

# **GUIDELINES FOR CONCENTRATION AND EXPOSURE-RESPONSE MEASUREMENT OF FINE AND ULTRA FINE PARTICULATE MATTER FOR USE IN EPIDEMIOLOGICAL STUDIES**

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## Foreword

There is increasing scientific and medical evidence that exposure to fine and ultra fine particulate matter could have relatively more significant health implications than exposure to larger particles or to other airborne pollutants. At present there is, however, not enough information available on the exposure-response relationship for fine and ultra fine particulate matter to consider appropriate guidelines, which would protect the whole population or at least the most susceptible groups. The WHO Guidelines for Air Quality, published recently, present the current knowledge on exposure-response relationships with respect to particles smaller than 10  $\mu\text{m}$ , but only marginal evidence for fine particles, defined as particles with an aerodynamic diameter below 2.5  $\mu\text{m}$ . The current difficulties relate to the scientific complexity of exposure assessment to fine particulate matter at all levels of approaches, including: instrumentation, measurement, modelling, model validation and data interpretation. The multitude of different instruments measuring different particle metrics makes a decision as to how to measure difficult. These difficulties are, however, often not realized to those who are outside the field of particle science, and who develop a simplistic view on particle measurements, based on limited knowledge acquired in this area. In addition, at present, there is not enough information available to explain the mechanisms by which inhaled particles cause a range of health effects. For those who undertake epidemiological studies, particle characterization can be costly, because extended time-series are needed for these studies.

These and other related issues should be brought to the attention of the scientific community undertaking new epidemiological studies, together with some broad guidelines to help the researchers in directing their studies. To facilitate this WHO undertook the task of developing the present guidelines.

Dr Richard Helmer

Director

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## Executive Summary

There is increasing scientific and medical evidence that exposure to fine and ultra fine particulate matter could have relatively more significant health implications than exposure to larger particles or to other airborne pollutants. At present there is, however, not enough information available on the exposure-response relationship for fine and ultra fine particulate matter to consider appropriate guidelines, which would protect the whole population or at least the most susceptible groups. One important reason for the current difficulties relate to the scientific complexity of exposure assessment to fine particulate matter at all levels of approaches, including: instrumentation, measurement, modelling, model validation and data interpretation. In particular:

- The range of parameters which could be measured to characterize airborne particles, as well as the choice of instruments to do this is such, that it is almost impossible, for those who are not experts in particle science, to take an informed decision as to what to measure and how to do it. The difficulty is, however, often not realized by those who are outside the field of particle science, and who develop a simplistic view on particle measurements, based on limited knowledge acquired in this area.
- At present, there is not enough information available to explain the mechanisms by which inhaled particles cause a range of health effects
- Particle characterization for epidemiological studies can be costly, because extended time-series are needed for these studies including parameters that are not routinely monitored. Inclusion of these parameters in a study programme could add to the costs and complexity of the programme. Due to budget limitation often only routine data is used, which does not necessarily expand the existing knowledge.
- These and other related issues should be brought to the attention of the scientific community undertaking new epidemiological studies, together with some broad guidelines to help the researchers in directing their studies.

To facilitate this WHO undertook the task of developing *Guidelines for Concentration and Exposure-Response Measurement of Fine and Ultra Fine Particulate Matter for Use in Epidemiological Studies* to be used by national and international organizations undertaking studies in this area.

## Review of Health Effect Studies

### Epidemiological Studies

Epidemiological studies conducted in the 1980s and 1990s, combined with analyses of health effects recorded during individual episodes of severely elevated air pollution levels, provided strong evidence for statistically significant associations between exposure to particulate matter and various types of health effects. Particulate matter was characterized in different ways in many of the studies, including total mass concentration (TSP – total suspended particulate) or its fractions such as PM<sub>10</sub> or PM<sub>2.5</sub> or its elemental or chemical composition. PM<sub>2.5</sub> fraction (or fine particles) is mass concentration of particles with aerodynamic diameters smaller than 2.5 µm, while PM<sub>10</sub> fraction is mass concentration of particles with aerodynamic diameters smaller than 10 µm (more precisely, the definitions specify the inlet cut-off for which 50% efficiency is obtained for these sizes). Coarse particles are then the fraction PM<sub>2.5</sub> - PM<sub>10</sub>. Ultra fine particles are those below 0.1 µm

Within most established networks, outdoor particles are measured by PM<sub>10</sub> and PM<sub>2.5</sub> (until recently also as TSP, total particle mass); therefore, most of the evidence of health effects of outdoor particles is based on these measures. TSP is almost entirely dominated by particles generated by mechanical processes such as dust resuspension, grinding, and mining. PM<sub>10</sub> is sometimes dominated by particles generated by mechanical processes and sometimes by accumulation mode particles, which is an aged fraction of the outdoor aerosol emitted by many sources such as industrial emissions, vehicle emissions, and power generation. In addition, a portion of the particles is of biogenic origin and generated from secondary processes such as photochemical processes. PM<sub>2.5</sub> is more likely to be dominated by accumulation mode particles, but can also include a significant fraction of mechanically generated particles. The relative contributions from different types of sources are very site specific.

There are many unanswered questions about how particles cause the health effects observed in epidemiological studies. Questions specifically refer to the mechanisms involved, the interaction between PM and gaseous co-pollutants, and the contribution of different sources to the causation of the effects. There are a number of hypotheses available, linking the health effects to, for example, the mass, the number of particles inhaled, or to their surface area or to the mass of trace components they carry. It is reasonable to expect that a number of mechanisms could be involved and linked to the different particle properties and causal of different health effects. Many of these hypotheses will still require a considerable amount of studies, mainly clinical, to be accepted or rejected. There are different potential mechanisms of cardiopulmonary responses to particle inhalation currently being discussed.

Gaps in knowledge and research needs in relation to the particle measurements for the purpose of epidemiological studies include:

- There is substantial evidence for the health effects of PM<sub>10</sub> and PM<sub>2.5</sub>; however, little is known on the health impact of other particulate matter properties such as ultra fine particles or the surface of particles.
- The sources and their fractional contribution to particles in outdoor air need to be determined as PM from different sources may exhibit different toxicity.
- Both acute and chronic health effect studies are needed to adequately assess the effects of rapidly changing aerosol mixtures in outdoor air.
- Multi-centre studies are needed to adequately address the role of various particle characteristics or the role of sources.
- Application of state-of-the-art statistical methodology, as well as adequate planning of studies, is needed as it would provide valuable insight into the role of particulate matter characteristics, and provide a general and not local interpretation of the findings

## **Exposure Studies**

The PM-exposure for an individual is the concentration of particulate matter (PM) with specified characteristics that exists in a person's breathing zone over a specified period of time. Humans are normally exposed to PM from several different sources.

In the developed world (in the absence of smoking), outdoor PM penetrating indoors is usually the most significant source of PM indoors. In the developing world, especially in rural areas, high indoor PM levels originate usually from indoor sources, mostly cooking on open fires.

### Exposure assessment methods

Exposure measurements for epidemiological studies can be broken down into a 2 x 2 matrix indoor and outdoor exposure and acute and chronic exposures. The majority of epidemiological studies relating PM exposure to health effects are concerned with the acute effects of outdoor or ambient exposure. Because people spend a majority of their time indoors, PM exposure in the indoor environment can be a significant part of their total exposure, and it is therefore important to be able to distinguish between PM generated by indoor sources and PM influenced by outdoor concentrations.

Exposures can be monitored and/or modeled. In addition, specific indicators can be used as surrogates of exposure. The advantages and disadvantages of different means for exposure assessment can be summarized as follows:

1. Exposure monitoring has the advantage that it produces real exposure data on real individuals in known and real life conditions. However, such an exposure-monitoring programme is normally quite an expensive and labor-intensive process and it also has the tendency to more or less select the subjects for the study and affect subject behaviour in the process, thus potentially modifying the exposure.
2. The advantage of exposure modeling is that it can be used to estimate past and future exposures, long-term exposures, and to compare e.g. population exposure differences of different urban development or air pollution mitigation alternatives. While there is a significant additional cost for each additional individual in exposure monitoring studies, the cost of exposure modeling is much less affected by the number of individuals or the size of the population (or the length of time) being modeled, thus favoring studies where the exposures of large numbers of individuals need to be assessed. While modeling individual exposures for specified days contain wide error margins, results become generally much more valid when population exposures over extended time periods are being modeled.
3. In principle, epidemiological studies need to estimate the exposures of large cohorts or populations of entire cities over long periods of time. So far, only crude exposure surrogates, usually based on centrally monitored outdoor air quality levels, and broad classification of the cohort members into some specific exposure groups (e.g. smokers and non smokers, homes with and without gas stoves, or individuals with and without occupational exposures) have therefore been used. Monitoring of the personal exposures in such epidemiological studies is clearly out of the question, but exposure-modelling techniques could be applied to improve exposure assessment from these exposure indicators.

## Relationship between personal exposures and outdoor concentrations

Exposure analysts share a general belief that, in order for community time-series epidemiology to yield information on the statistical association of ambient pollutant concentration, with a health response, there must be an association between personal exposure to a pollutant and the ambient concentration of that pollutant. Pooled values of total personal exposure to (non-ambient plus ambient) PM have a low correlation with ambient concentrations in cross-sectional settings. There the individual differences dominate the personal exposures and diminish the correlation.

One important reason for these poor correlations is that many of the studies were based on cross-sectional data, which means they included many individuals, who were generally monitored for only one or a few days and no distinction made between those with high exposures to indoor sources, such as smoking, from those with much lower exposures.

The relationship between personal exposure and ambient concentrations of PM is further complicated by the so-called “personal cloud” effect. This refers to the fact that personal exposure is generally found to be greater than the estimated time weighted average of indoor and outdoor concentrations.

However, within-person correlations over time are substantially higher and form the basis for the capacities to observe statistically significant relationships between health effects and ambient concentrations.

## Source apportionment from receptor measurements

In order to understand either the effects of particulate matter on health or to control the sources in order to mitigate health consequences, it is necessary to have an understanding of where the particles in the breathing zone are coming from, and then at the receiving end, how much individual sources contribute at the point of exposure. The two main categories of source apportionment techniques are based on chemical/elemental mass balance modelling and different factor analysis techniques. In general, databases containing more chemical detail and higher time resolution are needed to enable reliable source apportionment.

## Dosimetry

In the general framework for risk assessment, exposure is linked through dosimetry factors, dose and response factors to lifetime individual risk. Understanding of particle deposition in the respiratory tract is a very important aspect of framework for risk assessment, as it affects the dose received to the lungs and to the body in general.

The ultimate proof that the understanding of the lung deposition process is complete would be a consistency between the results obtained from experiments and from theoretical modeling. However, examination of the data reported in the literature on the experimental approach alone, reveals that there are significant discrepancies between the results obtained by different researches on aerosol deposition in the respiratory tract, not only for different types of aerosol, but also for the same types.

In terms of theoretical predictions, a comparison between different modelling approaches shows that, with general agreement as to the total deposition levels, there are often significant



discrepancies in the estimates for fractional penetration and deposition. The discrepancies for fractional penetration and deposition may question the reliability of the agreement for total deposition values.

### **Particle characterization for the purpose of exposure and health risk studies**

Airborne particulate matter is a mixture of solid particles and liquid droplets, which vary in concentration, nature and size distribution. The particles can be, for example, combustion products, dust or bioaerosols, and can act as carriers of adsorbed chemicals, bio-contaminants or condensed gases. A primary particle is a particle introduced into the air in solid or liquid form, while a secondary particle is formed in the air by gas-to-particle conversion of oxidation products of emitted precursors

Some of the most important physical properties of particles include: mass and mass size distribution, number and number size distribution, surface area, shape, hygroscopicity, volatility or electrical charge. Each of these characteristics is important in affecting particle dynamics and thus behaviour and fate in the air and in the human respiratory tract. Under specific circumstances each characteristic can become the leading one. However, the key characteristics are the first two and only these physical parameters will be discussed in this document. The most important chemical properties of particles that will be discussed include: elemental composition, secondary inorganic ions, carbonaceous compounds and organic composition.

#### Physical properties of particles

The size of airborne particles is significant as it determines their dynamic properties and thus behaviour in the air and fate during transport. In particular, the size strongly influences in which parts of the respiratory tract the particles are deposited. Larger particles (coarse mode), due to their higher inertia are deposited in the nasal area and in the upper parts of the respiratory tract. By contrast, smaller particles (accumulation mode and the even smaller ultra fine particles) can follow the airflow to the deeper parts of the respiratory tract, where they have a very high probability of depositing by diffusion, a very efficient deposition mechanism for small particles.

It is, however, not only the mass or number of particles in the particular size range that is important in relation to health risks, but also the composition of particles. The composition may determine in what way the respiratory tract reacts, or the body responds. The highest level of concentration of trace elements and toxins from anthropogenic sources and radioactivity from natural sources is related to the very small particles. The large particles, suspended by both anthropogenic and natural sources, carry components and elements mainly of crustal origin. Some particles can act as carriers of adsorbed chemicals or gases which can act as triggers for various health effects.

Fine particles are generated mainly from combustion processes, photochemical processes and gas to particle conversion and typically contain a mixture of soot, organic compounds, acid condensates, sulfates, nitrates, as well as trace metals and other toxic compounds. Coarse particles are generated mainly from mechanical processes including grinding, breaking and wear of material and dust resuspension and contain mostly earth crustal elements and compounds. In most cases, fine and coarse particles result from different generation processes; however, there are processes, which generate particles with broad size distributions. For

example, in close proximity to forest fires there are airborne combustion products of the fires, as well as large diameter particles that are entrained into the smoke column as a result of the turbulence and buoyancy generated by the fire. Sometimes, there is a correlation between fine and coarse airborne particles because the concentrations of both are influenced by meteorological conditions. In general, the occurrence and strengths of correlation depends on local emission sources and source mix. However, only limited information, or no information at all can be obtained about particle number from the measurements of particle mass.

### Chemical properties of particles

While particular types of sources always release certain elements (for example, lead by vehicles using leaded petrol), other elements are only released by specific sources (for example, barium is emitted only by motor vehicles using lubricants containing barium). Since most of the trace elements are non-volatile, associated with ultra fine particles and less prone to chemical transformations, they tend to undergo long-range atmospheric transport and remain as part of the primary form in which they were emitted.

In some cases it is not just the presence of a specific element that is of importance from the point of view of health effects, but the chemical form in which the element is present could play a role as well. Processes such as environmental transport and bioavailability are species dependent.

All combustion sources generate large amounts of volatile and semi-volatile organic compounds. Semi-volatile organic compounds can be present in the air either in the vapour or in particle form (solid or liquid). Exposure to many of the organic compounds emitted to the air has been associated with various types of health effects. Polycyclic Aromatic Hydrocarbons (PAH), some of which are strongly carcinogenic, are one class of compounds contained in the organic fraction of the fine particulate matter.

From the point of view of effects on human health, it could be of significance in what physical form the semi-volatile compounds are when they are inhaled. They could either be in vapour form, or could be associated with particles of specific sizes. There is very little information available on this, which is due not only to the recent emergence of interest, but mainly to the difficulties in investigating organic composition of small amounts of mass. The mass of particles in the ultra fine range is very small. In order to collect sufficient mass for standard organic chemistry analyses a long sampling time would be required. This usually is prohibitive for many studies on exposure or health effects.

### Markers and source signatures

In order to understand either the effects of particles on health or to control the sources in order to mitigate health consequences it is necessary to understand where the particles are coming from, and then at the receiving end, which amounts of what toxicity contribute at the site of particle measurement.

Source signatures or fingerprints are physical or chemical characteristics of emissions, which are specific for particular emission sources. They should be unique to these sources, which allows identifying every source. Source signatures include a specific suite of elements or

compounds and specific ratios of elements or isotopes, or compounds. A source marker, on the other hand, is used for quantification of exposures to a particular type of a source. The complexity related to source identification and apportionment is that on one hand outdoor air contains a dynamic mixture of pollutants emitted from various sources. This mixture undergoes continuous change in time as the interactions between the pollutants take place and as the components of the mixture are removed from the air due to the presence of various sinks. On the other hand, it is only rare that specific emission characteristics are unique to a particular source. More often there is a probability that emissions from other sources display some of these characteristics as well.

### Source apportionment

One important aspect of source characterization is quantification of emissions from specific source categories. This, in turn, enables the generation of inventories of emissions at local, regional and national levels, which is necessary for developing appropriate management and control strategies in relation to air quality and its impact on health.

### Spatial and temporal small-scale variation of aerosol parameters

Following formation, the mixture of emission products including particles, undergoes a range of physico-chemical processes, which change their chemical composition, physical characteristics and concentration in the air. Some of the emission components, such as, for example, combustion-related ones, are highly dynamic, while others, like mechanical dust, are less so. Particles measured away from the emission site, or particles generated indoors and measured some time after emission, would have different characteristics to those measured immediately after formation. The residence time of the emission products in the air depends on the nature of the processes they are involved in and varies from seconds or minutes to days or weeks. Larger particles (of a micrometer size range in aerodynamic diameter and more) are removed from the atmosphere mainly through gravitational settling, while smaller particles are removed by precipitation or diffusional deposition. While in the proximity to the emission site certain compounds could be of significance in relation to health effects, at a distance from the source, due to various processes that took place during transport, the relative significance may have changed. There is still very little information available on the fate of fine and ultra fine particles in the air.

### Association to other pollutants

In addition to particles, many emission sources, particularly combustion sources, also generate gases and vapours. The most common of them include:

- Inorganic gaseous: carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>),
- Volatile organic compounds (VOC): benzene, toluene, styrene, 1,3-butadiene, hydrocarbons (HC - in particular, chlorinated hydrocarbons and xylenes), very reactive toxic gases such as aldehydes-formaldehyde and acetaldehyde

- Ozone (O<sub>3</sub>) is a secondary pollutant that is generated in the air from its precursors including nitrogen oxides and hydrocarbons in the presence of light.

In general, ratios between outdoor concentrations of particulate matter and gases such as CO and NO<sub>x</sub> for example, are variable, reflecting contributions from various sources and atmospheric reaction processes.

### **Instrumental techniques for physical and chemical particle characterization**

Sampling for chemical analysis and mass measurement should in the first instance consider inlet design. The purpose of the inlet system is to provide a sample aerosol that is representative of outdoor air, to the various aerosol analysers and samplers applied. The inlet used for aerosol sampling should follow certain design guidelines so that comparable samples are obtained. Quality control for sampling should involve

- (1) Calibration,
- (2) Flagging of data with known abnormalities, and
- (3) Recording abnormalities.

Calibrations of sampling instruments include mass flow measurement calibration with a transfer standard (e.g., a bubble meter or mass flow meter). Leak tests of the sampling system should be done at least once a year, and more frequently, should problems develop. Analytical procedure quality control should consist of at least three steps:

- (1) Performance check by involving the lab in inter-laboratory inter-comparisons, as well as obtaining absolute standards if available,
- (2) Interspersing quality control standards with regular samples in a routine analysis sequence, and
- (3) Regularly scheduled repeat analyses of randomly selected samples.

Separate sets of flags must be developed for sampling/sample handling and analysis.

### Determination of particle mass

Particle mass concentration is the most commonly made measurement on aerosol samples. The most important methods for determination of particle mass include: gravimetric measurements, beta attenuation, vibrational microbalance method and optical scattering. These methods may be used to determine compliance with PM standards or, in the case of gravimetric analyses, to select certain samples for more detailed, and more expensive chemical analyses.

### Determination of chemical composition

The composition of aerosol particles is of interest in order to:

- (1) Explain and develop an inventory of the different sources of the mass observed
- (2) Identify potentially toxic components,

(3) Determine the sources of the PM, and

(4) Use this information to determine the effects of PM on health and welfare.

While any compositional measurement will address one or more of these goals, certain methods excel for specific tasks. In general, no single method can measure all chemical species, and comprehensive aerosol characterization programmes use a combination of methods to address complex needs. This allows each method to be optimized for its objective, rather than be compromised to achieve goals unsuitable to the technique. Such programmes also greatly aid quality assurance objectives, since confidence may be placed in the accuracy of a result when it is obtained by two or more methods on different substrates and independent samplers.

In general terms, methods for characterization of chemical composition of particles can be divided into two classes:

(1) Sample collection followed by laboratory analyses, and

(2) Near real time methods.

The most important features of both these classes of chemical analysis are summarized below.

The more commonly used methods for chemical analysis requiring sample collection can be divided into four categories:

- (i) Elements,
- (ii) Water-soluble ions,
- (iii) Organics and
- (iv) Carbon.

Material balance comparing the sum of the chemical species to the PM mass concentrations show that elements, water soluble ions, and organic and elemental carbon typically explain 65% to 85% of the measured mass and are adequate to characterize the chemical composition of measured mass for filter samples collected in most urban and non-urban areas. Some chemical analysis methods are non-destructive. These are preferred because they preserve the filter for other uses. Methods, which require destruction of the filter, are best performed on a section of the filter to save a portion of the filter for other analyses or as a quality control check on the same analysis method.

#### Recommendations in relation to instrumental techniques

As particle mass ( $PM_{10}$  or  $PM_{2.5}$ ) has been the standard for some time now, the greatest effort of instrument developers has been put into mass measurement, and on-line measurement of particle mass as an integral parameter actually exists for  $PM_{10}$  and  $PM_{2.5}$ . Extension of the  $PM_x$  series down to smaller cut-off diameters (e.g.  $PM_1$ ), would provide quite a useful picture of the mass size distribution and would be in line with former standards. No feasible method for recording these integral quantities below  $PM_1$  presently exist, and there is a great need of research and development here.

In view of the potential health effects of ultra fine particles, number concentration or surface area would be valuable parameters characterising the airborne particle load. In practice, it is a measure of the ultra fine particle load, because ultra fine particles typically dominate in number. Counters less delicate and less expensive than those based on the condensation principle are highly desirable.

There is presently no useful approach that could lead to an on-line monitor of the joint particle surface in outdoor air. If such an instrument existed, recording this quantity would certainly be of great interest for epidemiological studies. The quantity measurable on-line coming closest to the joint particle surface is the response of the epiphaniometer or of a diffusion-charger-electrometer combination. The latter is an inexpensive device.

In order to measure the entire ambient size range, it is necessary to combine instruments based on different physical principles and thus measuring different “equivalent diameters”. Therefore, there is great need for a simple size-measuring instrument that applies only one functional principle for the whole range.

Hygroscopicity and volatility of airborne particles are of relevance for behaviour of particles in atmospheric systems. The size dependence of these parameters has been measured with dual differential mobility analyser systems in atmospheric field studies. Less expensive instrumentation delivering more condensed data such as hygroscopicity factor of the ultra fine and one for the fine mode would be useful.

## 1. Introduction

There is increasing scientific and medical evidence that exposure to fine and ultra fine particulate matter could have relatively more significant health implications than exposure to larger particles or to other airborne pollutants. At present, however, not enough information is available on the exposure-response relationship for fine and ultra fine particulate matter, to permit consideration of appropriate guidelines, which would protect the whole population or at least the most susceptible groups. One important reason for the current difficulties relate to the scientific complexity of exposure assessment to fine particulate matter at all levels of approaches, including: instrumentation, measurement, modelling, model validation and data interpretation.

Connected to these difficulties are the difficulties in exposure-response assessment. Some specific problems include:

- (i) Lack of correlation between different particle monitoring and measurement approaches in particle epidemiological studies.
- (ii) Experimental difficulties in validation of lung deposition models and resulting problems with dose assessment.

In the last few years there has been a significant increase in national and international efforts towards extending the knowledge base on various aspects of exposure and exposure/health response relationship. Many new epidemiological studies have been undertaken to establish the links between the exposure to fine particles and health end points; the existing air quality and medical data have been examined with this focus in mind; and also various types of clinical studies have been undertaken to identify the mechanisms in which exposure to particles causes health effects. There are three key issues in relation to forthcoming studies, which if not addressed properly, may result in slowing the progress in developing understanding in this area, or lead to developing misconceptions, which could for long time misdirect control and management activities in this area. Compared to many other types of scientific endeavours, epidemiological studies take a long time to complete. Inadequately designed studies undertaken now, will result in inadequate outcomes in three to ten years or more from now. The key issues are:

- The range of parameters which could be measured to characterize airborne particles, as well as the choice of instruments to do this is such, that it is almost impossible for those who are not experts in particle science, to take an informed decision as to what to measure and how to do it. The difficulty is, however, often not realized by those who are outside the field of particle science, and who develop a simplistic view on particle measurements, based on limited knowledge acquired in this area. This could be the case if medical and epidemiological teams of experts are operating without support from particle experts. Thus the choice as to what particle characteristic to measure and what instrumentation to use, is often based on inadequate information, or depends on what is available to the research group in terms of instrumentation, as well as what instrumentation can be afforded from the budget for the project.
- At present, there is not enough information available to explain the mechanisms by which inhaled particles cause a range of health effects. There are a number of hypotheses available linking the health effects to, for example, the number of particles inhaled, or to their surface area or to the mass of trace components they carry. Many of these hypotheses will still require a considerable amount of study, mainly clinical, to be accepted or rejected.

Epidemiological studies are undertaken in principle to support the clinical studies, but also to provide quantification as to the exposure/health effects relationship. With only a limited amount of information available on the causes of health effects, epidemiological studies, in their design, should preferably include measurements of all parameters, which are now linked to any of the hypothesis available. For example, while earlier epidemiological studies were focused on the relation between PM<sub>10</sub> or PM<sub>2.5</sub> and health end points, there are now hypotheses that particle number could be an important factor, more directly linked to the health end points than particle mass fractions. If new epidemiological studies would not include investigations to follow up the modern hypotheses, there will be little progress in advancing knowledge in this area. This means that it is not just support from particle experts for the research team, but the research team should have the information available on what particle characteristics should be studied to advance the progress on understanding the health effects on exposure to airborne particulate matter.

- Epidemiological studies are usually costly, and often due to the budget limitations cannot address all the aspects of importance or all the population groups. For example, studies could be focused on some population groups, such as children in a certain age group, people susceptible to respiratory diseases due to some illnesses, or people exposed to some specific pollutants, rather than on the whole population. There could be also health effects of specific interest in different climatic zones or in different types of social and industrial environments. It is thus of a critical importance for speeding the process of knowledge acquiring and for reducing the costs involved, that studies are conducted in a manner, which would allow meaningful comparison of the results. This means that a certain level of commonality of study design has to be introduced in terms of particle characteristics investigated and instrumental techniques used.

These three issues should be brought to the attention of the scientific community undertaking new epidemiological studies, together with some broad guidelines to help the researchers in directing their studies. To address this need the WHO undertook the task of developing *Guidelines for Concentration and Exposure-Response Measurement of Fine and Ultra Fine Particulate Matter for Use in Epidemiological Studies* to be used by national and international organizations undertaking studies in this area.

**The objective of these guidelines is to improve:**

- 1) The state of knowledge on the links between exposure and health effects
- 2) The characterization of the relevant exposure in terms of its physical, chemical and biological source properties
- 3) The ability to inter-compare results of studies from different parts of the world

**Target audience**

The target audience for this guideline document includes:

- national and international bodies in developed and developing countries concerned with research funding and environmental management;



- the scientific community undertaking new epidemiological, experimental, exposure assessment studies and studies on the development of monitoring techniques.

### **The scope of the guidelines**

The guidelines will act as an important tool for funding bodies and research teams, undertaking concentration and exposure-response measurements in the area of airborne particulate matter with a focus on fine and ultra fine particles, and they should include identification of:

- The hypotheses and the links between exposure variables and health endpoints to be investigated
- The exposure characteristics that should be investigated
- The instrumental techniques for the measurements
- The experimental procedures and quality assurance
- Ways of raising awareness and how to apply the guidelines
- Process of updating the guidelines according to research progress

This document, therefore, is intended to improve the state of knowledge and the quality of the forthcoming exposure and epidemiological studies.

Outside the scope of this document are the following:

- A systematic review of either air quality situation in relation to airborne particles or the health evidence existing.
- A discussion and review of health effects related to the exposure to other airborne pollutants.

## **2. Review of Health Effects Studies**

Epidemiological studies conducted in the 1980s and 1990s, combined with analyses of health effects recorded during individual episodes of severely elevated air pollution levels, provided strong evidence for statistically significant associations between exposure to particulate matter and various types of health effects (Bascom et al. 1996; Brunekreef et al. 1995; Dockery and Pope 1994; Pope et al. 1995a; 1995b; Pope 2000a; 2000b; Schwartz 1994a). Particulate matter was characterized in different ways, in many of the studies, including total mass concentration or its fractions such as PM<sub>10</sub> or PM<sub>2.5</sub> or its elemental or chemical composition.

Within most established networks, outdoor particles are measured by PM<sub>10</sub> and PM<sub>2.5</sub> (until recently also as TSP, total particle mass, or black smoke, BS); therefore, most of the evidence of health effects of outdoor particles is based on these measures. TSP is almost entirely dominated by particles generated by mechanical processes such as dust resuspension, grinding, and mining. PM<sub>10</sub> is sometimes dominated by particles generated by mechanical processes and sometimes by accumulation mode particles, which is an aged fraction of the outdoor aerosol emitted by many sources such as industrial emissions, vehicle emissions, and power generation. In addition, a portion of the particles is of biogenic origin and generated from secondary processes such as photochemical processes. PM<sub>2.5</sub> is more likely to be dominated by accumulation mode particles, but can also include a significant fraction of mechanically generated particles. The relative contributions from different types of sources are very site specific.

Increases in all-cause mortality have been observed in studies of the acute and chronic effects of particulate matter. The increase in all-cause mortality is attributable to increases in respiratory disease and cardiovascular disease mortality (Pope and Dockery 1999; Schwartz 1994b). Consistent with the observation of increases in acute mortality, there was also an increase in hospital admissions for respiratory diseases and cardiovascular diseases in association with particulate air pollution (Bascom et al. 1996). Subpopulations consisting of susceptible individuals show increases in symptoms, medication use and physiological parameters consistent with an exacerbation of pre-existing respiratory or cardiovascular diseases.

Recent animal and human clinical studies are examining associations between exposure expressed in terms of particle mass and number, particularly of fine and ultra fine particles, and adverse effects. Toxicological studies have indicated that measures such as particle number or particle surface might be better indicators for ultra fine particles and that these particles potentially cause health effects (Chen et al. 1995; Oberdörster et al. 1992; 1994; Seaton et al. 1995). The evidence for health effects due to exposures characterized in terms of particle number, particle surface, or ultra fine particles from epidemiological studies is limited (MacNee and Donaldson 1999; Wichmann and Peters 2000). Two studies on adult asthmatics conducted in Erfurt, Germany (Peters et al. 1997) and Helsinki, Finland (Penttinen et al. 2001) suggested that decreases in peak expiratory flow rates were more strongly associated with ultra fine than with fine particles. In addition, a recent mortality study conducted in Erfurt, Germany suggested independent associations of ultra fine and fine particles with acute mortality (Wichmann and Peters 2000).

## 2.1 Epidemiology of acute health effects of particulate matter

Studies of acute health effects evaluate the impact of day-to-day or hour-to-hour variation in outdoor pollution on health. Studied outcomes span the range from mortality counts of populations to changes in physiological parameters or biomarkers of individuals.

### *Studies of short-term effects of particulate air pollution on mortality*

Mortality counts of large metropolitan areas have been a powerful source to assess the health effects of air pollution. In a study on particulate air pollution and daily death rate in Steubenville OH, Schwartz and Dockery (1992) found a 6 % increase in daily deaths when daily TSP levels increased from  $36 \mu\text{g}/\text{m}^3$  to  $209 \mu\text{g}/\text{m}^3$ . Similar associations were later observed in new time-series studies. Dockery and Pope (1994) summarized the U.S. studies published up to 1993 and observed on average a 1.0 % (range 0.7 - 1.6%) total mortality, 1.4% (0.8 - 1.8%) cardiovascular mortality and 3.5% (1.5 - 3.7%) respiratory mortality increase for  $10 \mu\text{g}/\text{m}^3$  increase in daily outdoor  $\text{PM}_{10}$ . HEI (1995) critically evaluated these studies and partly recalculated the results from original data, and as a result confirmed the original results. The results have also been replicated in China (Xu et al. 1994), in Lyon (Zmirou et al. 1996), Paris (Dab et al. 1996), Athens (Touloumi et al. 1996), Köln (Spix and Wichmann 1996), and Milan (Vigotti et al. 1996).

Association between particulate matter and increases in mortality have been shown consistently in more than 60 studies conducted in at least 35 cities throughout the world as recently reviewed by Pope (2000a). In particular these studies were able to reproduce the effects of particulate matter in locations with different climatic conditions and different sources of particulate matter. Studies of several geographical regions have been applied in the APHEA project (Air Pollution and Health: A European Approach), a project built on a database in 12 locations in 9 European countries (Katsouyanni et al. 1995). Combined analysis of the APHEA data from 5 western European cities indicates a 2 % increase in daily deaths resulting from a  $50 \mu\text{g}/\text{m}^3$  increase in daily  $\text{PM}_{10}$  level (Katsouyanni et al. 1997). This result was highly significant statistically, but the risk estimate is lower than in the American studies, possibly reflecting different PM characteristics or different mixtures and settings of air pollution exposures. Borja-Aburto et al. (1998) evaluated the association between mortality (all causes, cardiovascular and respiratory) and outdoor  $\text{PM}_{2.5}$  in Mexico City. Considering that outdoor  $\text{PM}_{2.5}$  level as typically being in the order of 60 % of  $\text{PM}_{10}$ , their mortality risk estimates fall between those of Dockery and Pope (1994) and Katsouyanni et al. (1997).

A larger effort was undertaken in the National Morbidity, Mortality, and Air Pollution Study (NMMAPS), which in its final stage compiles data from the 90 of the largest US cities (Samet et al. 2000a; 2000b). The study estimated a 0.5% increase in daily mortality associated with a  $10 \mu\text{g}/\text{m}^3$  increase in  $\text{PM}_{10}$  on the day before. The effect was independent of other co-pollutants. The power of the study was to provide combined estimates for the whole US as well as different regions. The largest effect estimates were seen in the northeastern United States.

NMMAPS and the continuation of the APHEA project are currently providing a powerful database; however, new studies will need to fill gaps of knowledge untouched by these large-scale studies (Table 2.3, p. 26). Areas of open questions include the role of:

- Sources

- Particle characteristics responsible for the effects observed in association with PM<sub>2.5</sub> and PM<sub>10</sub>.

In recent years, a German group suggested that the health effects of PM exposure may be related not only to PM<sub>2.5</sub> mass, for example, but possibly also to the number or mass of ultra fine particles (e.g. Peters et al. 1997; Wichmann and Peters 2000). In spite of their very small contribution to total PM mass, the ultra fine particles dominate particle numbers. This question is far from answered. The ultra fine PM numbers are not strongly correlated with, for example, PM<sub>10</sub> mass. One of the higher correlations observed was  $R = 0.6$ , i.e. variance in the number of ultra fine particles explained about 1/3 of the variation in PM<sub>10</sub> mass (Peters et al. 1997; Ruuskanen et al. 2001; Tiittanen et al. 1999). The ultra fine particle numbers can hardly explain or contradict the observed outdoor PM and health associations. They may, however, add important new information to the complex PM risk assessment.

An emerging field is mortality studies in cohorts of subpopulation of subjects with chronic diseases, as demonstrated by Sunyer et al. (2000). This approach provides evidence on the effects of particulate matter in presumed high-risk populations, and is likely to provide valuable insight to better reduce the health risks of populations. Time-series studies, however, leave one significant question open; namely, do air pollutants simply synchronize inevitable deaths by just a few days (harvesting), or do they also significantly reduce the life expectancies of affected individuals and populations?

### ***Design issues with time-series studies***

The following concerns with respect to design might arise:

- New studies should have sufficient power to detect small increases in relative risks shown by the numerous single-city as well as large, multiple-city studies. The NMMAPS study has shown that the effect estimates obtained at single locations vary around a common effect estimate (Samet et al. 2000a; 2000b). This also implies that a null result in a single city or region might not be contradictory to the overall effect. The average number of deaths, as well as the length of the time-series, determines the power of the studies. Exposure data and mortality counts should be available for at least 2 years. A minimum length of the time-series is necessary in order to allow appropriate modeling of season, a known potential confounder of the association between particulate air pollution and mortality or hospital admissions. Also power calculations should prove that the size of the study population is adequate. If different measures of outdoor particles are going to be compared, the correlation between these measures should be considered in estimating the power of the study to detect differences between the different measures.
- Mortality counts can be obtained without much additional data collection effort. The disadvantage is that they are collected for different purposes and the compliance with recording instructions cannot be monitored or influenced. Interpretation of the results with respect to specific diseases might be limited due to under or over-reporting of the specific diseases.
- Mortality studies of susceptible subgroups are providing promising new approaches, which use the case-crossover design (Sunyer et al. 2000). However, methodological concerns have been raised when comparing the results from time-series analyses and case-crossover

analyses (Greenland 1996; Navidi 1998; Bateson and Schwartz 1999). These concerns as well as new methodological discussions should be considered when planning new studies.

With respect to exposure assessment the following issues should be considered:

- A study area should form a geographical unit that can be characterized by one or a few central monitoring sites. In larger geographical regions, measurement stations should be selected to characterize population exposures, not individual sources. The correlation between the stations can be used as a criterion for the degree of heterogeneity in exposures present within the study area.
- Daily particle concentrations should be available in order to study the presence of lagged or cumulative effects.
- In case different particle characteristics are the main interest of the health effects study, the correlation between the different metrics of ambient particle exposures should be explicitly considered in the power calculations.
- Studies of detailed particle characteristics at multiple locations will be necessary in order to strengthen the potential role of other metrics. Newly introduced measures, such as the number of ultra fine particles, might be surrogates for different sources or particle characteristics in different locations. Therefore, a single location is not sufficient because the pollution mixtures vary between cities or regions.
- The response relationship between mortality and particulate air pollution appears to be linear or near linear at outdoor levels encountered in many cities today. There is evidence, however, that at high concentrations of outdoor particles, the dose-response relationship might flatten (Spix et al. 1993; Peters et al. 2000). These observations suggest that there is no threshold at low concentrations of outdoor particles that is without a public health risk. The dose-response curve needs to be addressed for other metrics of particulate matter specifically.

## **2.2 Studies of short-term effects of particulate air pollution on hospital admissions**

In addition to mortality data, many studies and reviews have also evaluated the association between the prevalence of symptoms, diseases and hospitalisation and PM air pollution. The results of most of these provide further support to the claims that existing levels of outdoor air PM pollution are causing adverse health effects (e.g. Dockery and Pope 1994; Hoek and Brunekreef 1994; Anderson et al. 1997; Pekkanen et al. 1997; Timonen and Pekkanen 1997). Hospital admission data provides a powerful tool to study the effects of particle air pollution on specific diseases or a combination of conditions such as respiratory and cardiovascular diseases. Again the NMMAPS study provides the largest database, analysing data of subjects older than 65 years in 14 metropolitan areas of the United States (Samet et al. 2000a; 2000b). Hospital admissions increased by 1% for cardiovascular disease and 2% for pneumonia and chronic obstructive lung disease in association with  $10 \mu\text{g}/\text{m}^3$   $\text{PM}_{10}$ . These associations have been the driving force to establish the link between cardiovascular disease exacerbation and outdoor air pollution. However, little evidence is available on the role of particles from different sources, and the impact of particle number concentrations or particle surface area is unknown (Table 2.3, p. 26).

### ***Design issues with hospital admission studies***

The concerns with respect to design are similar to those for short-term studies on mortality (see above) and will not be re-iterated here. In addition, the following may be considered.

- Hospital admission or discharge data can be obtained from administrative databases. The disadvantage is that they are often collected for billing purposes and therefore might also reflect the mandates of a health care system rather than true diagnoses. Interpretation of the results with respect to specific diseases might be limited due to under-reporting or over-reporting of the specific diseases.

The issues with respect to exposure assessment are also identical to those listed for studies on short-term effects of particulate air pollution (see above).

## **2.3 Studies of short-term effects of particulate air pollution in susceptible subpopulations**

Panel studies provide a powerful tool to study the day-to-day changes in health status in potentially susceptible subpopulations. Their aim is to provide evidence that early physiological changes or changes in biomarkers occur, which are consistent with disease exacerbation or mortality. For example, elevated levels of particulate air pollution have been associated with short-term responses such as decreased lung function, and increased respiratory symptoms such as cough, shortness of breath, wheezing, and asthma attacks (Pope 2000a; 2000b). Recent panel studies have also focused on cardiac endpoints and found air pollution to be associated with increased heart rate, decreased heart rate variability, and detection of arrhythmias by implantable defibrillators (Pope 2000a; 2000b). No associations between PM and blood oxygenation have been observed. Often these panel studies are combined with intermittent clinical examinations. They provide evidence on the biological mechanisms responsible for the exacerbation of chronic diseases by particle matter air pollution. They have been an important component in establishing the exacerbation of asthma by outdoor particulate air pollution (Bates 1995; Dockery and Pope 1994). In addition, they are currently playing a key role in establishing the biological mechanisms leading from inhalation of particles to exacerbation of cardiovascular disease.

### ***Design issues in panel studies***

The key design issues in these studies are:

- To select the appropriate subgroup. The goal is to select from the subgroup susceptible to particulate air pollution an unbiased sample for the purpose of the studies. This is with the view to quantify the health effects within this group to adequately predict the health risk of an entire population. However, often it is unknown who is most susceptible to ambient particulate air pollution, and therefore the selection of a somewhat heterogeneous group might be advantageous.
- To select outcomes variable enough to capture early responses to external factors. However, variability should be sufficiently low to characterize the physiological condition and not other uncontrolled or unknown influences. To select outcome events, such as heart rate variability, that are known risk factors for severe events (Task Force 1996). Thereby, a

logical link between exposure to outdoor particulate air pollution and severe outcomes such as myocardial infarction can be established. However, there is also the need for a plausible explanation about how the deposition of particulate matter in the airways/lung affects these risk factors.

- To select appropriate time for follow-up. The length of the study is determined by the variation in exposures. Normally a panel study should be conducted over 4 to 6 months in order to allow low and high exposures to occur and to be able to adjust for changes induced by season or meteorology. For example, the PEACE study, a large multi-center panel study in children with chronic respiratory disease, might have suffered from its short duration, because it started and ended with an air pollution episode in many locations (Roemer et al. 1998; 2000).

Most commonly, exposure is estimated at one or several central monitoring sites. In this case the issues discussed under studies of short-term effects of particulate air pollution on mortality (see above) apply. However, the limited number of study subjects might also allow personal or microenvironment measurements of particulate air pollution from outdoor origin (for detailed discussion see section on personal exposure assessment).

## **2.4 Ad hoc epidemiological efforts during environmental disasters such as forest fires**

Epidemiological data is needed to evaluate the impact of extreme exposure situations such as large forest fires (WHO/UNEP/WMO 1999). The health impact of environmental disasters such as forest fires in the developed world cannot be transferred to developing countries, because the underlying health of the populations differs substantially. Existing administrative health data can be an important source of data, and studies of short-term effects on mortality or hospital admissions could elucidate the health impact of environmental disasters, but since environmental disasters usually occur unexpectedly, it is only rarely possible. It would be optimal to have exposure as well as health data before, during and after the episode (WHO/UNEP/WMO 1999).

### ***Design issues in studies of environmental disasters***

Issues in studies of environmental disasters include the following:

- Completeness of the data is critical, as selective loss of data might bias the results of the study substantially.
- Access to the data and all relevant information is needed. Studies of potentially susceptible populations are often difficult because of lack of data before the disaster. However, studies documenting changes during and after the event might still be helpful to investigate the extent of the health impact and to characterize in more detail the impact on potentially frail subgroups of the population.
- Fast and efficient access to potentially susceptible populations during the environmental stresses is important.

- Knowledge about the recovery period is necessary to select the appropriate time after exposures.
- Data on time-varying potential confounders such as infectious diseases have to be collected and might be specific to the study area.

In cases of environmental disasters, studies usually have to rely on available measurements or quickly initiate simple and informative measurements in the locations struck by the disaster. Air pollution measurements might often not be available, but might be replaced by satellite images to characterize exposures over wider areas.

## **2.5 Epidemiology of chronic health effects based on longitudinal studies**

Studies of chronic health effects evaluate the impact of particle exposures over several years. These studies provide evidence on the impact of outdoor particulate air pollution on life expectancy as well as the development of chronic diseases or impaired physiological parameters.

In one of the first major prospective cohort study on the relationship between annual average pollution levels and adjusted mortality-rate ratios, a cohort of over 8000 adults in six cities followed over 14-16 years, Dockery et al. (1993) found that although many pollutants were associated with increasing mortality, the association was strongest for PM<sub>2.5</sub>. An increase in the annual average PM<sub>2.5</sub> level from 10 to 30 µg/m<sup>3</sup> was associated with a mortality increase of 26 % in total and 37 % in lung and heart disease.

In a larger cohort study on the associations of PM<sub>2.5</sub> levels and adjusted mortality rate ratios in 50 cities in cohorts of 295,000 individuals, Pope et al. (1995c) found that an increase of the annual average PM<sub>2.5</sub> by 24.5 µg/m<sup>3</sup> was associated with a 17 % increase in total mortality and 31 % increase in lung and heart disease mortality. The Health Effects Institute has recently reanalysed these studies and replicated their results (HEI 2000).

Concluding from these cohort studies, typical urban outdoor air levels of PM<sub>10</sub> and PM<sub>2.5</sub> appear to increase long-term death rates, i.e. reduce life expectancy (Brunekreef 1997; Pope 2000a; 2000b). These observed increases in long-term death rates cannot be explained by acute effects of air pollution, but rather relate to increased morbidity that results in earlier deaths.

This is also confirmed by studies that address long-term effects of air pollution on morbidity or physiologic measures such as lung function, which strongly predict survival. In the Seventh Day Adventists Cohort Study, the incidence of chronic bronchitis increased with long-term outdoor particulate levels (Abbey et al. 1991). In two other studies of the long-term effects of air pollution, lung function and morbidity of adults and children correlated with the long-term average outdoor particulate exposure (Ackermann-Lieblich et al. 1997; Braun-Fahrländer et al. 1997).

## **2.6 Studies of chronic health effects based on cross-sectional studies**

Cross-sectional studies collect information on exposure and health status at the same time. They attempt to assess exposures retrospectively either by questionnaire data or under the assumption that the concentration contrasts measured today have been constant over time. A goal of the



exposure assessment could be to correctly classify chronically exposed individuals and distinguish them from chronically unexposed individuals. These studies have provided evidence in the past on the impact of street traffic on lung function, respiratory symptoms, asthma and allergy prevalence (Duhme et al. 1996; Kramer et al. 2000; Oosterlee et al. 1996; van Vliet et al. 1997). The epidemiological issues in these studies are:

- To adequately assess how potential confounders such as socio-economic factors might influence living in areas with high-, medium-, or low- particulate air pollution exposures.
- To assess the health outcomes in a uniform and unbiased manner. Health problems of children might have caused parents to move out of areas heavily impacted by outdoor particulate air pollution.

With respect to exposure assessment the characterization of the exposure history needs to be designed carefully to adequately assess exposure gradients. For example, it is possible to measure particulate matter concentrations at schools in order to characterize children's exposures (Brunekreef et al. 1997).

## **2.7 Studies based on cohorts**

Studies based on cohorts have been a powerful tool to assess the chronic health effects of air pollution. A cohort is recruited and characterized with respect to major known risk factors for the outcome. Air pollution as well as health outcomes are monitored thereafter during the follow-up. In order to study air pollution, exposure gradients have to be created by selecting appropriate geographical regions. Geographical variation in exposures within a city or district is generally thought to be insufficient to allow study of long-term effects. Ideally the regions would differ only with respect to air pollution concentrations, but would otherwise be similar with respect to risk factor profiles. This is one of the obstacles that a multi-center cohort study in Europe would have to overcome, because regional differences are not only present with respect to air pollution, but also with respect to risk factor profiles influenced by cultural or inherited differences. Unfortunately, these studies are time consuming, costly and do not provide an assessment of the particulate air pollution mix present nowadays but a decade ago. In Europe, Asia and Africa these types of studies are completely missing, and therefore the chronic health effects of these quite different exposures might be under- or over-estimated. Retrospective studies might be of great merit, especially when well-characterized cohorts have been established in the past and relevant particulate matter indices have been measured. These studies have been conducted mostly with adults. However, to supplement the evidence from cross-sectional studies, cohort studies in children might be warranted based on existing birth cohorts.

The important design issues are:

- To adequately select the study areas in order to allow a wide range of exposure differences.
- To completely characterize the risk factor profiles for the outcomes of interest.
- To select a study population which stably resides in the study area to minimize attrition at follow-up. The outcomes might include mortality, hospital admissions, changes in physiological measures such as lung function or cardiac risk factor profiles, or symptoms.

- To completely assess all cases occurring in the study areas to have complete outcome ascertainment.

With respect to exposure assessment, the key issues are that the exposure contrasts are regional contrasts.

- Measurements should comprise at least PM<sub>2.5</sub> or PM<sub>10</sub>, but preferentially also other metrics of particle exposures over long time periods.
- Appropriate measurement sites should be selected.

## 2.8 Recommendations

### *Health endpoints*

Mortality assessment is usually the least expensive and relevant health endpoint for epidemiological studies. The use of mortality studies assumes that reasonable databases of mortality and air quality exist.

To study hospital admissions, it is essential to understand the biases in the country/community regarding hospitalizations, that at a minimum would include health care insurance, availability of hospital beds, and other socio-economic differences in utilization of hospital beds. Transportation or proximity to the hospital, as well as cultural factors, affect decisions to seek admission to hospital. There are also problems with differences in, for example, exposure, because of socioeconomic factors; those who are admitted to hospitals may have lower exposures than those who do not seek admission to hospital. These variables may limit the value of hospitalization data for epidemiological studies.

In studying children, school absence data may be a surrogate of health status, and easy to access. However, school absence may reflect accessibility to schools rather than health status of the pupils. For example, during a rain event, PM levels are lowered but roads may not be passable, thus preventing students from attending school.

### *Ambient Particle Measurements in Epidemiology Studies*

Epidemiological studies on the health effects related to particulate matter have used different indices of particulate exposure, and historically, this has depended largely upon the design and availability of samplers. For example the so-called “Total Suspended Particulate” fraction is defined by the design of the sampler (Wilson and Shu 1997).

A number of recently reported epidemiological studies have been compared with respect to the applied measurement methods of particulate matter. There are some interesting differences between studies carried out in Europe and the US, which arise from the availability of different sampling instrumentation in different countries. The US studies consistently have measurements for PM<sub>10</sub>, although this may be available only for every 6<sup>th</sup> day (that is, the minimal legal requirement) and frequently for PM<sub>2.5</sub>. In European studies many of the measurements available are TSP or black smoke (BS) and fewer sites seem to measure PM<sub>10</sub>. Currently widespread measurements of PM<sub>2.5</sub> in the US are uncommon in Europe, but will be increasingly available in the next few years.

The recommended minimum exposure measurements for new epidemiological studies in developing countries include an adequate measure of particle pollution, temperature, and relative humidity or dewpoint. The preferred measure of PM pollution is PM<sub>2.5</sub> (over TSP and PM<sub>10</sub>), but other measures of particulate pollution, including particle number or surface, would be useful. Adequate means for measurement of particle number do exist. Other valuable air pollution measures include SO<sub>x</sub> (SO<sub>4</sub> and SO<sub>2</sub>), CO, NO<sub>x</sub> (NO and NO<sub>2</sub>), O<sub>3</sub>, and elemental analysis. Obviously, for the daily time-series studies, daily monitoring of pollution and weather variables is required.

## 2.9 Toxicological studies

Toxicological studies, which involve controlled exposures of either humans or animals in laboratory settings, have been employed in attempts to evaluate the physicochemical properties of particulate matter (PM) which may be responsible for the health outcomes observed in epidemiological studies and to understand the underlying biological mechanisms for these outcomes.

### *Early Studies*

Early studies examining the toxicology of inhaled PM were largely focused on a limited number of chemical species. One such group, which received extensive attention was acidic sulphates, namely sulphuric acid and its partially neutralised products of reaction with ambient ammonia (Schlesinger 1999). Short-term exposures of healthy animals (with the exception of the guinea pig) to sulphuric acid at high concentrations, well above those found in outdoor air, did not alter standard tests of pulmonary function, nor did it result in pulmonary inflammation. However, lower levels were shown to alter non-specific airway responsiveness, as well as various aspects of respiratory tract physiology involved in lung defences, e.g., macrophage function. This latter may have been reflected in some evidence that sulphuric acid reduces resistance to bacterial infection, although this effect seems to depend upon the animal model used. Finally, chronic exposure produced alterations in numbers of epithelial secretory cells. The relative potency of acidic sulphate aerosols was related to their degree of acidity, indicating that observed responses were due to the hydrogen ion rather than to the sulphate.

Another chemical group examined extensively in early studies was the metals. These studies noted that acute or chronic exposures to pure metallic particles, e.g., arsenic, cadmium, copper, vanadium, iron, or zinc, could have various effects on the respiratory tract (Gardner and Graham 1997), although concentrations employed were much greater than those which would occur in the outdoor atmosphere. Some other types of particulate matter commonly used in earlier toxicological evaluations of PM included fly ash, volcanic ash, coal dust, carbon black, and titanium dioxide (Amdur 1996). Some of these particles were models of “nuisance” or “inert” dusts, i.e., those having low intrinsic toxicity, and were used to evaluate the occurrence of “non-specific” particle effects, i.e., responses which may be independent of the actual chemical nature of the material used. In general, only some inflammatory responses and mild pulmonary functional changes were noted following exposure to these particles, and this occurred only at high concentrations.

### ***Recent approaches***

More current toxicological studies have focused on the use of actual outdoor air PM and on various types of specific combustion-generated particles, and select constituents of these, increasing the relevance to actual outdoor inhalation exposures. In addition, the role of physical properties of PM, especially particle size, in modulating biological response has received much interest.

#### ***Outdoor air particles***

Exposures to outdoor particles have utilized both intratracheal instillation and inhalation techniques. For the former studies, outdoor PM samples collected on filters are resuspended in a vehicle, and a small volume of the resultant suspension is then instilled. These studies have provided some indication that outdoor PM could result in a pulmonary inflammatory response, which appears to be mediated through various cytokines. Furthermore, the responses seem to be related to bio-available transition metals (Dreher 2000). However, the doses used in these studies were generally quite high relative to outdoor concentrations. The most recent attempts to expose animals to lower concentrations of outdoor PM employed devices called concentrators, which allowed for the collection of PM from the air, coupled with direct inhalation exposure of animal models (Kim et al. 2000). These inhalation studies generally involved evaluation of various pulmonary and cardiac effects following exposure (Costa 2000). However, because of the variability in daily levels, and also in chemical makeup of outdoor PM even within one geographical region, studies using concentrated aerosols performed on different days may likely involve exposures to different concentrations of PM having different chemical composition. The inability to reproduce the same exposure conditions from day to day often makes the interpretation of findings somewhat complicated in terms of relating biological responses to specific PM components or exposure concentrations.

#### ***Combustion-generated particles***

A number of types of combustion-generated particles have received interest in toxicological studies. One type is diesel exhaust particles. These have been evaluated in terms of the relationship between exposure and alterations in aspects of immune function, especially the potential to modulate the induction or exacerbation of allergic airway disease (Cohen and Nikula 1999; Mauderly 2000). The inhalation or instillation, albeit at high concentrations, of diesel exhaust particles enhanced the production of antigen-specific antibodies, and also induced non-specific airway hyper-responsiveness.

Another class of particulate matter which has received attention in recent toxicological studies is fly ash, generally coal or residual oil fly ash (ROFA) (Dreher et al. 1997; Dreher 2000). Most such studies involved ROFA, which has a high content of water-soluble sulphate and metals. Studies with this material, rather than with pure metal particles as was done in the past, have allowed for the examination of the role of metals in biological responses to mixed chemical PM. The instillation of high doses of ROFA generally produced pulmonary inflammation, which was most likely due to aqueous leachable chemical constituents of the particles, generally metals. Furthermore, different biological effects were found to be due to different metal constituents, and were also influenced by the interaction between the metals and the acidity of the particles.

### ***Particle size and toxicity***

Most particles used in laboratory animal toxicology studies were in the fine particle mode, i.e., 0.1  $\mu\text{m}$  to 2.5  $\mu\text{m}$  in diameter. However, the great number and huge surface area of ultra fine particles (those  $< 0.1 \mu\text{m}$ ) in some outdoor PM atmospheres necessitated considering the size of the particle in assessing biological responses. Some studies have examined differences in toxicity between fine and ultra fine particles, with the general finding that the ultra fine particles show a significantly greater response at similar mass doses, as well as some differences in rates and pathways of clearance from the respiratory tract (MacNee and Donaldson 1999; Oberdörster et al. 1999). Furthermore, the amplitude of any biological response due to PM exposure may be dependent upon the total surface area, which is in contact with tissue, indicating that surface chemistry phenomena are also likely involved in PM-induced effects (Lison et al. 1997). Thus, size, as well as other physical properties of inhaled PM, may play a significant role in modulating a biological response in some cases, perhaps for some responses, and this may be independent of the specific chemical composition of the particles being evaluated. On the other hand, it is clear that all particles do not produce the same response, and particle composition likely does play a role in some of the adverse health effects associated with exposure to outdoor PM (Costa and Dreher 1997).

### ***Animal models of susceptibility***

Susceptibility to adverse health effects of PM can vary, depending upon a variety of host factors such as age, nutritional status, physiological activity profile, genetic predisposition, or pre-existent disease. Animal models of compromised hosts are useful in providing information about responses of sensitive human subpopulations. The most commonly used models are rodent models of human respiratory disease, although some studies have used animal models to evaluate the effect of age, nutritional manipulation and cardiovascular disease upon response to PM exposure (Kodavanti and Costa 1999; Muggenburgh et al. 2000; Mauderly 2000). Although such models cannot exactly duplicate a human disease, they can mimic certain features of the disease and can, thus, provide valuable insight into mechanisms of response in compromised animals. Some disease models are genetically derived, while drugs, chemicals or microbial exposures induce others. Although studies using compromised hosts are just emerging, they have provided evidence for enhanced susceptibility to inhaled PM in a number of cases. For example, particle-induced pulmonary inflammation was greater in old compared to young animals (Johnston et al. 1998), and pulmonary inflammation was enhanced in some animal models of disease compared to normals exposed to various PM (Costa and Dreher 1997).

### ***Toxicological endpoints and mechanisms of toxic effect***

While epidemiological studies have shown various health effects from exposure to outdoor PM, the mechanisms which underlie the toxicity from inhaled particles are not understood and, accordingly, have been the subject of intense investigation. Because these have not been elucidated, the toxicological endpoints evaluated in exposure studies cover a wide range of potential health outcomes (Dreher 2000; Costa 2000; Gilmour et al. 2000; MacNee and Donaldson 1999). The earliest studies concentrated on the induction of pulmonary inflammation, but more recent studies have assessed other endpoints as well. The role of airway epithelial cells and alveolar macrophages has received particular attention, because a PM-induced activation could result in the release of pro-inflammatory and pro-coagulant mediators and reactive oxidant species which may, in turn, interact

with other pulmonary cells and/or produce systemic responses. It is suggested that this process may be partly mediated through the modulation of intracellular signal transduction pathways.

Many studies have made use of *in vitro* exposure systems, which involve animal cells, human cells or cellular components exposed to various particles, including actual outdoor PM, soluble extracts of PM, or individual chemical constituents of PM (e.g., Kennedy et al. 1998; Bonner et al. 1998; Goldsmith et al. 1998; Hitzfeld et al. 1997). Such studies are useful in examining cellular and biochemical mechanisms of action by which PM may mediate health effects, with the recognition that cells may behave differently in tissues or within the whole organism, especially at dose levels that would occur under actual outdoor inhalation exposures conditions. Generally, *in vitro* exposures to non-cytotoxic concentrations of outdoor PM or fly ash, for example, have led to increased production of various cytokines, with these effects likely mediated, at least in part, through production of reactive oxygen species.

Some work has been done to examine the effects of PM on humoral (antibody) or cell-mediated immunity. A limited number of studies have examined the mechanisms underlying the enhancement of allergic airway disease by outdoor air PM other than diesel. The results suggest that outdoor PM or specific surrogates, such as ROFA, can up-regulate the immune response to inhaled antigen or can alter airway responsiveness.

Another approach to evaluating effects of PM on immune function involved assessing the ability of inhaled particles to modify resistance to bacterial infection, since some epidemiological studies have suggested that exposure to outdoor PM may be associated with increased prevalence of some acute lung disorders. Exposures to high concentrations of relatively inert particles have produced conflicting results; some particles had no effect on susceptibility to bacterial infection (Jakab 1993), while others decreased microbial clearance and the bacterial response of lymphocytes (Gilmour et al. 1989a; 1989b). In addition, while the pulmonary response to microbial agents may be altered by PM, the effect is dependent upon the specific microbial challenge and the animal model studied.

Recently, the ability of inhaled PM to produce effects beyond the respiratory tract has received attention. An increasing number of toxicological studies have examined the effects of PM on cardiovascular response, a potentially important pathway for acute health effects found in some epidemiological studies. Among the hypotheses that have been proposed to account for the non-pulmonary effects of PM are activation of neural reflexes, cytokine effects on cardiac tissue, alterations in blood coagulability, and perturbations in cardiac physiology, such as changes in heart rate or in heart rate variability (Killingsworth et al. 1997; Seaton et al. 1995; Sjögren 1997; Watkinson et al. 1998). However, an understanding of the pathways by which inhaled PM can produce systemic changes is far from clear.

### ***Coherence between epidemiology and mechanistic toxicology***

Epidemiological studies have found consistent associations between PM and adverse health outcomes in various geographic locations involving a range of populations. As toxicological studies are attempting to provide some biological plausibility for these associations, it is of interest to assess the extent of consistency between results of epidemiological and toxicological studies, i.e., coherence. The growing body of toxicological data is providing a degree of mechanistic plausibility for various epidemiological health outcomes. Some of these are shown in Table 2.1. In addition, there are a number of commonalities between epidemiological and toxicological studies in terms of specific components of outdoor PM which may be responsible for adverse health effects. Some of these are summarized in Table 2.2.

**Table 2.1** Mechanistic Plausibility: Some Examples of Coherence between PM-Exposure Associated Health Effects from Epidemiological and Toxicological Studies

Epidemiological Health Endpoints	Toxicological Health Endpoints	
	Concentrated Ambient	Specific PM Components
↑ Hypertension/Stroke	Δ PM Homeostasis (e.g., peripheral blood differentials)	Δ Blood Coagulation Factors: (UF Carbon) ↑ Platelets, WBC (Diesel Exhaust (whole))
↑ Ischemic Heart Disease ↑ Heart Attack	Δ Heart Rate Variability Δ EKG Wave Form Segments	↑ Arrhythmia Incidence: (ROFA)
↑ Acute Respiratory Infection (e.g., acute bronchitis, pneumonia)	↓ Mø ROI Production ↓ BALT Δ Pulmonary Cytokine Profile	↓ Mø ROI Production (Ammonium Sulfate) Δ Pulmonary Cytokines (Metals)
Exacerbation of COPD	-	↑ Airway Reactivity ( $H^+$ ) Δ Mucociliary Function ( $H^+$ )
↑ Respiratory Symptoms Δ Lung Function Indices	-	Pulmonary Inflammation (UF Metals) Δ Pulmonary Cytokines (Metals)

8 indicates increase in health endpoint; 9 indicates decrease in health endpoint;  
Δ indicates change in health endpoint

From: Schlesinger (2000)

**Table 2.2** Some Currently Hypothesized PM Physiochemical Properties Related to Biological Responses

PM Characteristic	Epidemiology	Toxicology
Mass concentration	Associated with health outcomes	Associated with biological responses
Particle size	Relative association with health outcomes often related to size mode (fine, coarse, ultra fine)	Different biological responses noted with different size modes
Metals	Utah Valley - effects from steel mill related to metals	ROFA: effects related to metals
Acidity	Some evidence for $H^+$ association with health outcomes	Various biological responses
Organics	Association of PM with lung cancer possibly due to carcinogenicity of organic fraction	Known mutagens/carcinogens
Biogenic PM	Possible association with health outcomes	Generally allergenic
Sulphate/nitrate salts	Association with some health outcomes (markers for $H^+$ )	Generally not very toxic at low concentrations
peroxides	?	High levels may produce biological effects
elemental C (soot)	?	Mutagenic/carcinogenic/irritant

From: Schlesinger (2000)

## 2.10 Clinical studies

Carefully controlled quantitative studies of exposed humans utilize laboratory atmospheric conditions, considered relevant to outdoor pollutant levels, or concentrated particles from the outdoor air, and document health-related effects that result from breathing the atmosphere. Advantage is taken of the highly controlled environment to identify responses to individual pollutants and characterize exposure-response relationships. In addition, the controlled environment provides an opportunity to study interactions among pollutants per se or with other variables such as exercise, humidity, or temperature. Insofar as individuals with acute and chronic cardiopulmonary diseases can participate in exposure protocols, potentially susceptible populations can be studied. However, controlled human exposures have important limitations: for practical and ethical reasons, studies are limited to small groups, presumably representative of larger populations, to short duration of exposure, and to pollutant concentrations expected to produce only mild and transient responses. Furthermore, acute transient responses seen in clinical studies may not predict chronic health effects of exposure to air pollution.



### ***Design issues with clinical studies***

Modern clinical studies use exposures to single pollutants, simple pollutant mixtures, or Concentrated outdoor Air Particles (CAPs). Studies generally involve exposure duration of 0.5 – 8 hours, and if feasible, a double blind, cross over design. Exposures are often conducted in environmentally controlled chambers (25-75 m<sup>3</sup> volume) with a single passage of the pollutant(s). The chamber setting offers special opportunities including normal activities, intermittent peak pollutant concentrations and unencumbered measurements of breathing. An alternative approach is the use of face masks or mouthpiece exposures of individual subjects in place of an exposure chamber. Such systems provide an opportunity to obtain quantitative information about the exposure, even to the extent of measuring total delivered dose. However, they are inherently less comfortable and limit the duration of exposure to 2 hours or less.

There is a major difference with regard to pollutant generation requirements between studies utilizing facemask or mouthpiece exposures and those conducted in relatively large environmental chambers. With the mouthpiece, a pollutant-air mixture must be produced that only slightly exceeds the individual subject's respiratory intake requirements, e.g., from 5 L min<sup>-1</sup> to 80 L min<sup>-1</sup> with exercise. In contrast, for chambers operating with a single pass (no recirculation), 5 to 25 m<sup>3</sup> min<sup>-1</sup> is the likely flow rate requirement, i.e., as much as 1,000 times greater. Given that the exposure duration is often longer for chamber studies, there is a need for much greater generation capacity than with mouthpiece or facemask studies.

Exercise performed either on a treadmill or bicycle is an important component of the exposure study. Exercise enhances the pollutant dose both by increasing ventilation and by causing a switch from nasal to oral breathing, effectively bypassing the nose. The nose may remove some particles and gases, variably reducing their delivery to the lower respiratory tract. In addition, the effect of exercise on airway drying may enhance the response to pollutants.

### ***Markers of response – endpoint assessment***

In clinical studies a variety of clinical and physiological outcome measures are used as tools for evaluating the site of injury. Collection of symptom data via questionnaires has emphasized simple verbal descriptions, incidence rates and ordinal scoring based on the numbers of symptoms reported and their severity. Questionnaires survey symptoms during exposure, immediately after exposure and occasionally 24 hours or longer after exposure.

Despite the development of newer and more direct measures of pulmonary effects on the airways, simple spirometry remains a mainstay in human clinical studies. The most commonly evaluated parameters obtained from spirometry are the forced vital capacity (FVC), forced expiratory volume in one second (FEV<sub>1</sub>), and the maximal flow-volume curve. Other tests of pulmonary mechanics include the measurement of airway resistance or its reciprocal, conductance, analysis of partial flow-volume loop, and flow rates at specific lung volumes. The testing of non-specific airway hyper-responsiveness has proven useful in assessing airway responses to low concentrations of environmental airway pollutants. Airway challenge studies have been used to assess the effects of pollutant exposure on airway responsiveness and to determine whether baseline levels of responsiveness predict lung function decrements in response to pollutant exposure. Utell et al. (1983) found a relationship between baseline airway responsiveness assessed by carbachol in asthmatic subjects and responsiveness to an inhaled sulphuric acid aerosol.

Fiberoptic bronchoscopy is widely used in clinical studies to characterize the nature of the airway response to single and repeated exposures to acid aerosols (Frampton et al. 1992), diesel exhaust (Salvi et al. 1999) and concentrated outdoor particles (Ghio et al. 2000). Bronchoscopic procedures have included bronchoalveolar, bronchial and proximal lavage; bronchial brush, endobronchial and transbronchial biopsies; and bronchial instillation (Utell and Frampton 2000a). Lavages have characterized the airway cellular response to particles and changes in cytokine levels while biopsy material can be used to examine cellular patterns of gene expression using immunologic staining and in situ hybridization. Following diesel exposure, in comparison with control air exposures, a significant increase was observed in epithelial leukocytes and mast cells, with increased expression of the adhesion molecules ICAM-1 and VCAM-1 in submucosal endothelium (Salvi et al. 1999).

In recent years, sputum induction has emerged as an alternative research tool for sampling the cells in epithelial lining fluid of the lower respiratory tract in humans. The results appear to be qualitatively similar to findings in the first aliquot of bronchoalveolar lavage fluid. Biochemical processes at the epithelial level may release gaseous products, some of which can be detected in the exhaled breath. Investigators have sampled for a variety of substances as markers of airway inflammation including hydrogen peroxide, carbon monoxide, and most recently nitric oxide (NO). The measurement of gases and volatile organic molecules in exhaled air shows promise as non-invasive markers of pollutant effects in clinical studies.

With the recent epidemiological observations that exposure to particulate matter affects cardiovascular function, clinical investigators have begun to incorporate continuous cardiac monitoring, or Holter recording, into protocols. Originally used to identify silent arrhythmias in cardiac patients, cardiac monitoring has revealed that both the pattern of variation in heart rate, or heart rate variability, and the pattern of electrical repolarization of the heart are markers of cardiac health or disease. Decreased heart rate variability as well as abnormalities in the duration, dynamics and heterogeneity of repolarization are established non-invasive predictors of arrhythmic events in patients with cardiovascular disease and in healthy subjects. In the clinical studies, participants undergo 24-hour, multiple lead ambulatory cardiac monitoring. The morphology of the ST segment and T-wave, duration of the QT interval and dispersion of repolarization as well as heart rate variability can be assessed. The heart rate variability analysis remains the most frequently used method to evaluate the influence of the autonomic nervous system.

Also following the observation of cardiovascular effects from exposure to particulate matter, investigators have begun to examine whether particle exposure could initiate a hypercoagulable state. To test the induction of the clotting mechanism, markers of coagulation, vascular injury, fibrinolysis and the acute phase response are being measured in plasma. Potential candidates include Von Willebrand factor, fibrinogen, C-reactive protein, and interleukin-6.

### ***Recent approaches***

Until recently, clinical studies have used commercially available nebulizers, which are widely available in pulmonary function laboratories or inhalation therapy to generate sulphate or nitrate aerosols. However, the need to study actual outdoor particles and various types of specific combustion-generated particles has resulted in a variety of new and unique technologies for clinical studies.

### ***Concentrated outdoor air particles***

Outdoor air contains a complex mixture of particles and gases containing a variety of chemicals at trace levels that may interact in causing health effects. A technology recently developed allows fine particles in the air to be concentrated in real time. Air is drawn through a series of virtual impactors designed so that particles less than 2.5  $\mu\text{m}$  in aerodynamic diameter are progressively concentrated up to 25- to 30-fold (Sioutas et al. 1995). Outdoor gases and particles in the ultrafine size range ( $<100$  nm diameter) are not concentrated using this methodology.

This instrument has been used to demonstrate effects of outdoor particulate matter in humans. For example, in a controlled exposure study to CAPs, it was reported that exposure of healthy elderly, but not young volunteers, resulted in decreased heart rate variability in both time and frequency domains (Devlin et al. 2000). However, exposure of young healthy volunteers to CAPs has caused increases in levels of blood fibrinogen, a clotting factor which has been reported as risk factor for ischaemic heart disease (Ghio et al. 2000). Although future generations of concentrators are likely to include ultrafine particles, there remain a number of potential problems. The actual exposure concentration and particle composition may vary day-to-day and even hour-to-hour, depending on changes in outdoor particle levels and sources during the experiment. Nevertheless, this technology introduces a way to study human responses to real outdoor particles.

### ***Diesel engine exhaust***

Another approach to the problem of combustion generated particles is illustrated by recent studies of exposure to diesel exhaust. Although diesel engines have improved efficiency and reduced emissions of carbon monoxide compared with gasoline engines, they generate large quantities of fine and ultrafine particles.

Healthy subjects have been exposed to dilute exhaust from an operating Volvo diesel engine in a specifically designed exposure facility (Salvi et al. 1999). Bronchoscopy with bronchoalveolar lavage and bronchial biopsy were performed six hours after exposure. As previously noted, the exposure increased epithelial leukocytes and mast cells in lavage with increased expression of adhesion molecules in submucosal endothelium. The diesel exposure induced airway inflammation in healthy subjects in the absence of effects on pulmonary mechanics.

Instillation of diesel exhaust particles into the nose has been shown to enhance the local ragweed-specific IgE response in subjects with allergic rhinitis and to drive the nasal cytokine response toward Th2 or allergic phenotype (Diaz-Sanchez et al. 1997). These findings raise concerns about diesel exhaust as a contributor to the increased prevalence of asthma and allergic rhinitis.

### ***Environmental tobacco smoke***

Using smoking machines, clinical studies have examined the role of environmental tobacco smoke (ETS) in the exacerbation of asthma (Weiss et al. 1999). Brief exposures to ETS produced symptoms such as eye and nasopharyngeal irritation. Blinding of ETS exposure is not feasible. Although only a few clinical studies with ETS have generated significant effects on FEV<sub>1</sub> or measures of airway responsiveness in asthmatics, there is evidence that individual

asthmatics and groups of asthmatics do respond to levels of ETS that do not elicit responses in healthy volunteers. Several factors limit the interpretation of these studies: duration exposures were generally brief; small sample sizes often constrained interpretation of the data; and often there was wide variability in response among ETS-exposed asthmatics. Nevertheless, ETS remains an important source of particulate matter exposure both outdoors and indoors and well designed clinical studies have much to offer in terms of characterizing responses in susceptible groups.

### ***Ultrafine particles***

The contribution of particle size to toxicity remains a key question in the study of particulate matter health effects. Although ultrafine particles contribute little to mass, they may be important in producing biological responses because of their high number concentration and surface area. The ultrafine particles (<100 nm diameter) may be important inducers of pulmonary and vascular effects because of their ability to evade macrophage phagocytosis, and to enter alveolar epithelial cells, the lung interstitium, and even pulmonary capillary blood (Frampton et al. 2001). In one protocol, healthy subjects were exposed for 2 hours to air and 2 concentrations of carbon ultrafine particles, 10 and 25  $\mu\text{g}/\text{m}^3$ , with intermittent exercise. The count median diameter of the particle was 27 nm. These studies demonstrated a remarkably high deposition fraction of 66% total deposition at rest increasing to 80% with exercise. In addition, mechanistic studies revealed a decrease in circulating blood monocytes 21 hours after exposure whereas the expression of ICAM-1 on blood monocytes was decreased almost immediately post exposure. These studies suggest that exposure to ultrafine particles at very low mass concentrations may cause effects on circulating leukocytes (Frampton et al. 2001). Because ultrafines may rapidly enter the circulation, the effects of ultrafine particles on blood leukocytes and cardiovascular function remain an important area of investigation.

### ***A mechanistic model***

To explain the cardiopulmonary associations with fine and ultrafine particles, a mechanistic schema linking particle exposure with both respiratory and cardiovascular effects is required. The mechanism will presumably require interaction between epithelium, endothelium and marginating leukocytes during the inflammatory response in the airways and the recognized role that the vascular inflammatory process plays in coronary artery disease.

Utell and Frampton (2000b) have proposed a model whereby airway epithelial injury activates local endothelial cells and circulating leukocytes, and induces release of tissue factor by circulating monocytes, partially activating the coagulation cascade. The combined effect of these processes could precipitate adverse cardiac events in individuals with critical coronary lesions. On the other hand, endothelial activation appears to be part of airway inflammation in asthma, and pollutant exposure is likely to increase expression of markers of endothelial activation. Ultimately, experimental studies are needed to test this and other hypotheses explaining the association between low-level particle exposure and health effects.

## 2.11 Conclusions

- There is substantial evidence for the health effects of PM<sub>10</sub> and PM<sub>2.5</sub>; however, little is known on the health impact of other particulate matter metrics such as ultra fine particles or the surface of particles.
- The sources contributing to particles in outdoor air might be important to distinguish more or less toxic particulate matter.
- Both acute and chronic health effect studies are needed to adequately assess the rapidly changing aerosol mixtures in outdoor air.
- Multi-centre studies are needed to adequately address the role of new particle measures or the role of sources.
- Application of state-of-the-art statistical methodology as well as adequate planning of studies would provide valuable insight into the role of particulate matter components, and provide a general and not local interpretation of the findings.

At present, there is not enough information available to explain the mechanisms by which inhaled particles cause a wide range of health effects. There are a number of hypotheses available, linking the health effects to for example the number of particles inhaled, or to their surface area or to the mass of trace components they carry. It is reasonable to expect that a number of mechanisms could be involved and linked to the different particle properties and causal of different health effects. Many of these hypotheses will still require a considerable amount of studies, mainly clinical, to be proved or disproved. There are different potential mechanisms of cardiopulmonary responses to particle inhalation currently being discussed.

There is no established mechanism to explain the relationship between pollutant exposure and excess cardiovascular mortality. Recent studies in healthy and compromised animals have suggested that inhalation of particulate matter may induce changes in cardiac rhythm or repolarization. Although there is little evidence to suggest that exposure to particulate air pollution has direct cardiac effects, penetration of very small particles (e.g., ultra fine particles) or their reaction products into the systemic circulation could induce inflammatory cytokine expression in the myocardium, resulting in myocarditis or epicarditis, or progression of coronary artery disease. Furthermore, an acute inflammatory response in the airway may be accompanied by an acute phase response, with increases in plasma viscosity and blood coagulation factors, such as fibrinogen, Factor VII, and plasminogen activator inhibitor. Such events could cause the observed increases in heart rate, changes in heart rate variability, contribute to congestive heart failure and arrhythmias, or precipitate coronary events in individuals with coronary artery disease (Utell and Frampton 1999).

Similarly, the mechanisms by which particles cause adverse effects in patients with asthma and COPD have not been determined. Particle exposure could contribute to progression of disease by enhancing inflammation. A mechanistic model for particle-induced lung inflammation involves injury to the epithelial cells by reactive oxygen species, possibly enhanced in the presence of metals, accompanied by activation of nuclear regulatory factors, leading to elaboration of proinflammatory cytokines, including IL-8 and IL-6, and increased expression of nitric oxide synthase with increased nitric oxide in exhaled air. This in principle could also result in

activation of vascular endothelium and circulating leukocytes. Alternatively, particles could increase susceptibility to infectious complications by impairing mucociliary clearance, by increasing adhesion of bacteria to epithelial cells, by impairing alveolar macrophage function, or by impairing specific or non-specific functions of the immune system (Utell and Frampton 1999).

There are many unanswered questions about how particles cause the health effects observed in epidemiological studies, specifically the mechanisms involved, qualitative relationships between PM and gaseous co-pollutants, and the identification of different sources linked to the effects. The open questions and research needs on health effects of particulate air pollution by epidemiological studies are captured in Tables 2.3 and 2.4.

**Table 2.3** Open research questions in studies of acute health effects of particulate air pollution.

Open Research Questions	Comments
<i>Studies of short-term effects of particulate air pollution on mortality.</i>	
Which sources are responsible for the observed PM <sub>10</sub> and PM <sub>2.5</sub> effects in a particular region?	The contribution of sources might vary from location to location and also their health relevance might vary depending on the general health of the population. Studies on other metrics should always include measurements of PM <sub>10</sub> and PM <sub>2.5</sub> , as they are currently the criteria pollutants for particulate matter.
What role do other metrics of particle exposure play such as number concentrations or surface area concentrations?	
Which subpopulations are susceptible to and die in association with outdoor particulate air pollution?	
<i>Studies of short-term effects of particulate air pollution on hospital admissions.</i>	
Which sources are responsible for the observed PM <sub>10</sub> and PM <sub>2.5</sub> effects in a particular region?	See above.
What role do other metrics of particle exposures play such as number concentrations or surface area concentrations?	See above.
Which accompanying conditions are increasing the likelihood of hospitalisation or re-hospitalisation on days with high concentrations of outdoor particles?	Identification of these conditions might be limited by the accuracy of the diagnoses collected for administrative and billing purposes.
<i>Studies of short-term effects of particulate air pollution in susceptible subpopulations.</i>	
Which sources are responsible for the observed PM <sub>10</sub> and PM <sub>2.5</sub> effects in a particular region?	See above.
What role do other metrics of particle exposures play such as number concentrations or surface area concentrations?	See above.
Are the potentially susceptible subpopulations showing changes in risk factor profiles or biomarkers, which are consistent with an increased risk of disease exacerbation in association with outdoor particulate air pollution?	
Are persons with both chronic respiratory and cardiovascular diseases particularly at risk on days with high outdoor levels of particles?	
<i>Ad hoc epidemiological efforts during environmental disasters such as forest fires</i>	
Are these extreme exposures causing health effects as would be predicted from studies available today?	
Are there population characteristics such as malnutrition, that make populations in developing countries even more susceptible to particulate air pollution?	This question might not be answered in an ad hoc study, but might need extensive epidemiological investigations. However, the results of these studies might be important to judge on the impact of environmental disasters.

**Table 2.4** Open research questions in studies of chronic health effects of particulate air pollution.

Open Research Questions	Comments
<i>Studies of chronic health effects based on cross-sectional data collection</i>	
Which sources are responsible for PM <sub>10</sub> and PM <sub>2.5</sub> effects in a particular region?	The contribution of sources might vary from location to location and also their health relevance might vary depending on the general health of the population.
What role do other metrics of particle exposures play such as number concentrations or surface area concentrations?	Studies of other metrics should always include measurements of PM <sub>10</sub> and PM <sub>2.5</sub> as they are currently the criteria pollutants for particulate matter.
<i>Studies of chronic health effects based on cohort data</i>	
Characterization of the chronic effects in children and newborn babies.	
Which sources are responsible for the observed PM <sub>10</sub> and PM <sub>2.5</sub> effects in a particular region?	See above.
What role do other metrics of particle exposures play such as number concentrations or surface area concentrations?	See above.



### **3. Exposure Studies**

The PM-exposure for an individual is the concentration of particulate matter (PM) with specified characteristics that exists in a person's breathing zone over a specified period of time.

Humans are normally exposed to PM from several different sources. These can be broken down into four basic (microenvironment) categories:

- 1) PM of outdoor origin from primary sources such as traffic and industry, wind blown dust from soil and from secondary sources such as PM produced by photochemical reactions.
- 2) PM generated by indoor sources, which include indoor combustion devices and re-suspension of general house-dust and pets.
- 3) PM from occupational sources, which cover a wide range of activities and they may be an extension of the domestic environment or they may be specific types of PM associated with the nature of the raw materials and the type of production process.
- 4) PM due to personal habits and activities and therefore including tobacco smoking, as well as general cleaning activities.

The division of human exposure in different microenvironments must be distinguished from the exposure from sources in the same microenvironments, as described above. Exposures in the different microenvironments are determined by the time spent in these microenvironments and the concentrations of PM in them. The PM in, for example, the residential microenvironment may originate from numerous outdoor sources, indoor sources, and personal activities of the exposed individual. In the developed world (in the absence of smoking), outdoor PM penetrating indoors is usually the most significant source of PM indoors. In the developing world, especially in rural areas, high indoor PM levels originate usually from indoor sources, mostly cooking on open fires (WHO 2000a).

Exposure measurements for epidemiological studies can be broken down into a 2x2 matrix: indoor and outdoor exposure and acute and chronic exposures (McMichael and Smith 1999). The majority of epidemiological studies relating PM exposure to health effects are concerned with the acute effects of outdoor or ambient exposure. Because people spend a majority of their time indoors, PM exposure in the indoor environment can be a significant part of their total exposure, and it is therefore important to be able to distinguish between PM generated by indoor sources and PM influenced by outdoor concentrations.

#### **3.1 Exposure monitoring, modelling and surrogates**

Exposures can be monitored, modeled, or specific indicators can be used as surrogates of exposure. Exposure monitoring has the advantage that it produces real exposure data on real individuals in known and real life conditions. However, an exposure monitoring programme covering a representative sample of the population is normally quite an expensive and labor-intensive process. Due to its invasive nature, it also has the tendency to more or less select the

subjects for the study and affect subject behaviour in the process, thus potentially modifying the exposure (Oglesby et al. 2000a).

The advantage of exposure modeling is that it can be used to assess past and future exposures, long-term exposures, and to compare e.g. population exposure differences of different urban development or air pollution mitigation alternatives. While there is a significant additional cost for each additional individual in exposure monitoring studies, the cost of exposure modeling is much less affected by the number of individuals or the size of the population (or the length of time) being modeled, thus favoring studies where the exposures of large numbers of individuals need to be assessed. While modeling individual exposures for specified days contain wide uncertainty margins, results become generally much more valid when population exposures over extended time periods are being modeled.

Fundamentally different logics have been applied in various approaches to exposure modeling. Physical (or deterministic) exposure models are based on logical/numerical constructs that attempt to mimic the physical and chemical reality that determines the exposure. Physical models can be expanded to quite different exposure settings and populations, as long as the model construct remains relevant for the study, but to be accurate, they tend to be very complex and require large databases. Empirical (statistical) models are usually based on best fit regression models of measured exposure vs. other measured parameters, which in principle are any parameters that are statistically significantly associated with exposure. Such models should not, without expert judgment or validation, be extrapolated from the original setting from which the data for the model was obtained. Probabilistic models are built on top of physical model constructs, but the input data, instead of being unique values, are drawn randomly from defined input data distributions (e.g. concentrations in homes of non-smokers, time spent in commuting by bus). Probabilistic models are quite useful for predicting the whole probability distributions of exposure. On the other hand, because of the random nature of data input, they cannot be used to predict the exposures of specific individuals.

Epidemiological studies would need to estimate the exposures of large cohorts or populations of entire cities over longer periods of time. So far, only crude exposure surrogates, usually based on centrally monitored outdoor air quality levels, and broad classification of the cohort members into some specific exposure groups (e.g. smokers and non smokers, homes with and without gas stoves, or individuals with and without occupational exposures) have therefore been used. Monitoring of the personal exposures in such epidemiological studies is clearly out of the question, but exposure-modelling techniques could be applied to improve exposure assessment from these exposure indicators. Further discussion about the validity and limitations of the use of centrally monitored outdoor air concentration as a surrogate of exposure is presented later in this chapter (Section 3.2).

### **3.1.1 Measurements of personal exposure**

The concentration of PM in the air inhaled by a person is not necessarily the same as that measured at a community outdoor air monitoring station. The concentration of PM near the breathing zone is called “personal exposure” and may be measured by a personal exposure monitor (PEM) carried by the person. There are several reasons why an individual’s personal exposure may be different from the outdoor concentration.

Firstly, the concentration of PM outside a person's home may be different from the concentration measured at a monitoring station. For some cities where sufficient information is available, PM concentrations measured at different pairs of stations (situated to measure community-wide pollution levels rather than individual source contributions) have been found to be highly correlated for PM<sub>2.5</sub> and PM<sub>10</sub>, although not for PM<sub>10-2.5</sub> (Wilson and Suh 1997). The average levels of PM<sub>2.5</sub>, however, are 40 – 60 % of PM<sub>10</sub>, depending on the location. These measures are, however, not always correlated, and often when correlated, the correlation is relatively weak

Secondly, people in developed countries spend on average over 90% of their time indoors, while people in the developing world over 70%. In the developed world the indoor microenvironment is usually protective in that the concentration of outdoor PM found indoors may be less than the concentration of ambient PM outdoors. In the developing world such protection from outdoor PM is usually minimal.

Thirdly, indoor sources, most importantly combustion of solid fuels for cooking and heating, and smoking, could significantly contribute to or even typically dominate the exposures – especially in developing countries and rural areas. Unless the air exchange rate is very high, the outdoor PM that infiltrates indoors will be removed by deposition more rapidly than it can be replaced. The ratio of PM of outdoor origin indoors to PM in outdoor air depends on the air exchange rate, and, also, on infiltration rate and deposition, both of which vary with particle size. The infiltration rate (concentration of particles per unit volume, penetrating from outside to inside in unit time) is at a maximum for particles in the accumulation mode (~ 0.3 to 0.7 µm aerodynamic diameter) and decreases for smaller (ultra fine) or larger (coarse-mode) particles.

Indoor sources of PM that contribute to personal exposure tend to produce ultra fine and coarse-mode particles rather than accumulation-mode particles. Important indoor sources are tobacco smoke, other open combustion for cooking and heating (ultra fine), cleaning-sweeping, dusting, vacuuming (coarse), and re-suspension due to walking on rugs (coarse).

The average infiltration of outdoor PM into indoor environments varies between buildings, between times of year, and depending on the weather situation (wind and temperature) and the behaviour of the occupants. This average infiltration may also differ significantly between different cities (e.g. 0.3 – 0.6) due to local climate and characteristics of the building stock. This fact may well explain some of the differences observed between the mortality and morbidity effects of outdoor PM levels in different cities.

### **3.1.2 PM exposure studies – a review**

On one hand recent epidemiological findings about the public health impacts of atmospheric PM and on the other hand the tremendous costs involved in significant reduction of the present PM levels in most regions of the industrialized world, lead to increasing demand for better information about.

- What chemical and physical characteristics of PM are most significant in relation to the health consequences observed,

- What environmental, micro-environmental and individual characteristics are most significant for personal PM exposures, and
- How much can the PM related health hazards be reduced by different control measures.

Personal exposure studies are needed to answer these questions. Provided below is a review of the PM exposure studies reported in the literature.

In an early study on non-occupational personal exposures to respirable particulate matter (RPM), 37 volunteers in Watertown MA and Steubenville OH carried personal samplers and filled time activity/diaries 12 h at a time (Dockery and Spengler 1981). This general study design has been repeated in all later PM exposure studies. The main result of this study was that the 12 h personal RPM exposure levels were in reasonably good agreement with the mean outdoor respirable particulate concentrations.

Some years later Sexton et al. (1984) assessed personal respirable particulate matter exposures of 48 volunteers in Waterbury Vermont. In this study homes were also equipped with similar indoor and outdoor micro-environmental RPM samplers. The main findings from the study were that outdoor particle level was not an important determinant of personal exposure, and personal exposures were on average higher than indoor air levels, which were again higher than outdoor air levels.

A total of 97 non-smoking volunteers in two rural Tennessee communities took part in personal RPM exposure measurement and modelling study conducted by Spengler et al. (1985). The volunteers carried personal samplers, their homes were equipped with indoor micro-environmental samplers, and outdoor levels were monitored by centrally located samplers in each of the towns. The new result was that the personal exposure levels of people who had been exposed to environmental tobacco smoke (ETS) were nearly twice as high as those of the non-exposed.

Lioy et al. (1990) monitored PM<sub>10</sub> in personal exposures and indoor microenvironments of 14 individuals and outdoor air in Phillisburg, NJ, in the Total Human Environmental Exposure Study (THEES). The new feature in the THEES study design was the fact that all study participants were monitored simultaneously for 14 consecutive days and nights. This design allowed exposure assessments across time and individuals (in epidemiological language) assessments of exposure variation at group level, and both within and between individuals. The former is relevant for longitudinal, the latter for cross sectional studies. In this first PM<sub>10</sub>-exposure study personal exposure levels were again higher than indoor and outdoor levels. Cross-sectional daily exposure levels were poorly associated with outdoor air levels but for group mean exposures, the association with outdoor air concentrations was strong. Individual longitudinal correlations between the personal and outdoor concentrations were statistically significant (with  $R > 0.75$ ) for only 6 out of the 14 subjects measured.

The U.S. EPA Particulate Total Exposure Assessment Methodology (PTEAM) study evaluated PM<sub>10</sub> exposures of the non-smoking population of Riverside, CA (Wallace et al. 1991; 1993; Clayton et al. 1993; Pellizzari et al. 1993; Thomas et al. 1993; Özkaynak et al. 1996). Personal PM<sub>10</sub> exposures, PM<sub>10</sub> and PM<sub>2.5</sub> concentrations inside and outside of the home and outdoor air

levels were monitored for the 178 study participants (a stratified probability sample including ETS-exposed and non-exposed from 10 to 70 years). Both gravimetric and elemental analyses were done. Daytime personal PM<sub>10</sub> exposure levels, as well as exposure levels of nearly all particle bound elements (except sulphur) were elevated relative to indoor and outdoor levels. Nighttime personal exposure levels were lower than outdoor but higher than indoor levels. Smoking, cooking, dusting and vacuuming were found to be the dominant indoor sources for high particle loads. PM concentrations in homes with ETS were considerably greater than those measured in homes without ETS. Cross sectional correlations of personal PM<sub>10</sub> exposures with central site outdoor concentrations were low for daytime but higher for nighttime exposures. (Clayton et al. 1993)

Backyard outdoor air PM<sub>10</sub> concentration showed a strong correlation with central site PM<sub>10</sub>, and personal 24 h exposure with residential indoor air, but the association between personal exposure and outdoor backyard air was weak, only 14 % of the variation of daily individual PM<sub>10</sub> exposures could be explained by respective variations in outdoor air PM<sub>10</sub>. However, for sulphur, which appeared to have no indoor or personal sources in Riverside, the outdoor air PM<sub>10</sub> bound sulphur explained 77 % of personal exposure (Özkaynak et al. 1996).

A large European multi-centre study to evaluate exposures to PM of urban dwellers in general and the role of ETS exposure in particular was conducted in Leeds (UK), Stockholm (Sweden), Bremen (Germany), Barcelona (Spain), Turin (Italy), Lisbon (Portugal) and Paris (France) (Phillips et al. 1994; 1996; 1997a; 1997b; 1997c; 1998a; 1998b). In the earliest study in Leeds, a personal sampler to collect “particles from all sources” - essentially TSP – was used. Later for the other cities (Stockholm ... Paris) a different RPM-sampler was selected. Only personal and no micro-environmental samples were collected in these studies. For the first time these results allow direct comparisons between cities, where the RSP exposures of non-smokers varied from 18 µg/m<sup>3</sup> in Stockholm to 54 µg/m<sup>3</sup> in Turin. Exposures were higher at work than in the home (except Stockholm). Smoking increased exposures relatively little in Barcelona and Lisbon, but in other cities the results were more in line with those reported from other studies, meaning that smoking was a significant contributor to exposure. Interestingly, the misclassification of the non-smoking/smoking status was also high (11 - 18 %) in Barcelona and Lisbon but modest (2-7 %) in the other cities (Phillips et al. 1998a), which might explain the observed differences between the impacts of smoking in the cities.

In the Netherlands, Janssen et al. (1997b; 1998; 1999) conducted a panel study in 1994-95 on personal PM<sub>10</sub> and PM<sub>2.5-3</sub> exposures and micro-environmental concentrations of primary school children and elderly adults in Amsterdam and Wageningen. Personal exposure of the participants was measured repeatedly a number of times, which allowed determinations of both individual regressions and cross sectional correlations between personal exposures and outdoor air concentrations. The cross sectional correlations of personal exposures with outdoor air concentrations were generally comparable to those reported in the THEES and PTEAM studies, poor overall, but significantly improved, when days with ETS exposure were eliminated, and the individual regression correlations were considerably better than the cross sectional correlations between personal PM exposures and outdoor air concentrations. Group exposures correlated quite well with outdoor air concentrations (extremely well for PM<sub>2.5</sub> among non-ETS exposed children).

A large-scale Research Triangle Institute study in Toronto had the principal objective to estimate the distribution of personal exposures of both smokers and non-smokers to manganese (from the use of gasoline additive, MMT, in Canada) in  $PM_{2.5}$ , but it also contributed broader information on personal exposures to  $PM_{2.5}$  (Pellizzari et al. 1999). Sampling was repeated for a new subset of the original sample monthly. The study showed that the cross sectional correlation of the personal exposure to outdoor air  $PM_{2.5}$  was low, but the results of the individual exposure - outdoor correlations from repeated sampling are not yet available.

The first large multi-centre personal  $PM_{2.5}$  (also CO, VOCs and  $NO_2$ ) exposure study was the European EXPOLIS study, where personal, home indoor and outdoor, and workplace concentrations of  $PM_{2.5}$ , 30 VOCs, CO and  $NO_2$  were measured from population samples ranging from 50 to 201 in six European cities (Athens, Basel, Grenoble, Helsinki, Milan and Prague). Identical equipment was used and the same operating protocols were followed in each centre, except Grenoble (Jantunen et al. 1998; Koistinen et al. 1999). The study design was based on random sampling of adult (25 - 55 year old) subjects, each monitored for 48 h. The new features in the EXPOLIS design were

- (i) Simultaneous sampling of populations of 6 cities in 6 countries;
- (ii) Sampling of multiple particulate and gaseous pollutants at the same time; and
- (iii) Sample timing, meaning that the samples were not collected for prefixed 24 or 12 hour periods (like THEES and others) or separately for day and night hours (like PTEAM), instead the workday, including commuting, and private time were monitored separately according to each subject's daily schedule.

The citywide annual average exposures (including smokers) differed widely between the cities from  $14 \mu g/m^3$  in Helsinki to  $48 \mu g/m^3$  in Milan. The workday exposures were higher (except in Basel) than private time exposures, with the biggest difference in Athens. In Helsinki the mean exposure of the smokers was nearly 3 times higher than of the non-smoke exposed (Rotko et al. 2000; Koistinen et al. 2000). The correlation between  $PM_{2.5}$  exposure and outdoor  $PM_{2.5}$  was non-existent for all smoke exposed. For the non-exposed this correlation was low during the workday, but much higher during private time. Comparison between the mean citywide long-term population exposure and the respective outdoor air  $PM_{2.5}$  showed a regression slope of essentially 1.0 and a very high correlation of 0.98. That is, annual average urban outdoor air  $PM_{2.5}$  level is an excellent predictor of long-term population exposure, although short-term outdoor air concentration is only a weak predictor of short-term individual exposures.

Oglesby et al. (2000b) analysed the elemental  $PM_{2.5}$  data from EXPOLIS Basel, to separately assess the exposure to  $PM_{2.5}$  from outdoor origin and of indoor origin. They found that the matter was more complicated than expected. While personal exposures to the spatially homogenous secondary outdoor PM (marked by  $SO_4^{2-}$ ) were strongly correlated with respective outdoor air levels, this correlation was weaker for traffic emitted PM, probably due to its spatial inhomogeneity and the activities of the exposed individuals.

In another study, Sarnat et al. (2000) investigated the exposures of 20 elderly non-smoking individuals living in Baltimore, MD, to  $PM_{10}$ ,  $PM_{2.5}$ ,  $SO_4^{2-}$ ,  $O_3$ ,  $NO_2$ ,  $SO_2$  and selected VOCs.

The 24 h measurements were repeated for each individual 12 times in the summer and in the winter of 1998-99. Only personal exposures were measured. The innovative feature of this PM exposure study was that two PEMs (similar as in PTEAM) were used, one to sample PM<sub>10</sub> at 2 L/min and other to sample PM<sub>2.5</sub> at 3.2 L/min. The cross sectional correlation between personal PM<sub>2.5</sub> exposures and outdoor PM<sub>2.5</sub> was relatively high for these individuals. During summer, the longitudinal Spearman's correlations varied highly between individuals, but were significant for 10 out of the 14, and the median correlation was as high as R = 0.76. In winter, the correlations were much weaker, and the median longitudinal correlation was R = 0.25. The interesting and new findings of this study are that the PM<sub>2.5</sub> exposures of elderly individuals with sedentary lifestyles are lower than outdoor air levels, and that while exposure to PM of outdoor origin and correlation between personal exposures and outdoor concentrations were reduced with decreasing ventilation, overall PM exposures were not reduced, probably due to increasing accumulation of fine PM from indoor sources.

Janssen et al. (2000) studied the PM<sub>2.5</sub> exposures of elderly non-smoking individuals with existing heart disease, and the relation of these exposures to outdoor PM<sub>2.5</sub> in Amsterdam and Helsinki. The exposure measurements were repeated biweekly 5 to 13 times for each participant. The results of this study agree well with those of Sarnat et al. (2000). The median (range) longitudinal Pearson correlation between personal PM<sub>2.5</sub> exposure and outdoor PM<sub>2.5</sub> was high both in Helsinki and Amsterdam. In Helsinki, but not in Amsterdam the mean PM<sub>2.5</sub> exposure level was lower than the mean outdoor PM<sub>2.5</sub>. Median exposures were below outdoor exposures both in Amsterdam and Helsinki.

Concluding from these two studies on elderly, non-smoking individuals with sedentary lifestyles, their personal PM<sub>2.5</sub> exposure levels are similar or below outdoor levels, and their personal exposure - outdoor PM<sub>2.5</sub>, correlations are on average high, but vary greatly between individuals and time of year.

A summary of the personal fine particulate matter exposure levels and corresponding levels measured in microenvironments such as homes, workplaces, adjacent outdoor environments and central outdoor air monitoring sites from the studies mentioned above are presented in Table 3.1. The table also includes data from the comprehensive review of indoor air PM studies of Wallace (1996).

**Table 3.1** The observed median levels for PM<sub>2.5</sub>, RPM and PM<sub>10</sub> in quoted American and European personal and micro-environmental PM exposure studies.

	PM <sub>2.5</sub> , RPM (µg/m <sup>3</sup> )	PM <sub>10</sub> (µg/m <sup>3</sup> )
Personal exposures	12 – 44	33 - 129
Home indoor levels	11 – 42	22 – 78
Home outdoor levels	8 – 40	18 – 83

Including data from developing countries would greatly increase the maximum levels for all of the measures in Table 3.1.

As a summary of the impacts of certain indoor activities on personal PM exposures and indoor concentrations, the most significant, at least in developed countries, is smoking. An average PM level increase in smoking vs. non-smoking environments is 30 - 40  $\mu\text{g}/\text{m}^3$  (Spengler et al. 1985; Sheldon et al. 1989; Clayton et al. 1993; Rotko et al. 2000; Koistinen et al. 2001) or doubling from the non-smoking level. Cooking increases PM exposures 7 - 26  $\mu\text{g}/\text{m}^3$  (Morandi et al. 1986; Clayton et al. 1993; Özkaynak et al. 1996), unvented kerosene heaters 5 - 30  $\mu\text{g}/\text{m}^3$  (Sheldon et al. 1989; Mumford et al. 1991) and wood stoves 0 - 10  $\mu\text{g}/\text{m}^3$  (Highsmith et al. 1988a; b; 1991; Sheldon et al. 1989; Santanam et al. 1990). Much higher PM concentrations are observed indoors in developing countries when biomass fuels are used for open-stove cooking and heating (WHO 2000a).

Table 3.2 presents a summary of the contributions of different sources to indoor and outdoor air PM. An application of source apportionment to determine the contributions of specific source categories to personal PM exposures is discussed in Section 3.3.

**Table 3.2** Summary of the contributions of different sources to indoor and outdoor air PM combined from the literature, quoted in the text. Note that, due to data availability, the contributions to indoor air levels are expressed in (%) of the total PM mass in indoor air, and to the outdoor air levels in ( $\mu\text{g}/\text{m}^3$ ). Except for smoking, other data are for conditions without smoking.

Source category	Range of indoor air (PM <sub>2.5</sub> - PM <sub>10</sub> )	Range of outdoor air (PM <sub>2.5</sub> - RPM)
smoking	24 - 71 %*	Negligible
cooking	25 - %*	2 - 3 ( $\mu\text{g}/\text{m}^3$ ) (frying fumes)
wood burning	3 - 21 %	1 - 4 ( $\mu\text{g}/\text{m}^3$ )
soil dust	4 - 50 %	1 - 23 ( $\mu\text{g}/\text{m}^3$ )
industry, heating	10 - 38%	4 - 6 ( $\mu\text{g}/\text{m}^3$ )
traffic emissions	5 - 30 %	5 - 17 ( $\mu\text{g}/\text{m}^3$ ) (mostly diesel)
secondary PM	Not available	11 - 22 ( $\mu\text{g}/\text{m}^3$ ) ( $\text{SO}_4^{=}$ , $\text{NO}_3^-$ , $\text{NH}_4^+$ )

\*where named activity takes place

### 3.1.3 Developing countries

A substantially smaller number of PM exposure studies have been conducted in the developing than in the developed countries (Smith et al. 1983; Mumford et al. 1987a; 1987b; Smith 1993). Indoor air quality studies have partly made up the missing data (Boleij et al. 1989; Collins et al. 1990; Raiyani et al. 1993; Li 1994; Brauer et al. 1996; Lee et al. 1997). It is important to realize that in cities of developing countries outdoor PM levels are usually very much higher due to dispersed heating with small scale solid fuel use, uncontrolled industrial emissions and the large quantities of non-catalyst two stroke engine vehicles. Indoor sources in the third world are a much more significant contributor to exposure than outdoor sources, particularly in rural areas. Unvented indoor combustion of solid fuels for cooking and heating is responsible for most of the very high indoor PM levels that have been observed.



In conclusion, while most of the PM exposure and health effects studies have focused on urban populations (mostly elderly individuals) in the developed world, most of the exposure - in terms of both the exposure levels and the numbers of individuals being exposed - and with all likelihood also the health consequences, occur in rural areas of developing countries, and the most affected populations are housewives and small children.

## **3.2 Relationships between personal exposures and outdoor concentrations**

Exposure analysts share a general belief that, in order for community time-series epidemiology to yield information on the statistical association of outdoor pollutant concentration, with a health response, there must be an association between personal exposure to a pollutant and the outdoor concentration of that pollutant. Several approaches have been suggested for rationalizing the paradoxical findings that correlations of pooled values of total personal exposure to (non-outdoor plus outdoor) PM have a low correlation with outdoor concentrations even though there is a statistically significant relationship between health effects and outdoor concentrations.

One important reason for these poor correlations is that many of the studies were based on pooled data, which means they included many individuals, who were generally monitored for only one or a few days and no distinction was made between those with high exposures to indoor sources such as smoking from those with much smaller exposures.

A better understanding of the relationship between personal exposure and outdoor concentrations is beginning to emerge from recent studies, which have followed individuals for extended periods of time.

The relationship between personal exposure and outdoor concentrations of PM is further complicated by the so-called “personal cloud” effect. This refers to the fact that personal exposure is generally found to be greater than the estimated time weighted average of indoor and outdoor concentrations, see Table 3.1. The size of the personal cloud is related to the level of activity of an individual and for PM<sub>10</sub> can be of the order of 50 µg m<sup>-3</sup> in people who are very active. By contrast sick or elderly persons because they are much less active, generate a much lower personal cloud. For PM<sub>2.5</sub> the personal cloud of non-smokers is much less pronounced, in average 0 – 7 µg/m<sup>3</sup> in the *EXPOLIS*-cities (Jantunen et al. 1999).

### **3.2.1 Longitudinal (same person, different days)**

Based on the longitudinal PM-exposure studies of Tamura et al. (1996) and Janssen et al. (1997a; 1998; 1999), the 1996 U.S. EPA PM Air Quality Criteria Document (US EPA 1996) pointed out that the correlation with outdoor PM concentration for a longitudinal series in which one person’s personal PM exposure was measured for several days was much higher than the correlation obtained from a pooled data set (different people, different days). Mage et al (1999) discuss this phenomenon in more detail. They explained why very low correlations with outdoor concentrations are obtained when people with very different non-outdoor exposures are pooled, even though their individual personal exposures are highly correlated with the outdoor concentrations. Wallace (2000) discusses this issue in a review of all then available studies with longitudinal data, and concluded that:

- For cohort studies in which each individual's daily health responses are obtained, it is clear that individual, longitudinal PM exposure data provide the appropriate indicator.
- The health responses of each individual can be associated with total personal exposure or components thereof.
- Also, the relationships of personal exposure indicators with outdoor concentration can be investigated.

### **3.2.2 Daily-average (same day, different people)**

In the case of community time-series epidemiology, it is not feasible to obtain experimental measurements of personal exposure for the millions of people over time periods of years that are needed to investigate the relationship between air pollution and infrequent health responses such as deaths or even hospital admissions. Epidemiologists must work with the aggregate number of health responses occurring each day and a measure of the outdoor concentration, which is presumed to be representative of the entire community.

Several analysts who have conducted community time-series epidemiology studies have discussed this issue and pointed out that the appropriate characterization of personal exposure that needs to have an association with outdoor concentrations is the daily community-average exposure (Schwartz and Levin 1999; Carrothers and Evans 2000; Samet et al. 2000a; Zeger et al. 2000; Dominici et al. 2000). The 1996 PM Air Quality Criteria for Particulate Matter (US EPA 1996) and Mage et al. (1999) make use of full matrix data sets from Tamura et al. (1996), Janssen et al. (1997a; 1998; 1999), and Lioy et al. (1990) to calculate a correlation between the daily average of all subject's personal exposures (sum) on a specific day and the outdoor concentrations on that day. For each of these three data sets, the regression of each day's daily average personal PM exposure against the outdoor PM concentration yields a higher correlation coefficient than either the pooled full matrix or the mean or median of the individual longitudinal regressions.

Outdoor concentration is an appropriate surrogate for personal exposure to outdoor fine (or accumulation mode) PM. Epidemiological studies of associations between long-term effects and long-term outdoor concentrations compare health outcome rates across cities with different outdoor concentrations. In non-smoking conditions in the developed world outdoor PM<sub>2.5</sub> is, indeed, for most populations the most significant source of PM<sub>2.5</sub> exposure. The highest exposures in the developed world as well as most PM exposures in the developing world, however, are not dominated by outdoor PM, but PM from indoor sources and personal activities, smoking, working, cooking, etc. Therefore, when individual level health outcomes are measured in small cohorts, it is necessary to measure both components of personal exposure and to determine if personal exposure to outdoor PM, personal exposure to non-outdoor PM, or total personal exposure (to outdoor plus non-outdoor PM) provide the best explanation of observed health effects.

### 3.2.3 Indoor-generated PM concentrations versus outdoor concentrations

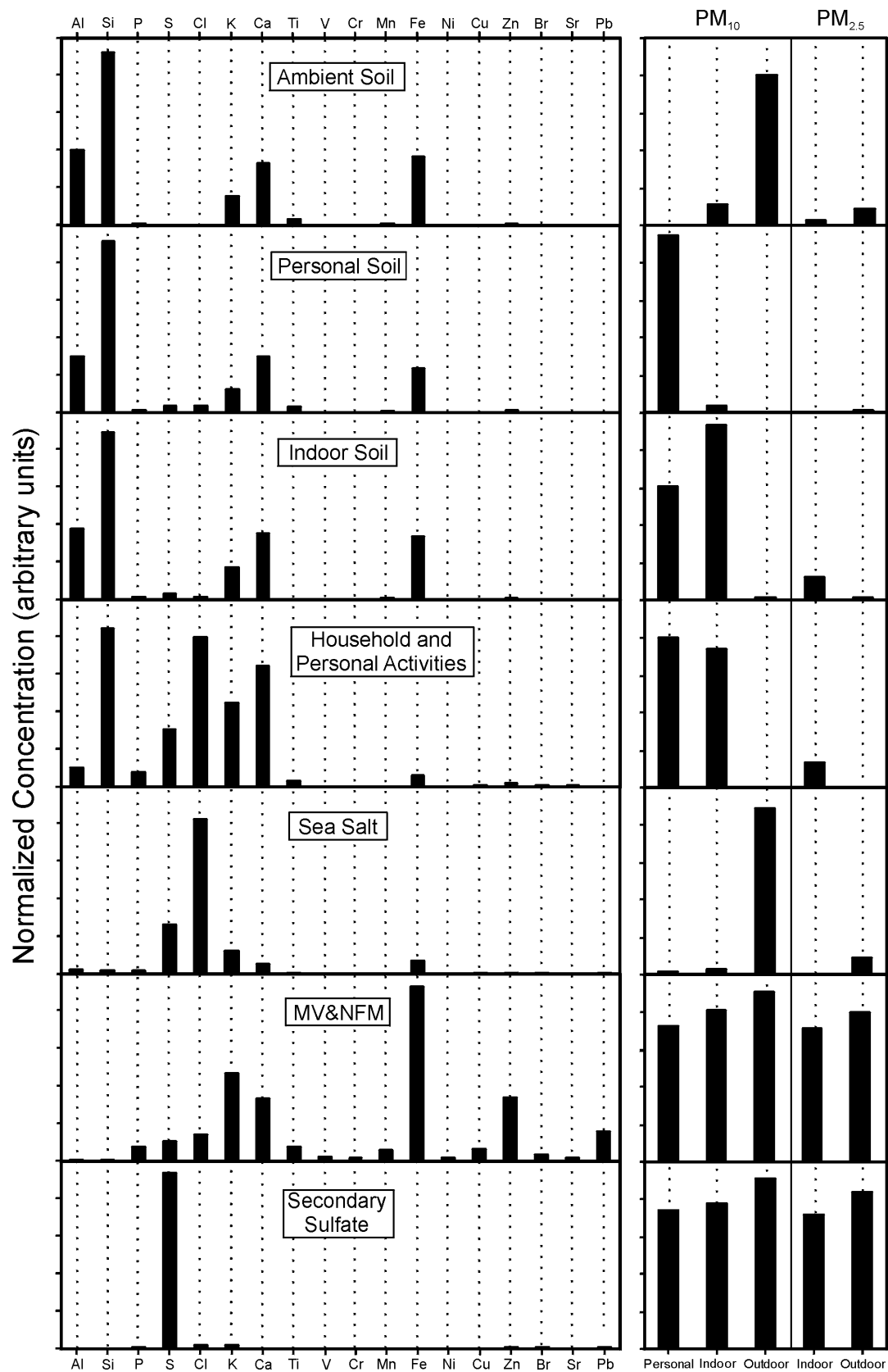
Mage et al. (1999) have shown that PM of outdoor origin and that of indoor origin appear not to be correlated in time. The authors took the PTEAM data set from Riverside, CA, at a time when the region had the highest annual mean concentration of outdoor PM<sub>10</sub>. Through measurements of air exchange rates between outdoor and indoor air, records of personal activity with respect to the fraction of time spent indoors and outdoors, the authors were able to estimate the exposure concentration of PM<sub>10</sub> generated by indoor sources and personal activities. A regression of estimated exposure to indoor PM<sub>10</sub> against local outdoor concentration was shown to be very poor. This led the authors to conclude that PM of indoor origin is unlikely to confound the basic linear relationship between health effects and outdoor concentrations.

### 3.3 Source apportionment from receptor measurements

Wilson et al. (2000) pointed out the importance of separating PM exposure into exposure to PM of outdoor origin and PM of indoor origin. Most of the health and concentration data that exists today applies to PM of outdoor origin, which may be controlled by regulating outdoor air sources. PM from indoor origin should be considered a separate issue for exposure, health and possible regulation.

In order to understand either the effects of particulate matter on health or to control the sources in order to mitigate health consequences it is necessary to have an understanding of where the particles in the breathing zone are coming from, and then at the receiving end, how much individual sources contribute at the point of exposure. Smith (1993) has shown that the same mass or number of particles emitted from different sources can have a 1,000,000-fold difference in population exposure. On the high risk extreme is mainstream tobacco smoke, out of which nearly ½ becomes someone's exposure, and on the low risk extreme the emissions of large power plants with high stacks. In between lie the indoor, neighbourhood and urban sources. The two main categories of source apportionment techniques are based on chemical/elemental mass balance modelling and different factor analysis techniques. These methods are discussed in more detail in Chapter 5.

The following example applies to the latter source apportionment technique. With a sufficient number of samples analysed with sufficient compositional detail, statistical techniques can be used to identify source category signatures and identify indoor and outdoor source categories and their contribution to indoor and personal PM. This has been demonstrated in a recent article in which positive matrix factorisation was used with XRF elemental data from the PTEAM database (Yakovleva et al. 1999). Seven source categories were identified. The elemental composition profiles and their contributions to personal, indoor, and outdoor concentrations for PM<sub>10</sub> and to indoor and outdoor PM<sub>2.5</sub> are shown in Figure 3.1. This study demonstrated that source categories associated with outdoor fine-mode particles were present at similar concentrations in outdoor, indoor, and personal samples (i.e., F and N ~1). Source categories associated with outdoor coarse-mode particles (soil and sea salt), however, did not appear to penetrate indoors significantly. Coarse-mode, soil-type particles were generated by two indoor source categories. One was the indoor soil dispersed throughout the house and the second was associated only with personal activity. Three-way PMF allowed differentiation of these two sources based on variation in time rather than variation in composition. An additional indoor source category, with a more complex composition than soil, was related to both household and personal activities. This approach has great promise. Databases containing more chemical detail and higher time resolution are needed to make the most of this technique which can easily be used to provide tracers for use in the tracer technique for separating outdoor and non-outdoor exposure. Such source apportionment techniques are equally applicable for data in the developing as well as the developed world.



**Figure 3.1** Elemental concentration profiles of source category factors from positive matrix factorisation and contribution of the seven source-categories to personal, indoor and outdoor concentrations. Source: Yakovleva et al. (1999).

## **4. Dosimetry**

In the general framework for risk assessment, exposure is linked through the dosimetry factors, dose and response factors to lifetime individual risk. Understanding of particle deposition in the respiratory tract is a very important aspect of framework for risk assessment as it affects the dose received to the lungs and to the body in general.

### **4.1 Particle deposition in the respiratory tract**

Factors influencing the deposition of inhaled particles can be classified into three main groups:

- 1) The physico-chemistry of aerosols
- 2) The anatomy of the respiratory tract
- 3) The airflow patterns in the lung airways

In relation to the first, the physico-chemistry of aerosols, the forces acting on a particle and its physical and chemical properties, such as size or size distribution, density, shape, hygroscopic or hydrophobic character and chemical reactions of the particle will affect the deposition. With respect to the anatomy of the respiratory tract, important parameters are the diameters, the lengths, and the branching angles of airway segments, which determine the deposition. Physiological factors include airflow and breathing patterns that influence particle deposition (Yeh et al 1976).

Large-size particles mainly deposit in the upper part of the respiratory tract due to impaction, interception, gravitational sedimentation, as well as turbulent dispersion. Very fine particles, such as generated through combustion processes, have a high probability of deposition in deeper parts of the respiratory tract, due to their high diffusivities.

The understanding of the mechanisms of particle deposition in the human respiratory tract and the ability to quantify the deposition in individual parts of the respiratory tract is of principal importance for dose assessment from inhalation of particles, which can then be used for risk assessment. Over the last three decades or so, a large number of studies have been conducted to investigate particle deposition in the human respiratory tract, with a somewhat larger number focused on theoretical modelling than on the experimental determination of the deposition.

### **4.2 Experimental studies on total lung deposition**

As presented in a review by Morawska et al. (1999), the small number of experimental studies of lung deposition for human subjects differ in the area of deposition investigated (total or various fractional depositions), type of aerosol inhaled, characteristics of the aerosol (age, size distribution, concentration, humidity, etc), type of inhalation (natural, artificial, controlled) and finally the experimental techniques and instrumentation used. These are combined with an uncertainty related to large inter-subject variability and, often, to the small number of subjects investigated (less than five in a number of studies). All these factors can have a significant effect on the outcome of the study and thus comparison of the results obtained from studies, which

differed in too many of the above variables becomes more of a speculation than a meaningful quantitative evaluation.

Most of the experimental studies conducted investigated total deposition as it can be measured directly and thus most accurately. The results from earlier experimental studies of nine investigators summarized by Lippman (1977) conducted under normal breathing conditions and mouthpiece inhalation indicated relatively low values of deposition, on average about 28% for particles of geometric diameter of about 0.1  $\mu\text{m}$ , and of about 18% for particles of 0.4  $\mu\text{m}$ . Heyder et al. (1973) reported even lower values of total deposition of about 0.1 in experiments conducted on deposition of di-2-ethylhexyl sebacate (DES) at controlled breathing conditions for particles in the size range of 0.2 – 1  $\mu\text{m}$ . Later studies on the deposition of the same aerosol (Heyder et al. 1986) conducted on controlled breathing for three subjects showed that for particles in the size range from 0.1 to 0.4  $\mu\text{m}$  total deposition for different breathing patterns varied from 0.12 (minimum for 0.4  $\mu\text{m}$  particles) to 0.51 (maximum for 0.1  $\mu\text{m}$  particles). From mainstream cigarette smoke inhalation experiments conducted on 11 subjects, Hinds et al. (1983) obtained much higher values of total deposition. The average total deposition was found to be 47% (range 22 – 75%), which was, however, concluded to be less than deposition values in the range from 0.7 to 100% for total deposition of mainstream smoke reported in different studies summarized by the authors. More recent studies by Strong et al. (1994) on inhalation of environmental tobacco smoke (ETS) of count median diameter (CMD) of 0.21  $\mu\text{m}$  by non-smoking subjects reported total deposition for nose breathing of  $(59 \pm 10)\%$ , for mouth breathing  $0.43 \pm 0.17$ , and for increased speed mouth breathing  $(22 \pm 8)\%$ . Very similar to these were the results obtained by Morawska et al. (1999) for total deposition of ETS in the size range from 0.1 to 0.5  $\mu\text{m}$  of  $(56.0 \pm 15.9)\%$  for natural nose breathing and  $(48.7 \pm 11.6)\%$  for natural mouth breathing.

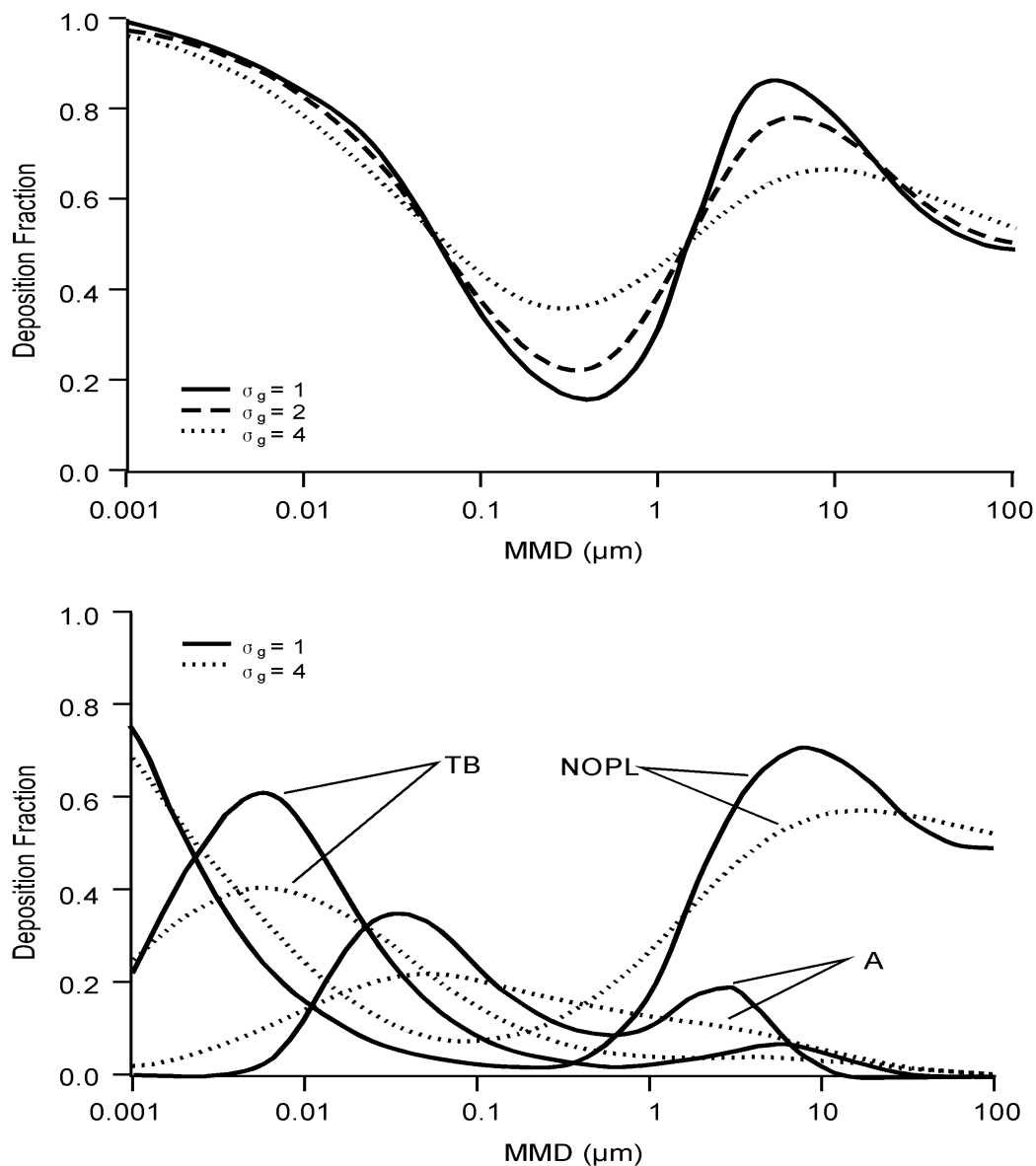
One hypothesis from the brief review above could be that, in general, lower values of total deposition are obtained for particles other than cigarette smoke and higher for cigarette smoke. However, this conclusion may not necessarily be justified, since deposition of different types of aerosols has not been conducted under the same conditions and in fact, the conditions were very different.

### **4.3 Modelling of particle deposition in the lung**

In terms of theoretical predictions, a comparison between different modelling approaches shows that, with general agreement as to the total deposition levels, there are often significant discrepancies in the values for fractional (i.e., regional and generation-by-generation) deposition (Hofmann 1996; Hofmann et al. 2001). The numerical models of particle deposition in the human lung that have been proposed are based on different morphometric lung models, utilize different deposition equations, and employ different computational techniques, it is thus not surprising that the resulting deposition fractions exhibit significant variations at the single airway generation level. Lack of agreement for fractional deposition, however, may put under a question mark the reliability of the agreement for total deposition values, since different combinations of fractional deposition values may lead to the same total deposition value.

Two commonly used lung deposition models are those of Yeh and Schum (1980) and Yu and Dju (1982). These models represent the respiratory tract as a branching network of airways, with each generation characterized by the number of airways and their length and diameter. Particle

deposition in each generation is computed by deterministic formulae, accounting for gravitational deposition, impaction, and diffusion. Interindividual variation of airway structure leading to variability in the model has been taken into account by including two random scaling factors (one for the tracheo-bronchial region and one for the alveolar region). It was shown that airway size is the single most important factor in the consideration of inter-subject variability of total and regional deposition under normal steady breathing conditions. Figure 4.1 presents calculated total and regional mass deposition from polydisperse aerosols (Yeh et al. 1993).



**Figure 4.1** Calculated mass deposition from polydisperse aerosols of unit density with various geometric standard deviations ( $F_g$ ) as a function of mass median diameter (MMD) for quiet breathing (tidal volume = 750 mL, breathing frequency = 15 min<sup>-1</sup>). The upper panel is total deposition and the lower panel is regional deposition (NOPL = Naso-oro-pharyngo-laryngeal, TB = Tracheobronchial, A = Alveolar). The range of  $F_g$  values demonstrates the extremes of monodisperse to extremely polydisperse. Source: Yeh et al. (1993).

These and other models of lung deposition, for example, Heyder et al. 1986, predict a minimum deposition at about 500 nm. From such models a deposition of 10-20% is expected in the predominant range of ETS particles. Modeling of ETS is often based on the assumption that saturated, spherical NaCl droplets have hygroscopic characteristics representative of cigarette smoke particles. This assumption provides results for total particle hygroscopic growth that predicts an increase in mass median diameters of about three times their original values. It is also assumed that hygroscopic growth of ETS is a dynamic process within the entire extrathoracic region (Martonen et al. 1994).

For mainstream smoke particles theoretical deposition models predict total deposition in the range of 5% - 50% for mouth breathing of monodisperse, non-hygroscopic aerosols, with most values falling around 20%<sup>9</sup>. For sidestream smoke Muller et al. (1990) predicted about 6% - 28% particle deposition. For particles less than about 200 nm MMD, the total deposition of hygroscopic particles is expected to be less than for non-hygroscopic particles (Persons et al. 1987). The enlargement of hygroscopic particles in the humid conditions of the lungs decreases the probability of deposition.

#### **4.4 Comparison between experimental and modelling approaches**

The ultimate proof that the understanding of the lung deposition process is complete would be a consistency between the results obtained from experiments and from theoretical modelling. However, examination of the data reported in the literature on the experimental approach alone, reveals that there are significant discrepancies between the results obtained by different researches on aerosol deposition in the respiratory tract, not only for different types of aerosol, but also for the same types. The discrepancies are not necessarily due to poor experimental design, but could result from different testing conditions, differences in the instrumentation used for particle measurements, or other factors. These factors can have a significant effect on the outcome of the study and thus comparison of the results obtained from studies which differed in too many of the above variables, becomes more speculation than a meaningful quantitative evaluation.

In terms of theoretical predictions, a comparison between different modelling approaches shows that, with general agreement as to the total deposition levels, there are often significant discrepancies in the values for fractional deposition. Lack of agreement for fractional penetrations may put under a question mark the reliability of the agreement for total deposition values.

All published deposition models have been validated by comparison with total and regional deposition data in human test subjects. However, as discussed by Hofmann et al. (2001), uncertainties still exist:

- Despite the generally good agreement with total deposition data, they are not strong proof of the validity of generation-based deposition models.
- The comparison with regional, i.e., bronchial and alveolar, deposition data suffers from the still missing unambiguous identification of the slow clearance phase observed in lung retention measurements; in contrast, the computation of regional deposition is based on lung morphometry and not on clearance.



- Although the different models predict substantial differences in deposition in individual airway generations, no experimental data presently exist which can be compared with the predicted data. In the near future, three-dimensional Single Photon Emission Computed Tomography (SPECT) data may provide at least part of this information (Hashish et al. 1998; Hofmann et al. 1997).

In addition, there is lack of models for people with lung and heart disease as well as smokers.

## 4.5 Links between exposure and dose

Dose is the amount of agent that enters a biological target over a specified time interval as intake or uptake (WHO 2000c). Applied dose is the amount of the agent directly in contact with the absorption barriers, such as the skin, respiratory tract and gastrointestinal tract (WHO 2000c). In general terms the dose depends on the exposure to the pollutants present in the air and the dosimetry factors.

Dosimetry factors characterize how much of the pollutant present in the air enters the body and is absorbed by different organs. This depends on the inhalation rate, absorption rate, average body weight, average lifetime, regional surface area of the lung, regional dose ratio, breathing pattern, and sex and age.

Dose is a function of exposure and dosimetry factors and quantifies the amount of substance available for interference with metabolic processes or biologically significant receptors. This applies to pollutants only but not to environmental conditions or environmental factors. Administered dose is the dose of the contaminant or its metabolites deposited in the body. Biologically effective dose is the dose received at the target cell.

Liu (1994) reviewed dose modelling. Standard dose models consist of algebraic equations that involve the major relevant variables. The dose for inhalation of chemicals in the air in particulate form is expressed as follows (Liu 1994):

$$D_p = \frac{C_p \times IR_a \times P_a \times RF \times ET \times EF \times ED}{BW \times AT}$$

where  $D_p$  is the dose from inhalation of airborne particles (mg/kg-day) and  $C_p$  is the chemical concentration of the airborne particles ( $\text{mg mg}^{-1}$ );  $IR_a$  is the inhalation rate ( $\text{m}^3 \text{h}^{-1}$ );  $P_a$  is the particle concentration in the air ( $\text{mg m}^{-3}$ );  $RF$  is the respirable fraction of particle (dimensionless);  $EF$  is the exposure frequency (days/year);  $ED$  is the exposure duration (years);  $BW$  is the body weight (kg);  $AT$  is the averaging time (days); and  $ET$  is the exposure time (hours/day).

Application of this equation in the dose, or more broader risk assessment to particles that is caused by virtue of the mass and nature of chemical components has been verified. However, application of this equation to other physical characteristics has not been verified. According to the current hypotheses, it could be particle number or surface area that is more directly linked to certain health effects. If these hypotheses are accepted, new approaches to dose quantification as a function of these characteristics may need to be developed.

## **5. Particle Characterization for the Purpose of Exposure and Health Risk Studies**

Airborne particulate matter is a mixture of solid particles and liquid droplets, which vary in concentration, nature and size distribution. The particles can be, for example, combustion products, dust or bioaerosols, and can act as carriers of adsorbed chemicals, bio-contaminants or condensed gases. A primary particle is a particle introduced into the air in solid or liquid form, while a secondary particle is formed in the air by gas-to-particle conversion of oxidation products of emitted precursors

The size of airborne particles is significant as it determines their dynamic properties and thus behaviour in the air and fate during transport and in particular, strongly influences in which part of the respiratory tract the particles are deposited. Larger particles, due to their higher inertia are deposited in the nasal area and in the upper parts of the respiratory tract. By contrast, smaller particles that can follow the airflow to the deeper parts of the respiratory tract have a very high probability of depositing in those parts by diffusion, which is a very efficient deposition mechanism for small particles.

It is, however, not only the number or mass of particles in the particular size range that is important, but also the composition of particles. The composition may determine in what way the respiratory tract reacts, or the body responds. The highest level of concentration of trace elements (Thomas and Morawska 2001) and toxins from anthropogenic sources and radioactivity from natural sources is related to the very small particles. The large particles carry components and elements mainly of crustal origin, mainly from natural sources. Some particles can act as carriers of adsorbed chemicals or gases which can act as triggers for various health effects.

In this chapter, particle physical and chemical properties will be discussed with the main focus on their relevance to exposure and human health studies. The properties will also be discussed in terms of their relation to the sources generating the particles. This will help to identify the parameters or their ranges that should be specifically targeted for various types of emission sources operating in the environment under investigation.

### **5.1 Physical characteristics**

Some of the most important physical properties of particles include:

- Number and number size distribution
- Mass and mass size distribution
- Surface area
- Shape
- Hygroscopicity
- Volatility
- Electrical charge

While each of these characteristics is important in terms of playing a role in affecting particle dynamics and thus behaviour and fate in the air and in the human respiratory tract and under specific circumstance can become the leading one, the key ones that are always critical are the first two and these will be discussed in this chapter in more detail.

### **5.1.1 Particle equivalent diameters**

One of the most basic particle properties is its size, most often characterized by particle diameter. Diameter is a characteristic of spherical objects, but in fact, only a small fraction of particles are spherical. Therefore a way of representation of particle irregular shapes has been introduced by means of particle equivalent diameter. Particle equivalent diameter is the diameter of a sphere having the same value of a physical property as the irregularly shaped particle being measured. Equivalent diameter relates to particle behaviour (such as inertia, electrical or magnetic mobility, light scattering, radioactivity or Brownian motion) or to particle properties (such as chemical or elemental concentration, cross-sectional area, volume to surface ratio). Therefore particle diameter determined experimentally depends on the choice of particle properties or behaviour measured.

The most commonly used equivalent diameters in application to exposure and health studies are aerodynamic (mainly for particles larger than 0.5  $\mu\text{m}$ ), diffusion (for particles smaller than 0.5  $\mu\text{m}$ ), light scattering (for various ranges from about 0.1  $\mu\text{m}$  and larger), and mass equivalent (mainly for larger particles). For example, aerodynamic (equivalent) diameter is the diameter of a unit-density sphere having the same gravitational settling velocity as the particle being measured. Understanding of which particle diameter is actually determined in a particular study is important for quantitative risk assessments and for comparison between different studies. For more details on particle equivalent diameters and methods for calculation of them see, for example, Willeke and Baron (1993).

### **5.1.2 Particle sizes and size distributions**

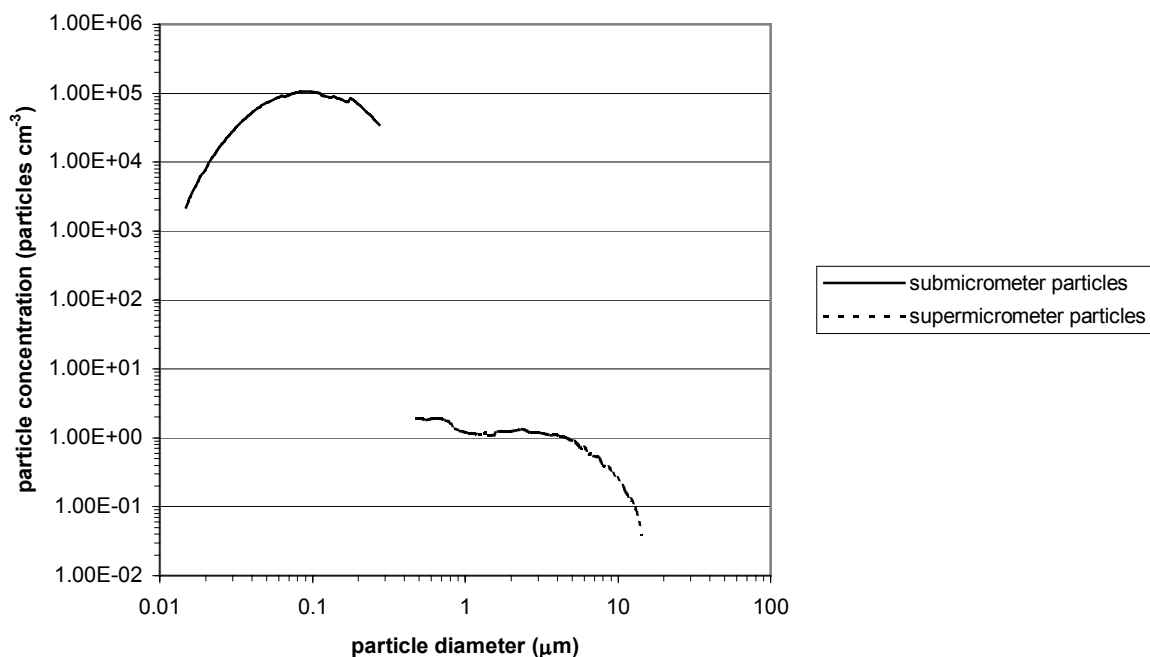
An important characteristic of airborne particles is their size distribution as it strongly affects particle behaviour and fate in atmospheric systems and their deposition in the human respiratory tract, and also determines the instrumentation to be used for particle detection. Almost all of the sources of particles in outdoor air generate particles with some distribution of the sizes, so called polydisperse aerosol, rather than particles of a single size, monodisperse aerosol. The spread of particle size distribution is characterized by an arithmetic or geometric (logarithmic) standard deviation

Size characterization most commonly used:

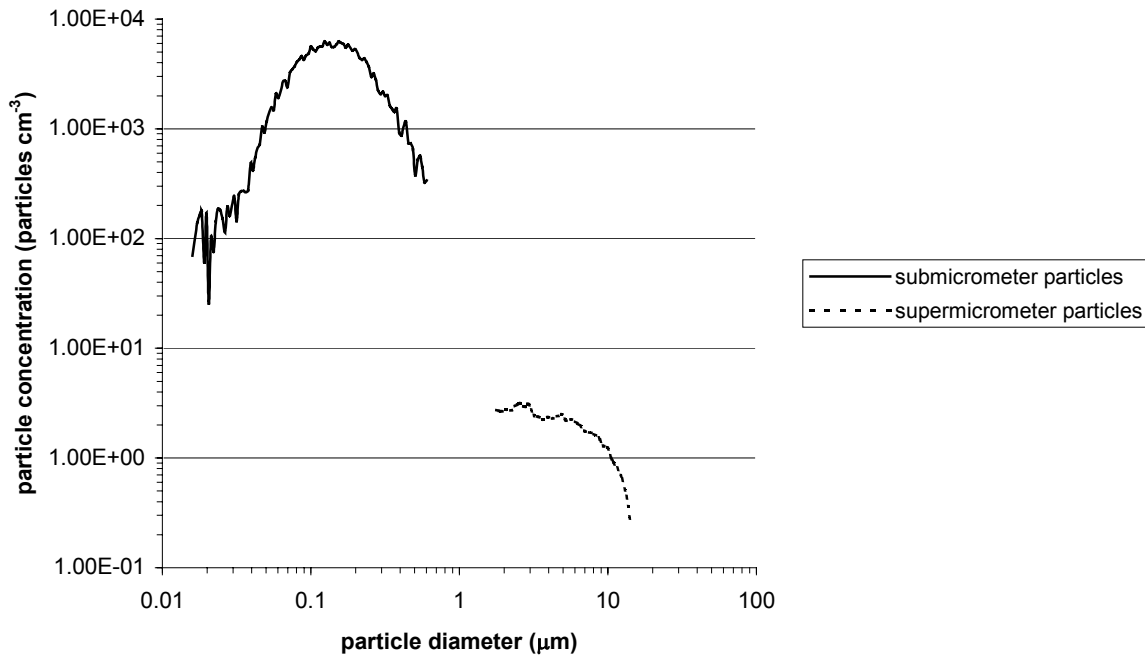
- Mean size - average of all sizes
- Median size - equal number of particles above and below this size. Often used are: count or number (equivalent terms) and mass median diameter CMD, NMD or MMD
- Mode size - size with the maximum number of particles

Particles generated by most sources have a lognormal size distribution, which means that the particle concentration versus particle size curve is “normal” (bell shaped) when the particles are plotted on a logarithmic scale. Geometric standard deviation characterises the width of the peak in the distribution. Particle size distributions often to contain one or more distinct peaks, called modes of the distribution. Willeke and Baron (1993) and Hinds (1999) give extensive

information on the use and interpretation of lognormal particle size distributions. As an example, typical size distributions of emissions from diesel vehicle emissions (Morawska et al. 1998a) and from environmental tobacco smoke (ETS) (Morawska et al. 1997) are presented in Figure 5.1 a and b. The distributions presented illustrate the point that different emission sources are characterized by different size distributions. While these distributions are not unique to these particle sources alone, if, however, a particular source has been characterized in terms of its size distribution, this information can help to identify its contribution to particle concentrations in outdoor air, expected areas in lung deposition and the instrumentation needed for their measurements. It has, however, to be kept in mind that size distributions change their shapes due to various factors affecting emission from the sources or the particles after the emission and thus the understanding of these factors is important for interpretation and using of the distributions.



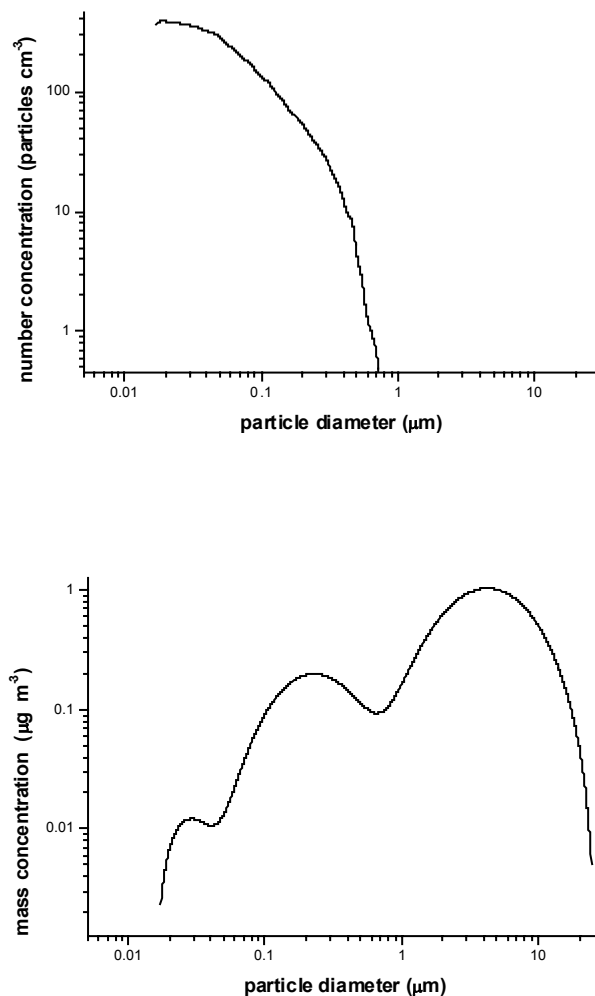
**Figure 5.1a** Size distribution of particles from a diesel bus running on low power, measured independently by two different instruments in the submicrometer and supermicrometer ranges (after Morawska, et al. 1998a).



**Figure 5.1b** Size distribution of side stream smoke produced by a human smoker. The measurements were performed independently by two different instruments in the submicrometer and supermicrometer ranges (after Morawska, et al. 1997).

There are no instruments that can measure the entire particle size range, from nanometers to tens of micrometers (see also Chapter 6) and usually there is a size range selected for investigations that depends on the objectives of the investigations. Various classifications and terminologies have been used to define particle size ranges. According to the most common definition used in aerosol science and technology, fine particles are defined as those with an aerodynamic diameter smaller than  $1\text{ }\mu\text{m}$  while ultra fine particles are those below  $0.1\text{ }\mu\text{m}$ . Accordingly, coarse particles are defined as being in the range between  $1$  and  $10\text{ }\mu\text{m}$  (Willeke and Baron 1993). The rationale behind this classification is, that one micrometer constitutes a natural division between particles, which are generated mainly from combustion processes and are smaller than particles, which are generated from mechanical processes. Obviously this definition is still somewhat arbitrary, as nature itself does not provide a perfect division. The minimum between the accumulation and coarse modes varies between  $1$  and  $2.5\text{ }\mu\text{m}$  depending for example on the relative humidity. In damp climates with low coarse mode concentrations, a separation at  $2.5\text{ }\mu\text{m}$  may be more likely, while in dry areas with high concentrations of coarse mode particles, separation will be more likely at  $1.0\text{ }\mu\text{m}$ . The terminology that has been used by the US Environmental Protection Agency (US EPA 1996) in the wording of the outdoor air quality standards included  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  fractions.  $\text{PM}_{2.5}$  fraction (or fine particles) is mass concentration of particles with aerodynamic diameters smaller than  $2.5\text{ }\mu\text{m}$ , while  $\text{PM}_{10}$  fraction mass concentration of particles with aerodynamic diameters smaller than  $10\text{ }\mu\text{m}$  (more precisely the definitions specify the inlet cut-offs for which 50% efficiency is obtained for these sizes). Coarse particles are then the fraction  $\text{PM}_{2.5} - \text{PM}_{10}$ . The US EPA definitions of fine and coarse particles are more commonly used for practical applications.

Particle distributions can be presented either in terms of number or mass distributions. In terms of number, the vast majority of airborne particles are in the ultra fine range. For example, in an urban environment where motor vehicle emissions are a dominant pollution source, over 80% or more of particulate matter in terms of number is in the ultra fine range (Morawska, et al. 1998b). The total mass of these particles is, however, often insignificant in comparison with the mass of a small number of large particles with which most of the mass of airborne particles is associated. This relationship between particle number and mass is presented in Figure 2 on an example of an urban air particle size distribution (Morawska 2000). This relationship was derived using measured particle number size distribution and calculating particle mass distribution assuming their sphericity and a density of the particles of  $1 \text{ g.cm}^{-3}$ .

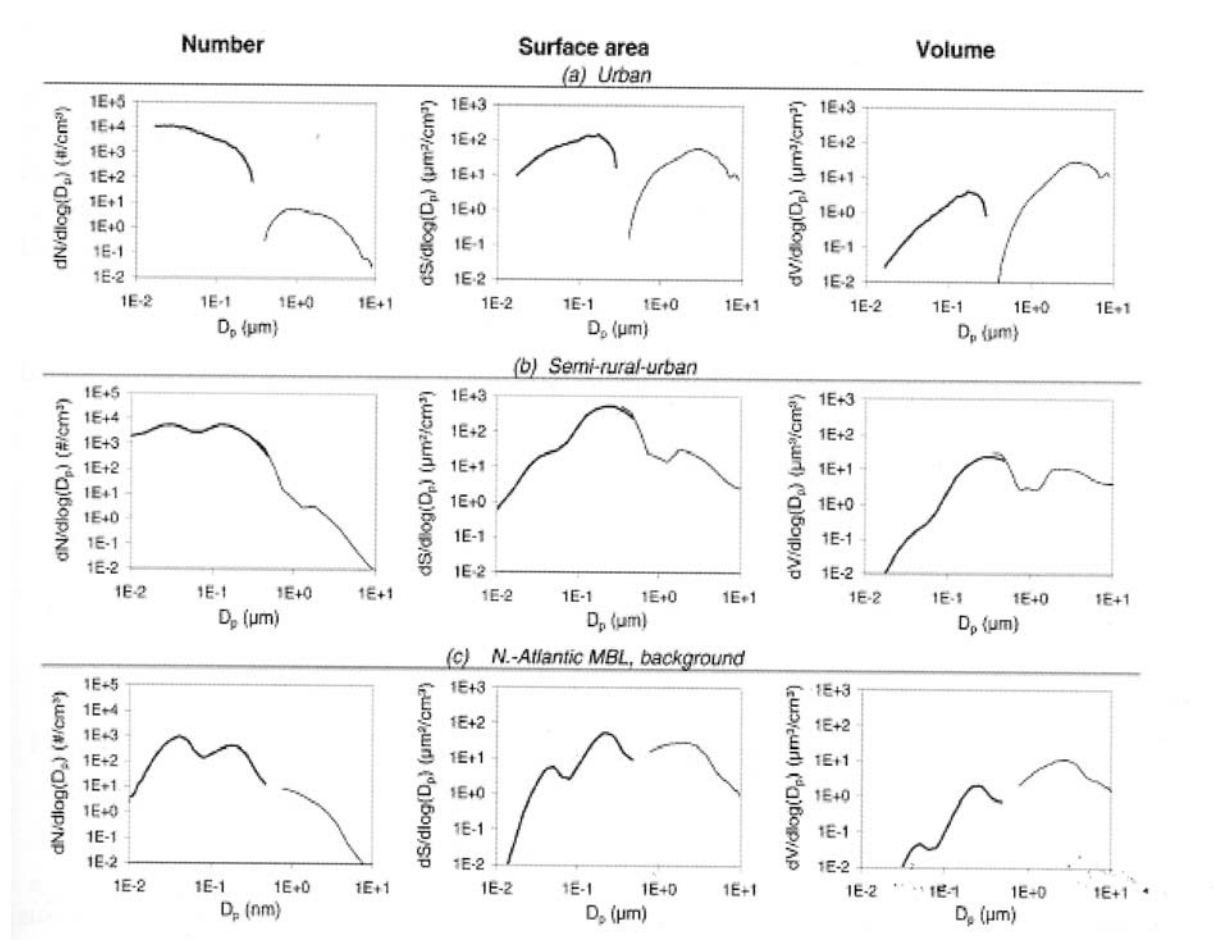


**Figure 5.2** Urban air particle number size distribution typically measured in Brisbane, Australia (upper diagram), and mass distribution (lower diagram) calculated from the number distribution (Morawska 2000).

This relationship between particle number and volume is presented in Figure 5.3 (adapted from Raes et al. 2000) for a number of outdoor conditions, including urban, semi-rural and North Atlantic polluted air. This relationship was derived using measured particle number size distribution and calculating particle volume distribution assuming their sphericity. Note that

particle size distributions are plotted as  $dN/d\log D_p$  and  $dV/d\log D_p$ , which is commonly used in representing size distributions of aerosols ( $D_p$  denotes the particle diameter). The figure illustrates in the first place the large variability in particle number and volume observed in conditions near or away from sources. Highest number and mass are observed in the urban environment. The occurrence of modes, arising from physical and chemical processes and from mixing is also clearly illustrated (Raes et al. 2000). Further, the figure shows that number and mass are distributed in a different way: in terms of number, the vast majority of airborne particles are in the ultra fine range. The semi-rural example (35 km away from an urban agglomeration) however shows that also the fine aerosol can contribute significantly to total aerosol mass.

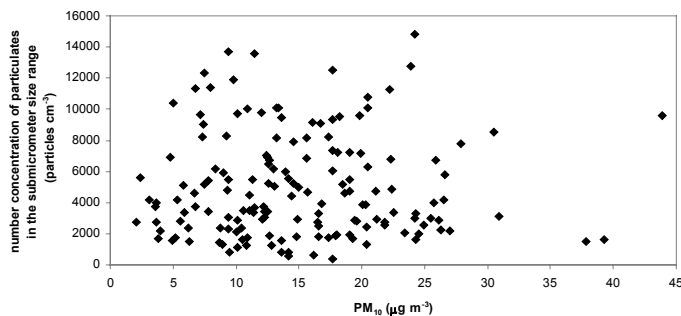
Figure 5.3 also clearly illustrates that the parameter “particle number concentration” has only a meaning when the lowest detected particle size (cut-off size) is mentioned. As indicated in chapter 6, various types of particle counters are available having cut-off diameters ranging from 3 nm to some 100 nm which would results in large deviations in measured concentrations for identical air samples.



**Figure 5.3** Number and volume size distributions observed at (a) an urban site (Milan, Italy); (b) a semi-rural-urban site (semi-rural area 35 km from Milan, Italy); (c) a remote marine site, 2 days downwind the European continent (Tenerife in the North-East Atlantic) (modified from Raes et al. 2000)

Fine particles are generated mainly from combustion processes, photochemical processes and gas to particle conversion and typically contain a mixture of soot, organic compounds, acid condensates, sulfates and nitrates, as well as trace metals and other toxins. Coarse particles are generated mainly from mechanical processes including grinding, breaking and wear of material and dust resuspension and contain largely earth crustal elements and compounds. While some processes result in generation of particles with a broad size distributions, covering both fine and coarse ranges (for example in close proximity to forest fires there are airborne combustion products of the fire as well as large diameter particles that are entrained into the smoke column as a result of the turbulence and buoyancy generated by the fire), in most cases, fine and large particles result from totally different generation process. Thus fine and coarse airborne particles, or particle number and mass are not always correlated, and often when correlated, the correlation is relatively weak. Figure 5.4 presents a scatterplot of particle data in terms of  $PM_{10}$  and particle number in the submicrometer size range collected over a period of two years in downtown Brisbane, Australia (Morawska et al. 1998b). As can be seen, there is no correlation between these two particle characteristics, which indicates that different sources contribute to generation of particles in the submicrometer range, which is predominant in particle number, and to larger particles, which predominate in mass. Various studies conducted on correlation between different particle characteristics and in particular on correlation between mass of particles in different size ranges, often point out to better correlations than presented here. The degree of correlation depends on specific local conditions, of which the degree of contribution from different sources is of a key importance. Better correlations are achieved for conditions when the majority of particles in the fine and coarse size ranges is related to the same source.

It is evident from above, that from the measurements of total particle mass only limited information, or no information at all can be obtained about particle number.



**Figure 5.4** Number concentration of particles in the size range 0.016 to 0.626µm versus  $PM_{10}$  mass concentration (Morawska et al. 1998 b)

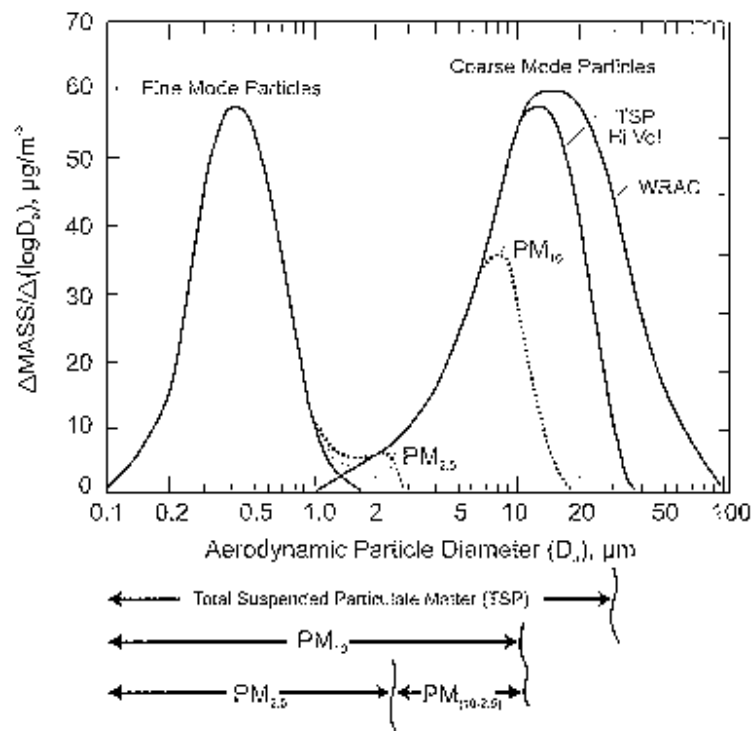
**In summary, it is important to bear in mind that:**

1. Particle size determines particle behaviour (ageing, transport, deposition) and that particle size and shape are:
  - Closely linked to formation and post formation processes
  - Often defined only to the extent that one can measure and calculate them



2. The fine and coarse mode particles:
  - Originate separately
  - Are transported separately
  - Have different chemical composition
  - Are removed from the atmosphere by different mechanisms
  - Require different detection techniques

Figure 5.5 present an example of a mass distribution of outdoor particulate matter as function of aerodynamic diameter. A wide-ranging aerosol collector (WRAC) provides an estimate of the full coarse mode distribution. Inlet restrictions of the high volume sampler for TSP, the PM<sub>10</sub> sampler, and the PM<sub>2.5</sub> sampler reduce the total mass reaching the sampling filter.



**Figure 5.5** An example of a mass distribution of outdoor particulate matter as function of aerodynamic particle diameter.

## 5.2 Chemical characterization

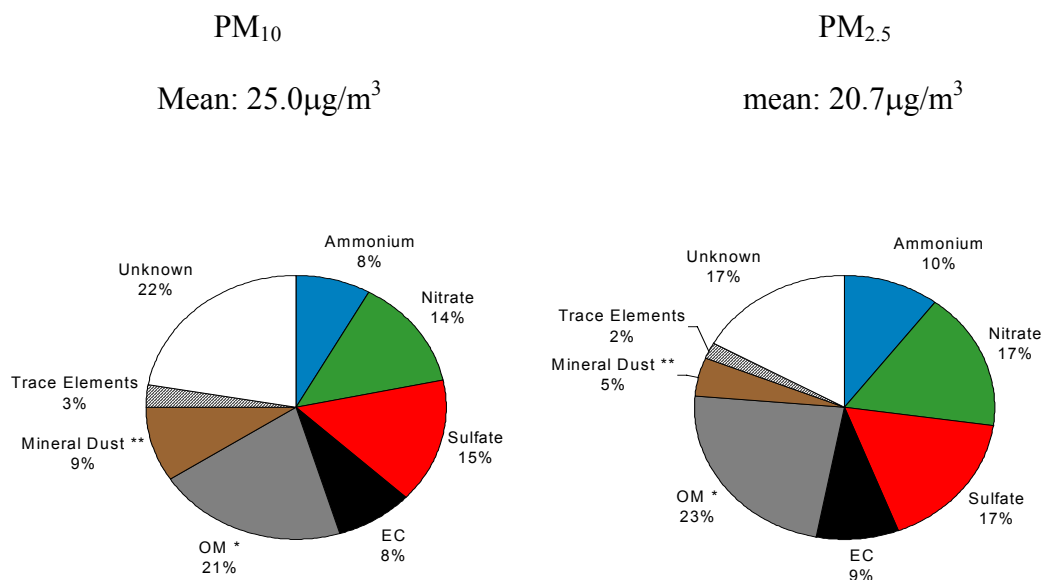
The most important chemical properties of particles that will be discussed in this chapter include

- Elemental composition
- Secondary inorganic ions
- Carbonaceous compounds
- Organic composition

As an example Figure 5.6 presents the major components of the atmospheric aerosol in Zurich, both for PM<sub>10</sub> and PM<sub>2.5</sub> (Hueglin 2000). It can be seen from figure 5.4 that the contributions to

PM<sub>10</sub> may be classified into three major classes each comprising about one third of the aerosol mass:

- i) Inorganic ions (mainly sulphate, nitrate and ammonium),
- ii) Carbonaceous aerosols (organic and elemental carbon), and
- iii) The remainder, composed of mineral dust and an 'unknown' component (mainly water, as will be shown below).



**Figure 5.6.** Pie chart of the major components of the atmospheric aerosol in Zurich; \*OM (organic material) is calculated from organic carbon using a factor of 1.4 to account for heteroatoms in OM; \*\* mineral dust is calculated from the aluminum content of the samples (Hueglin 2000).

Below different chemical properties of particles are described in more detail.

### 5.2.1 Secondary inorganic ions

The main atmospheric source of secondary particles is the oxidation of SO<sub>2</sub> and NO<sub>x</sub>. Oxidation of SO<sub>2</sub> always results in the formation of aerosol mass, due to the low H<sub>2</sub>SO<sub>4</sub> vapour pressure, and is in contrast to HNO<sub>3</sub>, which is distributed between the gas and aerosol phases. The chemical transformation of gases into particles depends on many factors including chemical reaction kinetics and physical factors such as plume mixing and dispersion, oxidant concentration, sunlight, catalytic aerosol surfaces etc. Despite this, the conversion rates of SO<sub>2</sub> are generally around 1 - 2% per hour and about 10 times higher for nitrate. SO<sub>2</sub> is emitted both by natural and anthropogenic sources. The largest source of secondary anthropogenic aerosol comes from fossil fuel emissions of SO<sub>2</sub> and subsequent conversion to H<sub>2</sub>SO<sub>4</sub>. Over continental surfaces, where gaseous ammonia is present (mainly from animal farming and catalyst cars) H<sub>2</sub>SO<sub>4</sub> forms NH<sub>4</sub>HSO<sub>4</sub> (acidic) and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (salt). These components may exist simultaneously. Examples of some chemical components and ions generated by selected emission sources that could be associated with particle form are presented in Table 5.1.

**Table 5.1.** Sources for various chemical components and ions in atmospheric aerosols

Source	Compound
Animal farming	NH <sub>3</sub>
Atmospheric transformation products of SO <sub>2</sub> , NO <sub>x</sub> and NH <sub>3</sub>	H <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>
Coal-fired boiler, Residual oil boiler	SO <sub>4</sub> <sup>2-</sup> , NH <sub>4</sub> <sup>+</sup>
Incinerator	NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>
wood smoke	nitrate, sulphate, NH <sub>4</sub>
meat charbroiling	nitrate, sulphate

### 5.2.2 Carbonaceous aerosols

The carbonaceous aerosol fraction comprises carbonate, a wide range of organic compounds (OC) and so-called elemental carbon (EC). In aerosol particles, organic molecules with an aromaticity ranging from 0.1 to 1 can be found. There is no clear border between OC and EC. However, the EC fraction can be defined from its optical properties or from the analytical conditions in which it evolves as CO<sub>2</sub>. It is important to define and measure EC accurately since it is an inert tracer of primary combustion aerosol. Combustion aerosols also contain organics. However, several other sources of particulate organic carbon have been identified. Primary sources include leaf abrasion, suspension of biological debris, etc. The production of secondary particulate organic carbon results from the gas-particle conversion of certain VOC oxidation products. Carbonate is usually a minor (ca. 5%) of the carbonaceous aerosol, except at sites where crustal aerosol is important.

### 5.2.3 Elemental composition

As explained above, particle properties very strongly depend on particle formation and post formation processes. This applies also to elemental composition of particles and for example, combustion of different types of fuels results in emissions of different trace elements that are present in the fuel material or in the lubricants used (in the case of emissions from motor vehicles). In most cases there is not just one specific element that is related to the combustion of a particular fuel, but a suite of elements. Mechanical processes, such as grinding, breaking, mining, mineral processing, dust re-suspension, etc, result in generation of particles containing predominantly crustal elements. Table 5.2 presents examples of the most common suites of elements related to common outdoor particle sources.

**Table 5.2** Characteristic elements emitted from various outdoor particle sources.

<b>Emission Source</b>	<b>Characteristic Elements Emitted</b>
<b>Road transport</b> Motor vehicle emissions Engine wear Catalytic converters Tyre wear Road side dusts	Br, Pb, Ba, Mn, Cl, Zn, V, Ni, Se, Sb, As Fe, Al Rare earths Zn EC, Al, Si, K, Ca, Ti, Fe, Zn
<b>Industrial facilities</b> Oil fired power plants Coal combustion Refineries Nonferrous metal smelters Iron and steel mills Plant producing Mn metal and Mn chemicals Copper refinery	V, Ni Se, As, Cr, Co, Cu Al, S, P, Ga V As, In (Ni smelting), Cu, Zn Pb Mn Cu
<b>Small combustion</b> Refuse incineration Wood smoke Meat charbroiling emissions	Zn, Sb, Cu, Cd, Hg, K, Pb Ca, Na, K, Fe, Br, Cl, Cu, Zn Na, Al, K, Sr, Ba, Cl
<b>Mineral and material processing</b>	Mg, Al, K, Sc and Fe, Mn.
<b>Sea spray</b>	Na, Cl, S, K
<b>Resuspended soil</b>	Si, V, Cr, Ca, Ti, Sr, Al, Mn, Sc

Morawska and Zang (2001) modified

While certain elements are always released by particular types of sources (for example lead by vehicles using leaded petrol), others are not (for example barium is emitted only by motor vehicles using lubricants containing barium). Since most of the trace elements are non-volatile, associated with ultra fine particles and less prone to chemical transformations, they tend to undergo long-range atmospheric transport and remain as part of the primary form in which they were emitted. To follow the trace elements to their potential emission sources, air parcel movement in the form of calculated backward trajectories is combined with the measured concentrations using various modelling methods (e.g. Gao et al. 1996).

A suite of elements and their concentrations released by a particular source may vary in time, dependently on the nature of the source and the surrounding environment. For example, while industrial outputs are not generally seasonally dependent, motor vehicle emissions could vary if fuel of different characteristics is used in different seasons and airborne concentrations of crustal material are greatly reduced during winter in areas covered with snow.

In some cases it is not just the presence of a specific element that is of importance from the point of health effects, but the chemical form in which the element is present. An example of this are lead compounds and in particular: lead from concentrate haulage as well as dust from smelter

storage piles would be unaltered galena (PbS); concentrate roasting is likely to produce lead sulphates and oxides (PbSO<sub>4</sub>, PbO); and blast furnace emissions could contain lead metal and oxides (Clevenger et al. 1991).

Speciation is the process of identification of various chemical forms of an element. Different chemical forms of an element have different physical and chemical properties. Processes such as environmental transport and bio-availability are species dependent.

Several authors have established that there is an increasing concentration of many toxic elements near the surface of the particle. For example arsenic, beryllium, cadmium, chromium, manganese, nickel, lead, tin, selenium, titanium, vanadium and zinc in atmospheric and ultra fine particles have been shown to increase in concentration with decrease in particles size in fly ash (Committee on the Medical Effects of Air Pollutants 1995). Linton et al. (1976) have shown that a number of elements exhibit significant increases in concentration near particles surfaces. The authors emphasize that conventional bulk analyses of particles provide a poor measure of the actual concentrations of many toxic trace elements that are in effective contact with the external environment of the particle. For a particle of an aerodynamic diameter of 1 µm, as much as 80% of the trace elemental mass is within the surface extractable layer.

#### **5.2.4 Water and hygroscopicity**

Atmospheric particles generally grow with relative humidity (hygroscopicity). Even out of clouds, aerosol particles therefore contain a significant amount of water. From growth factor measurements, it can be calculated for instance that a particle of NH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub> contains about 30% of water in mass at 50% relative humidity. The aerosol hygroscopicity decreases when hydrophobic (organic) substances are mixed with hydrophilic salts such as NH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>. However, water certainly contributes significantly to the outdoor PM mass concentration.

#### **5.2.5 Particle organic composition**

All of the combustion sources generate large amounts of volatile and semi-volatile organic compounds. Semi-volatile organic compounds can be present in the air either in the vapour or in particle form (solid or liquid). Exposure to many of the organic compounds emitted to the air has been associated with various types of health effects.

##### *Polycyclic aromatic hydrocarbons*

Polycyclic Aromatic Hydrocarbons (PAH), some of which are strongly carcinogenic, are one class of compounds contained in the organic fraction of the fine particulate matter. PAH compounds are synthesized from carbon fragments into large molecular structures in low-oxygen environments, such as occurs inside the flame envelope in the fuel-rich region of the flame structure. If the temperature is not adequate to decompose compounds upon exiting from the flame zone, then they are released into the free atmosphere and condense or are adsorbed onto the surface of particles. Many different combustion systems are known to produce PAH compounds. The most studied PAH is benzo[a]pyrene B[a]P that is a physiologically active substance that can contribute to the development of cancer in human cells. A compilation of the health effects of selected non-heterocyclic PAH has recently been published by WHO (1998). The PAHs considered in the document included: acenaphthene, acenaphthylene, anthracene, benzo[a]pyrene, benz[a]anthracene, dibenz[a,h]anthracene, fluoranthene, naphthalene,

phenanthrene, and pyrene. The US EPA introduced a list of the 16 priority PAHs that include: (Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthrene, Benzo(a) pyrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Cheysene, Dibenzo(a,h)anthracene, fluoranthene, fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene (Collier et al 1998).

High concentrations of PAHs have been found in soot generated from wood burning stoves and coal burning stoves (Mumford et al. 1987a). PAHs have also been found in gasoline and diesel soot, and the relative abundance of individual PAH species may be different for different types of soot. This makes it possible to use PAHs as source signatures of different types of fuels on one hand, but may also result in different health effects due to inhalation of emissions from different fuels.

### *Semi-volatile compounds*

Semi-volatile compounds include semi-volatile aliphatic hydrocarbons and particle related aliphatic hydrocarbons (Colombo et al. 1999). These compounds are emitted from diesel and gasoline engines (Simoneit 1985). Other types of semi-volatile compounds include guaiacol and its derivatives that result solely from the pyrolysis of wood lignin. Guaiacol and most of its derivatives appear to be relatively stable in the atmosphere. Therefore, these compounds can serve as unique tracers of wood smoke (Hawthorne et al. 1992). Another important semi-volatile example is that of 3-nitrobenzanthrone, a strongly carcinogenic compound present in diesel emissions. Organic acids of which the major constituents are monocarboxylic (emitted from combustion of fossil fuels and biomass) and dicarboxylic acids (Limbeck and Puxbaum 1999) can also contribute to source apportionment and have been linked to health effects.

From the point of view of the effect on human health it could be of significance in what physical form the semi-volatile compounds are when they are inhaled. They could either be in vapour form, or could be associated with particles of specific sizes. There is very little information available on this aspect, which is due not only to the recency of the interest, but mainly to the difficulties in investigating organic composition of small amounts of mass. Mass of particles in the ultra fine range is very small, and in order to collect sufficient mass for standard organic chemistry analyses, long sampling time would be required, which is prohibitive for many exposure or health effects studies.

Table 5.3 summarizes the most common volatile and semi-volatile organic compounds emitted from combustion sources.

**Table 5.3** Summary of the most common volatile and semi-volatile organic compounds emitted by a number of combustion sources (Cass 1998).

<b>Emission Source</b>	<b>Emitted Components</b>
<b>Environmental tobacco smoke</b>	Nicotine, iso-alkanes, anteiso-alkanes (anteiso-trioacontane, anteiso-hentriacontane, anteiso-dotriacontane, iso-tritriacontane),
<b>Road transport</b> Motor vehicle emissions         Tire dust   Natural gas powered motor vehicles	Hopanes and steranes (present in lubricating oil for diesel and gasoline vehicles, and in diesel) Black elemental carbon (present in a higher fraction in diesel emissions) High molecular PAHs: coronene and benzo[ghi]perylene (these are less specific) Styrene/butadiene copolymer, very high molecular weight even number n-alkanes, benzothiazole Some PAHs and oxyPAHs
<b>Vegetation burning</b>  Wood combustion	Retene, phytosterols, ligmens, phenalic compounds from lignins, diterponoids from resins
<b>Small combustion</b>  Meat charbroiling Natural gas fired home appliances	Cholesterol, supplemented by fatty acids Benz[a]anthracene
<b>Vegetative detritus</b>	High molecular weight n-alkanes ranging from C <sub>27</sub> – C <sub>34</sub> (high concentration of odd number n-alkanes)

### 5.3 Source markers and source signatures

In order to understand either the effects of particles on health or to control the sources in order to mitigate health consequences it is necessary to have an understanding of where the particles are coming from, and then at the receiving end, how much individual sources contribute at the point of particle measurement. Many anthropogenic and in particular combustion sources emit a very large number of compounds and products. For example, it was shown that over 4000 different compounds can be found in the smoke from tobacco combustion. It is usually not only impossible, but also not necessary to monitor all of these compounds. Instead only some of them, so called source markers and source signatures are used.

Source signatures or fingerprints are physical or chemical characteristics of emissions which are specific for particular emission sources, and which should be unique to these sources and thus through which this source can be identified. The complexity related to source identification and apportionment is that on one hand outdoor air contains a dynamic mixture of pollutants emitted from various sources. A mixture which undergoes continuous change in time as the interactions between the pollutants take place and as the components of the mixture are removed from the air due to the presence of various sinks. On the other hand, it is only rarely that specific emission characteristics are unique to a particular source. More often there is a probability that emissions from other sources display some of these characteristics as well. Source signatures include specific suite of elements or compounds and specific ratios of elements or isotopes, or compounds

Source marker on the other hand, is used for quantification of exposures to a particular type of a source. A suitable marker for quantifying concentrations of emissions from a particular source should be:

- unique or nearly unique to the source,
- similar in emission rates for a variety of fuels used,
- easily detected in air at low concentrations,
- in consistent proportion to compounds in the emissions that have effects on human health,
- in relation to organic compounds, must not evaporate into the gas phase over the transport time from source to receptor
- additionally, an ideal marker should also be easily (in real-time), accurately, and cost-effectively measurable.

### ***5.3.1 Markers of environmental tobacco smoke***

The application of markers as well as potential limitations of the technique are illustrated on the example of detection of environmental tobacco smoke (ETS) for which a number of markers have been used in the past to represent its concentrations in both field and chamber studies. Nicotine, carbon monoxide (CO), 3-ethenylpyridine, nitrogen oxides, pyridine, aldehydes, acrolein, benzene, toluene and several other compounds have been used or have been suggested for use as markers for vapour phase constituents of ETS. Respirable suspended particulate matter (RSP), solanesol, N-nitrosamines, cotinine, chromium, potassium are among the air contaminants used as markers for particle phase constituents of ETS (Leaderer and Hammond 1991). Elemental cadmium has been also suggested as a good marker (Wu et al. 1995). Most commonly, RSP, CO and nicotine are utilized as markers of ETS (Rando et al. 1992).

It is considered that the only markers used that may be related to actual exposure to ETS are nicotine and RSP concentrations. Both of these tracers, however, have potential problems. The use of nicotine as a marker of ETS is complicated by the fact that nicotine is found primarily in the gas phase (90%), making it a relatively poor particle marker (Eatough et al. 1989). Furthermore, gas phase nicotine is strongly basic and is removed from indoor environments at a faster rate than particle-phase nicotine or the particle portion of ETS. Thus, the concentration of gas-phase nicotine may underestimate exposure to the particle phase of ETS (Eatough et al. 1989). In addition, the fraction of nicotine in ETS varies with measurement conditions. For example, (5-10)% of ETS nicotine was found in the particle phase in a controlled atmosphere, while 20% was found in field environments (Eatough et al. 1989). The problem associated with



the use of RSP as a marker of ETS is that it is not unique to ETS, as it could come from other sources. Thus, using RSP as an ETS marker may overestimate ETS exposure. In many cases though, the elevated RSP level is significantly higher from ETS than from other sources. Therefore, RSP is still widely used as a marker of ETS.

## **5.4 Source apportionment - examples**

One important aspect of source characterization is quantification of emissions from individual pollution sources. This in turn enables generation of inventories of emissions at local, regional and national levels, which is necessary for developing appropriate management and control strategies in relation to air quality and its impact on health. Below are a few examples of emission inventories in relation to particulate matter.

The principal primary emissions in the UK are road transport, stationary processes and industrial processes, though the potential additional small contributors are high. Re-suspension is also significant for wind speeds rising above 5.4 m/s (QUARG 1996). In joint oil industry tests it was found that in the engines tested, diesels emitted 40-85 times as many particles on a mass basis. Gasoline engines both with and without catalysts were in the study, (Hall et al. 1998). The stationary combustion process that was traditionally widespread was coal burning, but this is in decline and in major cities is restricted by Clean Air acts, though in Belfast domestic coal burning still contributes significantly to emissions. The industrial processes that contribute most to particle emissions are acid processes, cement production, petroleum refining and incineration. The estimate for 1993 showed transport as contributing only 28% of the total calculated PM<sub>10</sub> emissions, though this rises to 80% in London (QUARG 1996).

Two main types of source apportionment have been used to quantify the proportions of contributing pollutants to PM<sub>10</sub> at a monitoring site. The first is the intuitive method of measuring the chemical inventory of constituents in the observed PM<sub>10</sub>, and from a knowledge of the chemistry of individual constituents, proportions of the latter can be estimated. Chow et al. (1996) used such a simple linear mixing model, which requires conservation of composition between source and receptor, but whilst making no assumption about transport or removal processes, requires an accurate knowledge of all significant source emission compositions. They were able to split out motor vehicles (30-42)%, road dust (25-27)% and marine aerosol (18-23)% as principal contributors, though the latter contribution was much higher at two of their marine background sites.

The second generic type of source apportionment uses multivariate methods, which extract information about the contribution of a source on the basis of the variability of chemical components. These need to be measured on a large number of samples, and the method relies on the principle that if a group of chemical constituents have a common origin, they should show a similar variation with time. The multivariate methods detect this common variability and infer source identity, and in contrast to the chemical mass balance method, quantitative chemical composition data for source emissions are not required. In practice there is a limit (about 8) to the number of categories that can be identified.

Harrison et al. (1996) carried out the latter type of source apportionment in Birmingham using analyses of 18 polycyclic aromatic hydrocarbons, (PAHs), fine and coarse particle, and 19 metal species. Principal component analysis was used to evolve from 35 inter-correlated variables 6

non-correlated principal components or factors, which were identified as sources. This was carried out on the fine fraction of the dichotomous sampler, ( $<2.1\mu\text{m}$ ). These were attributed to vehicles/road dust, oil combustion, secondary aerosol, incineration, vehicle emissions, and marine/road salt.

Simcik et al. (1999) also used multivariate statistics in source apportionment studies of PAHs in the coastal atmosphere of Chicago and Lake Michigan. They sampled PAHs in atmospheric vapor and particle phases using high-volume samplers and polyurethane foam for gas phase sampling. Using a modified factor analysis-multiple regression model, it was deduced that coal combustion accounted for  $(48 \pm 5)\%$  of the total PAH concentration, natural gas combustion  $(26 \pm 2)\%$ , coke ovens  $(14 \pm 3)\%$ , and gasoline and diesel vehicle emissions accounted for  $(9 \pm 4)\%$ . These results applied to urban and adjacent coastal atmosphere.

Hosiokangas et al. (1999) carried out receptor modelling using a factor analysis-multiple linear regression model. A dust episode in Kuopio, Finland was very strong during two sampling days, and had to be omitted from the analysis. The preferred model gave the following percentage contributions to  $\text{PM}_{10}$ ; soil and street dust 46-48%, heavy fuel oil burning (12-18)%, traffic exhaust (10-14)%, wood burning ca 11% and unidentified sources (15-25)%. During the spring dust episode days, the main contributor was soil.

It will be noted that only one of these studies has studied source apportionment in the fine fraction. Another study involving receptor modeling of fine aerosol was reported by Hueglin (2000). Since it is believed that the ultra-fine fraction may be the most injurious to health, it is of considerable interest to carry out source apportionment on the smallest particle size that is practical, recognizing that the problem of sample size and chemical characterization becomes more difficult as particle size declines. Kleeman and Cass (1998) have addressed this problem in a different way by constructing a mechanistic air quality model, which can predict the contribution of individual emission sources to both the size and the chemical composition distribution of particles. The Lagrangian aerosol trajectory model used examines the evolution of the size and chemical nature of the outdoor aerosol when gas-to-particle conversion processes are active. The model is claimed to describe all aerosol processes relevant to regional air pollution problems, including emissions, transport, deposition, gas-to-particle conversion and fog chemistry. Their results model one day in 1987, and noteworthy amongst their conclusions as the importance of vehicle emissions in the  $(0.1\text{-}0.2)\mu\text{m}$  range.

Künzli et al. (2000) noted that there are very few source apportionment studies of outdoor air pollution and that objective source-specific measures of PM have never been used in the epidemiological studies. Since then source specific measures of PM have been used and reported in the literature (Laden et al. 2000).

## **5.5 Spatial and temporal small-scale variation of aerosol parameters**

Following formation, the mixture of emission products including particles, undergoes a range of physico-chemical processes, which change their chemical composition, physical characteristics and concentration in the air. Some of the emission products, such as for example combustion related, are highly dynamic, while others, like mechanical dust, are less so. Particles measured away from the emission site, or particles generated indoors and measured some time after

emission, would have different characteristics to those measured immediately after formation. The residence time of the emission products in the air depends on the nature of the processes they are involved in and varies from seconds or minutes to days or weeks. Larger particles (of a micrometer size range in aerodynamic diameter and more) are removed from the atmosphere mainly through gravitational settling, while smaller particles by precipitation or diffusional deposition. For example, at a distance of 20 km from an extensive fire, while submicrometer particle concentration is significantly increased, there is no increase in particles over one micrometer, indicating the particles have been removed from the air plume, while travelling over this distance (WHO/UNEP/WMO 1999).

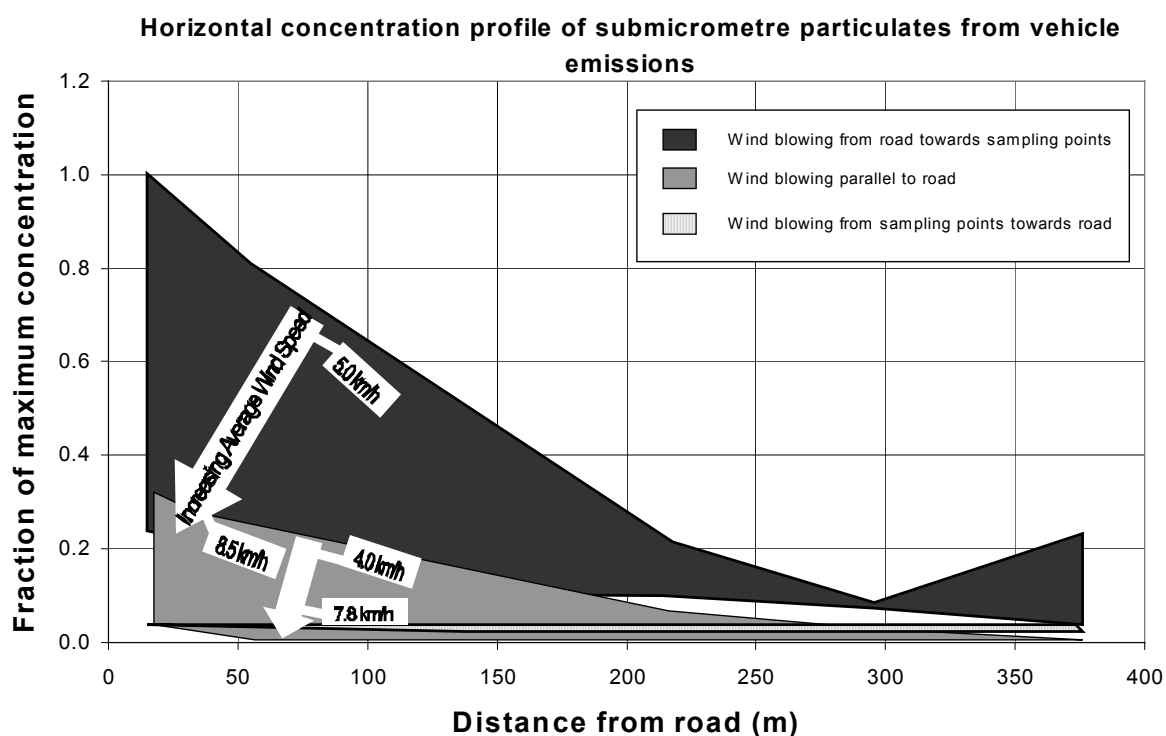
While in the proximity to the emission point certain compounds could be of significance in relation to health effects, at a distance from the source, due to various processes that took place during transport, the relative significance may have changed. For example, in a summary of the levels of exposures resulting from vegetation burning it was concluded that in the exposure to the population occurring due to distant large scale fires, mainly the particles and also to some extent PAHs are considered to be important from the health point of view, due to the elevated concentration at which they occur (WHO/UNEP/WMO 1999). The presence of other compounds emitted has not been considered significant at a larger distance from the fire due to the significant decrease in their concentrations.

There is still very little information available on the fate of fine and ultra fine particles in the air. In an urban environment, motor vehicle emissions usually constitute the most significant source of fine and ultra fine particles. There have been some studies conducted on behaviour of gaseous emissions at an increasing distance from the road, as well as on behaviour of mass concentrations of particles in terms of  $PM_{10}$  or  $PM_{2.5}$ , but very limited studies on particle number concentration. For example, from a study examining  $PM_{10}$ ,  $PM_{2.5}$ ,  $NO_2$ , black smoke, and benzene at a distance from a major motorway (Roorda-Knappe et al. 1998) it was concluded that  $NO_2$  and black smoke concentrations decrease with increased distance from a road of up to 300 m, whereas there is no significant decrease in concentrations of  $PM_{10}$ ,  $PM_{2.5}$ , and benzene. Janssen et al. (1997a) reached similar conclusions. The authors concluded that  $PM_{10}$  and  $PM_{2.5}$  concentrations were on average only 1.3 times higher near the road compared with the background readings, and black smoke (elemental carbon) readings were 2.6 times higher.

The measurements conducted by Hitchins et al. (2000) showed, as presented in Figure 5.7, that for conditions where the wind is blowing directly from the road, the concentration of submicrometer particle number decays to about half of the maximum (measured at the closest point to the road) at a distance of approximately (100 - 150) m from the road. For wind blowing parallel to the road, the reduction to half of the concentration occurs at (50 – 100) m. Total number concentrations of larger particles measured were not significantly higher than the average values for the urban environment, and decrease with distance from the road, reaching about 60% at 150 m from the road for wind from the road.  $PM_{2.5}$  levels also decrease with distance to around 75% for wind from the road and to 65% for wind parallel to the road, at a distance of 375 m.

These findings indicate that in relation to particle physical characteristics, while particle number and black smoke are closely related to motor vehicle emissions and are present at a distance up to 300 m from a road,  $PM_{10}$  or  $PM_{2.5}$  are to a lesser extent. Apart from vehicle emissions, also re-suspended road dust could contribute significantly to  $PM_{10}$  or  $PM_{2.5}$  and the degree of this

contribution is very site specific. In addition, the levels of Fe and Si (both elements are associated mainly with natural emission sources) are significantly higher in PM<sub>10</sub>, and to a lesser extent in PM<sub>2.5</sub> samples near the road.



**Figure 5.7** Compilation of total number concentration (size range 14.9 – 697 nm) for horizontal profile measurements for all wind conditions for two sites investigated. (Hitchins et al. 2000).

In a study recently conducted in Brisbane, Australia to identify the level of spatial distribution of pollutants between the stations of the urban monitoring network, a comparison between ambient concentrations of NO<sub>x</sub>, ozone and PM<sub>10</sub> was made for three stations of the network (Morawska et al. 2001). The best correlated between the three stations were ozone concentrations followed by NO<sub>x</sub> concentration, with the worst correlations observed for PM<sub>10</sub>. With a few exceptions correlations of all pollutants between the stations were statistically significant. The conclusion for Brisbane in relation to the assessment of population exposure is, that due to the very high correlation of ozone concentrations between the stations, data from any of the monitoring stations in the city can be used for exposure assessment equally well. In relation to NO<sub>x</sub> it would be better to use more localised data for human exposure assessment, but when it is not possible, due to the relatively high correlations between the stations, data from one station could still be used for exposure assessment. Applicability of the PM<sub>10</sub> monitoring data for exposure assessment is a complex issue. With the low correlation levels between the stations the recommendations would be that more localised data for PM<sub>10</sub> concentrations should be used, based on the knowledge of the local demographical factors. Yet, most of the correlations are statistically significant, which means that there is still merit in using the data from one station if relating the patients to the different areas they live, and thus different exposure levels proves to be impossible.

## 5.6 Association to other pollutants

In addition to particles, many emission sources, particularly combustion sources, also generate gases and vapours. The most common of them include:

- Inorganic gaseous: carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>),
- Volatile Organic Compounds (VOCs): benzene, toluene, styrene, 1,3-butadiene, hydrocarbons (HC - in a particular chlorinated hydrocarbons and xylenes), very reactive toxic gases such as aldehydes-formaldehyde and acetaldehyde
- Ozone (O<sub>3</sub>) is a secondary pollutant that is generated in the air from its precursors including nitrogen oxides and hydrocarbons in the presence of light.

Many of these pollutants have been independently associated with health impacts and have been subject of independent exposure and health studies. The discussion of these is outside the scope of this document. Knowledge of characteristics of these pollutants has, however a relevance to the studies of the effects of airborne particulate matter, as for example they could be used as additional indicators of specific source type as source markers or signatures.

In general, ratios between outdoor concentrations of particulate matter and gases such as CO and NO<sub>x</sub> for example are variable, reflecting contributions from various sources and atmospheric reaction processes. When only one source is present the ratios are more uniform and, when regression analyses were conducted for each monitoring site independently and for each season, a high degree of correlation was for example shown between PM<sub>10</sub> and PM<sub>2.5</sub> as well as between NO<sub>x</sub> and PM<sub>10</sub> or PM<sub>2.5</sub> (Airborne Particles Expert Group 1999).

## 5.7 Summary of aerosol parameters of potential relevance for health related issues

From the above discussion on particle chemical and physical characteristics, the relationship between different characteristics and the relationship between particle characteristics and those of atmospheric gases or vapours, the following recommendations can drawn as to the characteristics to be determined to advance knowledge on the links between exposure/dose and health effects. Table 5.4 provides a summary of the recommendations

**Table 5.4** Recommendations as to the characteristics to be determined to advance knowledge on the links between exposure/dose and health effects and justification for the recommendations.

Characteristics To Be Measured	Justification
Particle mass	<p>PM<sub>10</sub> Existing hypotheses of its effect on health, representative of the exposures to coarse particles, only occasional correlation with other particle physical characteristics</p> <p>PM<sub>2.5</sub> Existing hypotheses of its effect on health, represents respirable fraction of particles, in some environments, however, good correlation with PM<sub>10</sub></p> <p>PM<sub>1</sub> Existing hypotheses of its effect on health from combustion produces, representative of exposures to combustion particles, only occasional correlation with other particle physical characteristics</p>
Particle number	Existing hypotheses on its effect on health; lack of correlation with other particle physical characteristics such as mass.
Particle surface area	As an intermediate moment between number and mass. Existing hypothesis that the available amount of a toxic species is related to the surface area.
Particle number size distribution	Since most particle number is present in the ultra fine range, for many investigations particle size distribution does not need to be measured on a continuous basis, but on campaign basis to acquire general information for the study area.
Chemical composition	Existing hypotheses and recent evidence of its effect on health, only occasional correlation with other particle physical characteristics; those elements and compounds that are associated with local emission sources and their relation to health effects, should be particularly targeted;
Detailed size fractionated chemical composition	Existing hypotheses that different areas of deposition in the lung will result in different bio-availability of toxic, carcinogenic, etc substances and thus in different health effects

The effects of exposure to fine and coarse particles would differ not only due to their size and ability to penetrate to the different parts of the respiratory tract, but also to their significantly different chemical, and toxicological composition. For this reason studies aimed at linking the health effects to exposures to particles, should include characterization of as many atmospheric factors as practically possible, and the relationships between particles and other pollutants in complex air mixtures. It should be pointed out, however, that investigations of particle composition are costly and often requiring very specialized instrumentation. Thus at the design stage of a study, decisions have to be made which components of particle composition are to be investigated, based on the objective of the study, and understanding the local emission sources and other factors affecting exposures. An example of this could be differences in particle and in exposure characteristics in the vicinity of a busy road, compared to those near a quarry, thus requiring focus on different particle characteristics and developing different study designs.

## **6. Instrumental Techniques for Physical and Chemical Particle Characterization**

The objective of this chapter is to give an overview of methods of physical and chemical characterization of airborne particulate matter. The overview is not complete, but covers some techniques providing information of possible relevance for health effects. The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

### **6.1 Sampling for chemical analysis and mass measurement**

In the following sections an overview of the various methods for monitoring of suspended particulate matter is presented together with a brief discussion of the problems of each method. Some technical details of the monitoring methods mentioned below are given in Appendix 5.

A detailed overview on sampling issues and techniques is given by Vincent (1989) and by the EPA (US EPA 1996; US EPA 1999; US EPA 2001). For more technical details we refer to Vincent (1989).

Filtration is a commonly used method for collection of airborne particles. The conventional procedure involves drawing the air through the filter followed by digestion of the particles on the filter. Interferences to the aerosol sample encountered during the filtration stage include:

- the loss of particles passing through the pores of the filters
- the loss of particles from incorrect seals employed in the filter holder around the filter
- the loss or contamination of particles from the filter holder
- and aerosol transformations that may occur on the filter.

These interferences and the requirements of filter analysis methods are discussed in detail in Lehtimäki and Willeke (1993).

At the ultra-trace concentration levels consistent with atmospheric particulate matter it is vitally important that the levels of contamination from each of the components is kept to a minimum. The filter should be made of materials that do not add the concentration of elements under study. Berg et al (1993) analysed 19 filters from various manufacturers for 30 elements by ICP-MS to determine the most appropriate filter for ultra-trace metal analysis. The authors found that PTFE filters were the cleanest, whereas glass fibre filters contained a number of elements contributing to high blanks. Similar studies have been performed solely on glass fibre filters to evaluate the analytical blanks obtained as a result of the dissolution of the filter matrix (Wang et al. 1989).

#### **6.1.1 Inlet design considerations**

The inlet used for aerosol sampling should follow certain design guidelines so that comparable samples are obtained. The purpose of the inlet system is to provide a sample aerosol that is representative of outdoor air, to the various aerosol analysers and samplers applied. The US EPA requires, for measurement of particulate matter mass by the US Federal Reference Method, that the filter be maintained at a temperature near the outdoor temperature. Similar requirements are also made in the European reference method (CEN 1998). However, for other measurements of outdoor aerosol properties, aerosol-sampling equipment should be housed in a shelter that provides a controlled laboratory environment (temperature 15-30°C). However, consideration



should be given to changes in particle size and composition due to changes in temperature and relative humidity relative to the outdoor conditions. An omni-directional aerosol inlet, leading outside, is required. This can be achieved with a vertical configuration. The size of the entrance configuration must be well designed to provide a high inlet sampling efficiency for aerosol particles over a wide range of wind speeds. The cut-off diameter of the inlet and sampling line should match the European EN 12341 standard (CEN 1998) or the US-PM<sub>10</sub> standard (ambient conditions). At 10 m/s wind velocity, a 10 µm particle has a stopping distance of 0.23 cm. The inlet design must thus consider dimensions five times larger than the stopping distance to avoid particle losses. A cover mounted on top of the aerosol inlet should exclude drizzle, rain and snow. For indoor measurements, precautions related to wind speed and precipitation need not be met. Special care should be given to air splittings, bends and horizontal lines to avoid losses of large particles. We refer to the standards mentioned above for more details.

The aerosol mass is usually distributed into two major divisions called the fine mode and the coarse mode. The fine mode can be subdivided into an ultra fine or nuclei mode and the accumulation mode. Particles grow from the nuclei mode into the accumulation mode but under normal atmospheric conditions do not grow further into the coarse mode. The minimum separating the coarse and fine fractions does not always occur at the same diameter. In marine air, the minimum can be slightly below 1 µm diameter (aerodynamic diameter  $D_p$  for unit density spheres) while typical values in more polluted continental air are closer to 1.0 µm. The minimum may be as high as 2.5 µm in fog, clouds, or other high relative humidity conditions. The size cuts usually applied for mass determination and chemical analysis are  $D_p < 2.5\mu\text{m}$  (PM<sub>2.5</sub>) and  $D_p < 10\mu\text{m}$  (PM<sub>10</sub>). The cut-off size of 2.5 µm is chosen to discriminate against the coarse mode. Thus, the difference between PM<sub>10</sub> and PM<sub>2.5</sub> (PM<sub>10-2.5</sub>) reflects the coarse particles only, while PM<sub>2.5</sub> reflects the fine ones. While the ultra fine fraction (diameter < 0.1 µm) is also included here, its mass is always negligible. The size cuts can be accomplished with an impactor or a cyclone. For options that are currently available and for technical details see descriptions in the literature (US EPA 1996; US EPA 1999; US EPA 2001; Vincent 1989; CEN 1998). The device chosen should be characterized. Special considerations are required at sites that are frequently immersed in cloud or fog.

### **6.1.2 PM collection for chemical analysis and gravimetric mass determination**

The simplest sampling technique is to collect particles on filters, e.g. for 24-hour sampling periods. Different types of samplers and filters may be used, in either low-volume filter pack or high-volume samplers, depending on the specific components to be analysed. Sampling and analytical procedures should be standardized across the entire monitoring network, for which standard operating procedures (SOPs) need to be provided (US EPA 1987; US EPA 1999; CEN 1998). It is imperative that the monitoring activities be quality assured and the data quality controlled, preferably by qualified personnel. On a fixed schedule, such as monthly or quarterly, a survey of sample recovery rate for each measurement station should be maintained, which can be used as a basis for corrective actions if needed. Compliance with the standard operating procedures for sampling and analysis should be documented on the same schedule. A set of compliance criteria must be developed against which the check can be made. These documents should form part of the data together with the results from the sampling/analysis activities.

Quality control for sampling should involve

- (1) Calibration;
- (2) Flagging of data with known abnormalities; and
- (3) Recording abnormalities.

Calibrations of sampling instruments include mass flow measurement calibration with a transfer standard (e.g., a bubble meter or mass flow meter). Leak tests of the sampling system should be done at least once a year, and more frequently should problems develop. Analytical procedure quality control should consist of at least three steps:

- (1) Performance check by involving the lab in inter-laboratory inter-comparisons, as well as obtaining absolute standards if available;
- (2) Interspersing quality control standards with regular samples in a routine analysis sequence; and
- (3) Regularly scheduled repeat analyses of randomly selected samples.

Separate sets of flags must be developed for sampling/sample handling and analysis.

## **6.2 Methods for determination of mass**

### **6.2.1 Gravimetric measurement**

Particle mass concentration is the most commonly made measurement on aerosol samples. It is used to determine compliance with PM standards and to select certain samples for more detailed, and more expensive, chemical analyses. Gravimetric analysis is used almost exclusively to obtain mass measurements of filters in a laboratory environment. Detailed standardized procedures for mass analyses have been published in the European Standard EN 12341 and by the United States Environmental Protection Agency (US EPA 1987; US EPA 1999; CEN 1998). Gravimetry measures the net mass on a filter by weighing the filter before and after sampling with a balance in a temperature- and relative humidity-controlled environment. PM reference methods require that filters be equilibrated for 24 h at a constant (within  $\pm 5\%$ ) relative humidity between 20 and 40% and at a constant (within  $\pm 3^\circ\text{C}$ ) temperature between 15 and 30  $^\circ\text{C}$ . These are intended to minimize the liquid water associated with soluble compounds and to minimize the loss of volatile species. Nominal values of 30% RH and 15 to 20  $^\circ\text{C}$  best conserve the particle deposits during sample weighing.

### **6.2.2 Beta attenuation**

In the beta attenuation mass monitor (Marcias et al. 1976; Willeke and Baron 1993) particulate material is continuously collected on a foil, and the attenuation of beta radiation by the collected material is recorded. The collection process is repeated in fixed intervals, which leads to a quasi-continuous measurement of particulate mass vs. time. In contrast to optical absorption, the absorption of beta radiation is closely proportional to mass, and the proportionality constant is only weakly material dependent. Thus, although the physical quantity of mass is not directly determined, beta absorption can be calibrated for mass, with rather small errors arising from the

variability of the chemical species present. A disadvantage of the technique may be the requirement of the radioactive source, since the respective regulations of the country have to be followed. With the respective sampling head, the instrument can measure PM<sub>2.5</sub> or PM<sub>10</sub>. The gravimetric method mentioned under 6.2.1 enables calibration and quality control of this instrument.

### 6.2.3 Vibrational microbalance methods

A piezoelectric quartz crystal as used in wristwatches typically has a natural vibrational frequency (first harmonic) in the range of several MHz, which can be excited electrically. If aerosol particles are deposited on such a crystal, the frequency changes according to the respective mass. The sampling time required to collect a sufficient amount of material on the quartz surface is typically minutes. A serious disadvantage of this method is the change in sensitivity with loading, when more than one monolayer of particles has been collected. The measurement time before necessary cleaning is thus rather short. Strongly agglomerated particles are not measured correctly, because they do not firmly attach to the crystal.

These limitations are eliminated in the Tapered Element Oscillating Microbalance Mass Detector (TEOM) (Patashnik and Rupprecht 1980), which oscillates at much lower frequencies than the piezoquartz. The particle sample is collected in a filter mounted on the thin end of a tapered oscillating hollow element, which is fixed to a surface at its thick end. This element is electrically excited to oscillate in its natural frequency, which changes with the mass loading of the filter. The instrument can be equipped with a PM<sub>10</sub> or PM<sub>2.5</sub> sampling inlet. The inlet air is either heated to 50 °C to keep moisture in the vapour phase or dried with a diffusion dryer. In the latter case it only requires heating to 30 °C. This is recommended, when semi-volatile compounds like ammonium nitrate and volatile organics are present in significant concentration and should not be ignored. Mignacca and Stubbs (1999) reported a 22% higher signal at an equilibration temperature of 30°C, compared to 50°C. As a consequence, lower TEOM<sup>®</sup> concentrations are generally measured when compared to reference methods, a situation especially encountered during the colder seasons (Allen et al. 1997; Salter and Parsons 1999; Soutar et al. 1999; Muir 2000; King et al. 2000). Brook et al. (1999) also compared PM<sub>2.5</sub> data from TEOM<sup>®</sup> and dichotomous samplers and found a relatively small difference in the warmer months, while during the colder months, TEOM<sup>®</sup> values were lower by 23% on average. Ayers et al. (1999) compared 24-h PM<sub>2.5</sub> aerosol loadings determined by a TEOM<sup>®</sup> and manual gravimetric samplers in Australian cities. They found systematically lower results from the TEOM<sup>®</sup> by an average of > 30%, indicating that aerosol material is lost from the heated sample filter employed in the TEOM<sup>®</sup>. Using a diffusion dryer, which allows the temperature in the system to be reduced (Eatough et al. 1999), may minimize the problem.

### 6.2.4 Particle-bound water

A major fraction of the particles in the atmosphere are hygroscopic, and their size can be strongly dependent on the relative humidity (RH). In order to have samples that are size-segregated independent of outdoor RH, it is recommendable to bring the sample air to a reference RH prior to the size segregation step. Particle size is relatively insensitive to RH at humidities below 30-50%, so that the air stream does not have to be dried completely. The relative humidity can be controlled to 40% by heating the incoming air stream, including the measurement unit. Dew point temperatures in excess of 25°C can be expected in hot and humid environments, requiring the air to be heated over 40°C to achieve the desired RH. Under such conditions, significant

evaporation of volatile compounds, namely ammonium nitrate and volatile organics, may occur (see 6.3). To prevent loss of volatile species, we recommend the use of diffusion dryers, as used by Rupprecht and Patashnik for their mass measuring instrument TEOM or a dilution of the sample air with dry, particle-free air. If the relative humidity is reduced, as stated above, before entering the cut-off device, a cut-off size of 1  $\mu\text{m}$  will provide a better separation of the coarse and the fine particle modes.

### **6.2.5 Assessment of the particulate loading of the air by optical scattering**

Instruments are on the market that measure an integrated light scattering signal of all the particles sucked into the device, usually behind a  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  inlet, and that convert this signal into an approximate particle mass. For this conversion, assumptions have been made regarding the particle optical properties, and especially the size distribution of the particles. The reading on the instrument can be orders of magnitude wrong, if these assumptions are badly met. Using such instruments for scientific studies is therefore generally not recommended. In special cases, where continuous recording of the mass is required, and where the reading is periodically compared to a reference method indicating the actual mass, the response can be used to interpolate between the points of reference.

## **6.3 Determination of chemical composition**

The composition of aerosol particles is of interest to:

- (2) Explain and inventory the observed mass;
- (3) Identify potentially toxic components;
- (4) Determine the sources of the PM; and
- (5) Use this information to determine the effects of PM on health and welfare.

While any compositional measurement will address one or more of these goals, certain methods excel for specific tasks. In general, no single method can measure all chemical species, and comprehensive aerosol characterization programmes use a combination of methods to address complex needs. This allows each method to be optimized for its objective, rather than be compromised to achieve goals unsuitable to the technique. Such programmes also greatly aid quality assurance objectives, since confidence may be placed in the accuracy of a result when it is obtained by two or more methods on different substrates and independent samplers.

In general terms, methods for characterization of chemical composition of particles can be divided into two classes:

- (1) Methods that require sample collection followed by laboratory analyses; and
- (2) Near real time methods.

The most important features of both these classes of chemical analysis are summarized below. More details of instrumentation used for these analyses are provided in Appendix 5. It should be stressed that this summary is designed to be illustrative rather than exhaustive, since new methods are constantly appearing as old methods are being improved.

### 6.3.1 Sample collection methods

The more commonly used methods for chemical analysis requiring sample collection can be divided into four categories:

- (i) Elements;
- (ii) Water-soluble ions;
- (iii) Organic compounds; and
- (iv) Elemental carbon.

Material balance comparing the sum of the chemical species to the PM mass concentrations show that elements, water soluble ions, and organic and elemental carbon typically explain 65 to 85% of the measured mass and are adequate to characterize the chemical composition of measured mass for filter samples collected in most urban and non-urban areas. Some chemical analysis methods are non-destructive. These are preferred because they preserve the filter for other uses. Methods, which require destruction of the filter, are best performed on a section of the filter to save a portion of the filter for other analyses or as a quality control check on the same analysis method.

#### *Elemental analysis*

The most common interest in elemental composition derives from concerns about health effects and the utility of these elements to trace the sources of suspended particles. Instrumental neutron activation analysis (INAA), photon-induced x-ray fluorescence (XRF), particle-induced x-ray emission (PIXE), atomic absorption spectrophotometry (AAS), inductively-coupled plasma with atomic emission spectroscopy (ICP/AES), inductively-coupled plasma with mass spectroscopy (ICP/MS), and scanning electron microscopy with x-ray fluorescence (SEM/XRF) have all been applied to elemental measurements of aerosol samples. AAS and ICP/AES are also appropriate for ion measurements when the particles are extracted in deionised-distilled water (DDW). Since air filters contain very small particle deposits (20 to 100 Fg/cm<sup>2</sup>), preference is given to methods that can accommodate small sample sizes. XRF and PIXE leave the sample intact after analysis so that it can be submitted to additional examinations by other methods. Excellent agreement was found for the inter-comparison of elements acquired from the XRF and PIXE analyses (Cahill 1980). The details of the techniques are described in Appendix 5.

Table 6.1 identifies the elements commonly found in air using these methods with typical detection limits. The minimum detection limit for Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>=</sup> using ion chromatography is 50 ng/m<sup>3</sup>. The minimum detection limit for NH<sub>4</sub><sup>+</sup> using automated colourimetry is 50 ng/m<sup>3</sup>. The minimum detection limit for OC and EC is 100 ng/m<sup>3</sup> using thermal optical reflectance.

**Table 6.1** Instrumental detection limits for elements on particles

Minimum detection limit in ng/m <sup>3a</sup>						
Species	ICP/ AES <sup>b,d</sup>	AA Flame <sup>b,d</sup>	AA Furnace <sup>b</sup>	INAA <sup>b,e</sup>	PIXE <sup>f</sup>	XRF <sup>c</sup>
Be	0.06	2 <sup>d</sup>	0.05	NA <sup>g</sup>	NA	NA
Na	NA	0.2 <sup>d</sup>	< 0.05	2	60	NA
Mg	0.02	0.3	0.004	300	20	NA
Al	20	30	0.01	24	12	5
Si	3	85	0.1	NA	9	3
P	50	100,000	40	NA	8	3
S	10	NA	NA	6,000	8	2
Cl	NA	NA	NA	5	8	5
K	NA	2 <sup>d</sup>	0.02	24	5	3
Ca	0.04	1 <sup>d</sup>	0.05	94	4	2
Sc	0.06	50	NA	0.001	NA	NA
Ti	0.3	95	NA	65	3	2
V	0.7	52	0.2	0.6	3	1
Cr	2	2	0.01	0.2	2	1
Mn	0.1	1	0.01	0.12	2	0.8
Fe	0.5	4	0.02	4	2	0.7
Co	1	6 <sup>d</sup>	0.02	0.02	NA	0.4
Ni	2	5	0.1	NA	1	0.4
Cu	0.3	4	0.02	30	1	0.5
Zn	1	1	0.001	3	1	0.5
Ga	42	52	NA	0.5	1	0.9
As	50	100	0.2	0.2	1	0.8
Se	25	100	0.5	0.06	1	0.6
Br	NA	NA	NA	0.4	1	0.5
Rb	NA	NA	NA	6	2	0.5
Sr	0.03	4	0.2	18	2	0.5
Y	0.1	300	NA	NA	NA	0.6
Zr	0.6	1000	NA	NA	3	0.8
Mo	5	31	0.02	NA	5	1
Pd	42	10	NA	NA	NA	5
Ag	1	4	0.005	0.12	NA	6
Cd	0.4	1	0.003	4	NA	6
In	63	31	NA	0.006	NA	6
Sn	21	31	0.2	NA	NA	8

**Table 6.1 (cont'd)** Instrumental detection limits for particles on filters.

Minimum Detection Limit in ng/m <sup>3a</sup>						
Species	ICP/ AES <sup>b,d</sup>	AA Flame <sup>b,d</sup>	AA Furnace <sup>b</sup>	INAA <sup>b,e</sup>	PIXE <sup>f</sup>	XRF <sup>c</sup>
Sb	31	31	0.2	0.06	NA	9
I	NA	NA	NA	1	NA	NA
Cs	NA	NA	NA	0.03	NA	NA
Ba	0.05	8 <sup>d</sup>	0.04	6	NA	25
La	10	2,000	NA	0.05	NA	30
Au	2.1	21	0.1	NA	NA	2
Hg	26	500	21	NA	NA	1
Tl	42	21	0.1	NA	NA	1
Pb	10	10	0.05	NA	3	1
Ce	52	NA	NA	0.06	NA	NA
Sm	52	2,000	NA	0.01	NA	NA
Eu	0.08	21	NA	0.006	NA	NA
Hf	16	2,000	NA	0.01	NA	NA
Ta	26	2,000	NA	0.02	NA	NA
W	31	1,000	NA	0.2	NA	NA
Th	63	NA	NA	0.01	NA	NA
U	21	25,000	NA	NA	NA	1

<sup>a</sup>Minimum detection limit is three times the standard deviation of the blank for a filter of 1 mg/cm<sup>2</sup> area density.

ICP/AES = Inductively Coupled Plasma with Atomic Emission Spectroscopy.

AA = Atomic Absorption Spectrophotometry.

PIXE = Proton Induced X-ray Emissions Spectrometry.

XRF = Non-Dispersive X-ray Fluorescence Spectrometry.

INAA = Instrumental Neutron Activation Analysis.

<sup>b</sup>Concentration is based on the extraction of 1/2 of a 47 mm quartz-fiber filter in 15 ml of deionized-distilled water, with a nominal flow rate of 20 L/min for 24-h samples.

<sup>c</sup>Concentration is based on 13.8 cm<sup>2</sup> deposit area for a 47 mm ringed teflon-membrane filter, with a nominal flow rate of 20 L/min for 24-h samples with 100 sec radiation time.

<sup>d</sup>Harman (1989).

<sup>e</sup>Olmez and Harman (1989).

<sup>f</sup>Eldred et al. (1993).

<sup>g</sup>Not Available.

### *Analysis of water soluble ions*

The analysis for water-soluble ions can be divided into two main classes: ion chromatographic and automated colorimetric analysis.

Chromatographic methods make use of a *stationary phase* and a *mobile phase*. Components of a mixture are carried through the stationary phase by the flow of the mobile one. In Ion-exchange Chromatography, ionic components of the sample are separated by selective exchange with counter ions of the stationary phase. The use of ion exchange resins as the stationary phase brings about a classification based largely on geometry and size. IC can be used for both anions (fluoride [F<sup>-</sup>], chloride [Cl<sup>-</sup>], nitrite [NO<sub>2</sub><sup>-</sup>], bromide [Br<sup>-</sup>], nitrate [NO<sub>3</sub><sup>-</sup>], phosphate [PO<sub>4</sub><sup>-3</sup>], sulphite [SO<sub>3</sub><sup>=</sup>], sulphate [SO<sub>4</sub><sup>=</sup>]) and cations (potassium [K<sup>+</sup>], ammonium [NH<sub>4</sub><sup>+</sup>], sodium [Na<sup>+</sup>]) with separate columns.

Colorimetric methods involve the passing of radiation through an unknown sample solution and measurement of the absorbency of the solution for comparison with a set of standards. In the simplest form, daylight may commonly serve as the radiation source and the human eye as the detector. Automated colorimetric analysis (AC) applies different colorimetric analyses to small sample volumes with automatic sample throughput. Since IC provides multi-species analysis for the anions, AC most commonly measures ammonium.

More details on these methods can be found in Appendix 5. Table 6.2 identifies the water-soluble ions commonly found in air using these methods with typical detection limits.

**Table 6.2** Instrumental detection limits for water-soluble ions on particles

Species	Minimum Detection Limit in ng/m <sup>3a</sup>		
	IC <sup>b</sup>	AC <sup>b</sup>	TOR <sup>b</sup>
Cl <sup>-</sup>	50	NA	NA
NO <sub>3</sub> <sup>-</sup>	50	NA	NA
SO <sub>4</sub> <sup>=</sup>	50	NA	NA
NH <sub>4</sub> <sup>+</sup>	NA	50	NA
OC	NA	NA	100
EC	NA	NA	100

IC = Ion Chromatography.

AC = Automated Colorimetry.

TOR = Thermal Optical Reflectance.

<sup>a</sup> Minimum detection limit is three times the standard deviation of the blank for a filter of 1 mg/cm<sup>2</sup> area density.

<sup>b</sup> Concentration is based on the extraction of 1/2 of a 47 mm quartz-fiber filter in 15 ml of deionized-distilled water, with a nominal flow rate of 20 L/min for 24-h samples.

### *Analysis of organic compounds*

Organic compounds comprise a major portion of airborne particles in the atmosphere. Specific groups of organic compounds (e.g., polycyclic aromatic hydrocarbons, PAHs) have also been implicated in human health effects. However, due to the very complex composition of the organic fraction of atmospheric aerosols, the detailed composition and atmospheric distributions of organic aerosol constituents are still not well understood.

For organic analysis, PM is most frequently collected on quartz-fiber filters that have been specially treated to achieve low "carbon blanks". Outdoor organic PM has also been collected on a variety of particle sizing devices, such as low pressure impactors and Micro Orifice Uniforms Deposit Impactors ("MOUDI"). However, the task of sampling organic compounds in airborne particles is complicated by the fact that many of these compounds have equilibrium vapour pressures so that the concentration in the gas phase is of the same order of magnitude as the concentration in the condensed phase. This implies a temperature- and concentration-dependent distribution of such organic compounds between particulate and vapour phases. It also suggests that artefacts may occur during the sampling process. Volatilisation would cause the under-estimation of the particle-phase concentrations of organic compounds. Conversely, the adsorption of gaseous substances on deposited particles or on the filter material itself would lead



to over-estimation of the particle-phase fraction. In addition chemical degradation of some organic compounds may occur during the sampling procedure.

Since the organic fraction of airborne particulate matter is typically a complex mixture of hundreds to thousands of compounds distributed over many organic functional groups, its chemical analysis is an extremely difficult task (Appel et al. 1977; Simoneit 1984; Flessel et al. 1991; Hildemann et al. 1991; Li and Kamens 1993; Rogge et al. 1993a; 1993b; 1993c). Analyses of organic compounds generally begin with solvent extraction of the particulate sample. A variety of solvents and extraction techniques have been used in the past. One common method is sequential extraction with increasingly polar solvents, which typically separates the organic material into non-polar, moderately polar, and polar fractions (Daisey et al. 1982). This step is usually followed by further fractionation using open-column liquid chromatography and/or high-performance liquid chromatography (HPLC) in order to obtain several less complicated fractions (e.g., Schuetzle and Lewtas 1986; Atkinson et al. 1988). These fractions can then be analysed further with high resolution capillary-column gas chromatography (GC), combined with mass spectrometry (GC/MS), Fourier transform infrared (GC/FTIR/MS) or other selective detectors.

Much of the recent work on the identification of nonpolar and semi-polar organics in airborne samples has used bioassay-directed chemical analysis (Schuetzle and Lewtas 1986), and has focused on identification of fractions and compounds that are most likely to be of significance to human health. In particular, PAHs and their nitro-derivatives (nitroarenes) attracted considerable attention due to their mutagenic and, in some cases, carcinogenic properties. More than 100 PAHs have been identified in the PM<sub>2.5</sub> fraction of outdoor particulate matter (Lee et al. 1981). While most of the nitroarenes found in outdoor particles are also present in primary combustion-generated emissions, some are formed from their parent PAH in the atmospheric nitration reactions (e.g., Arey et al. 1986; Zielinska et al. 1989; Ramdahl et al. 1986).

Little work has been done to date to chemically characterize the polar fraction in detail, even though polar material accounts for up to half the mass and mutagenicity of soluble outdoor particulate organic matter (Atherholt et al. 1985; Gundel et al. 1994). Until recently the polar fraction has remained analytically intractable, since very polar and labile species interact with conventional fractionation column packing materials and cannot be recovered quantitatively. Recently, very polar particulate organic matter has been successfully fractionated using cyanopropyl-bonded silica (Gundel et al. 1994), with good recovery of mass and mutagenicity (Kado et al. 1989). However, outdoor particulate polar organic material cannot be analysed with conventional GC/MS because of GC column losses resulting from adsorption, thermal decomposition, and chemical interactions. New analytical techniques, such as HPLC/MS and MS/MS, need to be applied if the chemical constituents of polar particulate organic matter are to be identified and quantified.

Most of the recent work on the identification of particulate organic matter has focused on mutagenic and carcinogenic compounds that are of significance to human health. Relatively little work has been done to characterize individual compounds or classes of compounds that are specific to certain sources of organic aerosol. In urban and rural atmospheres, as well as in the remote troposphere, organic composition corresponding to chemical source profiles for of plant waxes, resin residues, and long-chain hydrocarbons from petroleum residues have been found (e.g., Gagosian et al. 1981; Simoneit 1984; Mazurek et al. 1987; 1989; 1991; Simoneit et al. 1991). However, a variety of smaller, multi-functional compounds characteristic of gas-to-particle conversion have also been observed (e.g., Finlayson-Pitts and Pitts 1986). These compounds tend to be present in the polar fraction of outdoor organic aerosol particles, having

been formed from atmospheric chemical reactions of less polar precursors. Little is currently known about the chemical composition of this polar fraction due to the serious analytical difficulties mentioned above.

Recent advances in infrared optics and detectors have resulted in the quantitative determination of the major functional groups (e.g., sulphate, nitrate, aliphatic carbons, carbonyl carbons, organonitrates, and alcohols) in the atmospheric aerosol (Allen et al. 1994). The advantages of functional analysis in source apportionment are that the number of functional groups is much less than the number of organic compounds to be classified.

Appendix 5 provides some details about the individual methods for analysis.

#### *Analysis of organic and elemental carbon*

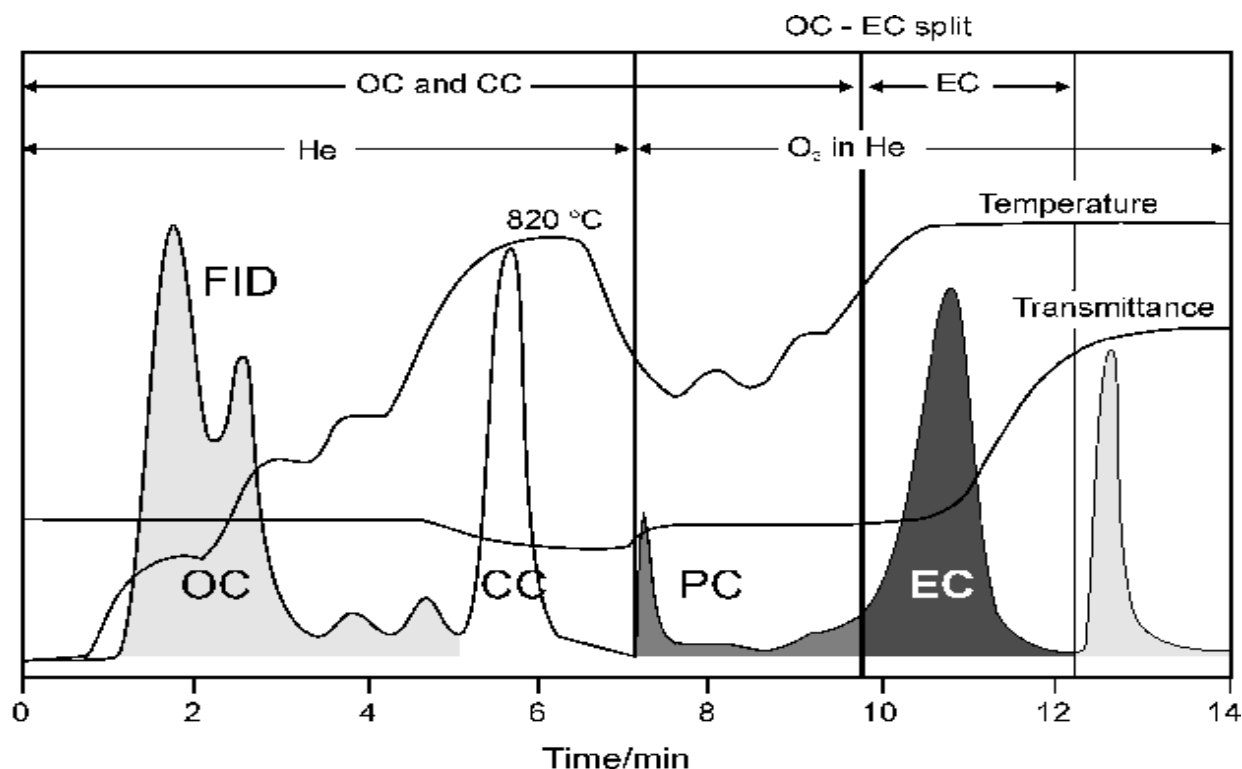
Elemental/Organic Carbon, Soot, or Particulate Organic Matter. Total carbon in aerosol particles (TC) can be expressed as the sum of organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC), with the contribution of CC to TC usually on the order of 5% or less, for particulate samples collected in urban areas (Appel 1993). In thermal separation methods, thermally evolved OC and EC are oxidised to CO<sub>2</sub> and quantified either by non-dispersive infrared detection or electrochemically, or the CO<sub>2</sub> can be reduced to CH<sub>4</sub> and quantified via flame ionisation detection (FID). The various methods give similar results for TC, but not for EC or OC.

In a methods comparison study (Countess 1990), it was shown that it is necessary to minimize or correct for pyrolytically generated EC (“char”), and that CC found in wood smoke and automobile exhaust samples may interfere with some of the thermal methods.

Pyrolytic char is corrected for in Thermal/Optical Reflectance (TOR) and Thermal/Optical Transmission (TOT) methods for the quantification of OC and EC on quartz fibre filter deposits. In thermal-optical carbon analysis (Birch and Cary 1996; Chow et al. 1993) punches from a quartz sampling filter are inserted into the carbon analyser and heated in a helium atmosphere to volatilise organic carbon. Then, the temperature is reduced, and oxygen is added to the carrier gas, so that desorbed compounds are then oxidised to CO<sub>2</sub>, reduced to methane, and measured in a flame ionisation detector. In order to account for the portion of the OC that is pyrolyzed, a He-Ne laser monitors the sample reflectance (or transmittance). As the pyrolysis occurs, the sample gets darker, and the reflectance decreases. Then, as elemental carbon is removed, the filter lightens, and the reflectance increases until all carbon has been removed from the filter. The split between organic and elemental carbon is considered to be the point at which the reflectance regains its pre-pyrolysis value, with material removed prior to this point being considered organic, and that after, elemental. In the TOR method the reflectance is monitored throughout the analysis and the TOR detection limit for EC and OC is 100 ng/m<sup>3</sup>.

The TOT is similar to the TOR with the primary difference being that light transmission rather than reflectance is monitored on the filter throughout the analysis. The TOT method of Birch and Cary (1996) consists of a two-stage process, with the first stage being conducted in a pure helium atmosphere, and the second stage conducted in a 10% oxygen-helium mix. The temperature is ramped to about 820 EC in the helium phase, during which organic and carbonate carbon are volatilized from the filter. In the second stage, the oven temperature is reduced, and then raised to about 860 EC. During the second stage, pyrolysis correction and EC measurement are made. Figure 6.1, an example of a thermogram, shows temperature, transmittance, and FID

response traces. Peaks are evident that correspond to OC, CC, EC, and pyrolytic carbon (PC). As can be seen in this figure, the high temperature in the first stage allows for decomposition of CC. The ability to quantify PC is particularly important in high OC/EC regions (like wood smoke-impacted airsheds), allowing for the volatilization of any remaining complex organic compounds so they are not apportioned to the EC phase.



**Figure 6.1** This thermogram, for a sample containing rock dust (a carbonate source) and diesel exhaust, shows three traces that correspond to temperature, filter transmittance, and FID detector response. Peaks correspond to organic (OC), carbonate (CC), pyrolytic (PC), and elemental (EC) carbon. The rightmost peak is a methane calibration peak. (Birch and Cary 1996).

The National Institute for Occupational Safety and Health (NIOSH) Method 5040 for monitoring elemental carbon as a marker for particulate diesel exhaust is based upon a TOT method analyser (Birch and Cary 1996), while the OC/EC method specified for the IMPROVE network is the TOR method (Chow et al. 2001). Chow et al. (2001) compared the OC, EC, and TC measurements from NIOSH and IMPROVE methods. The two methods differ in that temperature and atmospheric controls that are used to accomplish carbon speciation, in addition to the use of light transmission in the case of the NIOSH method, as compared to light reflectance in the IMPROVE method, of the filter is measured during the analysis. The IMPROVE thermal protocol specifies organic carbon fractions at 120, 250, 450, and 550 °C in a non-oxidizing atmosphere (He), and elemental organic fractions at 550, 700, and 800 °C in an oxidizing atmosphere. The NIOSH method differs in its thermal protocol, which has organic carbon fractions at 250, 500, 650, and 850 °C in a non-oxidizing atmosphere (also He), and elemental carbon fractions at 650, 750, and 850 °C in an oxidizing atmosphere. The high temperature before addition of oxygen in the NIOSH method is to quantify particulate carbonate, which

evolves between 650 and 830 °C (Birch and Cary 1996). The two methods also differ in the specified residence times at each temperature set point. The residence times at each set point are typically longer for the IMPROVE analysis compared to the NIOSH analysis.

Chow et al. (2001) analysed 60 quartz filter samples that represented a wide variety of aerosol compositions and concentrations. The TC measurements from each protocol were in good agreement, with no statistically significant differences. A statistically significant difference was observed in the fraction of TC that is attributed to EC, as determined by the IMPROVE and NIOSH thermal evolution protocols, with the IMPROVE EC measurements typically higher by approximately a factor of 2 than the NIOSH EC measurements. This difference was attributed to the 850 °C temperature step in the non-oxidizing atmosphere in the NIOSH protocol. Chow et al. compared the OC for each method and found that the two methods showed good agreement when the 850°C non-oxidizing temperature step in the NIOSH method was not included in determination of OC. There was also a difference between the reflectance and transmittance detection methods in the pyrolysis adjustment, although this difference was most noticeable for very black filters for which neither reflectance nor transmittance was able to accurately detect further blackening by pyrolysis. Because OC and EC are operationally defined parameters, Chow et al. pointed out that it is importance to retain ancillary information when reporting EC and OC by these analytical methods, so that comparisons can be made among measurements taken at different site using these two methods.

In 1986, the Carbonaceous Species Methods Comparison Study (CSMCS) was conducted in Los Angeles, CA, during which a number of methods for the measurement of this species were intercom pared. The CSMCS was mentioned in the 1996 PM AQCD (US EPA 1996). Hansen and McMurry (1990) specifically compared two very dissimilar methods for aerosol elemental carbon—collection of impactor samples backed by a quartz fiber after-filter, followed by EC analysis by oxidation in helium over a  $\text{MnO}^2$  catalyst, and real-time measurements using an aethalometer (an optical absorption technique)—and found good agreement between these two, very different methods. The CSMCS inter-laboratory precision for total carbon was 4.2% (Turpin et al. 2000). However, because the split between OC and EC is operationally defined, there was substantial inter-laboratory variability in OC and EC (e.g., 34% for EC [Turpin et al. 1990]). A recent inter-comparison in Europe showed that these discrepancies for the determination of EC are still present, with up to a facto of ten between the lowest and the highest value (Schmid et al. 2001). The implications for data analysis are

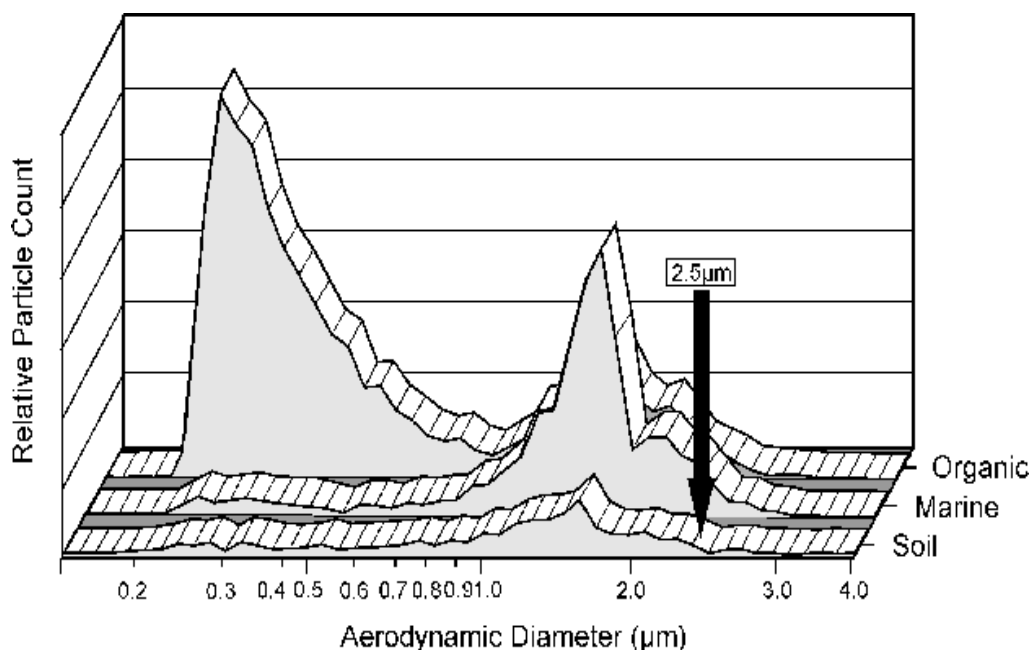
- (1) The analysis method used must be reported with particulate carbon data; and
- (2) Comparative analyses should not be conducted with data analysed by more than one carbon analysis method unless the mutual compatibility of the methods has been demonstrated.

### **6.3.2 Continuous measurement of chemical components of PM**

#### *Measurements of Individual Particles*

Recently, several researchers have developed instruments for real-time in situ analysis of single particles (e.g., Noble and Prather 1996; Gard et al. 1997; Johnson and Wexler 1995; Silva and Prather 1997; Thomson and Murphy 1994). Although the technique varies from one laboratory to another, the underlying principle is to fragment each particle into ions using either a high

power laser or a heated surface and to then use a time-of-flight mass spectrometer (TOFMS) to measure the ion fragments in a vacuum. Each particle is analysed in a suspended state in the air stream (i.e, without collection), avoiding sampling artefacts associated with impactors and filters. By measuring both positive and negative ions from the same particle, information can be obtained about the chemical composition, not just the elemental composition, of individual particles of known aerodynamic diameter. This information is especially useful in determining sources of particles. An example of the type of information that can be determined is shown in Figure 6.2.



**Figure 6.2** Size distribution of particles divided by chemical classification into organic, marine, and crustal.

Since particles are analysed individually, biases in particle sampling (the efficiency of particle transmission into the sensor chamber as a function of size; particle size measurement, and detection of particles prior to fragmentation) represent a major challenge for these instruments. Moreover, the mass spectrometer has a relatively large variability in ion yields (i.e., identical samples would yield relatively large differences in MS signals [Thomson and Murphy 1994]); therefore, quantitation is inherently difficult (Murphy et al. 1997). Quantitation will be even more challenging for complex organic mixtures because

- (a) A large number of fragments are generated from each molecule; and
- (b) Ion peaks for organics can be influenced or obscured by inorganic ions (Middlebrook et al. 1998).

Nonetheless, scientists have been successful in using these techniques to identify the presence of organics in atmospheric particles and laboratory-generated particles (i.e., as contaminants in laboratory-generated sulphuric acid droplets) as well as the identification of specific compound classes such as PAHs in combustion emissions (Castaldi and Senkan 1998; Hinz et al. 1994; Middlebrook et al. 1997; Middlebrook et al. 1998; Murphy et al. 1997; Neubauer et al. 1997; Noble and Prather 1998; Reilly et al. 1998; Silva and Prather 1997).

Until recently, single particle ATOFMS systems have only been able to characterize particles that are larger than approximately 0.2 to 0.3  $\mu\text{m}$  in diameter. The work of Wexler and colleagues (Carson et al. 1997; Ge et al. 1998) have developed a single particle, TOFMS instrument that it is able to size, count and provide chemical composition on individual particles ranging in size from 10 nm to 2  $\mu\text{m}$ .

Noble and Prather (1996) used ATOFMS to provide compositionally resolved particle size distributions. Their instrument is capable of analysing, at typical outdoor concentrations, size and chemical composition of 50 to 100 particles/min, and up to 600/min at high particle concentrations. Data storage requires are met using a Pentium 90 MHz personal computer.

#### *Automated Fine Particulate Nitrate*

An integrated collection and vapourisation cell was developed by Stolzenburg and Hering (2000) that provides automated, 10-min resolution monitoring of fine particulate nitrate. In this system, particles are collected by humidified impaction process and analysed in place by flash vapourisation and chemiluminescent detection of the evolved nitrogen oxides. In field tests in which the system was collocated with two US Federal Reference Method (US FRM) samplers, the automated nitrate sampler results followed the results from the US FRM, but were offset lower. The system was also collocated with a Harvard EPA annular denuder sampler (HEADS), as well as a SASS speciation sampler (MetOne Instruments). In all these tests, the automated sampler was well correlated to other samplers, with slopes near 1 (ranging from 0.95 for the US FRM to 1.06 for the HEADS) and correlation coefficients ranging from 0.94 to 0.996.

#### *Semi-continuous Carbon Analysis*

Several instruments have been developed that collect and analyse atmospheric organic PM with better than 2-h time resolution. An “in situ carbon analyser” measured total particulate organic and elemental carbon (i.e., Fg of carbon/ $\text{m}^3$ ) with 1 to 2 h resolution in Glendora and Claremont, CA, during 1986 and 1987 (Turpin and Huntzicker 1991; Turpin and Huntzicker 1995) and Atlanta, GA, during 1999 (Supersite experiment; unpublished). This in situ carbon analyser collects particulate matter on a quartz fiber filter mounted in a thermal-optical transmittance carbon analyser (Turpin et al. 1990). The material on a quartz fiber filter behind a Teflon filter in the second sampling port provides an estimate of the positive sampling artefact (i.e., gas adsorption on the quartz sampling filter). It does not correct for the negative sampling artefact due to vaporization of semivolatile organic compounds.

An automated carbon analyser with 15-min to 1-h time resolution is now commercially available (Rupprecht et al. 1995) and has been operated in several locations, including the Atlanta Supersite. It collects samples on a 0.1  $\mu\text{m}$  impactor downstream of an inlet with a 2.5  $\mu\text{m}$  cut point. Use of an impactor eliminates gas adsorption that must be addressed when filter collection is used. However, this collection system may experience substantial particle bounce, and a sizeable fraction of EC is in particles  $< 0.2 \mu\text{m}$ . In the analysis step carbonaceous compounds are removed by heating in filtered outdoor air. Carbonaceous material removed below 340 EC is reported as organic carbon, material removed between 340 and 750 EC is reported as elemental carbon. Turpin et al. (2000) comment that it would be more appropriate to report carbon values obtained by this method as “low-” and “high-temperature” carbon, since some organics are known to evolve at temperatures greater than 340 EC (e.g., organics from wood smoke). Hering (unpublished) has modified this system. Higher collection efficiencies are obtained for smaller particles by growing the particles by humidification prior to impaction.

## 6.4 Measurement of physical parameters other than mass

Physical Particle Characterization refers to measuring physical and geometrical descriptors of the particles like mass, number and diameter. These quantities are measurable by on-line methods and thus generally more easily accessible than chemical information.

### 6.4.1 Number concentration measurement

The safest and the only direct way of measuring particle number concentration is by counting particles in a given volume. In optical particle counters (OPCs) the light scattered by single particles is recorded. This is done by directing a constant aerosol flow through the focus of a light beam and by collecting a portion of the scattered light into a detector. Each particle then produces a pulse of the detector output and the number of pulses during fixed time intervals yields the particle concentration  $N$ . This technique only detects particles large enough to deliver a scattering signal in the measurable range. The cut-off size for most OPCs is above  $0.1\ \mu\text{m}$ . In order to register all particles in the relevant size range, condensation particle counters (CPCs) are used. A CPC contains a particle magnifier, in which a liquid condenses on the particles, growing them to a size detectable by an OPC, which follows in a continuous flow arrangement. CPCs detect particles down to a diameter of  $10\ \text{nm}$  or even  $3\ \text{nm}$ . Most CPCs are very sensitive to shock or motion but provided they are properly drained and dried out before being used, they are quite suitable for many field measurements.

The lower cut-off size of particle counters is of great importance, especially if a significant amount of the particles are smaller than the cut-off. This is the case, even for a cut-off of  $10\ \text{nm}$  in environments where fresh aerosols from combustion are present, e.g. in cities, where automobiles are a major source. In order for the response of particle counters to be comparable, the counting efficiencies must be precisely known as function of particle size. For most instruments the counting efficiencies are near unity for most of the size range and steeply fall to zero, when the particle size is reduced to the minimum size certified. The critical size defining this cut-off curve may vary considerably from instrument to instrument, even within the same series. Comparison and inter-calibration of the counting instruments used is therefore essential. A calibration procedure is described by Wiedensohler et al. (1997).

There is presently no alternative to CPCs for particle concentration measurement. All other existing methods like those measuring collective extinction or scattering from an aerosol probe require information on particle size, shape and composition to derive the true number concentration.

### 6.4.2 Size measurement

#### 6.4.2.1 Size separation by impactors

Impactors are devices primarily used for determination of size dependent particle composition. Multistage impactors (Willeke and Baron 1993) consist of several stages, each composed of an orifice and an impaction plate opposite to it. Between orifice and plate the flow performs a  $90^\circ$  bend. Due to their inertia, large particles follow the flow less well than small ones. Particles above a certain aerodynamic size impinge on the plate, where they stick. The nozzle-plate geometry and the gas pressure at each particular stage define the cut-off diameter. Thus, particles are separated according to their aerodynamic diameters. The smallest diameters separable with

commercial impactors are some tens of nanometers. In order to obtain the particle size distribution, the masses of the deposits of each stage must be determined gravimetrically.

Impactors have been developed, which use quartz microbalances (see section 6.2.3) to give a direct measure of the deposited mass on each stage, and thus deliver a discrete approximation of the aerodynamic size distribution directly (Chuan 1976). These devices suffer from the restrictions concerning mass loading and poor response to agglomerated particles mentioned in 6.2.3.

#### ***6.4.2.2 Time of flight-aerodynamic sizing***

Besides impactors, so-called aerodynamic sizing instruments yield the distribution of particle sizes. In these instruments, the aerosol sample is accelerated in the flow through an accelerating orifice. The aerodynamic size of a particle determines its rate of acceleration, with larger particles accelerating more slowly due to increased inertia. As particles exit the nozzle, they cross through two partially overlapping laser beams in the detection area. Light is scattered as each particle crosses through the overlapping beams. Part of the scattered light is collected into a photo detector, which converts the light pulses into electrical pulses. The time between these is related to their velocity and the aerodynamic diameter is calculated for each particle detected. The smallest particle diameter to be measured this way is typically around 0.5  $\mu\text{m}$ . The TSI Model 3320 is an example of such an instrument (TSI 2000a). It also measures the scattering peak height, which provides additional information related to the composition of the particle.

#### ***6.4.2.3 Mobility measurement***

The mobility equivalent diameter distribution is measured in a so-called differential mobility analyser (DMA) (Fissan et al. 1983). The particles must be electrically charged to apply this technique. The aerosol is subjected to an electric field, usually perpendicular to the laminar flow. Due to the resulting electrostatic force on the particles, they are deflected. The deflection depends on their size, and particles of a certain size land at a slit, where they are separated from the rest of the aerosol. The particle size extracted depends on the electric field. Scanning the field and measuring the number concentration of the extracted particles can determine the size distribution of an outdoor aerosol determined quasi continuously.

A variety of DMA models are on the market. Among others, they are sold as measurement systems called the Differential Mobility Particle Sizers (DMPS) and the Scanning Mobility Particle Sizers (SMPS) (TSI 2000a). They contain a diffusion charger, a DMA and condensation particle counter. The recorded function is automatically converted to the particle size distribution by a suitable algorithm. The difference between the DMPS and SMPS systems consists of the time required for recording of a mobility distribution. This takes less than a minute with an SMPS system and several minutes with a DMPS system, which provides more precise size distribution data. The inlets are usually equipped with impactors with a 1- $\mu\text{m}$  cut-off. This defines a well-defined maximum size, which is required for data reduction. Different data reduction algorithms have been applied in these systems, leading to significantly different results. The size distributions obtained with them must therefore still be regarded as approximations. When using several sizing instruments in a field study, these must be inter-calibrated. The largest particle size measured by commercial systems is 1  $\mu\text{m}$ . The diameters obtained by mobility analysis are called “mobility equivalent diameters”.



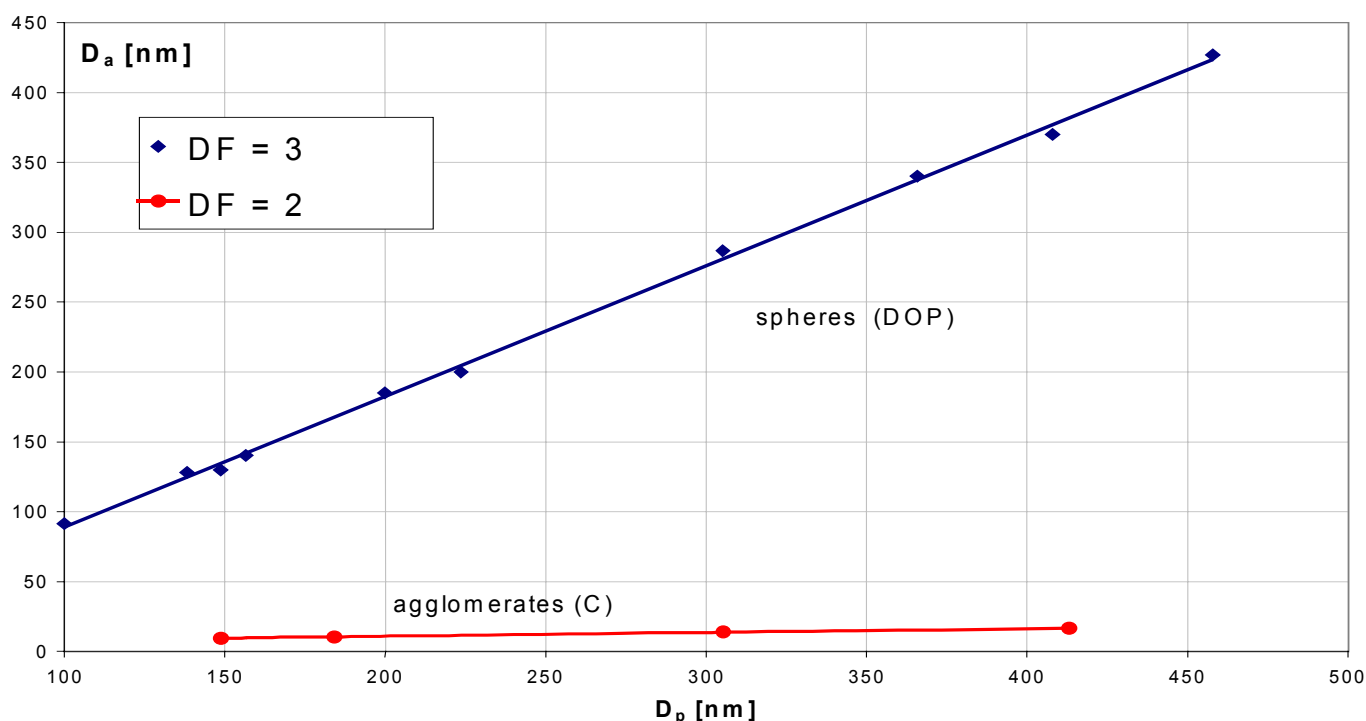
#### 6.4.2.4 Optical sizing instruments

Optical sizing instruments use the fact that the light scattered by a particle under a given radiation depends on its size. The smallest particle sizes measurable are around  $0.1\ \mu\text{m}$ . While the mobility equivalent diameter only depends on the particle geometry, and the aerodynamic diameter depends on geometry plus density, any optical diameter depends very much on the composition of the particle in addition to its geometry. Forward scattering instruments minimize this dependence, but their sensitive size range is restricted to supermicrometer particles.

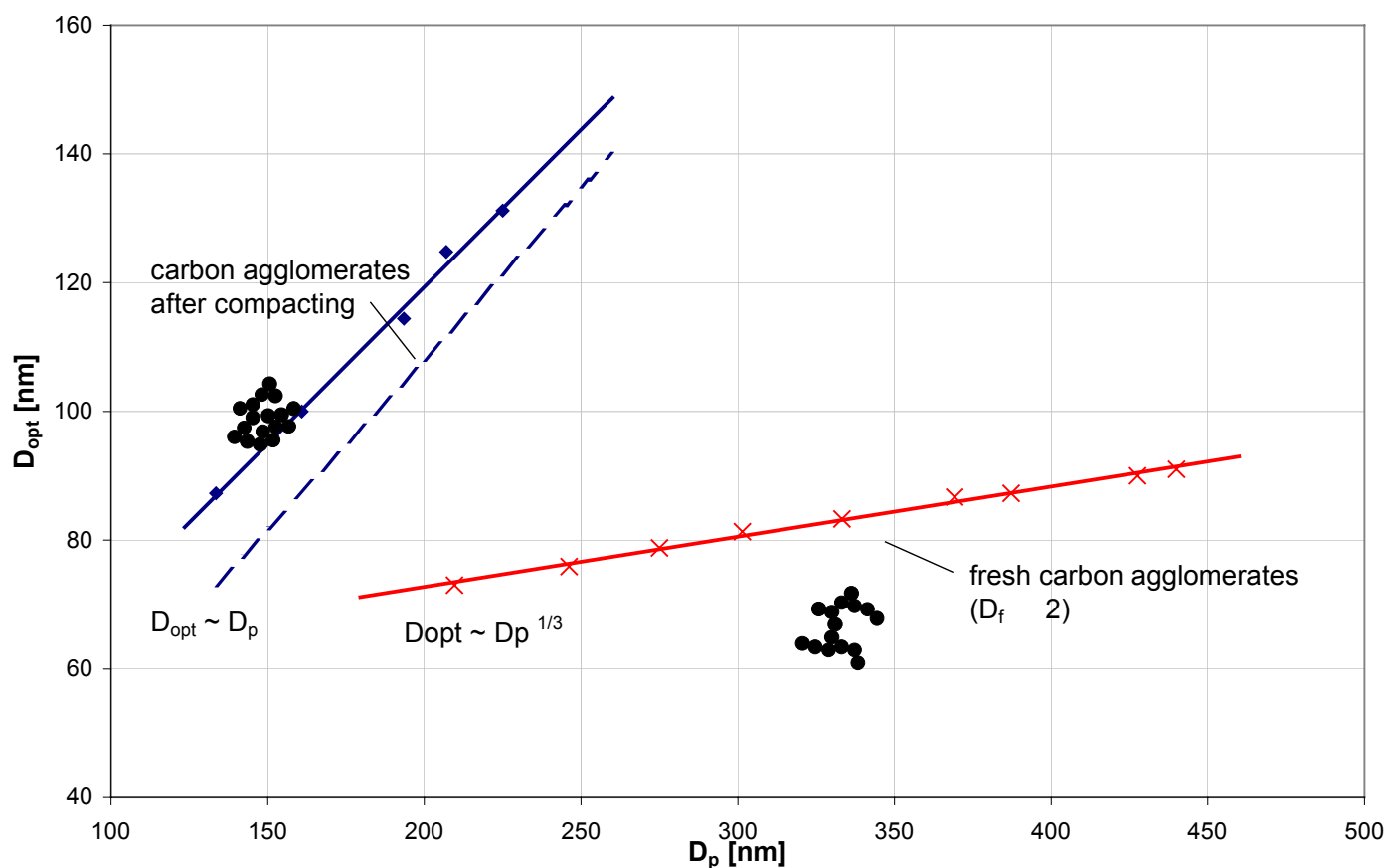
#### 6.4.2.5 Combining instruments of different physical principles

Mobility analysis is restricted to particles smaller than  $1\ \mu\text{m}$  with the charging techniques applied today. For the large particle end of the spectrum, aerodynamic methods are used. The aerodynamic particle sizer measures from  $0.5\ \mu\text{m}$  upwards and thus has an overlap with the mobility analysers on the market. Optical sizing is used as an alternative to cover the range from approximately  $0.3\ \mu\text{m}$  and up.

When combining these techniques to cover the whole outdoor size range from a few nanometers to  $10\ \mu\text{m}$ , it is often not considered that the methods determine different physical quantities. Figs. 6.3a and 6.3b illustrate, how fundamentally different the meaning of the aerodynamic, the mobility equivalent and an optical scattering equivalent diameter is, if the particles are not spherical, but have the typical fractal-like structure of fresh agglomerates (fractal dimension  $\leq 2$ ) (Schmidt-Ott and Wuestenberg 1995). By definition, these three diameters coincide only for the case of spheres. Fractal-like shapes are at least as abundant as spherical droplets in a city atmosphere, in which combustion processes like in Diesel engines are a major source.



**Figure 6.3a** Aerodynamic diameter,  $D_a$  vs. mobility equivalent diameter,  $D_p$  of spherical droplets (fractal dimension  $DF=3$ ) and fresh carbon agglomerates (fractal dimension  $DF\approx 2$ )



**Figure 6.3b** Optical scattering diameter,  $D_{opt}$  vs. mobility equivalent diameter,  $D_p$  of fresh carbon agglomerates (fractal dimension  $DF \approx 2$ ) and agglomerates compacted into close packings.

#### 6.4.2.6 Calibration of sizing instruments.

There are presently no national or international standards for aerosol sizing instruments. Absolute calibration is usually based on comparison with electron micrographs of deposited particles. Absolute precision of the particle size is of minor importance in epidemiological studies, whereas the agreement of the performance of the instruments is crucial. Intercomparison studies are therefore essential.

### 6.4.3 Particle surface related measures

#### 6.4.3.1 Gas adsorption methods

The classical way of measuring the joint surface of particles is via gas adsorption, which is usually referred to as the BET method. The amount of inert gas (usually nitrogen) adsorbed to a cooled sample is measured as a surface proportional quantity. A typical particle mass of 1 g as a powder is required for these methods. If the particles are sampled from the air with a high volume sampler at  $1.5 \text{ m}^3/\text{min}$ , it would require 50 days to obtain 1 g, if the air contains  $10 \mu\text{g}/\text{m}^3$  of particulate matter. This example demonstrates that conventional gas adsorption methods are far from capable of delivering data with a time resolution as required for epidemiological studies

#### 6.4.3.2 *The epiphaniometer and the diffusion-charger-electrometer combination*

The epiphaniometer (Gäggeler et al. 1989) is a sensor, the response of which is related to what has been referred to as “Fuchs Surface” or “active surface” of aerosol particles.

In a continuous flow arrangement, the aerosol is sucked passed a piece of the isotope  $^{227}\text{Ac}$ . This isotope decays to form  $^{219}\text{Rn}$ , which emanates out of the material as a gas. Within 4 minutes  $^{219}\text{Rn}$  decays into  $^{211}\text{Pb}$ . These atoms diffuse in the gas and stick to any surface they hit. Thus the particles pick up atoms of this lead isotope with a probability connected to their size and geometrical shape. The aerosol of these radioactively marked particles flows through a capillary, where all unattached  $^{211}\text{Pb}$  atoms are removed by attachment to the wall, and is then directed through a filter, where all particles are held back.

The  $^{211}\text{Pb}$  attached to them is detected quantitatively by means of its characteristic  $\alpha$  radiation. The sensor signal is the number of  $\alpha$  particles detected per unit time. The response time is in the order of some minutes, and the detection limit of the device is about  $60 \text{ ng/m}^3$  for  $0.8 \text{ }\mu\text{m}$  particles and below that for smaller particles.

The response of this instrument is proportional to the flux of molecules diffusing in the gas to the particles, where the molecules have the property of sticking at the first collision. If only spherical particles of one size were present, the response would be proportional to the square of the particle diameter for particles much smaller than the molecule mean free path ( $\lambda=0.066 \text{ }\mu\text{m}$  under normal conditions) and proportional to the diameter for particles larger than  $\lambda$ . Thus the epiphaniometer delivers a signal proportional to the joint particle surface only for very small spherical particles. A drawback of the epiphaniometer is that it requires radioactive material.

A Diffusion-Charger-Electrometer Combination (DCE) (see e.g. Willeke and Baron. 1993) practically yields the same information as the epiphaniometer (Schmidt-Ott et al. 1990; Keller et al. 2000). It is considered as probably the simplest device producing a particle dependent signal. Leading it through a zone flooded with small ions charges an aerosol. This process is called diffusion charging (Büschler et al. 1994). As the lead atoms in the epiphaniometer, the ions attach to the particles. In a continuous flow arrangement, the aerosol is then passed through a so-called aerosol electrometer (Willeke and Baron 1993), which measures the current carried by the particle charge. The response of this simple sensor is afflicted with the same problem as the epiphaniometer concerning the physical meaning of its response. A great advantage of the charger-electrometer combination lies in the simplicity of its construction associated with a low price. Charger-electrometer combinations are commercially available and are occasionally called Fuchs Surface Sensors.

The sensor “counts” particles, where large ones contribute more strongly to the response than small ones. More precisely, the sensor weights the particle count with the diameter to the power of  $x$ . A good approximation for  $x$  is  $x=1.5$ , if only ultra fine particles are measured (smaller than  $0.1 \text{ }\mu\text{m}$  in diameter) (Schmidt-Ott and Kauffeldt 1999), and  $x=1.1$  is a value which can be used in the sense of an approximation for the range  $0.01 \text{ }\mu\text{m}$  to  $10 \text{ }\mu\text{m}$  (Woo et al. 2001). The measurement of particle number corresponds to  $x=0$  and for particle volume or mass,  $x=3$ . A DCE thus provides a signal, which is intermediate between number and mass. It can be regarded as a rough approximation of the joint particle diameter. If all particles in a unit volume of air would be aligned in a chain, the chain length would approximately represent the DCE signal. For non-spherical particles, the relevant diameter is the mobility equivalent diameter.

There is presently no published calibration procedure, although such a procedure could be carried out quite easily using a monodisperse aerosol of particles carrying single elementary charges and comparing with the number concentration. For epidemiological studies using several DCE instruments, absolute calibration of the signal is of minor importance. If several instruments are used, inter-comparison of the instrument responses prior to recording of data and periodically during the study is essential.

#### **6.4.4 Discussion of instrumentation for physical particle analysis**

In connection with epidemiological studies it would be most desirable to measure a relevant set of integral parameters for physical characterization of an aerosol. Ideally, the standards should be based on unambiguous basic physical or geometric quantities such as mass, volume, surface or number. If epidemiological studies show correlations between integral parameters and health effects, such parameters would provide a useful starting point in the search for physiological effects, especially if the integral parameters directly refer to basic properties of probable relevance in physiological models or hypotheses. Examples of such descriptors are the total particle surface area and the particle number concentration. On the other hand, a measuring procedure, which is simple and cheap, has some attractiveness, because a dense area-wide network of measuring stations will often be desirable. Table 6.3 summarizes the physical quantities of probable relevance for health effects and comments on the instrumental means available today for this purpose.

**Table 6.3** Physical parameters of potential relevance for assessing health effects due to PM

Quantity Measured	Weighting of Diameter ( $D_p$ )	Off-Line Measurement?	On-Line Measurement?	Absolute Standard Available?	Remarks
Mass	$D_p^3$	Yes	Yes	Yes	On-line measuring instruments are rather expensive, see 6.2.1 for standard
Joint Surface	$D_p^2$	No	No	No	--
Joint Diameter	$D_p^1$	No	No	No	--
Number Concentration	$D_p^0$	No	Yes	Yes	Rather expensive instruments
Joint Attachment Coefficient	$D_p^{1.16}$	No	Yes	Yes	The diffusion charging electrometer combination is a relatively inexpensive method. The epiphaniometer is an alternative for very low concentrations
Size Distribution	--	Yes	Yes	Yes	Mobility equivalent diameter below 1 $\mu\text{m}$ and aerodynamic diameter above 0.1 $\mu\text{m}$ ; Expensive equipment required.

Woo et al. (2001) have demonstrated that from the three integral parameters number, mass and the DCE response an estimate of the “total surface” can be derived in addition to mass and number, as well as an approximate size distribution. This is an alternative to measurement of a complete size distribution by an expensive DMA based system. It must be kept in mind that the value of this “total surface” is an equivalent one based on unrealistic assumptions such as spherical particle shape. It does not account for pores or the “inner surface” of agglomerates, which may well be very important for health effects. Nevertheless, number, mass and the DCE response give a good physical representation of an ambient aerosol condensed into 3 parameters using technology available today. In cases where budget limitations do not allow determination of more than one physical parameter, the DCE response is a compromise reflecting both the fine and the ultra fine particle fractions.

#### **6.4.4.1 Needs in research and development**

As particle mass ( $PM_{10}$  or  $PM_{2.5}$ ) has been the standard for some time now, the greatest effort of instrument developers has been put into mass measurement, and on-line measurement of particle mass as a integral parameter actually exists for  $PM_{10}$  and  $PM_{2.5}$ . Extension of the  $PM_x$  series down to smaller cut-off diameters, e.g.  $PM_1$ , would provide quite a useful picture of the mass size distribution and would be in line with former standards. No feasible methods for recording these integral quantities below  $PM_1$  presently exist, and there is a great need of research and development here.

In view of the suspected health effects of ultra fine particles, number concentration is a valuable parameter characterizing the airborne particle load. In practice, it is a measure of the ultra fine particle load, because ultra fine particles typically dominate in number. Counters less delicate and less expensive than those based on the condensation principle are highly desirable.

There is presently no useful approach that could lead to an on-line monitor of the joint particle surface in outdoor air. If such an instrument existed, recording this quantity would certainly be of great interest for epidemiological studies.

Due to the problems pointed out in Section 6.4.2.5, in order to measure the entire ambient size range, it is necessary to combine instruments based on different physical principles and thus measuring different “equivalent diameters”. Therefore, there is great need for a simple size-measuring instrument that applies only one functional principle for the whole range.

Hygroscopicity and volatility of airborne particles are of probable health relevance. The size dependence of these parameters has been measured with dual DMA arrangements in atmospheric field studies. Less expensive instrumentation delivering more condensed data such as a hygroscopicity factor of the ultra fine and one for the fine mode would be useful.

## **6.5 Conclusions**

Unambiguous integral parameters characterizing environmental aerosols, which can be continuously measured, are number and mass. The clear definition of these quantities leaves freedom to instrument developers in choosing the functional principle and in developing less expensive instruments than the existing ones. In addition, the response of a diffusion charger electrometer combination (DCE) is a useful parameter. Here the meaning of the response is not straightforward, and the method is defined more easily than the response. Woo et al. (2001) have

demonstrated that from these three parameters (number, mass and the DCE response) an estimate of the “total surface” can be derived in addition to mass and number, as well as an approximate size distribution. It must be kept in mind that the value of this “total surface” is an equivalent one based on unrealistic assumptions such as spherical particle shape. Similar to the surface parameter derived from a mobility distribution, it does not account for pores or the “inner surface” of agglomerates, which may well be very important for health effects. Nevertheless, number, mass and the DCE response give a good physical representation of an ambient aerosol condensed into 3 parameters using technology available today. It is therefore proposed to measure mass according to the PM<sub>10</sub> and/or PM<sub>2.5</sub> standard as well as the total number and the DCE response for continuous physical aerosol characterization.

As a final note, a point to consider when planning and conducting measurements is: What can be measured may not be what is hoped to be measured.

## Appendix 1

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## Appendix 2

### Acronyms

AAS	Atomic Absorption Spectrophotometric
AC	Automated Colorimetry
APHEA	Air Pollution and Health: A European Approach
APS	Aerodynamic Particle Sizer
ATDSR	Agency for Toxic Substances and Disease Registry (USA)
BALT	Bronchus-Associated- Lymphoid Tissue
BS	Black smoke
BW	Body weight
CaCO <sub>3</sub>	Calcium carbonate
CAPs	Concentrated outdoor Air Particles
Cd	Cadmium
CH <sub>4</sub>	Methane
CMD	Count Median Diameter
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
COPD	Chronic Obstructive Pulmonary Disease
CPC	Condensation Particle Counters
Cu	Copper
DDW	Deionised-distilled water
DMA	Differential Mobility Analyser
DCE	Diffusion-Charger-Electrometer Combination
DMPS	Differential Mobility Particle Sizers
EC	Elemental carbon
EPA	US Environmental Protection Agency
ETS	Environmental Tobacco Smoke
FRM	Federal Reference Method (US)
H <sup>+</sup>	Hydrogen ion associated with acid aerosol exposure
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
HC	Hydrocarbons
HEI	Health Effects Institute
HiVol	High Volume Sampler
HNO <sub>3</sub>	Nitric acid
IL6	Interleukin-6
IL8	Interleukin-8
INAA	Instrumental Neutron Activation Analysis
ISO	International Standards Organization
MHz	Megahertz
MMD	Mass Median Diameter
Mn	Manganese
Mø	Pulmonary Macrophage
µm	Micrometer
µg	Microgram
MTB	Methylthymol Blue
NaCl	Sodium chloride
NMD	Number Median Diameter
NMMAPS	National Morbidity, Mortality, and Air Pollution Study
NH <sub>3</sub>	Ammonia
NH <sub>4</sub> <sup>+</sup>	Univalent ammonium radical

NH <sub>4</sub> HSO <sub>4</sub>	Ammonium bisulphate
(NH <sub>4</sub> ) <sub>2</sub> HSO <sub>4</sub>	Ammonium hydrogen sulphate
NH <sub>4</sub> NO <sub>3</sub>	Ammonium nitrate
Ni	Nickel
NO	Nitrogen oxide
NO <sub>2</sub>	Nitrogen dioxide
NO <sub>3</sub> <sup>-</sup>	Nitrate
NO <sub>x</sub>	(NO and NO <sub>2</sub> )
O <sub>3</sub>	Ozone
OC	Organic carbon
OEH	Occupational and Environmental Health, WHO, PHE, Geneva
OM	Organic material
OPC	Optical Particle Counters
PAH	Polycyclic Aromatic Compounds
Pb	Lead
PEACE	Pollution Effects on Asthmatic Children in Europe
PEM	Personal Exposure Monitor
PHE	Department for Protection of the Human Environment, WHO, Geneva
PM	Particulate matter
PTEAM	Particulate Total Exposure Assessment Methodology (USEPA)
RH	Relative humidity
RPM	Respirable particulate matter
ROFA	Residual oil fly ash
ROI	Reactive Oxygen Intermediates
RSP	Respirable Suspended Particulate Matter
SEM	Scanning electron microscope
SMPS	Scanning Mobility Particle Sizer
Si	Silicium
SPECT	Single Photon Emission Computed Tomography
SO <sub>2</sub>	Sulphur dioxide
SO <sub>4</sub> <sup>=</sup>	Sulphate ion
SO <sub>x</sub>	SO <sub>4</sub> and SO <sub>2</sub>
SOPs	Standard Operating Procedures
STEM	Scanning transmission electron microscope
TC	Total carbon
TEM	Transmission electron microscope
TEOM	Tapered Element Oscillating Microbalance
THEES	Total Human Environmental Exposure Study
TSP	Total Suspended Particles
UNEP	United Nations Environment Programme
US EPA	United States Environmental Protection Agency
UF	UltraFine size range
V	Vanadium
VAPS	Versatile Air Pollution Samples
VOCs	Volatile Organic Compounds
WBC	White Blood Cells
WHO	World Health Organization
WRAC	Wide-Ranging Aerosol Collector
XRF	X-ray fluorescence
Zn	Zinc

## Appendix 3

### Glossary

Accumulation mode particles	A mode in the atmospheric particle size distribution, formed primarily by coagulation of smaller particles (Willeke and Baron 1993).
Administered dose	The amount of an agent that is actually ingested, inhaled or applied to the skin (WHO 2000c).
Adverse health effects	Change in morphology, physiology, growth, development or life span of an organism exposed to air pollution, which results in impairment of functional capacity or impairment of capacity to compensate for additional stress or increase in susceptibility to the harmful effects of other environmental influences (WHO 1994).
Aerodynamic (equivalent) diameter	Diameter of a unit-density sphere having the same gravitational-settling velocity as the particle in question (Willeke and Baron 1993).
Aerosol	A suspension in a gaseous medium of solid particles, liquid particles or solid and liquid particles having a negligible falling velocity (ISO 1994).
Air shed	A body of air bounded by topography and meteorology in which a contaminant, once emitted, is contained (SEQRAQS Steering Group 1998).
Algorithm	A sequence of algebraic and logical operations that produces an approximation to a mathematical or physical problem (Burden et al. 1981).
All-cause mortality	Death rate due to all causes.
Alveolar	Pertaining to an air sac of the lungs (alveolus, CMD 1997)
Alveolar macrophage	A monocyte (= a mononuclear phagocytic (= able to ingest and digest bacteria, protozoa, cells and cell debris and dust particles) white blood cell) that has left the circulation and settled and matured in the alveoli (air sacs of the lung) (CMD 1997).
Anthropogenic	Produced by human beings or activities.
Applied dose	Amount of an agent directly in contact with the body's absorption barriers, such as the skin, respiratory tract and gastrointestinal tract, and therefore available for absorption (WHO 2000c).
Arrhythmia	Irregularity or loss of rhythm, esp. of the heartbeat (CMD 1997).
Bias	Any Effect at any stage of investigation or inference tending to produce results that depart systematically from the true values (Sackett 1979)
Biogenic	Produced by living organisms (CMD 1997).

Biologically effective dose	The amount of a substance that reaches a particular tissue.
Biomarker	Any parameter that can be used to measure an interaction between a biological system and an environment agent, which may be chemical, physical or biological (WHO 1993).
Biomass	Organic substance of biotic origin: either living organisms or dead substances such as wood, crop residues, or animal dung.
Birth cohort	A cohort study with participants recruited at birth.
Black smoke	Surrogate for suspended particles used in UK and is defined according to a special measuring procedure, indicating the density of blackness on a certain filter system.
Blood coagulation	The process of clumping together of blood cells to form a clot (CMD 1997).
Blood coagulation factors	The various factors involved in the coagulation process. At present 13 factors are used (CMD 1997).
Blood oxygenation	Saturation or combination with oxygen of the blood (CMD 1997).
Breathing zone	Zone where inhaling and exhaling takes place (adapted from CMD 1997).
Carbon dioxide	A colourless, odourless, non-combustible gas, formula $\text{CO}_2$ . It is approximately 50% heavier than air, of which it is a normal constituent. It is formed by certain natural processes (see carbon cycle) and by the combustion of fuels containing carbon, and it has been estimated that the amount in the air is increasing by 0.27% annually. Only in the most exceptional circumstances do local concentrations of carbon dioxide in air rise to levels that are dangerous to health, but it plays a significant role in the decay of building stones and in corrosion (WHO 1980).
Carbon monoxide	A colourless, almost odourless, tasteless, flammable gas, formula $\text{CO}$ . It is produced, <i>inter alia</i> , by the incomplete combustion of organic materials (e.g. in automobile engines) and normally occurs in trace amounts in the atmosphere. At concentrations exceeding about $100 \text{ cm}^3/\text{m}^3$ (0.01%) it is highly toxic. Its affinity for hemoglobin (with which it forms carboxyhemoglobin) is between 200 and 300 times that of oxygen, and it has the effect of reducing the oxygen-transport capacity of hemoglobin and leading to death by asphyxiation. Concentrations of carbon monoxide in city streets (arising mainly from motor vehicle exhausts) can be sufficiently high to cause concern, as can those resulting from tobacco smoking in unventilated rooms (WHO 1980).
Carbonaceous particles	Particles consisting mostly of carbon compounds
Cardiac end points	Target parameters pertaining to the heart.
Cardiovascular	Pertaining to the heart and blood vessels (CMD 1997).
Cardiovascular disease	See “cardiovascular” and “disease”.

Case control study	Longitudinal (relating to more than one point in time) epidemiological study of people with a disease or other outcome variable of interest (cases) and a suitable control group (WHO 1993).
Case-crossover design	Case control study in which the experimental design changes case-group and control-group in the second phase of the study, to eliminate group-specific confounders.
Chemical composition	The contents of particles of chemical elements.
Cilia	Threadlike projections from the free surface of epithelial cells such as lining the trachea and bronchi (CMD 1997).
Ciliated	Possessing cilia (CMD 1997).
Coagulation	The process of clumping together of blood cells to form a clot (CMD 1997). Coagulation is the process whereby aerosol particles collide with each other due to a relative motion between them, and adhere to form larger particles. Coagulation leads to a decrease in particle number concentration and to an increase in particle size, and leaves the total particle mass unaffected.
Coarse particle fraction	The particle size fraction between 2.5 and 10 micrometer.
Cohort study	Study of the incidence (occurrence of new cases) of disease or other health outcome in a group of people (a cohort) initially free of disease or other outcome, who are classified into subgroups according to exposure to a potential cause of disease or health outcome (WHO 1993).
Combustion	A chemical reaction in which a material combines with oxygen with the evolution of heat: “burning”. The combustion of fuels containing carbon and hydrogen is said to be complete when these two elements are all oxidized to carbon dioxide and water. Incomplete combustion may lead to (1) appreciable amounts of carbon remaining in the ash; (2) emission of some of the carbon as carbon monoxide; and (3) reaction of the fuel molecules to give a range of products of greater complexity than that of the fuel molecules themselves (if these products escape combustion they are emitted as smoke) (WHO 1980).
Community time series epidemiology	Epidemiological studies that assess the impact of exposures on day-to-day variation in health events within a community.
Condensation	A process with more vapour molecules arriving at a particle’s surface than leaving the surface, resulting in a net growth of the particle (Willeke and Baron 1993).
Confounder	Variable that influences an health effect apart from air pollution. In particular, a confounder is associated with the exposure and the outcome and effect estimates would be biased if the variable would be neglected in the analyses.

COPD (chronic obstructive pulmonary disease)	A disease process that decreases the ability of the lungs to perform ventilation. Diagnostic criteria include a history of persistent dyspnea on exertion, with or without chronic cough, and less than half of normal predicted maximum breathing capacity. Diseases that cause this condition are chronic bronchitis, pulmonary emphysema, chronic asthma, and chronic bronchiolitis (CMD 1997).
Coronary artery disease	Disease of one of a pair of arteries that supply blood to the myocardium of the heart (CMD 1997).
Correlation coefficient	Measure of mutual relationship between two variables (Snedecor 1976).
Correlation-sectional study	An epidemiological study that measures exposure and prevalence of disease at the same time (WHO1993).
Count median diameter	A diameter for which equal number of particles is above and below this size.
Cross-sectional study	An epidemiological study that measures exposure and prevalence of disease at the same time (WHO1993).
Crustal elements	Elements derived from a crustal origin
Cumulative effects	Health effects that increase if exposures last several days.
Cut-off diameter	Diameter of particle which has 50% probability of being removed by the device or stage and 50% probability of passing through (Willeke and Baron 1993).
Cyclone	A device in which particles are removed by centrifuginal forces in a cyclonic path (Willeke and Baron 1993).
Cytokine	One of more than 100 distinct proteins produced primarily by white blood cells. They provide signals to regulate immunological aspects of cell growth and function during both inflammation and specific immune response (CMD 1997).
Defibrillator	An electric device that stops quivering or spontaneous chaotic contraction of individual muscle fibres (threadlike structure) of the heart (CMD 1997)
Deliquescent	Becoming liquefied or moist by absorbing of water from the air (CMD 1997).
Dewpoint temperature	The temperature to which a given parcel of air must be cooled at constant pressure and constant water-vapour in order for saturation to occur. Any further cooling usually results in the formation of dew (WMO 1992).
Diesel exhaust	Diesel exhaust emissions contain hundreds of chemical compounds, which are emitted partly in the gaseous phase and partly in the particulate phase of the exhaust. The major gaseous products are carbon dioxide, oxygen, nitrogen, and water vapour; carbon monoxide, sulphur dioxide, nitrogen oxides, and hydrocarbons and their derivatives are also present. Benzene and toluene are present in the lower range (percentage weight) in the gaseous part of the hydrocarbon fraction. Other gaseous exhaust compounds are low-

relative-molecular-mass polycyclic aromatic hydrocarbons. A main characteristic of diesel exhaust is the release of particles at a rate about 20 times greater than that from gasoline-fuelled vehicles. The particles are composed of elemental carbon, organic compounds adsorbed from fuel and lubricating oil, sulphates from fuel-sulphur, and traces of metallic components. Most of the total particulate matter appears to occur in the submicrometer range, between 0.02 and 0.5  $\mu\text{m}$  (WHO 1996).

Diffusion (equivalent) diameter	Diameter of a sphere with the same diffusional properties as the particle in question.
Disease	A pathological condition of the body that presents a group of clinical signs, symptoms, and laboratory findings peculiar to it and setting the condition apart as an abnormal entity differing from other normal or pathological condition (CMD 1997).
Dose	<ol style="list-style-type: none"> <li>The amount of a substance to which a person is exposed (ATDSR 1999).</li> <li>The amount of a contaminant that is absorbed or deposited in the body of an exposed organism for an increment of time – usually from a single medium (NRC 1991).</li> <li>The amount of substance available for interaction with metabolic processes or biologically significant receptors after crossing the outer boundary of an organism.</li> </ol>
Dose assessment	Process of determining dose and the uncertainty included in the dose estimate through the use of exposure scenarios, bioassay results, monitoring data, source information and pathway analysis (adapted from USDOE 2000).
Dose-response curve	<ol style="list-style-type: none"> <li>A mathematical relationship between the dose administered or received and the incidence of adverse health effects in the exposed population (AIHA 2000).</li> <li>A quantitative relationship between administered, applied, or internal dose and probability of occurrence of a health effect or effects (US EPA 1992).</li> </ol>
Dose-response relationship	<ol style="list-style-type: none"> <li>The relationship between the dose of a pollutant and the response (or effect) on a biological system (CARB 2000; ODEQ 1999)</li> <li>A correlation between a quantified (exposure) dose and the proportion of a population that demonstrates a specific effect (response) (SRA 1999; USDOE 2000).</li> </ol>
Dosimetry	Process of measuring or estimating dose (US EPA 1992).
Electrometer	Device that measures the current carried by the particle charge.
Elemental analysis	Chemical analysis of elements in a particle sample.
Elemental composition	The contents of elements in particles.

A form of squamous epithelium consisting of flat cells that line the

Endothelium	blood and lymphatic vessels, the heart, and various other body cavities (CMD 1997).
Endpoint	A health indicator used in an epidemiological study as the dependent variable.
Environmental Tobacco Smoke (ETS)	ETS is generated by the combustion of tobacco products. ETS is a complex mixture of over 4000 compounds. These include over 40 known or suspected human carcinogen, such as 4-aminobiphenyls, 2-naphthylamine, benzene, nickel, and a variety of PAH and N-nitrosamines. A number of irritants, such as ammonia, nitrogen oxides, sulphur dioxide, various aldehydes, and cardiovascular toxicants, such as carbon monoxide and nicotine are also present (WHO 2000b).
Epicarditis	Inflammation of the outermost layer of the heart wall (OCCMD 1998).
Epidemiological studies	Studies pertaining to epidemiology.
Epidemiology	The science of the distribution and determinants of health-related states and events in populations, and the application of the science to the control of health problems (CMD 1997).
Epidermis	The outermost layer of the skin (CMD 1997).
Epithelium	The layer of cells forming the epidermis of the skin and the surface layer of mucous and serous membranes (CMD 1997).
Equivalent diameter	Particle equivalent diameter is the diameter of a sphere having the same value of a physical property as the irregularly shaped particle being measured
Exacerbation	Aggravation of symptoms or increase in the severity of a disease (CMD 1997).
Exposure	Exposure to a chemical is the contact of that chemical with the outer boundary of the human body. The outer boundary of the human body is the skin and the openings into the body such as the mouth, the nostrils, and punctures and lesions in the skin (WHO 1999).
Exposure assessment	Quantitative or qualitative evaluation of the contact of a chemical with the outer boundary of the human body, which includes consideration of the intensity, frequency and duration of contact, the route of exposure (e.g. dermal, oral or respiratory), rates (chemical intake or uptake rates), the resulting amount that actually crosses the boundary (a dose), and the amount absorbed (internal dose) (WHO 1999).
Exposure gradient	Change in the value of exposure per unit distance in a specified direction (Webster 1994).
Exposure indicator	A characteristic of the environment measured to provide evidence of the occurrence or magnitude of a response indicator's exposure to a chemical or biological stress (USDOE 2000).



Exposure-response relationship	The relationship between the amount of a chemical at the absorptive surfaces of an organism and <ul style="list-style-type: none"> <li>a. a specific adverse effect, or</li> <li>b. the incidence of an adverse effect</li> </ul> (adapted from JHU 1999, US EPA 1997a).
Extrathoracic region	Region outside the chest (CMD 1997).
Factor VII	A coagulation factor in normal blood that is formed in the kidney under the influence of vitamin K (MWMD 1995).
Fibrinogen	A protein synthesized by the liver and present in blood plasma that is converted into fibrin (a whitish, filamentous protein) through the action of thrombin and in the presence of calcium ions. This process is the basis for blood clotting. Fbrinogen is also called factor I (CMD 1997).
Fine particles	Particles with aerodynamic diameters below 2.5 micrometer
Fly ash	Particles of ash entrained in flue gas produced by fossil fuel combustion (Willeke and Baron 1993).
Fractal dimension	A measure of the complexity of a particle's shape (Willeke and Baron 1993).
Fractal-like structures	Strongly agglomerated particles usually exhibit such structure. For a set of agglomerated particles with a similar history it is characterized by approximate validity of the scaling law $M \sim D_p^{D_f}$ , where M is the agglomerate mass and $D_p$ is the agglomerate diameter. The constant $D_f$ is called fractal-like dimension (Schmidt-Ott 1988).
Fractional deposition (regional & generation-by-generation)	Factors that determine the amounts of particle deposition within the various regions comprising the body (Subcommittee on Airborne Particles, 1978)
Geometric diameter	Diameter on a logarithmic size scale, where a given ratio of the sizes appears as the same linear distance (Willeke and Baron, 1993).
Geometric mean	A measure of central position. The geometric mean of n quantities equals the nth root of the product of the quantities (Snedecor 1967)
Geometric standard deviation	Characterises the width of the peak in the distribution. In naturally occurring aerosols the geometric standard deviation tends to vary from about 2 to 4 $\mu\text{m}$ , with 84% of the distribution being of size less than that specified by the median diameter multiplied by the geometric standard deviation. A measure of dispersion (variability) usually used for deviation data that are approximately symmetric on the log scale, as in the log-normal distribution (Department of Health Committee on the Medical Effects of Air Pollutants, 1995)
Gravimetry	Gravimetry measures the net mass on a filter by weighing the filter before and after sampling (US EPA 1997a).
Gravitational deposition	Particle motion in gravitational field.
Gravitational settling	Particle motion in gravitational field.

Harvesting	Extended air pollution episodes might deplete the pool of susceptible individuals; as a consequence, the remaining population might appear less vulnerable in a period after the episode.
Health endpoints	see Endpoint
Heart rate variability	Variability of the heart rate; a measure of autonomic nervous system control.
Hygroscopicity	the ability of particles to absorb water. This effect may result in a substantial increase in the diameter of the particles.
IL-6	A cytokine released by lymphocytes that mediates the acute phase response (adapted from CMD 1997).
IL-8	A cytokine produced by many cell types that acts as a neutrophil chemoattractant (CMD 1997).
Impactor	A device in which aerosol particles with sufficiently high inertia in a deflected air stream are impacted onto a surface (Willeke and Baron 1993).
Impinger	A device in which aerosol particles are removed by impaction the aerosol particles into a liquid (Willeke and Baron 1993).
Lagged effects	Health effects that do not occur on the same day of exposures but after exposures one or several days earlier.
Laminar flow	Gas flow with a smooth, nonturbulent pattern of streamlines, with no streamline looping back on itself (Willeke and Baron 1993).
Leak tests	Test assuring that the aerosol measurement equipment including tubings and connections is airtight, usually by reducing the pressure inside and observing whether it remains constant.
Leukocytes	A protein synthesized by the liver and present in blood plasma that is converted into fibrin (a whitish, filamentous protein) through the action of thrombin (CMD 1997).
Log normal distribution	A skew distribution of values X such that log X is normally distributed (Snedecor 1967).
Lung deposition models	Representation of the respiratory system used to make quantitative estimates of particle deposition. (Willeke and Baron, 1993). Models based typically on estimation of the physical behaviour of aerosol particles in a simplified anatomical model of the lung (Department of Health Committee on the Medical Effects of Air Pollutants, 1995)
Lung morphometry	The measurement of lung forms (CMD 1997).
Mainstream cigarette smoke	Smoke exhaled by the smoker (WHO 2000b).
Mass aerodynamic median diameter	Same as the mass median diameter except the stated diameter is the aerodynamic diameter (Department of Health Committee on the Medical Effects of Air Pollutants, 1995).
Mass concentration	The concentration of particles in air expressed as mass per unit volume (Department of Health Committee on the Medical Effects of Air Pollutants, 1995)

Mass distribution	Term used to characterize the distribution of sizes of particles in an aerosol (Department of Health Committee on the Medical Effects of Air Pollutants, 1995)
Mass median diameter	The size where half the mass of the aerosols in the mass distribution are contained in the particles smaller than the stated diameter and half in the larger particles (Department of Health Committee on the Medical Effects of Air Pollutants 1995)
Median diameter	Equal number of particles above and below this size
Microenvironment	Well-defined surrounding such as the home, office or kitchen that can be treated as uniform in terms of stressor concentration (US EPA 1997a)
Mobility equivalent diameter	Diameter of a spherical particle with the same dynamic mobility as the particle in question. (Willeke and Baron, 1993).
Mode	Value occurring most often in a distribution of values; peak value of a distribution (Willeke and Baron, 1993). A mode in the particle size distribution may be defined as a peak in the distribution, which can be described by a lognormal function for the mass distribution of the atmospheric aerosol (John, 1993).
Molecule mean free path	The mean distance a molecule travels before colliding with another molecule (Willeke and Baron, 1993).
Monodisperse aerosol	Composed of particles with a single size or small range of sizes. (Willeke and Baron, 1993).
Morbidity	The number of sick persons or cases of disease in relationship to a specific population (CMD 1997).
Mortality	The death rate; the ratio of the number of deaths to a given population (CMD 1997).
Mucocillary	Pertaining to ciliated mucosa (CMD 1997).
Mucocillary clearance	The elimination of a substance from tissue layers by cilia motion.
Multi-center study	Epidemiological studies that are conducted at multiple locations with the same design by one group of investigators.
Myocardial infarction	A condition caused by partial or complete of one or more of the coronary arteries. Synonym: heart attack (CMD 1997).
Myocarditis	Inflammation of the myocardium (CMD 1997).
Myocardium	The middle layer of the walls of the heart, composed of cardiac muscle (CMD 1997).
Nitrate.	See <i>nitric acid</i>
Nitric acid	A colourless or yellowish fuming liquid, formula $\text{HNO}_3$ . It is highly corrosive and the vapour is very hazardous. Nitric acid and nitrates (mainly ammonium nitrate) occur in the atmosphere in the form of aerosols: the acid is formed from oxides of nitrogen and then reacts with ammonia to form ammonium nitrate (WHO 1997).
Nitric oxide	See <i>nitrogen oxides</i> .
Nitrogen	A gaseous element, atomic number 7, relative atomic mass 14.0067, symbol N. It is the principal constituent of air (78% by volume).
Nitrogen dioxide	See <i>nitrogen oxides</i> .

Nitrogen oxide synthase	Synthase=Synthetase=An enzyme that acts as a catalyst for joining two molecules with the loss or splitting off of a high-energy phosphate group (CMD 1997). NO synthase to be defined from text.		
Nitrogen oxides	A series of seven compounds, of which only three are of any significance in the atmosphere. <i>Dinitrogen oxide</i> (nitrous oxide), formula N <sub>2</sub> O, is a colourless gas that is believed to play an important role in the nitrogen cycle. It is the most abundant atmospheric nitrogen compound and a greenhouse gas but is of no significance as a pollutant. <i>Nitrogen oxide</i> (nitric oxide), formula NO, is a colourless poisonous gas that reacts readily with oxygen (and very rapidly with O <sub>3</sub> ) to form the dioxide. It is formed in combustion processes, e.g. in furnaces and internal combustion engines. NO is an active participant in the atmospheric reactions that lead to the production of <i>photochemical smog</i> . Nitrogen dioxide, formula NO <sub>2</sub> , is a reddish-brown poisonous gas. At ordinary temperatures the vapour is an equilibrium mixture of NO <sub>2</sub> and the dimer N <sub>2</sub> O <sub>4</sub> (dinitrogen tetroxide); on heating, the latter dissociates and the NO <sub>2</sub> content increases. Above 140 <sup>0</sup> C, the NO <sub>2</sub> dissociates into NO and oxygen (WHO 1997). In the air pollution literature, the term “nitrogen oxides” and the formula NO <sub>x</sub> are used for the mixture of NO and NO <sub>2</sub> in the air (WHO 1997).		
Nucleation	The process of forming a central point about which matter is gathered (CMD 1997). Nucleation is the process whereby new aerosol particles are spontaneously formed from gaseous species, usually when photochemical reactions lead to a sufficiently high concentration in the gas phase of species which have a low vapour pressure and which would occur in liquid or solid state at ambient conditions, e.g. sulphuric acid (H <sub>2</sub> SO <sub>4</sub> ), nitric acid (HNO <sub>3</sub> ). Cloud nucleation refers to the rapid condensation of water vapour onto aerosol particles to form cloud droplets.		
Nucleation particles	(nuclei)	mode	Smallest mode in atmospheric particle size distribution, formed by condensation of atmospheric gases or emissions from hot processes, typically containing particles <0.1 μm in size (Willeke and Baron 1993).
Optical scattering diameter	The diameter of a calibration particle that scatters as much light in a specific instrument as the particle being measured (Willeke and Baron 1993).		
Oxygen	A gaseous element, atomic number 8, relative atomic mass 15.9994, symbol O. Oxygen is a colourless, odourless gas which supports combustion in air. Molecular oxygen (O <sub>2</sub> ) constitutes 20.95% by		

volume of dry air in the lower part of the atmosphere. O<sub>2</sub> is essential for the maintenance of almost all forms of life. Above an altitude of 20 km atomic oxygen appears in significant amounts and at 100 km it is in the predominant form. For the tri-atomic form of oxygen, see *ozone*.

Ozone	The tri-atomic allotrope of oxygen; a pale blue gas with a distinctive pungent odour, formula O <sub>3</sub> . It is a highly reactive oxidising agent and is very poisonous, and is considered a serious pollutant at concentrations much in excess of 125 µg/m <sup>3</sup> (WHO 1980). It is naturally occurring in the atmosphere. It occurs at large concentrations in the upper atmosphere, where it is formed by the action of solar ultraviolet radiation. In the troposphere, O <sub>3</sub> is mostly formed by photochemical reactions involving hydrocarbons and nitrogen oxides.
Panel study	An epidemiological or toxicological study performed with volunteers.
Particle	Small discrete mass of solid or liquid matter (ISO 1994).
Particle aerodynamic diameter	Diameter of a sphere of density 1 g/cm <sup>3</sup> with the same terminal velocity due to gravitational force in calm air as the particle, under the prevailing conditions of temperature, pressure and relative humidity (ISO 1995).
Particle bound elements	Elements that attach themselves to the atmospheric particles (Department of Health Committee on the Medical Effects of Air Pollutants 1995)
Particle size distribution	The distribution of equivalent diameters of particles in a sample or the proportion of particles for which the equivalent diameter lies between defined limits (Willeke and Baron 1993).
Peak expiratory flow rate	See rate.
Pearson correlation	Measure of the degree of closeness of the linear relationship between two variables (Snedecor 1967).
Personal exposure	The concentration of PM near the breathing zone.
Personal exposure (monitor)	Aerosol sampling systems designed to be worn on the body during normal activities (US EPA 1997a)
Photodetector	Light-sensitive sensor
Plasma viscosity	The state of being sticky or gummy of the liquid part of the lymph and of the blood (adapted from CMD 1997).
Plasminogen	A protein found in many tissues and body fluids. Important in preventing fibrin clot formation (CMD 1997).
Plasminogen activator	A substance that induces activity of plasminogen (adapted from CMD 1997).
Plasminogen inhibitor	A substance that inhibits activity of plasminogen (adapted from CMD 1997).

PM reference methods	Usually refers to the US Federal Reference Methods for PM <sub>2.5</sub> or PM <sub>10</sub> , precisely detailed techniques for collecting particles on a filter, equilibration at specified temperatures and pressures, and weighing on a microbalance, including temperature limits during collection and storage. Could refer to any standard technique to which other measurements are compared.
PM <sub>10</sub>	Mass concentration of particles collected by a sampler with a 50% cut-point at an aerodynamic particle diameter of 10 micrometers, mostly particles with aerodynamic particle diameters of 10 micrometers or less.
PM <sub>2.5</sub>	Mass concentration of particles collected by a sampler with a 50% cut-point at an aerodynamic particle diameter of 2.5 micrometers, mostly particles with aerodynamic particle diameters of 2.5 micrometers or less.
Polydisperse aerosol	Composed of particles of a range of sizes (Willeke and Baron 1993).
Population exposure	Average exposure of a population.
Power calculation	The estimate of the probability of making the correct decision of selecting the true nature of events, given a sample of appropriate size (adapted from Yamane 1973).
Prevalence	The number of cases of a disease present in a specified population at a given time (CMD 1997).
Primary fine particles	Particles that have been emitted into the atmosphere as particles, as opposed to secondary particles, which are formed in the atmosphere from gas-to-particle conversion of gaseous precursors. Most common examples of primary particles are sea-salt, road and desert dust, soot and carbonaceous particles from combustion.
Proinflammatory cytokine	A cytokine that favours inflammation.
Rate	The speed or frequency of occurrence of an event, usually expressed with respect to time or some other known standard (CMD 1997). <i>Death rate</i> or <i>mortality rate</i> is the number of deaths in a specified population, usually expressed per 100 000 population, over a given period, usually 1 year. <i>Morbidity rate</i> is the number of cases per year of certain diseases in relation to the population in which they occur. <i>Infant mortality rate</i> is the number of deaths per year of live-born infants less than 1 year of age divided by the number of live births in the same year. <i>Peak expiratory flow rate</i> is the maximum rate of exhalation during forced expiration, measured in litres per second or litres per minute.
Reactive oxygen species	Oxygen radicals or Epoxides.
Regression	Statistical term to describe the linear relationship between a dependent variable Y and an independent variable X (Snedecor 1967)

Regression slope	The rate of units of the dependent variable Y per unit of the independent variable X (Snedecor 1967).
Relative humidity	The ratio of the quantity of water vapour present in the atmosphere to the quantity which would saturate at the existing temperature (WMO 1992).
Repolarization	Recovery of the resting membrane potential after a depolarization (here of the heart muscle).
Respirable particulate matter	Mass concentration of particles of sizes below 5 micrometer, most likely to be deposited in the pulmonary portion of the respiratory tract (adapted from SRA 1999).
Respiratory disease	Diseases of the respiratory tract such as for example chronic obstructive bronchitis or asthma.
Retrospective	Relating to a review of past events (Webster 1994).
Risk assessment	A conceptual framework that provides the mechanism for a structured review of information relevant to estimating health or environmental outcomes (WHO 1999).
Risk factor	An element in the environment or a chemical, psychological, physiological, or genetic elements, thought to predispose an individual to the development of a disease (adapted from CMD 1997).
Risk factor profile	A summary of risk factors.
Secondary fine particles	Particles which are formed in the atmosphere from gaseous precursors (gas-to-particle conversion). They are usually formed from gases in three ways: Nucleation (i.e, gas molecules coming together to form a new particle). Condensation of gases onto existing particles. By reaction of absorbed gases in liquid droplets.
Sidestream smoke	Smoke emitted from the smoldering tobacco between puffs (WHO 2000b).
Source apportionment	Method of assessment of the contributions to air pollution concentrations of individual emitting sources.
Spearman's correlation	Ordinary correlation coefficient between ranked values of two variables (Snedecor 1967).
Submicrometer	Particles with aerodynamic diameters smaller than one micrometer.
Sulphate	A salt of sulphuric acid, H <sub>2</sub> SO <sub>4</sub> (WHO 1980).
Susceptible individuals	Individuals exhibiting disease signs and symptoms when exposed.
Time lag	see <i>lagged effects</i> .
Time series study	Epidemiological or ecological study of the health state of a population exposed e.g. to air pollutants.
Toxicology	Division of medical and biological science concerned with toxic substances, detecting them, studying their chemistry and pharmacological actions, and establishing antidotes and treatment of toxic manifestations, prevention of poisoning, and methods for

	controlling exposure to harmful substances (CMD 1997).
Trace elements	Elements in trace quantities.
Tracheo-bronchial region	Region concerning the trachea proper (windpipe) and the bronchus (one of the two large branches leading from the trachea proper to the lung) (adapted from CMD 1997; Webster 1994).
Transfer standard	secondary calibration standard
TSP (total suspended particulates)	Mass concentration of particles of all sizes collected on a glass fibre filter by a high volume samplers (WHO 1987).
Ultrafine	Particles with aerodynamic diameters below 0.1 micrometer.
Unbiased	See bias
Unit density spheres	Spheres of density $1 \text{ g cm}^{-3}$
Variability (statistical)	Statistical term to describe the individual deviations of items in a sample from some centrally located number such as the sample mean (adapted from Snedecor 1967).
Vascular endothelium	The cellular tissue lining the blood vessels (CMD 1997).
Volatile organics	Organic compounds that are vapourizable at low temperatures and combustible at or below $600^{\circ}\text{C}$ (EEH 1974).



## Appendix 4

### JOINT WHO - EC-JRC Expert Meeting

#### "Guidelines for Concentration and exposure -response measurement of fine and ultra-fine particulate matter for use in epidemiological studies"

JRC - Ispra - Italy

20/11/2000 - 22/11/2000

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## **Appendix 5**

### **Some technical details on Instrumental Techniques for Chemical Particle Characterization**

#### **Elemental analysis**

The most common interest in elemental composition derives from concerns about health effects and the utility of these elements to trace the sources of suspended particles. Instrumental neutron activation analysis (INAA), photon-induced x-ray fluorescence (XRF), particle-induced x-ray emission (PIXE), atomic absorption spectrophotometry (AAS), inductively-coupled plasma with atomic emission spectroscopy (ICP/AES), inductively-coupled plasma with mass spectroscopy (ICP/MS), and scanning electron microscopy with x-ray fluorescence (SEM/XRF) have all been applied to elemental measurements of aerosol samples. AAS and ICP/AES are also appropriate for ion measurements when the particles are extracted in deionised-distilled water (DDW). Since air filters contain very small particle deposits (20 to 100  $\mu\text{g}/\text{cm}^2$ ), preference is given to methods that can accommodate small sample sizes. XRF and PIXE leave the sample intact after analysis so that it can be submitted to additional examinations by other methods. Excellent agreement was found for the inter-comparison of elements acquired from the XRF and PIXE analyses (Cahill, 1980).

#### **X-ray fluorescence of trace elements**

In x-ray fluorescence (XRF) (Dzubay and Stevens 1975; Hammerle and Pierson 1975; Jaklevic et al. 1977; Torok and Van Grieken 1994), the filter deposit is irradiated by high energy x-rays that eject inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent x-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration.

XRF methods can be broadly divided into two categories: wavelength dispersive x-ray fluorescence (WDXRF), which utilizes crystal diffraction for observation of fluorescent x-rays, and energy dispersive x-ray fluorescence (EDXRF), which uses a silicon semiconductor detector. The WDXRF method is characterized by high spectral resolution, which minimizes peak overlaps. It requires high power excitation to overcome low sensitivity, resulting in sample heating and potential degradation. Conversely, EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures.

XRF methods can be further categorized as direct/filtered excitation, where the x-ray beam from the tube is optionally filtered and then focused directly on the sample, or secondary target excitation, where the beam is focused on a target of material selected to produce x-rays of the desired energy. The secondary fluorescent radiation is then used to excite the samples. The direct/filtered approach has the advantage of delivering higher incident radiation flux to the sample for a given x-ray tube power, since about 99% of the incident energy is lost in a secondary

fluorescence. However, the secondary fluorescence approach produces a more nearly monochromatic excitation that reduces unwanted scatter from the filter, thereby yielding better detection limits.

XRF analysis of air particulate samples has had widest application to samples collected on membrane-type filters such as Teflon- or polycarbonate-membrane filter substrates. These membrane filters collect the deposit on their surfaces, thus eliminating biases due to absorption of x-rays by the filter material. These filters also have a low area density which minimizes the scatter of incident x-rays, and their inherent trace element content is very low.

Larger particles collected during aerosol sampling have sufficient size to cause absorption of x-rays within the particles. Attenuation factors for fine particles ( $PM_{2.5}$ , particles with aerodynamic diameters equal to or less than  $2.5\ \mu m$ ) are generally negligible (Criss 1976), even for the lightest elements, but these attenuations can be significant for coarse fraction particles (particles with aerodynamic diameters from  $2.5$  to  $10\ \mu m$ ). Correction factors for XRF have been derived using the theory of Dzubay and Stevens (1975) and should be applied to coarse particle measurements.

### **Particle induced X-ray emission of trace elements**

Particle induced X-ray emission (PIXE) is another form of elemental analysis based on the characteristics of x-rays and the nature of x-ray detection (Cahill et al. 1987; 1989). PIXE uses beams of energetic ions, consisting of protons at an energy level of 2 to 5 MeV (Mega-electron-Volt), to create inner electron shell vacancies. As outer electrons fill inner electron shell atomic vacancies, the emitted characteristics of x-rays can be detected by wavelength dispersion (which is scattering from a crystal) or by energy dispersion (which involves direct conversion of x-rays).

The development of focusing energetic proton beams (proton microprobes) has expanded the application of PIXE from environmental and biological sciences to geology and material sciences. PIXE analysis is often used for impactor samples or small filter substrates, since proton beams can be focused to a small area with no loss of sensitivity (Cahill and Wakabayashi 1993).

Very thick filters or thick particle deposits on filter substrates scatter the excitation protons and lower the signal-to-noise ratio for PIXE. X-ray analysis methods, such as PIXE and XRF, require particle size diameter corrections (for low atomic number targets) associated with a spherical particle of a given diameter (typically particles with aerodynamic diameters  $>2.5\ \mu m$ ) and compositions typical in outdoor aerosol studies. These analyses also require correction for sample loadings that reflect the passage of x-rays through a uniform deposit layer.

PIXE analysis can provide information on one of the widest range of elements in a single analysis, since x-ray results require two or three separate anodes. However, attempts to improve sensitivity of PIXE analysis may result in damage to Teflon-membrane filters. Recent developments (Malm et al. 1994) using PIXE analysis at moderate sensitivity plus single anode XRF analysis at high sensitivity for transition/heavy metals have achieved the minimum detectable limits of less than  $0.01\ ng/m^3$ . With the addition of hydrogen analysis (a surrogate for organic matter), almost all gravimetric mass concentrations can be explained (Cahill et al. 1987).

XRF and PIXE are the most commonly used elemental analysis methods owing to their non-destructive multi-element capabilities, relatively low cost, high detection limits, and preservation

of the filter for additional analyses. XRF sometimes needs to be supplemented with INAA when extremely low detection limits are needed, but the high cost of INAA precludes this method from being applied to large numbers of samples. AAS is a good alternative for water-soluble species, especially for low atomic number. ICP/AES analysis is a viable alternative, but it is less desirable because of the sample extraction elements such as sodium and magnesium, but it requires large dilution factors to measure many different elements expense and the destruction of the filter.

### **Instrumental neutron activation analysis of trace elements**

Instrumental neutron activation analysis (INAA) (Dams et al. 1970; Zoller and Gordon 1970; Olmez 1989; Ondov and Divita 1993) basically involves irradiation of a thin membrane filter sample in the core of a nuclear reactor for periods ranging from a few minutes to several hours. Bombardment of the sample with neutrons induces a nuclear reaction of the stable isotopes in the sample. The energies of the gamma rays emitted by the decay of this induced radioactivity are used to identify them, and therefore, their parents. With the use of prepared elemental standards, the amount of parent element in the sample can be determined since the intensity of these gamma rays are proportional to their number.

The gamma-ray spectra of radioactive species are usually collected with a high-resolution germanium detector utilizing commercially available amplifiers and multi-channel analysers. Typical detector efficiencies range from 10 to 40% relative to a  $3 \times 3$  in. sodium iodide detector. Detector system resolution, measured as the full-width at half-maximum for Table 4.4, the 1,332 KeV gamma-ray peak of  $^{60}\text{Co}$ , should be less than 2.3 KeV in order to provide adequate resolution between isotopes of neighbouring energies.

In order to obtain a full suite of elemental analysis results (often over 40 elements), multiple counting periods and irradiations are performed on the same sample (e.g., two irradiations would produce elements separated into short- and long-lived decay products).

The power of INAA is that it is not generally subject to interferences like XRF or PIXE due to a much better ratio of gamma ray peak widths to total spectral width, by a factor of about 20. INAA does not quantify some of the abundant species in outdoor particulate matter such as silicon, nickel, tin, cadmium, mercury, and lead. While INAA is technically non-destructive, sample preparation involves folding the samples tightly and sealing it in plastic, and the irradiation process makes the filter membrane brittle and radioactive. These factors limit the use of the sample for subsequent analyses by other methods. The technique also suffers from the fact that a nuclear reactor is usually used as a source of neutrons. However, since the advent of high-resolution gamma-ray detectors, individual samples can be analysed for numerous elements simultaneously, most at remarkably trace levels without the need for chemical separation. This greatly diminishes the danger of contamination due to excessive sample handling and introduction of chemical reagents used for separation procedures.

### **Microscopy analysis of particle composition**

Electron microscopy includes the:

- (1) Transmission electron microscope (TEM);

- (2) Scanning electron microscope (SEM), and;
- (3) Scanning transmission electron microscope (STEM).

The SEM and STEM use accelerated electrons to strike the sample. As the electron beam strikes the samples, various signals (e.g., secondary, backscattered, and Auger electrons, characteristic x-rays, photons, and cathodoluminescence) are generated. These signals can be collected to provide highly detailed information on a point-by-point basis. The secondary electron signal yields a sample image with three-dimensional perspective, high depth of field, and illuminated appearance. Back-scattered electron images are used to separate phases containing elements of different atomic number.

The information obtained from scanning microscopy analyses is usually considered to be qualitative, due to the limited number of particles counted. To achieve a quantitative analysis, a sufficient number of particles must be properly sized and identified by morphology and/or chemistry to represent the entire sample. The selection of filter media, optimal particle loadings, and sample handling methods are also of importance. In this manner, the microscopic characteristics can be directly and reliably related to the bulk or macroscopic properties of the sample.

Microscopic analysis requires a high degree of skill and extensive quality assurance to provide quantitative information. The technique is complex and expensive when quantitative analysis is required. The evolution of computer technology has allowed for quantitative analysis of particle samples of an entire population of features. With advanced pattern recognition methods, data from individual particle features can be sorted and summarized by size and composition, permitting improved quantitative source apportionment (Bruynseels et al. 1988; Hopke and Casuccio 1991). Casuccio et al. (1983) summarized the pros and cons of automatic scanning electron microscopy.

Recent development of the SEM/XRF allows analysis of elemental compositions and morphological information on small quantities of material (Bruynseels et al. 1988). Coupled with statistical data analysis, computer controlled scanning electron microscopy shows promise for identifying and quantifying complex pollution sources in the field of receptor modelling source apportionment (e.g., Griffin and Goldberg 1979; Janocko et al. 1982; Johnson et al. 1981; Massart and Kaufman 1983; Hopke 1985; Derde et al. 1987; Saucy et al. 1987; Mamane 1988; Dzubay and Mamane 1989).

### **Atomic absorption spectrophotometric (AAS) and inductive coupled plasma atomic emission spectro (ICP/AES) photometry analyses for trace elements**

In atomic absorption spectrophotometric (AAS) analysis (Buttgereit 1973), the sample is first extracted in a strong solvent to dissolve the solid material; the filter or a portion thereof is also dissolved during this process. A few millilitres of this extract are introduced into a flame where the elements are vaporized. Most elements absorb light at certain wavelengths in the visible spectrum, and a light beam with wavelengths specific to the elements being measured is directed through the flame to be detected by a monochromator. The light absorbed by the flame containing the extract is compared with the absorption from known standards to quantify the elemental concentrations. AAS requires an individual analysis for each element, and a large filter or several filters are needed to obtain concentrations for a large number of the elements specified

in Table 4-3. AAS is a useful complement to other methods, such as XRF and PIXE, for species such as beryllium, sodium, and magnesium that are not well quantified by XRF and PIXE. Airborne particles are chemically complex and do not dissolve easily into complete solution, regardless of the strength of the solvent. There is always a possibility that insoluble residues are left behind and soluble species may co-precipitate on them or on container walls.

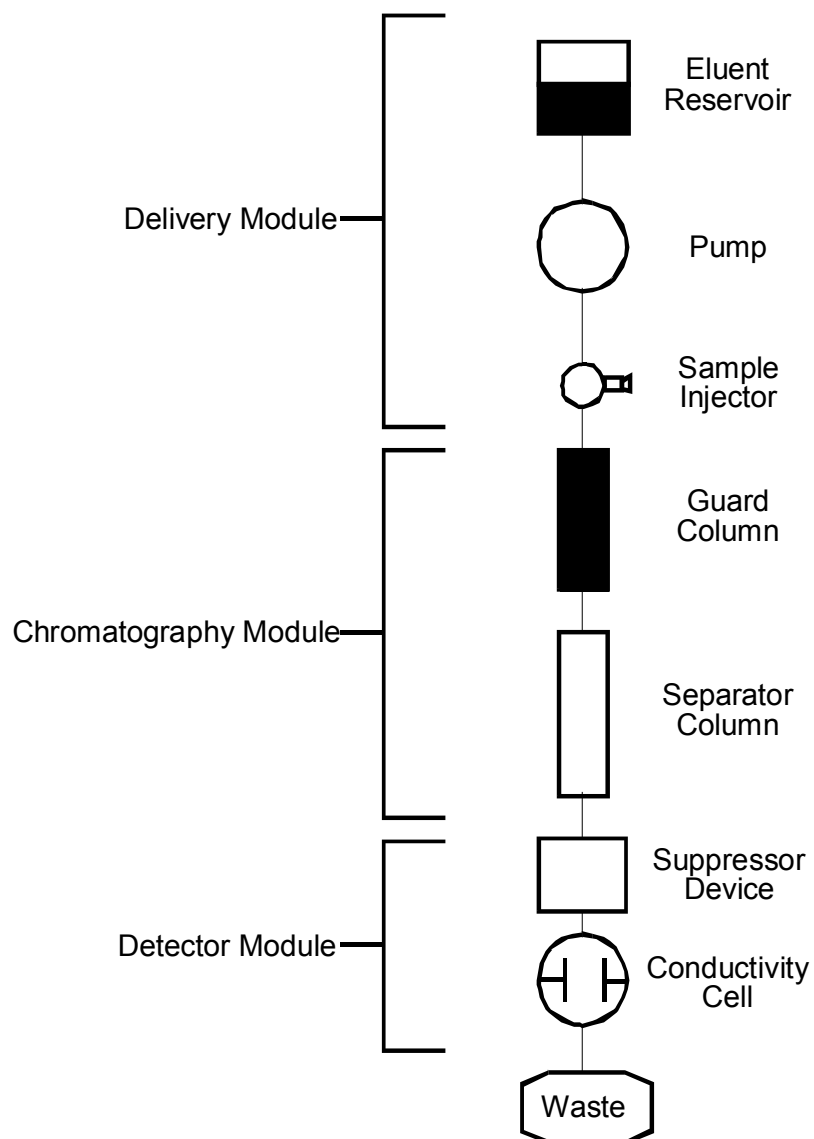
In inductive coupled plasma atomic emission spectrophotometric (ICP/AES), (Lynch et al. 1980; Harman 1989), the dissolved sample is introduced into an atmosphere of argon gas seeded with free electrons induced by high voltage from a surrounding Tesla coil. The high temperatures in the induced plasma raise valence electrons above their normally stable states. When these electrons return to their stable states, a photon of light is emitted which is unique to the element, which was excited. This light is detected at specified wavelengths to identify the elements in the sample. ICP/AES acquires a large number of elemental concentrations using small sample volumes with acceptable detection limits for atmospheric samples. As with AAS, this method requires complete extraction and destruction of the sample.

## **Analysis for water-soluble ions**

### **Ion chromatography**

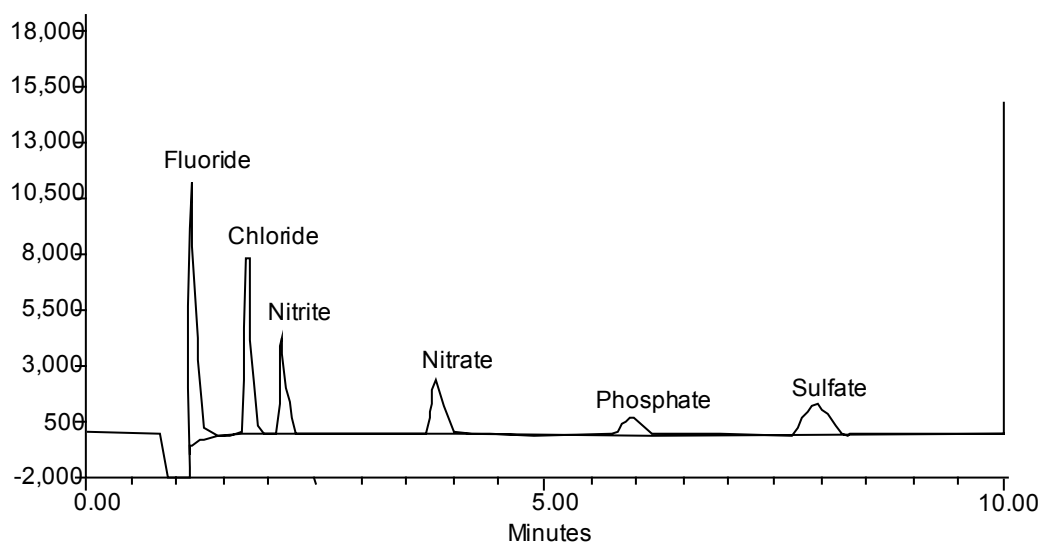
Ion chromatography (IC) can be used for both anions (fluoride  $[F^-]$ , chloride  $[Cl^-]$ , nitrite  $[NO_2^-]$ , bromide  $[Br^-]$ , nitrate  $[NO_3^-]$ , phosphate  $[PO_4^{3-}]$ , sulphite  $[SO_3^{2-}]$ , sulphate  $[SO_4^{2-}]$ ) and cations (potassium  $[K^+]$ , ammonium  $[NH_4^+]$ , sodium  $[Na^+]$ ) with separate columns. In IC the sample extract passes through an ion exchange column that separates the ions in time for individual quantification, usually by an electro conductivity detector. Figure A.5.1 shows a schematic representation of the IC system. Prior to detection, the column effluent enters a suppressor column where the chemical composition of the element is altered, resulting in a lower background conductivity. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. IC is especially desirable for particle samples because it provides results for several ions with a single analysis and it uses a small portion of the filter extract with low detection limits.





**Figure A.5.1** Schematic representation of an ion chromatography system.

Water-soluble chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulphate ( $\text{SO}_4^{2-}$ ) are the most commonly measured anions in aerosol samples. Figure A.5.2 shows an example of an IC anion chromatogram. IC analyses can be automated by interfacing to an automatic sampler that can conduct unattended analysis of as many as 400 samples (Tejada et al. 1978).



**Figure A.5.2** Example of an ion chromatogram showing the separation of fluoride, chloride, nitrite, nitrate, phosphate, and sulphate ions.

Several independent quality assurance (QA) standards should be used to check the calibration curve. The standards that are traceable to NIST simulated rainwater standards are: Environmental Resource Associates (ERA, Arvada, CA) custom standards containing the anions measured at a concentration of 100 Fg/ml, ERA Waste Water Nutrient Standard, ERA Waste Water Mineral Standard, and Alltech individual standards at 200 Fg/ml. The QA standards are diluted in DDW to concentrations that are within the range of the calibration curve.

Calibration curves are performed weekly. Chemical compounds are identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. The QA standards are analysed at the beginning of each sample run to check calibrations. A DDW blank is analysed after every 20 samples and a calibrations standard is analysed after every 10 samples. These quality control (QC) checks verify the baseline and calibration respectively.

### **Automated colorimetric analysis for ammonium, nitrate, and sulphate**

Automated Colorimetry (AC) applies different colorimetric analyses to small sample volumes with automatic sample throughput. Since IC provides multi-species analysis for the anions, AC most commonly measures ammonium.

The AC system is illustrated schematically in Figure 4-29. The heart of the automated colorimetric system is a peristaltic pump, which introduces air bubbles into the sample stream at known intervals. These bubbles separate samples in the continuous stream. Each sample is mixed with reagents and subjected to appropriate reaction periods before submission to a colorimeter. The ion being measured usually reacts to form a coloured liquid. Beer's Law relates the liquid absorbance to the amount of the ion in the sample. A photo multiplier tube measures this absorbance through an interference filter specific to the species being measured.

The standard AC technique can analyse .60 samples per hour per channel, with minimal operator attention and relatively low maintenance and material costs. Several channels can be set up to simultaneously analyse several ions. The methylthymol blue (MTB) method is applied to analyse sulphate. The reaction of sulphate with MTB barium complex results in free ligand, which is measured colourimetrically at 460 nm. Nitrate is reduced to nitrite that reacts with sulphanilamide to form a diazo compound. This compound is then reacted to an azo dye for colorimetric determination at 520 nm. Ammonium is measured with the indophenol method. The sample is mixed sequentially with potassium sodium tartrate, sodium phenolate, sodium hypochlorite, sodium hydroxide, and sodium nitroprusside. The reaction results in a blue-coloured solution with an absorbance measured at 630 nm. The system determines carry-over by analysis of a low concentration standard following a high concentration. The percent carry-over is then automatically calculated and can be applied to the samples analysed during the run.

## Appendix 6

### Some technical details on Instrumental Techniques for Physical Particle Characterization

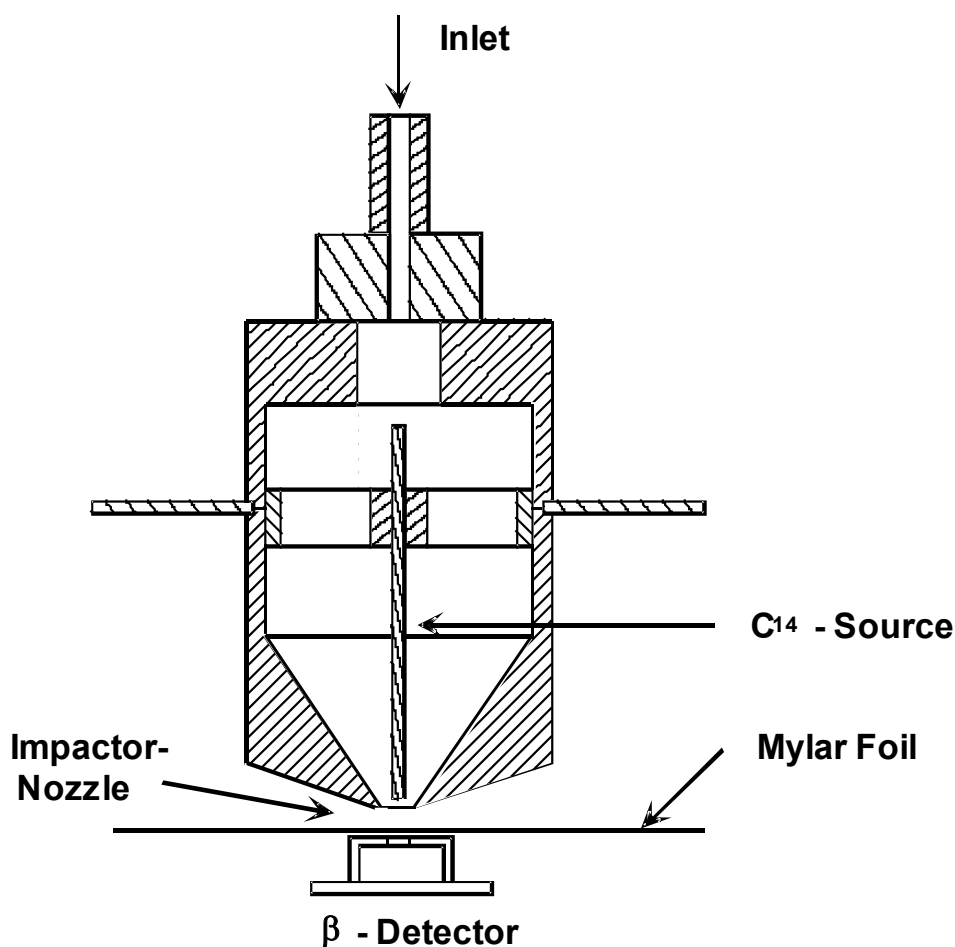
#### Determination of mass

##### Beta attenuation

The principle of the beta attenuation mass monitor (Marcias and Husar 1976) is illustrated in figure A.6.1. The response is the attenuation of beta radiation by a collected sample between the beta source and the detector. This attenuation is approximately related to the collected mass by

$$\ln\left(\frac{I}{I_0}\right) \approx -K_b \cdot Q \cdot t \cdot c_m$$

where  $I_0$  is the intensity measured before the sampling begins,  $I$  is the intensity after sampling,  $K_b$  is the sensitivity coefficient of the device,  $Q$  is the aerosol mass flow, from which the particles are collected by impaction or electrostatic deposition,  $t$  is time and  $c_m$  is the mass concentration. The response time depends on the concentration  $c_m$  measured and is typically in the range of minutes. A disadvantage of the technique may be the requirement of the radioactive source.



**Figure A.6.1** Particulate Mass Measurement by  $\beta$  Absorption

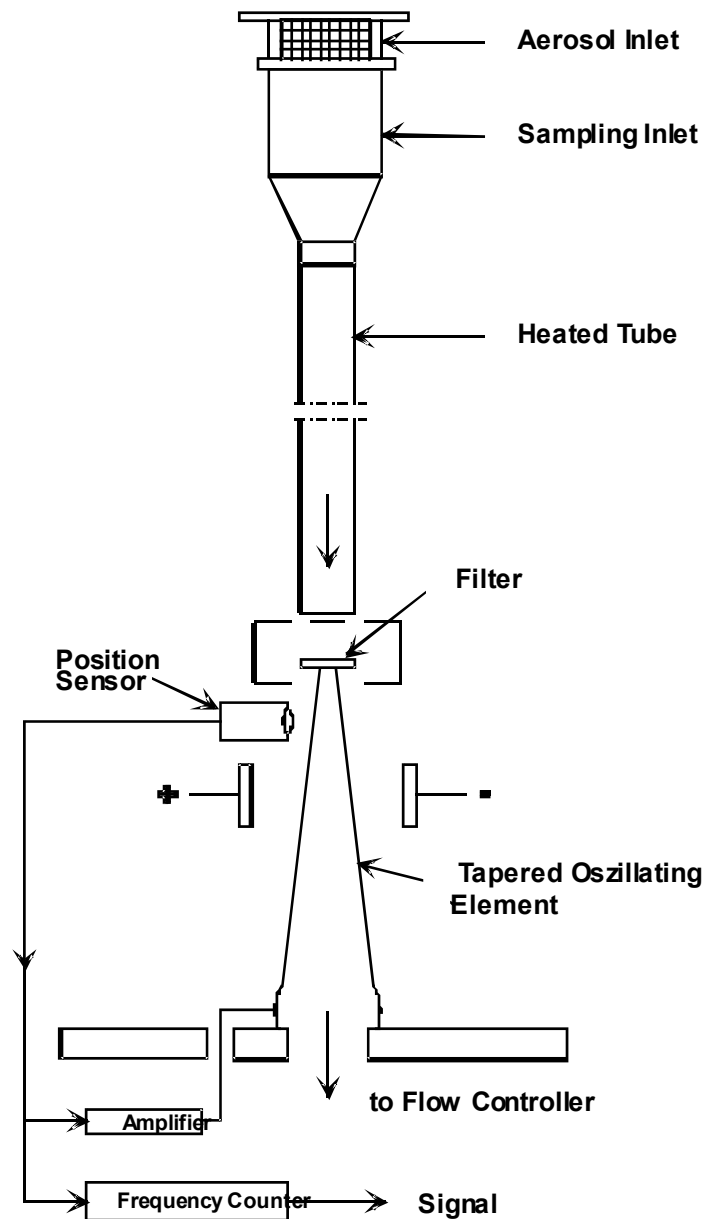
### Vibrational microbalance methods

If aerosol particles of mass  $\Delta m$  are deposited on a piezoelectric quartz crystal, the frequency changes by the measured value of

$$\Delta f = K_q \cdot Q \cdot t \cdot c_m$$

where  $K_q$  is the sensitivity. The sampling time required to collect a sufficient amount of material on the Quartz surface is typically minutes. A serious disadvantage of this method is the change in sensitivity with loading. This disadvantage is eliminated in the TEOM (Patashnik and Rupprecht 1980). Figure A.6.2 shows the principle components of the system. The particle sample is collected in a filter mounted on the thin end of a tapered oscillating hollow element, which is fixed to a surface at its thick end. This element is electrically excited to oscillate in its natural frequency, which changes with the mass loading of the filter according to the equation above. The

inlet air is heated to 50 °C to keep moisture in the vapour phase. Alternatively it can be used with a diffusion dryer, which only requires heating to 30 °C .



**Figure A.6.2** Tapered Element Oscillator Microbalance

## Measurement of physical parameters other than mass

### *Number concentration measurement*

In optical particle counters (OPCs) the light scattered by single particles is recorded. This is done by directing the aerosol flow through the focus of a light beam and by collecting a portion of the scattered light into a detector. Each particle then produces a pulse of the detector output and the number  $n$  of pulses during a certain time  $t_p$  is proportional to the particle concentration  $N$  through

$$N = \frac{n}{Q \cdot t_p}$$

where  $Q$  is the volume flow rate. This technique only detects particles large enough to deliver a scattering signal in the measurable range. The cut-off size for most OPCs is above  $0.1 \mu\text{m}$ . In order to register all particles in the relevant size range, condensation particle counters (CPCs) are used. A CPC contains a particle magnifier, in which a liquid condenses on the particles, growing them to a size detectable by an OPC, which follows in a continuous flow arrangement. CPCs detect particles down to a diameter of  $10 \text{ nm}$  or even  $3 \text{ nm}$ . Most CPCs are very sensitive to shocks or motion and are therefore not suitable for most field measurements. TSI Incorporated has a portable CPC on the market (TSI 2000c). This instrument has a cut-off size of  $10 \text{ nm}$ .

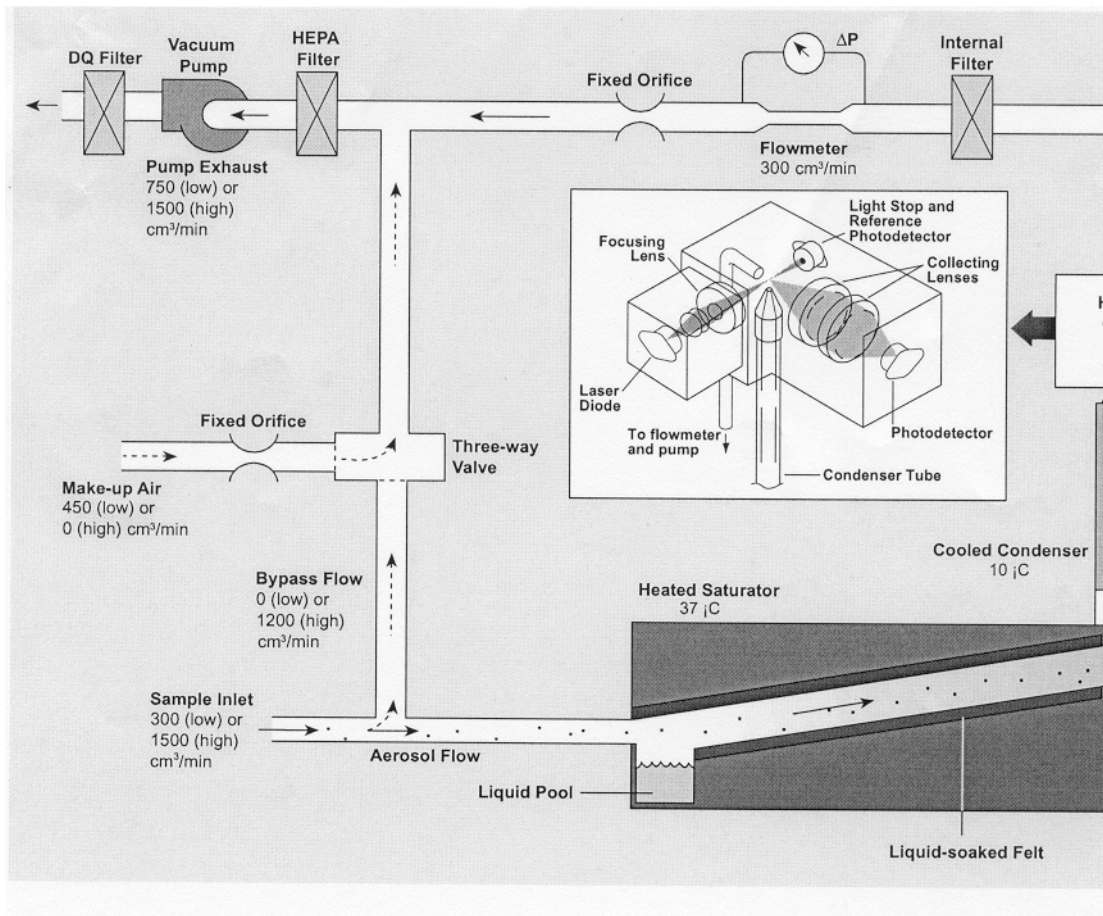


Figure A.6.3 shows the concept of this instrument.

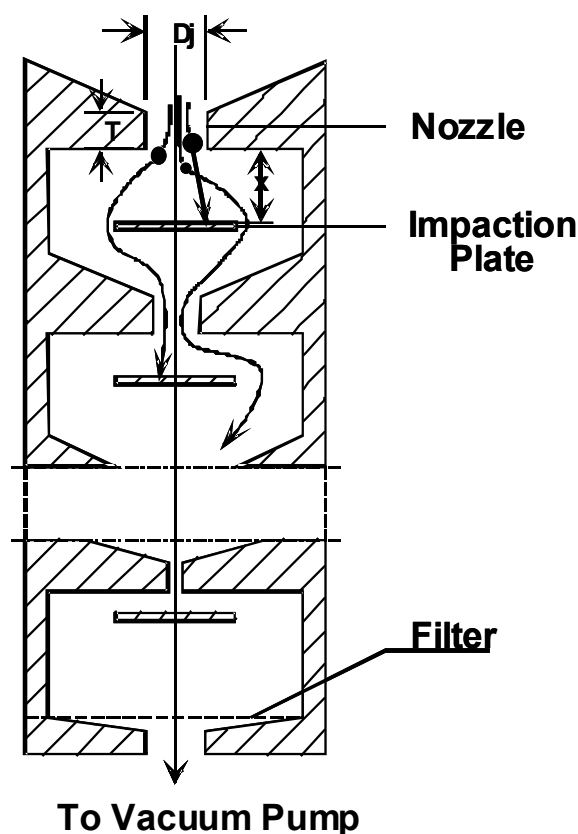
**Figure A.6.3.** Condensation Particle Counter

## Size measurement

### Size separation by impactors

Figure A.6.4 schematically shows the structure of a multistage impactor. Each stage consists of an orifice and an impaction plate. Between orifice and plate the flow performs a 90° bend. Due to their inertia, small particles follow the flow better than large ones. Particles above a certain aerodynamic size impinge on the plate, where they stick. The nozzle-plate geometry and the gas pressure at each particular stage define the cut-off diameter. Thus the particles are separated according to their aerodynamic diameters. The smallest diameters separable with commercial impactors are some tens of nanometers. In order to obtain the particle size distribution, the masses of the deposits of each stage must be determined gravimetrically.

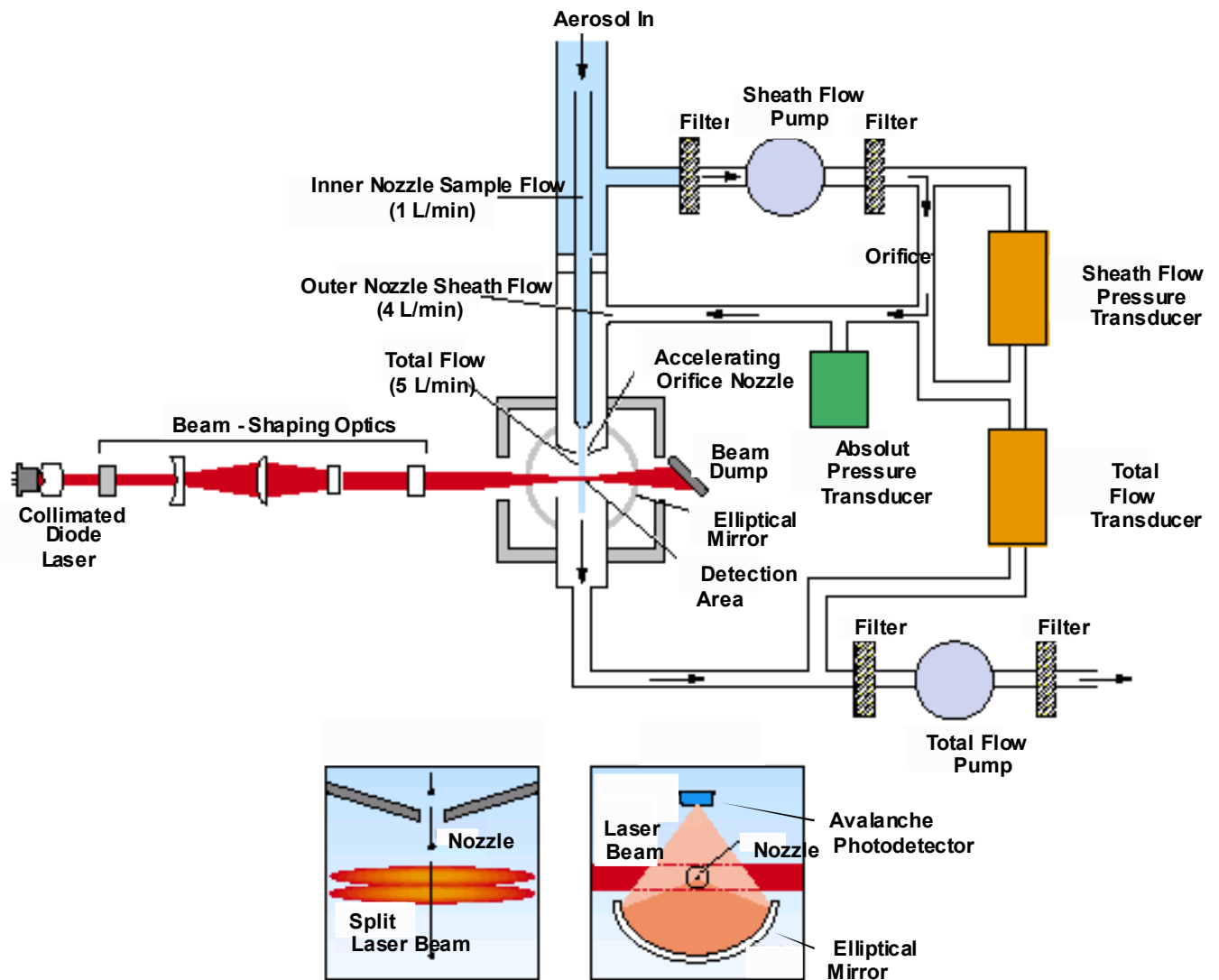
Variable pressure impactors have been used as single-stage size spectrometers [6.7]. The particles are charged and the current carried to the impaction stage by the depositing particles is measured as function of size. From this measured relationship, the aerodynamic diameter distribution can be derived.



**Figure A.6.4** Multistage Impactor

Laboratory models have been used for size determination down to diameters in the range of a few nanometers.





**Figure A.6.5** Principle of the aerodynamic Particle Sizer

Figure A.6.5 illustrates the operation principle of aerodynamic sizing instruments. The smallest particle diameter to be measured this way is typically around  $0.5 \mu\text{m}$ .

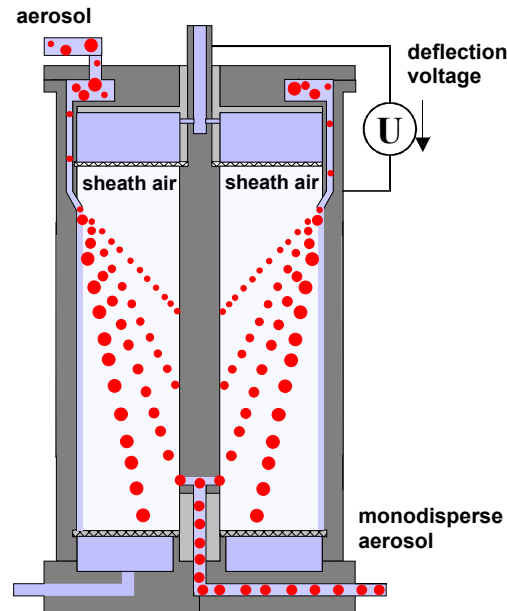
#### *Mobility measurement*

The differential mobility analyser (DMA) (Fissan et al. 1983) is illustrated in Figure A.6.6. The aerosol enters the cylindrical arrangement through an annular slit and performs an axial laminar flow. Charged particles are deflected towards the centre rod by a radial electric field. Particles essentially having the same mobility exit through the slit in the centre rod.

More precisely, particles are extracted that have a narrow mobility distribution, the mean of

which is defined by the deflecting voltage applied between the centre rod and the outer cylinder.

To obtain the size distribution, the number concentration of the exiting particles is measured as function of this voltage. If the charge distribution of the particles is known, the size distribution can be calculated from this function.



**Figure A.6.6** Differential Mobility Analyser (DMA)

## Particle surface related measures

### *The epiphaniometer*

The epiphaniometer mentioned in section 6.4.3.2 measures the surface of aerosol particles. This measurement yields the integrated attachment coefficient  $\eta$  of the particles in an aerosol.  $\eta$  is defined by the diffusion current of molecules to the particle surface, where the molecules stick to the particles with unit probability at each collision.  $\eta$  is defined by the attachment rate

$$\frac{dN_m}{dt} = \eta \cdot N \cdot N_m$$

where  $N$  is the particle concentration and  $N_m$  is the sticking molecule concentration. The epiphaniometer signal is given by the integrated attachment coefficient

$$\bar{\eta} = \frac{1}{N} \int_0^{\infty} \eta(D_p) \cdot f(D_p) dD_p,$$

Here  $f(D_p)=dN/dD_p$  is the particle size distribution.  $\eta(D_p)$  is a well-known function for spherical particles (Fuchs 1989).  $\eta$  is proportional to  $D_p^2$  of a spherical particle, if  $D_p \ll \lambda$ , i.e. if  $D_p$  is much smaller than the mean free path  $\lambda$  of the air molecules ( $\lambda=0.066 \mu\text{m}$  under normal conditions) and proportional to  $D_p$  for  $D_p \gg \lambda$ . Thus under normal conditions, i.e. under air of 1 bar, the epiphaniometer delivers a signal proportional to the joint particle surface only for very small particles. Another prerequisite is that the particles are of convex shape, which means in particular that they should not be fractal-like agglomerates and they should not have pores. The epiphaniometer thus delivers no surface proportional signal, since most inhalable particles in the environment are non-spherical agglomerates, and particle sizes range from a few nanometers to tens of micrometers, i.e. the size distribution extends to either side of  $\lambda$ . For a polydisperse aerosol it is not possible to derive the particle surface or volume from the epiphaniometer response, even if the particles are considered as spheres. The response is a measure of the interaction of the gas molecules with the particles in terms of the number of collisions they perform per unit time. Note that multiple collisions do not occur in the attachment process, so that only the outer particle surface is “seen”, and shielded parts like pores or the interior of clustered agglomerated particles do not contribute. The part of the particle surface contributing to the instrument’s response has been termed “active” surface with regard to chemical gas-particle interactions. This view is only justified for reactions that take place with unit probability at every collision (reaction coefficient = 1). Most reactions have reaction coefficients near zero, e.g.  $10^{-6}$ , and the total geometric surface of a particle contributes.

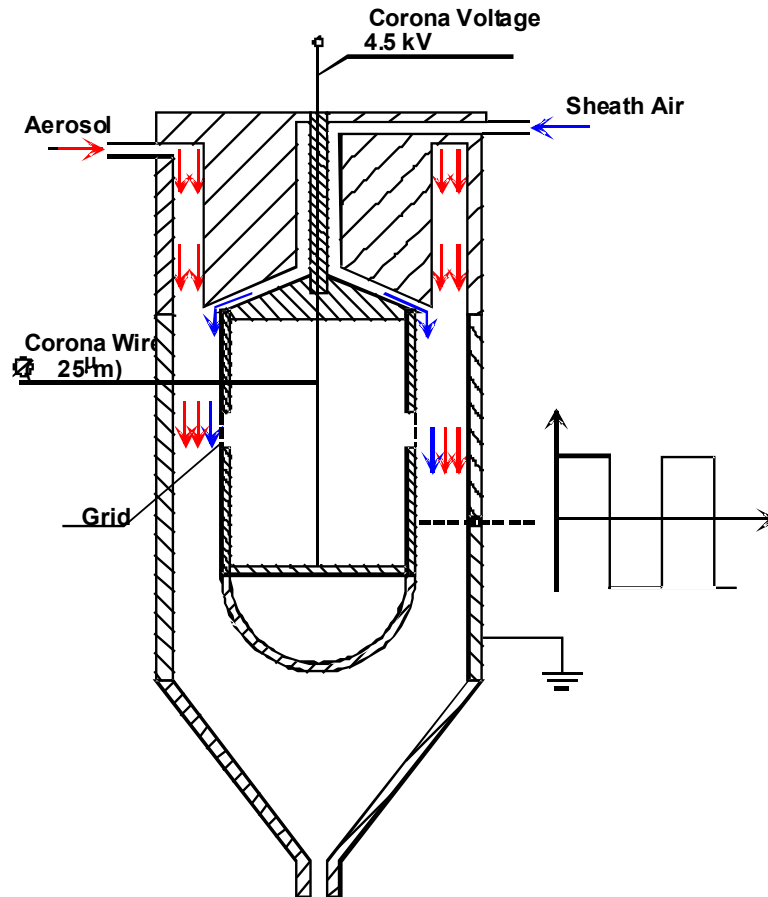
Due to the fact that the epiphaniometer’s signal is not related to basic physical or geometrical descriptors of the particle in a simple way, and that the “active” surface only deserves this designation for a very special and rare case of chemical gas-particle interaction, the instrument has not been widely applied. Another reason is that the same particle information can be obtained in other ways not involving radioactive material. It has been shown that the mobility or the diffusion coefficient of a particle is quite exactly proportional to the inverse of the attachment coefficient  $\eta$  (Schmidt-Ott et al. 1990; Keller et al. 2001). Thus  $\eta$  can also be determined from a mobility distribution. Furthermore, it is easy to measure the coefficient  $\beta$  for the attachment of ions to particles, and it turns out that  $\eta \sim \beta$ .

### ***Diffusion charger-electrometer combination***

As the lead atoms in the epiphaniometer, the ions attach to the particles according to an equation analogous to the formulae for the integrated attachment coefficient above, where  $N_m$  is replaced by the ion concentration  $N_i$  and  $\eta$  is replaced by the ion attachment coefficient  $\beta$ . Figure A.6.7 shows the principle of a unipolar diffusion charger (Büscher et al. 1994; Schmidt-Ott 1999). In a continuous flow arrangement, the aerosol is then passed through a so-called aerosol electrometer (Willeke and Baron 1993), where the particles are collected in a filter surrounded by a Faraday cup. The current  $I_p$  flowing from the cup to ground is measured and corresponds to the current of charged particles coming out of the charger.  $I_p$  is proportional to the integral analogous to  $\eta$ . Thus the response of this simple sensor is afflicted with the same problem as the epiphaniometer concerning the physical meaning of its response. A great advantage of the charger-electrometer combination lies in the simplicity of its construction associated with a low price.

Below 0.1  $\mu\text{m}$ , the response of a diffusion charger electrometer (DCE) sensor has been shown to follow

$$I_{DCE} = \text{const}_1 \cdot \int_0^{D_p(\text{max})} D_p^{1,5} \cdot dN$$



**Figure A.6.7** Diffusion Charger, Schmidt-Ott and Kauffeldt (1999).

Woo et al. (2000) have recently shown that for the wide range between 0.01  $\mu\text{m}$  and 10  $\mu\text{m}$  the approximate relation

$$I_{DCE} = \text{const}_2 \cdot \int_0^{D_p(\text{max})} D_p^{1,16} \cdot dN$$

can be given. Note that  $D_p$  in this equation is the “ion attachment equivalent” diameter, which is almost identical to the diffusion or mobility equivalent diameter.

## Appendix 7

### Problems in Measuring Particulate Matter<sup>1</sup> Problems in Measuring Particulate Matter Mass

#### Background

The EPA decision to revise the PM standards by adding daily and yearly standards for PM<sub>2.5</sub> has led to a renewed interest in the measurement of atmospheric particles and also to a better understanding of the problems in developing precise and accurate measurements of particles. Unfortunately, it is very difficult to measure and characterize particles suspended in the atmosphere. Chow (1995), McMurry (2000), and US EPA (1996; 2000) contain excellent reviews of sampling and analytical techniques for particulate matter (PM).

The U.S. Federal Reference Methods (FRM) for PM<sub>2.5</sub> and PM<sub>10</sub> provide relatively precise (10 %) methods for determining the mass of material remaining on a Teflon filter after equilibration. However, numerous uncertainties remain as to the relationship between the mass and composition of material remaining on the filter, as measured by the FRMs, and the mass and composition of material that exists in the atmosphere as suspended PM. The goal of a PM indicator might be to measure accurately what exists as a particle in the atmosphere. However, this is not currently possible, in part because of the difficulty of creating a reference standard for particles suspended in the atmosphere. As a result, EPA defines accuracy for PM measurements in terms of agreement of a candidate sampler with a reference sampler. Therefore, intercomparisons of samplers become very important in determining how well various samplers agree and how various design choices influence what is actually measured.

There are five general areas where choices must be made in designing an aerosol indicator. These include treatment of semi volatile components; selection of an upper cut point; separation of fine-mode and coarse-mode PM; treatment of pressure, temperature, and relative humidity; and assessment of the reliability of the measurement technique. In many cases choices have been made by default and with inadequate understanding of the consequences. As a result, measurement methods developed by different organizations may give different results when sampling the same atmosphere, even though the techniques appear to be identical.

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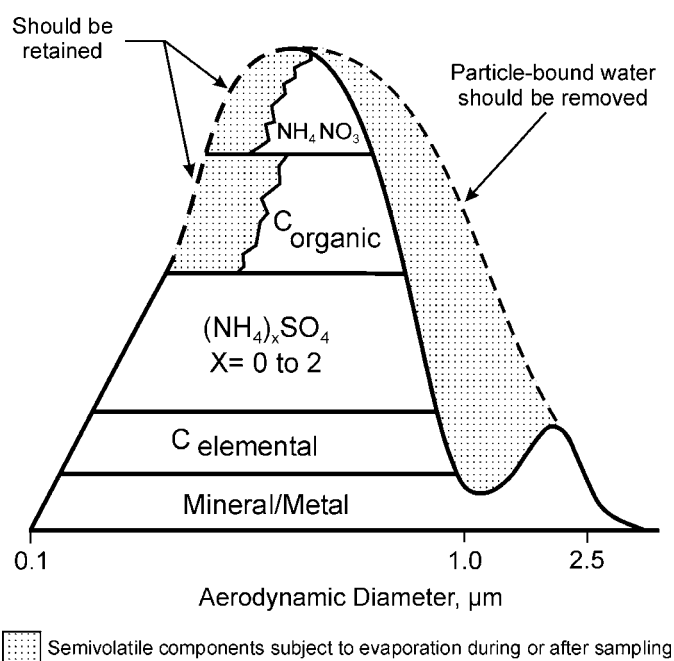
<sup>1</sup> This Appendix is based on material prepared for inclusion by the U.S. EPA in the updated EPA document, Air Quality Criteria for Particulate Matter (AQC PM). Further revisions of these materials are expected to be made in response to external review by the Clean Air Scientific Advisory Committee (CASAC) for incorporation into a final version of the AQC PM, expected to be completed in early 2002. Authors contributing to this material are William E. Wilson, U.S. EPA; Candis Claiborn, Washington State University; and Barbara Turpin, Rutgers University.

## Treatment of semi-volatile components of PM

Current filtration-based mass measurements lead to significant evaporative losses, during and possibly after collection, of a variety of semi-volatile components (i.e., species that exist in the atmosphere in dynamic equilibrium between the condensed phase and gas phase). Important examples include ammonium nitrate, semi-volatile organic compounds, and particle-bound water. This problem is illustrated in Figure A.7.1.

Possible approaches that have been used to address the problem of potentially lost semi-volatile components include the following, which will be discussed in more detail in subsequent sections:

1. Collect/measure all components present in the atmosphere in the condensed phase except particle-bound water. (Examples: Brigham Young absorptive sampler, Harvard pressure drop monitor. Both require preconcentration of the accumulation mode and reduction of outdoor humidity.).
2. Stabilize PM at a specified temperature high enough to remove all particle-bound water. This results in loss of most of the semi-volatile PM. (Examples: TEOM operated at 50 °C, beta gauge with heated inlet.).
3. Equilibrate collected material at fixed, near-room temperature and low relative humidity to remove particle-bound water. Accept loss of an unknown but possibly significant fraction of semi-volatile PM. (Example: U.S. Federal Reference Method and most filter-weighing techniques. There is also information to suggest that the equilibration process removes not all particle-bound water.).



**Figure A.7.1** Schematic showing major non-volatile and semi-volatile components of  $\text{PM}_{2.5}$ . Semi-volatile components are subject to partial to complete loss during equilibration or heating. The optimal technique would be to remove all particle-bound water but no ammonium nitrate or semi-volatile organic PM.

The amount of semi-volatile material lost is dependent on the concentration and composition of the semi-volatile components and is, therefore, also dependent on season and location. The amount of semi-volatile material lost has been found to be significant in air sheds with high nitrate, wood smoke, or secondary organic aerosols.

### **Upper cut point**

A technique must be used that gives an upper cut-point, and its standard deviation, that is independent of wind speed and direction (the classical high volume sampler head was unsatisfactory because of radial asymmetry). A separation that simulates the removal of particles by the upper part of the human respiratory system would appear to be a good choice (i.e., measure what gets into the lungs). The ACGIH-ISO-CEN penetration curve for thoracic particles, with a 50% cut-point at 10  $\mu\text{m}$  aerodynamic diameter (AD), would be an appropriate choice. (Thoracic particles are able to pass the larynx and penetrate into the bronchial and alveolar regions of the lung.) Some countries, however, use  $\text{PM}_{10}$  to refer not to samplers with a 50% cut at 10  $\mu\text{m}$  AD but samplers with 100% rejection of all particles greater than 10  $\mu\text{m}$  AD. Such samplers miss too much of the thoracic PM. The US  $\text{PM}_{10}$  separation curve, while sharper than the thoracic curve, is probably satisfactory both for regulatory and health risk monitoring. It has the advantage of reducing the problem of maintaining the finite collection efficiency specified by the thoracic penetration curve for particles larger than 10  $\mu\text{m}$  AD.

### **Cut point for separation of fine-mode and coarse-mode PM**

Fine-mode and coarse-mode particles differ not only in size and morphology (e.g., smooth droplets versus rough solid particles) but also in formation mechanisms; sources; and chemical, physical, and biological properties. They also differ in terms of dosimetry (deposition in the respiratory system), toxicity, and health effects as observed by epidemiological studies. The many reasons for wanting to collect fine and coarse particles separately and considerations as to the appropriate cut point for separating fine and coarse particles were discussed in Chapter 3 of the 1996 PM AQCD (US EPA 1996). A review of atmospheric particle-size-distribution data did not provide a clear or obvious rationale for selection of an appropriate cut point. Depending on conditions, a significant amount of either fine- or coarse-mode material may be found in the intermodal region between 1 and 3  $\mu\text{m}$ . However, the analysis of the existing data did demonstrate the important role of relative humidity in influencing the size of the accumulation mode.

At high relative humidity, such as that found in fog and clouds, hygroscopic fine-mode particles will increase in size due to accretion of particle-bound water. Under these conditions, some, originally sub-micrometer, fine-mode PM may be found with an AD above 1  $\mu\text{m}$ . At very low relative humidity, coarse-mode particles may be fragmented into smaller sizes and small amounts of coarse-mode PM may be found with an AD below 1  $\mu\text{m}$ . Thus, a  $\text{PM}_{2.5}$  sample will contain most of the fine-mode material, except during periods of RH near 100 %. However, especially under conditions of low RH, it may contain 5 to 20% of the coarse-mode material below 10  $\mu\text{m}$  in diameter. A cut point of 1.0  $\mu\text{m}$  would reduce the misclassification of coarse-mode material as fine, but under high RH conditions could result in some fine-mode material being misclassified as coarse. A reduction in RH, either intentionally or inadvertently, will reduce the size of the fine mode. A sufficient reduction in RH will yield a dry fine-particle mode with very little material

above 1.0  $\mu\text{m}$ . Studies of the changes in particle size with changes in relative humidity suggest that only a small amount of accumulation mode particles will be above 1  $\mu\text{m}$  in diameter at RH below 60% but a substantial fraction will grow above 1  $\mu\text{m}$  for RH above 80% (Hitzenberger et al. 1997; McMurry and Stolzenburg 1989; US EPA 1996).

It is desirable to separate fine-mode PM and coarse-mode PM as cleanly as possible in order to properly allocate health effects to either fine-mode PM or coarse-mode PM and to correctly determine sources by factor analysis and/or chemical mass balance. For example, sulphate in the fine-mode is associated with hydrogen and/or ammonium ions; sulphate in the coarse mode is associated with basic metal ions. The sources are different and the health effects are likely to be different. Transition metals in the coarse mode are likely to be associated with soil and tend to be less soluble than transition metals in the fine mode, which may be found in fresh combustion particles.

The current practice of separating fine-mode and coarse-mode particles at 2.5  $\mu\text{m}$  does not provide an adequate separation for exposure or epidemiological studies or for the determination of source categories to guide control strategy, especially in areas where winds cause high concentrations of wind blown soil. A possible approach, which would provide much better separation of fine-mode PM and coarse-mode PM, would be to dehumidify the air stream to some fixed humidity that would remove all or most particle-bound water without evaporating semi-volatile components and make the cut near 1  $\mu\text{m}$  AD. New techniques have been developed for both integrated and continuous measurement of fine particulate matter that reduce particle-bound water but retain semi-volatile nitrate and organic compounds. These techniques require reduction of RH prior to collection. With such techniques,  $\text{PM}_{1.0}$  would be an appropriate cut point.

### **Treatment of pressure, temperature, and relative humidity**

There are a variety of techniques for defining (or ignoring) the pressure, temperature, and relative humidity during or after sampling.

#### *Temperature and pressure:*

- a. Sample volume based on mass or volumetric flow corrected to standard temperature and pressure (273  $\mu\text{K}$  and 1 atm.) (former EPA technique for  $\text{PM}_{10}$ ).
- b. Sample volume based on volumetric flow at outdoor conditions of temperature and pressure (current EPA technique for  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ).

#### *Temperature during collection:*

- a. Heat enough to remove all particle-bound water (i.e., TEOM at 50  $^{\circ}\text{C}$ ).
- b. Heat several degrees to prevent condensation of water in sampling system.
- c. Try to maintain sampler near ambient temperature.
- d. Maintain sampler at constant temperature inside heated/air conditioned shelter.



*Temperature after collection:*

- a. No control
- b. Constant Temperature (room temperature)
- c. Store at cool temperature (4 °C)

*Relative humidity:*

Changes in relative humidity cause changes in particle size of hygroscopic or deliquescent particles. Changing relative humidity by adding or removing water vapour affects measurements of:

- a. Particle number, particle surface area and particle size distribution
- b. Amount of overlap of fine-mode and coarse-mode particles

Changing relative humidity by intentional or inadvertent changes in temperature affects above measurements plus:

- c. Amount of ammonium nitrate and semi-volatile organic compounds lost.

Studies of relationships between personal/indoor/outdoor measurements present special problems.

Indoor environments are typically dryer than outdoors and may be warmer or, if air-conditioned, cooler. These differences may change particle size and the amount of volatilisation of semi-volatile components. Such changes between indoors and outdoors will complicate the comparison of indoor to outdoor concentrations, the modelling of personal exposure to all particles, and exposure apportionment by the disaggregation of personal exposure into exposure to particles of outdoor origin and exposure to particles of indoor origin.

**No way to determine accuracy**

Precision is typically determined by comparison of collocated samplers or through replicate analyses, while accuracy is determined through the use of traceable calibration standards. Unfortunately, no standard reference calibration material or procedure has been developed for suspended PM. Therefore, it is not possible to establish the absolute accuracy of a PM monitoring technique. Inter-comparison studies, to establish the precision of identical monitors and the extent of agreement between different types of monitors, are essential for establishing the reliability of PM measurements. Inter-comparison studies have contributed greatly to our understanding of the problems in PM measurement. Such studies will be discussed as they apply to specific measurement problems, monitoring instruments, or analytical techniques.

Measurement errors of concern in PM<sub>10</sub> sampling that arise due to uncertainty tolerances in cut point, particle bounce and re-entrainment, impactor surface overloading, and losses to sampler internal surfaces were discussed in detail in the 1996 PM AQCD (US EPA 1996). Measurement errors of concern in PM<sub>2.5</sub> sampling arise because of our inability to assess accuracy in an absolute sense due to a lack of primary calibration standards or procedures, because of the use of an operational definition of PM<sub>2.5</sub> as a surrogate for fine particles, and because of problems associated with trying to measure the mass of particles as they exist in the air rather than what remains after collection on a filter.

Because of the difficulties associated with determining the accuracy of PM measurements, EPA has sought to make US FRM measurements equivalent by specifying operating conditions and, in the case of PM<sub>2.5</sub> samplers, by specifying details of the sampler design. Thus, both the PM<sub>10</sub> as well as PM<sub>2.5</sub> standards are defined with consistency of measurement technique, rather than accuracy of the true mass concentration measurement, in mind (McMurry 2000). It is acknowledged in the Federal Register (1997) that, “because the size and volatility of the particles making up outdoor particulate matter vary over a wide range and the mass concentration of particles varies with particle size, it is difficult to define the accuracy of PM<sub>2.5</sub> measurements in an absolute sense . . .” Thus, accuracy is defined as the degree of agreement between a field PM<sub>2.5</sub> sampler and a collocated PM<sub>2.5</sub> reference method audit sampler (McMurry 2000). (See the description of the Federal Reference Method (US FRM) for PM<sub>2.5</sub>.) As mentioned earlier, volatilisation losses, during sampling or post-sampling handling, of some organic compounds as well as ammonium nitrate can lead to significant underestimation of the true fine particulate mass concentration in some locations. Sources of error in the measurement of true PM<sub>2.5</sub> mass also arise due to adsorption or desorption of semi-volatile vapours onto or from collected PM, filter media, or other sampler surfaces; neutralization of acid or basic vapours on either filter media or collected PM; and artefacts associated with particle-bound water.

During the past 25 years, there have been advancements in the generation and classification of monodisperse aerosols, as well as in the development of electron microscopy and imaging analysis, that have contributed to the advancement in aerosol calibration (Chen 1993). Still, one of the limitations in PM sampling and analysis remains the lack of primary calibration standards for evaluating analytical methods and for intercomparing laboratories. Klouda et al. (1996) examined the possibility of resuspending the NIST Standard Reference Material 1649 (Urban Dust) in air for collection on up to 320 filters simultaneously, using SRI International's dust generation and collection system. However, the fine component is not resuspended and the semi-volatile component has evaporated so this material is not a suitable standard for suspended PM. Little additional work in this area has been reported.

Methods validation was discussed in the 1996 PM AQCD (US EPA 1996), and the usefulness of intercomparisons and "internal redundancy" was emphasized. For example, a number of internal consistency checks are applied to the IMPROVE network (Malm et al, 1994). These include mass balance, sulphur measurements by both proton induced X-ray emission (PIXE) and ion chromatography (IC), and comparison of organic matter determined by combustion and by proton elastic scattering analysis (PESA) analysis of hydrogen. Mass balances compare the gravimetrically determined mass with the mass calculated from the sum of the major chemical components (i.e. crustal elements plus associated oxygen, organic carbon, elemental carbon, sulphate, nitrate, ammonium, and hydrogen ions). Mass balances are useful validation techniques, however, they do not check for, or account for, artefacts associated with the absorption of gases during sampling, or the loss of semi-volatile material during sampling. The mass balance check may appear reasonable even if such artefacts are present, since only the material collected on the filter is included in the balance.

## **Problems associated with semi-volatile particulate matter**

It is becoming increasingly apparent that the semi-volatile component of PM may significantly impact the quality of the measurement, and can lead to both positive and negative sampling artefacts. Losses of semi-volatile species, like ammonium nitrate and many organic species, may

occur during sampling; due to changes in temperature, relative humidity, or composition of the aerosol; or due to pressure drop across the filter (McMurry 2000). Gas phase organic species, both volatile and semi-volatile species may adsorb onto, or react with, filter media and/or collected PM, leading to a positive sampling artefact. Quartz fibre filters have a large specific surface area upon which adsorption of gases can occur. A number of other types of filters (e.g., stretched Teflon membrane filters) have much smaller exposed surface areas (Turpin et al. 1994) and appear to be subject to less adsorption (Kirchstetter et al. 2000; Turpin et al. 1994). Tsai and Huang (1995) observed positive sulphate and nitrate artefacts on high volume PM<sub>10</sub> quartz filters and attributed the artefacts to interactions between acidic gases SO<sub>2</sub>, HONO and HNO<sub>3</sub> and both the filter media (either glass fibre or quartz) and the coarse particles collected on the filter. Volatilisation losses have also been reported to occur during sample transport and storage (Chow 1995). Evaporative losses of particulate nitrates have been investigated in laboratory and field experiments (e.g., Wang and John 1988), and in theoretical studies (Zhang and McMurry 1992). It has been known for some time that volatilisation losses of SVOC can be significant (e.g., Eatough et al. 1993).

The theory describing phase equilibrium of SVOC continues to be developed. Liang et al. (1997), Jang et al. (1997), and Strommen and Kamens (1997) have modelled the gas/particle partitioning of SVOC on inorganic, organic, and outdoor smog aerosols.

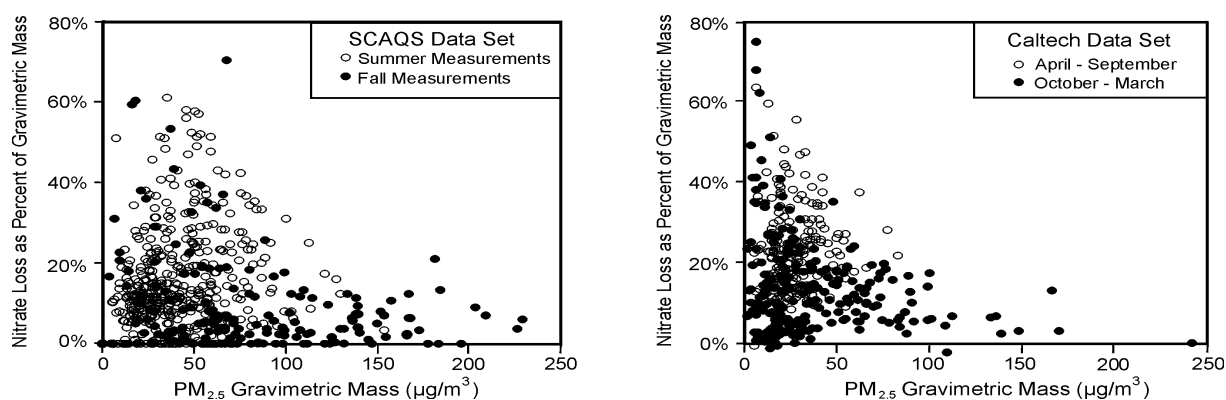
Adsorption of organic vapours onto quartz filters is recognized as a source of positive sampling error. This artefact has been examined in experiments in which two quartz fibre filters were deployed in series. The second quartz filter may indicate gaseous VOC adsorbed on both filters (positive artefact) or SVOC evaporated from particles on the first filter and subsequently adsorbed on the second filter (negative artefact), or a combination of both effects. Unless the individual compounds are identified, the investigator does not know what to do with the loading value on the second filter (i.e., to add or subtract from the first filter loading value).

The developing state of the art in which diffusion denuder technology is being applied to SVOC sampling (e.g., Eatough et al. 1993; Gundel et al. 1995), as well as for sampling of gas and particulate phase organic acids (Lawrence and Koutrakis 1996a; 1996b), holds promise for improving our understanding of SVOC sampling artefacts. In a denuder-based system, gas-phase organics are removed by diffusion to an adsorbent surface (e.g., activated carbon, special polymer resins, etc.). Particles are then collected on a filter downstream of the denuder and the remaining organic vapours (i.e., from denuder breakthrough and volatile losses from the collected particles) are collected in an adsorbent downstream of the filter (e.g., charcoal or carbon impregnated filters, polyurethane foam, or polystyrene-divinylbenzene resin (XAD)).

Finally, Eatough et al. (1999) have reported on a batch sampler (the Particle Concentrator Brigham Young University Organic Sampling System, or PC-BOSS) and a continuous sampler (Real-Time Air Monitoring System or RAMS), which attempt to correct simultaneously for volatilisation losses of both nitrate and SVOC. These samplers are discussed in more detail later in this Appendix.

## Particulate nitrates

It is well known that volatilisation losses of particulate nitrates (e.g., Zhang and McMurry 1992; see also Hering and Cass 1999), and references therein) occur during sampling on Teflon filters. The impact on the accuracy of atmospheric particulate measurements from these volatilisation losses is more significant for  $PM_{2.5}$  than for  $PM_{10}$ . The US FRM for  $PM_{2.5}$  suffers loss of nitrates, similar to the losses experienced with other simple filter collection systems. Sampling artefacts due to the loss of particulate nitrates represents a significant problem in areas that experience high amounts of nitrogen species, like southern California. Hering and Cass (1999) examined the errors in  $PM_{2.5}$  mass measurements due to volatilisation of particulate nitrate by looking at data from two field measurement campaigns conducted in Southern California by the Southern California Air Quality Study (SCAQS, Lawson 1990), and the 1986 CalTech study (Solomon et al. 1992). In both these studies, side-by-side sampling of  $PM_{2.5}$  was conducted. One sampler collected particles directly onto a Teflon filter. The second sampler consisted of a denuder to remove gaseous nitric acid followed by a nylon filter that absorbs any  $HNO_3$  that evaporates from the ammonium nitrate. In both studies, the denuder consisted of MgO-coated glass tubes (Appel et al. 1981). Fine particulate nitrate collected on the Teflon filter was compared to fine particulate nitrate collected on the denuded nylon filter. In both studies, the  $PM_{2.5}$  mass lost due to volatilisation of ammonium nitrate represented a significant fraction of the total  $PM_{2.5}$  mass. The fraction of mass lost was higher during summer than during fall (17% versus 9% during the SCAQS study, and 21% versus 13% during the CalTech study) (Figure A.7.2). In regard to percentage loss of nitrate, as opposed to percentage loss of mass discussed above, Hering and Cass (1999) found that nitrate remaining on the Teflon filter samples was on average 28% lower than that on the denuded nylon filters.



**Figure A.7.2** Amount of ammonium nitrate volatilised from Teflon filters, expressed as a percentage of the measured  $PM_{2.5}$  mass, for the SCAQS and CalTech studies, for spring and fall sampling periods.

Source: Hering and Cass (1999).

Hering and Cass (1999) also analysed these data by extending the evaporative model developed by Zhang and McMurry (1987). The extended model utilized by Hering and Cass (1999) takes into account dissociation of collected particulate ammonium nitrate on Teflon filters into nitric acid and ammonia, via three mechanisms: scrubbing of nitric acid and ammonia in the sampler

inlet [John et al. (1988) showed that clean PM<sub>10</sub> inlet surfaces serve as an effective denuder for nitric acid], heating of the filter substrate above ambient temperature during sampling, and pressure drop across the Teflon filter. For the sampling systems modelled, the flow-induced pressure drop was measured to be less than 0.02 atmospheres, and the corresponding change in vapour pressure was 2%, so losses driven by pressure drop were not considered to be significant in this work. Losses from Teflon filters were found to be higher during the summer compared to the winter, higher during the day compared to night, and reasonably consistent with modelled predictions.

Finally, during the SCAQS study, particulate samples were also collected using a Berner impactor and greased Tedlar substrates, in size ranges from 0.05 to 10 µm in aerodynamic diameter. The Berner impactor PM<sub>2.5</sub> nitrate values were much closer to those from the denuded nylon filter than those from the Teflon filter, with the impactor nitrate being approximately 2% lower than the nylon filter nitrate for the fall measurements, and approximately 7% lower during the summer measurements. When the impactor collection was compared to the Teflon filter collection for a non-volatile species (sulphate), the results were in agreement.

It should be noted that during these inter-comparison studies, filters or collection surfaces were removed immediately after sampling and placed into vials containing a basic extraction solution. Therefore, losses that might occur during handling, storage, and equilibration of filters or impaction surfaces were avoided. The loss of nitrate observed from Teflon filters and impaction surfaces in this study, therefore, is a lower limit compared to losses that might occur during the normal processes involved in equilibration and weighing of filters and impaction surfaces. Brook and Dann (1999) measured particulate nitrate in Windsor and Hamilton, Ontario, Canada by three techniques: a single Teflon filter in a dichotomous sampler, the Teflon filter in an annular denuder system (ADS), and total nitrate including both the Teflon filter and the nylon back-up filter from the ADS. The dicot Teflon filter averaged only 13% of the total nitrate. The Teflon filter from the ADS averaged 46% of the total nitrate. The authors conclude that considerable nitrate was lost from the dicot filters during handling, which included weighing and XRF measurement in vacuum.

Kim et al. (2000) also examined nitrate-sampling artefacts by comparing denuded and undenuded quartz and nylon filters, during the PM<sub>10</sub> Technical Enhancement Program (PTEP) in the South Coast Air Basin of California. They observed negative nitrate artefacts (losses) for most measurements; however, for a significant number of measurements they observed positive nitrate artefacts. Kim et al. (2000) pointed out that random measurement errors make it difficult to measure true amounts of nitrate loss.

Several diffusion denuder samplers have been developed to account for the nitrate lost due to volatilisation from filters, many of which were discussed in the 1996 PM AQCD (US EPA 1996). Eatough et al. (1999a) developed a high-volume diffusion denuder system in which diffusion denuder and particle concentrator techniques were combined. The particle concentrator reduces the flow through the denuder so that the denuder can be operated for weeks without a loss of collection efficiency, thus making the sampler suitable for routine field sampling. The system was evaluated for the collection of fine particulate sulphate and nitrate in Riverside, CA (Eatough et al. 1999b). Concentrations of PM<sub>2.5</sub> nitrate obtained from the PC-BOSS agreed with those obtained using the Harvard-EPA Annular Denuder Sampler, HEADS (Koutrakis et al. 1988b).

In atmospheres with high sulphate and low ammonia, the PM tends to be acidic ( $\text{NH}_4\text{HSO}_4$  or  $\text{H}_2\text{SO}_4$ ) and nitric acid remains in the vapour phase. In atmospheres with lower sulphate and higher ammonia, there may be sufficient ammonia to fully neutralize the  $\text{H}_2\text{SO}_4$  and also react with  $\text{HNO}_3$  to form  $\text{NH}_4\text{NO}_3$  particles. Therefore, loss of nitrate will be a bigger problem in the areas with low  $\text{SO}_2$  emissions and high ammonia emissions. However, as  $\text{SO}_2$  emissions are reduced in areas that currently have high  $\text{SO}_2$  emissions, nitrate may become a larger fraction of the suspended PM.

### **Semi-volatile organic compounds**

Semi-volatile organic compounds (SVOC) can similarly be lost from Teflon filters due to volatilisation, and can also cause the  $\text{PM}_{2.5}$  mass to be significantly underestimated. Like particulate nitrates, the US FRM for  $\text{PM}_{2.5}$  will suffer loss of SVOC, similar to the losses experienced with other simple filter collection systems. It has been suggested that attempting to correct for the losses of SVOC during sampling by deploying a second quartz filter directly behind either a quartz or Teflon filter can significantly underestimate the volatilisation losses compared to a denuded filter sample (e.g., Eatough et al. 1993). Using their multichannel diffusion denuder sampling system (BOSS), Eatough et al. (1995) reported that, for samples collected at the South Coast Air Quality Management District sampling site at Azusa, CA, changes in the phase distribution of SVOC could result in a loss on average of 35% of the particulate organic material. At present, there are limited data available specifically on the fraction of  $\text{PM}_{2.5}$  mass lost during sampling onto Teflon filters due to volatilisation of organic species, and even less on the regional differences in the volatilisation losses of SVOC. Cui et al. (1998) found that losses of SVOC from particles in the Los Angeles Basin during the summer were greater during the day than at night. Cui et al. (1998) determined that on average, 62 and 42% of the particulate organic material was semi-volatile organic compounds lost from particles during sampling for daytime and nighttime samples, respectively.

In addition to their contribution to suspended PM mass, SVOC are also of interest because of their possible health effects. SVOC include products of incomplete combustion such as polycyclic aromatic hydrocarbons (PAHs) and polycyclic organic matter, which have been identified as a hazardous air pollutant. PAHs have also been suggested as alternative particulate tracers for automobile emissions, since the phase-out of organo-lead additives to gasoline means that lead is no longer a good tracer for automobiles (Venkataraman et al. 1994). PAHs are also emitted during biomass burning, including burning of cereal crop residues and wood fuels (Jenkins et al. 1996; Roberts and Corkill 1998).

Several investigators have observed that collection of particles on a filter can result in underestimation of particulate organic compounds due to losses of semi-volatile organic material during sample collection (negative sampling artefact) (Eatough et al. 1993; Tang et al. 1994; Eatough et al. 1995; Gundel et al. 1995; Finn et al. 1999). Positive sampling artefacts can also occur due to the adsorption of gases onto the filter materials (e.g., Gundel et al. 1995). There appears to be a larger positive artefact due to adsorption of organic vapour onto quartz fibre filters than to Teflon filters (Turpin et al. 1994; Chow et al. 1994; 1996; Eatough et al. 1996; Finn et al. 1999). When samples for organic analysis are collected on quartz fibre filters, the amount of adsorbed organic vapour on the quartz filter is sometimes estimated by the amount collected on a second quartz fibre filter behind the first, or by the amount collected on a quartz fibre filter placed behind a Teflon filter in a parallel sampling port (Novakov et al. 1997). Many, but by no means

all, investigators subtract this adsorption estimate from the front filter quantity to obtain the mass of collected particulate organic (Turpin et al. 2000). Kirchstetter et al. (2000) report that adsorptive properties of quartz fibre filters vary with lot number, and therefore front and back-up filters should be taken from the same lot. Recent literature suggests that a Teflon-quartz back-up filter appears to provide a better estimate of the adsorption of gases on a quartz fibre front filter than does a quartz-quartz backup, and that the difference between these two adsorption estimates can be substantial for short durations (Kirchstetter et al. 2000; Turpin et al. 2000). The typically lower organic carbon loadings on quartz-quartz back-up filters, relative to Teflon-quartz back-up samples collected concurrently, is believed to occur because adsorption on the quartz front filter acts to reduce the gas-phase concentration downstream until gas phase B adsorbed phase equilibrium has been achieved in the vicinity of the front quartz filter surface. Since Teflon filters have little affinity for organic vapours, this equilibrium occurs almost instantaneously for Teflon filters, and the Teflon-quartz back-up filter is exposed to the outdoor concentration of organic vapours from the beginning of the sampling period.

### **Use of denuder systems to measure semi-volatile compounds**

Phase distribution of semi-volatile organic species has been the subject of several studies that have employed denuder technology (see Gundel et al. 1995; Gundel and Lane, 1999) to directly determine the phase distributions while avoiding some of the positive and negative sampling artefacts associated with using backup quartz filters. In an ideal system with a denuder that is 100% efficient, the gas phase would be collected in the denuder and the particle phase would be the sum of the material collected on the filter and the adsorbent downstream. Denuder collection efficiency depends upon the denuder surface area, the diffusivity and vapour pressure of the compound, the temperature and flow rate of the air stream, and the presence of competing species, including water vapour (Cui et al. 1998; Kamens and Coe, 1997; Lane et al. 1988). In a system with denuder collection efficiency less than 100%, the collection efficiency must be known in order to accurately attribute adsorbed organics from denuder breakthrough to the gas phase and adsorbed organics volatilised from collected particles to the particle phase. In calculating the overall phase distributions of SVOC PAH from a denuder system, the collection efficiency for each compound is needed.

For measuring particulate phase organic compounds, the denuder-based sampling system represents an improvement over the filter/adsorbent collection method (Turpin et al. 1993). Some researchers, however, have reported that denuder coatings themselves can introduce contamination (Mukerjee et al. 1997), or the adsorbed species may be difficult to remove from the coating (Eatough et al. 1993).

In a study conducted in southern California (Eatough et al. 1995), the Brigham Young University Organic Sampling System (BOSS) (Eatough et al. 1993) was used for determining POM composition, and a high-volume version (BIG BOSS) (flow rate 200 lpm) was utilized for determining the particulate size distribution and the chemical composition of SVOC in fine particles. The BOSS, a multi-channel diffusion denuder sampling system, consists of two separate samplers (each operating at 35 lpm). The first sampler consists of a multi-parallel plate diffusion denuder with charcoal-impregnated filter papers as the collection surfaces, followed by a two-stage quartz filter pack, followed by a two-stage charcoal-impregnated filter pack. The second sampler operating in parallel with the first consists of a two-stage quartz filter pack, followed by the parallel plate denuder, followed by the two-stage charcoal-impregnated filter

pack. The filter samples collected by the BOSS sampler were analysed by temperature-programmed volatilisation analysis. Eatough et al. (1995) also operated a two-stage quartz filter pack alongside the BOSS sampler. The BIG BOSS system (Tang et al. 1994) consists of four systems (each with a flow rate of 200 lpm). Particle size cuts of 2.5, 0.8, and 0.4  $\mu\text{m}$  are achieved by virtual impaction, and the sample subsequently flows through a denuder, then is split, with the major flow (150 lpm) flowing through a quartz filter followed by an XAD-II bed. The minor flow is sampled through a quartz filter backed by a charcoal-impregnated filter paper. The samples derived from the major flow (quartz filters and XAD-II traps) were extracted with organic solvents and analysed by gas chromatography and GC-mass spectroscopy. The organic material lost from the particles was found to represent all classes of organic compounds.

Eatough et al. (1996) operated the BOSS sampler for a year at the IMPROVE site at Canyonlands National Park, Utah, alongside the IMPROVE monitor and alongside a separate sampler consisting of a two-stage quartz filter pack. They found that concentrations of particulate carbon determined from the quartz filter pack sampling system were low on average by 39%, and this was attributed to volatilisation losses of SVOC from the quartz filters. In another study conducted with the BOSS in southern California, losses of 35% of the POM, on average, were found and attributed to losses of the SVOC during sampling (Eatough et al. 1995).

The PC-BOSS system of Eatough et al. (1999) includes a virtual impactor upstream of the denuder to improve the denuder collection efficiency by removing a majority of the gases from the aerosol flow (i.e., gases and particles smaller than 0.1  $\mu\text{m}$  are removed with the major flow of the virtual impactor and the remaining aerosol enters the denuder). Particulate OC estimates are corrected for particle losses of 46 to 48% in the inlet. The denuder is comprised of charcoal-impregnated cellulose fibre filter material, and denuder collection efficiencies of greater than 98% are reported for organic gases that adsorb on quartz and charcoal-impregnated filters.

Turpin et al. (1993) developed a sampling system based upon a diffusion separator, which corrects for the loss of semi-volatile organic compounds during sampling by removal of most of the gas phase material from the particles in a diffusion separator sampling system. Unlike the previously mentioned systems, wherein the particulate phase is measured directly, in the system of Turpin et al. the gas-phase is measured directly. In the laminar flow system, outdoor, particle-laden air enters the sampler as an annular flow. Clean, particle-free air is pushed through the core inlet of the separator. The clean air and outdoor aerosol join downstream of the core inlet section, and flow parallel to each other through the diffusion zone. Because of the much higher diffusivities for gases compared to particles, the SVOC in the outdoor air diffuse to the clean, core flow. The aerosol exits the separator in the annular flow, and the core flow exiting the separator now contains a known fraction of the outdoor SVOC. Downstream of the diffusion separator, the core exit flow goes into a PUF plug, where the SVOC is collected. The adsorbed gas phase on the PUF plug is extracted with supercritical fluid  $\text{CO}_2$ , and analysed by gas chromatography/mass-selective detection (GC/MSD). The gas-phase SVOC is thus determined. Ultimately, to determine particulate phase SVOC concentrations, the total compound concentration will also be measured, and the particulate phase obtained by difference. The system was tested for the collection of PAH. The diffusional transport of gas-phase PAHs and particle concentrations agreed well with theory. Breakthrough was problematic for low molecular weight PAHs ( $\text{MW} < 160$ ). Detection limits ranged from 20 to 50 pg of injected mass for all PAHs.



### *Effect of diffusion denuders on the positive quartz filter artefact*

To account for the volatilisation losses of semi-volatile organic compounds, Turpin et al. (1994) recommended that a quartz filter be placed behind a Teflon filter in a parallel sampler. Addition of a vapour trap (e.g., polyurethane foam plug) downstream of the filter was also suggested as a method to collect semi-volatile organic compounds. However, it was noted that addition of some type of trap behind the Teflon filter collected both vapour phase organics as well as “blow-off” from the Teflon filter [i.e., material vaporized from particles collected on Teflon filter (Van Vaeck et al. 1984)]. Kim et al. (2000) used a quartz filter behind a Teflon filter recently to account for positive organic artefacts in the South Coast Air Basin. They found that, on an annual average basis, 30% of the PM<sub>2.5</sub> organic carbon concentration is positive artefacts.

The adsorption of organic compounds by a second quartz filter has been shown to be reduced, but not eliminated, in samples collected in the Los Angeles Basin, if a multi-channel diffusion denuder with quartz filter material as the denuder collection surface preceded the quartz filters (f, 1990). This artefact can be further reduced by the use of activated charcoal as the denuder surface and use of a particle concentrator to reduce the amount of gas phase organic compounds relative to condensed phase organic compounds (Cui et al. 1998; 1997; Eatough 1999). Recent experiments (Cotham and Bidleman 1992; Cui et al. 1998; Eatough et al. 1995; 1996) have shown that the quartz filter artefact can result both from the collection of gas phase organic compounds and from the collection of semi-volatile organic compounds lost from particles during sampling. Thus, results available to date suggest that both a “positive” and a “negative” artefact can be present in the determination of particulate phase organic compounds using two tandem quartz filters.

The relative importance of adsorption of organic vapours and volatilisation from filter-collected particulate matter continues to be a topic of active debate. The relative importance of positive and negative artefacts will be different for denuded and undenuded filters, and will depend on collection face velocity, sample loading, and the vapour pressure of the compounds of interest. Evidence for a substantial positive sampling artefact for total particulate OC follows. Undenuded quartz-quartz and Teflon-quartz back-up filters have been reported to collect 10 to 50% of the organic mass found on quartz front filters that remove particulate matter with essentially 100% efficiency (Turpin, et al. 2000). Larger percentages were found for samples with shorter collection times and for cleaner locations. Kirchstetter et al. (2000) and Turpin et al. (2000) argue that the quantity of organic material on a quartz back-up filter provides an estimate of the positive artefact (i.e., adsorbed organic vapours), but provides no information about the negative artefact (i.e., volatilised particulate organics). This argument is based on profiles of thermal carbon analyses (i.e., plots of evolved carbon with temperature created during Evolved Gas Analysis, EGA) and the following argument. Material volatilised from the collected particles will not add significantly to the loading on the quartz backup filter unless the particle-to-particle mass ratio is low and the rate of volatilisation is great enough to significantly increase the organic particle concentration passing through the back-up filter (Zhang and McMurry 1987). Evaporative losses of a given species only become significant (according to theory) when the particle-to-particle mass ratio is greater than one (i.e., moderate particle pressure), and therefore will not be effectively collected on a quartz fibre back-up filter.

A *net* positive artefact for total particulate organic carbon was reported by Novakov et al. (1997), whose filter-based aircraft measurements had carbon loadings that exceeded the total aerosol

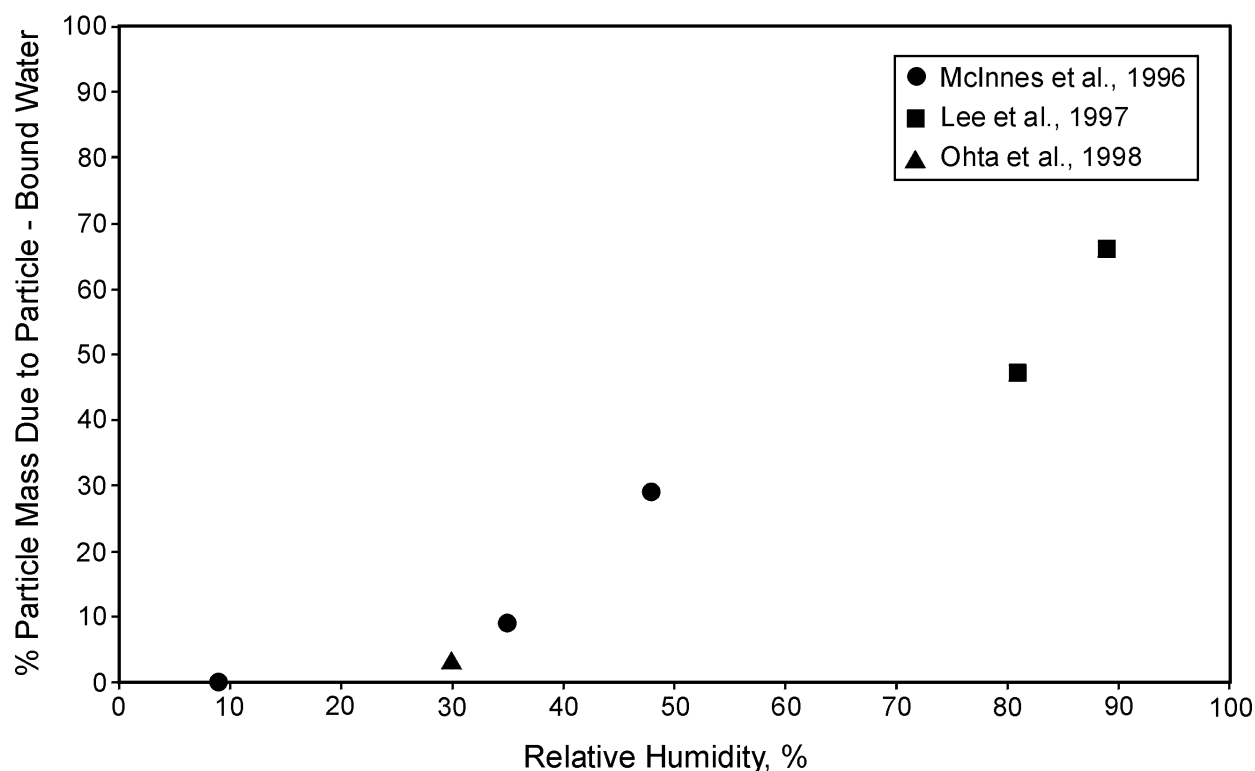
mass. Novakov compared estimates of adsorption based on examination of EGA thermograms and estimates of adsorption obtained from quartz-quartz back-up filters. He concludes that, if anything, the quartz-quartz back-up filter underestimates the positive sampling artefact. Also, both McDow and Huntzicker (1990) and Turpin et al. (1994) observed that subtraction of the Teflon-quartz backup filter (adsorption estimate) from the quartz front filter loading removed the face velocity dependence of the particulate organic carbon concentrations obtained at face velocities of 20, 40 and 80 cm/s. Kirchstetter et al. (2000) reported that the organic carbon content of a denuded quartz filter collected in Berkeley, CA was comparable to the carbon content of a concurrently collected undenuded quartz filter after subtraction of the matching Teflon-quartz backup (i.e., after correction for the positive artefact). As a result, they concluded that volatile losses must not be important for this sample. (Some denuder breakthrough was noted in this study.)

Evidence of a *net* negative artefact is provided by Lewtas et al. (2001), who emphasized that if particulate OC had been measured on a denuded quartz filter without an adsorbent downstream, the negative bias would be large. Their data showed that the sum of a denuded quartz filter and absorbent downstream (average =  $9.1 \mu\text{g}/\text{m}^3$ ) was greater than a colocated undenuded quartz filter (average =  $7.7 \mu\text{g}/\text{m}^3$ ) in a PC-BOSS sampler after correction for losses (46 to 48%) in the virtual impactor inlet. A net negative artefact for total particulate OC has been reported by Eatough and colleagues in a number of studies (e.g., Cui et al. 1998; Eatough, 1999).

### **Particle-bound water**

It is generally desirable to collect and measure ammonium nitrate and semi-volatile organic compounds. However, for many measurements of suspended particle mass, it is desirable to remove the particle-bound water before determining the mass. In other situations it may be important to know how much of the suspended particle's mass or volume is due to particle-bound water. The water content of PM is significant and highly variable. Moreover, there is significant hysteresis in the water adsorption-desorption pathways (Seinfeld and Pandis 1998), further complicating the mass measurement.

The results of several of the above studies, in which aerosol water content as a function of relative humidity was determined, are summarized in Figure A.7.3. In this figure, the results of Lee et al. (1997), McInnes et al. (1996), and Ohta et al. (1998) are included. Relative humidity ranged from 9% (at which the aerosol water content was assumed to be zero, McInnes et al. 1996) to 89%, at which the aerosol water content was determined to be 66% by mass (Lee et al. 1997). Koutrakis et al. (1989) and Koutrakis and Kelly (1993) have also reported field measurements of the equilibrium size of atmospheric sulphate particles as a function of relative humidity and acidity at the stage for which the cut size was  $0.047 \mu\text{m}$ , where the cut size was 10.7% larger than the non-hygroscopic particle cut size. They concluded that flow-induced RH changes would have only a modest effect on MOUDI cut sizes at  $\text{RH} < 80\%$ .



**Figure A.7.3.** Aerosol water content expressed as a mass percentage, as a function of relative humidity.

Hitzenberger et al. (1997) collected atmospheric aerosol in the size range of 0.06 to 15  $\mu\text{m}$  in Vienna, Austria, using a nine-stage cascade impactor and measured the humidity-dependent water uptake when the individual impaction foils were exposed to high RH. They observed particle growth with varying growth patterns. Calculated extinction coefficients and single scattering albedo increased with humidity.

Hygroscopic properties, along with mixing characteristics, of submicrometer particles sampled in Los Angeles, CA, during the summer of 1987 SCAQS study and at the Grand Canyon, AZ, during the 1990 Navajo Generating Station Visibility Study were reported by Zhang et al. (1993).

They used a tandem differential mobility analyser (TDMA; McMurry and Stolzenburg 1989) to measure the hygroscopic properties for particles in the 0.05 to 0.5  $\mu\text{m}$  range. In their experimental technique, monodisperse particles of a known size are selected from the atmospheric aerosol with the first DMA. Then, the relative humidity of the monodisperse aerosol is adjusted and the new particle size distribution is measured with the second DMA. At both sites, they observed that monodisperse particles could be classified according to “more” hygroscopic and “less” hygroscopic. Aerosol behaviour observed at the two sites differed markedly. The “less” hygroscopic particles sampled in Los Angeles did not grow to within the experimental uncertainty (2%) when the RH was increased to 90%, whereas at the Grand Canyon, the growth of the “less” hygroscopic particles varied from day to day, but ranged from near 0 to 40% when the RH was increased to 90%. The growth of the “more” hygroscopic particles in Los Angeles, CA, was dependent on particles size (15% at 0.05  $\mu\text{m}$  to 60% at 0.5  $\mu\text{m}$ ), whereas at the Grand Canyon, the “more” hygroscopic particles grew by about 50%, with the growth not varying significantly with particle size. By comparison of the TDMA data to impactor data, Zhang et al.

(1993) surmised that the more hygroscopic particles contained more sulphates and nitrates, while the less hygroscopic particles contained more carbon and crustal components.

Although most of the work to date on the hygroscopic properties of atmospheric aerosols has focused on the inorganic fraction, the determination of the contribution of particle-bound water to atmospheric particulate mass is greatly complicated by the presence of organics. Saxena et al. (1995) observed that particulate organic compounds can also affect the hygroscopic behaviour of atmospheric particles. They idealized the organic component of aerosol as containing a hydrophobic fraction (high-molecular weight alkanes, alkanolic acids, alkenolic acids, aldehydes, and ketones) and a hydrophilic fraction (e.g., lower-molecular weight carboxylic acids, dicarboxylic acids, alcohols, aldehydes, etc.) that would be likely to absorb water. They then analysed data from a tandem differential mobility analyser in conjunction with particle composition observations from an urban site (Claremont, CA) and from a non-urban site (Grand Canyon, AZ) to test the hypothesis that, by adding particulate organics to an inorganic aerosol, the amount of water absorbed would be affected, and the effect could be positive or negative, depending on the nature of the organics added. They further presumed that the particulate organic matter in non-urban areas would be predominantly secondary and thus hydrophilic, compared to the urban aerosol that was presumed to be derived from primary emissions and thus hydrophobic in nature. Their observations were consistent with their hypothesis, in that at the Grand Canyon, the presence of organics tended to increase the water uptake by aerosols, whereas at the Los Angeles site, the presence of organics tended to decrease water uptake.

Non-equilibrium issues may become of important for the TDMA, as well as for other methods of measuring water content. While approach to equilibrium when the RH is increased is expected to be rapid for pure salts, it may be much slower for aerosols containing a complex mix of components (Saxena et al. 1995). For example, if an aerosol contains an organic film or coating, that film may impede the transport of water across the particle surface, thus increasing the time required for equilibrium (Saxena et al. 1995). Insufficient time to achieve equilibrium in the TDMA could result in underestimation of the water content.

## **Monitoring Programmes of the U.S. EPA**

### **The Federal Reference Methods for equilibrated mass**

Federal Reference Methods (US FRM) have been specified for measuring PM<sub>10</sub> (Code of Federal Regulations 1991a,b) and for measuring PM<sub>2.5</sub> (Code of Federal Regulations 1999a). The US FRM for PM<sub>10</sub> has been discussed in previous PM AQCD=s and will only be briefly reviewed. The PM<sub>10</sub> US FRM defines performance specifications for samplers in which particles are inertially separated with a penetration efficiency of 50% at an aerodynamic diameter of 10 - 0.5  $\mu\text{m}$ . The collection efficiency increases to  $\approx 100\%$  for smaller particles and drops to  $\approx 0\%$  for larger particles. Particles are collected on filters; mass concentrations are determined gravimetrically; and sample volumes are adjusted to standard conditions (1 atm and 25<sup>0</sup> C). Measurement precision for 24-h samples must be  $\sim 5 \mu\text{g}/\text{m}^3$  for PM<sub>10</sub> concentrations below 80  $\mu\text{g}/\text{m}^3$ , and 7% above this value.

As opposed to the performance-based US FRM standard for PM<sub>10</sub>, the new US FRM for PM<sub>2.5</sub> specifies certain details of the sampler design, as well as of sample handling and analysis, while other aspects have performance specifications. The PM<sub>2.5</sub> US FRM sampler consists of a PM<sub>10</sub>

inlet, an oil-soaked impaction substrate to remove particles larger than 2.5  $\mu\text{m}$ , and a 47 $\mu\text{m}$  polytetrafluoroethylene (PTFE) filter with a particle collection efficiency greater than 99.7%. The sample duration is 24 h, during which the sampler temperature is not to exceed ambient temperatures by more than 5  $^{\circ}\text{C}$ . After collection, samples are equilibrated for 24-h at temperatures in the range of 20 to 23  $^{\circ}\text{C}$  ( $\pm 2$   $^{\circ}\text{C}$ ) and at a relative humidity in the range of 30 to 40% ( $\pm 5\%$ ) in order to remove particle-bound water. Filters are weighed before and after sampling under the same temperature and relative humidity conditions. For sampling conducted at ambient relative humidity less than 30%, mass measurements at a relative humidity down to 20% are permissible (Code of Federal Regulations, 1999a).

The US FRM also allows for Class I, II, and III equivalent methods for  $\text{PM}_{2.5}$  (Code of Federal Regulations, 1999b). Class I equivalent methods use samplers with relatively small deviations from the sampler described in the US FRM. Class II equivalent methods include “all other  $\text{PM}_{2.5}$  methods that are based upon 24-h integrated filter samplers that are subjected to subsequent moisture equilibration and gravimetric mass analysis.” Class III equivalent methods include filter-based methods having other than a 24-h collection interval or non-filter-based methods such as beta attenuation, harmonic oscillating elements, or nephelometry (McMurry 2000).

The strength of the  $\text{PM}_{2.5}$  US FRM is that specification of all details of the sampler design ensures that measurements at all locations if done properly, should be comparable. For example, the US FRM requires maintenance because the oil-soaked impaction substrate could otherwise become loaded with coarse particles. Failure to do so could lead to coarse particle bounce, thus artificially increasing the fine particle concentrations. Moreover, the specification of a  $\text{PM}_{10}$  inlet requires the oil-soaked impaction substrate to collect particles between 2.5 and 10  $\mu\text{m}$ . The implication is that, during sampling periods of high coarse PM concentrations, the impaction substrate could become overloaded, leading to particle bounce. If an inlet with a cut point diameter smaller than 10  $\mu\text{m}$  were specified, coarse particle bounce could potentially be reduced, and perhaps the maintenance frequency could be reduced (McMurry 2000).

Since the implementation of the  $\text{PM}_{10}$  standard in 1987 (Federal Register 1987) considerable information has accumulated on the factors that affect the quality of the data gathered from the EPA reference method for  $\text{PM}_{10}$ . These include inlet losses of coarse fraction particles (e.g., Anand et al. 1992); biases in concentrations due to differences between samplers in large particle cut points that are within the EPA-s specified acceptable tolerances (Ranade et al. 1990); and particle bounce tolerances and re-entrainment leading to as much as 30% errors (Wang and John 1988). The sampling issues associated with cut point tolerances are predictable, and the manufacturers have since dealt with the particle bounce and re-entrainment problems voluntarily by recommending operational procedures including oiling of impact surfaces and regular cleaning. The 1996 PM AQCD (USEPA 1996) concluded that the  $\text{PM}_{10}$  sampling systems can be designed such that concentration measurements are precise to  $\pm 10\%$ . For  $\text{PM}_{2.5}$ , cut point tolerances are not expected to affect the mass concentration as much as for  $\text{PM}_{10}$ , since the 2.5- $\mu\text{m}$  cut point generally occurs near a minimum in the mass distribution (e.g., Figure 5.5).

The  $\text{PM}_{2.5}$  mass concentration will be affected, on the other hand, by other sampling issues mentioned but not discussed extensively in the previous 1996 PM AQCD (USEPA 1996). These issues have been discussed earlier in this chapter and include gas/particle and particle/substrate interactions for sulphates and nitrates (e.g., Appel et al. 1984); volatilisation losses of nitrates (Zhang and McMurry 1992); semi-volatile organic compound (SVOC) artefacts (e.g., Eatough et al. 1993); and relative humidity effects (e.g., Keeler et al. 1988).

Several studies have now been reported, during which the US FRM was collocated with other PM<sub>2.5</sub> samplers in inter-comparison studies. During the Aerosol Research and Inhalation Epidemiology Study (ARIES) several PM<sub>2.5</sub> samplers were collocated at a mixed industrial-residential site near Atlanta, GA (Van Loy et al. 2000). These samplers included a standard PM<sub>2.5</sub> US FRM, a TEOM with Nafion drier, a particulate composition monitor (PCM) (Atmospheric Research and Analysis, Cary, NC), a high-volume carbon sampler operated by the Desert Research Institute, a HEADS sampler, and a dichotomous sampler for coarse PM. The PCM sampler has three channels, all of which have PM<sub>10</sub> cyclone inlets. The first two channels both have two denuders preceding a 2.5- $\mu$ m WINS impact and filter packs. The first denuder is coated with sodium carbonate to remove acid gases, and the second is coated with citric acid to remove ammonia. The third channel has a carbon coated parallel-plate denuder preceding the WINS impactor. 24-h mass measurements from the US FRM, PCM, and TEOM samplers, as well as reconstructed PM<sub>2.5</sub> mass (RPM) were compared for a 12-mo period. The slopes for the TEOM-FRM, PCM1-FRM, and RPM-FRM correlations were 1.01, 0.94, and 0.91, respectively, while the y-intercepts for each were 0.68, 0.04, and 0.98. Particulate sulphate measurements on the FRM Teflon filter, the PCM Teflon filter, and PCM Nylon filter were nearly identical. Nitrate results from the three filters were much less consistent, with the US FRM collecting substantially less nitrate than that collected on either the denuded nylon filter or a denuder followed by a Teflon-nylon filter sandwich. Particulate ammonia measurements were also compared, and showed more scatter than the sulphate measurements, but less than the nitrate measurements.

An inter-comparison of both PM<sub>10</sub> and PM<sub>2.5</sub> mass measurements was conducted during the 1998 Baltimore PM Study (Williams et al. 2000). PM monitors were collocated at a residential indoor, residential outdoor, and outdoor monitoring site within Baltimore County, MD. PM samplers included TEOMs, PM<sub>2.5</sub> FRMs, cyclone-based inlets manufactured by University Research Glassware (URG), and Versatile Air Pollution Samplers (VAPS). Personal Environmental Monitors (PEMs; MSP, Inc.) were also included but will not be discussed in this section. The VAPS sampler is a dichotomous sampler operating at 33 lpm (one coarse particle channel at 3 lpm, and two fine particle channels at 15 lpm, each). In the configuration employed during this study, one fine particle channel was operated with a Teflon filter, backed by a nylon filter and preceded by a sodium carbonate coated annular denuder; the second fine particle channel has a quartz filter preceded by a citric acid-coated annular denuder; and the coarse particle channel had a polycarbonate filter followed by a Zefluor filter for flow distribution. Differences in PM<sub>2.5</sub> mass concentrations between the samplers, although not large, were attributed to potential particle nitrate, denuder losses, and loss of SVOC for some samplers. Differences between coarse particulate mass concentrations, on the other hand, varied widely between the instruments.

In another inter-comparison study, Tolocka et al. (2000) examined the magnitude of potential sampling artefacts associated with the use of the USFRM by collocating FRMs alongside other chemical speciation samplers at four U.S. cities. The locations included a high nitrate and carbon, low sulphate site (Rubidoux, CA); high crustal, moderate carbon and nitrate site (Phoenix); high sulphate, moderate carbon, and low nitrate (Philadelphia); and low PM<sub>2.5</sub> mass (Research Triangle Park, NC). The use of Teflon and heat-treated quartz filters was also examined in this study. The Teflon filters collected less nitrate than the heat-treated quartz filters. Filters in samplers using denuders to remove organic gases collected less organic PM than filters in samplers without denuders.