spectrophotometry using a calibration curve from standard sulphide solutions. Ozone and some reducing agents such as SO ₂ can have some interfering effect ⁵⁰ . Recommended exposure period is between 2 and 4 weeks, so not suitable for short-term episodes. The usual applications, benefits and limitations of diffusive sampling apply.	The LoD for the Gradko diffusion tubes analysed by visible spectrophotometry is stated as approx 0.23 µg m ⁻³ (0.16 ppb) for a 2-week exposure period.	The expanded uncertainty of the analytical determination of Gradko diffusion tubes by visible spectrophotometry is stated as ±10%. No data on sampling uncertainty.
Period-averaged sampling	Pumped (active) sampling of hydrogen sulphide through an impinger bottle with absorption in cadmium hydroxide suspension; analysis by visible spectrophotometry.	Although there is currently no CEN, ISO or BS standard method covering this technique, a custom and practice method exists: ISC method 42402-01-70T <i>Methylene Blue Method</i> ⁵¹ .	Air bubbled through an alkaline suspension of cadmium hydroxide (10 ml) in a midget impinger (25 ml capacity) with coarse-porosity frit. The sulphide is precipitated as cadmium sulphide (the sulphide suffers rapid air oxidation in aqueous alkaline solution) and Arabinogalactan is added to minimise photo-decomposition. The collected sulphide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction with a strongly acid solution of N,N-dimethyl- <i>p</i> -phenylenediamine and ferric chloride. Extended sampling (e.g. 24-h integrated samples) should be avoided as losses can result and analysis should be completed within 24 h. The methylene blue reaction is highly specific for sulphide at ambient concentrations. Some interferences occur ⁷² from nitrite (>0.3 ppm) and ozone (15% at 57 ppb).	Method range 2-200 µg m ⁻³ (2-144 ppb). When sampling at the maximum recommended rate of 1.5 l min ⁻¹ for 2 h, the LoD is 1.1 µg m ⁻³ (0.14 ppb).	Precision stated as ±12%.

⁵⁰ Gradko Technical Data Sheet TDS4, available from http://www.gradko.co.uk/outdoor_ambient_air.shtml

⁵¹ Lodge JP (ed), *Methods of Air Sampling & Analysis*, 3rd Edn., Intersociety Committee, Lewis Publ Inc, 1989.

Real-time monitoring	Measurement of hydrogen sulphide by continuous UV-fluorescence analyser.	There is currently no CEN, ISO or BS standard method covering this technique. A CEN working group (SC3/WG 3) is considering a European Standard method for determination of hydrogen sulphide in ambient atmospheres by spectrophotometry and by GC-FPD.	Direct-reading continuous measurements may be made using a UV-fluorescence SO ₂ analyser coupled to an H ₂ S converter unit containing a scrubber ⁵² to remove SO _x and a catalyst to convert H ₂ S passing through the scrubber into SO ₂ .	Range ⁵³ 0-50 ppb to 0-2 ppm total reduced sulphur. The lower detection limit (about 0.5 ppb) and relatively fast response time (less than 180 sec) lend this approach to monitoring intermittent peak concentrations.	No data available
Real-time monitoring	Measurement of total sulphides by continuous flame-photometric analyser.	There is currently no CEN, ISO or BS standard method covering this technique.	Continuous flame-photometric analysers are in widespread use for the continuous determination of total sulphur species in ambient air. These instruments detect not only sulphur dioxide, but also hydrogen sulphide and other sulphur-containing compounds such as mercaptans. Total reduced S can be obtained by difference by simultaneous determination of total S by FPD, and total S less SO _x using a second FPD with a catalytic scrubber.	No data available	No data available
Real-time monitoring	Measurement of hydrogen sulphide by continuous sampling with batch analysis by gas chromatography (GC).	There is currently no CEN, ISO or BS standard method covering this technique. An Australian national standard exists: AS 3580.8.1-1990: <i>Methods for Sampling and Analysis of Ambient Air – Determination of Hydrogen Sulphide – Automatic Intermittent Sampling – Gas Chromatographic Method</i> . A CEN working group (SC3/WG 3) is considering a European Standard method for determination of hydrogen sulphide in ambient atmospheres by spectrophotometry and by GC-FPD.	Automatic method for the measurement of hydrogen sulphide. Conditioned air sample introduced to gas chromatograph. Any gaseous compound with a similar retention time to hydrogen sulphide on the GC column potentially interferes.	Approximately 3 ppb (5 mg m ⁻³) to 2 ppm (3 mg m ⁻³)	No data available
Real-time monitoring	Measurement by continuous direct-reading electrochemical analyser.	There is currently no CEN, ISO or BS standard method covering this technique.	Sampled gas passed through electrochemical cells where the current produced is proportional to the concentration. Electrochemical analysers usually have a poorer analytical performance than UV fluorescence analysers, but are usually more portable (sometimes	Typical ⁵⁴ range 0-10 ppm, LoD 100 ppb, response time (T ₉₀) <40 sec.	Typical repeatability ±1% of signal.

⁵² Manufacturers literature: Horiba Instruments Ltd.

⁵³ Manufacturer's data sheet, Teledyne API.

			battery powered) and considerably cheaper.		
Real-time monitoring	Measurement of total sulphides by continuous flow colorimetric analyser.	There is currently no CEN, ISO or BS standard method covering this technique.	Other automatic methods include a continuous flow H ₂ S analyser based on the methylene blue colorimetric method.	Typical range of 0-100 ppb and LoD of 2 ppb	No data available

Notes:

Passive diffusion samplers - the general performance requirements for all diffusive samplers used for the determination of the concentration of gases and vapours in ambient air, irrespective of the nature of the sorption process and the analytical determination, are covered by BS EN 13528:2002: *Ambient air quality. Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods. Part 1 - General requirements; Part 2 - Specific requirements and test methods; Part 3 - Guide to selection, use and maintenance.*

⁵⁴ Manufacturer's data sheet, StreetBox Urban Pollution Monitor, Signal Ambitech, Signal Group Ltd.

Table 14.14: Volatile organic sulphur compounds (including mercaptans, carbon disulphide)

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Pumped (active) sampling of mercaptans through an impinger bottle with absorption in cadmium hydroxide suspension; analysis by spectrophotometry.	Although there is currently no CEN, ISO or BS standard method covering this technique, a custom and practice method exists: ISC method 43901-01070T for mercaptans ⁵⁵ .	This is the principal manual method for the determination of low molecular weight mercaptans in ambient air. Measured volume of air is aspirated through aqueous mercuric acetate-acetic acid solution. Mercaptans react with N,N-dimethyl- <i>p</i> -phenylenediamine (DMPDA) and ferric chloride in strongly acid solution to produce a red complex, which is measured spectrophotometrically. If hydrogen sulphide is also present at a significant level some turbidity in the solution will result which must be filtered off before analysis.	For a 200 l air sample the LoD of CH ₃ SH is 5 µg m ⁻³ (3 ppb). Without modifying these sample volumes, the range ¹⁶ of the method is 2-100 ppb.	Precision is ±3% for the C ₁ to C ₆ mercaptans.
Period-averaged sampling	Pumped (active) sampling of mercaptans onto an impregnated filter; analysis by GC-FPD.	Although there is currently no CEN, ISO or BS standard method covering this technique, a custom and practice impregnated filter method for mercaptans exists ⁵⁶ .	The sample (volume 100 l) is collected on a treated filter paper (glass-fibre impregnated with HgOAc). Analysis is by GC-FPD. This method is similar to the OSHA method IMIS 1220 for ethanethiol and there are a number of workplace methods (e.g. NIOSH 2542) that could be adapted (e.g. increase volume sampled) for ambient air applications.	No data available	No data available
Period-averaged sampling	Pumped (active) sampling of carbon disulphide onto solid sorbent tubes; analysis by GC-FPD, GC-PID or GC-TCD.	There is currently no CEN, ISO or BS standard method covering this technique. Custom and practice is to use modified workplace methods (e.g. MDHS 15 or NIOSH 1600).	Sampling onto charcoal adsorption tubes at 500 ml min ⁻¹ ; may need to be modified for ambient levels (e.g. increase volume sampled); validated analytical end method suitable for most ambient samples: solvent (toluene) desorption followed by GC, with FPD specified as standard (although a PID or thermal conductivity detector can also be used).	NIOSH 1600 estimated LoD: 0.02 mg per sample.	MDHS 15 workplace method has a precision of about ±10%.
Real-time monitoring	Measurement of H ₂ S, CH ₃ SH, CS ₂ and COS by continuous sampling with batch analysis by chromatographic sulphur gas analyser (GC-FPD or GC-PID).	There is currently no CEN, ISO or BS standard method covering this technique.	Mainly used for SO ₂ but also able to separate and determine H ₂ S, methyl mercaptan (CH ₃ SH), carbon disulphide (CS ₂) and carbonyl sulphide (COS). Sulphur compounds separated on a suitable column and quantified by FPD. GC-PID systems are also commercially available. Silica-gel based columns (e.g. Chromosil 310) can be used in the analysis of CS ₂ and COS, but not for mercaptans since the latter are too strongly retained.	LDL of about 5-10 ppb.	No data available
Real-time monitoring	Measurement of total sulphur molecules by continuous flame-photometric analyser.	There is currently no CEN, ISO or BS standard method covering this technique.	Method in widespread use for the continuous determination of sulphur-containing molecules in ambient air. These instruments respond to total S species in air (i.e. includes sulphur dioxide and hydrogen sulphide as well as organic sulphur-containing compounds such as mercaptans). Well suited for unattended operation in the field.	Fast response instruments. Non-specific unless catalytic scrubbers used. Good lower detection limits.	No data available
Real-time monitoring	Measurement of total reduced organic sulphur species by continuous PID.	Currently no CEN, ISO or BS standard method covers this technique.	PID responds to reduced organic sulphur species. Well suited for unattended operation in the field.	Response factors vary more than for FIDs but PIDs much more sensitive. Good LoDs.	No data available

⁵⁵ Lodge JP (ed), *Methods of Air Sampling & Analysis*, 3rd Edn., Intersociety Committee, Lewis Publ Inc, 1989.

⁵⁶ Knarr & Rappaport, *Anal. Chem.*, (52) p 733, 1980.

Table 14.15: Benzene, 1,3-butadiene and other speciated hydrocarbons/VOCs

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Sampling of benzene, 1,3-butadiene and other hydrocarbons by pumped (active) sampling; analysis by gas chromatography.	<p>BS EN 14662:2005 <i>Ambient air quality. Standard method for measurement of benzene concentrations.</i></p> <p>Part 1- Pumped sampling followed by <u>thermal</u> desorption and gas chromatography.</p> <p>Part 2 - Pumped sampling followed by <u>solvent</u> desorption and gas chromatography.</p>	<p>The European reference method for benzene (CEN standard EN14662) is in five parts, each describing a different method. Part 3 of the standard describes a methodology for measurements of benzene with automated GCs; the other four parts of the CEN standard cover manual sampling of benzene, by either pumped sampling or by diffusive sampling. The Directive 2008/50/EC requires manual measurements for reporting purposes to be made by pumped sampling rather than by diffusive sampling in view of the former's inherently better measurement uncertainty.</p> <p>The UK Non-Automatic Hydrocarbon Network uses the Part 1 (pumped sampling/thermal desorption method) to monitor ambient benzene concentrations to assess compliance with UK Objectives, as well as with the corresponding EC Air Quality Directive Limit Value. Until 2007, 1,3-butadiene was also monitored to assess compliance with the UK Air Quality Strategy Objective. The data obtained provide a useful addition to the semi-continuous measurements from the Automatic Hydrocarbon Network. As the Objectives and Limit Values for benzene relate to the annual average concentration, it is not necessary to use a monitoring method with short time resolution. Sampling is therefore undertaken using pumped samplers, with sampling period of two weeks. Ambient air is pumped through sampling tubes containing a proprietary absorbent (Carbopack X), using purpose-built pump units that switch between two tubes to produce two nominally identical samples covering each fortnight. Every fortnight, the tubes are changed, and the exposed tubes sent for analysis by GC.</p> <p>The Part 2 (pumped sampling/solvent desorption) method is based on sampling on sample tubes typically containing 100 mg of activated charcoal and desorption using carbon disulphide. Alternative sorbents to activated charcoal may be used provided that the equivalence in performance characteristics of the procedure is demonstrated. Alternative desorption solvents to carbon disulphide may be used provided that the equivalence in performance characteristics of the procedure is demonstrated</p> <p>Typical benzene interferents include: methylcyclopentane, 2,2,3-trimethylbutane, 2,4-dimethylpentane, tetrachloromethane cyclohexane, 2,3-dimethylpentane, 2-methylhexane, 3-</p>	<p>These parts of EN 14662 are valid for measurement of benzene concentrations in the range approx 0.5 – 50 µg m⁻³ for an air sample of 1 m³ volume, typically collected over a period of 24 hours. In practice, the upper limit of the useful range is set by the capacity of the sorbent and by the linear dynamic range of the GC.</p> <p>From the performance criteria in the standard (Part 1), the LoD is approximately 0.5 µg m⁻³, based on the mass of benzene in the blank and a 10 l air sample volume.</p>	<p>Measurements made to the European reference method using compliant/ equivalent instruments will have an expanded uncertainty at the Limit Value that does not exceed the Data Quality Objective (DQO) of 25% for benzene.</p> <p>An expanded relative uncertainty of ± 16.6% is stated in the standard (Part 1) from combining the uncertainties specified for the performance requirements.</p>

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
			ethylpentane, trichloroethene and n-heptane.		
Period-averaged sampling	Sampling of benzene and other hydrocarbons by diffusive (passive) sampling; analysis by gas chromatography.	BS EN 14662-4:2005 <i>Ambient air quality. Standard method for measurement of benzene concentrations.</i> Part 4 - Diffusive sampling followed by <u>thermal</u> desorption and gas chromatography Part 5 - Diffusive sampling followed by <u>solvent</u> desorption and gas chromatography (See also Note on passive sampling)	Part 4 of EN 14662 gives the method for sampling and analysis of benzene in air by diffusive sampling (onto Carboxograph, Carboxopack, Chromosorb, Tenax or Poropak), thermal desorption and capillary gas chromatography. Part 5 uses activated charcoal and carbon disulphide solvent, but alternative sorbents and desorption solvents may be used provided that the equivalence in performance characteristics of the procedure is demonstrated.	The standard covers measurement of benzene in the concentration range of approximately 0.5 – 50 µg m ⁻³ in an air sample typically collected over a period of several days to several weeks. The LoD in practice is dependent on the noise level of the detector and blank levels in analyte and sorbent tubes. The latter are typically sub ng for sorbents such as graphitised carbon, but higher levels of aromatic hydrocarbons have been noted in other sorbents.	The standard states a range of component uncertainties that when combined and expanded fulfill the Data Quality Objective (DQO) of 25% for benzene.
Period-averaged sampling	Sampling of volatile organic compounds (VOCs) by pumped (active) sampling onto sorbent tube; analysis by thermal desorption/capillary gas chromatography.	BS EN ISO 16017-1:2001 <i>Indoor, ambient and workplace air. Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Pumped sampling.</i>	Part 1 of the European reference method for VOCs (EN16017) is appropriate for a wide range of compounds, including hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols. A number of sorbents are recommended for the sampling of these VOCs, each sorbent having a different range of applicability. Very polar compounds will generally require derivatisation, very low boiling compounds will only be partially retained by the sorbents, depending on ambient temperature, and can only be estimated qualitatively. Semi-volatile compounds will be fully retained by the sorbents, but may only be partially recovered. Compounds for which this standard has been tested are given in tables. The standard may be applicable to compounds not listed, but in these cases it is advisable to use a back-up tube containing the same or a stronger sorbent.	Part 1 of this standard is applicable to the measurement of airborne vapours of VOCs in a concentration range of approximately 0.5 µg m ⁻³ to 100 mg m ⁻³ per individual compound. The LoD in practice is dependent on detector noise and blank levels in analyte and sorbent tubes. The latter range from: typically sub-ng (for Tenax GR and carbonaceous sorbents such as Carboxopack/Carboxotrap, carbonized molecular sieves and molecular sieves such as Spherocarb, or pure charcoal); at low ng levels for Tenax TA; and at 5-50 ng levels for other porous polymers such as Chromosorbs and Poropaks.	Dependent on sorbent, but repeatability and reproducibility for Chromosorb are 12% and 37%, respectively.
Period-averaged sampling	Sampling of volatile organic compounds (VOCs) by diffusive (passive) sampling onto sorbent tube; analysis by thermal desorption/capillary gas	BS EN ISO 16017-2:2003 <i>Indoor, ambient and workplace air. Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas</i>	Application is as for Part 1, above.	Part 2 of this standard is applicable to the measurement of airborne vapours of VOCs in a mass concentration range of approximately 2 µg m ⁻³ to 100 µg m ⁻³ per individual	Dependent on sorbent, but precision of the analysis stage for different compounds is up to about 6% for Chromosorb.

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
	chromatography.	<i>chromatography. Diffusive sampling</i> (See also Note on passive sampling)		organic compound for an exposure time of 8 h, or 2 µg m ⁻³ to 300 µg m ⁻³ for an exposure time of four weeks. The LoDs in practice are determined by the factors described in Part 1 of this standard.	
Real-time monitoring (quasi-continuous)	Measurement of benzene, 1,3-butadiene, toluene, ethylbenzene, <i>m</i> - and <i>p</i> -xylenes, <i>o</i> -xylene and other hydrocarbons by automated in-situ gas chromatography.	BS EN 14662:2005 <i>Ambient air quality. Standard method for measurement of benzene concentrations. Part 3 - Automated pumped sampling with in situ gas chromatography.</i>	Part 3 of the European reference method EN14662 describes an automated GC method that can be used for demonstrating compliance with the EU Directive Limit Value for benzene with a one calendar-year reference period. Continuous ambient monitoring systems used to report results for this purpose must be product-certified or covered by type approval: CAMSs certified under MCERTS meet the performance criteria in the CEN standards and the relevant Directive Data Quality Objective (DQO). MCERTS instrument-certification can be extended beyond benzene to include (but not limited to) the following: (in the C ₂ -C ₆ group) ethane, ethene, propane, propene, iso-butane, n-butane, acetylene, trans-2-butene, 1-butene, cis-2-butene, 2-methyl butane, n-pentane, 1-3 butadiene, trans-2-pentene, 1-pentene, 2-methyl pentane, n-hexane, isoprene and (in the C ₆ -C ₁₂ group) 2,2,4-trimethyl pentane, n-heptane, toluene, n-octane, ethyl benzene, <i>m</i> -xylene, <i>p</i> -xylene, <i>o</i> -xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3-trimethyl benzene. In the UK, the Automatic Hydrocarbon Network uses automatic GCs to report against the annual-mean EU Directive Limit Value for benzene and the Air Quality Strategy Objectives for benzene and 1,3-butadiene. Although it is not necessary to use a monitoring technique with short time resolution for comparison with the annual-average Limit Value and Objectives, the hourly output of these instruments allows the data to be reported in near real time to the public through a range of media. Currently the Network runs with some sites using Environnement VOC71M analysers configured to measure benzene, 1,3-butadiene, toluene, ethylbenzene, <i>m</i> - and <i>p</i> -xylenes and <i>o</i> -xylene; and other sites using automated Perkin Elmer GCs measuring a wider range (at least 27) of hydrocarbons ⁵⁷ .	The standard covers benzene concentrations in the range 0 µg m ⁻³ to 50 µg m ⁻³ . The Automatic Hydrocarbon Network measures benzene to LoD of 0.1 ppb (0.3 µg m ⁻³) and this is typical of the LoDs of type-approved instruments listed in the standard.	Measurements made to the European reference method using compliant/ equivalent (e.g. MCERTS-certified) instruments will have an expanded uncertainty at the Limit Value that does not exceed the DQO of 25% for Benzene. In general ⁵⁸ , ratified hourly data from the Automatic Hydrocarbon Network have an uncertainty (at 95% confidence) of ±10% for concentrations above 0.5 µg m ⁻³ and ±0.05 µg m ⁻³ for concentrations below 0.5 µg m ⁻³ .

Passive diffusion samplers - the general performance requirements for all diffusive samplers used for the determination of the concentration of gases and vapours in ambient air, irrespective of the nature of the sorption process and the analytical determination, are covered by BS EN 13528:2002: *Ambient air quality. Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods.* Part 1 - *General requirements*; Part 2 - *Specific requirements and test methods*; Part 3 - *Guide to selection, use and maintenance.*⁵⁷ *Air Pollution in the UK: 2007*, AEA

Table 14.16: Halogenated volatile organic compounds

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Sampling of volatile organic compounds (VOCs) by pumped (active) sampling onto sorbent tube; analysis by thermal desorption/capillary gas chromatography.	BS EN ISO 16017-1:2001 <i>Indoor, ambient and workplace air. Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Pumped sampling.</i>	This standard is appropriate for a wide range of VOCs, including halogenated hydrocarbons. (See Table 14.15 for further details)	The standard is applicable to the measurement of airborne vapours of VOCs in a concentration range of approximately 0.5 µg m ⁻³ to 100 mg m ⁻³ per individual compound. The lower limit of the range in practice is dependent on the noise level of the detector and blank levels in analyte and sorbent tubes. (See Table 15 for further details).	Dependent on sorbent, but repeatability and reproducibility for Chromosorb 106 are 12% and 37%, respectively.
Real-time monitoring (intermittent, non-continuous)	Measurement of halogenated hydrocarbons by portable gas chromatography.	There is currently no CEN, ISO or BS standard method covering this technique.	Portable GC-FID or GC-PID systems can separate and quantify a selection of pre-targeted halogenated hydrocarbons.	Although these instruments are popular for workplace monitoring, their lower detection limits extend down to the low ppb level expected in ambient monitoring.	No data available
Real-time monitoring	Measurement of halogenated hydrocarbons by continuous sampling with batch analysis by automated in-situ gas chromatography.	There is currently no CEN, ISO or BS standard method covering this technique. However, the determination follows the same approach as BS EN 14662:2005 for benzene and hydrocarbons.	Halogenated hydrocarbons can be determined by automatically-cycling GC systems, using a suitable pre-concentration technique such as cryogenic trapping to provide a concentrated sample for analysis. These systems are suitable for unattended operation in air quality monitoring networks.	No data available	No data available
Real-time monitoring	Measurement of specific halogenated hydrocarbons by continuous ion mobility spectroscopy (IMS).	There is currently no CEN, ISO or BS standard method covering this technique.	Continuous direct-reading analysers based on ion mobility spectroscopy (IMS) have been developed for measuring low levels of specific halogenated compounds ⁵⁹ .	Capable of measuring down to about 5 ppb	No data available

report for Defra and the Devolved Administrations ⁵⁸ *Ratification of data produced by the UK Ambient Automatic Hydrocarbon Air Quality Network, 1 July 2005 to 30 September 2005*, AEAT report for Defra, January 2006.

⁵⁹ Manufacturer's literature: Environmental Technologies Group, Inc.

Table 14.17: Formaldehyde and other aldehydes

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Pumped (active) sampling of formaldehyde through water in an impinger bottle; analysis by spectrophotometry.	Although there is currently no CEN, ISO or BS standard method covering this technique, a custom and practice chromotropic acid method for formaldehyde exists ^{60,61} .	Air is sampled at 1 l min ⁻¹ through distilled water (20 ml) contained in each of two coarse-fritted bubblers arranged in series. Colorimetric procedure: chromotropic acid (4,5-dihydroxy-2,7-naphthalene disulphonic acid) and sulphuric acid are added and the purple coloured dye formed from the reaction is determined spectrophotometrically at 580 nm.	Range 0.1-2.0 µg m ⁻³ HCOH for a 40 l air sample. Sensitivity can be increased ten-fold by sampling directly into chromotropic acid-sulphuric acid solution. For longer term measurements, sample >100 l with larger impingers containing greater volumes of absorbing reagent. Alternatively, the MBTH method should be used.	No data available
Period-averaged sampling	Pumped (active) sampling of aliphatic aldehydes through MBTH in an impinger bottle; analysis by spectrophotometry.	Although there is currently no CEN, ISO or BS standard method covering this technique, a custom and practice MBTH method for water soluble aliphatic aldehydes exists ^{62,63} .	Not specific to formaldehyde. The measured concentration should be multiplied by 1.25 ±0.10 to correct for the higher aldehydes, giving a better estimate of total aldehydes in ambient air. The air is sampled at 0.5 l min ⁻¹ for 24 h through a fritted bubbler (capacity >75 ml, porosity 40-80 µm) containing MBTH (0.05% aqueous solution). Aldehydes react to form an azine which is subsequently oxidised using ferric chloride-sulphamic acid reagent to form a blue dye. Measured spectrophotometrically at 628 nm using a calibration solutions prepared from standard solutions of formaldehyde. The aldehydes present can be identified by separating out the individual colorimetric components by thin-layer chromatography (TLC) ¹⁰⁵ . Although aromatic amines, carbazoles, hydrazones and a number of other compounds react with MBTH, most of them are not gaseous or are insoluble in aqueous solution and should not interfere.	Method range is 0.03-0.7 µg m ⁻³ of HCOH. Efficiency for a single bubbler is 84%; two in series recommended.	Precision stated as ±5%.
Real-time monitoring	Measurement of specific aldehydes by continuous ion mobility spectroscopy (IMS).	There is currently no CEN, ISO or BS standard method covering this technique.	Continuous direct-reading analysers based on ion mobility spectroscopy (IMS) have been developed for measuring low levels of specific aldehyde compounds ⁶⁴ .	Capable of measuring down to about 5 ppb.	No data available

⁶⁰ Clayton & Davis, *HMIP Manual on Environmental Sampling and Analysis*, WSL report LR680/LR756 (PA), 1989.

⁶¹ Harrison RM, *Handbook of Air Pollution Analysis*, Second Edition, Ed. Harrison RM & Perry R, London, 1986.

⁶² Pengelly M I, Groves J A, Foster R D, Ellwood P A, and Wagg R M, *Development of a Method for Measuring Exposure to Resin Acids in Solder Fume*, Ann. Occup. Hyg., Vol 38, No. 5, pp 765-776, 1994.

⁶³ Clayton & Davis, *HMIP Manual on Environmental Sampling and Analysis*, WSL report LR680/LR756 (PA), 1989.

⁶⁴ Manufacturer's literature: Environmental Technologies Group, Inc.

Table 14.18: Polycyclic aromatic hydrocarbons (PAHs)

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	24-hour duration pumped (active) sampling of PAHs onto filters and traps; analysis by gas chromatography with mass spectrometry (GC-MS).	BS EN 15549:2008 <i>Air quality. Standard method for the measurement of the concentration of benzo(a)pyrene in ambient air.</i>	<p>This is the European reference monitoring method for demonstrating compliance with the EU 4th Daughter Directive Target Value set for the “marker” PAH, benzo(a)pyrene (B[a]P). The Directive requires that the reported result is a calendar-year average of concentrations of (B[a]P) in PM₁₀ samples taken over individual 24-hour periods. In order for member states to assess ambient air concentrations and deposition rates, other PAHs are required to be monitored at a limited number of sites where B[a]P is monitored. These compounds should include at least:</p> <ul style="list-style-type: none"> • benzo(a)anthracene • benzo(b)fluoranthene • benzo(j)fluoranthene • benzo(k)fluoranthene • indeno(1,2,3-cd)pyrene • dibenz(a,h)anthracene <p>Defra operates a PAH Network, which now uses Digitel DH-80 high volume aerosol samplers to allow 24-hour samples of the PM₁₀ fraction to be collected on glass-fibre filters. A smaller number of sites use a modified sampler that, in addition to a glass-fibre filter, has a polyurethane foam (PUF) filter to collect vapour-phase PAHs.</p> <p>The glass-fibre filter (and, where relevant, PUF filter) is extracted and analysed by GC-MS. The method provides data on 39 PAH species. (Note that for the filter-only method, the results are only a representation of the PAHs retained by the filter. For some of the more volatile PAH compounds, this represents only a small fraction of the total.)</p>	<p>The standard covers B[a]P concentrations in the range from approx 0.04 ng m⁻³ to 20 ng m⁻³.</p> <p>The lower limit of the range in practice is dependent on the noise level of the detector and variability in the filter blanks, but is required to be less than 0.04 ng m⁻³.</p>	<p>Measurements made to the European reference method using compliant/ equivalent instruments will have an expanded uncertainty at the Limit Value that does not exceed the Data Quality Objective (DQO) of 60% for B[a]P.</p> <p>Uncertainty for the analysis is estimated to be 20%.</p>
Period-averaged sampling	14-day duration pumped (active) sampling of PAHs onto filters; analysis by GC-MS or HPLC.	<p>Analysis stage may be covered by either:</p> <ul style="list-style-type: none"> • BS EN 15549:2008; • ISO 12884:2000 <i>Ambient air - Determination of total (gas and particle-phase) polycyclic</i> 	<p>For applications other than demonstrating compliance with the Directive Target Value, it is common to collect samples over longer periods, often enabling the sample to be subdivided for analysis of dioxins and furans and PCBs, as well as PAHs.</p> <p>For example, prior to the 2007 upgrade to samplers able to collect samples over the 24-hour period</p>	Range covered is approximately 0.05 ng m ⁻³ to 1000 ng m ⁻³	Precision and uncertainty will vary with sample volume and analyte concentration. The ISO 12884:2000 standard states that precision and

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
		<p><i>aromatic hydrocarbons - Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analysis;</i> or</p> <ul style="list-style-type: none"> • ISO 16362:2005 <i>Ambient air - Determination of particle-phase polycyclic aromatic hydrocarbons by high performance liquid chromatography.</i> 	<p>required by the Directive, Defra's PAH Network had from its inception used a modified Anderson GPS-1 Pesticide Sampler to collect both gas and particle-phase PAHs on glass fibre and PUF filters, respectively, over a 14-day sample period. Successive samples are combined to give quarterly samples for analysis. The sample extracts have been analysed for PAHs using either high performance liquid chromatography (HPLC) or GC-MS⁶⁵.</p> <p>The London-Wide Environment Programme (LWEP) PAHs Survey⁶⁶ uses a different sampling approach, whereby a filter pack containing a quartz-fibre filter in conjunction with a polyurethane foam plug was connected to the by-pass flow of TEOM PM₁₀ instrument.</p>		<p>uncertainty should be no worse than $\pm 25\%$, and uncertainty $\pm 50\%$, respectively.</p>

⁶⁵ Polycyclic Aromatic Hydrocarbon Monitoring and Analysis Network: 2000-2003, AEAT report to Defra, 2005.

⁶⁶ London Wide Environmental Programme Polycyclic Aromatic Hydrocarbon Survey 2005-06, Bureau Veritas Report Ref: BV/IAQ/AGG04101.

Table 14.19: Dioxins & furans (PCDDs & PCDFs) and polychlorinated biphenyls (PCBs)

Type of monitoring	Monitoring technique	Standard method	Comments	Reported LoD and range	Reported uncertainty
Period-averaged sampling	Pumped (active) sampling of dioxins and furans and PCBs (and PAHs if required) onto filters and traps; analysis by gas chromatography with mass spectrometry (GC-MS) or electron capture (GC-ECD).	Analysis stage covered by BS EN 1948-3:2006 <i>Stationary source emissions. Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs. Identification and quantification of PCDDs/PCDFs.</i>	<p>The following procedure, used to routinely measure polychlorinated dibenzo-<i>p</i>-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) as part of Defra's Toxic Organic Micropollutants (TOMPs) Network, can be considered the current best practice method. It is used to provide information to government on UK sources and likely exposures and to assess long-range transport of persistent Organic Pollutants (POPs) under the UNECE protocol.</p> <p>The TOMPs Network uses a modified Andersen GPS-1 high volume sampler to collect PCDDs/Fs and PCBs at the same time. Samples are obtained over fortnightly periods and combined to give quarterly samples for analysis⁶⁷. The sorbent trap and filter set is extracted with dichloromethane and toluene. After removal of a proportion of the extract for PAHs analysis⁶⁸, the remaining sample is chromatographically separated and cleaned-up for PCDDs/Fs and PCBs analysis by the following end-methods:</p> <ul style="list-style-type: none"> <input type="checkbox"/> Gas chromatography coupled with high-resolution mass spectrometry (GC-HRMS) for the PCDDs/Fs and for those PCBs with dioxin-like effects, in accordance with analytical method EN1948-3:2006; <input type="checkbox"/> Low-resolution mass spectrometry or GC with electron capture detector (GC-ECD) for the other PCBs. 	The LoDs for individual congeners are between 0.1 and 9 pg m ⁻³ .	Uncertainty for the analysis is estimated to be 25%.

⁶⁷ *Toxic Organic Micropollutant Monitoring 1999 to 2000*, AEAT report for DETR, 2001, available at www.airquality.co.uk

⁶⁸ Extracts of samples are also analysed for PAHs as part of the PAH Network (though samples for demonstrating compliance with the EU Directive Target Value must be obtained from samplers that can collect samples over the 24-hour period)

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- 18 Sheppard V. and Shutt M., 'Toolbox Macro'. Available at <http://www.environment-agency.gov.uk/business/regulation/127216.aspx>
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Annex A Acronyms

ACCU	Automated Cartridge Collection Unit
AQC	Air quality criteria
AURN	Automatic Urban & Rural Network
BS	British Standard
CAM	Continuous Ambient Monitoring System
CERL	Central Electricity Research Laboratories
CH ₄	Methane
CLAG	Critical Loads Assessment Group
CO	Carbon monoxide
COMEAP	Committee on the Medical Aspects of Air Pollution
DA	Devolved Administration of Scotland, Wales & Northern Ireland
DEFRA	Department of the Environment, Food & Rural Affairs
DIAL	Differential absorption LIDAR
DOAS	Differential optical absorption spectroscopy
EAL	Environmental Assessment Level
EDAX	Energy dispersive analysis by X-rays
ELPI	Electrical low-pressure impactor
EMEP	European Monitoring and Evaluation Programme
EPAQS	Expert Panel on Air Quality Standards
EPR	The Environmental Permitting (England and Wales) Regulations 2010
EU	European Union
FID	Flame ionisation detector
FPD	Flame photoionisation detector
FTIR	Fourier transform infrared (spectrometry)
GC	Gas chromatography
H ₂ S	Hydrogen sulphide
ISO	International Standards Organisation
LDL	Lower detection limit
LIDAR	Laser interferometry detection and ranging
MCERTS	Environment Agency's Monitoring Certification Scheme

MS	Mass spectrometry
NDIR	Non-dispersive infrared (spectrometry)
NDUV	Non-dispersive ultraviolet (spectrometry)
NO _x	Various oxides of nitrogen
PAHs	Polynuclear aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo- <i>p</i> -dioxins
PCDFs	Polychlorinated dibenzofurans
PID	Photoionisation detector
PM ₁₀	Suspended particles of diameter up to 10 µm
QA/QC	Quality assurance/quality control
SEM	Scanning electron microscope
SO ₂	Sulphur dioxide
SODAR	Sonic detection and ranging
TEOM	Tapered element oscillating microbalance
TOMPS	Toxic Organic Micropollutants (monitoring programme)
TSP	Total suspended particulates
UKAS	United Kingdom Accreditation Service
UV	Ultraviolet

Annex B Data Analysis Techniques

B.1 Pollution rose analysis

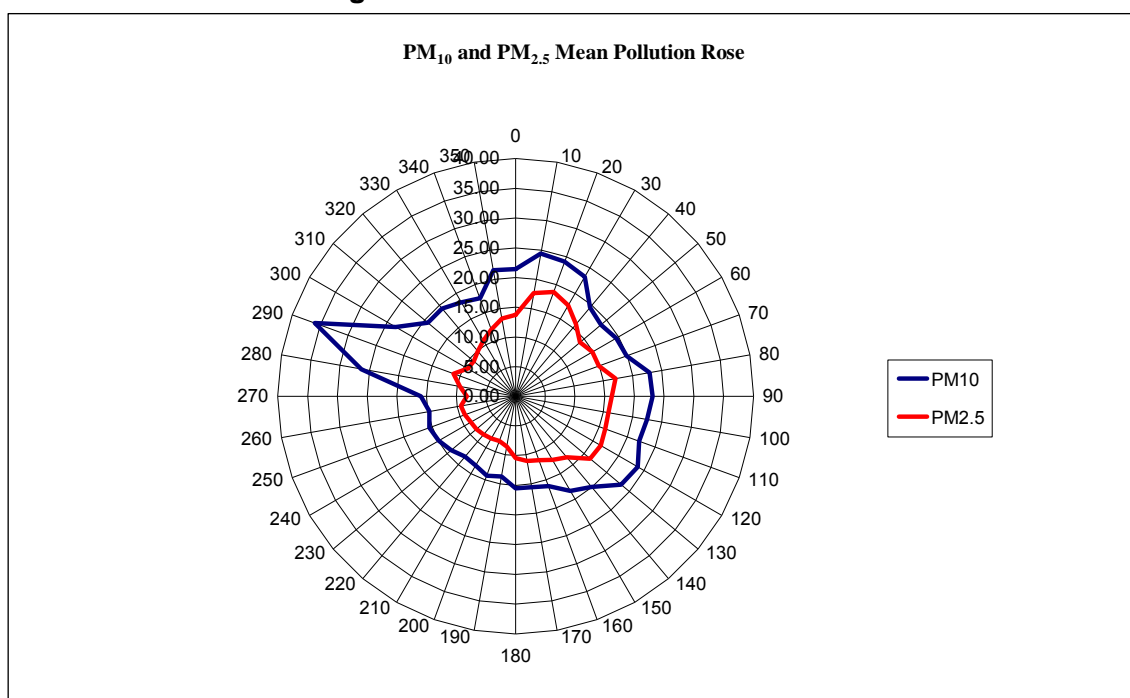
Plotting a pollution rose can provide an insight into the direction of pollution sources relative to the position of the monitoring location. To achieve an effective pollution rose, concentration measurements must be collected concurrently with wind direction measurements.

The averaging period of these measurements should be short enough that the wind direction value is representative of the concentration measurement i.e. 15 minutes/hourly. If the averaging period is too long then each averaged wind direction value will have a much greater degree of uncertainty as the wind directions will have varied during the period. If the averaging time is too short, i.e. significantly shorter than the expected time that it would take for the pollutant to travel from source to monitor, then it is possible that the wind direction measurement at the time the pollutant is measured is not representative of the average wind direction during the whole time the pollutant travelled to the monitor.

The plot is achieved by dividing the data into wind direction sectors and then plotting the wind direction sector against the mean of all the concentration measurements taken when the wind was recorded as coming from that sector. The presentation of this can be a conventional bar chart or can be a radial plot, which tends to be easier to interpret as directional biases in concentration appear to point in the direction of the sources. It is this radial representation of the data from which the name 'rose' comes.

Figure B.1 shows examples of mean pollution roses for PM₁₀ and PM_{2.5}. By plotting the two pollution roses on the same figure it makes it easier to visually compare the data and the plot clearly shows that between 280° - 290° there is a prominent source of PM₁₀ although it is not a particularly prominent source of PM_{2.5}. This indicates that the source provides particulate in the coarse fraction between PM₁₀ – PM_{2.5}, but not as much in the fine fraction less than PM_{2.5}. Such evidence would tend to rule out a combustion source and probably supports an assumption that the particulate source in this direction is a consequence of wind blown fugitive emissions.

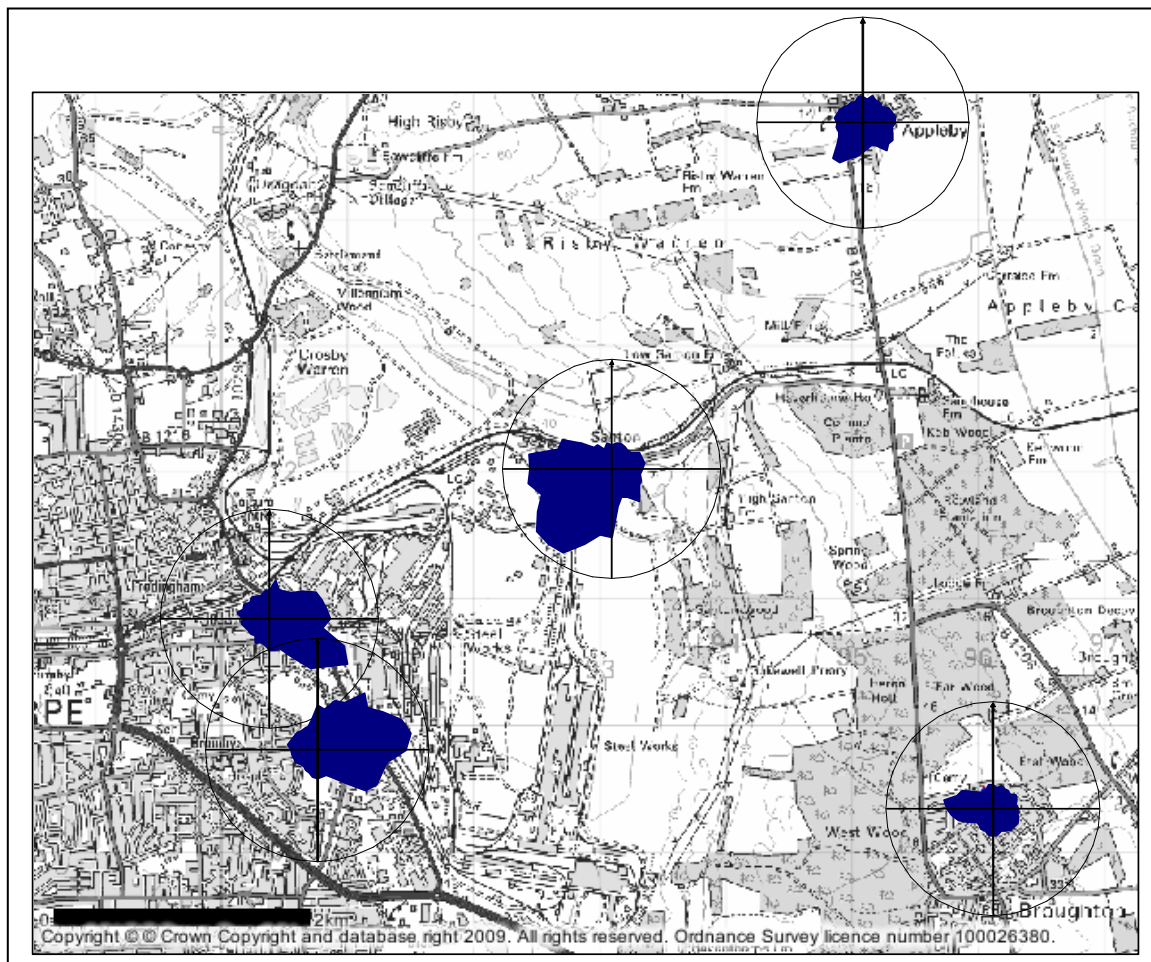
Figure B.1 : Particulate Pollution Roses



B.2 Triangulation analysis

Multiple monitoring locations can help pinpoint sources of emission within a given area. Figure B.2 shows PM₁₀ pollution roses for 5 different monitoring locations in and around Scunthorpe. The figure clearly shows that each of the pollution roses has a bias that points toward the steelworks, which is the main source of PM₁₀ emissions in the area. By positioning monitors at strategic points in and around the steelworks itself, this technique can aid in the identification of the particular processes within the steelworks that are producing the greatest PM₁₀ emissions. This information is invaluable when deciding where to allocate mitigation effort so that it has the greatest impact in reducing emissions.

Figure B.2 : PM₁₀ triangulation plot



B.3 Percentile rose analysis

Percentile analysis provides a method of looking at the distribution of concentrations within a data set. Microsoft Excel calculates percentiles by first sorting the concentrations into ascending order and then ranking each concentration. It then interpolates the value of a particular percentile from the calculated ranking i.e. it calculates the concentration below which a certain percentage of concentrations fall. For example, at the 95th percentile, 95% of the data will lie below this value and 5% of the data will lie above it.

In order to produce radial percentile roses, the data is first divided into the required wind sectors and then the data in each sector undergoes separate percentile analysis. By calculating the concentration of a pollutant at different percentiles for different wind sectors,

you are able to visually examine the distribution of pollutant concentrations at a particular monitoring site. This in turn will provide information on the source that may be influencing levels at the monitoring site.

By breaking each 10° wind sector down into a number of different percentiles it can be seen whether biases are present in all of the percentiles or just certain ones, which can tell you whether a source is affecting the monitoring site relatively continuously or just intermittently. For example, a bias that is observed in all of the percentiles (Figure B.3) suggests that the source in that particular 10° wind sector is emitting relatively continuously as it is influencing a large percentage of the sector's data.

Whilst a bias that is only observed in the higher percentiles (Figure B.4) suggests that the source is intermittent as it only affects a small percentage of the sector's data, i.e. it doesn't affect concentrations at the monitoring site every time the wind is coming from this direction. Occasionally, a bias is observed in the lower percentiles that is not evident in the higher percentiles (Figure B.5). This suggests that the source is relatively continuous, as it is affecting a large percentage of the data, but it also tells you that the source is not causing appreciably high concentrations at the monitoring site.

Figure B.3 shows a bias between 280° – 300° that is evident in all of the percentiles.

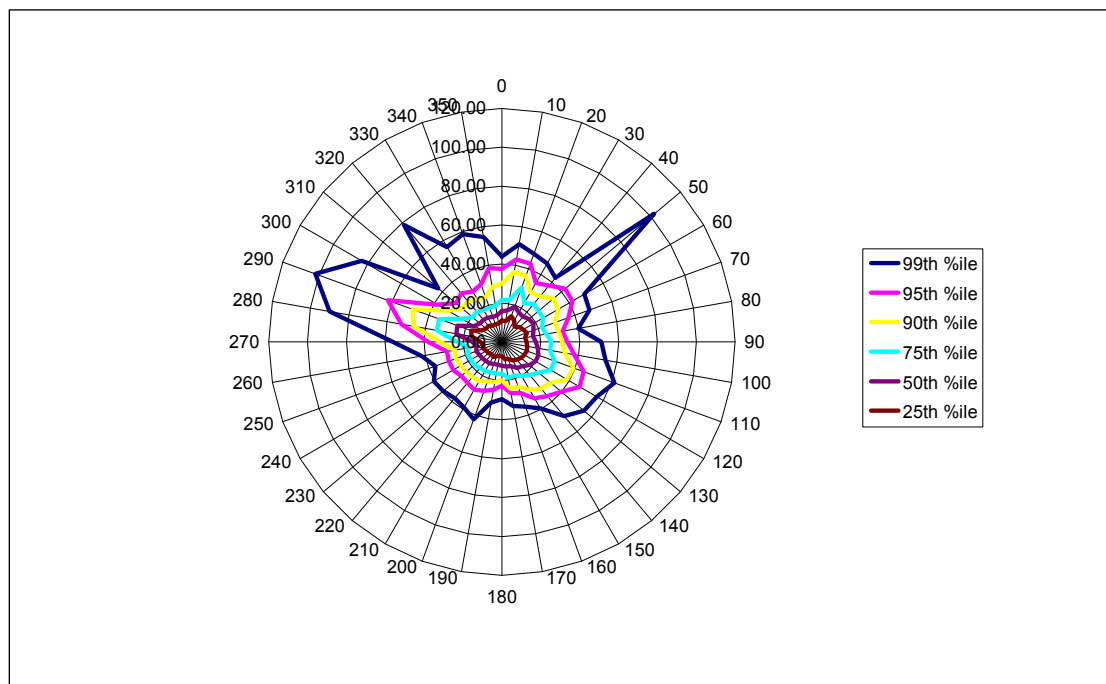


Figure B.4 shows a bias at 260° that is only evident in the 99th percentile.

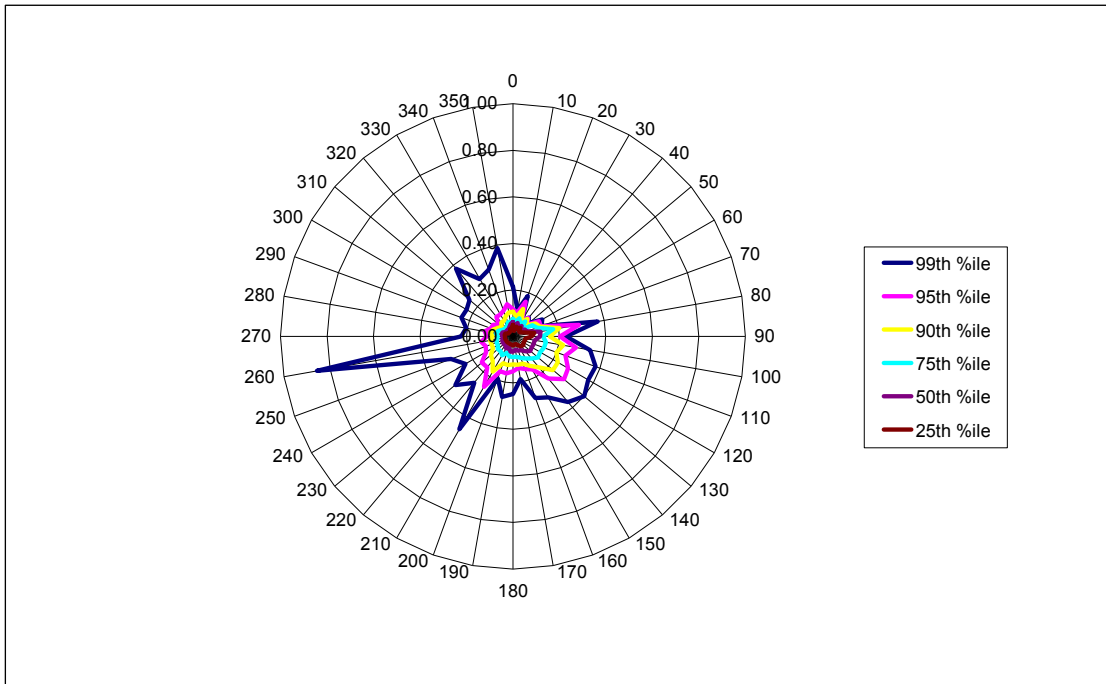
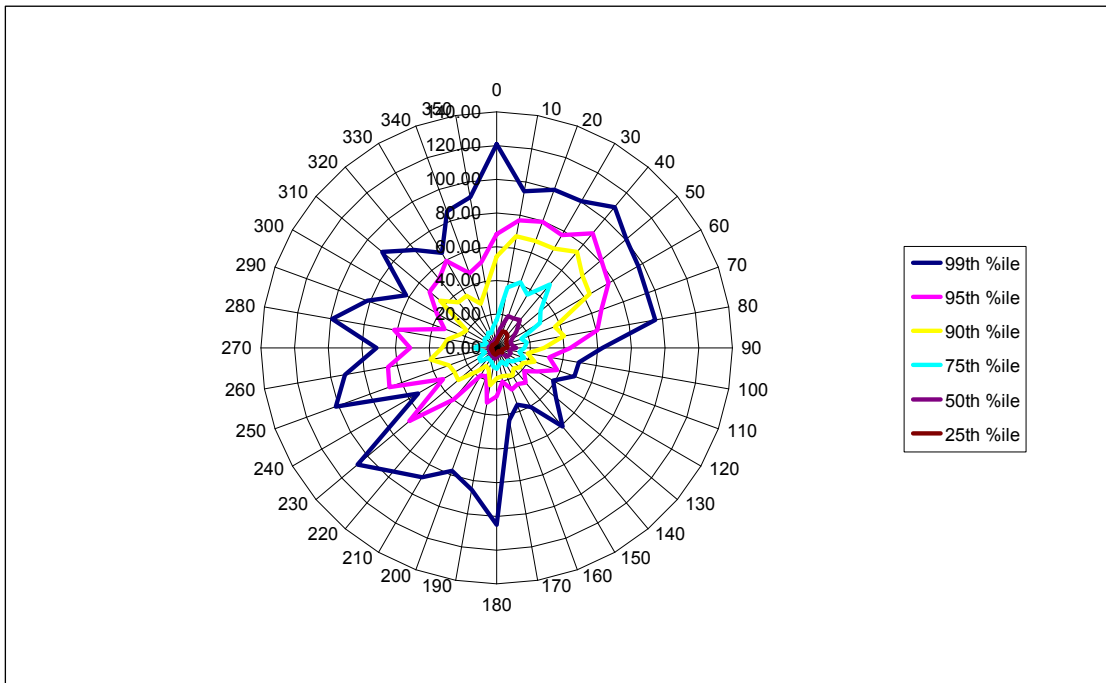


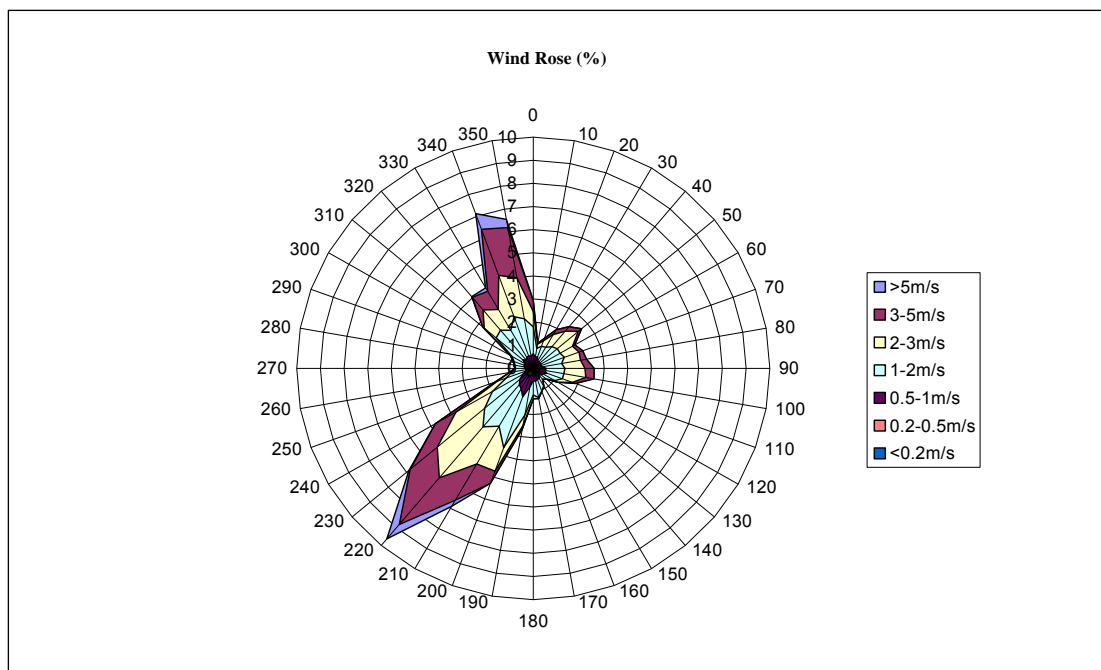
Figure B.5 shows a bias between 20° – 50° that is only evident in the lower percentiles.



B.4 Frequency roses

The frequency rose shows, for each wind direction, the number of times or the fraction of the total time that a given level is exceeded (>) or conversely not reached (<). Figure B.6 shows a typical wind rose showing the frequency distribution of wind speed at a particular monitoring location for each of the wind sectors.

Figure B.6 : Wind Rose



B.5 Diurnal variation

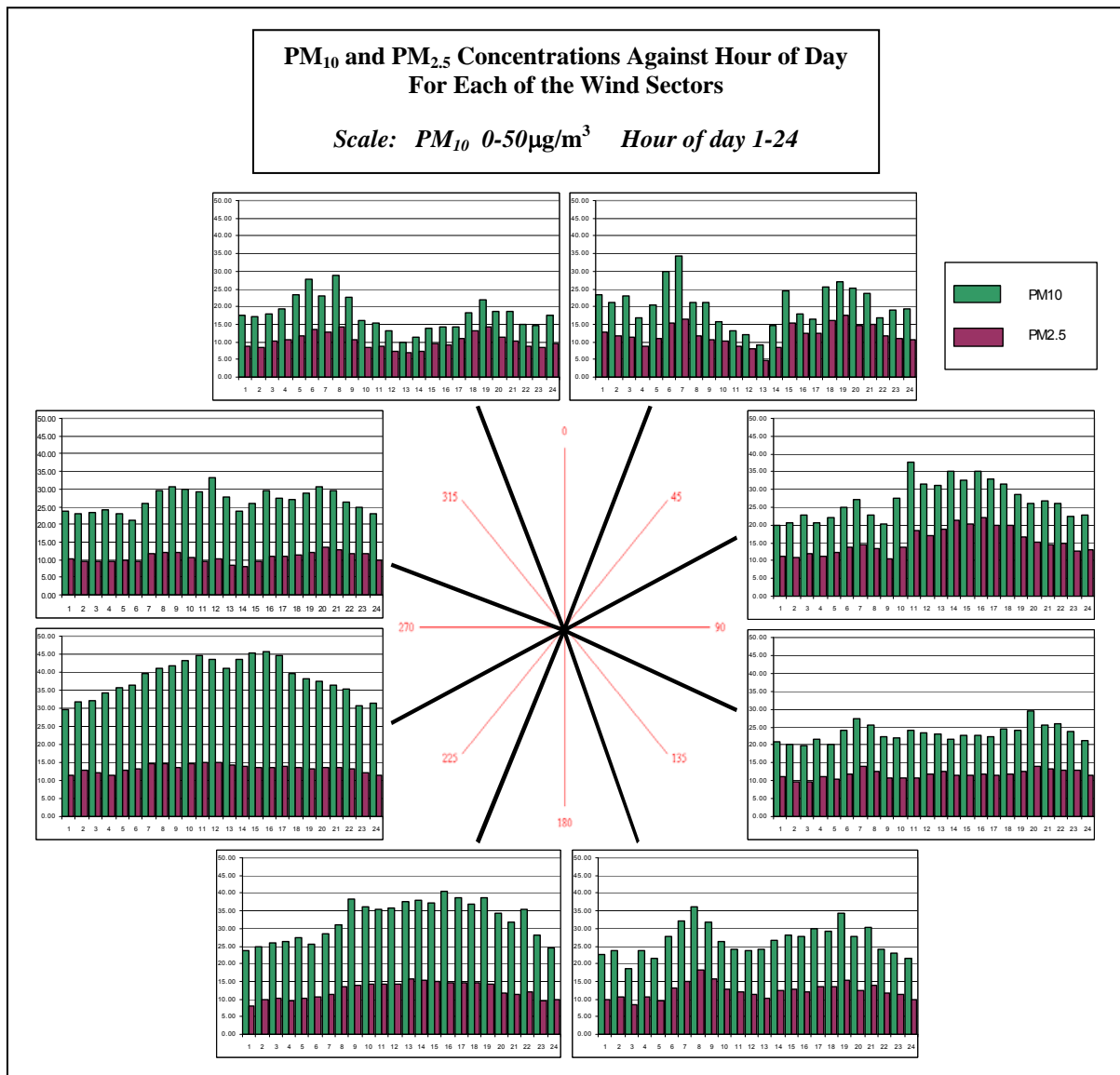
Diurnal variation is the averaged temporal distribution of pollutant concentrations through the 24 hours of the day. The technique generally involves taking the data of the monitoring period (or part of the monitoring period) and dividing it up into 24 sets each representing data collected within one of the hours of the day. The mean concentration is then plotted against the hour of the day.

Consideration of the diurnal distribution of concentration levels can provide useful information about the sources contributing to the ambient levels in each sector. Traffic generated pollutants often show a diurnal profile that matches the traffic flow levels. This generally takes the form of a double peak pattern, which correspond to the morning and afternoon/evening rush hours. Industrial emissions are usually characterised by more elevated concentrations during the hours with the greatest amount of solar heating of the ground, due to increased convective mixing bringing stack emissions to ground level. Changes between BST and GMT occur twice per year and provide an opportunity to identify sources whose emissions and inputs are specifically linked to day time working patterns – e.g. road-traffic sources – and to distinguish them from other more continuously-emitting sources e.g. continuous industrial process

Figure B.7 shows that the charts for the sectors 180° – 225° and 225° – 270° suggest that there may be a stack or other source of PM₁₀ and PM_{2.5} influencing their profile, which is characterised by elevated concentrations around midday. The charts for 315° – 360° and 0°

– 45° show a characteristic double peak profile suggesting that these sectors are heavily influenced by traffic related emissions.

Figure B.7 : Particulate diurnal variation plot

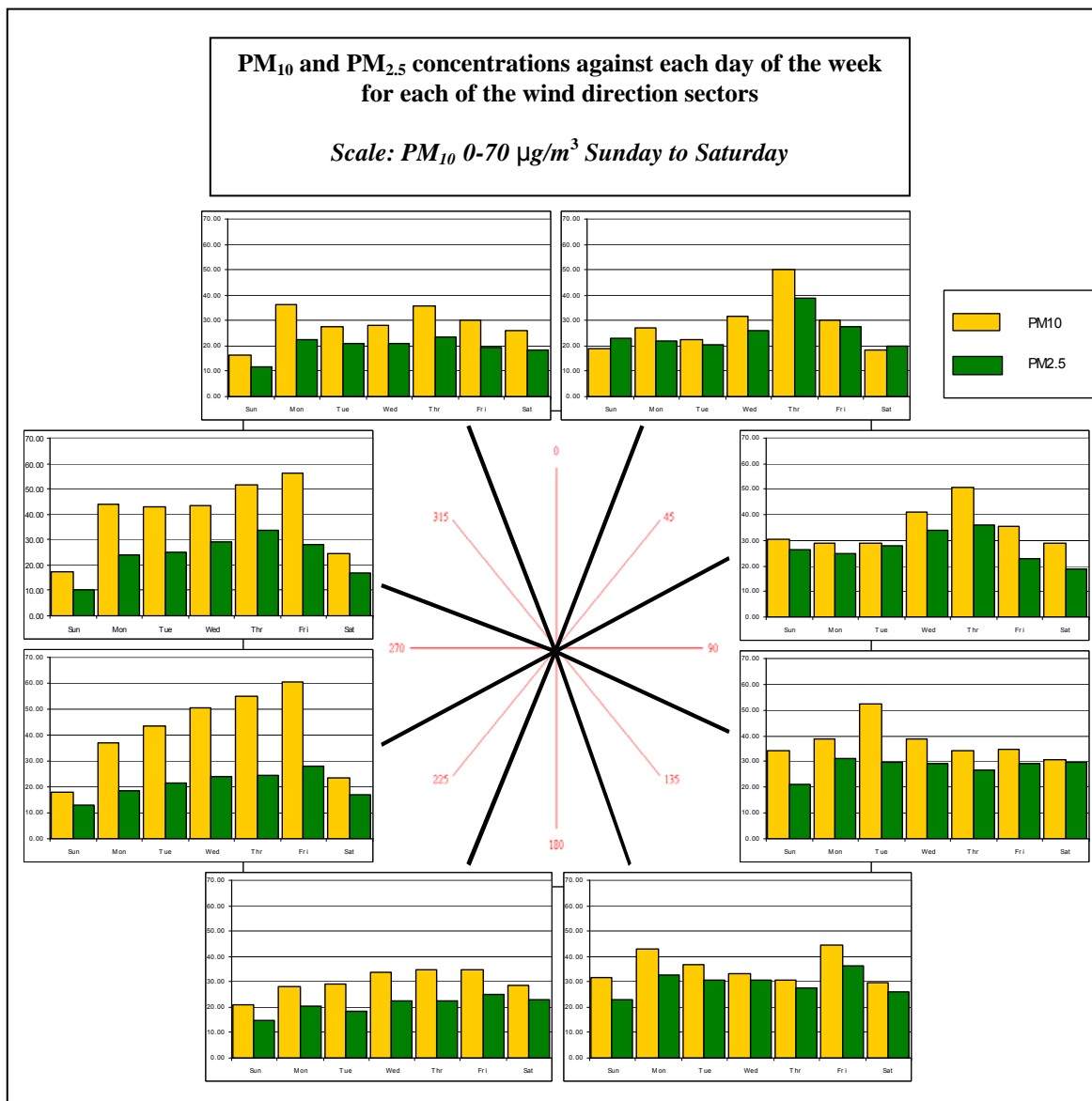


B.6 Weekly variation

Weekly variation is the averaged temporal distribution of pollutant concentrations through each day of the week. The technique divides the data set into the 7 days of the week. This can provide useful information about the working practices of individual process activities within the sector of interest.

Figure B.8 shows that the charts for the wind sectors between 180° – 360° all show lower levels on the weekend, but higher levels on the Saturday than on the Sunday. This may reflect the working patterns within these wind sectors, suggesting that occasionally work is carried out on a Saturday.

Figure B.8 : Particulate weekly variation plot



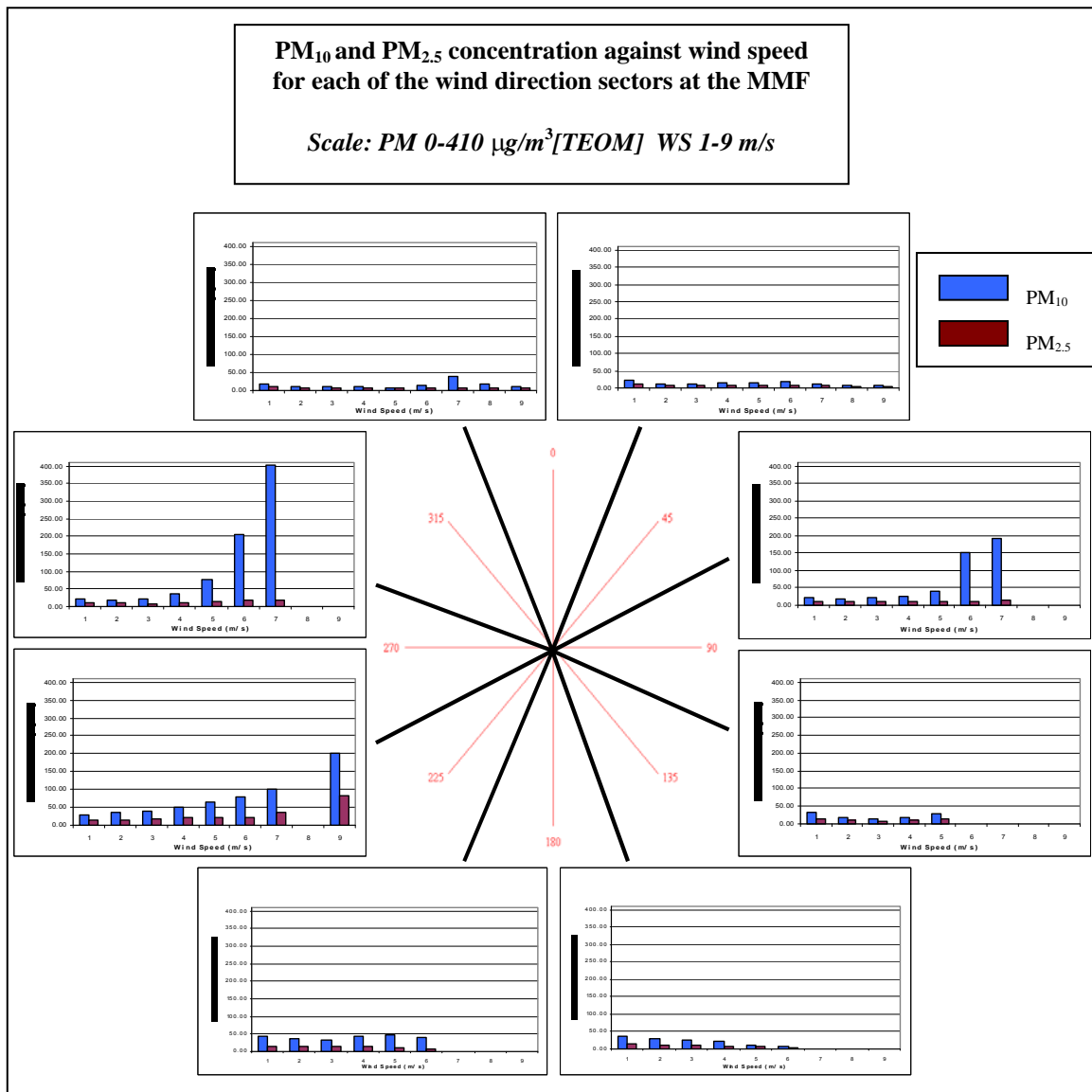
B.7 Wind speed versus pollutant concentration analysis

Wind speed plays an important role in the dispersion of air pollutants. Higher wind speeds generate more mechanical turbulence, which has the effect of distributing emissions more rapidly through the mixed boundary layer of the atmosphere. The relative concentrations

measured at different wind speeds can provide insight to the nature of contributing sources. By examining and contrasting average concentrations measured at different wind speeds for each 45° sector, information may be provided about the number, distance and height of release of impacting emissions.

Figure B.9 shows that the plots for the wind sectors 45° – 90° and 270° – 315° show levels of PM₁₀ that increase with increasing wind speed. This is not observed in the PM_{2.5} data. This suggests that the sources in these sectors are not combustion sources and could possibly be the result of wind blown dust because rapid rise with wind speed is consistent with wind erosion. The plot for the wind sector 225° – 270° show levels of PM₁₀ and PM_{2.5} that increase with increasing wind speed. This suggests that the source(s) in this sector is an elevated combustion source, such as a stack release. The plot for the wind sectors 135° – 180° shows levels of PM₁₀ and PM_{2.5} that decrease with increasing wind speed. This suggests that the sources in this wind sectors are low level combustion sources, such as traffic emissions.

Figure B.9 : Particulate wind speed variation plot

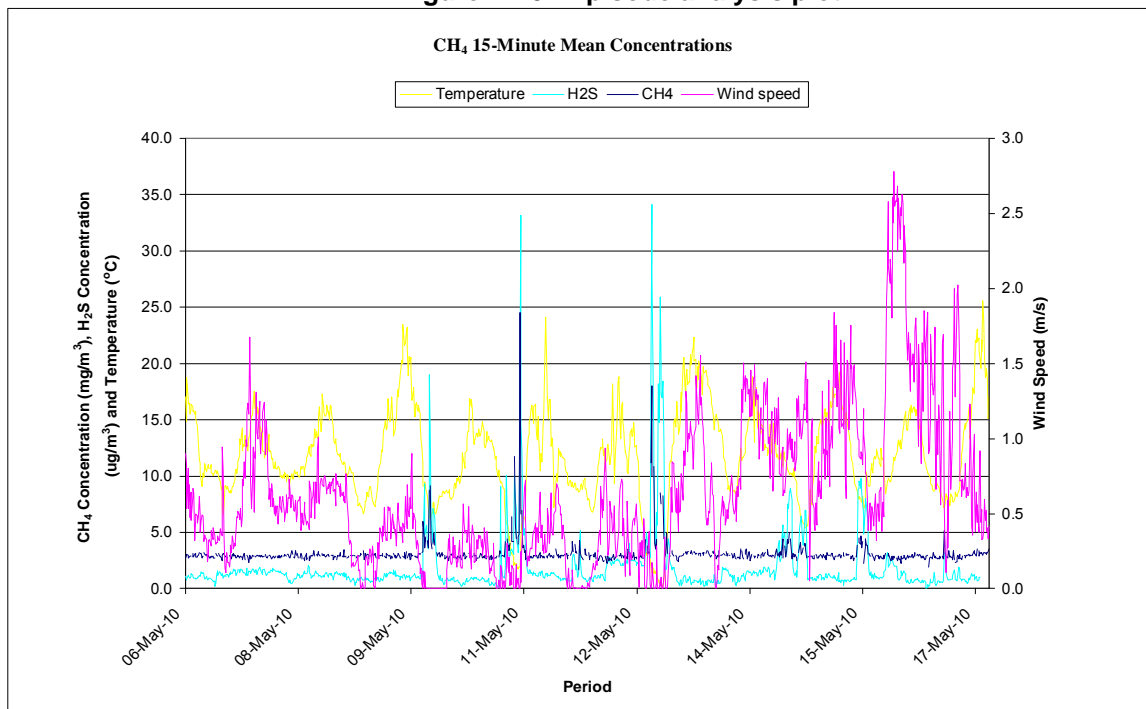


B.8 Episode/Event analysis

Episode or event analysis looks more closely at the occasions of high pollutant concentrations in an effort to identify the conditions that may have given rise to such events.

The peaks in methane (CH_4) and hydrogen sulphide (H_2S) concentrations in Figure B.10 generally occur at night when the temperature and wind speed drop (poor dispersion), suggesting that the pollution events occur during particularly stable conditions, when dispersion may be reduced by the presence of nocturnal inversion layers. The fact that the H_2S and the CH_4 events follow each other so closely suggests that they are both from the same source.

Figure B.10 : Episode analysis plot



B.9 Multiple time series analysis

Multiple time series plots (see Figure B.11) are useful for visually showing correlation between individual pollutant events.

Figure B.11 : Multiple time series plot

