Methods for monitoring particulate concentrations

Key points

- The measurement of concentrations of PM in ambient air is not straightforward. There are a variety of techniques available for measuring mass concentrations, but due to the complex nature of PM, the method that is selected can significantly influence the result.

- The TEOM analyser is widely used for monitoring PM_{10} concentrations in the UK. This continuous sampler provides real-time data with a short time resolution that can be used for providing public information. For the TEOM to be used as a USEPA equivalent method for PM_{10} measurement, a default adjustment factor ($1.03 *$ TEOM reading $+ 3$ µg m^{-3}) must be applied. All TEOM analysers in the UK, both for PM_{10} and $PM_{2.5}$, are set up with this default factor included.

- Due to the need to eliminate the effect of changing humidity on the mass measurement, the TEOM is required to maintain the sample filter at an elevated temperature which may lead to losses of semi-volatile species such as ammonium nitrate. This has led to reported differences in concentrations of PM between the TEOM and the European reference method for PM_{10} measurement, which uses an unheated, filter-based gravimetric sampler.

- The European reference method for PM_{10} measurement, EN 12341, does not fully address the issue of semi-volatile losses and so can give inconsistent results. The draft reference method for $PM_{2.5}$ measurement, prEN 14907, is intended to reduce this problem and will also provide the basis for a revised PM_{10} measurement reference method.

- Intercomparison trials between the European reference method and various other methods, including the TEOM, are being carried out in the UK. As an interim measure, a default scaling factor (also known as correction factor) of 1.3 is currently applied to all TEOM PM_{10} data in the UK national networks in an attempt to account for these losses.

- If the reference method were changed so that only the non-volatile component of the particle mass were measured, this would lead to great improvements in the consistency and practicality of measurements for regulatory purposes. These 'core particulate' measurements could be supplemented by specific monitoring techniques to determine the volatile and other particle mass components as required.

- Monitoring of PM_{10} concentrations, based largely on the TEOM analyser, is carried out on a national scale on behalf of Defra and the Devolved

Administrations and at a regional or sector-specific scale on behalf of local authorities, the Highways Agency and the power generation industry. These networks are subject to rigorous quality assurance and quality control procedures.

- Data from 240 PM_{10} monitoring sites operating in 2003 – including sites at kerbside, roadside, urban background/centre, industrial and rural/remote locations – have been collated within a spreadsheet pro forma for this report Fifteen of these sites have co-located $PM_{2.5}$ analysers.

- National networks also exist to measure concentrations of black smoke, PAHs, heavy metals and major ions (such as sulphate, nitrate and chloride).

- As part of a research programme funded by Defra and the Devolved Administrations, continuous measurements of particulate nitrate and organic and elemental carbon, together with total and fractionated particle number concentrations (predominantly ultrafine particles), are carried out at a number of sites in the UK.

- The monitoring of PM in the UK is dominated by PM_{10} mass measurements. Only limited data are available for particle number, size, surface area and morphology.

5.1 Introduction

376. The complex nature and composition of airborne PM has been described in detail in Chapter 2. In the absence of a confirmed toxicological route for the effects of particles on human health, the relative importance of the different components of the particle mass is, as yet, unknown. This presents a significant challenge for the measurement of particulate concentrations in the ambient atmosphere and, to a large extent, the method selected for the collection and determination of particle mass determines the mass concentration that is subsequently reported. For this reason it is essential to state precisely the method by which the reported measurements have been made.

5.2 Overview of PM monitoring methods

5.2.1 Introduction

377. There is a variety of monitoring methods available for the measurement of mass concentrations of PM in ambient air. These include both direct reading instruments, which provide continuous measurements of particle concentrations, and filter-based gravimetric samplers that collect the particulate material onto a filter, which must then be weighed subsequently in a laboratory.

378. Commonly used methods in the UK for the mass measurement of PM in ambient air include:

- filter-based gravimetric samplers (including the European reference sampler);

- Tapered Element Oscillating Microbalance (TEOM) analysers;

Box 5.1 Units of measurements

With gaseous pollutants it is possible to express concentrations as an amount fraction – the ratio of pollutant molecules to the total number of air molecules – for example, with units of nanomoles per mole (nmol/mol) or, more commonly, parts per billion (ppb).

This is not possible for PM, and measurements are always given in units of particulate mass per unit volume of air (typically $\mu g \ m^{-3}$). When these units are used without specifying the temperature and pressure of the air, the same 'packet' of air will have a different concentration as these properties of the air change. The European legislation for PM requires that the air volume used must be at the same ambient air temperature and pressure as at the time of sampling.

In practice this means that appropriate corrections need to be made if the flow rate used to calculate the sampled volume is not based on the actual volume of sampled air.

As is described in more detail within this chapter, different measurement techniques, although nominally measuring the same PM, may treat the airstream in different ways, leading to significantly different results. For clarity, all mass measurements of PM_{10} and $PM_{2.5}$ in this report are expressed as $\mu g \ m^{-3}$ for both gravimetric and TEOM analysers. If any 'correction factor' has been applied to the data, this is explicitly stated. For example, where data from TEOM analysers have been 'corrected' by applying a factor of 1.3, these data are reported as $\mu g \ m^{-3}$ (TEOM * 1.3).

- ß-attenuation analysers;

- optical analysers;

- black smoke method; and

- personal samplers.

379. A summary of the various advantages and disadvantages of each method is provided in Table 5.1. Annex 4 provides a summary of the PM_{10} and $PM_{2.5}$ measurement techniques that are used in the monitoring networks across Europe.

378. Alongside these measurement techniques, which directly or indirectly monitor particulate mass, other types of measurements are routinely made.

381. Various methods are available to quantify the soiling aspect of nuisance dust. These are discussed briefly in Section 5.6.

382. Ultrafine particle measurements quantify the number of particles below ~100 nm. These are described in Section 5.7. Chemical analysis of the PM can be carried out for a very wide range of components and chemical properties using many analytical techniques. Within the UK, PAHs, such as benzo[a]pyrene; metals, especially lead, nickel, arsenic and cadmium; and major ions, especially sulphate, are analysed routinely, generally in the PM_{10} size fraction. These measurements are described in Section 5.8.

5.2.2   Size-selective inlet heads

383.   Both gravimetric and automated instruments, apart from those that use optical methods, rely on a size-selective inlet to exclude unwanted larger particles before the concentration of PM is quantified.

384.   The selection is achieved using aerodynamic principles: a convoluted route forces the larger particles to move outside the path followed by smaller particles and they can then be prevented from travelling on to the filter. Designs use either an impactor, where the larger particles collect on to a flat plate, or a cyclone, where they collect on the inner surface of a ring.

385.   Impactor designs need more regular cleaning to prevent the build up of piles of dust that would change the cut-off characteristic and more regular application of grease to prevent the larger particles bouncing off and continuing on to the filter.

386.   No design can have an infinitely sharp cut-off, with all particles below 10 μm, for example, being let through and all particles above that size rejected. Inlets are designed so that 50% of particles of the critical size are rejected, but the curve of percentage rejected versus particle size varies between designs. Cyclones generally have a less sharp cut-off curve than impactors, and the reference design is, therefore, usually an impactor.

387.   The cut-off characteristics depend on the speed of the air passing through the inlet, so that control and calibration of the flow is necessary for the correct size fraction as well as for the correct sampled volume. Some specific inlets are mentioned in Section 5.3.1.

5.3 PM_{10} monitoring methods

5.3.1   Filter-based gravimetric samplers

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

- superhigh volume sampler – the WRAC (Wide Range Aerosol Classifier);

- high-volume sampler – the HVS PM_{10} sampler (68 m^3 h^{-1});

- low-volume sampler – the LVS PM_{10} sampler (2.3 m^3 h^{-1}).

389.   Each of these samplers consists of a PM_{10} sampling inlet that is directly connected to a filter substrate and a regulated flow controller. Following completion of the sampling period, the PM_{10} mass collected on the filter is determined gravimetrically. The filter is conditioned at 20°C and 50% relative humidity prior to weighing.

390.   The WRAC sampler is usually regarded as a 'primary standard' and is not suitable for deployment in the general ambient environment. Within the UK, the low volume sampler (often referred to as the kleinfiltergerat or KFG) has been most widely used.

391. It is important to emphasise that the PM_{10} concentration measured by the reference method is simply that – it is not an absolute measure of PM_{10} mass in the atmosphere. The reference method will be subject to both positive (for example, due to an increase in particle-bound water) and negative artefacts (for example, due to loss of semi-volatile compounds) during sampling.

392. A number of samplers based on the low-volume sampler have been designed to allow automatic filter changing after each 24-h period, so that the instrument does not need to be visited each day. This includes a system that incorporates eight separate PM_{10} sampling heads connected to a central pump via a solenoid switching system (PNS-X8, IND) and a sequential sampler that uses an automatic exchange mechanism (SEQ47/50, Leckel). Although these types of samplers are more convenient to operate, there is the potential for an unquantified loss of semi-volatile compounds if the filter is exposed to the fluctuating conditions in the ambient environment following the end of sampling period.

393. There is a wide range of other filter-based gravimetric samplers available that are based on principles similar to the reference method. Within the UK, the Partisol sampler (R&P) has been used in a wide number of studies. The instrument operates at a lower sampling volume ($1 \text{ m}^3 \text{ h}^{-1}$) than the LVS reference sampler, and incorporates a USEPA-approved PM_{10} size selective inlet. The instrument is available as both a single filter sampler (Partisol 2000) and as a 16-day sequential sampler (Partisol 2025).

394. A number of UK research workers have also used the MiniVol sampler (Airmetrics). This is a portable sampler operating at $0.3 \text{ m}^3 \text{ h}^{-1}$ and is powered from a rechargeable battery, allowing it to be easily deployed in the field. The sampler may be configured to collect either PM_{10} or $PM_{2.5}$ samples depending upon the impactor that is selected. Mass determination is by subsequent weighing of the filter.

5.3.2 TEOM analysers

395. The TEOM analyser is widely used in both the UK and throughout the rest of the world for measuring continuous concentrations of PM. The instrument is based on the principle that the frequency of oscillation of a glass, tapered tube (element) changes by an amount that is directly proportional to the mass of the tube. Therefore, any change in mass of the tube, due to the deposition of particles onto a small filter affixed to one end, will result in a change in the resonant frequency – this change is proportional to the additional mass.

396. Air is sampled at 16.7 l min^{-1} through a USEPA-approved PM_{10} size selective inlet. A sample splitter divides the flow, carrying 3 l min^{-1} to a 16 mm PTFE-coated quartz filter. Both the manifold inlet and tapered element are maintained at 50°C to minimise errors associated with the evaporation and condensation of water on the filter.

397. In order for the TEOM to be used as a USEPA-equivalent method for PM_{10} measurement, a default adjustment factor ($1.03 * \text{TEOM reading} + 3 \text{ μg m}^{-3}$) must be applied to the raw data. This adjustment factor was derived to account for moisture equilibration differences between the TEOM and the HI-vol sample media. The adjustment factor was determined at sites where non-volatile PM

Table 5.1 Summary of advantages and disadvantages of principal PM sampling methods.

Technique	Advantages	Disadvantages	Estimated precision[a]
Filter-based gravimetric samplers	The reference method for PM_{10} specified in the EU First Daughter Directive.	High operating costs. Time resolution of the measurement is limited to 24-h. Reporting requirements of the EU First Daughter Directive cannot be met and results can only be provided some days after the sample was collected.	$\pm 2 \mu g\ m^{-3}$
TEOM analysers	Provide real-time data with short time resolution (<1 h) that can be used for public information. Improved precision compared to the reference method.	Preheated air stream causes a greater loss of semi-volatiles compared to the reference method. High capital cost.	$\pm 0.5\ \mu g\ m^{-3}$
ß-attenuation analysers	Provide real-time data with short time resolution (<1 h) that can be used for public information.	If a heated inlet is used some semi-volatile material may be lost. Unheated samplers may suffer from interference due to the presence of water. Analyser contains a radioactive source.	$\pm 3\ \mu g\ m^{-3}$, but depends on analyser type
Optical analysers	Portable and often battery operated. Can measure several size fractions simultaneously.	Depends on assumptions about particle characteristics, which may vary from place to place and time to time.	Depends on analyser type
Black smoke	Simple, robust, inexpensive and easy to maintain. Long time series of existing data.	Measures an index rather than a gravimetric concentration. Calibration factor not appropriate to the current mix of pollution sources. Time resolution of the measurement is limited to 24-h.	$\pm 2\ \mu g\ m^{-3}$, may be higher at current typical concentrations
Personal samplers	Portable samplers that can easily be deployed in the field and used to determine personal exposure to particulate concentrations.	As above, depending on measurement method used. All personal exposure analysis is very labour-intensive.	According to technique employed, as above

[a] The precision stated refers to when the sampler is used to determine PM_{10} mass over an averaging period of 24-hours.
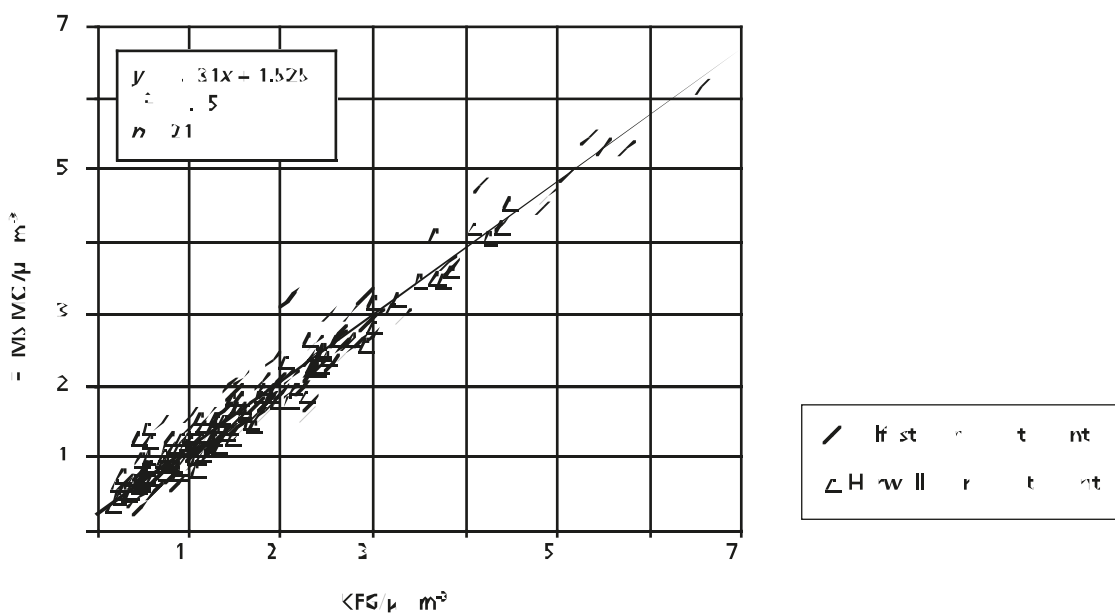
dominated and is intended to reflect the filter character more than the PM. It is understood that USEPA has no general policy on the use of this empirical adjustment factor for $PM_{2.5}$ measurements. All TEOM analysers in the UK measuring both PM_{10} and $PM_{2.5}$ are currently set up with this default adjustment factor included. In addition, TEOM analysers within the UK networks are set to report concentrations corrected to 293K and 101.3 kPa.

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

399. To attempt to overcome these problems, two innovations to the TEOM have become available in recent years. A TEOM analyser equipped with a Sequential Equilibration System (SES) incorporates a Nafion dryer, which reduces the relative humidity of the sample stream. This allows the instrument to operate at the lower temperature of 30°C, thereby reducing the loss of volatile components.

400. A more recent development, the Filter Dynamics Measurement System (FDMS) independently measures the volatile component of the incoming air sample. The incoming air stream passes through a size selective inlet and a SES dryer before it is alternately switched every six min between the TEOM microbalance sensor unit and a purge filter system held at 4°C. The purge filter effectively removes aerosols from the sample stream before it passes to the sensor unit. The system then adjusts the final mass concentration by reference to any mass change that occurred during the purge cycle, for example, if a decrease in mass was measured during the purge cycle, then this would be added back to the mass measurement reported with particle-laden air.

401. FDMS analysers have been deployed on a trial basis at two locations in the UK: at Belfast (from 1 October 2003) and Harwell (from 20 November 2003). Figure 5.1 shows a comparison of the 24-h mean PM_{10} concentrations measured by the FDMS with a co-located reference sampler (KFG) up until May 2004. Regression analysis was performed using an orthogonal approach. These data form a preliminary assessment, and there is an intention to include FDMS analysers in the detailed equivalence programme described in Section 5.4.3.

5.3.3 ß-attenuation analysers
402. ß-attenuation particle analysers are the most widely used method for measuring ambient PM_{10} concentrations in national networks across Europe (see Annex 4). However, they are less widely employed within the UK networks, where use of the TEOM analyser is more common (Section 5.10.). The ß-attenuation analyser uses measurement of the reduction in intensity of ß particles passing through a dust-laden filter. This reduction in intensity is due to absorption of ß particles by the dust collected (and the filter material). The relationship between radiation absorbed and mass of dust collected closely follows an exponential relationship

Figure 5.1 Comparison between FDMS and reference KFG samplers at Belfast and Harwell.

that is reasonably independent of the chemical composition of typical PM found in the atmosphere. Some ß-attenuation monitors are calibrated using foils based on quartz dust.

403. Although the exact configuration varies from analyser to analyser, the sample is collected onto a filter or filter tape and a radioactive source (typically carbon 14, krypton 85 or promethium 147) is positioned above the sample, with a detector below to measure the radiation absorbed. In some units the particle mass can be monitored continuously, whereas in others the sample is collected for a discreet period (typically 30 or 60 min) before the mass is determined. Absorption due to the clean filter is accounted for either by the sequential measurement of clean and exposed filters or using a dual chamber arrangement.

404. In addition to the mass measurement, measurement of the volume of air sampled is necessary to calculate particle concentration. The determination of volume is normally achieved by the use of flow controllers and flow measurement devices, as in other automatic monitors.

405. Particle size selection is determined by the inlet and the flow rate used. Hence, ß-attenuation analysers can measure total suspended particles (TSP), PM_{10} or $PM_{2.5}$ (or other size fractions), depending on the inlet head used. Although the filter material in ß-attenuation monitors is not generally heated, in some analyser's configurations the inlet system is heated to reduce relative humidity in the sample and, therefore, minimises the water content of the aerosol mass. However, this is likely to lead to loss of semi-volatile material, as in the TEOM.

406. Studies of intercomparisons of ß-attenuation analysers and gravimetric samplers have been reviewed (EC Working Group on Particulate Matter, 2001). The report concluded that the factor relating ß-attenuation analysers to the reference gravimetric sampler varied from study to study and depended on whether the sample was heated or not, the analyser calibration and the season (winter or

summer). However, in general, the factor was close to one in systems without heated inlets and approximately 1.3 with heated inlets during the winter season and closer to one in the summer season.

407. Monitoring with an unheated ß-attenuation analyser (the Met One beta-Attenuation Monitor, or BAM 1020) is carried out by a number of local authorities in the UK. Although no systematic long-term collocation studies comparing the BAM, TEOM and reference sampler have been carried out, consistent evidence shows that the BAM measures significantly higher PM_{10} concentrations than the reference sampler or the TEOM * 1.3 (see Annex 5).

408. This effect is also demonstrated in Section 6.2.3, where both TEOM * 1.3 and BAM data have been used to generate a concentration surface across London. It is evident that the concentrations generated by the BAM measurements are anomalous compared with the TEOM * 1.3 data.

5.3.4 Optical analysers

409. Optical particle monitors utilise the interaction between airborne particles and visible, infrared or laser light.

410. Nephalometer and/or transmissometers are commonly used in the USA to determine visibility loss due to airborne particulate material, especially in national park areas. Transmissometers operate over a long open path of 1–10 km and measure total light extinction by determining the loss of light (due to scattering and absorption of the intervening atmosphere) from an artificial light source of known luminescence. Nephalometers, which operate over a short closed path, measure light scattering, which is responsible for the majority but not all of the total light extinction.

411. Of more relevance to measuring particle concentrations, some newer light scattering devices use laser light scattering to both count and size classify PM. The advantage of this approach is that a single analyser with a TSP inlet can monitor particles of a range of sizes, including PM_{10}, $PM_{2.5}$ and PM_1, simultaneously. However, the particle counts need to be converted to mass by calculation using a range of assumptions whose validity may vary due to the nature of the particles sampled. In an attempt to overcome this problem, some analysers also collect the particles sampled onto filters for subsequent gravimetric analysis. These results can then be used to 'calibrate' the optical results for the particular application.

412. Often these analysers are small, lightweight and battery operated and hence are readily portable and very useful for short-term measurements and 'screening' of a number of locations to build up knowledge of particle distribution in both space and time.

413. Optical monitors are not used in the national monitoring networks in the UK, although particle counters – which utilize optical techniques (see Section 5.6) – are used in research programmes for Defra and the Devolved Administrations. Portable optical particle monitors are often used in screening studies and for workplace and indoor particle monitoring programmes.

5.3.5 Black smoke method

414. The methodology for monitoring particulate material as black smoke was developed more than 50 years ago, when domestic smoke was a major cause of particle pollution in the UK. The method is fully described in ISO 9835. PM is collected on a filter paper over a 24-h period and the darkness of the stain is measured by a reflectometer. The inlet size (30–50 mm diameter), sample tube (<8 m of 6.5 mm PVC tube) and the sample flowrate (2 m^3 per day) define the fraction of material collected, and this is generally taken as approximately PM_4. The monitoring equipment is relatively simple, robust and inexpensive.

415. The 'darkness' of the stain is measured on a standard reflectometer. The darkness reading is converted to a measure of particulate material in the atmosphere by reference to one of two standard calibration curves: the OECD curve and the British Standard curve. The calibration curves convert reflectance measurements to µg m^{-3} of black smoke, which can then be converted to black smoke concentration (µg m^{-3})[1].

416. In practice, however, no meaningful universal relationship can be derived between reflectance and black smoke since the relation can change from place to place and from time to time. The 'concentrations' of black smoke derived from this method should, therefore, be considered to be an index of black smoke rather than an absolute measure in mass terms. The precision of the method is high, typically about 2 µg m^{-3} for concentrations >5 µg m^{-3}. However, many concentration measurements in the UK are now lower than this and are likely to be less precise.

417. Despite the shortcomings of the methodology, many epidemiological studies still find clear links between black smoke concentrations and the effects on human health (see Chapter 3). In addition, there is a vast body of black smoke measurement data in the UK and throughout the world, stretching back to at least 1961. In the UK, over 1000 monitoring sites operated during 1962–1980; at the present time, 123 sites are still in operation. This provides a rich source of research data. Section 5.10.2 gives further information on the UK Black Smoke Monitoring Network.

5.3.6 Personal samplers

418. An increasingly wide range of measurement techniques for various metrics of PM are being applied to personal exposure analysis. The requirement of exposure analysis is that sampling should be from the breathing zone of an individual, which extends approximately 30 cm from their nose and mouth, and moves with them from one microenvironment to the next. Portable equipment ranges in size and weight from passive badge samplers (Brown *et al.*, 1995; Wagner and Leith, 2001), although these techniques have not been very widely used, to high-volume pumps, 16 l min^{-1} from a pump weighing ~3 kg (Adams *et al.*, 2001a). Low-volume active sampling is used for integrated measurement over daily or longer averaging times (Jantunen *et al.*, 1998), whereas high-volume sampling allows shorter times to be investigated, such as commuting periods (Adams *et al.*,

---

[1] The British Standard curve is used within the UK, except when results are reported to the EC, when they are reportedin OECD units, as required by Directive 80/779/EEC(British Standard= OECD Standard * 0.85).

2001b). Particle size selection for these filter sampling techniques is achieved by conventional impactor or cyclone techniques or specially designed more lightweight methods such as the conical inhalable sampler using treated foam to remove particles larger than 10 or 2.5 μm at a given low or high flow rate. Condensation particle counters (for example, TSI P-Trak) and optical particle counters (for example, Grimm) are portable and may be used for personal exposure measurement. They also have the advantage of providing time resolutions as high as 1 Hz, if required, to identify the frequency, duration and severity of peak exposures and higher moments of the personal exposure distribution function.

5.4 Comparison of PM_{10} monitoring methods

5.4.1 Introduction

419. The reference method describes a uniform approach to the measurement of PM_{10} concentrations, but provides a number of practical difficulties for monitoring, particularly within national networks. Filter-based gravimetric samplers rely heavily on human resources for servicing, particularly if the filters are exchanged on a daily basis, and for subsequent weighing of the filters. The quality assurance must be more strictly enforced, simply due to the additional potential pathways for error (for example, sample handling, transfer, storage and weighing). In addition, as the filters have to be taken to the laboratory for weighing, there are several days delay (as a minimum) between sample collection and reporting. This is disadvantageous to the protection of public health and contravenes the reporting requirements of the Daughter Directive.

420. For these reasons, monitoring of PM in the UK has been largely founded on the TEOM analyser (as described in Section 5.10). Studies to investigate the relationship between the TEOM analyser and the reference method are ongoing and are described in Section 5.4.3 below.

5.4.2 EU Working Group paper on equivalence

5.4.2.1 Background

421. For all air pollutants covered by European Ambient Air Directives, the Directives specify a reference method for carrying out the measurements. These methods are, in principle, set out in sufficient detail to meet the Data Quality Objectives of the Directives within European Committee on Standardisation (CEN) standards, many of which exist in draft form and are due for publication in 2005. PM_{10} measurement is an exception to this, as the CEN standard EN 12341 was published in 1998 (European Committee on Standardisation (CEN), 1998), before the relevant Ambient Air Directive, and it, therefore, does not explicitly address the Data Quality Objectives for PM_{10}.

422. At the same time as specifying a reference method, the Ambient Air Directives also contain the statement:
'A Member State may use any other method which it can demonstrate gives results equivalent to the above method.'

423. For PM$_{10}$ this is extended by the statement:
'... or any other method which the Member State concerned can demonstrate displays a consistent relationship to the reference method. In that event the results achieved by that method must be corrected [scaled] by a relevant factor to produce results equivalent to those that would have been achieved by using the reference method.'

424. For non-reference methods for all pollutants and, in the case of PM$_{10}$ also for non-reference methods with a scaling factor, there is a need to be very clear about what is meant by results being 'equivalent' to those of the reference method. The EC set up a Working Group to produce a guidance document covering this issue. A final draft document was published in 2004 (EC Working Group on Guidance for the Demonstration of Equivalence, 2004).

5.4.2.2 *The equivalence procedure for PM$_{10}$ in EN 12341*

425. The CEN standard EN 12341 contains a procedure for determining whether non-reference instruments are equivalent to the reference method. However, the procedure states that it is not to be used to determine the equivalence of automated methods. It also uses relatively crude statistical procedures to assess field trial data, and the equivalence criteria are not directly linked to the Data Quality Objectives. It is, therefore, not greatly helpful for current or future purposes of complying with the Ambient Air Directive. It is expected to be replaced in due course with an equivalence procedure based on the EC Guidance Document, described below.

5.4.2.3 *The equivalence procedure for PM$_{10}$ in the draft EC Guidance Document*

426. The draft EC Guidance Document on Equivalence (EC Working Group on Equivalence, 2003) has the general aims of determining whether candidate (non-reference) methods are capable of fulfilling the Data Quality Objectives (especially measurement accuracy/uncertainty) and of ensuring that only suitable methods are employed for official reporting purposes with sufficient ongoing quality control to ensure that the Data Quality Objectives are met during routine use.

427. In principle, equivalent methods should not require less rigorous implementation than the reference method, whose requirements are set out in detail in CEN standards.

428. For PM (both PM$_{10}$ and PM$_{2.5}$), the draft EC Guidance Document specifies two approaches for determining whether a candidate method is equivalent, depending on whether the method differs in minor or major ways from the reference method. Where minor variations – such as non-standard storage of filters or non-standard filter weighing conditions within manual methods, otherwise similar to the reference method – are proposed they can be evaluated by laboratory trials that determine the worst case effect on the measurements.

429. Major variations, such as any automatic methods, must be evaluated from field trials involving side-by-side reference and candidate instruments. The draft document proposes:

- two reference instruments;

- two candidate instruments;

- operation of the candidate instruments as they would be at a standard field site;

- at least four distinct field comparisons containing at least 40 measurement days each; and

- adequate coverage of the full range of expected measurement conditions in the field – PM concentration, PM composition, temperature, humidity and wind speed.

However, the draft guidance document also allows that data from previous parallel measurements with two reference instruments may be taken into account (obviating the need for simultaneous measurements of both two reference and candidate instruments) where that previous data is obtained under equivalent conditions to those given in the Guidance document.

430. Equivalence can only be declared for the range of conditions covered during the field tests. For instruments without a scaling factor, it is determined by quantitative tests covering:

- agreement between the duplicate reference instruments (to provide a check that they have been used correctly);

- agreement between the duplicate candidate instruments (to check repeatability);

- the regression slope between the average reference measurement and the average candidate measurement (which must be close to one); and

- the uncertainty of individual candidate measurements – a combination of repeatability, the uncertainty of the reference method, deviation of the regression line from ideal slope and intercept and the deviation of individual data points from the regression line – which is compared to the Data Quality Objectives.

431. These tests must be passed for the entire set of measurement data, and also for the distinct comparisons separately, so that anomalous performance in one set of conditions will not be masked by other more favourable conditions.

432. In line with the special allowance for scaling factors to be applied to PM instruments, all the candidate data may be adjusted for a constant offset, a constant factor or both, which would then be applied in the same way to all data collected for official monitoring. After data have been scaled, the tests listed above must be passed, again both for the entire dataset and for the distinct comparisons separately. In addition, an extra term relating to the correction is added to the uncertainty of the individual measurements.

5.4.3 The UK PM$_{10}$ intercomparison exercise

433. An intercomparison study between the TEOM analyser and the reference sampler commenced in 1999 (Casella Stanger, 2004). It is important to note that this study predated the draft EC Guidance Document described above.

434. The study focused on six monitoring sites within the UK Automatic Urban and Rural Network (see Section 5.9), representative of the geography, particle concentrations and sources in the UK. These were:

- Marylebone Road (Kerbside – London);

- Thurrock (Urban Background – SE England);

- Harwell (Rural – Oxfordshire);

- Port Talbot (Industrial – Wales);

- Glasgow Centre (Urban Centre – Scotland);

- Belfast Centre (Urban Centre – Northern Ireland).

435. The conclusions of the study are that the TEOM analyser generally reports lower PM_{10} concentrations than the reference sampler. The ratio of TEOM and reference sampler concentrations varies from site-to-site and from season-to-season. The lowest seasonal ratios (close to unity) are consistently observed at Port Talbot (presumably influenced by local emissions from the nearby steelworks) and the highest ratios (approximately 1.4 to 1.5) are observed at Thurrock. In general, higher ratios are observed in the winter than in the summer.

436. The application of the 'default' 1.3 scaling factor that is currently applied to TEOM data in the UK provides a variable level of agreement with the reference sampler. The default factor provides a reasonable result for many sites when long-term averages are considered, but does not give an accurate indication of the number of exceedence days.

437. Regression analysis (based on Reduced Major Axis) indicates R^2 values generally within the range of 0.6 to 0.9 (examples are shown in Figure 5.2), although the relationships are both site and seasonally dependent. The poorest relationship has been consistently observed at Harwell, with R^2 values in the range of 0.36 to 0.63. An analysis of time series data indicates that, in general terms, the TEOM and the reference method compare reasonably well on a day-to-day basis for much of the time, but measured levels may diverge significantly particularly when concentrations are elevated.

438. Although the intercomparison study meets the general requirements of the draft EC Guidance Document in terms of the range of expected environmental conditions and the number of field comparisons, the study has not included side-by-side reference and candidate instruments. It has, therefore, not been possible to determine the 'between-instrument' uncertainties. However, in order to provide an initial indication as to how the TEOM analyser might perform, and to inform the requirements for any future work, the data from the intercomparison study have been evaluated using the statistical approach in the draft Guidance Document and assumptions[2] for 'between-instrument' uncertainties.

439. The expanded uncertainty of the full dataset following scaling is 30.5%, which exceeds the requirement for measurement uncertainty (25%) stated in the

---

[2] For the KFG reference sampler this was assumed to be the maximum allowable uncertainty of ≤ 1 μg m^{-1}.

Daughter Directive, and the TEOM analyser fails the test. This conclusion must be considered with the following points in mind:

- The reference sampler used in this study was fitted with an automatic filter switching mechanism to avoid daily site servicing. Although this was consistent with general network operations, there is the potential for losses of semi-volatile material post-sampling, as the filters remain exposed in the ambient environment for up to seven days.

- Filters were transported to the laboratory by post, which may have incurred further losses of semi-volatiles.

- Given the potential for these losses, it has not been possible to conclude whether the stringent criterion for the 'between-instrument' uncertainty of the reference sampler has been met.

440. In light of these results, Defra started a more detailed evaluation exercise in 2004, which will include a wide range of co-located candidate samplers. It is expected that preliminary results will be reported in late 2005.

441. Notwithstanding the outcome of the proposed evaluation exercise, it is noted that if the reference method were changed so that only the non-volatile component of the particle mass was determined, this would lead to a great improvement in both the consistency and practicality of measurements of PM for regulatory purposes. In the event that the semi-volatile, or any other mass component not within this 'core particulate' were deemed important, then these could be measured by additional specific monitoring techniques at a representative number of sites.

5.5 Measurement of $PM_{2.5}$ (and PM_1) concentrations

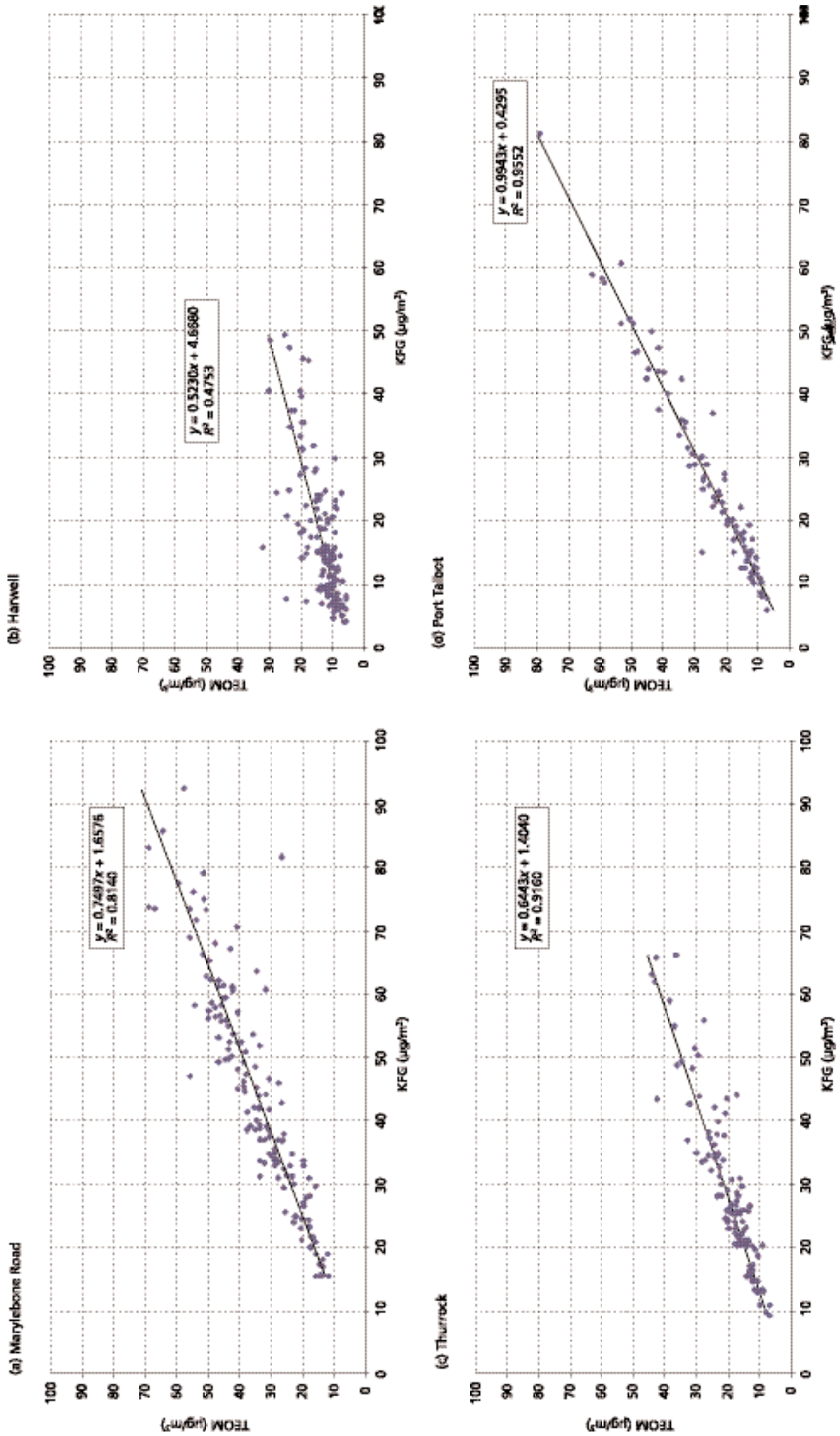### 5.5.1 Methods of measurement

442. The $PM_{2.5}$ fraction of PM differs from the PM_{10} fraction solely in the size of the particles included. The fundamental difference in methods for $PM_{2.5}$ compared to PM_{10} measurement in most cases is, therefore, just the design of the size-selective inlet. The methods used for PM_{10}, described in Section 5.2 can, therefore, be adapted for use with $PM_{2.5}$ with no other changes[3]. The exceptions to this are instruments that use optical methods, which determine the size fraction by means other than a size-selective inlet. However, optical instruments for $PM_{2.5}$ are essentially similar to those for PM_{10}, with commercial instruments capable of monitoring the different size fractions in a rapid cycle.

443. The size-selective inlets for $PM_{2.5}$ measurements are generally designed to operate at the same sampling flow rate as those for PM_{10}, so that the instruments can be converted for the different size fractions with minimal effort.

444. In practice, the measurement of $PM_{2.5}$ differs from PM_{10} because there will be a smaller quantity of PM to measure, and the coarse fraction, which tends to consist of windblown dust and other non-volatile material, is excluded. Both these factors make accurate $PM_{2.5}$ measurement more difficult than PM_{10} measurement.

---

[3] As described in Sections 5.3.2, all TEOM analysers measuring $PM_{2.5}$ are set up with the USEPA default adjustment factor (TEOM *1.03 +3 µg m^{-3}).

Figure 5.2 Regression (Reduced Major Axis) plots for the four sites used in the UK intercomparison study (October 1999 to March 2000). At the mean TEOM concentrations measured at each site in 2002, the regression equations below represent gravimetric:TEOM factors of 1.27 (Marylebone Road), 1.20 (Harwell), 1.45 (Thurrock) and 0.99 (Port Talbot).

(a) Marylebone Road

(b) Harwell

(c) Thurrock

(d) Port Talbot

445. Instruments for measurement of PM_1, a yet smaller size fraction, follow the same principles as those for $PM_{2.5}$ and PM_{10} measurement.

5.5.2 Development of CEN reference method for $PM_{2.5}$

446. The European Ambient Air Directives require Member States to make measurements of $PM_{2.5}$ and the EC mandated the standardisation body CEN to specify the reference method to be used. In line with the European reference method for PM_{10} measurement, the method was required to be based on the collection of the $PM_{2.5}$ fraction of ambient PM on a filter, with mass determination by weighing.

447. The standard will, therefore, include one or more designs of size-selective inlet, with associated parameters for flow control; specifications for conditioning, transporting and weighing the filters; additional quality assurance and quality control requirements; and a methodology for calculating the measurement uncertainty. It will also contain a procedure for determining whether non-reference methods give equivalent results to those of the reference method, which will closely follow the EC Guidance Document on Equivalence.

448. Apart from the different inlet design(s), the major operational differences from the PM_{10} reference method, EN 12341, are expected to involve stricter measures to minimise losses of semi-volatile PM from the filter during and after sampling and other filter artefacts affecting the measured mass, issues that were not fully appreciated when EN 12341 was written.

449. The draft standard prEN 14907 was completed in December 2003 and is passing through a process of consultation, revision and voting by Member States. The process is coordinated through national standardisation bodies, BSI in the UK.

450. During the drafting of the standard, a major series of field trials involving candidate reference instruments – operated under the proposed stricter conditions of the new standard – together with selected automatic instruments, was carried out. Nine locations across Europe were used, including Teddington in SW London. This location also included a TEOM FDMS instruments. The initial results of these trials have not yet been published.

5.6 Measurement of nuisance dust

451. Nuisance dusts may be generated by a wide range of activities, including road traffic, construction and demolition work, mineral extraction processes and industry. These emissions can cause soiling of surfaces such as car bodywork and window ledges and can give rise to considerable public concern. There is no precise definition of nuisance dust, or how to measure it, and no standard criterion for assessment has been established.

452. A variety of monitoring techniques have evolved. These involve the determination of the mass of dust deposited over a given area or determination of the soiling of a surface by reduction in surface reflectance or gloss. A more detailed description of these methods is given elsewhere (for example QUARG,1996).

5.7 Measurement of ultrafine particles

5.7.1 Particle number measurements

453. Ultrafine particles are commonly defined as those particles that are <0.1 μm in diameter. Such particles contribute very little to particle mass, but contribute significantly to the total number of particles. It is common practice to measure ultrafine particles in terms of the particle number concentration. The conventional light scattering instruments normally used to measure particle number concentrations cannot detect ultrafine particles. Within the UK, the Condensation Particle Counter (CPC, TSI) has been used in a number of studies. The CPC is based on the principle that supersaturated vapour will condense on small particles. The sampled aerosol passes through a chamber that is saturated with *n*-butyl alcohol vapour and then to a cooled condenser where the alcohol condenses onto the particles, which causes them to grow in size. The particles are then counted in an optical detector. Depending upon the configuration of the CPC, the analyser is capable of measuring particles within the range of 0.003–2.0 μm. Within the UK, measurements within the range ~0.007–2.0 μm have been routinely carried out.

454. Size-fractionated particle number concentrations may be carried out using a Scanning Mobility Particle Sizer (SMPS, TSI). The SMPS uses a ^{85}Kr ß particle source to impart a bipolar equilibrium charge on the polydisperse aerosol before passing to the electrostatic classifier of a differential mobility analyser (DMA), where the particles are separated according to their electrical mobility. By varying the air flow rate and the voltage in the DMA, the monodisperse aerosol exiting the classifier can be controlled to within a narrow, specified size range. The monodisperse aerosol then enters a CPC where the particle concentration is determined. The size ranges that can be measured using the SMPS are dependent upon the equipment configuration and user-defined parameters. Within the UK, measurements within the range 11–450 nm have been routinely carried out.

5.7.2 Measurement of particle surface area

455. The measurement of particle surface area is not straightforward, principally because airborne particles have a complex morphology. Two main approaches have been used. The first method attaches labelled atoms to the particle surface and then measures the mass transfer. The principal drawback of this method is that the rate of attachment within a polydisperse aerosol is not directly related to the particle surface area: there will be a transition from the molecular bombardment regime for particles smaller than the mean free path of the gas molecules to a diffusion-limited regime for the larger particles. The epiphaniometer is based on this approach and attaches gaseous ^{211}Pb atoms onto the aerosol particles, which are then collected onto a filter and determined by an α-counter. The measured signal is proportional to the exposed Fuchs surface of the aerosol particles (Fuchs, 1964).

456. The second method is to use measurements of particle number size distributions, which may then be converted to surface area based on assumptions regarding particle geometry. This may, for example, include measurements carried out using the SMPS for the smaller particles, in tandem with a suitable instrument for

measuring the larger particle size fractions (such as the Aerodynamic Particle Sizer, TSI).

5.8 Measurement of metals, PAHs and major ions

457. Samples of PM collected using the techniques described in Section 5.2 can be subjected to chemical analysis for the subsequent determination of metals, PAHs and major ions (most commonly sulphate). These days, measurements of metals and sulphate are based on the PM_{10} size fraction, although historically, monitoring of these species in the UK were based on the M-type sampler[4]. PAH monitoring is currently based on use of a modified pesticide sampler, which also has a cut-off of approximately PM_{15}. When the 4th EU Daughter Directive is agreed and implemented, it is likely that the network will need to change to PM_{10}-based sampling.

5.8.1 Metals

458. Particles containing the analytes nickel, arsenic, cadmium and lead are sampled by drawing a known volume of ambient air through a cellulose filter held within a high- or low-volume sampler. The filter is dissolved in a solution of HNO_3 and H_2O_2 by microwave digestion in a closed vessel. This sample is then analysed for metals content by inductively coupled plasma-mass spectrometry (ICP-MS).

459. ICP-MS is a technique that employs an argon plasma to ionise a sample as it is introduced. The ions produced are then analysed by a mass spectrometer. The ICP-MS analyses all elements of interest effectively simultaneously and can also automatically correct for molecular and isobaric interferences.

5.8.2 PAH

460. Samples are collected using polyurethane foam plugs and filter papers to capture PAHs in the volatile and non-volatile phases, respectively. The fortnightly samples are extracted using dichloromethane and then bulked to give a single sample. The concentrations of 32 individual PAHs are determined from the quarterly samples using gas chromatography with mass spectrometric detection.

5.8.3 Major ions

461. Samples are collected onto filters (generally cellulose acetate) with subsequent aqueous extraction and analysis by ion chromatography. In some sampling systems, a denuder is incorporated into the sample stream to remove potential interference from acid gases.

5.9 Continuous monitoring of speciated PM

462. Conventionally, measurements of speciated PM are carried out by subsequent chemical analysis of the exposed filter. However, an increasing number of direct-reading analysers are now available, which permit continuous measurements for

---

[4] The performance of the M-type sampler is strongly windspeed-dependent, although at average windspeeds for the UK, the sampling is close to that of a PM_{10} sampler.

a range of particulate species including nitrate, sulphate and elemental/organic carbon. These instruments have the advantage of providing measurements over much shorter time resolutions (1 h or less) and can provide valuable data in tracking diurnal trends and pollution episodes.

463. Carbon particulate analysers (for example, Series 5400, R&P) are based on a thermal CO_2 analysis technique similar to that used in many laboratories. Ambient air passes through a size-selective inlet and the particulate material is collected onto a cartridge contained within a temperature-regulated oven. Differentiation between the organic and elemental carbon component is achieved by oxidising the sample at an intermediate temperature (340°C for organic carbon) and a final high burn temperature (750°C for elemental carbon). The analyser is capable of providing data with a 2-h time resolution.

464. Several analysers are available for the continuous analysis of particulate nitrate and sulphate (Series 8400N, R&P; 9000A Ambient Ion Monitor, URG). Ambient air is drawn through a size-selective inlet and then passes through a denuder to remove interfering acid gases. To achieve a high collection efficiency of very small secondary aerosol, the particles are then enlarged by passage through a humidifier or saturation chamber. The final determination is then by flash volatilisation and measurement of NO_X or SO_2 or by injection into an ambient ion detector.

5.10 The UK monitoring networks

465. Measurement of the mass of PM in the atmosphere (mainly as PM_{10}, but including some $PM_{2.5}$ monitoring) is carried out on both a national and regional scale using a range of monitoring techniques. National networks are also established to monitor black smoke and ultrafine particles and to collect and analyse particulate material for the determination of PAHs, metals and sulphate concentrations. These networks are described in the following sections.

5.10.1 Monitoring networks for PM_{10} and $PM_{2.5}$

466. Networks for monitoring PM are operated at both national level, on behalf of Defra and the Devolved Administrations, and at regional and sector-specific levels. The vast majority of these sites monitor PM_{10}, although a few also monitor $PM_{2.5}$. The TEOM analyser is by far the most common method of measurement in the UK, although some sites use sequential gravimetric samplers and some attenuation analysers.

467. The locations of all sites that were operational in December 2003 and have provided PM data for this study are shown in Figure 5.3. The structures of the various monitoring networks are summarised in Table 5.2.

468. The national research network provides additional monitoring of PM_{10} and $PM_{2.5}$ with a range of gravimetric samplers at nine sites that are part of the AURN and LAQN National Monitoring Networks (see Section 5.9.1.3).

5.10.1.1 UK networks
469. The UK networks are comprised of monitoring sites within both the AURN and the LAQN. The AURN contains a number of monitoring sites that are directly

Table 5.2 Summary of PM monitoring networks (2003).

Networks	Managment unit	Quality assurance and control responsibility	Number of PM$_{10}$ monitoring locations	Number of PM$_{2.5}$ monitoring locations
UK networks				
AURN	Cesella Stanger	Netcen	66	3
LAQN[a]	Kings College ERG	Netcen	5	1
Regional networks				
LAQN				
KAQM	King's College ERG	NPL/ERG	64	5
HBAPMN	King's College ERG	NPL/ERG	18	0
SAQSG	King's College ERG	NPL/ERG	14	0
	King's College ERG	ERG	8	0
Other networks				
Birmingham	Birmingham CC	Birmingham CC	4	1
Calibration Club	Netcen	Netcen	41	2
Highways Agency[b]	TRL	TRL	5	2
Heathrow Airport[c]	Netcen	Netcen	2	0
JEP/Innogy	Casella Stanger	Casella Stanger/NPL	2	1
JEP/Powergen	Power Technology	Power Technology	2	0
Defra/Developed Administrations research	Casella Stanger	Casella Stanger	9	8

Key: KAQN, Kent Air Quality Network; HBAPMN, Hertfordshire and Bedfordshire Air Pollution Monitoring Network; SAQSG, Sussex Air Quality Steering Group; Birmingham CC, Birmingham County Council; Kings College ERG, Kings College Environmental Research Group This table summarises information from the PM monitoring networks used in this report. It is not a complete list of all networks in the UK. [a]A number of sites in this network have been affiliated into the national networks. [b]The Victoria Street site was operated for the Highways Agency up to 2001. From 2003 onwards, this site has been operated for TfL. [c]The Heathrow Airport site is also part of the LAQN and the Heathrow Harlington site is also part of the AURN.

funded by Defra and the Devolved Administrations, together with additional sites that are owned and operated by other organisations (mainly local authorities) and which have been affiliated into the network. The LAQN consists solely of affiliated local authority monitoring sites. The first PM$_{10}$ measurements at six sites in the UK commenced in 1992 and through the years, the number of monitors has steadily increased to the present number of 71. Initially all sites used TEOM analysers, although one ß-attenuation analyser was introduced into the network in 1998[5]. During 2001–2002 additional sites were established in order to meet the requirements of the First Daughter Directive and sequential gravimetric analysers were installed at these seven new PM$_{10}$ monitoring sites. Thus, although some sites have been operating for 10 years or more and can provide invaluable information on long-term trends over this period, data are limited to a considerably shorter period at the majority of monitoring sites. In 2003, four automatic PM$_{2.5}$ monitoring sites (see Section 5.9.1.4) were incorporated into the national network.

[5] A Met One ß-attenuation monitor (BAM 1020), which has an unheated inlet.

Figure 5.3 The Location of (a) PM_{10} and (b) $PM_{2.5}$ 2003 monitoring sites.

(a)

(b)

AURN
AURN + Defra/DA Research
LAQN
KAQN
HBAPMN
SAQSG
Birmingham CC
Calibration Club
Highways Agency - TRL
Transport For London - TRL
Heathrow Airport
JEP - Innogy
JEP - Powergen

Table 5.3 Summary of PM$_{10}$ monitoring stations in the UK national networks (2003).

Site type	AURN	LAQN
Kerbside	1 (0)[a]	2 (1)
Roadside	7 (0)	1 (0)
Urban	23 (0)	1 (0)
Background Urban centre	23 (1)	0 (0)
Suburban	4 (0)	1 (0)
Industrial	4 (0)	0 (0)
Rural/remote	4 (2)	0 (0)
Total	66 (3)	5 (1)

[a]The number of sites with co-located PM$_{2.5}$ analysers is shown in parentheses.

470. Monitoring stations are classified according to their location; a summary of the PM monitoring sites is provided in Table 5.3. Details of the site-type definitions used in the UK are provided in Annex 3 of the AQEG report on NO$_2$ (AQEG, 2004). Further details on the national monitoring network sites and measurement data can be found at www.airquality.co.uk.

471. Automatic data are collected from the network sites on an hourly basis and, after initial validation, are disseminated to the public and the media via the Air Quality Communications Unit. Daily data from the sequential gravimetric samplers are available after the filters have been collected from the analyser and returned to the laboratory for conditioning and weighing.

472. There is a relatively small percentage of roadside and kerbside monitoring sites in the national network (~10%). This is because the networks were developed primarily to monitor urban and rural background pollution, to which most of the population is exposed. However, in recent years, there has been increased interest in roadside pollution levels and a much higher percentage of the more recent sites added to the network have been in this site category. It is possible that many more roadside sites will be required if some of the currently proposed revisions to the EU First Daughter Directive are agreed; however, at present these are still under discussion within the EU.

5.10.1.2 *Regional networks*

473. Regional networks are operated or coordinated by King's College ERG, DoE Northern Ireland and the Welsh Assembly Government, on behalf of local authorities. The operation of the ERG networks mirrors that of the national networks, with routine data polling and validation and subsequent quality assurance and control to provide ratified datasets. A summary of the site types

Table 5.4 Summary of PM$_{10}$ monitoring stations in regional UK networks (2003).

Site type	LAQN[a]	KAQMN	HABAPMN	SAQSG
Kerbside	5	2	—	5
Roadside	34 (2)[b]	8	4	—
Urban Background	16(1)	6	10	3
Urban Centre	—	—	—	—
Suburban	9 (2)	1	—	—
Industrial	—	—	—	—
Rural	—	1	—	—
Total	64 (5)	18 (0)	14 (0)	8 (0)

[a]These sites are not part of the UK network (see Table 5.3). [b]The number of co-located PM$_{2.5}$ sites is given in parentheses.

within these networks is provided in Table 5.4. In Northern Ireland the majority of local authority air quality monitoring sites are part of the Netcen calibration club and have been included under this heading in the tables in this section and in the data proforma.

5.10.1.3 Other networks

474. Birmingham City Council operates a number of PM$_{10}$ and PM$_{2.5}$ monitoring sites. The site at Hodge Hill has one of the longest time series of PM$_{2.5}$ data in the UK: it commenced in 1994. These data have been made available to AQEG.

475. Some local authority monitoring stations throughout the UK form part of the Calibration Club network within which data handling and data quality assurance and control are undertaken centrally by Netcen, on behalf of the individual authorities.

476. Other monitoring networks are orientated towards monitoring air quality close to particular emission sources. Examples of such monitoring networks used in this report are those operated by the power generators, Heathrow Airport Ltd and the Highways Agency (monitoring sites close to very busy roads). As with national and regional networks, these other networks have recognised procedures for data quality assurance.

477. In addition, Defra and the Devolved Administrations operate a research network of particle measurements with a range of gravimetric samplers. These measurements are not part of the AURN and the data are not fully ratified. The network is primarily intended to investigate the relationship between gravimetric samplers and automatic particle analysers that are operated within the AURN (see Section 5.4.3).

478. A summary of the site types within these other networks is given in Table 5.5.

Table 5.5 Summary of PM_{10} monitoring stations in other UK networks (2003).

Site type	Birmingham	Calibration Club	Highways Agency/TfL	Heathrow Airport Ltd[a]	JEP/ Innogy[b]	JEP/ Powergen	Defra/ Devolved Administrations research[c]
Kerbside	—	—	1 (1)[d]	—	—	—	1 (1)
Roadside	3	21 (2)	4 (1)	—	—	—	—
Urban background	1 (1)	15	—	—	—	—	3 (2)
Urban centre	—	—	—	—	—	—	4 (4)
Suburban	—	—	—	—	—	—	—
Industrial	—	4	—	—	—	—	—
Rural	—	—	—	—	1 (1)	2	1 (1)
Special: Rural kerbside	—	—	—	—	—	—	—
Suburban roadside	—	—	—	—	—	—	—
Airport	—	1	—	2	—	—	—
Total	4 (1)	41 (2)	5 (2)	2 (0)	1 (1)	2 (0)	9 (8)

[a]Data have been provided for more sites for earlier years. [b]The Heathrow Airport site is also part of the LAQN; the Heathrow Harlington site is also part of the AURN. [c]Data for PM_{10} and $PM_{2.5}$ are from a range of gravimetric samplers. [d]The number of co-located $PM_{2.5}$ sites is given in parentheses.

5.10.1.4 *$PM_{2.5}$ monitoring networks*

479. Monitoring within the UK national networks is supplemented by measurements of $PM_{2.5}$ to fulfil the requirements of the First Daughter Directive and to support policy development. Some regional and other networks also include $PM_{2.5}$ monitoring, as indicated in Tables 5.2 to 5.5. In the Defra/Devolved Administration research network, $PM_{2.5}$ monitoring is primarily undertaken with filter-based gravimetric methods (Partisol), with the instruments equipped with $PM_{2.5}$ Sharp-Cut Cyclone (SCC) heads. In each case, the $PM_{2.5}$ instrument is located with a PM_{10} instrument of identical type, so that relevant information on the fine ($PM_{2.5}$) and coarse (PM_{10}–$PM_{2.5}$) fractions can be determined. At two sites, Harwell and Marylebone Road, PM_{10} and $PM_{2.5}$ monitoring is undertaken with both gravimetric and TEOM analysers.

480. A summary of the $PM_{2.5}$ monitoring sites is provided in Table 5.6.

Table 5.6 PM$_{2.5}$ monitoring sites (2003).

Network	Site	Site type	TEOM	Partisol
AURN	London, Bloomsbury	Urban centre	✓	
	Rochester (Stoke)	Rural		
AURN and Defra/Devolved Administration research	Marylebone Road	Kerbside	✓	✓
	Belfast Centre	Urban centre		✓
	Birmingham Centre	Urban centre		✓
	Glasgow Centre	Urban centre		✓
	London North Kensington	Urban background		✓
	Manchester Piccadilly	Urban centre		✓
	Port Talbot	Urban background		✓
	Harwell	Rural	✓	✓
LAQN	Bexley 2– Belvedere	Suburban	✓	
	Bexley 3 – Thamesmead	Suburban	✓	
	Ealing 2 – Acton Town Hall	Roadside	✓	
	Greenwich Bexley 6 – A2 Falconwood	Roadside	✓	
	Hackney 4 – Clapton	Urban background	✓	
Birmingham CC	Birmingham Hodge Hill	Urban background	✓	
Calibration club	Norwick Golding Place	Roadside	✓	
	South Cambs Bar Hill	Roadside	ß-guage	
Highways Agency	Victoria	Kerbside		✓
	M25	Roadside	✓	
JEP/Innogy	Rosehurst Farm	Rural	✓	

5.10.2 Black smoke monitoring network

481. The Smoke and SO$_2$ Network was set up in 1961 and was then known as the National Survey. It constituted the backbone of the UK's air pollution monitoring during a period when the main pollutants of concern were smoke and SO$_2$. Monitoring sites were equipped and operated by participating organisations, primarily local authorities, who participated at their own expense. By the mid-1960s there were over 1,200 sites and the network size remained relatively stable until the early 1980s. Levels of smoke and SO$_2$ decreased substantially throughout the 1960s and 1970s, and in 1982 the National Survey underwent a major reorganisation. The total number of sites was reduced to around 470 and existing rural sites became the separate Rural Network.

482. The Network has continued to operate in this format, although the number of monitoring sites has gradually reduced to 123 at the end of 2003.

483. All daily data for the smoke network back to 1961 are available on www.airquality.co.uk and earlier data are available in printed annual reports.

5.10.3 PAH monitoring network

484. PAH concentrations were originally monitored as part of the Toxic Organic Micropollutant Network on behalf of Defra and the Devolved Administrations. Four on-going sites were established in the early 1990s (Hazelrigg, London, Manchester and Middlesbrough) to monitor long term trends of dioxins, PCBs and PAHs. Two rural sites (High Muffles and Stoke Ferry) were added in 1996 to investigate more fully rural concentrations of these species.

485. More recently, the UK PAH monitoring network, operated on behalf of Defra and the Devolved Administrations, was established. This is comprised of 25 sites in total: the six sites mentioned above and a further 19 sites located in areas of high domestic fuel use, roadside locations, major urban areas and close to a selection of major industrial plants. These sites monitor a range of PAH compounds as follows:

- at all sites: acenaphthene, fluorene, phenanthrene, anthracene, pyrene, benz[a]anthracene, chrysene, benz[b]fluoranthene, benzo[a]pyrene and benzo[ghi]perylene;

- additionally at London and Middlesborough: acenaphthylene, fluoranthene, benzo[k]fluoranthene, indeno[123,cd]pyrene and dibenzo[ah/ac]anthracene;

- additionally at Manchester and Hazelrigg: fluoranthene/methylphenanthrene, dibenzo[ah/ac]anthracene/benzo[k]fluoranthene and coronene;

- since 2000 the following extra PAHs have been measured at sites other than Hazelrigg, High Muffles, Manchester and Middlesbrough: anthanthrene benzo[e]pyrene, benzo[b]naph[2,1-d]thiophene, benzo[c]phenanthrene benzo[k]fluoranthene, benzo[j]fluoranthene, coronene, cyclopenta[c,d]pyrene, dibenzo[ae]pyrene, dibenzo[ah]pyrene, dibenzo[ai]pyrene, dibenzo[al]pyrene, fluorene, 5-methyl chrysene, methylphenanthrenes/methyl anthracenes/4,5-methylene phenanthrene and retene.

486. A detailed analysis of the data for benzo[a]pyrene was undertaken in 2001 in support of the development of the UK National PAH objective within the UK Air Quality Strategy (Coleman *et al*. 2001) and data are available at www.airquality.co.uk.

5.10.4 Heavy metals monitoring networks

487. The monitoring of a range of up to 16 elements in urban areas is undertaken by the multielement monitoring network. This commenced in 1976 with 20 sites in 17 towns and cities throughout the UK. After two years, the monitoring was reduced to five sites: London Brent, Glasgow, central London[6], Leeds and Motherwell. These sites remain in operation today (see below for current details),

---

[6] Minster House, Vauxhall 1976 to 1990; Bridge Place, Victoria 1990 to 2000; Horseferry Road, Westminster from June 2002 onwards.

with the addition of a site in Cromwell Road in London in 1990. Additionally, one rural site, at Eskdalemuir in Scotland, was added to the multielement network in 2000.

488. Since 2003, monitoring of PM_{10} particulate trace elements, including heavy metals, has been conducted at a network of ten rural sites across the UK, with weekly sampling and analysis of filter samples using ICP-MS for trace elements and ion chromatography for major elements. Details of the network can be found at www.heavymetals.ceh.ac.uk.

489. Monitoring of particulate lead has historically been undertaken in the lead-in-petrol survey: this commenced in 1985 with two rural and four urban sites. Following the ban on sales of leaded petrol in 2000, the network was reduced to two urban sites – Manchester and Cardiff – where monitoring still continues.

490. When the first EC Directive on Lead in Air was introduced in 1982, a number of short term surveys of lead at industrial premises were undertaken. From the results of these surveys, three industrial locations were selected for long-term monitoring (eight sites in total). These monitoring sites have been in operation from 1985/6 to the present day.

491. When the new Daughter Directive considerably reduced the limit value for lead in air concentrations, a similar 12-month screening exercise of industrial premises was carried out in 2000. In preparation for the introduction of the 4th Daughter Directive on arsenic, cadmium, nickel and mercury, measurement of these elements was also included. In 2002, monitoring at a number of these sites recommenced at five locations: Avonmouth, Hallen Village (Avonmouth), Swansea, Sheffield and Runcorn.

492. In 2003, the operation of all of these networks, with the exception of the Rural Trace Element Network, has been rationalised into a single integrated programme, with a common sampling and analysis structure. Monitoring at all sites is now conducted on a weekly basis, using Partisol 2000 samplers equipped with PM_{10} size selective inlets, and subsequent extraction and analysis conducted using techniques consistent with the CEN WG14 proposed reference method.

493. Data for all these survey are available at www.airquality.co.uk, with the exception of the industrial monitoring undertaken during 2000, which are available at www.stanger.co.uk/airqual/metals.

5.10.5 Major ions and elemental and organic carbon in PM

494. Sulphate in particulate material was monitored at eight rural sites (Eskdalemuir, Stoke Ferry, Lough Navar, Barcome Mills, Yarner Wood, High Muffles, Strathvaich Dam and Glen Dye) as part of the UK Acid Deposition Monitoring Networks. Monitoring started in the early to mid-1980s at most sites, but at Eskdalemuir, monitoring started in 1973. In November 2001, three of the sites were closed (Stoke Ferry, Strathvaich Dam and Glen Dye). Four of the remaining sites are also part of the UK automatic Urban and Rural Monitoring Network - Yarner Wood, Lough Navar, High Muffles, Eskdalemuir.

Table 5.7 Ultrafine particle monitoring sites.

Site	Site type	CPC	SMPS
Marylebone Road	Kerbside	✓	✓
London Bloomsbury	Urban centre		✓
Belfast Centre	Urban centre	✓	
Birmingham Centre	Urban centre	✓	
Glasgow Centre	Urban centre	✓	
London North Kensington	Urban background		
Manchester Piccadilly	Urban centre	✓	
Port Talbot	Urban background	✓	
Harwell	Rural		✓

495. The results are reported and analysed in the reports for the Network (Hayman *et al.*, 2003) and data are available at www.airquality.co.uk.

496. Rural sulphate measurements are also undertaken as part of the Nitric Acid Monitoring Network. This network has been in operation since September 1999 and provides data on nitric acid, particulate nitrate and other species (gaseous sulphur dioxide and hydrogen chloride and particulate sulphate, chloride, sodium, magnesium and calcium), as part of the UK Acid Deposition Monitoring Programme. Measurements are made on a monthly basis at 12 rural locations using the CEH DELTA denuder and filter system. The denuder and filter samples are extracted and analysed using ion chromatography. Information on the monitoring programme and the measurements can be found in Hayman *et al.*, 2003 or at http://www.edinburgh.ceh.ac.uk/cara/networks.htm.

497. Daily urban sulphate in particulate measurements were initially undertaken at 20 sites throughout the UK during the period 1976–1978. From 1978, monitoring continued at five sites for a further year. In 1979, four of these sites were closed and a new site opened at the central London Laboratory in Vauxhall Bridge Road. Monitoring at the site in Brent continued until 1980 to provide some overlap with the new site in Vauxhall Bridge Road. This site moved a short distance to Bridge Place in 1990. Data from this site continued until 1996, although data capture was generally poor. Particulate material was collected on Whatman 40 filter on a daily basis at a nominal flow rate of 3 l min^{-1}. The filters were returned to the laboratory for analysis. The data are available at www.airquality.co.uk.

498. Measurements of daily mean sulphate, nitrate and chloride have been carried out on behalf of Defra and the Devolved Administrations since September 2001

at four sites (Marylebone Road, London North Kensington, Belfast Centre and Harwell). Samples are collected using Partisol 2025 PM$_{10}$ samplers, with subsequent laboratory analysis. Measurements of continuous elemental and organic carbon are also carried out at these four sites, together with measurements of continuous nitrate at Harwell and Belfast.

5.10.6 Ultrafine particles

499. Monitoring of both total and fractionated particle number concentrations are carried out on a routine basis at a number of national network sites. This network is summarised in Table 5.7.

5.11 Measurement uncertainty and quality assurance control

500. The general principles of quality assurance and control applied to national air quality monitoring networks were described in the AQEG report on NO$_2$ measurements (AQEG, 2004). These principles, including those detailed in site operator's instruction manuals (Netcen, 2003), 6-monthly site audit visits and data ratification procedures apply equally to the measurements of particulate material, but there are significant differences in the detail.

501. In contrast to the measurement of gaseous species, no reference material is available for ambient particle samplers and, hence, no routine calibrations of the analysers can be performed. At the 6-monthly audit visits, the flow rate through the analyser size selective inlet is measured and, in the case of the TEOM analysers, the flow rate through the filter is also measured. Also, in the case of TEOM analysers, the tapered element calibration constant is determined using preweighed filters. Both the determination of flows and the tapered element calibration constant are undertaken using UK Accreditation Scheme (UKAS)-accredited methods.

502. For the gravimetric samplers used in the national network, the weighing of the filters is also undertaken using UKAS-accredited method during the process of data ratification. Any unusual data are checked carefully and additional information such as analyser status outputs, measurements of other pollutants at the same site, measurements of particulate material at nearby sites, known local effects such as nearby industry or bonfires and so on are investigated to assess whether the data are valid and reliable. The hourly data in the Air Quality Information Archive are marked as provisional until this process of data ratification is complete.

503. As discussed above, there are no reference materials available for calibration of ambient particle analysers to establish traceability of the measurements to metrology standards. The quality assurance and control procedures in use for the UK Network measurements ensure high quality data for PM, as measured by a standard TEOM instrument. For EU reporting purposes, the uncertainty of the data needs to comply with the Data Quality Objectives that refer to PM as measured by the reference method, which can be significantly different. Calculating this uncertainty, is therefore, not straightforward. This issue, which does not arise for measurements of other air pollutants, is being addressed by the EU Working Group on Equivalence (described in Section 5.3.2) and by other European initiatives.