In this section of the report, a review is presented of the sampling equipment and methodology that was employed to make the particle concentration measurements discussed in this report. The concentration parameter commonly used is the mass concentration of the PM_{10} fraction, which is similar to those particles which penetrate the larynx and enter the thoracic region of the respiratory system. It is the particulate matter capable of passing an inlet of defined characteristics with a 50% sampling efficiency at 10 µm aerodynamic diameter – to a fair approximation PM_{10} is particulate matter smaller than 10 µm aerodynamic diameter. Other concentration metrics used are the mass concentrations of the $PM_{2.5}$ or PM_1 fractions. Some quoted data has been obtained using older instruments sampling "total suspended particulate" (TSP). Unfortunately these data are of limited use, as TSP is an old specification for airborne particles, and is not necessarily relevant to those particles that can enter the human respiratory system. Its definition is specific to a given type of instrument, the performance of which varies with windspeed and particle size distribution.

Sampling instruments generally fall into two complementary categories: a) direct-reading instruments which provide continuous measurements of particle concentration, normally logged as 1 hr averages; and b) simple gravimetric filter samplers, which collect particles on a filter for a given length of time (normally 24 hrs) from which the mass concentration is obtained some days later after the filter has been weighed. The collected sample can also be analysed chemically to determine the composition of the sampled particles.

In order to give some structure to this review, it is convenient to consider four main types of sampling situation:

1) Measurements of particle levels in the ambient atmosphere as part of national and other sampling networks.
2) *Ad-hoc* measurements of particle levels in the ambient atmosphere to study specific topics.
3) Regulated measurements of emissions from power stations and other industrial processes where the emission is controlled through a chimney or exhaust duct.
4) Laboratory-based measurements of the emission of particles from vehicle exhausts.

The aim is to review the reliability of the methods in terms of the mass concentration measurements obtained, and to discuss how the characteristics of the sampling methods may affect the conclusions drawn.

2.1 MEASUREMENTS FROM NATIONAL NETWORKS IN THE UK

The Department of the Environment, Transport and the Regions undertake PM_{10} measurements automatically and continuously at 47 urban and three rural sites. In addition, $PM_{2.5}$ are measured at four sites and particle numbers at three sites. The mass concentration of the PM_{10} fraction of ambient airborne particles is determined continuously using a Tapered Element Oscillating Microbalance (TEOM). This device uses the principle that the frequency of mechanical oscillation of an element, such as a tapered glass tube, is directly proportional to the mass of the tube. Changes in the effective mass of the tube (due to the deposition of particles on a small filter fixed to the free end of the tube) is reflected in a change in the resonant frequency. In the environmental version of the instrument (Model 1400A), air at 16.7 l/min is sampled through a SA 246b PM inlet, and transported through an insulated metal pipe to a sample divider, where a 3 l/min sample is passed through the 16 mm PTFE coated quartz fibre filter (Pallflex). The inlet and sensing arrangement are held at a temperature of 50°C to minimise errors from the evaporation and condensation of water on the filter. Recently, a different type of direct-reading monitor has been providing PM_{10} data onto the national Automatic Urban Network

(AUN) network from the affiliated site at Belfast East. This is a MetOne BAM 1020 β-attenuation mass monitor and uses the attenuation of β-particles by airborne particles collected on a filter tape to give mass concentration measurements. Its minimum sampling time is one hour, and it has the advantage of retaining the particle samples for future chemical analysis.

A direct-reading instrument has many advantages over simple gravimetric filter samplers, associated with its ability to give real-time, mass concentration measurements. Once set up, the manpower involved in obtaining hourly, daily and weekly mass concentration data is limited to a two-weekly visit to check and if necessary to change the filter in the TEOM. It can be used to give information on diurnal trends, to track the passage of pollution episodes. In addition, it has sufficient sensitivity to provide hourly measurements of the $PM_{2.5}$ and PM_1 fractions. The main drawback with the TEOM instrument is associated with the requirement to keep the filter at a constant temperature of 50°C. This has led to differences between mass concentrations given by the TEOM and co-located gravimetric filter samplers, for which the collection filters are unheated and are therefore at ambient temperatures. The effect of this difference is variable, being dependent upon the location, the environmental conditions and the magnitude of the concentration. Generally, the TEOM gives lower particle concentration values than the gravimetric samplers. Some comparative data have been collected for the TEOM with co-located gravimetric samplers (Partisol). This allows the preliminary examination of the relationship between gravimetric and TEOM monitors, shown in Table 2.1, and Figures 2.1 and 2.2 (DETR *et al.*, 1999). The data from Ribble Valley (Table 2.1 and

Figure 2.1 Comparison of PM_{10} concentrations (µg m^{-3}) measured by TEOM and Partisol instruments at Ribble Valley, April to September, 1997.

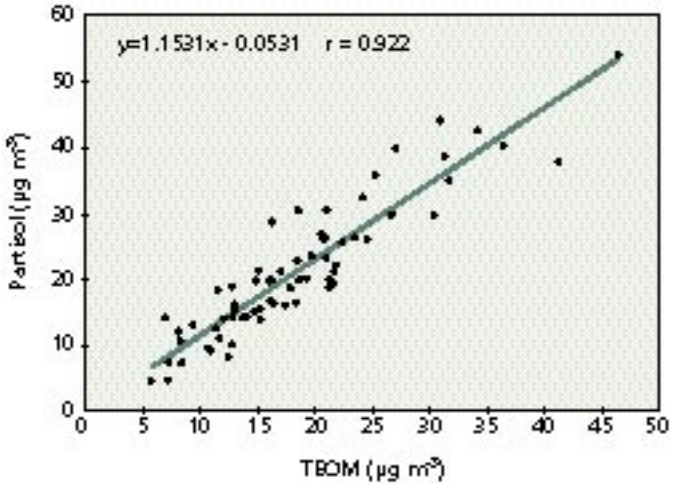
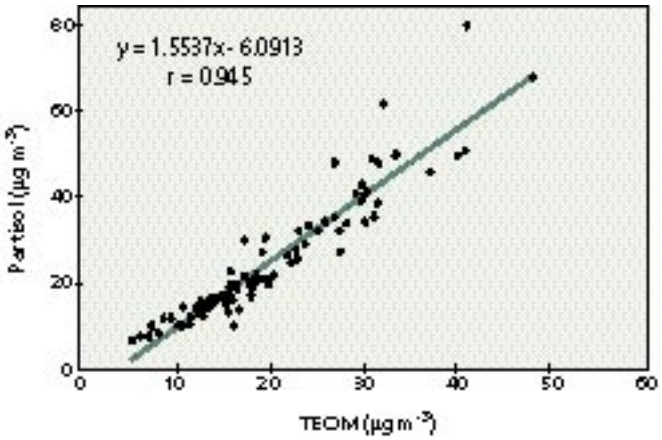


Figure 2.1), which are subject to some influence of industrial sources, show a reasonably good fit to a linear relationship with a minimal intercept. In this situation the Partisol data are consistently about 15% higher that the TEOM mass measurements. The data from Cornwall (Table 2.1 and Figure 2.2) illustrate a different situation in which the data are best fitted by a curvilinear relationship. Attempts to fit by linear regression suggest a substantial intercept which is not borne out by examination of the data. Thus, both the slope and intercepts suggested by linear regression of these data are very misleading. At a Partisol measured concentration of 50 µg m^{-3} the TEOM is reading about 38 µg m^{-3}, indicating Partisol results about 32% higher than the TEOM broadly consistent with the relationship found in South Yorkshire. Thus, at concentrations around the air quality standard, the extent of under-reading by the TEOM relative to the Partisol indicated by the data in Table 2.1 is around 15-30%. Further longer term studies have been established by the Department of the Environment,

Table 2.1 Regression equations for Partisol and TEOM from the First Phase Air Quality Review and Assessment Studies (DETR *et al.*, 1999)

Local Authority		Correlation Coefficient, r
Ribble Valley	Partisol = 1.15 x TEOM - 0.05	0.92
South Yorkshire	Partisol = 1.3 x TEOM	0.89
Cornwall	Partisol = 1.55 x TEOM - 6.09	0.94
London Kerbside	Partisol = 1.2 x TEOM - 3.1	0.92

Figure 2.2 Comparison of PM_{10} concentrations (µg m^{-3}) measured by TEOM and Partisol instruments at Cornwall, April to October, 1997.



Transport and the Regions to provide a rigorous analysis of the relationship between concentrations from these two sampler types. It is most probable that this difference is associated with the evaporation of semi-volatile species such as ammonium nitrate and some organic compounds. Therefore, in source apportionment studies using data obtained from TEOMs, care must be taken when predicting the secondary particle contribution to the total mass concentration. It is useful to bear in mind that the UK air quality standard for PM_{10} of 50 µg m^{-3} as a maximum 24 hour running average was recommended by the Expert Panel on Air Quality Standards using the results of an epidemiological study which used data from a TEOM instrument (EPAQS, 1995). There is therefore a consistency between the monitoring method and the standard, and hence any underestimation of PM_{10} by the TEOM relative to other sampling methods does not imply a relaxation in the protection of public health.

The Black Smoke and SO_2 monitoring networks have been in operation for over 30 years and have successfully monitored the massive decline in the concentrations of these pollutants resulting from the implementation of the Clean Air Acts. Despite the introduction of PM_{10} measurements into the national network, the measurement of Black Smoke is still carried out at 226 sites. The instrument comprises a downward-facing funnel into which air is drawn at about 1.5 l/min. The sampled particles are transmitted some 2 m down glass and plastic tubing to be collected on a Whatman No 1 filter paper. The quantity of dust is assessed by means of light reflectance, with the black particles produced from incomplete combustion of fossil fuels contributing most to the measurement. The equivalent mass concentration is then estimated by use of a Standard Smoke Curve. The results obtained using this method will be biased strongly towards black particles, and only particles < 4 µm will reach the filter and hence are sampled efficiently. However, as a means of measuring the contribution to particles in the atmosphere, these attributes (darkness and size) are beneficial as only the black particles are detected and the majority of smoke particles are below 1 µm. The conversion from reflectance to mass concentration is the weak link if the concentration of all airborne particles is required, as the white particles and those larger than 4 µm will be appreciably underestimated.

The National Acid Deposition Network includes 8 sites as part of the European Monitoring and Evaluation Programme (EMEP) where SO_2 concentrations and particulate sulphate levels are measured on a daily basis. The inlet and particle transmission to the Whatman 40 filter are very similar to the Black Smoke method. Consequently, it is doubtful whether particles larger than 4 µm will reach the filter for analysis. This is, however, sufficient to give high collection efficiency for secondary sulphates, of which the vast proportion falls below this size cut.

Measurements of particulate ammonium have just been established by the Department of the Environment, Transport and the Regions.

2.2 *AD-HOC* MEASUREMENTS

A wide range of instruments have been used in studies in the UK to investigate specific topics, the results from which are used in this report. Apart from the use of TEOMs described above, they are

generally gravimetric devices in which particles are collected onto filters for periods of 24 hours to 1 week, after which the filters are returned to the laboratory for weighing. The results give the average mass concentration of particles over the sampling period. Some of the instruments used to gather data referred to in this report include:

- *R & P Partisol*: which samples ambient air at 16.7 l/min through a PM_{10}, $PM_{2.5}$, or PM_1 sampling head, with particles being collected on an unheated 47 mm filter.
- *Graseby Andersen Hi-Vol PM_{10}:* which samples at 1200 l/min through a PM_{10} sampling head onto an unheated 25 cm by 20 cm glass fibre filter.
- *EnviroTechnology MiniVol:* this can operate on battery power to sample at 5 l/min through an unvalidated sampling head designed to select PM_{10} particles for collection on an unheated 47 mm filter.
- *Graseby Andersen Lo-Vol dichotomous sampler:* samples at 16.7 l/min through a PM_{10} sampling head and then uses a virtual impactor arrangement to provide two separate samples on 37 mm filters - one with particles of aerodynamic diameter less than 2.5 µm and the other with particles in the 2.5 - 10 µm range.
- *Andersen cascade impactor:* separates particles into eight size bands between 0.43 and 9 µm, and uses a preseparator at the entry to select particles less than 10 µm at the flow rate of 28.3 l/min. Particles are collected on quartz fibre filters for weighing and chemical analysis.
- *R & P ACCU:* this is a set of eight unheated 47 mm filter holders which uses the 13.7 l/min of sampled air that the TEOM discharges. Unfortunately, the connections between the sampling inlet and the filters are via plastic pipes of variable length, and so inevitably particles of all sizes will be lost to the internal walls leaving the samples collected on the filters to be of an uncertain size fraction.

These samplers provide mass concentration measurements and also provide samples for compositional analysis. Although none of the instruments has a heated line, there is still the possibility of losing some volatile particles, especially ammonium nitrate, if the filters are not changed regularly and the conditions of transport, storage and analysis are not carefully controlled. This has the potential to produce an uncontrolled error into the determination of semi-volatile species, dependent upon the history of the sample.

Other aerosol samplers include the Rotheroe and Mitchell Acid Sampler used since the early 1970s (Eggleton & Atkins, 1972) to collect one hourly samples of particles for the determination of the sulphate, nitrate and the ammonium content. This instrument uses a roll of Whatman 41 filter paper to collect sequential hourly samples at 250 l/min. Ambient air is sampled through a mushroom shaped inlet designed to prevent the entry of particles larger than 100 µm, although there are no data on its sampling performance as a function of windspeed and particle size. The filter tape is interleaved with Melinex film to avoid cross-contamination of the samples. However, unless the filter tape is kept cool and returned to the laboratory for analysis very quickly, there is again the potential to lose some of the semi-volatile nitrate species.

2.3 REGULATED MEASUREMENTS OF STATIONARY EMISSION SOURCES

The measurement of particulate emissions from stationary sources, such as power stations and other major industries, is specified by British Standard BS 3405, with improved standards published by the International Standards Organisation (IS 9096). This method involves the use of an isokinetic sampler positioned inside the chimney with a long transmission pipe connecting to a filter holder positioned outside the stack. This has the benefit of allowing the collected sample to be maintained at a temperature lower than that within the stack, thereby minimising the loss of collected material by volatilisation. However, the method suffers from considerable particle losses on the internal walls of the transmission pipe between probe entry and filter. The internal walls of the pipe

must be washed and the deposited particles combined with those on the filter. The accuracy of the method is ±25 %. Very rarely is the PM_{10} fraction measured - it is normally the total emitted particulate concentration that is measured with the isokinetic system. Estimation of the PM_{10} fraction is then determined from knowledge of the particle size distribution. This estimate is reasonable provided that the process does not change. However, considerable uncontrolled errors could arise if the size distribution of the emitted particles does change.

A situation where the PM_{10} fraction is measured is in the testing of various types of solid fuel. Here, a single cyclone is positioned at the entry of the sampling probe to select the 10 µm particles to give an estimate of the PM_{10} fraction.

2.4 MEASUREMENTS OF THE EMISSION OF PARTICLES FROM VEHICLE EXHAUSTS

Measurements of the emissions of particles from vehicle exhausts are generally carried out in the laboratory using Constant Volume Sampling (CVS) dilution tunnels to condition the exhaust and make it suitable for sampling. Isokinetic sampling is nominally carried out, although the system requirements specified in the relevant EC Directive (70/220/EEC) can lead to significant errors for the large particles, with virtually no particles of aerodynamic diameter larger than 5 µm being measured. However, as most particles emitted from vehicle exhausts are considerably less than 1 µm diameter, this inadequacy may not be important, apart from during the removal of large agglomerated particles from the internal walls of the exhaust system during start up. The main uncontrolled variable in the measurements is the length of flexible pipe connecting the tail pipe to the dilution tunnel. This should be kept as short as possible, but the existence of both front and rear wheel drive vehicles poses considerable problems to the test houses. Finally the filters are required to be kept at a temperature of below 52°C so as to limit the losses of semi-volatile materials from the filter during collection.

References

DETR, *et al.*, (1999) *The First Phase Air Quality Review and Assessment Studies - a summary.* Department of the Environment, Transport and the Regions, Welsh Office, Scottish Office, Department of Environment for Northern Ireland, in press.

Eggleton, A.E.J and Atkins, D.H. (1972) *Results of the Tees-side Investigation*. Report AERE-R6983. AEA Technology.

EPAQS (1995) *Particles.* Department of the Environment Expert Panel of Air Quality Standards, HMSO, London.

Note to Readers

This Chapter seeks only to indicate some of the equipment choices available to those wishing to measure airborne particulate matter. It makes no attempt to be exhaustive, and some commercial instruments have not been included. Omission of an instrument should not be inferred as conveying any opinion by the Expert Group and equally, inclusion does not constitute an endorsement by Airborne Particles Expert Group.