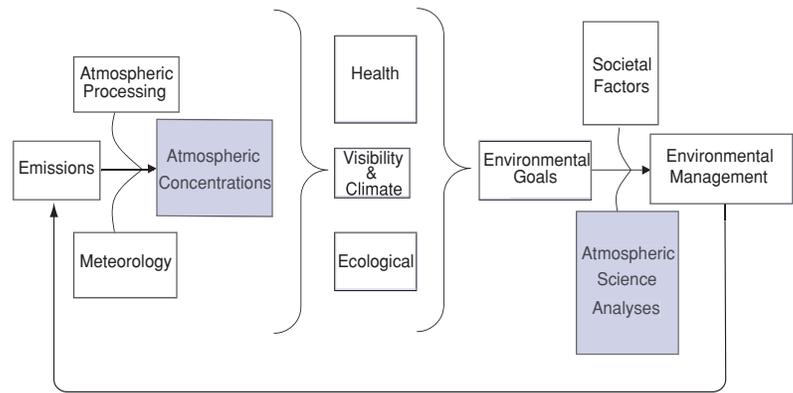


## CHAPTER 5

# Particle and Gas Measurements

*Principal Authors: Fred Fehsenfeld, Don Hastie, Judith Chow, and Paul Solomon*



Measurements provide fundamental information for evaluating and managing the impact of PM on air quality. As illustrated in Figure 5.1, data obtained through measurements form the foundation of all approaches used to define and mitigate PM problems. Diverse measurements are required by different users to meet a variety of needs:

- 1) To monitor **exposure**. (*Who has the problem?*) Exposure monitors document actual human exposure to indoor and outdoor pollution.
- 2) To determine specific causes of **health effects**. (*What is the problem?*) Initial emphasis focuses on testing related to the eleven hypotheses listed in Textbox 2.5. The wide array of measurements that are needed to determine the connection between health effects and specific PM properties are enumerated in Appendix B, Table B.1. *Measurements of novel PM properties are needed to test hypotheses regarding causal agents for human health effects.*
- 3) To monitor **visibility impairment**. (*Is the problem visible?*) Fine particles in the atmosphere reduce local visibility, increase regional haze, and affect climate change.
- 4) To monitor **compliance**. (*Where is the problem?*) Measurements document locations where standards are exceeded.
- 5) To develop reliable **source attribution**. (*Who or what is causing the problem?*) Measurement techniques, modeling, and data analysis use measurement data to identify the sources of PM pollution.

- 6) To establish **program evaluation**. (accountability) (*Are air-quality goals being met? If not, where and when are shortfalls occurring?*) Measurements monitor the atmospheric distributions of regulated pollutants and pollutant precursors, and the trends in those distributions.
- 7) To provide information for **scientific understanding** required for analysis and forecasting. (*Is the problem understood?*) Measurements are used to establish if the sources and atmospheric chemical and physical processes that shape PM concentrations are sufficiently well understood; to explain failures to attain desired air quality; and to suggest alternative management strategies. Measurements also support research to develop an air-quality forecast system that can predict air-quality problems and issue appropriate guidance, warnings, or alerts.

To provide the measurement data for these and other applications, different types and configurations of instruments have been developed and deployed. However, data acquisition, analysis, and interpretation are interrelated activities. A full understanding of available sampling and analysis strategies, and a determination of their uncertainties and costs, are required before acceptable measurement techniques can be specified to meet PM measurement user-community needs. This chapter briefly describes the measurement techniques available, explains how the information obtained through measurements is applied, and discusses the confidence that can be placed in the data based on current uncertainty estimates. More detailed

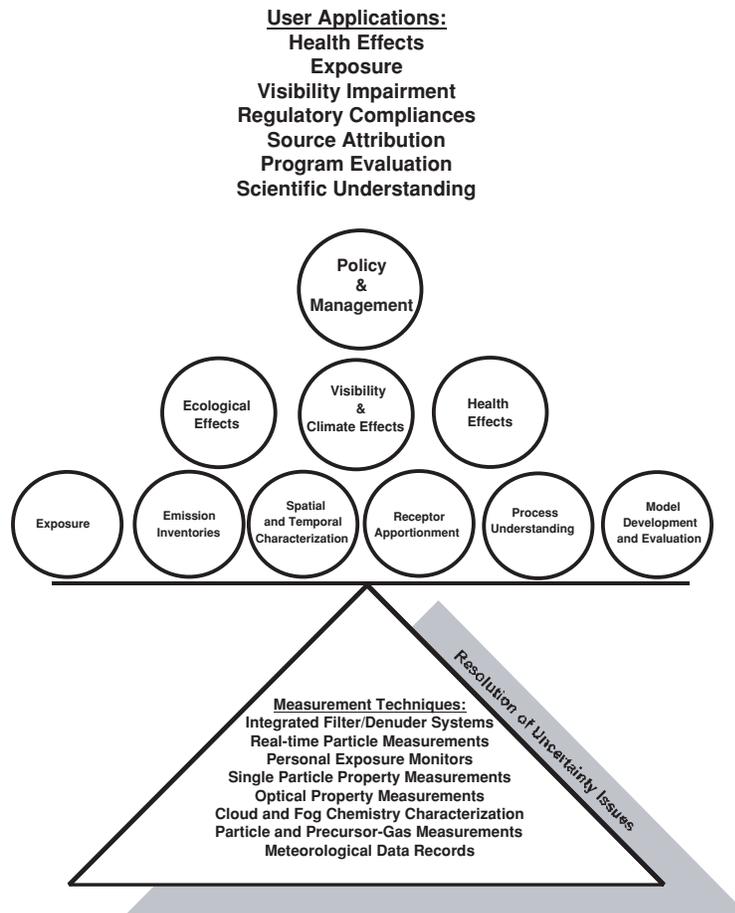


Figure 5.1. Relationships of data-measurement techniques, air-quality management tools, and user applications.

descriptions of measurement techniques and applications are given in Appendix B.

Data obtained through measurements quantify the observable properties of particles: size and size distribution, mass, chemical composition, and optical characteristics. Measurements of other variables – for example, cloud-water content, atmospheric chemistry, and meteorological conditions – also characterize the behavior of particles in the atmosphere, document particle sources and relationships to other pollutants, and provide data on meteorology related to PM formation, removal, and transport. Information obtained on particle characteristics is applied according to the user’s needs. Examples of particle characteristics are as follows:

**Size/Number** - Investigators concerned about health effects have focused on particles with diameters less than 10  $\mu\text{m}$  and less than 2.5  $\mu\text{m}$ , including ultrafine particles with diameters ranging from 0.001  $\mu\text{m}$  to 0.1  $\mu\text{m}$ . Monitors that determine human exposure to fine particles use particle inertia to partition particles into different size ranges or measure size directly using methods such as optical sensing. Investigators examining visibility degradation, regional haze, or long-range transport need measurements of particles in a range of sizes from about 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$ , since particles in this range scatter and adsorb light efficiently and have the longest atmospheric residence times.

**Mass** - Several techniques measure the mass of particles in a given size range in sampled air. Particle inertia is used to separate particles into

different size fractions. After separation, particles are usually collected on a filter and the mass is determined gravimetrically. Frequently such mass-based selection methods inadvertently alter the observed PM mass by allowing desorption of volatile compounds from the particles or sorption of ambient gases on the collected particles and/or the collection substrate.

**Chemical composition** - Many of the hypothesized causes for health effects are related to the chemical composition of PM. Chemical composition also determines the scattering and light-absorbing properties of particles that contribute to visibility reduction. The chemical components include major ions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ); alkali ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and alkali earth ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) metals; BC; OC; sea salt; trace elements, including transition metals; other minerals; and biological particles.

Three groups of techniques developed to determine particle composition are 1) methods, which collect particles on suitable substrates for subsequent laboratory analysis; 2) real-time techniques, which collect particles, detect certain chemical constituents, and give on-line information concerning the amount of the detected compounds; and 3) single-particle measurements, which give semi-quantitative, real-time information regarding the chemical composition of each particle detected.

**Optical properties** - Measurements of the optical properties of particles characterize temporal trends and spatial distributions of particles that impair visibility, and link the visual effects of those particles to their sources through particle composition or other properties. The fundamental particle properties related to visibility are light scattering and absorption. Particles with size ranges from  $0.1\ \mu\text{m}$  to  $1\ \mu\text{m}$  are most efficient at scattering light, while BC contained in aerosol is the most effective light-absorbing PM component.

Aside from the measurement of particle size, mass, composition, and optical properties of aerosols, additional measurements are required to explain the fate of aerosols in the atmosphere, their sources, and

their relation to other pollutants. Since PM concentrations are strongly affected by the presence of fogs and clouds, measurements of fog- and cloud-water content and composition are important for characterizing the formation and accumulation of PM in air. Measurements that quantify gas-phase compounds, such as  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_x$  or  $\text{NO}_y$ , and VOCs, which are precursors to PM formation, are needed. Other gas-phase measurements are required to determine the relation between atmospheric copollutants and PM. Finally, meteorology affects all of the processes related to PM formation, loss, and transport. The understanding of PM and PM relationships to precursor compounds and to copollutants requires measurements of meteorological parameters: wind speed, wind direction, temperature, and relative humidity.

## 5.1 CURRENTLY AVAILABLE TECHNOLOGY AND INSTRUMENT CAPABILITIES

Eight measurement techniques are described: 1) integrated denuder and gravimetric filter-based systems; 2) real-time particle measurement techniques; 3) personal exposure monitors; 4) single-particle property measurements; 5) optical properties of aerosols and long-path optical measurements; 6) fog- and cloud-water measurements; 7) gas-phase fine-particle and copollutant precursor measurements; and 8) meteorological measurements.

### 5.1.1 Size-Selective Inlets

Before particles can be collected and measured they must enter the sampler through an inlet, where size-fractionation may occur. Size-selective inlets define the particle-size fraction being sampled and are typically the inlets for many of the measurement techniques described in the following sections. These inlets usually rely on inertial separation of large (heavy) particles from small (light) particles to obtain size fractionation. Five approaches for size separation are in use currently and are illustrated in Figure 5.2.

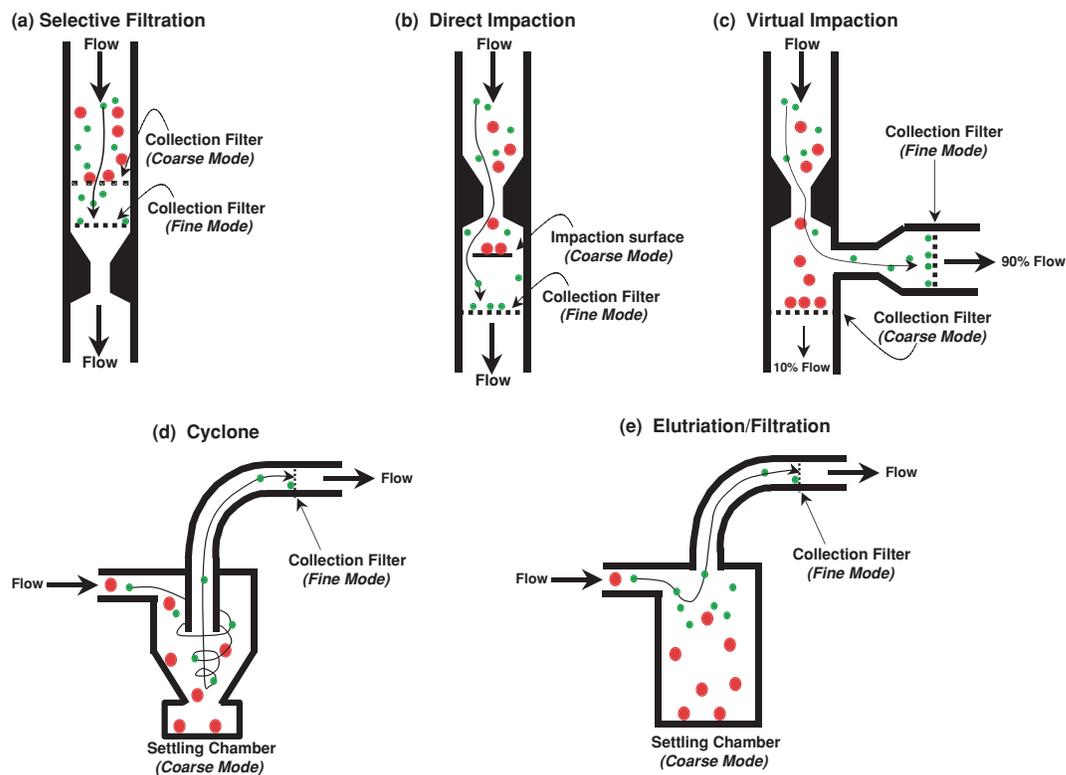


Figure 5.2. Inlets used for particle size separation, illustrating the separation and collection of the smaller (fine mode) particles from larger (coarse mode) particles. The fine mode collection filter is often replaced by a variety of measurement devices.

- 1) Selective filtration inlets use a filter as the particle fractionator (see Figure 5.2a). As air is sampled through the filter, light particles follow the streamlines of the flow through small pores in the filter into the device where they are collected or measured. The larger particles are collected on the surface of the filter.
- 2) Direct impaction uses a collecting surface in the flow stream to collect large particles (see Figure 5.2b). This surface is placed orthogonal to the direction of flow. The momentum of heavy particles carries them to this surface, across a stable boundary layer, where they are collected; particles below the cut-point follow the streamlines of the flow around the surface into the device where they are collected or measured. Multiple stages may be employed to collect PM in several size ranges.
- 3) Virtual impaction uses a collection nozzle rather than a collection surface as in direct impaction (see Figure 5.2c). Small particles, below the cut-point, follow the major flow, which is diverted orthogonally to the inlet flow and into the major flow channel. Heavier particles, those above the cut-point, continue straight into the collection probe, across a stable boundary layer near its top (the virtual surface) following the minor flow (typically 5-10%), and are then collected or measured downstream.
- 4) Cyclones use a conical chamber into which air enters from the side along the inside circumference to impart centrifugal motion to particles in the chamber (see Figure 5.2d). Flow out of the chamber is tangential to the rotating gas in the chamber. The radial momentum imparted to the heavier particles allows them to impact the walls of the cyclone and be collected by gravitational settling, while lighter particles follow the tangential flow out of the cyclone where they can be collected or measured.
- 5) Elutriation/impaction inlets place a large chamber in the flow path (see Figure 5.2e). The

flow exits the chamber through the top. Gravitational settling of the heavier particles carries them to the bottom of the chamber where they are collected; the lighter particles migrate to the top of the chamber from which they exit into the device in which they are measured.

All routine monitoring techniques use these methods to sort particles by size, with impactors and cyclones used most widely. These devices must operate with minimal maintenance over extended periods in all types of weather. Since a large particle may have as much material as hundreds or thousands of smaller particles, a likely source of error in these measurements is the mobilization or re-entrainment of the collected larger particles followed by their migration into the measurement device. These problems are reduced by surface design (e.g., virtual impactors) or surface coatings, which effectively retain the larger particles, and by careful maintenance of the inlet system. However, coatings often interfere with chemical analysis. Low-flow impactors and cyclones are used most commonly for ambient sampling (1 m<sup>3</sup>/hr) in urban and rural areas and for personal monitoring (0.1 m<sup>3</sup>/hr). High-volume samplers are used to improve detection limits and/or time resolution.

### 5.1.2 Integrated Denuder and Gravimetric Filter-Based Systems (substrate- and absorbent-based measurements) for Mass and Composition Sampling

Time-integrated denuder and gravimetric filter-based systems are used to collect PM to determine particle mass and composition<sup>1</sup>. Such systems, in use for decades, have undergone steady progress in reducing interferences and artifacts in mass and composition measurements, thereby improving precision, accuracy, and detection limits. Measurements made using integrated denuder and filter systems have long sampling times (typically several hours to 24 hours), and laboratory analysis of these samples is labor-intensive and time-consuming. In addition, the time delay and sample handling between collection and analysis provide the opportunity for added error (e.g.,

loss of semivolatile species or contamination by absorbing gas-phase compounds), and contribute to delays in data reporting.

Integrated systems allow for the determination of a large set of PM properties. Sampling systems typically include size-selective inlets, denuders, and filters, along with the necessary connecting lines, flow controllers, and flow meters. The simple diagram shown in Figure 5.3 illustrates the principles of this sampling approach. The air sample is introduced through a size-selective inlet that limits the PM size distribution to the range of interest. The sample then passes into separate channels where PM is collected on different filter types, which are subsequently used to determine properties of sampled PM. For example, in Figure 5.3, four channels collect PM for analysis of: 1) the organic compounds present in the sampled particles; 2) the PM mass and elemental composition; 3) the ionic composition; and 4) the semivolatile NO<sub>3</sub><sup>-</sup> components. Because semivolatile VOC (SVOC) and NH<sub>4</sub>NO<sub>3</sub> may be present in the sample, and because the gaseous fractions can interfere with the collection of PM on filters, denuders are used to remove the gas-phase fraction from the sampled air before the PM filter. The PM is then collected on a suitable substrate or filter. Since the SVOC and NH<sub>4</sub>NO<sub>3</sub> may evaporate from the collected particles, an adsorbing or reactive backing-filter may be placed after the primary filter to capture the compounds that evolve from the primary filter. After exposure, the filters and denuder are removed for chemical analysis. Atmospheric concentrations are obtained by dividing the mass loading measured on the filter by the total volume of air that passes through the filter. The principal analysis components for these systems are given in Appendix B, in Table B.2 and the accompanying text.

Specialized versions of these samplers have been successfully developed for use as personal exposure monitors (c.f., Section 5.1.4). In addition, integrated samplers also have been adapted for use aboard aircraft. However, because of the long sampling times required by time-integrated denuder and filter-based systems, they are not able to resolve the valuable short-duration information concerning the

<sup>1</sup> Integrated denuder and gravimetric filter-based systems include the U.S. Federal Reference Method and other gravimetric methods commonly in use in regulatory or compliance networks to determine size-resolved bulk particle mass.

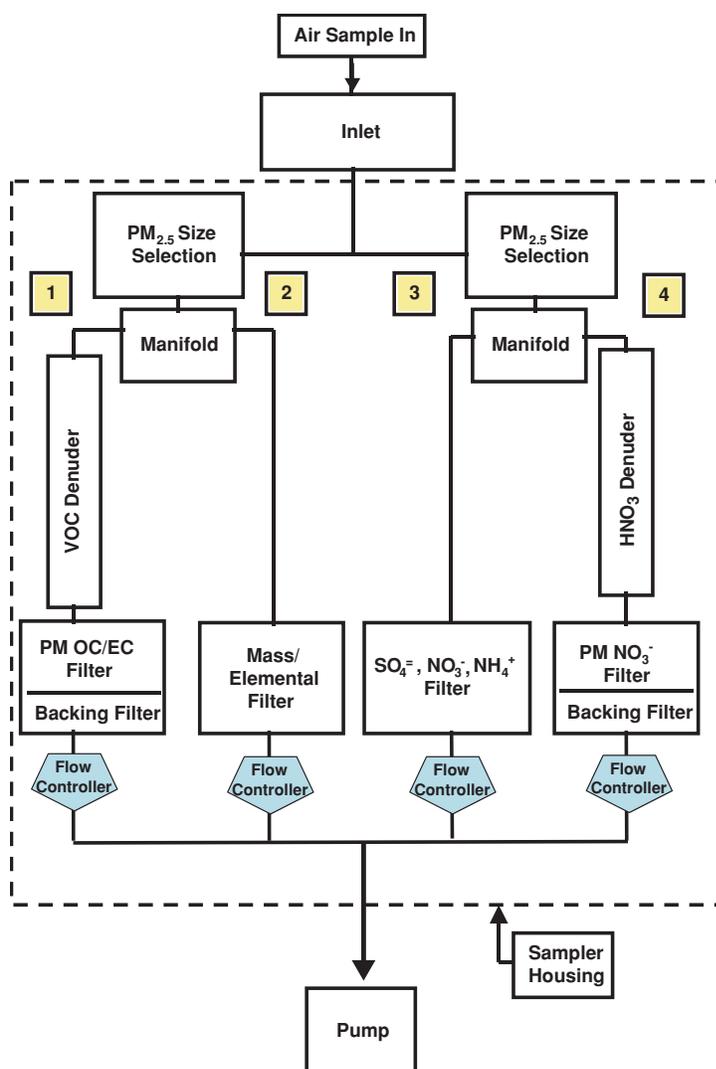


Figure 5.3. Representative denuder and filter sampler for collecting  $PM_{2.5}$ .

chemical and physical properties of the atmosphere encountered by fast-moving aircraft.

***Denuders and Their Gas-Phase Measurements.***

Denuders are placed in the sampling system to remove selected gases while transmitting particles. Typically denuders are cylinders coated with a substance that absorbs and retains the selected gases. Molecules in the gas phase diffuse rapidly to the denuder surface where they are absorbed, while particles diffuse much less rapidly and pass through the denuder to the filter where they are collected. The absorbed gas-phase compound concentrations can be obtained for laboratory analysis by extracting denuders in a solvent. Denuders can be used as part of, or immediately behind, size-selective inlets to remove gases that might interfere with the PM

measurement (positive interference), or to quantify the concentrations of gases that are precursors to secondary PM formation. In addition, denuders may be placed after the filter to capture semivolatile gases that may evaporate from PM collected on the filters (negative interference). The removal and collection of  $SO_2$ ,  $HNO_3$ , and  $NH_3$  by denuders are well developed and characterized. However, the collection and analysis of organic gases using denuders is particularly difficult due to the wide range of physical and chemical properties exhibited by this family of compounds. This has been the focus of much recent study.

***Substrate- and Absorbent-Based Measurements of Particle Chemical Composition.*** The principal method used in integrated systems to determine size-

selected PM properties is filtration. Filters for collecting PM are selected based on the gravimetric and chemical analyses to be undertaken. Most systems use a Teflon-membrane or quartz-fiber filter followed by an absorbent or a chemically treated filter (i.e., a filter impregnated with a reactive material). Particle mass is usually obtained by determining the weight of particles collected on the front filter. The second filter collects vapors that pass through the first filter or that are released by the particles collected on the first filter. Chemical analysis to determine particle composition includes bulk analysis and particle-scanning analysis.

Stable species (e.g.,  $\text{SO}_4^{2-}$ ) and trace elements (e.g., Al, Si, Ca, Fe, Mn, Ti) can be collected with minimal sampling bias on filters. A wide variety of compounds that contain trace elements can be detected in PM, including metals such as Cr, Mn, Co, Ni, Cd, Hg, Be, As, Se, Sb, and Pb, which may be related to the potential health effects noted in Textbox 2.5.

Labile species, such as  $\text{NH}_4\text{NO}_3$  and SVOC existing in gas and particle phases in the atmosphere, require specialized filter-sampling protocols that typically use denuders and reactive collection substrates. Methods that use only filters for collecting these species may suffer from sampling artifacts associated with the capture of gas-phase species during sampling (often referred to as a “positive artifact”) or the loss of compounds from collected PM (often referred to as a “negative artifact”). Combined denuder-filter methods are required to provide the least biased measurements of semivolatile components in aerosols: for example,  $\text{NO}_3^-$ ,  $\text{HNO}_3$ ,  $\text{NH}_4^+$ ,  $\text{NH}_3$ , and SVOC.

Overall, measurements of carbonaceous material are most challenging and prone to errors owing to PM volatility, interferences from gaseous organic species, limitations with collection and analytical methods, and lack of accepted primary and transfer standards (c.f., Turpin, et al., 2001). The most common method used to quantify the bulk carbon/organic content of collected PM is thermal oxidation. In this method the sample is heated and sequentially less volatile organics are evolved and oxidized. Eventually, graphitic carbon in the sample is oxidized. In each case the carbon in the collected sample is evolved

from the particles and detected as  $\text{CO}_2$ . The result is a measure of EC, often described as BC or soot, and OC. Both of these terms are operationally defined (Chow et al., 2001). In this chapter we distinguish between EC as determined by thermal methods and BC as determined by optical methods but continue, in accordance with Textbox 1.2, to apply the term BC when no distinction is required. The organic compounds that compose OC contain carbon plus other elements such as oxygen and hydrogen. Because these other elements are typically not measured, it is commonly assumed that organic mass concentrations can be inferred by multiplying the measured carbon mass by a factor that accounts for other associated elements. This factor is typically assumed to be 1.4, but may be as high as 2.2, depending on particle composition (Turpin, et al., 2001).

*Improved methods are needed to measure OC and BC concentrations and to identify and quantify organic PM species, especially those important as source tracers or health effects markers. More information on the relationship between the carbon content of OC and OC mass concentrations is also needed. Effort should be made to characterize the composition of primary and secondary organic species associated with anthropogenic and biogenic source emissions.*

Beyond the determination of the BC and OC fractions, the identification of the exact chemical composition of these carbonaceous fractions is desirable. Organic aerosols emitted by different sources have distinct chemical signatures. Therefore, measurements of organic speciation at a receptor can provide valuable insights into the origins of ambient OC. However, the measurement problem becomes much more challenging. The carbonaceous material in PM can include thousands of compounds covering a vast range of properties. The most sophisticated laboratory methods available can identify only 10 to 20 percent of the total organic-carbon mass by compound; such measurements are expensive and require highly trained personnel. Furthermore, only a few laboratories in North America are equipped to carry out such analyses.

Two strategies have been applied to the determination of organic species. In the first, the organic

compounds that are evolved by heating the collection filter can be analyzed by mass spectrometry. Although the organic compounds contained on the filter may be altered or partially decomposed during the heating process, the evolved material contains information concerning the identity of the substances that are contained in the OC fraction.

A second, more commonly used approach involves the selective and quantitative removal of various classes of organic fractions or species from the filter by solvent extraction. Separation often is based on the chemical affinity of different organic-compound classes (e.g., polar vs non-polar). The fractions can be analyzed by GC-MS or LC-MS to quantify individual compounds, a number of which are important source tracer species (Schauer et al., 1996).

**Impactors.** Cascade impactors represent a special class of substrate- and absorbent-based techniques for composition sampling. These instruments are used to obtain size-resolved measurements in ambient chemistry and visibility studies. These devices use a series of impactor stages as described in the inlet section above, with each subsequent stage designed to collect smaller particles, thus, providing a series of size-resolved particle samples over a range of particle sizes (e.g., Marple and Olsen, 2001). The substrate on the impactor stage can be removed and analyzed for the mass and composition of the collected particles. By having the collector surfaces move continuously in a stepwise fashion, time-resolved measurements can be obtained.

A special type of impactor, the dichotomous sampler, uses virtual impaction to separate the particles into two size fractions, typically into fine ( $<PM_{2.5}$ ) and coarse ( $PM_{10-2.5}$ ). In this device, which has been widely used in routine monitoring, particles are drawn in through a single inlet. The flow splits inside the impactor. A smaller portion of the flow continues along a straight path, while the larger flow is diverted into a separate channel (Figure 5.2c). The particle-size distribution is determined by the flow rate and the configuration of the flow splitter or virtual impactor. The particles in each channel are collected on appropriate filters and analyzed for mass and composition.

### 5.1.3 Continuous and Semi-continuous Real-time Measurements

For specific PM properties, continuous and semi-continuous real-time measurements have a faster time response (seconds to an hour) than the integrated methods (6 to 24 hours) and often afford real-time quantification of the specific property that is measured. Thus, continuous and semi-continuous measurements give much more information concerning the sources and atmospheric processes that shape PM formation and transport because they add temporal variability to these analyses. In addition, information on short-term variations may be useful in assessing health effects and validating models. The suite of chemical species that can be measured is continually evolving with the incorporation of new methods of detection. Significant progress has been made in the past several years on developing instrumentation for real-time measurements of PM mass and composition, and some of these instruments have been commercialized. Many continuous methods use size-selective inlets that restrict sampling (c.f., Section 5.1.1) to particles smaller than a certain size.

McMurry (2000) describes measurements of aerosol properties (e.g., cloud-condensation nuclei, particle-number concentration, refractive index, particle-size distribution, size-resolved composition). Available devices to measure physical properties over short durations ( $< 1$  hour) and under conditions where continuous measurements may or may not be correlated with, or predictive of, integrated denuder and filter system measurements are discussed by Watson et al. (1998). Many of these measurements require collocated comparisons with well-established filter-based measurements to define their comparability.

*Where reliable, low-cost and effective methods exist, filter samplers should be replaced with instruments that provide continuous, real-time information on PM mass and composition.*

Continuous in-situ PM measurements can be classified, based on the properties they measure, into three categories: 1) mass (inertial mass, beta-ray attenuation, pressure drop); 2) size distribution and mobility (electrical mobility, aerodynamic mobility);

and 3) chemical components including carbonaceous compounds, (BC and OC), ions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ) and elements (such as Si, Fe, Ca, Mg, and Ti). Examples of continuous and semi-continuous real-time measurements are reviewed in Appendix B, Table B.3 and the accompanying text. Discussions of recent developments are provided in the following subsection.

**Mass and Mass Equivalent.** Williams et al. (1993) have described a variety of dynamic principles used in continuous mass sampling techniques. These continuous measurements determine particle mass by measuring changes associated with 1) the inertia imparted to a dynamic element by collected particles; 2) electron attenuation through a surface by particles collected on the surface, and 3) pressure drop across small pores in a filter due to collected particles. The methods are reviewed in Appendix B, Table B.3a.

The continuous inertial methods in use include the widely used TEOM (tapered element oscillating microbalance) and the PEMB (piezoelectric microbalance). The TEOM element oscillates at a characteristic frequency when an electric field is applied and optically measures frequency shifts due to the increasing inertial mass of particles accumulating on the collector. The PEMB measures the shift in the resonant frequency of a piezoelectric crystal as mass is added to the surface of the crystal by the accumulating particles. Electron attenuation devices (beta gauges) measure the increasing attenuation of electrons emitted from a radioactive source by particles accumulating on a filter. Pressure-drop systems measure the pressure drop across a filter as the filter loads and its pores become clogged. Significant progress has been made in the past several years on developing instrumentation for real-time and/or continuous measurements of PM mass and composition, and some of these instruments have been commercialized. The availability and capabilities of commercialized real-time instrumentation will evolve substantially in the next few years, and efforts should be made to replace filter samplers as these methodologies mature.

**Size Distribution and Mobility.** A wide range of techniques and protocols are used to measure particle sizes ranging from  $<0.003 \mu\text{m}$  to  $>10 \mu\text{m}$ . Examples of continuous and semi-continuous real-time

measurements of PM size-distribution and mobility are reviewed in Appendix B, Table B.3b and the accompanying text. Particle size is typically reported as “diameter.” However, the different measurement techniques often define even this most fundamental parameter in different ways, as shown in the box (McMurry, 2000).

**Aerodynamic diameter**, which is measured by inertial methods such as impactors and cyclones, depends on particle shape, density, and size.

**Electrical mobility diameter**, which is obtained by electrostatic mobility analyzers, depends on particle shape and size, and is obtained by the rate of migration of charged particles in an electrostatic field.

**Optical diameter**, which is obtained by light scattering detectors, depends on particle refractive index, shape, and size.

Quantitative determination of the particle-size distribution is difficult to achieve. Sampling losses of particles  $>1 \mu\text{m}$  by inertial impaction, and of particles  $<0.1 \mu\text{m}$  (ultrafine) by diffusion deposition, present a major challenge in particle-size measurements. The effects of humidity and particle volatility on the determined size also must be considered. Calibration aerosols of known size distribution are often difficult to create and methodologies have not been standardized, making comparison between different measurements difficult.

To measure particle sizes down to approximately  $0.1 \mu\text{m}$ , optical and aerodynamic particle counters are commercially available and can be used for continuous monitoring. Unfortunately, most current real-time instruments for measuring particle-size distributions below  $0.1 \mu\text{m}$  are expensive and require continuous oversight, frequent calibration and maintenance, and considerable expertise to run with good accuracy and precision. Airborne measurements also require attention to the effects of high-velocity sampling inlets, rapid pressure changes, and spatially varying particle characteristics. Despite these difficulties, recent developments in particle-size sampling show promise for continuous or semi-continuous measurements.

For monitoring purposes, considerable effort needs to be made to ensure that particle-size distributions can be acquired on a long-term basis at urban and non-urban locations. Such measurements allow the role of particle size to be associated with health effects, and provide valuable information concerning the optical effects and likely residence time of the particles in the atmosphere. Even the most developed of available techniques require fairly complex devices and specific training to calibrate and to perform comprehensive data processing. Efforts have been made to develop standardized calibration devices and to generate calibration aerosol for collocated comparisons of different techniques.

**Chemical Components.** Continuous measurements of carbonaceous compounds, ions, and metals are described below.

*Carbonaceous compounds: BC, EC, and OC.* As mentioned earlier, the most challenging aspect of PM composition determination involves the carbonaceous fraction, which includes hundreds of organic compounds. Examples of continuous and semi-continuous real-time measurements of PM composition are reviewed in Appendix B, Table B.3c and the accompanying text. No real-time technique is available that can adequately speciate OC. Hence, measurements usually are restricted to major carbon fractions and labeled accordingly, OC or BC. As for time-integrated denuder and filter based measurements (see Section 5.1.2), OC and BC/EC measurements involve collecting particles on a substrate (e.g., a filter or impaction plate) for enough time to achieve the desired sensitivity. This is typically several minutes to an hour depending on the concentration of carbon-containing compounds in the collected particles. The substrate or plate is then heated in a controlled atmosphere to first volatilize the OC, then (in the case of EC measurements) further heated to burn off the EC. The OC and EC evolve to CO<sub>2</sub> gas, which can be measured directly by a non-disperse infrared detector, or converted to CH<sub>4</sub> and measured by a flame-ionization detector. As with the time-integrated denuder and filter-based systems, the mass of organic material is approximated by adjusting the evolved carbon mass by an appropriate factor.

*Cost-effective techniques for obtaining more detailed spatial and temporal information on carbonaceous PM species should be developed.*

Other approaches also are under development. In one such technique total organic carbon is measured by collecting particles into purified water and analyzing the aqueous medium. Although such techniques are only under development, they have the potential for time resolution on the order of seconds. However, they may be restricted only to the analysis of soluble organic components. The PAS2000 real-time polycyclic aromatic hydrocarbon (PAH) monitor measures particle-bound PAH based on the ionization of particles and their detection with an electrometer. The photoionization method for particle-bound PAH is reproducible, but at present can be related only to absolute concentrations of particle-bound PAH via collocated filter samples (Watson and Chow, 2002). More information regarding these systems can be found in Appendix B.

Identifying the origins of organic aerosols, understanding their transformations in the atmosphere, and understanding their effects will require measurements of speciated OC, and such measurements are needed with better spatial and temporal resolution than is currently possible. Although significant advances are expected in the near future, permitting more widespread measurements of OC and BC, instrumentation for continuous measurement of speciated OC is likely further off in the future.

*More effort should be made to characterize the composition of primary and secondary organic species associated with anthropogenic and biogenic source emissions.*

*Ionic component of PM.* The ionic component (particularly SO<sub>4</sub><sup>=</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) of PM is often a significant fraction of the total PM mass. Ion chromatography permits speciation and quantitative measurement of these and other ionic species (Chow and Watson, 2001). Filter extractions are analyzed with a dual channel ion chromatography for a range of ions, including cations (e.g., NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>), inorganic anions (e.g., Cl<sup>-</sup>, SO<sub>4</sub><sup>=</sup>, and NO<sub>3</sub><sup>-</sup>), and organic acids (e.g., formate, acetate, and oxalate).

Efforts have been made to collect ambient particles directly into purified water for on-line ion-chromatography analysis. In all cases, diffusion denuders need to be placed upstream of the instrument to remove potentially interfering gases such as  $\text{SO}_2$ ,  $\text{NH}_3$ , and  $\text{HNO}_3$ . The newer techniques can have high sampling rates (six samples per hour) but generally result in lower sensitivities. Continued developmental work is required for reliable real-time inorganic  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  measurements. Additional emphasis also is needed on  $\text{NH}_4^+$  and other anions and cations.

Other technology is being developed to measure the ionic components of PM. These alternative techniques are based on the choice of detectors and the constraints that these detectors place on the device. Real-time  $\text{SO}_4^{=}$  detectors have been developed based on the use of a flame-photometric detector widely used to measure gaseous sulfur compounds. Commercially available continuous  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  analyzers have been developed which involve the flash vaporization of particles collected by impaction onto a filament, followed by chemiluminescence detection of nitrogen oxides for  $\text{NO}_3^-$  or by ultraviolet absorption of  $\text{SO}_2$  for  $\text{SO}_4^{=}$ . Finally, online PM mass spectrometry using thermal volatilization followed by electron-impact or chemical ionization (Section 5.1.5) is found to give quantitative size-resolved real-time measurements of the ionic species contained in PM.

*PM Metals.* Many of the techniques used to identify the metals contained in PM collected on filters are being adapted for continuous time-resolved measurement using moving filter strips. Detection methods include X-ray fluorescence and proton-induced X-ray emission. In each case, the metals are identified by the emission of X-rays from the metals that are excited in the sample. In addition, collection and flash vaporization followed by detection using atomic-absorption spectrometry, emission spectrometry and mass spectrometry is being developed to measure the metals in PM. These same detectors are used to distinguish the soluble metals contained in PM sampled into a solvent stream. Online laser desorption/ionization mass spectrometry (Section 5.1.5) has been used to detect the presence of metals, but the measurement has not been made quantitative.

#### 5.1.4 Personal Exposure Monitors

The devices described in the previous two sections are used for monitoring PM and its chemical properties in ambient air. However, individuals are subject to non-ambient exposures in their homes, indoor workplaces, and stores (Williams et al., 2000a,b,c). With this in mind, some of the techniques that were described in the two previous sections have been adapted to monitor personal exposure. The sampling has focused on mass as well as specific pollutants that could have potentially significant human-health effects, such as combustion emissions, tobacco smoke, acid aerosols, and vapor-phase organics.

Personal-exposure monitors are designed to be carried by an individual and to record the exposure of that individual to pollution. The typical PM monitor is intended to obtain time-integrated measurement of PM over a 24-hour sampling period. To make these devices sufficiently portable, the methods used for ambient-air monitoring are altered to reduce the size, weight, and power consumption. Current technology is able to produce a measurement device that weighs no more than one kilogram. Recent comparisons have achieved agreement with FRM collectors of  $\pm 20$  percent for  $\text{PM}_{2.5}$  mass concentration (Evans et al., 2000). In addition, measurements of the principal ionic components of PM have comparability within a factor of two of fixed ambient monitors, which is often adequate for their intended purposes.

Although most personal monitoring has focused on 24-hour collection, devices are being developed to give real-time continuous monitoring to estimate individual exposure to short-term (one minute) variations in PM concentrations. This is useful not only to determine the impact of brief high exposures but also to directly identify and characterize PM sources. Because of the sensitive nature of personal-exposure monitoring and the engineering required to miniaturize these devices, operation of the personal-exposure monitors requires highly skilled research personnel, but allows subjects to wear the monitor without extensive training.

### 5.1.5 Single-Particle Measurement Capabilities

The ability to measure properties of a single particle, rather than of a bulk collection of particles, has opened the way for more detailed understanding of the characteristics of particles and the chemical processes responsible for their formation and transformation. Development of automated scanning electron-microscope and X-ray fluorescence analyses (McMurry, 2000) has made it possible to perform elemental analysis on statistically significant numbers of particles for a reasonable number of samples.

More recently, single-particle mass-spectrometers have been developed that allow real-time detection of the chemical composition of individual particles. These approaches analyze the basic chemical and physical properties of individual particles and can be used to assess the sources of the particles and the history of atmospheric processes that determine their composition. Of particular value is their ability to provide information on the internal vs. external mixing of different aerosol components. Additional details concerning these techniques are given in Appendix B and listed in Table B.4. Also, Middlebrook et al. (2003) have discussed the operating principles of three of these instruments and compared the results obtained from their measurements. However, the use of single-particle measurement methods is limited because they are technologically sophisticated, costly, and the data thus far are only semi-quantitative.

A technique related to single-particle spectrometers, the aerosol mass-spectrometer, provides size-resolved, quantitative measurements of those PM components that are volatile at temperatures less than about 700°C. This technique operates in two modes: 1) to obtain size distributions associated with a limited number of PM components, and 2) to determine bulk concentrations of a larger number of PM components.

### 5.1.6 Optical Properties of Aerosols and Long-Path Optical Measurements

Issues associated with visibility, radiative transfer, and climate have motivated the use of optical long-path measurements, and in combination with other

instruments also can contribute to other aspects of particle monitoring. Measuring optical properties of fine particles and visibility requires a combination of in-situ and long-path techniques. The principal techniques that are used are listed in Appendix B in Table B.5 and the accompanying text.

***In-situ measurements of light scattering and light absorption.*** The in-situ properties of primary interest are aerosol light scattering and absorption. The light-scattering coefficient is measured directly by integrating nephelometers. In this device, a collimated beam of light passes through a chamber containing the sampled air. Scattering by the particles reduces the intensity of the light. The reduction in the intensity of the light by aerosol scattering is influenced by a combination of particle size and density. A number of vendors produce robust, field-ready versions of this instrument suitable for monitoring applications.

The most commonly used technique for monitoring light absorption measures the attenuation of light transmitted through the particles that are deposited on a filter. Time resolution can be achieved by depositing the particles on a filter-paper tape. The commonly used aethalometer and the particle soot absorption photometer convert optical attenuation to BC; however, conversion to mass concentrations requires use of an absorption coefficient, which is empirically determined.

These methods are adequate for routine measurements of the integral optical properties of aerosols related to visibility reduction. In most cases, sample air must be drawn from a sample inlet to the instrument, which means that care must be taken to avoid particle losses. Changes in relative humidity also affect light-scattering measurements, requiring measurement and, in general, control of sample relative humidity. Particles larger than a few micrometers in diameter are difficult to characterize quantitatively, due to inlet effects and optical truncation in the scattering measurement. More work is needed to characterize measurement artifacts of the filter-based methods for light absorption, to develop methods to determine the RH-dependence of aerosol light absorption, and to develop calibration and reference standards. Several new in-situ techniques, including cavity ring down cells, photo

acoustic cells and direct extinction cells, are under development. These show promise for fast-response online measurements of aerosol scattering and absorption.

***Long-Path Measurement Techniques: Remote sensing and visibility.*** The in-situ measurements described above give the visibility-relevant properties of air at the location of the sampling inlet. The long-path measurements described below indicate the burden and, in some cases, the particle distribution in a column of air.

Sun-tracking photometers measure the vertical optical depth by observing the transmission loss between the sun and the instrument. They obtain information about the average size-distribution of the particles in the column. Interpretation of the size distributions should be limited to general rather than detailed features, because the results are typically quite sensitive to measurement errors and data retrieval algorithms. Shadow-band radiometers measure both direct and diffuse radiation and provide information similar to that obtained from a sun photometer, but with less accuracy. Automated spectral sun photometers and shadow-band radiometers are commercially available, and are standard instruments in some radiation-monitoring networks. Radiative-transfer and climate issues usually motivate the use of these instruments, but they also can contribute to pollution research, especially in combination with other instruments.

Telephotometers or teleradiometers measure the contrast reduction of a distant reference target due to the intervening haze. The results are closely applicable to human perception, but depend on lighting conditions. Scene cameras are even more attuned to visual perception and less quantitative than telephotometers in terms of quantifying the optical properties of PM. Transmissometers measure the one-way transmission loss, and hence the average extinction coefficient, along a path. Transmissometers designed for long-term operational use are commercially available, and are used as a standard instrument in the IMPROVE network. Transmissometers often have been used at airports, where the design is optimized for low visibility.

Long-path measurements are becoming available that can provide spatial resolution. The lidar (light

detection and ranging) uses a laser to transmit a pulse of light into the atmosphere. The small portion that is scattered back from the air is detected as a function of time, or equivalently, of distance from the device. The information provided by current instruments is qualitative, indicating the approximate distribution of particles in the atmosphere. This information is extremely valuable for locating aerosols and determining the thickness of the layers. Lidar can operate from the surface or from aircraft. Automated, eye-safe lidars are commercially available along with new emerging research prototypes.

Recent research has shown the value of data from various lidar systems for inferring profiles of the physical properties of particles, such as  $PM_{2.5}$  and even the size distribution. The influence of relative humidity on the distribution and optical properties of aerosols and their behavior with height in the atmosphere can be studied using simultaneous lidar measurements of water vapor and aerosol backscatter or extinction. In addition, the lidar is capable of determining the depolarization ratio of backscattered light, a source of information relatively untapped in aerosol studies. The depolarization ratio indicates the morphology of particles by specifying the degree to which particles are non-spherical. Finally, coupling lidar measurements with other measurements (for example, a spectral sun photometer) can greatly enhance the available information. Additional development and evaluation of such methods should yield valuable dividends for future aerosol studies.

*Network applications of light scattering and absorption.* Prior to 1994, visual range was recorded hourly by human observations. In the United States and Canada, human observations were replaced with automated light scattering instruments in automated surface observing (or weather) systems (ASOS/AWOS). The automated sensors measure the extinction coefficient as one-minute averages. The visibility sensor operates on a forward-scatter principle, since forward-scatter measurements were found to correlate better with transmissometer extinction coefficients than backscatter measurements. Currently, the ASOS/AWOS data are provided as 18 specified visual ranges with a visual range upper bound of 10 miles, even though the instrument can provide meaningful data up to 20

30 miles. The raw visibility data need to be filtered to eliminate and correct for weather influences (fog, precipitation), high humidity, and visual range threshold. However, ASOS/AWOS data have great potential in aiding PM<sub>2.5</sub> mapping if adequate algorithms are developed to relate the forward scattering measured by these devices to fine-particle concentrations.

*Satellite measurements.* Several techniques exist for detecting aerosols from space using passive remote-sensing methods. Each method has its own advantages and disadvantages. Satellite techniques are at present most suited to define patterns of aerosol distributions and may be useful in evaluating total aerosol optical depth for comparison with total aerosol optical depth as computed by models. They usually provide the only information available in remote areas and can offer global coverage. However, current satellite sensors measure only relative concentrations of PM in the lower atmosphere.

Visible and near-infrared techniques also have been tested for detecting dust aerosols. The total ozone mapping spectrometer (TOMS) uses the ultraviolet part of the electromagnetic spectrum and has the ability to distinguish between absorbing and non-absorbing PM. A 20-year record is available globally, both over land and ocean. A major advantage of this technique is the availability of aerosol coverage, since the surface ultraviolet reflectivity is low and nearly constant over both land and water. However, the TOMS aerosol product is not sensitive to aerosols below 1 km, and the spatial resolution of the instrument is on the order of 40 by 40 km<sup>2</sup>.

Although the accuracy of direct concentration measurements of the boundary layer from satellites is problematic, other satellite data can be used to characterize the physical atmosphere in which aerosols are produced. For example, atmospheric water is critical to the evolution and growth of particles and their ultimate optical and chemical properties. Visible and infrared measurements from polar orbiting satellites can be used to characterize cloud distributions and liquid water properties. Clouds and their physical properties are highly parameterized in models and satellite data potentially have the temporal and spatial resolution to replace

the uncertain cloud characterizations produced in models. Satellites also have the potential to provide characteristics of the surface (moisture availability, albedo, heat capacity) that will ultimately improve the fidelity of PM modeling (e.g., Jones et al., 1998).

### 5.1.7 Chemical Analysis of Cloud and Fog Chemical Composition

Fog and cloud droplets collect local particles and soluble gaseous compounds. The amount of particulate matter in the air after the droplets evaporate can either increase or decrease (c.f., Pandis et al., 1998). While fog and cloud water have been sampled for a number of years, in the last few years multiple size-fractionating droplet collectors have been employed and the collected water analyzed for its chemical composition (Collett et al., 1998). These measurements allow for a better understanding of the chemistry within fogs and clouds, and of its variation with droplet size as a function of location, elevation, and time of day.

Fog- and cloud-water collectors are designed to collect water droplets ranging from 2 to 50 μm. Droplets typically are collected by impaction, either passively or actively. Passive collectors use ambient air movement to bring the droplets to the collector. Active collectors either draw air across the collection surface or move the surface through the air.

Fog- and cloud-water collectors are either bulk collectors, which collect all droplet sizes, or size-selective collectors, which collect the droplets in several discrete size ranges. Depending on the flow rates and liquid-water content of the fogs, sampling durations as short as 5 minutes can be achieved using active strand collectors. Size-selective collectors have been developed to collect cloud droplets in as many as five droplet size ranges. In addition, these samplers employ impaction either through multiple nozzle impactor plates or several impaction strings of different size.

Counterflow virtual impactors (Figure 5.2c) have been applied to inertially separate cloud droplets and ice crystals from ambient air, evaporate the water from them, and chemically examine the residue particles and evaporated gases. Such studies show

promise in understanding the role of particles as ice nuclei and cloud-condensation nuclei, and for studying the relationship between cloud chemistry and PM processed through clouds

Bulk and size-fractionated fog and cloud-water samples can be analyzed for liquid-water content and chemical components, including inorganic and organic anions and cations. In general, the analytical methods for determining concentrations of these species in fogs and clouds are well established and summarized in Seigneur et al. (1998). Analytical limits of detection and analytical uncertainties are given in Collett et al., (1998). Intercomparisons to estimate the liquid-water content in fogs indicate agreement among the methods of about 10 percent. Important chemical species analyzed in fog and cloud water include inorganic anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{=}$ ), inorganic cations ( $\text{H}^+$  [i.e., pH],  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$ ), total iron (FeX) and manganate (MnX), low molecular-weight organic anions (e.g., formate, acetate, and others), formaldehyde, S(IV), hydroxymethanesulfonic acid, hydrogen peroxide, and organic peroxides.

### 5.1.8 Gas-Phase PM Precursors, Ozone, Ozone Precursors, and Oxidants

The salient features of techniques currently available to measure the ambient concentrations of gas-phase PM precursors, ozone, ozone-precursors (including the odd-hydrogen free radicals), and oxidation products of these compounds are listed in Appendix B, Tables B.6.

Many PM precursors are also those that lead to tropospheric ozone. Several essential measurement methods are well developed (e.g., those for ozone, NO,  $\text{NO}_2$ ,  $\text{NO}_y$ , CO,  $\text{SO}_2$ , and  $\text{C}_1$ - $\text{C}_8$  hydrocarbons). Routine measurements made in urban monitoring networks can reliably use low-cost commercially available instruments that measure these species, especially for compliance purposes, although higher sensitivity and improved selectivity are desired for measurements outside urban areas. However, aircraft measurements needed for understanding chemical processes and model development and evaluation require performance found only in the most sophisticated, research-grade instruments. Parrish

and Fehsenfeld (2000) recently reviewed most of these techniques, their capabilities, and their limitations.

### 5.1.9 Meteorological Measurements

Accurate measurements of meteorological parameters at ground level and aloft are essential for understanding and modeling PM sources, chemistry, transport, and deposition. Major field programs have stimulated new insight in the complexity of the meteorological processes that control air quality and the need for better observations and models. Central to these studies has been the need for observations of horizontal and vertical transport and mixing, temperature, moisture, radiation, and the surface-energy budget. The meteorological measurements required for this research were reviewed recently (Seigneur et al., 1998). Ground-level methods for most measurements are routine, precise, accurate, and inexpensive. They are deployed in all monitoring networks and are well understood.

In contrast, measurements aloft are more complicated, difficult to operate and maintain, expensive, of lesser known accuracy (calibration methods are not straightforward), and relatively new. Unique insights into boundary-layer mixing and mesoscale or synoptic-scale transport processes can be made only with the application of these techniques. In addition, measurements aloft provide essential information about the distribution of PM and PM precursors, particularly the long-range transport of particles with sufficiently long atmospheric lifetimes to be transported thousands of kilometers from their sources. Much of the long-range transport may occur in transport layers in or above the planetary boundary layer. These measurements often are made in combination with routine observing networks. Indeed, profiling measurements provide important information that can be used to determine the best location for surface-based monitoring stations. Information concerning the measurement of meteorological parameters for critical parameters such as temperature, humidity, wind speed and direction, mixing height and solar radiation is given in Appendix B in Table B.7 and the accompanying text.

## 5.2 MEASUREMENT UNCERTAINTY AND VALIDATION

Estimated uncertainties of measurements made by instruments deployed in fine-particle monitoring networks are listed in Tables 5.1, 5.2, and 5.3.

The multitude of measurable parameters that may be necessary to define PM (e.g., size, mass, number, and composition) makes determining the uncertainty inherent in most particle measurements considerably more challenging than is the case for gas-phase measurements. In general, the uncertainty of any measurement consists of two parts: precision (random error) and accuracy (systematic error). Precision or reproducibility allows for estimates of random errors. These errors usually are determined for combined field and laboratory operations by collecting collocated replicate samples or by propagating individual instrument errors through all components of the measurement process. Accuracy or systematic error usually results in the largest uncertainty, since it incorporates instrument or method accuracy and includes the coupled effects of measurement interferences, artifacts, and detection limit. Interferences are constituents in the atmosphere that are detected in the measurement as the compound of interest in the case of gas-phase compounds or as the target property of interest in the case of PM. By contrast, artifacts are unintended alterations (gain or loss) in the compound of interest in the case of gas-phase compounds, or as the target property of interest in the case of PM in the course of the measurement or during collection and analysis of the sample. Detection limit is determined by the amount of a constituent that is required to be detectable above the intrinsic noise of the measurement technique and establishes the volume of air needed and the time required to make a measurement.

### 5.2.1 Estimation of Particle Measurement Uncertainty

With the possible exception of mass, it is difficult to determine the absolute accuracy in the measurement of PM properties. Mass can be considered an exception, but only by definition in a regulatory context as described later, and not in terms of certified

Standard Reference Material (SRM, e.g., those prepared by NIST). Appropriate reference materials or standards for many particle-phase components that can account for the entire sampling and analysis process, and which are representative of many of the complex properties of atmospheric particles, are not routinely available or suitable for use with many PM measurement techniques. In general, the chemical properties of PM are referenced to a known level of that chemical component supplied to the system during the final stage of chemical analysis. It is this aspect of the determination of PM properties that is given as “accuracy” in Tables 5.1, 5.2, and 5.3. Although progress is being made in the development of calibration sources of known size with known physical-chemical properties (McMurry, 2000), many challenges remain in making a routine, absolute determination of true atmospheric PM properties and composition. Since SRMs are not available for most PM properties, the accuracy of the method relative to ambient is unknown and is estimated only by the convergence of several methods, also typically of unknown accuracy. Thus, while the gravimetric methods for mass may be regulatory-standard methods, they are not standard methods to judge accuracy or bias in the more classical analytical sense. As well, there are SRMs for the chemical analysis of sampled inorganic species, such as  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ , which provide confidence that the sampled material is appropriately analyzed. As with mass, the absolute determination of these properties in the atmosphere cannot be verified, since standards to test the complete sampling and analysis system are unavailable.

For this reason, measurement uncertainty (or perhaps more appropriately, consistency or comparability) is usually determined by comparisons among several methods that are aimed at determining similar properties of the sampled particles. Hence, for PM, convergence of methods through intercomparison studies, rather than calibration to a known standard as a guide to measurement uncertainty, is relied upon. Several such studies have been conducted over the past twenty years to determine the equivalence and comparability of PM mass and its chemical components (Seigneur, 1998). These studies provide equivalency or comparability among the methods tested, but not bias relative to a known standard or

Table 5.1. Estimated uncertainty in measurements of the physical properties of PM.

Compared Property	Analytic Method Accuracy <sup>a</sup>	Precision <sup>b</sup>	Range of Comparability <sup>c</sup>	Time Resolution	Comments <sup>d</sup>
Mass (PM <sub>2.5</sub> )	±5 percent	±10 percent	within 20 percent	24-hr	Accuracy refers to gravimetric analysis only. There is no consideration of sampling artifacts. Adequate collocated precisions and comparability can be achieved among filter mass measurements if care is taken. (Watson and Chow, 2002; Solomon et al., 2003.)
Mass (coarse)	±5 percent	±10 percent	within 20 percent	24-hr	Accuracy refers to gravimetric analysis only. There is no consideration of sampling artifacts.
Size distribution (coarse, fine, ultrafine)	25 percent		within 25 percent	5 min	Accuracy based on comparison of integrated size distributions with integral measurements (e.g. total number).

<sup>a</sup> Accuracy is defined as the ability of the laboratory methods to correctly measure the samples of a standard reference material.

<sup>b</sup> Precision is defined as the coefficient of variation of repeated measurements obtained by identical collocated samplers in the field.

<sup>c</sup> The range of observed levels of comparability across techniques involved in field comparisons designed to test comparability.

<sup>d</sup> Estimates based on authors' experience unless a citation is given.

absolute particle metric for that property. The consistencies among evaluated techniques for measurements of specific properties are listed in Tables 5.1 through 5.3. In addition, references to the studies that have determined consistency among the instruments used for PM measurement are listed in Appendix B, Section B.3.

Tables 5.1, 5.2, and 5.3 indicate the level of confidence that has evolved in these measurements; that is, the comparability of the measurements of the physical properties and chemical composition for measurements made using integrated and, in some cases, continuous samplers operated side-by-side. It should be noted that the values listed in these tables represent current, state-of-the-art methods and that historical measurements are probably less accurate and precise. The particle transmission and collection properties of the inlet and particle volatilization in these integrated samplers have been identified as important factors that influence comparability between the different measurement methods (Chow, 1995; Solomon et al., 2003). Careful maintenance of the sampler and handling, storage, and analysis of the samples can minimize the influence of these parameters on uncertainty; however, they often are

found to be as important as sampler design in determining the differences among systems. Differences in analysis methods also may result in significant differences in reported concentrations, which are important when, for example, data are compared across networks (e.g., National PM<sub>2.5</sub> Chemical Speciation Network and IMPROVE).

## 5.2.2 Mass and Size Distribution

The standard gravimetric techniques used to determine PM mass for many regulatory purposes involve filter collection and weighing. While such methods are relatively simple and inexpensive to implement, they require manual operation, provide limited time resolution, are prone to sampling interferences, and, due to human intervention required for weighing, are subject to other sampling errors that cannot be quantified. The gravimetric filter-based methods, such as the FRM for PM<sub>2.5</sub>, have been shown to be biased low, under certain conditions, due to the loss of semivolatile compounds (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SVOC) during sampling. Thus, while the PM<sub>2.5</sub> FRM is a reference method for compliance purposes, it is not a suitable reference method to

Table 5.2. Uncertainty in measurements of the chemical composition of PM: acids and inorganics.

Compared Property	Accuracy <sup>a</sup>	Precision <sup>b</sup>	Range of Comparability <sup>c</sup>	Time Resolution	Comments <sup>d</sup>
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	±5 percent	±10 percent	within 10 percent	3- to 24-hr	Generally good agreement among many methods (Solomon et al, 2003).
Nitrate (NO <sub>3</sub> <sup>-</sup> )	±5 percent	±10 percent	within 35 percent	3- to 24-hr	Significant differences among methods. Comparison involved measurements from both integrated systems and continuous measurements. (Solomon et al., 2003)
Chloride (Cl <sup>-</sup> )	±10 percent	±30 percent	50 percent	3- to 24-hr	
Organic acids	±5 percent	±10 percent	unknown	3- to 24-hr	
Ammonium (NH <sub>4</sub> <sup>+</sup> )	±5 percent	±10 percent	within 30 percent	3- to 24-hr	Ammonium comparability similar to sulfate in PM dominated by ammonium sulfate or bi-sulfate (Solomon et al., 2003)
Alkali Metals (Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> )	±5 percent	±10 percent	within 30 percent	3- to 24-hr	
Alkali earth metals (Mg <sup>2+</sup> , Ca <sup>2+</sup> )	±5 percent	±10 percent	within 30 percent	3- to 24-hr	

<sup>a</sup> Accuracy is defined as the ability of the analytic method to correctly measure the samples of a standard reference material.

<sup>b</sup> Precision is defined as the coefficient of variation of repeated measurements obtained by identical collocated samplers in the field.

<sup>c</sup> The range of observed levels of comparability across techniques involved in field comparisons designed to test comparability.

<sup>d</sup> Estimates based on the authors' experience unless a citation is given.

determine the accuracy of mass concentrations relative to what is actually in the air.

Continuous techniques for accurate measurements of mass that avoid such sampling errors are needed. These methods are being developed but will require considerable evaluation before they are ready for operation in routine networks. *SRM are not available for most PM properties, so accuracy of the method relative to actual ambient PM is unknown and only estimated by convergence of several methods also typically of unknown accuracy. Thus, the FRM methods for mass are regulatory standard methods, but are not standards to judge accuracy or bias in a more classical sense.*

### 5.2.3 Aerosol Chemical Composition

Non-volatile inorganic aerosol components such as SO<sub>4</sub><sup>2-</sup> can be measured with acceptable precision and

comparability among methods (i.e., within 10 percent). More labile compounds (e.g., NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and organic compounds) as well as BC are measured considerably less well. Organic-PM measurements (OC or OC species) are especially prone to error due to sampling artifacts, which include both the volatilization of semivolatile compounds from collected deposits of particles and the adsorption or absorption of organic gases on sampling substrates or collected particle deposits during sampling. It is likely that positive and negative artifacts and interferences occur during sampling, handling, and storage, and the relative magnitudes of these effects vary with environmental variables and sampling parameters (e.g., filter type, flow rate, sampling time). It is important to understand the magnitude of these artifacts and interferences so as not to bias the ability to manage air quality.

*More effort is needed to understand properties of organic aerosols and their gas-phase precursors,*

Table 5.3. Uncertainty in measurements of the chemical composition of PM: carbon and organics.

Compared Property	Accuracy <sup>a</sup>	Precision <sup>b</sup>	Range of Comparability <sup>c</sup>	Time Resolution	Comments <sup>d</sup>
<b>Organic carbon (OC)</b>	±10 percent	±20 percent	within 20-50 percent	3- to 24-hr	Serious problems have been identified using evolved gas analysis to determine total organic carbon in PM. Net positive artifacts (1-4 µg/m <sup>3</sup> ) with use of quartz-fiber filters also has been observed consistently. (Huebert and Charlson, 2000; Solomon et al., 2003)
<b>Black Carbon (BC) or Elemental carbon (EC)</b>	±10 percent	±20 percent	within 20 percent to 200 percent	3- to 24-hr	Serious problems have been identified using evolved gas analysis to determine elemental carbon in PM. Wide range in comparability is due to use of different analysis methods. (Huebert and Charlson, 2000; Solomon et al., 2003)
<b>Total carbon</b>	±10 percent	±10 percent	within 20 percent	3- to 24-hr	Adequate collocated precisions and comparability can be achieved among filter carbon measurements if care is taken. (Watson and Chow, 2002.)
<b>Organic (speciated)</b>	unknown	unknown	unknown		Involves extraction of organic fractions, based on polarity or other properties followed by GC-MS analysis (Schauer et al., 1996). To date a maximum of only 20 percent of the organic mass has been identified as individual species.
<b>Trace elements</b>	±5 percent	±10 percent	10-30 percent depending on species	3- to 24-hr	Comparability based on XRF analysis for PM collected on Teflon filters and species observed above their detection limit, primarily sulfur and crustal related species. (Solomon et al., 2003)
<b>Transition metals</b>	±5 percent	±10 percent	10-30 percent depending on species	3- to 24-hr	Comparability based on XRF analysis for PM collected on Teflon filters and species observed above their detection limit, primarily sulfur and crustal related species. (Solomon et al., 2003)
<b>Biological PM</b>	unknown	unknown	unknown		

<sup>a</sup> Accuracy is defined as the ability of the analytical method to correctly measure the samples of a standard reference material.

<sup>b</sup> Precision is defined as the coefficient of variation of repeated measurements obtained by identical collocated samplers in the field.

<sup>c</sup> The range of observed levels of comparability across techniques involved in field comparisons designed to test comparability.

<sup>d</sup> Estimates based on authors' experience unless a citation is given.

*including factors that govern the gas-particle partitioning of semivolatile organic compounds, the hygroscopicity of particulate organic compounds, and the proclivity of gas-phase organic precursors to form secondary organic PM.*

#### 5.2.4 Uncertainties in Routine Gas-phase Measurements Used for Network Monitoring

The instruments and techniques available for the measurement of atmospheric concentrations of ozone and PM precursors, and other related trace gases are briefly described in Section 5.1.8 with additional

detail given in Appendix B, Table B.6a. Uncertainty estimates are given in Table 5.4. There is a long evaluation history for instruments used to measure these gas-phase compounds. These instrument validations were in response to the need for reliable measurements that could be used to understand and monitor acid deposition, urban and regional photochemical air quality, climate change, and stratospheric-ozone depletion. As new techniques were devised, they were field tested to demonstrate worthiness and to determine the necessary housekeeping procedures (calibration, zeroing, routine maintenance). Several studies have been conducted over the past twenty years to determine the accuracy of these measurements (Parrish and Fehsenfeld, 2000).

With regard to uncertainties in the measurement of gas-phase compounds, two issues require serious attention. The first pertains to calibration procedures used for routine measurements. In particular, the approaches used to calibrate important measurements, such as ozone, NO, and NO<sub>2</sub>, can lead to serious errors under some circumstances and in certain locations. Problems include the ability to reliably generate standards at low concentrations (ppt range) and deliver them through the inlet to the instrument. A careful review of calibration procedures used in routine monitoring networks should be undertaken.

The second issue involves measurement uncertainties associated with VOC sampling. Apel et al. (1999) identified large uncertainties for many of these VOCs. The approaches used to measure VOCs are discussed briefly in Appendix B (Section B.2.6). Serious problems have been observed in routine measurements of high molecular-weight VOCs, which have a high probability of participating in particle formation. Clearly one of the most critical needs of the ambient VOC measurement community is a rigorous field intercomparison of measurement techniques. Such an intercomparison will define more clearly measurement capabilities and identify prevalent problems that must be addressed.

## 5.3 MEASUREMENT STRATEGIES AND NETWORK ISSUES

The instruments described in the preceding sections eventually must be assimilated into a capable and cost-effective measurement system and strategy. An effective measurement strategy requires a complement of long-term routine measurements, short-term or special studies, and intensive field studies. Every measurement is not needed everywhere all the time, but a wide variety of measurements may be needed at some locations some of the time.

The design and implementation of the strategy must account for differences in measurement objectives: 1) to understand the composition and distribution of PM in the atmosphere, 2) to determine pollution effects, and 3) to provide the information needed for effective management. The system must identify when and where PM problems exist and the severity of these problems. The measurements must provide information concerning the sources, transport, and transformation of atmospheric PM. They must identify the sources, and monitor the distributions of, precursors that are involved in the generation of the PM pollution. Finally, they must provide data for developing and evaluating “receptor-based” and “emission-based” chemical-transport models (and the modules contained within these models) used to determine and test possible abatement strategies for PM pollution.

### 5.3.1 Deployment of Measurement Technology

*Routine Surface-Network Observations.* Monitoring networks at selected surface sites are vested with the primary responsibility for characterizing PM concentration and distribution for the purposes of air-quality management. The objectives, measurements, and design criteria for existing air-quality networks in Mexico, Canada, and the United States have been discussed extensively elsewhere (Demerjian, 2000; U.S. EPA, 2002). The information provided by the existing networks is

Table 5.4. Uncertainty in routine measurements of gas-phase compounds. References for the intercomparisons to establish limits can be found in Parrish and Fehsenfeld (2000).

Compared Property	Accuracy	Time Resolution	Comments
<b>Sulfur dioxide (SO<sub>2</sub>)</b>	±10 percent	1 min.	Pulsed-fluorescence at 190-230 nm and fluorescence at 220-400 nm. Instrument currently in wide use for routine monitoring. Standard reference material available for through-the-inlet calibration. Recent studies indicate considerable advances in measurement of sulfur compounds. Similar results with longer-time resolution by filter pack measurements with potassium-carbonate-impregnated filters followed by ion chromatography analysis.
<b>Ammonia (NH<sub>3</sub>)</b>	±10 percent	1-hr	Based on citric acid coated denuder sampling followed by ion chromatography analysis. Method currently used in research studies and networks. Careful handling of denuders required for optimum results. Newer techniques for ammonia measurement are being developed that promise significant improvements in ammonia measurement. Development of fast-response techniques must be accompanied by inlet designs that reduce ammonia uptake on inlet.
<b>Ozone</b>	±1 ppbv	1 min.	UV absorption at 254 nm, based on intercomparison of ozone measurements. Instrument in wide use currently for routine monitoring. Absolute calibration base on Beers' Law. Potential interferences in the standard UV absorption technique from VOCs such as the aromatic compounds benzene and toluene don't appear to be a problem. However, a clean, properly operating UV absorption instrument provides an absolute measurement of ozone. Additional calibration procedures only should identify field instruments needing cleaning and/or repair, never to alter instrument measurement results.
<b>Carbon monoxide (CO)</b>		1 min	There are presently a variety of instruments that are capable of measuring CO. The choice of instrument depends on the accuracy, precision, and frequency demanded of the measurements. Non-dispersive infrared absorption has proven to be satisfactory for most ground-based measurements. Instrument currently in wide use for routine monitoring. Standard reference material available for through-the-inlet calibration. The modified commercial NDIR instrument is capable of continuous, unattended measurements at 1-ppbv precision for one hour averaging times of the slowly varying ambient CO levels.
<b>Nitric oxide (NO)</b>	±30 percent	1 min	NO measurements are made in current networks and high-quality, commercially available instruments exist to make these measurements. The reliability of chemiluminescence technique to measure NO has been well established through several instrument intercomparisons. Standard reference material available for through-the-inlet calibration. Instrument currently in wide use for routine monitoring.
<b>Nitrogen dioxide (NO<sub>2</sub>)</b>	±30 percent	1 min	The reliability of chemiluminescence/photolysis technique to measure NO <sub>2</sub> has been well established through several instrument intercomparisons. Standard reference material available for through the inlet calibration. A high time resolution converter for NO <sub>2</sub> measurements by photolysis-chemiluminescence promises a significant improvement in the measurement of this compound.
<b>Nitric acid (HNO<sub>3</sub>)</b>	±10 percent	1 hr	Routine monitoring usually done with denuders directly or denuder difference method and ion chromatographic analysis. The evaporation of nitric acid from ammonium nitrate containing aerosols can interfere with gas phase measurement. Calibration is an issue. Method is used currently in research studies and networks. The development of fast-response sampling techniques must be accompanied by improved inlet design to reduce nitric acid uptake on sampling lines. Several semi-continuous methods likely suitable for routine networks are emerging.
<b>Reactive nitrogen oxides (NO<sub>y</sub>)</b>	±30 percent	1 min	NO <sub>y</sub> measurements are made in current networks and high-quality, commercial instruments exist to make these measurements. Converter reduces NO <sub>y</sub> to NO and detects NO by chemiluminescence. Technique has been well established through several instrument intercomparisons and is in wide use for routine monitoring. Calibration at very low levels is an issue. The development of fast-response sampling techniques must be accompanied by improved inlet design to reduce nitric acid uptake on sampling lines.

reviewed in Chapter 6. In meeting the air-quality information needs over all of North America, it is clearly in the interest of the three countries that the designs of these monitoring networks provide compatible information and meet diverse needs with maximum efficiency.

*Monitoring networks that provide compatible information for Canada, the United States, and Mexico, and that meet diverse needs with maximum efficiency, need to be designed.*

Several networks are in operation. They are aimed at various PM-related problems: harm to human health, ecosystem damage, degradation of visibility, and influence on global climate. The primary responsibilities of the existing networks are to document the severity and extent of the problem and to measure progress in its control. As described in Chapter 6, the existing networks have significantly advanced the understanding of the spatial and temporal patterns of PM concentration and composition. The sites in these networks are chosen and the instrumentation is selected to ensure that their primary goals are met. The network measurements are typically made on a nearly continuous basis throughout the year; although for PM a one-day-in-three or a one-day-in-six, 24-hr average sampling schedule often is used. Although the measured data typically vary according to the objectives of each network, there are significant elements of commonality in the instrumentation used in these networks.

Some networks measure a suite of PM components, including  $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , OC, BC, and a variety of elements that represent crustal contributions, as well as gas-phase precursors ( $\text{NO}_x$ , VOC,  $\text{SO}_2$  and  $\text{NH}_3$ ) that are responsible for the formation and evolution of PM in the atmosphere. In some cases the network measurements also include ozone and ozone precursors ( $\text{NO}_x$ , VOC and CO). The measurements made in these networks, apart from their specified monitoring objectives, are useful for diagnostic air-quality applications: tracking effectiveness of control strategies, source identification and apportionment, and evaluation of chemical and physical process understanding. Additionally, information to support these objectives will be obtained by continuous methods, which are

rapidly emerging to measure specific PM components, such as mass,  $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and trace elements. Continuous methods for carbonaceous compounds, however, are still research activities.

Current instruments, their temporal resolution, and spatial deployment are sometimes inadequate for these additional tasks, specifically for tracking trends and feeding receptor-modeling applications. Moreover, daily operation of the instruments in the network requires significant commitment of personnel resources for maintenance, quality assurance, data archiving, and reporting. Routine monitoring requires reliability, operational simplicity, and low cost. However, this monitoring also requires significant human intervention to reduce and analyze the measurements (Chow, 1995). These factors often result in insufficient time resolution to meet desired objectives.

Clearly, the length of monitoring needed depends upon monitoring objectives. An adequate baseline period may require several years (three or more) of data to specify current conditions and to provide sufficient data for use in designing the most efficient and effective monitoring programs. Most of the regulatory standards require at least three years of data for compliance monitoring. For the assessment of control programs by means of trend analyses, monitoring information is typically needed over a decade or more (see Chapter 6). In this respect, the evaluation of control measures imposes different requirements than does the characterization of population PM exposure over shorter periods.

Requirements for sampling duration and frequency for regulatory monitoring are dictated in part by the forms of the ambient air-quality standards. Twenty-four-hour measurements made once every three to six days have been judged adequate for determining compliance with the 24-hr and annual PM standards. However, 24-hr measurements typically provide little scientific insight into either the formation of secondary PM species or the linkages between emission sources and the eventual PM distribution.

Sampling frequency also affects statistical robustness. The collection of 24-hr PM samples once every six days provides representative but incomplete

information for PM frequency distributions. The use of one-day-in-six sampling frequency is thought to introduce potential errors in estimating annual means (Chapter 6).

In addition, characterization of population PM exposure within acceptable uncertainty imposes significant requirements on the number and location of monitors. As discussed in Chapter 6, average-annual urban PM<sub>10</sub> and PM<sub>2.5</sub> concentrations may show factor-of-two variations over distances of approximately 10 to 20 km and 50 to 100 km, respectively. A variety of statistical methods is available for spatially allocating monitoring stations. The design criteria to accomplish this have recently been presented (U. S. EPA, 2002)

Efforts to establish scientific bases for network design have not yet been incorporated into redesign of the existing networks. The new U.S. National Air Monitoring Strategy (<http://www.epa.gov/ttn/amtic/stratdoc.html>) appears to offer the prospect of integrating current single-pollutant monitoring approaches to better address the management of linked, multi-pollutant air-quality issues <sup>2</sup>.

Some important monitoring requirements are not being met, or cannot be met until technology evolves. Virtually no speciated carbon measurements exist except for limited, special studies. Measurement of individual PM carbon compounds holds the potential for substantially improving knowledge of source contributions to ambient OC and BC concentrations. Precursor and copollutant gas measurements are necessary for fully understanding the production and evolution of PM in the atmosphere. This full suite of measurements is not available in as many locations as is required. Demerjian (2000) concluded that the monitoring information needed to provide scientific understanding compared with that needed strictly for air-quality management becomes critical for secondary pollutants. In the case of secondary pollutants, understanding the relative effectiveness of emission control strategies requires analyses of data that are capable of revealing the relations between the production of secondary species and their precursor concentrations.

Finally, the measurements made at surface monitoring sites have significant inherent limitations in providing information required for source apportionment and chemical-transport model evaluation. The concentrations of chemically active constituents can be influenced strongly by surface exchange and lead to vertical concentration gradients. The measurement requirements including the ancillary meteorological measurements needed to account for these effects are extremely demanding and cannot be accomplished with presently available network measurements. In addition, the measurements made at ground sites in populated areas are sensitive to nearby sources. Some of these limitations can be overcome with the addition of ground-based instruments that can provide vertical-profile measurements of chemical composition and meteorology.

***Special studies and intensive field studies.*** Routine surface-based monitoring networks alone are neither sufficient nor cost-effective approaches to providing all of the information required by users with different needs (Figure 5.1). To overcome some of the limitations of routine monitoring networks, other approaches, (e.g., special and intensive field studies), are necessary. Three general types of special studies can play a critical role in improving the overall capability of atmospheric-science tools.

1) *Intercomparison studies* are aimed at determining the capability, reliability and/or consistency of the measurement techniques used to characterize the atmospheric concentration of individual gas-phase compounds or specific chemical and physical properties of sampled particles. As discussed earlier, comparisons are critical for PM and related species since field standards are not available for through-the-inlet calibration. These studies also provide an arena to test the proficiency of new measurement techniques and to estimate the confidence, comparability, and reliability of existing techniques (c.f., Section 3.2). The atmospheric-science community addresses measurement uncertainties in an arduous but effective way: formal, rigorous, and unbiased inter- and intra-method instrument comparisons. There have been many such special

<sup>2</sup> This monitoring strategy is specifically focused on the National Air Monitoring Stations (NAMS), the State and Local Air Monitoring Stations (SLAMS), the Photochemical Air Monitoring Stations (PAMS), and IMPROVE.

studies, carried out at ground sites and in aircraft, devoted specifically to the assessment of instrument capability, reliability, and comparability.

2) *Source-characterization studies* are used to pinpoint sources, to identify their emissions, and to evaluate emission inventories using receptor-modeling methods (c.f., Chapter 7).

3) *Major field intensives* use a comprehensive collection of measurements, including research techniques, to characterize source emissions and to better understand chemical and meteorological processes. These studies are especially useful for evaluating chemical-transport models (c.f., Chapter 8). These two types of studies are often carried out in a region that has routine monitoring sites. The studies involve altering the sampling frequency of the routine measurements and/or deploying additional measurement techniques at selected locations for the duration of the special study.

Intensive field programs have been used effectively for several years, to fill gaps in the understanding of processes and sources that shape the distribution of gas-phase and PM pollution, and to provide information needed to critically evaluate model performance. These studies use an array of advanced instruments operated by teams of scientists that cooperate to carry out these large field campaigns. The intensive measurement periods are followed by an extended period of analysis and interpretation by the scientists involved in the study as well as others in the scientific community.

To achieve greater cost effectiveness, the goals of all three special-study types can, and often are, merged into one integrated intensive field study involving ground sites, aircraft, and specific source measurements. The studies are carried out over periods ranging from several weeks to more than a year, and typically involve one or more highly instrumented ground sites along with satellite ground sites that are less highly instrumented and distributed over the region of interest. The major ground sites need sufficient measurements in a highly variable atmosphere to reduce the degrees of freedom in interpretation and quantification of the important processes and sources. The measurement sites are chosen to best identify important sources or processes

that shape atmospheric composition and pollution accumulation, and may be collocated at previously established network monitoring sites. The distributed ground sites and aircraft permit the study to be placed in a regional context. In addition, aircraft measurements allow investigation through the boundary layer and above. The studies are supported by detailed estimates of the local and regional emissions of compounds of interest, which often have much higher temporal resolution than the information supplied to national emission-inventory programs. Specific source-type measurements may include, for example, tunnel studies or continuous emission monitoring of major point sources. These studies have provided the modeling community with the range of data that is required to test current models (see Chapter 7 and Chapter 8). In addition, receptor models (see Chapter 7) have been used with these data to uncover problems with emission inventories. Because these studies are expensive and require elaborate planning, they occur infrequently (for a given region, perhaps one or twice a decade).

### 5.3.2 Future Requirements for Measurement Strategies

PM represents a large collection of components, whose identity and source are poorly understood. Thus the current situation with regard to developing PM measurement strategies and monitoring networks is substantially different from that encountered with gas-phase pollution monitoring. The characteristics of the particles that cause harmful effects are not yet well established. For this reason, the measurement strategies and networks required to monitor these properties are not yet fully defined and implemented. There is a need for a basic suite of chemical measurements at spatially representative, or unique, sites to provide the full picture of PM formation, transport, and trends. For example, a minimum suite includes PM mass, speciation of the six major components ( $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , OC, BC, crustal species), ground-level ozone, and precursor species ( $\text{NO}_x$ ,  $\text{SO}_2$ , VOCs and  $\text{NH}_3$ ).

The source-receptor relationships that determine PM concentration and visibility are similar; thus networks and field studies should be designed to permit particle

concentrations and visibility relationships to be studied simultaneously. As new measurement technology emerges, it must be adapted to maximize the information-gathering capacity and utility of the existing and planned measurement platforms and sites. The development of accurate, real-time (measurement time of a few seconds or less) instruments opens opportunities for both airborne instruments (on manned and unmanned aircraft and balloons) and ground-level instruments (on vans, boats, and trains) that can make measurements with better spatial resolution and coverage. It will be necessary to increase the reliability and operational simplicity of the techniques so that they can be more easily adapted to operational needs. This includes the development of methods to calibrate these measurements, along with the development and maintenance of calibration and certified reference standards. The measurement strategies that use these resources must be aimed at providing data products and data-product formats that fulfill specific needs and can be readily and easily used.

Where networks are responsible for compliance, the principle of accountability should be incorporated into network design and the interpretation of network data. This means that the changes in emissions should be reflected in the data, and those changes should be compatible with expected changes based on a theoretical understanding of atmospheric processes and CTM predictions.

There is a natural synergism between PM research and research involving other air pollutants. The most effective management of these copollutants requires the combined understanding of the sources and processes that are responsible for them and the relationships between them. Measurement programs aimed at the study of PM should include sufficient scope to address the questions associated with these linkages.

## 5.4 SUMMARY

### *Measurement Uncertainty*

The large number of properties needed to fully define PM (e.g., size, mass, number, and

composition) makes the determination of the uncertainty inherent in any of the particle measurements more challenging than for gas-phase measurements. Appropriate reference materials or standards for many particle-phase components are limited and virtually unavailable for in-the-field through-the-inlet calibration. For this reason, measurement uncertainty (or perhaps more appropriately, consistency or equivalency) is determined by comparisons among several methods that determine similar properties of sampled particles. Hence, for PM, convergence of methods is used rather than calibration to a known standard, as a guide to measurement uncertainty. However, measurement accuracy relative to what actually exists in air is undefined by current methods. Considerable research is required to develop in-field certified calibration methods and reference standards, and may not be possible or feasible for all particle properties.

Comparisons of PM mass measurement using filter-based methods indicate that  $PM_{2.5}$  mass determinations are comparable to within 20 percent. The measurements of the stable ionic components, such as  $SO_4^{2-}$ , are comparable within 10 percent. The measurement of important volatile and semivolatile PM components, including  $NH_4NO_3$  and SVOCs is much less certain, even with the use of denuders and reactive filters.

The measurement of particulate carbon and carbon-containing species by filter/denuder-based methods is especially problematic. Measurements of organic compounds in PM are prone to errors due to particle volatility, interferences from gaseous organic species, limitations with analytical methods, and lack of calibration and certified reference standards. It is likely that both positive and negative artifacts and interferences occur during sampling, and there is no consensus as to the net effect of these interferences and artifacts. Recent studies using quartz-fiber filters indicate a net positive artifact for OC in the range of 1-4  $\mu g/m^3$  under the variety of conditions examined. It is likely that the relative magnitudes of these effects vary as a function of a number of variables. For these reasons, current organic speciation explains only 10 percent to 20 percent of total organics in PM. A list of all the estimated uncertainties in integrated denuder and filter systems is given in Tables 5.1 through 5.3.

### Integrated Denuder and Gravimetric Filter-Based Systems

Integrated denuder and filter-based systems have been widely used to measure PM mass, PM chemical composition and PM precursor gases (e.g.,  $\text{HNO}_3$  and  $\text{NH}_3$ ). These systems typically consist of an inlet and subsequent particle-size separating device to allow only particles of interest to be collected; a denuder to remove potential gas-phase interferences if the species of interest is semivolatile (e.g.,  $\text{NH}_4\text{NO}_3$ ); an inert or reactive collection substrate, often composed of Teflon, quartz-fiber, or nylon; followed by a vacuum pump to pull air through the system and a device to monitor and regulate the flow. Several different size-fractionating modules are available, as well as denuders and collection media. Denuders and reactive filters to measure  $\text{NO}_3^-$  and/or  $\text{HNO}_3$  are fairly well developed, although new designs require significant testing. The collection of organic aerosols is still quite challenging. However, the chemical measurements using these systems in combination with well-established analytical methods are capable of identifying and quantifying the major components ( $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , OC, BC, and crustal-related species) of the collected mass. While filter/denuder based systems are robust and relatively easy to use, their application in national PM monitoring networks is limited because they are labor intensive and costly. As described below, continuous measurements would be expected to reduce cost and to provide unique data in terms of temporal resolution.

### Continuous and Semi-continuous Measurements

Instrumentation is needed to measure aerosol composition semi-continuously or continuously in real-time. While suitable real-time bulk mass instruments are available now, measurement techniques for PM chemical components are emerging rapidly. Real-time instruments also can be less expensive to operate than filter-based sampler systems and can provide valuable information on diurnal trends. While filter measurements are relatively simple and inexpensive to implement, they require manual operation, provide poor time resolution, and are subject to sampling errors that cannot be quantified. Continuous and semi-continuous real-time methods supply high-frequency,

short-duration measurements needed to improve understanding of the formation, redistribution, and loss of atmospheric PM, as well as the sources of this material and the relation between PM and human health. They also facilitate timely communication to the public. Significant progress has been made in the past several years to develop instrumentation for real-time measurements of PM mass and composition, and some of these instruments have been commercialized. However, sampling errors and uncertainty in continuous and semi-continuous composition measurements still need to be better identified and quantified before wide use in routine monitoring networks. The availability and capabilities of commercialized real-time instrumentation will evolve substantially in the next few years, and as greater confidence in these methods is achieved, efforts should be made to replace filter samplers.

### Personal Exposure Monitors

Techniques have been adapted to monitor actual personal exposure. These monitors are designed to be carried by an individual and record the actual exposure of that individual to particulate matter. The sampling has focused on mass and collection of environmental pollutants having potentially significant human-health effects such as combustion emissions, tobacco smoke, acid aerosols, and vapor-phase organics. Although most personal monitoring has focused on 24-hr collection, devices are being developed for real-time continuous monitoring to determine individual exposure to short-term (one minute) variations in PM concentrations to determine the impact of brief high exposures and to identify and characterize PM sources. These small, lightweight devices have uncertainties of about 20 percent for mass and about 20 percent for stable particle-phase components (e.g.,  $\text{SO}_4^{=}$ ).

### Single-Particle Measurements

During the past ten years, the ability to measure properties of a single particle in near-real time, rather than just the properties of a bulk collection of particles over an integrated time period, has opened the way for more detailed understanding of particle morphology and chemical composition. Of particular value is the information provided on the mixing of

different aerosol components. Currently, the techniques are only semi-quantitative. As a consequence, these methods are not used in routine monitoring applications. It is possible that particle mass-spectrometry will evolve a capability to provide accurate real-time measurements of size-resolved composition, but much more research will be required to develop and evaluate the potential for such measurements. Single-particle analysis by scanning electron microscopy (SEM) also has evolved, allowing for simultaneous detailed observations of particle morphology, size, and chemical composition, providing valuable insights for source apportionment of ambient, micro-environmental, and human-exposure studies.

#### Optical Properties of Aerosols and Long-Path Optical Attenuation

Issues associated with visibility, radiative transfer, and climate have motivated the use of optical long-path measurements. In combination with other instruments these techniques also can contribute to other aspects of PM monitoring. Satellite techniques are currently most suited to define global aerosol-distribution patterns. Satellite techniques usually provide the only information available in remote areas and can offer global coverage, but typically measure only relative concentrations of a PM in the atmosphere. Satellites also have the potential to monitor cloud distributions and characteristics of the surface such as moisture availability, albedo, and heat capacity. Such measurements can ultimately improve the fidelity of PM modeling.

Routine surface-based visibility measurements provide data on total extinction and the major components of extinction – light scattering and light adsorption. Along with the chemical composition of PM from filter-based or continuous methods the contributions to light extinction can be apportioned to emission sources. The ASOS/AWOS visibility measurements and the ancillary meteorological data represent a valuable resource for air-quality investigations as well. Resources should be made available to the agencies that operate and evaluate the ASOS/AWOS network to make the data more widely available and in a form that represents the full dynamic range of the instruments.

#### Analysis of Cloud and Fog Chemical Composition

Fog and cloud droplets collect local aerosols and soluble gaseous compounds. Cloud-chemistry measurements allow for a better understanding of the chemistry within fogs and clouds and the variation with droplet size as a function of location, elevation, and time of day. Along with ambient PM measurements, fog and cloud measurements allow for an improved knowledge of the impact of water droplets on PM concentrations during and after fog and cloud occurrence. Studies show that clouds and fog can play a significant role in PM formation, either increasing or decreasing particle loading after the event. Intercomparisons to estimate liquid-water content in fogs indicate agreement among the methods of about 10 percent. In addition, important chemical species can be analyzed in fog and cloud water within several droplet size ranges. The non-volatile fraction of the chemical compounds in cloud water can be determined to within 10 percent.

#### Gas-Phase PM and Copollutant Precursors

Techniques are available to measure the ambient concentrations of gas-phase particle precursors, ozone, ozone precursors, and oxidation products of these compounds in the atmosphere. In general, the measurement methods and calibration procedures are well developed and adequate for most studies. Several intercomparisons have been conducted over the past twenty years to determine the equivalence and comparability of measurement methods for these species. The measurement methods for routine monitoring application are well developed for ozone, NO, NO<sub>2</sub>, NO<sub>y</sub>, CO, and SO<sub>2</sub>. These measurements can be made routinely with uncertainties of less than 30 percent. A list of all the estimated uncertainties in the relevant gas-phase measurements was given in Table 5.4.

The VOCs are of particular interest in connection with measurement uncertainties. They constitute a very large class of compounds generally defined as volatile at standard temperature and pressure. VOC measurements are difficult to perform because of the extreme complexity of the organic mixtures that may be present in the atmosphere. Although the C<sub>1</sub>-C<sub>6</sub> hydrocarbons usually can be determined with uncertainties of less than 20 percent, difficulties

associated with VOC measurements increase with complexity of the compound, and depend on whether carbon bonds in the VOC are saturated and whether the VOC is oxygenated. Serious problems have been observed for higher molecular weights, ( $\geq C_8$ ) particularly NMHCs, which have a high probability of participating in particle formation. Clearly, one of the most critical needs of the ambient VOC measurement community is a rigorous field intercomparison of measurement techniques. Such an intercomparison will more clearly define measurement capabilities and identify prevalent problems that must be addressed.

#### Meteorological Measurements

Ground-level methods for meteorological observations are routine, precise, accurate, and inexpensive. They are deployed in all monitoring networks and are well understood and appreciated by most scientists who use them. In addition, accurate measurements of meteorological parameters aloft are essential for understanding and modeling PM sources, chemistry, transport, and deposition. New insight has been gained from measurements aloft regarding the complexity of the meteorological processes that control air quality and the need for better observations and models. However, these measurements are more complicated, difficult to operate and maintain, expensive, difficult to calibrate, and relatively new. NOAA maintains a sparse national network of radar profilers to measure wind speed and direction aloft in the U.S. Midwest and along both coasts for tracking severe weather. This network also can provide valuable information for air quality management.

## 5.5 POLICY IMPLICATIONS

The ultimate deployment of measurements must consider the level of confidence needed in the data, the uncertainty associated with the measurements, the resolution of the data, and the intended use of the information. Multiple measurement strategies – routine, special study, intensive periods – are required to estimate human exposure, support epidemiological studies, identify the sources and understand the evolution of aerosols in the atmosphere, and track the success of

implementation. *Implication:* The intended purpose of the data should drive selection of the measurement method, and the spatial and temporal resolution of the measurement. The most effective measurement strategy requires a complement of long-term routine measurements, focused special studies and intensive field studies.

There is a need for a basic suite of chemical measurements at spatially representative sites to provide the full picture of PM formation, transport, trends, and impacts. For example, a minimum suite would be: PM mass (fine and coarse), speciation of the six major components ( $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ , OC, BC, crustal material), ground-level ozone, the precursor gases ( $NO_x$ ,  $SO_2$ ,  $>C_7$  VOCs, and  $NH_3$ ),  $HNO_3$  and CO, with meteorological measurements. *Implication:* A focused suite of measurements is necessary to characterize the limiting processes and chemical reagents leading to particle formation and growth, to link ambient concentrations and exposure to sources, and to illustrate the short- and long-term impact of management strategies.

The large number of properties needed to fully define PM (e.g., size, mass, number, and composition) as well as the impact of related parameters (e.g., gases, meteorological variables) makes it challenging to determine the uncertainty inherent in any of the particle measurements. At present, PM measurement uncertainty for many properties is estimated by instrument comparisons among different methods which determine similar properties of sampled particles. *Implication:* The science community relies on convergence of methods, not absolute calibration, as a guide to measurement certainty. Currently, measurement confidence varies according to the specific particle characteristic that is being measured and even the conditions under which it is being measured.

Significant progress has been made in the past several years to develop instrumentation for real-time, continuous measurements of particle mass and composition. Comparability studies indicate that filter-based methods and continuous measurements each have useful roles to play in managing and tracking PM. However, continuous real-time methods can supply additional information that can improve understanding of the formation, redistribution and

loss of PM in the atmosphere, the sources of that PM, and the relation between PM and human health. *Implication:* Over the next few years the availability and capability of routine real-time, continuous instrumentation will improve substantially. Efforts should be made to augment and/or replace the filter methods with these continuous methods.

Measurement confidence and ability to characterize the carbon fraction, speciated organics, the semivolatile species, the relative amounts of OC and BC, and the relative contributions of primary and secondary carbon is evolving, but limited. *Implication:* The carbon fraction is typically 1/5 to 1/2 of the total particle mass, and the limited information about this major component handicaps understanding of PM formation and evolution, and inhibits the development of management strategies.

The health-research community (including epidemiological, toxicological and clinical researchers) is restricted to investigations of the impacts of PM characteristics that can be measured, and require sufficient data from these measurements to assess health impacts. Of the many hypothesized causal elements of PM impacts, there are only sufficient ambient data to test about half. Measurements of many of the potential causal agents also require highly trained investigators. *Implication:* Progress in elucidating causal mechanisms and the sources that may be most responsible for PM health impacts are contingent upon the development and monitoring of the hypothesized elements. Population-level studies typically require relatively long-term data sets to achieve statistically significant results.

Investigation and assessment of health impacts have been based upon PM data obtained from gravimetric methods and are the basis of current ambient PM standards. Numerous advanced measurement methods are emerging that can measure additional PM properties, e.g., single-particle mass spectrometry, particle density, ultrafine particle size and number distribution, and size-resolved composition. *Implication:* New PM mass and composition measurements related to health impacts need to be linked to the historical context, and will provide insights into the fundamental properties and relative source contributions of particles providing

the ability to differentiate between sources, local versus regional contributions, primary versus secondary aerosol constituents, and natural versus anthropogenic contributions.

The gravimetric filter-based methods (for example, the U.S. Federal Reference Method) may underestimate or overestimate the concentration of  $PM_{2.5}$  due to loss of volatile components or the adsorption of gases. These losses or gains may be significant under certain circumstances and the parameters that affect these variables and related amounts are only now being quantified. *Implication:* Uncertainty in the gravimetric characterization of PM mass can impact the status of compliance within a given region. A better understanding of the uncertainty of these gravimetric methods for  $PM_{2.5}$  is needed to determine if national standards are being achieved.

## 5.6 REFERENCES

- Apel, E.C., Calvert, J.C., Gilpin, T.M., Fehsenfeld, F. C., Parrish, D.D., Lonneman, W.A., 1999. The Non-Methane Hydrocarbon Intercomparison Experiment (NOMHICE): Task 3. *Journal of Geophysical Research* 104, 26,069-26,086.
- Chow, J.C., 1995. Critical review: measurement methods to determine compliance with ambient air quality standards for suspended particles. *Journal of the Air and Waste Management Association* 45, 320-382.
- Chow, J.C., Watson, J.G., 2001. Ion chromatography. In *Elemental Analysis of Airborne Particles*, Landsberger, S. and Creatchman, M., eds. Gordon and Breach, Newark, NJ, pp. 97-137.
- Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merrifield, T., 2001. Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Science and Technology* 34, 23-34.
- Collett, J.L., Hoag, K.J., Pandis, S.N., 1998. The influence of drop size-dependent fog chemistry and aerosol production and deposition in San Joaquin Valley fogs. Prepared for the California Regional PM10/PM2.5 Air Quality Study c/o the

## CHAPTER 5

- California Air Resources Board, Technical Support Division, Sacramento, CA.
- Demerjian, K.L., 2000. A review of national monitoring networks in North America. *Atmospheric Environment* 34, 1861-1884.
- Evans, G.F., Highsmith, R.V., Sheldon, L.S., Suggs, J.C., Williams, R.W., Zweidinger, R.B., Creason, J.P., Walsh, D., Rodes, C.E., Lawless, P.A., 2000. The 1999 Fresno particulate matter exposure studies: comparison of community, outdoor, and residential PM mass measurements. *Journal of the Air and Waste Management Association* 50, 1887-1896.
- Huebert, B.J., Charlson, R.J., 2000. Uncertainties in data on organic aerosols. *Tellus* 52B, 1249-1255.
- Jones, A.S., Guch, I.C., Vonder Haar, T. H., 1998. Data assimilation of satellite-derived heating rates as proxy surface wetness data into a regional atmospheric mesoscale model. Part I: methodology. *Monthly Weather Review* 126(3), 634-645.
- McMurry, P.H., 2000. A review of atmospheric aerosol measurements. *Atmospheric Environment* 34, 1959-1999
- Marple, V.A., Olson, B.A., 2001. Inertial, gravitational, centrifugal, and thermal collection techniques. In *Aerosol Measurement: Principles, Techniques and Applications*, Second Edition, Baron, P.A. and Willeke, K., eds. Van Nostrand Reinhold, New York, NY.
- Middlebrook, A.M., Murphy, D.M., Lee, S.H., Thomson, D.S., Prather, K.A., Wenzel, R.J., Liu, D.Y., Phares, D.J., Rhoads, K.P., Wexler, A.S., Johnston, M.V., Jimenez, J.L., Jayne, J.T., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Hering, S.V., Weber, R.J., Jongejan, P., Slanina, J., and Dasgupta, P.K., 2003. A comparison of particle mass spectrometers during the 1999 Atlanta Supersite Experiment. *Journal of Geophysical Research*, in press.
- Pandis, S., Lillis, D., Collett, J., Richards, R.L., 1998. Fog effects on PM concentration and composition in the SJV. Prepared for the California Regional PM10/PM2.5 Air Quality Study c/o the California Air Resources Board, Technical Support Division, Sacramento, CA.
- Parrish, D.D., Fehsenfeld, F.C., 2000. Methods for gas-phase measurements of ozone, ozone precursors and aerosol precursors. *Journal of Geophysical Research* 34, 1921-1957.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30, 3837-3855.
- Seigneur, C., Pun, B., Prasad, P., Louis, J-F., Solomon, P.A., Koutrakis, P., Emery, C., Morris, R., White, W., Zahniser, M., Workshop, D., Tombach, I., 1998. Guidance for the performance evaluation of three-dimensional air quality modeling systems for particulate matter and visibility, Appendix A: Measurement methods. Prepared for the American Petroleum Institute, Washington, DC by Atmospheric Environmental Research, Inc., San Ramon, CA.
- Solomon, P.A., Baumann, K., Edgerton, E., Tanner, R., Eatough, D., Modey, W., Marin, H., Savoie D., Natarajan, S., Meyer, M.B., Norris, G., 2003. Comparison of integrated samplers for mass and composition during the 1999 Atlanta Supersites project. *Journal of Geophysical Research*, in press.
- Turpin, B.J., Saxena, P., Andrews, E., 2001. Measuring and simulating particulate organics in the atmosphere: Problems and prospects. *Atmospheric Environment*, 34, 2983-3013.
- U.S. EPA, 2002. National Air Quality Monitoring Strategy. Available at [www.epa.gov/ttn/amtic/stratdoc.html](http://www.epa.gov/ttn/amtic/stratdoc.html).

- Watson, J.G., Chow, J.C., Moosmüller, H., Green, M.C., Frank, N.H., Pitchford, M.L., 1998. Guidance for using continuous monitors in PM<sub>2.5</sub> monitoring networks . Report No. EPA-454/R-98-012. Prepared by U.S. Environmental Protection Agency, Research Triangle Park, NC.
- Watson, J.G., Chow, J.C., 2002. Comparison and evaluation of in-situ and filter carbon measurements at the Fresno Supersite. *Journal of Geophysical Research*, Submitted for publication.
- Williams, K.R., Fairchild, C.I., Jaklevic, J.M., 1993. Dynamic mass measurement techniques. In *Aerosol Measurement: Principles, Techniques and Applications*, Willeke, K. and Baron, P.A., eds. Van Nostrand Reinhold, New York, NY, pp. 296-312.
- Williams, R., Suggs, J., Zweidinger, R., Evans, G., Creason, J., Kwok, R., Rodes, C., Lawless, P., and Sheldon, L., 2000a. The 1998 Baltimore particulate matter epidemiology-exposure study: Part 1. Comparison of ambient, residential outdoor, indoor and apartment particulate matter monitoring. *Journal of Exposure Analysis and Environmental Epidemiology* 10, 518-532.
- Williams, R., Suggs, J., Creason, J., Rodes, C., Lawless, P., Kwok, R., Zweidinger, R., and Sheldon, L., 2000b. The 1998 Baltimore particulate matter epidemiology-exposure study: Part 2. Personal exposure assessment associated with an elderly study population. *Journal of Exposure Analysis and Environmental Epidemiology* 10, 533-543.
- Williams, R., Creason, J., Zweidinger, R., Watts, R., Sheldon, L., and Shy, C., 2000c. Indoor, outdoor, and personal exposure monitoring of particulate air pollution: the Baltimore elderly epidemiology-exposure pilot study. *Atmospheric Environment* 34, 4193-4204.

## CHAPTER 5