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Continuous and Semicontinuous Monitoring Techniques for Particulate Matter Mass and Chemical Components: A Synthesis of Findings from EPA's Particulate Matter Supersites Program and Related Studies

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) established the Particulate Matter (PM) Supersites Program to provide key stakeholders (government and private sector) with significantly improved information needed to develop effective and efficient strategies for reducing PM on urban and regional scales. All Supersites projects developed and evaluated methods and instruments, and significant advances have been made and applied within these programs to yield new insights to our understanding of PM accumulation in air as well as improved source-receptor relationships. The tested methods include a variety of continuous and semicontinuous instruments typically with a time resolution of an hour or less. These methods often overcome many of the limitations associated with measuring atmospheric PM mass concentrations by daily filter-based methods (e.g., potential positive or negative sampling artifacts). Semicontinuous coarse and ultrafine mass measurement methods also were developed and evaluated. Other semicontinuous monitors tested measured the major components of PM such as nitrate, sulfate, ammonium, organic and elemental carbon, trace elements, and water content of the aerosol as well as methods for other physical properties of PM, such as number concentration, size distribution, and particle density. Particle mass spectrometers, although unlikely to be used in national routine monitoring networks in the foreseeable future because of their complex technical requirements and cost, are mentioned here because of the wealth of new information they provide on the size-resolved chemical composition of atmospheric particles on a near continuous basis. Particle mass spectrometers likely represent the greatest advancement in PM measurement technology during the last decade. The improvements in time resolution achieved by the reported semicontinuous methods have proven to be especially useful in characterizing ambient PM, and are becoming essential in allowing scientists to investigate sources of particulate pollution and to probe into the dynamics and mechanisms of aerosol formation in the atmosphere.

IMPLICATIONS

Significant advances in the measurement of PM chemical and physical properties have resulted as an outcome of EPA's PM Supersites Program over the last 5–7 yr. This paper focuses on continuous methods for these parameters and provides recommendations addressing the question "Are there routine monitoring techniques that are at a stage of understanding and operational skill that should be instituted in routine monitoring networks so that we will have better information in a few years?" Application of continuous methods with greatly improved time resolution has already led to understanding more thoroughly atmospheric processes leading to PM accumulation in air and the linkages between PM sources and ambient concentrations of PM observed at receptor locations. Air quality managers can use this information in network design, and thus, to develop more cost-effective and efficient strategies for reducing PM to below the levels of the national Ambient Air Quality Standards to protect public health and ecosystems from the adverse effects of particulate matter.

INTRODUCTION

Numerous epidemiological studies have found persistent associations between ambient concentrations of particulate matter (PM) and significant adverse health effects.[1] An improved understanding of factors influencing human exposure to PM is important for the development of effective control strategies designed to reduce the health impacts of airborne particulate matter.[2] This requires a better understanding of the composition and physical properties of $PM_{2.5}$ (particles less than 2.5 μm aerodynamic diameter [AD]), which depends on high-quality measurements of size, concentration, composition, other parameters of $PM_{2.5}$, and related species.

The U.S. Environmental Protection Agency (EPA) responded to this need with an ambient monitoring research program, commonly referred to as the Particulate Matter Supersites Program.[3] The primary goals of the program are to provide unprecedented physicochemical

characterization of ambient PM that contributes to a better understanding of PM sources and formation mechanisms, support health effects and exposure research, and conduct development and testing of novel state-of-the-art sampling methods of PM mass and chemical speciation. Atlanta, GA, and Fresno, CA, were chosen as initial Supersites Projects[4,5] for Phase I on the basis of their ongoing and planned research activities and their distinctively different airsheds. In January 2000, Phase II started with Supersites Projects in Baltimore, MD; Fresno, CA; Houston, TX; Los Angeles, CA; New York, NY; Pittsburgh, PA; and St. Louis, MO.

This paper focuses on the third goal of testing methods, specifically in this case, for near continuous measurement of physical and chemical PM properties. Many of the methods developed and/or tested through the Supersites Program are capable of resolving PM size and composition at high time resolution (hourly or shorter), but had not been thoroughly evaluated or previously deployed in regulatory monitoring networks. The need to develop monitors that measure particle properties in relatively short time intervals is important for improving our understanding of adverse health impacts, atmospheric chemistry, and sources of PM. This is because sources, meteorology, and atmospheric processes of PM pollutants often vary on time scales substantially shorter than 24 hr. The daily averaging times used in many current networks tend to smooth out much of this variability, which limits our understanding of the factors influencing PM accumulation in air and exposures that result in the adverse impact of PM. Moreover, attempting to routinely obtain a better time resolution for ambient particle concentrations for large monitoring networks is presently impractical with the traditional time-integrated measurements that are based on field sampling and subsequent laboratory analysis of particle mass or chemical composition.

The purpose of this paper is to review results from the evaluation of continuous and semicontinuous methods for the measurement of mass, chemical composition, and physical properties of PM with an emphasis on the question, "Are there advanced monitoring techniques that should be instituted into routine networks so that we will have better information in a few years?" Many of the studies reviewed in this paper have been published in one of the special journal issues on research performed within the Supersites Program,[6–9] and although this review is not limited to those papers, it is not an exhaustive review of the work conducted over the last 5–7 yr.

The first part of this paper covers methods measuring physical properties of ambient PM. One section describes development and testing of continuous methods for the direct measurement of mass concentration. The aim of these methods was to minimize potential positive or negative sampling artifacts (e.g., absorption or volatilization of semi-volatile compounds) associated with collecting atmospheric PM on a filter. Also reviewed in this section are mass monitors developed for PM size ranges different from $PM_{2.5}$, including ultrafine and coarse PM mass. In the following section, the indirect measurement of mass concentration is described from the combination of size distribution data obtained by different methods. Lastly, the first part reports on performance studies of a new water-based condensation particle counter (WCPC) for total number concentration, an approach to measure the density of particles in a given size range, and a system to measure the water content of ambient aerosol by comparison of ambient (wet) and dried size distributions.

The second part describes near continuous methods related to the determination of the chemical composition of PM in ambient air. Reviewed in this section are semicontinuous methods for sulfate, nitrate, elemental carbon (EC), organic carbon (OC), and trace elements. In addition, particle mass spectrometry (MS) methods are briefly mentioned.

PHYSICAL PROPERTIES OF PM

Continuous Gravimetric Methods for Mass Concentration

Continuous and integrated methods for mass have been developed with two different objectives. Some methods were developed, at least initially, to be comparable to the Federal Reference Method (FRM) for $PM_{2.5}$ mass. These are methods that might be considered as Federal Equivalent Methods (FEMs) and provide regulatory related data on a daily basis or even an hourly basis. However, the FRM is a regulatory standard and not an analytical standard (Fehsenfeld et al.[10]) and has been found to be influenced by sampling artifacts (e.g., loss of semi-volatile material) under certain conditions as described later in this paper. Other methods, and often the goal of the continuous methods developed and evaluated within the Supersites Program, include measuring the actual PM mass as found in ambient air, by accounting for loss of semi-volatile species, water retention, or other sampling and analysis artifacts. Methods based on both types of approaches are described below.

Tapered Element Oscillating Microbalance (TEOM). The TEOM monitor provides a continuous measure of collected mass.[11] It uses a filter for particle collection and is therefore subject to the same artifact and interference problems that other filter-based methods suffer, including negative artifacts from the loss of semi-volatile material collected during sampling, and positive artifacts from absorption or adsorption of gaseous components on deposited particles and/or the filter media. The original version of the TEOM was operated with the filter heated to 50 °C to eliminate or limit the interference from particle-bound water.[11,12] Heating to a controlled temperature is also necessary to make the response of the sensor, which is sensitive to temperature, more stable, resulting in reproducible measurements of ambient coarse PM (PM_{10}) or $PM_{2.5}$. However, the heating results in enhanced losses of semi-volatile material from the collected particles.[12]

Real-Time Ambient Mass Sampler (RAMS). To address the issue of semi-volatile losses during sampling with the TEOM, a real-time monitor was developed using a TEOM with a "sandwich" filter, which was designed to retain semi-volatile material evaporating from collected particles.[13–15] The RAMS[13] represents the first attempt to measure $PM_{2.5}$ mass free of both positive and negative sampling artifacts. The complexity of the system described

below begins to suggest how difficult it is to measure artifact-free $PM_{2.5}$ mass.

The RAMS removes gas-phase components from the stream of sampled air to avoid positive artifacts on the TEOM filter and then uses a reactive filter to capture any semi-volatile material that may evaporate from the particles during sampling. This is accomplished in multiple steps. First, a 2.5-μm cut point cyclone is followed by a particle concentrator that removes 70% of the gas-phase, thereby concentrating fine particles.[15–17] An annular denuder then removes nitrogen dioxide (NO_2) and part of the ozone (O_3) from the remaining gas-phase. The denuder is followed by a Nafion diffusion dryer to remove water. The sample flow is then split into two equal parts and delivered to two nearly identical sampling lines, one of which is preceded with a quartz-fiber (QF or quartz) filter and represents a blank for online correction. Both lines then include a Brigham Young University Organic Sampling System (BOSS) diffusion denuder[17] to remove gas-phase compounds that can be absorbed by charcoal, followed by an additional annular denuder to remove NO_2 formed in the BOSS denuder and another Nafion diffusion dryer. The sample stream finally passes the TEOM sandwich filter, in which a Teflon filter is backed up by a charcoal-impregnated filter (CIF) to adsorb ammonium nitrate (NH_4NO_3) and semi-volatile organic compounds lost from particles during sampling.

The RAMS has been evaluated in a number of locations where semi-volatile material was a significant fraction of the ambient PM. Two of these sets of studies are highlighted below, and additional discussions are given in following sections in comparison to other samplers where the RAMS is considered the historical reference sampler. The RAMS was evaluated in Salt Lake City, UT,[18] during three intensive sampling periods (winter 1999–2000, summer 2000, and winter 2000–2001). In these studies, a RAMS was collocated with a TEOM monitor (50 °C in summer and 30 °C in winter) and a Particle Concentrator-Brigham Young University Organic Sampling System (PC-BOSS[19]) diffusion denuder-integrated sampler. The PC-BOSS is the filter-based, time-integrated counter part to the RAMS and uses filters rather than a TEOM to collect particles. Mass is determined gravimetrically in the laboratory. Excellent agreement, based on linear regression of 24-hr averaged data across all three study periods (R^2 = 0.90, slope of 1.00 ± 0.02, and zero intercept), was observed between the RAMS and sum of the species from the PC-BOSS. The sum of the species as measured by the PC-BOSS provides a good estimate of nonvolatile and semi-volatile PM mass excluding water (see Long et al.[18] and references within). Similar regression statistics were observed for shorter average sampling periods as well. One-hour average $PM_{2.5}$ RAMS versus TEOM data showed statistically significant differences between the two methods with lower values reported by the TEOM by as much as 31% for samples collected during the winter study and 42% for samples collected during summer with R^2 in the range of 0.4–0.6. These differences were due to a loss of semi-volatile material from the TEOM sampler, which as described by Long et al.[18] and discussed later in this paper, appeared to be a reasonable estimate of nonvolatile $PM_{2.5}$ mass. Filter-based FRM $PM_{2.5}$ concentrations were found to under-report $PM_{2.5}$ only during warm dry periods. Loss of semi-volatile material from the TEOM when operated at 50 °C is well established in the literature and has motivated the research community and the manufacturer to implement additional measures to ensure improved mass measurements by the TEOM by minimizing losses of semi-volatile material and the influence of water. These methods are discussed in the following sections.

The RAMS also was tested in a series of field studies by comparing its concentrations to those obtained with a TEOM and a PC-BOSS.[13] These studies occurred in the dry winter climate of Provo, UT; in the humid summer climate of Philadelphia, PA; and in Atlanta, GA, during the 1999 Atlanta Supersites project.[5] In Atlanta, the TEOM was heated at 30 °C and preceded by Nafion dryer to reduce relative humidity (RH) to below 40%. At the other two sites, the TEOM was heated to 50 °C without a dryer. On average, the TEOM reported 82% of RAMS $PM_{2.5}$ concentrations in Provo and Atlanta, whereas in Philadelphia, the TEOM varied more, measuring 50–85% of RAMS concentrations (see Table 1). The higher content of semi-volatile material found in Philadelphia indicated that the higher $PM_{2.5}$ mass determined with the RAMS was due to both semi-volatile nitrate and organic material not measured by the TEOM.

Table 1. Comparison of RAMS and TEOM monitoring data (μg/m^3).

Sample Location	RAMS $PM_{2.5}$ Average	TEOM $PM_{2.5}$ Average	TEOM Monitor % of RAMS $PM_{2.5}$
Provo, UT			
December 11–15	23.9	19.3	81
Philadelphia, PA			
July 17–18	54.1	36.0	67
July 22–29	41.9	27.4	65
July 22–24	48.0	40.6	85
July 25–29	37.3	18.5	50
Atlanta, GA			
August 8–11	44.5	37.2	84

Notes: Measurements were conducted in Provo, UT, in December 1998; Philadelphia, PA, in July 1999; and Atlanta, GA, in August 1999 during the 1999 Atlanta Supersites Project. Reprinted with permission from Eatough et al.[13] Copyright 2001 American Association for Aerosol Research.

Sample Equilibration System (SES) TEOM. To minimize volatilization associated with the 50 °C TEOM, it was operated at 30 °C; however, water removal was limited, and in a variety of environments 30 °C was not sufficient for stable operation. To help overcome these problems, a SES was developed in which the 30 °C TEOM was preceded by a diffusion dryer.[20] When sampling generated particles of ammonium sulfate, copper sulfate, and potassium nitrate in the laboratory, Schwab et al.[21] observed that the 30 °C TEOM with a dryer clearly responded to step changes in humidity; however, the mass gain was less than that without the dryer and just slightly higher than the bare tapered element sensor with no filter. Results also indicated that most of the mass gain appeared to be due to water collected by the filter because only a slight increase in mass was observed with a particle-laden filter as compared with a clean filter. The 30 °C SES-equipped TEOM was even less sensitive to changes in humidity at a lowered flow rate of 1 min^{-1} as compared with the usual flow rate of 3 min^{-1}, likely because of the Nafion dryer being more efficient at removing water at the lower flow rate.

The SES TEOM, RAMS, and Continuous Ambient Mass Monitor (CAMM[22]) were operated in comparison studies in Atlanta, Baltimore, and Pittsburgh by Lee et al.[23] The CAMM is described later in this paper. Among the continuous samplers, the SES TEOM was in best agreement with the FRM mass concentrations (with $R^2 \geq 0.9$ and slopes close to 1 at all three sites), suggesting that both had similar losses of semi-volatile materials. This is consistent with results from other studies that reveal the TEOM loses semi-volatile aerosol components during sampling. The RAMS appeared to measure total ambient PM, including semi-volatile materials. The mass differences observed between the RAMS and either the CAMM or SES TEOM could be accounted for by the loss of NH_4NO_3 and semi-volatile organic material.

Lee et al.[24] also evaluated the SES TEOM (at 30 °C) during the summer in Houston, TX, and winter in Seattle, WA, and compared it to collocated RAMS, CAMM, and filter-based samplers. Measurements were obtained after 30 or 60 min of sampling. Reasonably good agreement was observed between pairs of the continuous mass samplers (see Table 2). RAMS measurements had slightly higher, but comparable $PM_{2.5}$ mass to the integrated filter measurements in warm and dry conditions in Houston (slope = 1.10 at R^2 = 0.89), whereas RAMS $PM_{2.5}$ mass concentrations appeared to be slightly lower, but comparable to filter-based mass during cold and humid periods in Seattle (slope = 0.92 at R^2 = 0.78). Similar dependence on RH and temperature was found for differences between RAMS and SES TEOM in Houston, which suggested that the loss of semi-volatile NH_4NO_3 contributed to the mass difference. An explanation could be that volatilization of semi-volatile materials from the filter-based measurements of $PM_{2.5}$ is expected to decrease during the colder winter period.[18] The results also corroborate the earlier finding that setting the TEOM at a lower temperature than the standard configuration would still lose semi-volatile materials.

Differential TEOM. The Differential TEOM (D-TEOM) was developed by Patashnick et al.[25] to further minimize positive and negative sampling artifacts, including effects observed with humidity. Initially, the system consisted of an inlet, dryer, two electrostatic precipitators (ESPs), and two TEOM monitors in parallel. In its commercial form, ambient aerosol is sampled through a standard inlet followed by a diffusion dryer, which is followed by an ESP and then a single TEOM. When the ESP is turned on, all particles are collected by the ESP[26] and the mass change detected by TEOM is due to potential negative or positive sampling artifacts as described above. The ESP is switched on and off with a switching time that is long enough for measurable volatilization to occur but sufficiently short enough not to allow influence by atmospheric changes. These assumptions were confirmed for NH_4NO_3.[27] In these laboratory studies, the dynamics of volatilization from the D-TEOM was examined at two operating filter temperatures: 30 °C and 35 °C. Results showed that losses of NH_4NO_3 from the TEOM filter occurred on a time scale that was longer than the 5-min cycle time used by the D-TEOM. This was important because it established that vaporization measured during the alternate 5-min periods could be used effectively as a reference baseline value for particle mass measurements. Thus, the D-TEOM is self referencing,[25] where the measurement with the ESP turned on was used to correct the prior measurement of

Table 2. Deming slopes and intercepts for $PM_{2.5}$ mass between pairs of continuous mass samplers.[a]

$PM_{2.5}$ Mass		$[Y] = b^*[X] + a$				
[*Y*]	[*X*]	*b*	*a*	Error	R^2	N
Houston						
[CAMM]	[Adj RAMS]	0.93 ± 0.03	3.14 ± 0.74	6.10	0.81	203
[30 °C TEOM]	[Adj RAMS]	0.92 ± 0.03	1.52 ± 0.77	6.37	0.80	204
[30 °C TEOM]	[CAMM]	1.01 ± 0.03	−1.91 ± 0.79	5.89	0.83	204
Seattle						
[CAMM]	[RAMS]	1.07 ± 0.05	1.03 ± 0.55	4.39	0.61	362
[30 °C TEOM]	[RAMS]	0.95 ± 0.03	1.24 ± 0.38	3.24	0.72	362
[30 °C TEOM]	[CAMM]	0.87 ± 0.03	0.55 ± 0.37	3.01	0.74	361

Notes: Measurements were conducted in Houston, TX, during the summer in conjunction with the 2000 TexAQS and in Seattle, WA, during the winter, January–February 2001 (from Lee et al.[24]). Reprinted with permission. Copyright 2005 American Association for Aerosol Research. [a]Uncertainties are 95% confidence intervals. The error is the standard error of the regression. R^2 = correlation coefficient; N = number of samples.

PM when the EPS was off. This configuration has been tested in several studies, as described below.

Schwab et al.[21] also tested a D-TEOM during their laboratory studies of the SES TEOM. Their analysis indicated that the D-TEOM could be a robust technique for the continuous real-time measurement of ambient aerosol mass, even in the presence of semi-volatile components and condensable gases, such as sulfur dioxide (SO_2) and NO_2. Figure 1 shows the response of the D-TEOM to laboratory-generated NH_4NO_3. Note that the calculated D-TEOM mass concentration measurements report the presence of NH_4NO_3 during generation and a mass concentration of zero afterward. Note also that the negative mass measured when the ESP is turned on is an estimate of the loss of semi-volatile material.

Hering et al.,[27] Jaques et al.,[28] and Lee et al.[29] performed field evaluations of the D-TEOM in Southern California in locations with high nitrate concentrations, including Claremont and Rubidoux, the latter having some of the highest nitrate concentrations in the country. Jaques et al.[28] field-tested two collocated $PM_{2.5}$ D-TEOM monitors in Claremont, CA, from September 2001 to August 2002. The D-TEOM monitors used 5-min switching periods for the ESP at a TEOM sensor temperature of 30 °C; 24-hr time-integrated mass concentrations of the D-TEOM were compared with collocated Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corp.) and dichotomous Partisol (Dichotomous Partisol-Plus, Rupprecht and Patashnick (R&P) Model 2025; R&P is now part of Thermal Electron, Inc.) gravimetrically determined mass measurements. A high correlation (R^2 = 0.94, slope = 0.98) between the 24-hr integrated concentrations of the two D-TEOMs was obtained, indicating the high precision of the instruments. Comparison of the 5-min data showed that the response of the two instruments tracked each other well, that significant changes in ambient PM levels occurred on a time scale as short as 15 min, and that these changes are successfully tracked by the D-TEOM.[28] $PM_{2.5}$ mass concentrations from collocated MOUDI and Partisol samplers correlated well with the D-TEOM (R^2 = 0.86 and 0.83, respectively). The Partisol measured lower $PM_{2.5}$ concentrations than the MOUDI, whereas the D-TEOM measurements were higher than the MOUDI, suggesting that the MOUDI still encounters loss of semi-volatile species, including semi-volatile organics, albeit less than typically observed by integrated filter measurements.[30] Also in Claremont, Hering et al.[27] showed that under ambient conditions (February–June 2002), the vaporization reference signals (negative artifact measured by the reference) from the D-TEOM tracked well the ambient particulate nitrate concentration measured with a collocated cascaded Integrated Collection and Vaporization System (ICVS)[31] (Figure 2). The ICVS is described later in this paper.

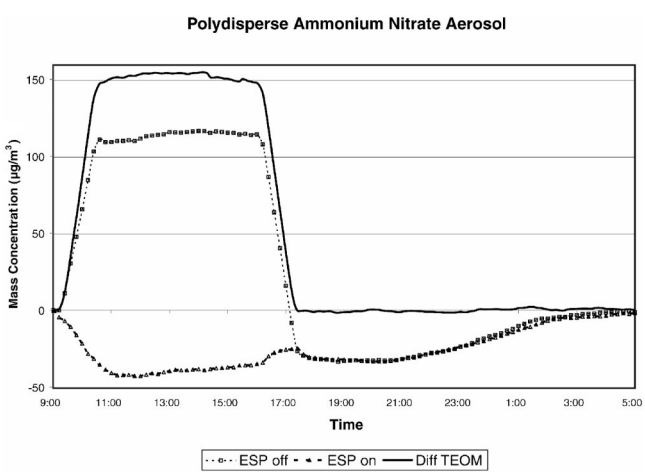

Figure 1. Generation and evaporation of NH_4NO_3 aerosol measured using the D-TEOM monitor. Atomization of the NH_4NO_3 solution began at 9:10 a.m. and ended at 4:35 p.m. Data in this plot are 1-hr running average values. Notice that the calculated D-TEOM mass concentration measurements report the presence of NH_4NO_3 during generation and mass concentration of zero afterward. Adapted with permission from Schwab et al.[21] Copyright 2004 Air & Waste Management Association.

In nearby Rubidoux, CA, Lee et al.[29] compared the $PM_{2.5}$ mass obtained by the D-TEOM with that of the RAMS, CAMM, and FRM Partisol, the latter an integrated filter-based method for $PM_{2.5}$ mass. The D-TEOM performed better in measurements of semi-volatile species than the CAMM or RAMS, and the RAMS typically measured more $PM_{2.5}$ mass than the CAMM. The FRM showed significant loss of semi-volatile material. Near artifact-free NH_4NO_3 was measured by a collocated Harvard-EPA annular denuder (HEADS)[32] and the measured nitrate was approximately equivalent to the difference of D-TEOM and FRM mass concentrations.

Schwab et al.,[21] Hering et al.,[27] Jaques et al.,[28] and Lee et al.[29] concluded that the D-TEOM monitor provides a good estimate, under the high nitrate conditions tested, of the actual ambient PM present on a near-continuous basis.

Filter Dynamics Measurement System (FDMS). The FDMS[33] was developed to account for loss of semi-volatile species relative to the previously mentioned TEOM methods. However, the FDMS uses a cold filter at 4 °C to remove particles and obtain particle-free air, rather than an electrostatic precipitator. The air is first conditioned with an SES diffusion dryer to remove water, after which the FDMS uses a switching cycle of 6 min, alternately sampling ambient and particle-free air. The loss or gain of semi-volatile material by the TEOM sensor is then accounted for by the period of particle-free air, similar to that of the D-TEOM. The FDMS was tested by Grover et al.[34] in two field studies to determine how well it measured total fine PM, including the semi-volatile ammonium (NH_4^+), nitrate, and organic material. Results from the FDMS were compared with results from a TEOM heated to 30 °C, D-TEOM, RAMS, and integrated PC-BOSS sampler in Lindon, UT, in February 2003. In July of the same year, the FDMS was compared with a TEOM (50 °C), RAMS, and PC-BOSS in Rubidoux, CA. A continuous R&P nitrate monitor (R&P Model 8400N) and a continuous Sunset carbon analyzer (Sunset Laboratories Inc.) were collocated in Rubidoux with the continuous mass monitors. The FDMS and D-TEOM monitors needed little attention from site operators during their studies and appeared to be rugged units. Results from these studies indicated that on average the FDMS and D-TEOM monitors both measured total $PM_{2.5}$, including the semi-volatile PM. However, for

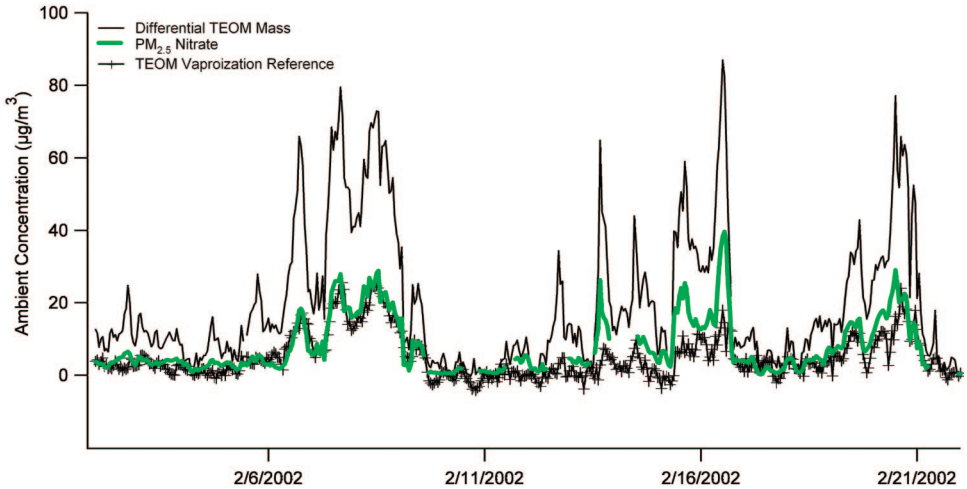

Figure 2. Hourly $PM_{2.5}$ mass and vaporization reference signals from the mean of collocated D-TEOM monitors, compared with hourly $PM_{2.5}$ NO_3 measured with the cascaded ICVS system during a wintertime period of relatively high NO_3 concentrations. The TEOM vaporization reference signal is the negative of the mass concentration measured during the particle-free measurement cycle. Adapted with permission from Hering et al.[27] Copyright 2004 Elsevier, *Atmospheric Environment*.

short-term high concentration episodes (38 of 474 data points), the FDMS was on average 21 $\mu g/m^3$ higher than the D-TEOM (noting that general concentrations ranged from 20–60 $\mu g/m^3$). Excluding these peak periods, the FDMS was on average only 1.2 $\mu g/m^3$ higher than the D-TEOM at an average $PM_{2.5}$ concentration of 35 $\mu g/m^3$, and the two methods were well correlated (R^2 = 0.85). Results from Grover et al.[34] also indicated that the FDMS agreed better with the RAMS and PC-BOSS measurements than did the D-TEOM, even during peak periods, although, in general, the comparisons were within expected uncertainties. Therefore, the authors recommended additional studies to determine whether the D-TEOM or FDMS is more accurate.

Grover et al.[34] also compared the 30 °C and 50 °C TEOM systems and FRM to the FDMS. Both of the heated TEOM samplers reported consistently lower $PM_{2.5}$ concentrations than the FDMS. In the case of the 50 °C TEOM, the difference was similar or slightly lower than the summed concentration of semi-volatile organics and NH_4NO_3, indicating almost complete loss of semi-volatile matter for this heated TEOM, which suggests a potential continuous method for measuring either the nonvolatile or semi-volatile components of PM mass, as illustrated in Figure 3.

$PM_{2.5}$ and PM_{10} Beta Attenuation Monitor (BAM). The BAM provides a direct continuous measurement of PM ($PM_{2.5}$ or PM_{10}) mass in air on the basis of the absorption of beta particles by PM deposited on a filter. In general, RH does

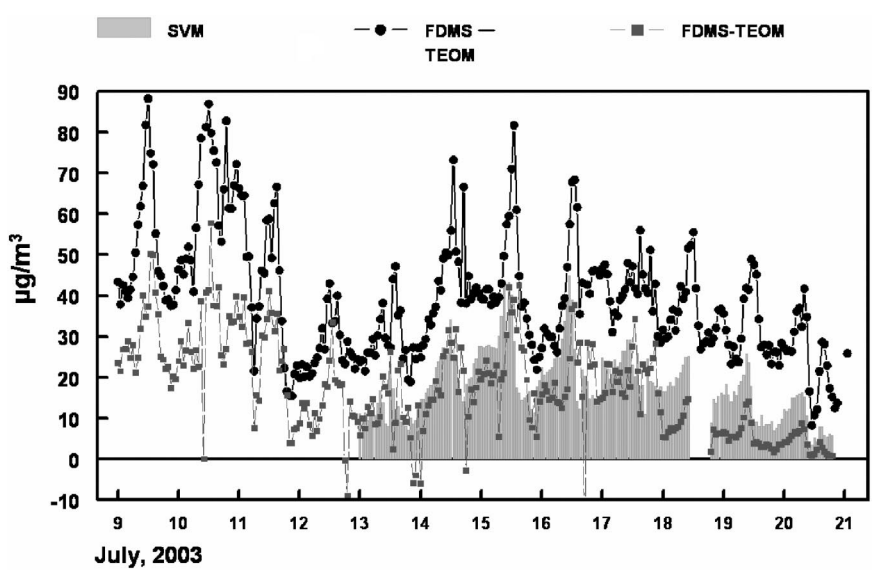

Figure 3. Data from the Rubidoux, CA, July 2003 study. The circles indicate 1-hr average FDMS $PM_{2.5}$ mass, the squares the difference between 1-hr average FDMS and a 50 °C TEOM monitor $PM_{2.5}$ mass, and the bars the sum of 1-hr average R&P $PM_{2.5}$ NH_4NO_3 mass measurements and the modified Sunset monitor semi-volatile organic material (SVOM) mass measurements. This sum is indicated as SVM, semi-volatile material. Reproduced/modified by permission of American Geophysical Union.[34] Copyright 2005 American Geophysical Union.

not affect the measurement so the filter is not intentionally heated, as with the TEOM. BAM monitors are commercially available from several vendors. The BAM employs a radioactive beta source (typically ^{14}C or ^{85}Kr) that emits beta particles that are absorbed by the PM collected on a filter that is located between the source and detector. The filter is a continuous tape that advances at specified times or particle loadings. The absorption is proportional to the amount of PM collected on the filter. The newly advanced filter is used as a reference. A more detailed description of the BAM is given by Wen et al.[35] The standard BAM has not changed much during the last 5 yr so further discussion of the standard BAM will not be given here. However, a BAM designed to measure ultrafine PM is discussed below and represents a significant new development employing the BAM monitor.

Ultrafine Mass Monitor (UF BAM). Ultrafine PM mass concentrations vary drastically over short time scales in the atmosphere and are potentially toxic,[36,37] thus, having important human health implications. Chakrabarti et al.[38] modified a BAM to measure quasi-ultrafine (i.e., <0.15 μm or $PM_{0.15}$) mass concentrations nearly continuously. The ultrafine BAM (UF BAM) is preceded by a 0.15-μm cut point impactor, which is designed to have a very low-pressure drop. The UF BAM was tested at a downwind receptor site in the Los Angeles Basin in Claremont, CA. It was operated using a 2-hr cycle and collocated with a Scanning Mobility Particle Sizer (SMPS), Aerodynamic Particle Sizer (APS), and MOUDI. The UF BAM and MOUDI were in excellent agreement (R^2 = 0.92, slope = 0.97), as shown in Figure 4. The SMPS, however, underestimated UF BAM $PM_{0.15}$ levels, with the underestimation being highest in early morning and nighttime and least toward the middle of the day. The authors suggested that this could be caused by differences in the classification of fractal-structured UF particles. Several fractal-agglomerate particles, with effective densities substantially lower than 1 g/cm^3,[39] may be detected by the UF BAM on the basis of their aerodynamic diameter (AD), but could be classified by the SMPS in higher size ranges on the basis of their physical or mobility diameter.[40] No correlation (R^2 = 0.001) was found between the $PM_{2.5}$ mass concentrations, as determined by the SMPS, APS, and $PM_{0.15}$ mass concentrations, thereby indicating that ultrafine mass concentrations, at least in Los Angeles, are independent of $PM_{2.5}$ concentrations. Little or no correlation was observed between concurrently measured particle number concentrations measured by the sum of the SMPS size channels, and the $PM_{0.15}$ (UF BAM) mass concentrations (R^2 = 0.06). These findings demonstrate the need for a continuous UF mass monitor to ensure effective assessment of the short-term variations in UF aerosols.

CAMM. The CAMM for $PM_{2.5}$ is described by Babich et al[22]. The measurement principle is based on an increased drop in pressure across a membrane filter (Fluoropore) during particle sampling. The pressure drop is proportional to the mass of the PM deposited. After passing through a $PM_{2.5}$ inlet, the airstream is dried below 40% RH using a Nafion diffusion dryer to remove particle-bound water (PBW) followed by collection of the particles on a filter tape at a flow rate of 0.3 min^{-1}. The tape advances about every 30–60 min so that particles remain close to equilibrium with the sampled air during collection. This also results in minimal volatilization and adsorption artifacts during sampling. The CAMM has a detection limit above 5 μg/m^3 for $PM_{2.5}$ concentrations averaged over 1 hr.[22] The performance of this monitor was investigated in a series of field studies conducted in seven cities with presumably different $PM_{2.5}$ chemical composition.[22] Twenty-four 1-hr CAMM measurements were averaged and compared with Harvard Impactor (HI) 24-hr $PM_{2.5}$ integrated measurements. On the basis of 211 valid sampling days, the measurements obtained from the HI and the CAMM were highly correlated (R^2 = 0.90). The average CAMM-to-HI concentration ratio was 1.07 ± 0.18. Other comparisons of the CAMM with the D-TEOM, SES TEOM, and RAMS were discussed in previous sections.

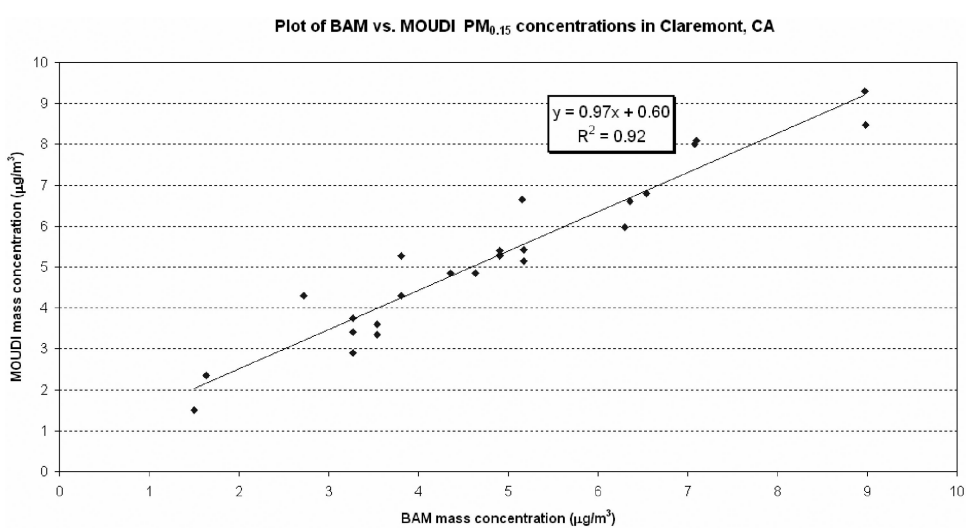

Figure 4. Plot of BAM (integrated over 4-hr periods) vs. MOUDI $PM_{0.15}$ concentrations in Claremont, CA. Adapted with permission from Chakrabarti et al.[38] Copyright 2004 American Association for Aerosol Research.

Coarse PM TEOM and BAM. Two continuous PM_c samplers ($PM_c = PM_{10}–PM_{2.5}$, i.e., particles in the size range between $PM_{2.5}$ and PM_{10}) are commercially available, one using the TEOM, and the other using the BAM as the detector. Both methods measure PM_c directly on filters. An indirect method using the APS is also discussed below. The PM_c TEOM[41] was developed and evaluated as part of the Southern California Supersites Project, and therefore is described in more detail here. The operating principle of the PM_c TEOM is based on enriching particles in the 2.5–10 μm range by a factor of approximately 25, while leaving fine mass ($PM_{2.5}$) at its ambient level. The resulting aerosol mixture is then sampled with a standard TEOM at 2 min^{-1}, the response of which is dominated by the contributions of the coarse PM, due to concentration enrichment. The enrichment of coarse particles is achieved with a PM_{10} sampling inlet operating at 50 min^{-1} followed by a 2.5-μm cut point round nozzle virtual impactor whose ratio of minor to total flow is 25 (Figure 5). This represents the ideal ratio, and wall losses and other factors may slightly influence it up or down. This continuous coarse particle monitor (CCPM) was tested in Los Angeles in a field comparison with integrated sampling methods using a MOUDI and a Partisol (Dichotomous Partisol-Plus, R&P Model 2025) employing sampling times from 90 to 210 min. Coarse mass concentration measured by the CCPM and either MOUDI (Figure 5) or Partisol were well correlated (with $R^2 = 0.88$ and 0.85, respectively) and had ratios between 26 and 27.[41] There was no difference observed in the response of the CCPM when the TEOM was heated to either 30 or 50 °C under the atmospheric conditions tested. Misra et al.[41] showed that the enriched concentrations allow for reliable measurements at time intervals as short as 5 min and suggested that its simplicity and reliability make it ideal for use in large scale monitoring networks. The PM_c BAM monitor also separates fine from coarse particles using a virtual impactor, but it operates at an inlet flow rate of 16.7 min^{-1} with a concentration factor of 10 rather than 25. In the commercial BAM, coarse and fine particles are measured with a time resolution of 1 hr.

Recent studies[42] were conducted by EPA at four locations (Research Triangle Park, NC [January 2003], Gary, IN [March 2003], Phoenix, AZ [May 2003, January 2004, May 2005], and Riverside, CA [July 2003]), to evaluate the PM_c TEOM and PM_c BAM (Kimoto Electric Co. Ltd., Japan) as potential FRM or FEM samplers. An APS was initially included in the study to provide size distribution data to understand better potential differences between the two direct reading PM_c samplers, but results suggested it might also prove suitable as a PM_c sampler as described below. The initial field comparisons in 2003 and 2004 (before modifications as mentioned below) indicated that the prototype commercial PM_c TEOM was low by 20–30% (TEOM/reference) under some conditions and relative to the reference method (PM_{10} FRM minus $PM_{2.5}$ FRM); however, the results were highly correlated (>0.95). The low values were believed to result from three factors. First, the inlet on the prototype PM_c TEOM had a cut point of 9 μm rather than 10 μm. Secondly, the TEOM was heated to 50 °C, as is the case for the standard TEOM. This latter effect may have resulted in the loss of semi-volatile coarse particle components, which in this size range could be organic species such as lower molecular weight polycyclic aromatic hydrocarbons (PAHs).[43] Finally, the concentration conversion ratio may have been too high, using the ideal value rather than one adjusted for wall losses.[41] R&P subsequently increased the cut point of the inlet from 9 to 10 μm, lowered the operating temperature from 50 °C to 40 °C, and modified the concentration conversion algorithm to more accurately reflect influences on the ratio, such as wall losses, from 25:1 to 23:1. Preliminary results from the 2005 study in Phoenix indicate better agreement for the PM_c TEOM with the reference method, on average, agreement within 5% and $R^2 > 0.98$. Recently, R&P also has developed a fine and coarse particle sampler employing the FDMS (PM_c FDMS) approach, which should minimize the loss of volatile species from the coarse and fine particles.

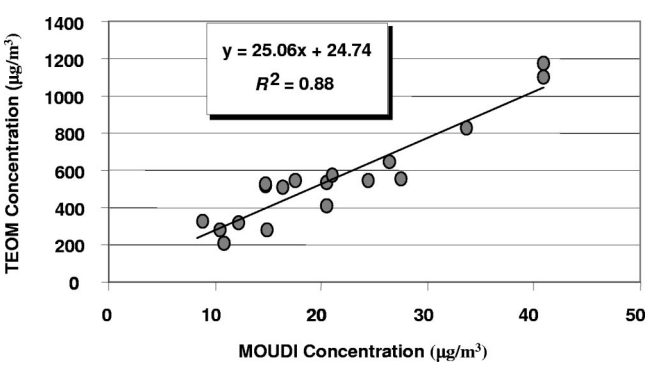

Figure 5. Comparison of 50 °C TEOM and MOUDI coarse particle data for sampling in Los Angeles during the Los Angeles Supersites Project. Ideal concentration factor for the PM_c TEOM is 25. Adapted with permission from Misra et al.[41] Copyright 2001 Air & Waste Management Association.

The PM_c BAM (enrichment factor 10) had good agreement to the difference method for PM_c in all the studies reported to date[42] (regression slopes between 0.88 and 1.17, with R^2 values exceeding 0.95); however, $PM_{2.5}$ was significantly overestimated at all locations and times of year by at least 40%. PM_{10} values were also higher than those obtained by the PM_{10} FRM. Laboratory studies with Arizona road dust and sodium chloride confirmed the overestimation for $PM_{2.5}$ as well as the good agreement for PM_c. The PM_c BAM was modified before the 2005 studies. The modifications included reduction for the $PM_{2.5}$ deposition area and a change from mass flow control to volumetric flow control. In the 2005 Phoenix study, the PM_c continued to agree well, but $PM_{2.5}$ was still significantly overestimated.[42]

As noted above, an APS was initially included in the study design to provide size distribution data to better understand potential differences between the two direct reading PM_c samplers. However, the APS had reasonably good agreement with the difference method at most locations; slopes with the FRM difference method within 10% and $R^2 > 0.85$, with the exception of Gary, IN, where the APS was low by 30%. Subsequently, a heater was installed to stabilize the RH to below 45%, as transport losses of large hygroscopic particles in humid environments were determined to be part of the reason for the low values. However, the RH in Phoenix in 2005 was

below 45% most of the time so the smart heater modification was not enabled. Operational problems also plagued the APS during the 2005 Phoenix study.

The 2005 field studies in Phoenix, AZ, and Birmingham, AL, also included other samplers. Besides the modified PM_c TEOM, PM_c BAM, and APS, the study included a GRIMM Technologies, Inc. instrument based on detecting single particles by light scattering, as well as the PM_c FDMS as mentioned above. Preliminary results for these samplers as observed in the 2005 Phoenix study are presented in Vanderpool et al.[42] Results for the 2005 Birmingham, AL, study are not yet available.

Continuous Indirect Methods for Mass Concentrations

SMPS-APS. The size distributions of a SMPS and APS can be combined to obtain a unified size distribution covering particle sizes from a few nanometers up to 10 μm. Stanier et al.[44] provide an excellent example of the use of these combined systems for Pittsburgh, where strong diurnal patterns are observed showing the direct effect of particle sources such as traffic and other combustion sources as well as atmospheric nucleation that appears to be regional in nature and occurs on 30–50% of the days. These number-based size distributions (number of particles/cm^3 in specific size bins) can be used to calculate volume and mass concentrations as indicated below. The SMPS (Model 3934 and 3936) typically measures aerosol particles in the size range from 10 to 800 nm. These size ranges can be adjusted by adjusting the aerosol and sheath air flows of the instruments. A newer version of this instrument, the TSI Nano-SMPS, which uses a shorter-length differential mobility analyzer (nano-DMA, Model 3085), allows classification of particles in the size range of 3–150 nm. The lower detectable size range of this instrument is important in atmospheric studies investigating aerosol formation mechanisms. Examples include nucleation events as well as exposure assessment studies conducted inside or near freeways and busy roadways, where a larger fraction of the aerosol is associated with sub-10 nm particles.[45,46] The Model 3321 APS spectrometer provides high-resolution, real-time aerodynamic measurements of particles from 0.5 to 20 μm.

Aerosol volume concentrations are determined from the number-based size distributions measured by the SMPS-APS system, assuming that all particles are perfect spheres. Conversion of volume concentration to mass concentration also requires an estimate of particle density. For $PM_{2.5}$ mass, the shape factor is often assumed to be 1 and the density from approximately 1.5 to 1.6 g/cm^3.[40,47] Estimates of particle density for PM_c seem to range between 2 and 2.2 g/cm^3.[40]

The ability of this method to accurately measure PM_{10}, $PM_{2.5}$, and/or PM_c concentrations was evaluated by Shen et al.[40] and Khlystov et al.[47] In these studies, the SMPS-APS was tested in comparison with other continuous PM measurement devices and with time-integrated mass samplers at various sites in the Los Angeles Basin and in Pittsburgh, respectively. Size distributions between the SMPS and APS were merged based on algorithms by Sioutas et al.[48] in Los Angeles and for Pittsburgh on the basis of Shen et al.[40] as well as a second approach fitting the APS to SMPS size distributions to yield a size correction factor that was related to the ratio of particle density and the shape factor.

Both studies indicated good agreement between $PM_{2.5}$ gravimetric mass and that estimated from the size distribution data. Results from Pittsburgh[47] indicated an average standard error of approximately 20% using the alternative algorithm and an average aerosol effective density of 1.5 g/cm^3. However, results from both studies also indicated a significant difference (little correlation) between the measured mass for lowest stages of the MOUDI (<0.15 μm) and the SMPS mass estimates. This discrepancy may be due to particle bounce in the MOUDI, causing larger particles to be collected in lower stages, and/or the effect of shape and density of local vehicular emissions in Los Angeles on the measurement of particle mobility by the SMPS. The latter would result in its underestimation of the mass below 0.1 μm relative to the MOUDI. These results are also consistent with other findings in Los Angeles near Claremont, CA,[38] as noted earlier, in which the SMPS also underestimated mass below 0.15 μm in comparison to the UF BAM monitor. Results from Los Angeles[40] are shown in Figure 6.

Shen et al.[40] also compared the APS results to PM_{10} measurements obtained by a Partisol sampler and found a weaker association between the SMPS-APS and Partisol for PM_{10} than for $PM_{2.5}$, likely driven by the poor efficiency of the APS for measuring coarse particle mass. Their results and those cited within ref 40 indicated that, relative to gravimetric methods (impactors), the APS both overestimates and underestimates PM_c mass because of overcounting across all size ranges (2.5–10 μm) and loss of particles because of wall losses in the APS. The latter has a significant influence for particles above 5 μm. These findings corroborated the results of previous studies.[49,50] However, more recent results by Vanderpool et al.[42] in comparing the APS to the FRM difference method for PM_c (described above) indicate better agreement for PM_c between these two methods.

Watson et al.[51] compared size distribution data collected in Fresno, CA, by an SMPS (TSI Model 3936L10) and an optical particle counter (OPC; PMS Lasair 1003) to hourly mass concentrations obtained by a $PM_{2.5}$ BAM. The SMPS measured the size distribution between 9 and 392 nm, the OPC between 0.1 and 2 μm. The SMPS and OPC agreed well (R^2 = 0.95 and slope = 0.79) in the overlapping range of their size distributions. The OPC particle concentrations, however, were systematically higher by an average of approximately 20%. The authors speculated that the longer residence time for the SMPS in the heated trailer environment (relative to the colder ambient temperatures in winter) could result in an apparent loss of SMPS particles from the overlapping region. No attempt was made to combine the size distributions by the two instruments or to convert them to volume and mass concentrations. However, they found a high correlation between the number concentration for particles greater than 0.3 μm, as measured by the OPC, with $PM_{2.5}$ measured by the BAM (R^2 = 0.91), as shown in Figure 7.

Results from the studies reviewed here suggest that size distribution data can be used to estimate $PM_{2.5}$ mass concentrations, but not ultrafine or coarse particle mass.

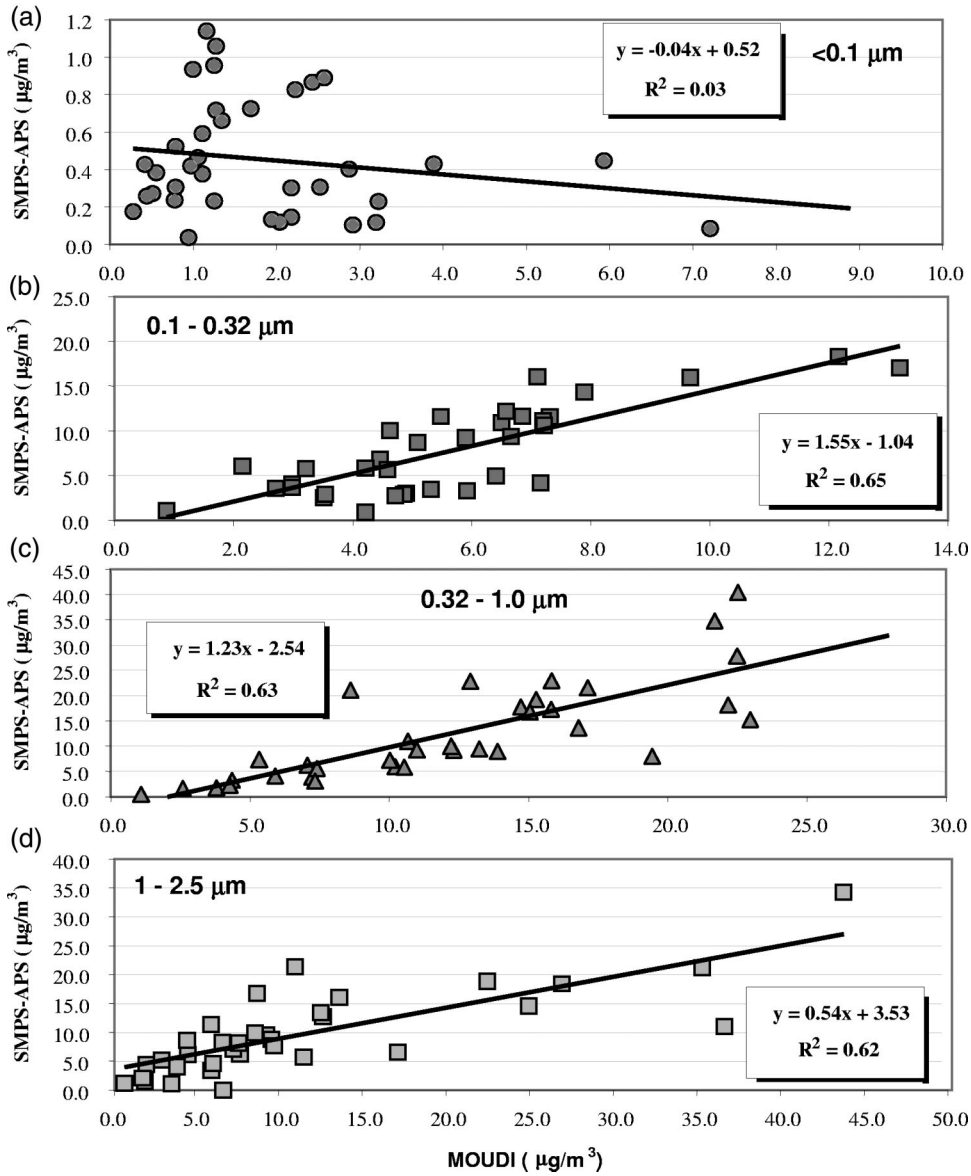

Figure 6. Time-integrated, size fractionated mass concentration of SMPS-APS compared with those measured gravimetrically by the MOUDI. (a) <0.1 μm, (b) 0.1–0.32 μm, (c) 0.32–1.0 μm, and (d) 1–2.5 μm. Adapted with permission from Shen et al.[40] Copyright 2002 Elsevier, *Atmospheric Environment*.

Results for PM_{10} also show a significant difference between PM_{10} mass estimated by the SMPS-APS and gravimetrically determined PM_{10} related to the measurement efficiency of the APS for coarse particles.

Size Distribution and Number Concentration

McMurry[52] provides a thorough review of well-established methods for obtaining size distribution and total number concentration data as well as other physical properties of PM. Here we focus on newer methods that were developed and/or evaluated as part of the Supersites Program and related studies. A discussion of the SMSP and nano-SMPS is given above.

WCPC. A new water-based laminar-flow condensation particle counter WCPC has been developed (Aerosol Dynamics Inc. and Quant Technologies, LLC)[53,54] and is commercially available (TSI, Inc.). The WCPC uses water rather than butanol to grow particles by condensation to a size where they can be counted by optical means. The use of water is particularly advantageous because it is a safer chemical than butanol, which is combustible, has a strong odor, and could contaminate other concurrent measurements. In this method, the wetted condenser walls are warmer than the air entering it, creating a condition of high supersaturation within the aerosol stream with rapid condensation of water vapor onto the particles. In contrast, because of the relatively low mass diffusivity of the butanol vapor, the butanol CPCs employ condenser walls that are cooler than the entering air to create the zone of supersaturation. The saturated butanol vapor then condenses onto the particles where they are grown and can be counted optically.

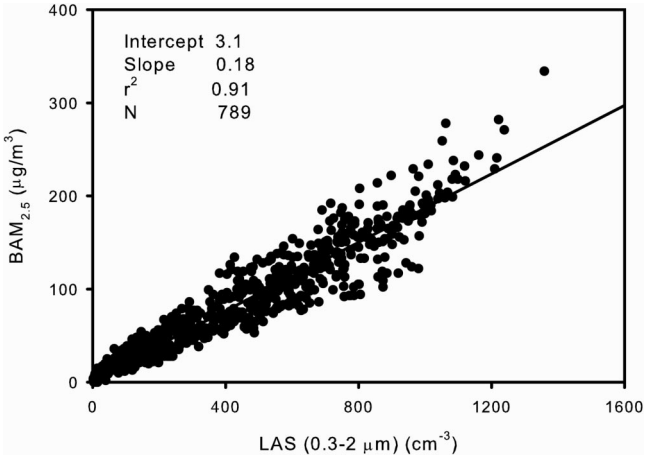

Figure 7. The relationship between a $PM_{2.5}$ BAM (Met One 1020) and OPC (PMS Lasair Laser Aerosol [LAS 1003] Spectrometer) particle concentrations (0.3–2 μm). Adapted with permission from Watson et al.[51] Copyright 2002 Air & Waste Management Association.

The WCPC (Model 3785) has an aerosol-sampling rate of 1 L/min and a lower detection limit near 5 nm. Calibration of this instrument with aerosol from a freeway tunnel and with ambient aerosol shows lower detection cut points of 4.3–4.8 nm, similar to the 5-nm cut point obtained for ammonium sulfate and NH_4NO_3 aerosol[54] (Figure 8a). Somewhat higher cut points are found for laboratory-generated hydrophobic organic aerosols.[53] The time response of the instrument is characterized by an exponential decay time constant of 0.35 sec, which is faster than for other unsheathed instruments.

Biswas et al.[55] compared the performance of the WCPC (a prototype of the TSI WCPC Model 3875) to the widely used TSI CPC Model 3022A (TSI Inc.), a butanol-based CPC, to varying particle composition, concentrations, and size. Results of the study indicated good correlation between the WCPC and butanol-based CPC (R^2: 0.74–0.99). Good agreement was found between the two instruments for particle concentrations up to 40,000/cm^3, with ratios of WCPC to CPC3022A concentrations varying between 0.8 and 1.2 (Figure 8b). Because of differences in the photometric mode calibration of these instruments, this ratio drops to 0.6–0.8 between 40,000 and 100,000/cm^3. The photometric mode of these counters is used at higher number concentrations, during which multiple particles are present in the scattering volume, and the particle concentration is derived from the light scattered from the cloud of particles within the scattering volume.

In addition to the TSI Model 3785 WCPC, three other water-based CPCs are commercially available: Models 3781, 3782, and 3786. All WCPCs operate based on the same principle as the 3785. The 3786 UF WCPC detects particles as small as 2.5 nm with an extended concentration range to as high as 100,000/cm^3 with single-particle counting. The 3782 is similar to 3785 but operates at a lower flow rate, and thus, detects particles at a higher concentration range in the single count mode than the 3785. The 3781 was designed to detect particles at concentrations up to 5×10^5 particles/cm^3 in a single count mode, with a Dp_{50} of 6 nm. These WCPC instruments are relatively new commercial methods and require additional field and laboratory testing before use in routine monitoring networks.

Particle Density

Particle density is crucial in determining where particles of a given size deposit in the respiratory system. Particle density also is an important property of aerosols because it is required to convert measured number distributions to mass distributions and to relate AD to Stokes diameter. Bulk particle density is often estimated from the measured chemical composition of PM. However, this method has considerable uncertainty because the mass balance is not always complete, organic species have a wide range of densities, and particle shape is unknown but often inaccurately assumed to be spherical, which is often not an

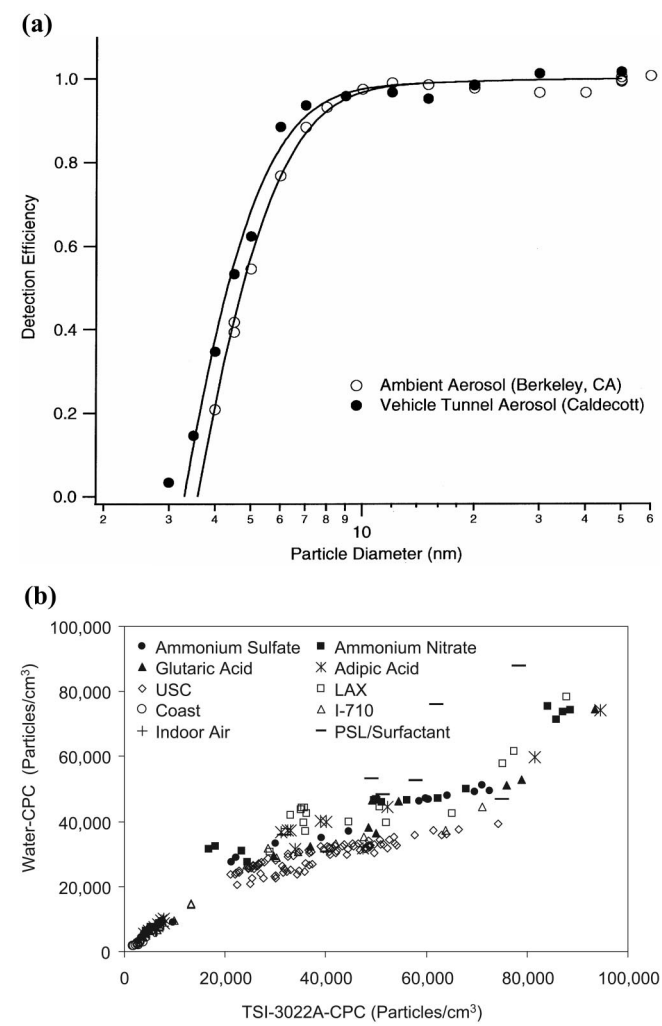

Figure 8. (a) Detection efficiency of the WCPC for atmospheric aerosols from Berkeley, CA, and for vehicular particulate sampled from a freeway traffic tunnel. Measurements obtained by reference to a UF CPC. Lines show fit to the data (adapted from Hering et al.[54]). Reprinted with permission. Copyright 2005 American Association for Aerosol Research. (b) Correlation between WCPC and a butanol-based (TSI-3022A) CPC in the photometric mode transition range (adapted from Biswas et al.[55]). Reprinted with permission. Copyright 2005 American Association for Aerosol Research.

accurate assumption. Other methods of determining particles density take advantage of the fact that particle effective density can be found if one of the following combinations is known: mobility size–aerodynamic size, mobility size–particle mass, or aerodynamic size–particle mass. A brief summary of the methods is given in McMurry et al.[52] and Ristimaki et al.[56]

McMurry et al.[39] describe a method for measuring particle density on the basis of first selecting particles of a known electrical mobility with a DMA and then measuring their mass using an aerosol particle mass analyze[57] (APM, now available commercially, Model APM-10, Kanomax USA). The APM classifies particles according to their mass to electrical charge ratios. Classification occurs between the narrow annular spaces, also termed the operating space, available between two rotating coaxial cylindrical electrodes. Particles thus experience both radial electrical and centrifugal forces, which act in opposite directions. When the forces balance each other, the particles will penetrate through the rotating cylinders to the downstream detector. For spherical particles, the electrical mobility equivalent diameter equals the geometric diameter. Density is determined by knowing the geometric diameter and the mass. For nonspherical particles, their measurements can provide insightful information on dynamic shape factors, fractal agglomerate content, and "effective" densities. McMurry et al.[39] used this technique to measure the effective density of ambient aerosols in Atlanta, GA, during August 1999. Their study showed that particles of a given mobility (~0.1 μm and 0.3 μm AD) often have several distinct densities and shapes, the most abundant of which consists of spherical hygroscopic particles with effective densities in the range from 1.54 to 1.77 g/cm^3 at 3–6% RH. These values agreed to within approximately 5% of values calculated based on the measured size-resolved composition. Particles that were more and less massive than these were also observed. The less massive particles had effective densities of 0.25–0.64 g/cm^3 and the more massive particles had effective densities of 1.7–2.2 g/cm^3. McMurry and co-authors[39] hypothesize that the less massive particles consist of chain agglomerate soot.

Ristimaki et al.[56] described the use of the electrical low pressure impactor (ELPI), which measures AD in near real time, in combination with an SMPS, which measures mobility diameters. These measurements are performed in parallel, as opposed to the McMurry et al. method above, and then the two size distributions are compared to estimate the density of particles measured. Using test aerosols of known density, Ristimaki et al. showed that the SMPS-ELPI could provide a reasonable estimate of submicron particle densities. Geller et al.[58] compared density estimates using an SMPS-ELPI with those obtained with a DMA-APM.[39] Agreement to within approximately 10% was observed for each method for aerosols of known density, with better agreement between the methods (~5%) for ambient aerosols. Results indicated that as particle sizes increase from 50 to approximately 400 nm, their effective densities decreased; this was especially true near freeways and in particular the freeway with the higher fraction of diesel vehicles.[58] In addition, as particle sizes increased, two or more density peaks occurred at a given size. In general, particle densities for 50-nm particles were greater than 1 g/cm^3 and decreased to less than 0.5 g/cm^3 as particle sizes increased to near 300–400 nm. Variations regarding these findings occurred depending on the site location; near one of the two freeways (gasoline-dominated vs. a relatively high fraction [25%] of diesel vehicles), a source-influenced site at the University of Southern California (USC), and a receptor site in Riverside, CA. Results indicated that as the particle size increased, the particles consisted more of chain-like agglomerates as suggested by McMurry et al.[39] Fractal shape factors also were estimated in both of these studies.

Particle-Bound Water (PBW)

A number of methods have been described in the literature for the uptake of water associated with ambient particles. Both laboratory and field studies have been conducted and are briefly summarized in Stanier et al.[59] For example, one of the most common methods used to date is the hygroscopic tandem DMA (H-TDMA).[60] The H-TDMA consists of two DMA units in series, one operated under dry conditions following a drying column and the other at RH approaching 90%. Particles of a given size are usually classified into two types by this method: less hygroscopic and more hygroscopic.[60] Switching of the first DMA size range allowed more than one particle size to be examined. Authors typically report a growth factor, which is the ratio of the humidified to dry particle diameters; however, the water content of the aerosol is typically not determined by this method because it is limited to particles of only a few sizes.

Dry and Ambient Aerosol Size Spectrometer (DAASS). An automated system to measure the water content of ambient aerosol (3 nm to 10 μm) and its hygroscopic growth, the DAASS, has been designed and was tested for 1 yr in Pittsburgh.[59] In this method, a nano-SMPS, SMPS, and APS sampled in parallel and measured overlapping size distributions from 3 nm to 10 μm. The SMPS and APS size distributions were merged as described by Khlystov et al.[47] The system alternately sampled ambient and dried air with a switching period of 7 min. RH was controlled to 30% using Nafion dryers. The difference in ambient and dry size distributions and the corresponding integrated volumes reveal the physical state of the aerosol and is expressed as a growth factor (ratio between ambient and dried volumes) or an absolute amount of aerosol water every 15 min, after having measured one ambient and one dry size distribution. In the laboratory, the DAASS was tested first with ammonium sulfate and good agreement with the known hygroscopic properties of these particles was achieved. Preliminary results from the field study showed that the water content of the particles was between zero and 20 μg/m^3 (0–50% of the ambient, hydrated mass). Figure 9 shows an example of ambient and dried size distributions. Discussions of extended field results in Pittsburgh are given by Khlystov et al.[61] who found that the seasonal behavior of aerosol water content followed that of the aerosol acidity, so that in summer at lower RH (even below 30% RH), particles could contain more water than in winter at higher RH because the

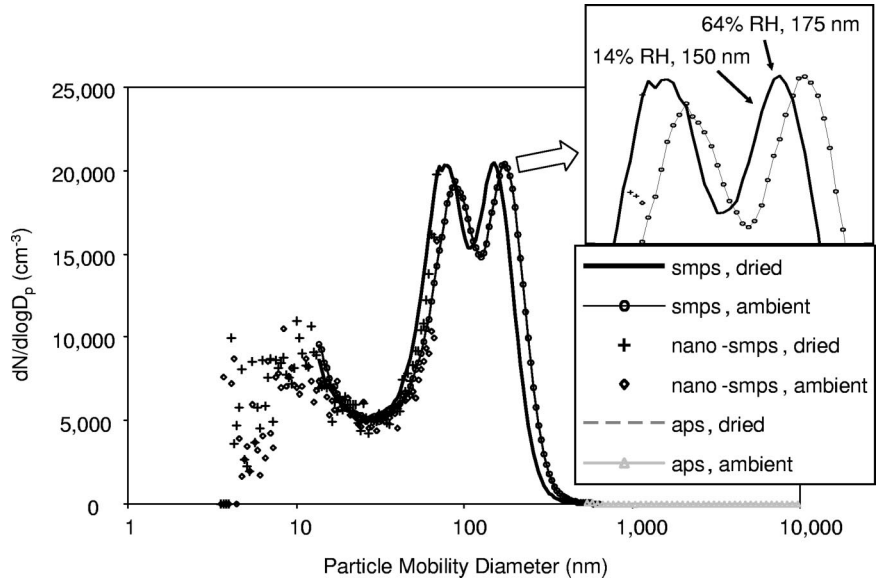

Figure 9. Dried and ambient number size distributions measured during the Pittsburgh Air Quality Study. Shown are 1-hr averages for 10:00–11:00 p.m. EST on July 3, 2001. Each of the distributions is the average of four ambient and four dried distributions (adapted from Stanier et al.[59]). Reprinted with permission. Copyright 2004 American Association for Aerosol Research.

summer aerosol was more acidic. The relationship between water content and aerosol acidity is illustrated in Figure 10 for hourly data obtained in Pittsburgh during July 2001, where the maximum in water content occurs during periods of greatest aerosol acidity.[62] The acidity ratio is calculated as:

$$\text{Acidity Ratio} = 2[SO_4^{-2}]/[NH_4^+]$$

where $[SO_4^{-2}]$ is the measured molar concentration of aerosol sulfate, and $[NH_4^+]$ is the measured molar concentration of NH_4^+. A ratio of approximately 1 indicates

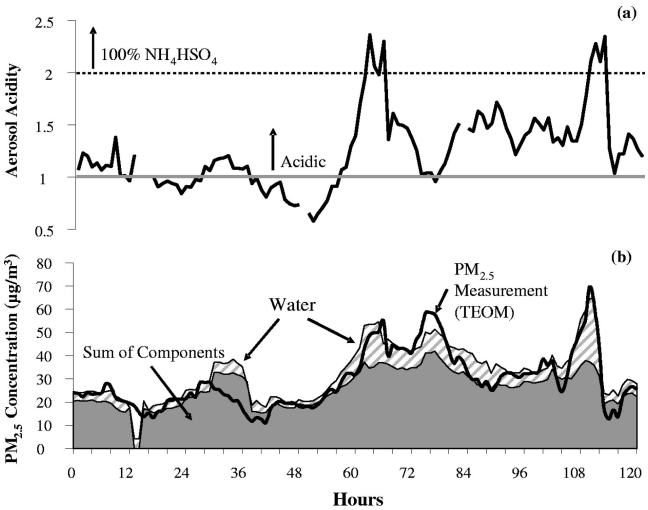

Figure 10. Hourly atmospheric (a) acidity (acidity ratio = $2[SO_4^{-2}]/[NH_4^+]$) and (b) $PM_{2.5}$ mass balance for July 20–25, 2001. Data are from continuous instruments. Aerosol acidity >1 indicates acidic conditions; aerosol acidity >2 indicates 100% NH_4HSO_4. Water estimates are from DAASS measurements. Data illustrate that mass balance discrepancy is accounted for by measured aerosol water and generally corresponds to acidic conditions (adapted with permission from Rees et al.[62]). Copyright 2004 Elsevier, *Atmospheric Environment*.

neutral conditions; ratios greater than 1 indicate acidic conditions when some bisulfate is likely present; and ratios of 2 or greater indicate that all of the sulfate present is likely in the form of bisulfate.

The seasonal variation in water content is illustrated in Figure 11.[62] The average water content for the summer was approximately 16% (3.9 $\mu g/m^{-3}$) of the $PM_{2.5}$ mass, whereas in the winter it was approximately 8% (0.9 $\mu g/m^{-3}$) of the $PM_{2.5}$ mass.[62] Rees et al.[62] were able to achieve a $PM_{2.5}$ FRM mass balance (daily average) within the uncertainties of the data using hourly data, including results from the DAASS along with improved estimates of the loss of semi-volatile chemical components (Figure 11). However, it should be noted that the organic matter (OM)/OC factor of 1.8 used by Rees et al.[62] may be highly uncertain and variable, depending on season and time of day, as the OC composition varies over the course of these periods because of its differing sources and formation mechanisms. Use of 1.8 likely minimizes the uncertainty, because the likely range of the OM/OC ratio is from 1.4 to 2.1[63]

PM CHEMICAL COMPOSITION

The major chemical components of PM typically include anions (sulfate and nitrate, sometimes chloride and organic acids), cations (NH_4^+, sometimes water-soluble sodium, potassium, calcium, and magnesium); carbon, including OC (actually composed of hundreds of compounds) and elemental carbon (EC); and a series of trace elements. Methods to measure these species, typically on a 1-hr time resolution or better, are described below.

Anion and Cation Monitoring

Thermal Reduction with Detection by Gas Analyzers. In these systems, the chemical components of PM are heated to sufficient temperatures, usually in the presence of a catalyst, to form a gas-phase species of lower oxidation state (e.g., sulfate is measured as SO_2 and nitrate is measured as oxides of nitrogen [NO_x]). The resulting gas species are

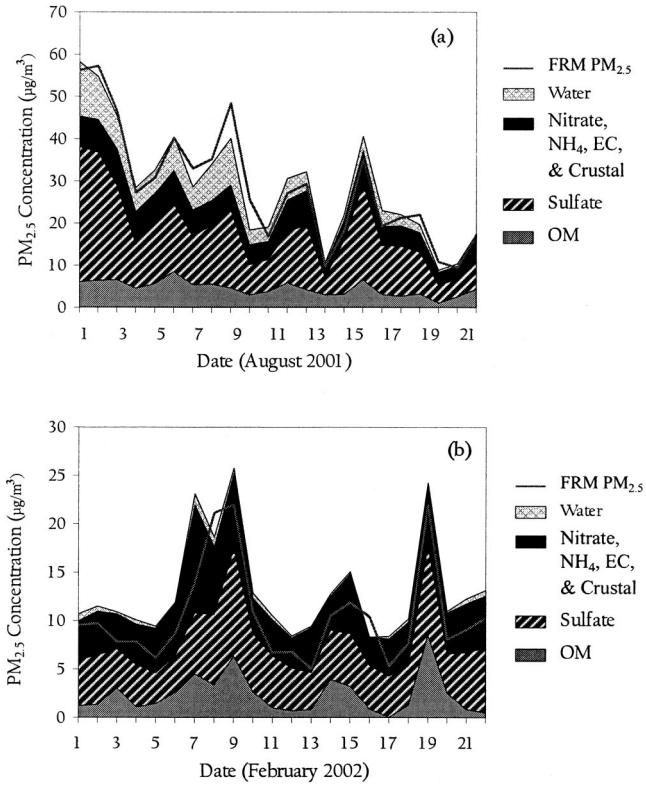

Figure 11. Time series of daily mass balances with estimated water content for (a) August 2001 and (b) February 2002. Water estimated from DAASS measurements extrapolated to a 35% relative humidity to reflect FRM filter conditioning. OM is defined as 1.8 × OC (adapted with permission from Rees et al.[62]). Copyright 2004 Elsevier, *Atmospheric Environment.*

then measured by an appropriate continuous gas monitor as described below. These methods do not measure the species of interest directly and conversion efficiencies are not always 100% so calibration factors are needed to convert the measured species to the desired species and to ambient concentrations.

ICVS. An automated system for the measurement of fine particulate nitrate in the atmosphere was developed by Stolzenburg and Hering,[64] the ICVS. A similar system was developed for sulfate[65] and prototypes of both systems were evaluated during the 1999 Atlanta Supersites Project.[66] Results from Atlanta showed good agreement between the ICVS methods for sulfate and nitrate with other continuous methods and 24-hr averaged filter-based methods. However, generally more scatter was observed in these comparisons, than with the ion chromatography (IC)-based methods, with R^2 values usually near 0.7. The higher variability may have been due to the different analytical techniques employed where the ICVS method indirectly measures sulfate and nitrate as the thermally desorbed gases SO_2 and NO_x, respectively.

R&P has commercialized both systems (Model 8400N for nitrate and 8400S for sulfate). As with the prototype, particles are grown by condensation of water to sizes large enough for efficient impaction on the collection strip. This process greatly reduces particle bounce from the collection strip and minimizes NH_4NO_3 volatilization before collection. Following humidification, particles are collected by impaction on either a stainless steel or a Nichrome strip for nitrate or a platinum strip for sulfate. After an 8-min sampling period, the material collected on the strip is flash vaporized into a nitrogen carrier gas and the generated gases of interest are then detected by either an ozone-chemiluminescence detector with molybdenum (Mo) catalyst for NO_x generated from the nitrate or SO_2 by ultraviolet (UV) fluorescence for sulfate. Both systems use a 2.5-μm sharp-cut cyclone as the inlet followed by a honeycomb denuder (ChemComb Model 3500 Speciation Sampling Cartridge, Thermo Electron Corp.) that can be coated with different gas-phase adsorbing compounds to remove interfering gases. The humidifier follows the denuder. The system operates with a time resolution of 10 min.

Stolzenburg and Hering[64] have reported laboratory and field evaluations of the prototype nitrate system. Laboratory studies indicated collection efficiencies of 95% and higher for particles with diameters greater than 0.1 μm; collection efficiencies for the sulfate system appear to be greater than 90%. High correlations between 24-hr average ICVS and denuder-filter measurements were observed for nitrate using the pre-commercial instrument ($R^2 > 0.94$) at three sites (Denver, CO; Rubidoux, CA; and Bakersfield, CA) with slopes from 0.96 to 1.06 and data recovery exceeding 97% during the field study.[64] Wittig et al.[67] evaluated the commercial sulfate and nitrate monitors (R&P 8400S and R&P 8400N, respectively) in Pittsburgh from June 2001 to March 2002. They found reasonable correlations ($R^2 > 0.83$) with EPA speciation sampler 24-hr average sulfate and nitrate results as reported directly by the commercial instrument (Figure 12a). However, after additional corrections were made to the data (e.g., blank, calibration, software correction, gas analyzer efficiency), the commercial units (8400N and 8400S) still reported values lower (slopes of 0.83 for nitrate and 0.71 for sulfate) than the filter-based methods, the latter of which were used as the reference measurement. Results were better below approximately 2 μg/m^3 for nitrate and sulfate (Figure 12b). The short-term results (24-hr average) were calibrated to the 24-hr filter-based measurements to obtain improved estimates of temporally resolved nitrate and sulfate during the study period (Figure 12c). They used these data to investigate short-term phenomena in Pittsburgh that could not have been revealed with the 24-hr filter data. This information was used to determine daily and diurnal seasonally averaged variations of the gas-to-particle partitioning of nitrate, as illustrated in Figure 13.

The R&P 8400N also was evaluated in east Baltimore from February to November 2002.[68] The continuous nitrate data were compared with 24-hr denuder/filter-based measurements employing 47-mm nylon filters preceded by a MgO denuder to remove nitric acid.[69] On average, the R&P 8400N was 33% lower than the 24-hr filter-based measurements, suggesting a conversion efficiency considerably lower than one, assuming negligible positive artifact of the denuded filter measurement (i.e., 100% MgO denuder efficiency). Results indicated that the NO_x monitor was sensitive to the absolute pressure of gas in the analytical cell requiring corrections for cell pressure to the

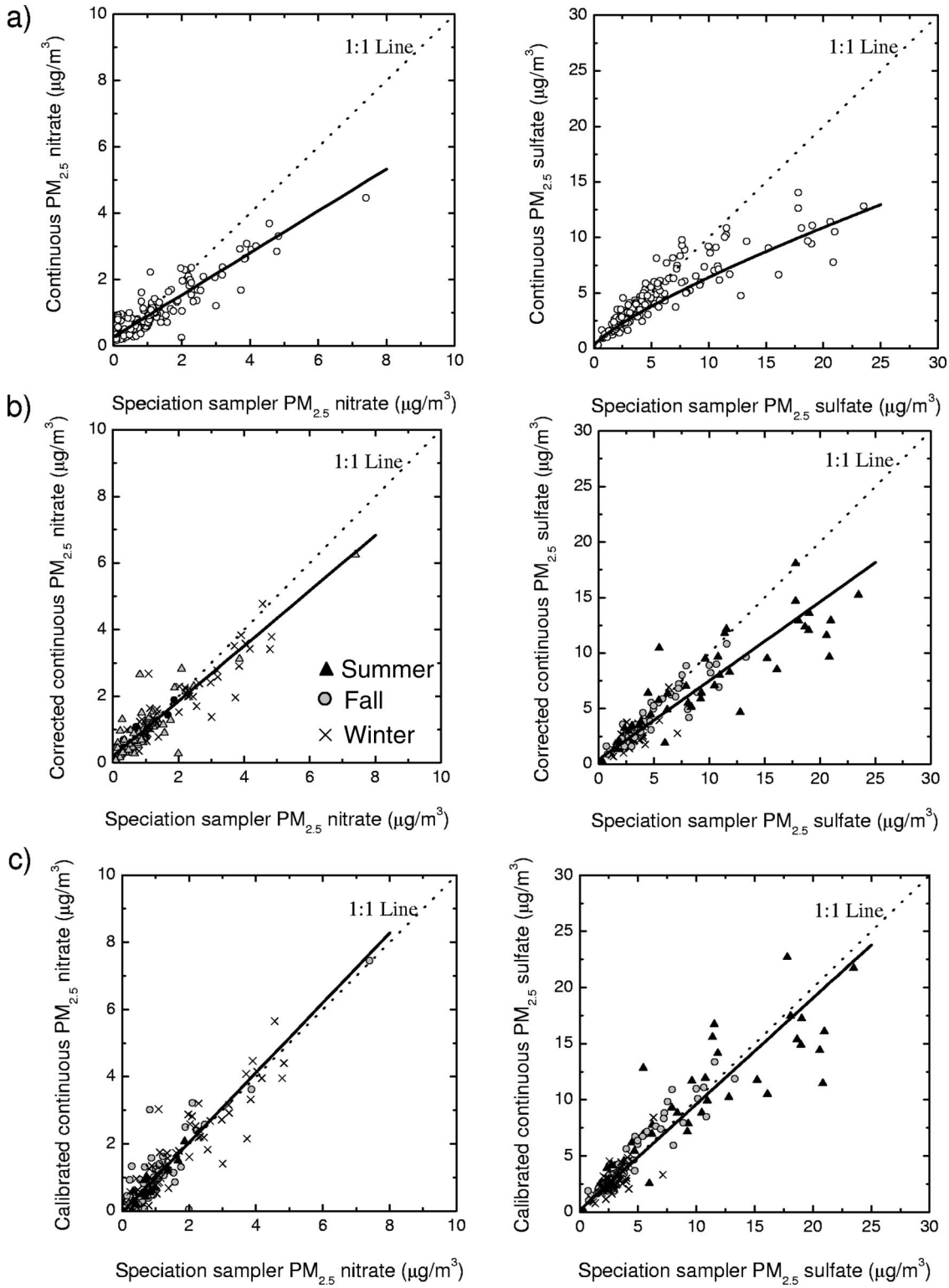

Figure 12. (a) Comparison of the daily averages of the instrument reported (raw measurements) semicontinuous NO_3 (R&P 8400N) and sulfate (R&P 8400S) with the corresponding values of the filter-based speciation sampler from July 2001 to March 2002. The linear correlation (black line), $y = 0.63x + 0.27$ μg/m^3 with $R^2 = 0.82$ was obtained for NO_3. The nonlinear correlation (black line), $y = x^{0.79} + 0.23$ μg/m^3 with $R^2 = 0.86$ was obtained for sulfate. Also shown are the 1:1 lines (dashed lines) (adapted from Wittig et al.[67]). Copyright 2004 Elsevier, *Atmospheric Environment*. (b) Comparison of the daily averages of the corrected semicontinuous NO_3 and sulfate with the corresponding values of the filter-based speciation sampler from July 2001 to March 2002. The linear correlation (black line), $y = 0.83x + 0.20$ μg/m^3 with $R^2 = 0.84$ was obtained for NO_3 and the linear correlation (black line), $y = 0.71x + 0.42$ μg/m^3 with $R^2 = 0.83$ was obtained for sulfate. Also shown are the 1:1 lines (dashed lines). Reprinted with permission from Wittig et al.[67] Copyright 2004 Elsevier, *Atmospheric Environment*. (c) Comparison of the daily averages of the calibrated semicontinuous NO_3 and sulfate with the corresponding values of the filter-based speciation sampler from July 2001 to March 2002. The linear correlation (black line), $y = 1.04x - 0.04$ μg/m^3 with $R^2 = 0.83$ was obtained for NO_3, and the linear correlation (black line), $y = 0.94x + 0.17$ μg/m^3 with $R^2 = 0.84$ was obtained for sulfate. Also shown are the 1:1 lines (dashed lines). Reprinted with permission from Wittig et al.[67] Copyright 2004 Elsevier, *Atmospheric Environment*.

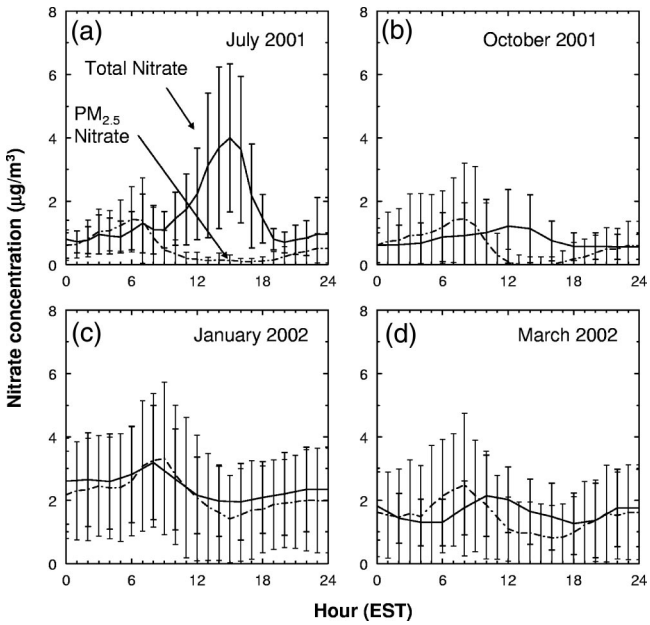

Figure 13. Average diurnal gas-to-particle partitioning of NO_3 for (a) July 2001, (b) October 2001, (c) January 2002, and (d) March 2002. Also shown is the standard deviation of the hourly measurements used to compute monthly average diurnal profiles. $PM_{2.5}$ NO_3 diurnal profiles were computed from the final corrected semicontinuous NO_3 measurements. Total ($PM_{2.5}$ + gas) NO_3 diurnal profiles were computed from the steam sampler 1- to 2-hr measurements (adapted with permission from Wittig et al.[67]). Copyright 2004 Elsevier, *Atmospheric Environment*.

data. Measurements also were corrected for ambient temperature. Precision for both 10-min and 24-hr average data were less than 10%. Detection limits ranged from 0.17 and 0.24 μg/m^3 for the 10-min and daily average results. Conclusions suggested that an independent filter-based measurement (denuded Nylon or Teflon with adsorbing backup) is needed to calibrate the data, as was suggested by Wittig et al.[67] Grover et al.[34] also used the R&P 8400N nitrate monitor in their field studies with the RAMS in Lindon, UT, and Rubidoux, CA. They found that the R&P 8400N nitrate concentrations were low with respect to the PC-BOSS fine PM nitrate (zero-intercept slope of 0.65 ± 0.07, intercept of 3.3 ± 2.4 μg/m^3, R^2 = 0.73) with the largest differences observed at higher concentrations as reported by the authors. The authors indicated that the lower values were likely due to incomplete volatilization of sampled NH_4NO_3.

EPA has been evaluating the R&P 8400N and 8400S at five sites since mid-2002 (Five-Cities Study). The sites included locations where the monitors were tested under different air quality and meteorological conditions. The sites were located at existing state air monitoring sites with existing filter-based chemical speciation samplers. The sites were located in Phoenix, AZ; Chicago, IL; Seattle, WA; Deer Park, TX; and Indianapolis, IN. These evaluations were focused on operational aspects of the samplers as used by state employees and comparisons to EPA's STN filter-based results. Part of the evaluation included performance audits by an independent EPA laboratory located in Montgomery, AL.[70] EPA conducted five audits on the R&P samplers. Five aqueous standards containing varying amounts of nitrate (KNO_3) and sulfate $(NH_4)_2SO_4$ were provided to the site operators to evaluate the 8400N and 8400S, respectively. In the fifth nitrate audit sample, one of the blind audit mixtures contained nitrate from four different salts as well as sulfate from ammonium sulfate. This last solution was included to test the instrument's response to different forms of nitrate that may occur in ambient air. All the single salt solutions showed low recoveries. The mixed nitrate audit sample consistently had the lowest values at all sites for its challenge of the 8400N. The results obtained from the audits are consistent from year-to-year. Precision was excellent with triplicate samples, usually varying by less than a few percent. Results were linear with correlation coefficients usually greater than 0.95. However, significant intercepts were observed and recoveries of the standard (linear regression slopes) were low for nitrate, often by 20–35%, especially at higher concentrations similar to the results presented in Figure 12, a and b. The greatest difference for nitrate is for deposits greater than 50 μg on the flash strip (~2–5 μg/m^3 based on 24-hr sampling using the $PM_{2.5}$ FRM or Met One sampler flow rates). Regression slopes below this nitrate level were typically within 10% of unity. Regression slopes for sulfate also were low by up to 50% with significant intercepts. Sulfate results also showed more variability in slopes. Data at all sites were recalculated using the calibration curves from the blind audit samples and nearly identical results were obtained for all sites with slopes of essentially one. This latter analysis suggests the data can be adjusted to provide useful data.

Data from the Five-Cities Study also were compared with collocated STN filter data at each of the sites.[71] Significant differences were observed between the filter-based data and results from both the R&P 8400N and the R&P 8400S at most of the sites. For nitrate, the difference was negative at four sites and positive at the Houston site, whereas for sulfate, the difference was negative at four sites and positive at the Seattle site. The nitrate response appeared to be nonlinear, with a greater disparity evident at higher ambient nitrate concentrations. Looking at operational aspects of the monitors, the most time-consuming activity for both the nitrate and sulfate monitors were data acquisition and data processing. Running aqueous standards and dealing with flash strips were the next most time-consuming activities.

Cascade ICVS. The collection stages of a cascaded impactor were added to the ICVS to allow for size-resolved nitrate measurements.[31] Particles were collected by humidified impaction on three impactor stages (2.5–1, 1–0.5, and 0.5–0.08 μm) after the initial $PM_{2.5}$ size cut. Sampling times and analysis steps were the same as the single stage ICVS. Laboratory tests showed slightly better recoveries for sodium nitrate than for NH_4NO_3.[31]

The cascade ICVS was evaluated by Fine et al.[72] in Southern California. The instrument was employed at two sites: in Rubidoux, CA, from July to September 2001, and in Claremont, CA, from September 2001 to February 2002; both downwind receptor locations east of downtown Los Angeles. The cascaded ICVS was collocated with

a MOUDI and a HEADS sampler at these sites. Both size-resolved and total $PM_{2.5}$ nitrate concentrations (24-hr averages) were compared among the different sampling techniques. The cascaded ICVS monitor and HEADS $PM_{2.5}$ nitrate measurements were well correlated (R^2 = 0.79) with a geometric mean of the ratios of cascaded ICVS to HEADS of 0.90. The size-fractionated nitrate data from the semicontinuous nitrate monitor was consistently higher than the corresponding MOUDI stages, most likely due to volatilization of NH_4NO_3 from the MOUDI impaction substrates. Among the three stages, better agreement was observed in the upper stage (1–2.5 μm size range), in which a portion of the nitrate may exist as nonvolatile sodium nitrate. Fine et al.[72] underlined the importance of the continuous nature of the data generated by the cascaded ICVS and demonstrated its use in generating spatial and temporal profiles of size-fractionated particulate nitrate, which in turn helped determine the sources and formation mechanisms of atmospheric particulate nitrate.

ARA Continuous Nitrate Monitor. In this system,[73] fine particulate nitrate and NH_4^+ are obtained using a three-channel, continuous differencing approach developed by ARA (Atmospheric Research and Analysis, Inc.). Fine particles are obtained using a sharp-cut cyclone inlet (BGI, Inc.), followed by two annular denuders, one coated with sodium carbonate, the other with citric acid (URG). These denuders are followed by two carbon honeycomb denuders (MAST Carbon Ltd.). This combination of denuders removes a wide range of interfering species, including reduced nitrogen, nitrogen oxides, and volatile organic compounds. The carbon honeycomb denuder, in particular, reduces NO_y by 90–99% and significantly dampens short-term variability (e.g., spikes from passing vehicles). This latter property of the denuder makes it possible to resolve small (50 ppt) differences between channels with high temporal resolution. The sample is then split into the three channels. Baseline is measured in Channel 1 (CH1) after the sample is passed through a KCl-impregnated cellulose filter, which is followed by a commercial Mo mesh catalyst heated to 350 °C. CH1 thus measures the instrument's dark current and any residual gas-phase NO_y not removed by the inlet, filters, and denuders.

Channel 2 (CH2) is the same as CH1 except the KCl filter is removed. The signal from CH2 includes baseline NO_y plus particulate nitrogen species that were converted to NO. Channel 3 (CH3) is similar to CH1; however, the filter in CH1 is replaced by a ceramic tube containing approximately 5 g of platinum (Pt) wire gauze heated to 600 °C. CH2 and CH3 each include separate Mo converters operated at 350 °C. The hot Pt catalyst quantitatively oxidizes NH_4^+ to NO and NO_2, whereas the Mo catalyst reduces nitrate (NO_3^-), NO_2, and residual NO_y to NO.

NO produced by each of the converters was quantified via NO-ozone chemiluminescence with a Thermo-Environmental Model 42Ctl NO/NO_x analyzer. Each channel was measured for 10 sec in sequential order and an average was determined for each channel every minute. The system was zeroed (four times per day) along with daily single-point calibrations. NO_3 and NH_4^+ were then operationally defined as CH2-CH1 and CH3-CH2, respectively.

Weber et al.[66] compared a prototype two-channel version of the ARA method to other continuous NO_3 methods during the 1999 Atlanta Supersites Project. The prototype analyzer used dual sodium hypochlorite-coated annular denuders for NO_x removal instead of carbon honeycomb denuders. The sodium hypochlorite denuders exhibited variable removal of NO_x (20–60%), and therefore, were much less effective at dampening the baseline signal. Hourly comparisons were made among the individual instruments, each instrument to a mean of all the continuous methods and to the 24-hr average of the continuous data to the filter-based daily samples with comparison on a 24-hr basis and to the mean of the 24-hr average data. In comparing hourly data, the ARA nitrate instrument was the least correlated with the other monitors ($R^2 \leq 0.3$), had the largest absolute relative difference to the mean of the hourly data, and the most scatter, which appeared to be independent of concentration. However, nitrate values were low in Atlanta (on average <0.5 μg/m^3) so the larger scatter by the ARA method might be due to the approach of measuring a difference between two similar values, NO_x with and without nitrate after conversion to NO_x, resulting in higher uncertainties. Comparisons to the 24-hr filter data are slightly better. The instrument operated in its current configuration as described above (activated carbon vs. hypochlorite denuders) has demonstrated much better performance, with typical R^2 values in the range of 0.95–0.97 for 24-hr comparisons with filter data.[74]

Thermo Electron 5020/Harvard School of Public Health (HSPH) Continuous Sulfate Monitor. Allen et al.[75] developed a continuous flow sulfate monitor based on thermal reduction and detection by an SO_2 monitor. The system is commercially available (Model 5020 SPA; Thermo Electron Co.). The method is based on the conversion of particulate sulfate to SO_2 via thermal reduction in a range of 800–1000 °C. The reduction reaction is catalyzed by stainless steel, which is critical to the conversion of particulate sulfate to SO_2 gas. Drewnick et al.,[76] utilizing an earlier research version, used a stainless steel tube heated in a tube furnace to a temperature of 900 °C. The commercial version uses a quartz tube containing a stainless steel rod, which is heated to 1000 °C. The higher temperature provides a more efficient conversion of sulfate to SO_2. The SO_2 is quantified by a high-sensitivity pulsed-fluorescence SO_2 analyzer (Model 43S; Thermo Environmental Instruments Inc. [now Thermo Scientific]). Interfering gas-phase species are removed immediately after the $PM_{2.5}$ sharp-cut cyclone using a carbonate coated annular denuder and a honeycomb carbon denuder. The commercial unit has a stated response time of 110 sec and a detection limit of 0.5 μg/m^3 for a 15-min average sample.

Only a few comparisons of the Harvard/Thermo Electron continuous sulfate analyzer have been published. One uses the early research method as designed by Allen and the other tests pre-production and production versions of the instrument. Employing the early method, Drewnick et al.[76] compared the early version to three other continuous sulfate instruments during summer

2001 at the PMTACS-NY Supersites in Queens. The instruments used in the comparison were the R&P 8400S, the particle-into-liquid sampler coupled with an ion chromatographic (IC) detector (PILS-IC), and an aerosol mass spectrometer (AMS). Comparisons among the continuous methods were excellent with $R^2 > 0.9$ and recoveries in the range of 0.97 to 1.03. Comparisons of all continuous methods to the 6- and 24-hr filter-based methods also were well correlated on average ($R^2 > 0.85$); however, sulfate recovery among all the continuous methods relative to the filter methods was only approximately 85%. Slopes in the comparison of the Harvard/Thermo sulfate analyzer for the 6- and 24-hr average data range between 0.67 and 0.79 with correlation coefficients (R^2) in the range of 0.85 to 0.9. Combinations of factors were discussed for these lower recoveries, including sampling artifacts by the filter methods and inlet cut point and transport losses, and less than unity conversion efficiencies for the continuous monitors. Similar results for the pre-production and production versions of the Thermo 5020 have been recently reported by Schwab et al.[77] These field tests were conducted at a rural site in Pinnacle State Park, NY[77] and employed several different filter-based samplers. Field and first time laboratory results were consistent with the previous results and with each other indicating recoveries of approximately 80% as indicated in Figure 14, a and b. Laboratory results also indicated that metal sulfate salts (Ca, Na, and K) had even lower conversion efficiencies (4–63%) so results in locations impacted by these salts would likely be biased low. However, work by Allen et al.[78] in St. Louis using the pre-production Thermo 5020 indicated nearly 100% conversion efficiency compared with sulfate measured on Teflon filters and as measured by the PILS-IC. Reasons for these differences are being evaluated.

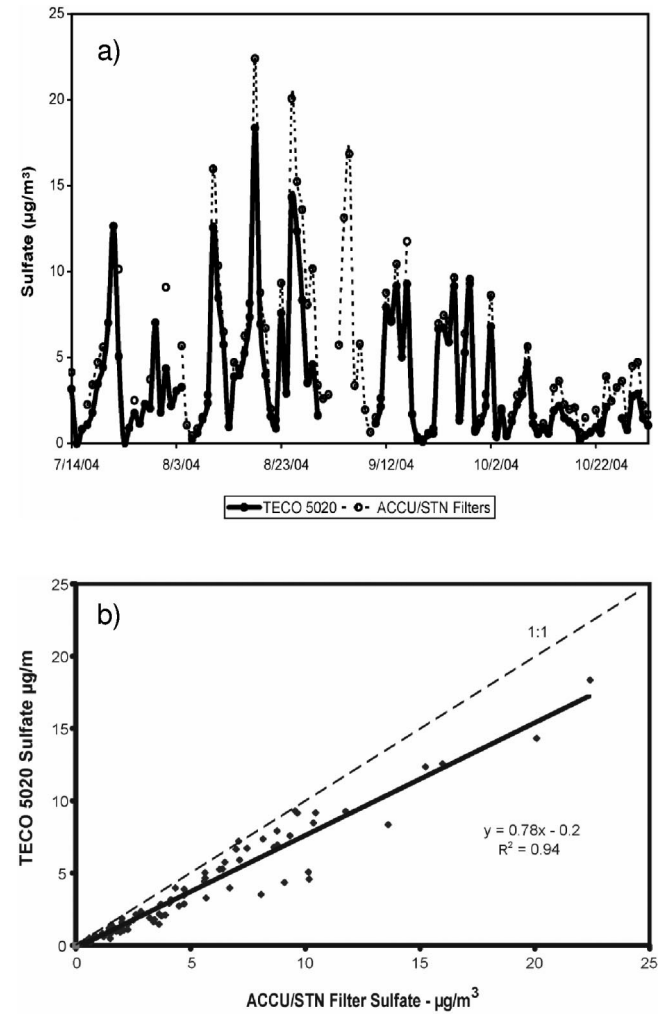

Figure 14. (a) Time series plot of the 24-hr averaged 5020 sulfate and filter sulfate from the combined ACCU/STN dataset collected at the Addison field site. (b) Correlation plot of the 24-hr data from Addison, along with the 1:1 line for reference, and the linear regression line and equation (adapted from Schwab et al.[77]). Reprinted with permission. Copyright 2006 American Association for Aerosol Research.

Methods Based on Analysis by IC. Weber et al.[66] compared five continuous prototype/research instruments for the measurement fine particle nitrate and sulfate at the Atlanta Supersites Project. The instruments were compared between each other on an hourly basis and to the average of the hourly data, as well as to the filter-based 24-hr integrated measurements. The comparison included three IC-based units and two thermal reduction/gas detection instruments as described above. In two of the IC-based systems,[79–82] particles were grown by condensation of water onto the particles under high RH conditions, collected by impaction, and followed by analysis of the flowing stream by IC. These methods are referred to in the literature as the PILS-IC (Applikon Analytical)[79,80] and the steam jet aerosol collector (SJAC; MARGA, Applikon Analytical).[81,82] In the third IC-based system (referred to here as the parallel plate sampler (PPS; Dionex Corp.),[83] particles were collected on one of two pre-washed glass fiber filters for 15-min sampling periods each after passing through a $PM_{2.5}$ cyclone and a wet parallel plate denuder to remove interfering gas-phase species. The filter was then automatically extracted with water followed by IC analysis. Alternating the use of two filters allowed for continuous collection, one channel collected while the other was being analyzed. Besides sulfate and nitrate, other inorganic and organic species (e.g., F^-, Cl^-, Br^- and acetate, formate, and oxalate) can be quantified directly by these IC-based systems, an advantage over the thermal reduction methods.

Good agreement was observed among comparisons of the hourly IC-based methods during the 1999 Atlanta Supersites Project with R^2 values ranging between 0.75 and 0.9 for nitrate and 0.85 and 0.95 for sulfate.[66] Relative differences to the mean of the hourly data ranged between 25 and 30% for nitrate and 8 and 15% for sulfate. Relative differences to the mean of daily filter-based sulfate and nitrate data ranged between 17 and 26%. For both nitrate and sulfate, the variability among the continuous data was less than among the filter-based data, suggesting that the continuous methods might be less susceptible to sampling artifacts. In addition, several of these prototype instruments have been commercialized along with improvements that were suggested from the outcome of the Atlanta Supersites Project. Additional details of the comparison can be found in Weber et al.[66]

During the PMTACS-NY campaign, several online aerosol analysis instruments were deployed together with gas-phase and filter sampling techniques. Drewnick et al.[76] reported on the intercomparison of four continuous $PM_{2.5}$ sulfate instruments during the summer of 2001 in Queens, New York. These instruments were compared with one set of 6-hr and three sets of 24-hr collocated filter-based chemical speciation measurements. The continuous instruments included an AMS, PILS-IC, a continuous R&P sulfate monitor (R&P 8400S), and a Thermo 5020/HSPH continuous sulfate monitor (described above). Excellent agreement was observed among the samplers with slopes close to 1 and R^2 values >0.9, as illustrated in the time series presented in Figure 15. In addition, continuous data were well correlated with the filter-based measurements (R^2 = 0.86–0.98); however, the continuous instruments recovered only approximately 85% of the sulfate mass collected by the filter techniques. The authors attributed this deviation to a combination of positive sampling artifacts associated with the collection of aerosols on filters (e.g., collection of particles with diameters greater then 2.5 μm, absorption or adsorption of gases on the filters) and/or potential losses associated with the continuous measurements (inlet line losses, limited collection efficiency for small particles below ~0.1 μm).

The SJAC was compared with denuder filter-based methods in several measurement studies as well as to a thermo-denuder method as described in Slanina et al.[82] In most cases, linear regression results had slopes close to 1, small intercepts, and $R^2 > 0.9$. Laboratory tests using generated aerosols in cloud chambers also showed excellent agreement between the filter-based methods, a thermo-denuder method, and the SJAC.[82] Other comparisons are described above in the previous anion and cation monitoring sections.

Major Carbon Components—Elemental Carbon (EC) or Black Carbon (BC) and OC

Two continuous instruments have been developed and are commercially available to simultaneously measure the major components of particulate carbon in air, EC and OC. The sum of OC plus EC is referred to as total carbon (TC). A third instrument provides estimates of water-soluble carbon. Continuous methods for determining BC on the basis of an absorption measurement in units of 1/m, which can be converted to ambient concentrations in $\mu g/m^3$ by applying an absorption coefficient, also are described below. These include the Aethalometer and photoacoustic spectrometer (PAS).

OC and EC Based on Thermal-Optical Absorption (TOA) Methods. Two continuous methods have been developed for the determination of OC, EC, and TC. One method is based on the National Institute for Occupational Safety and Health (NIOSH) method[84] and is available from Sunset Laboratories, Inc. The other method is slightly different, as described below, and is available from R&P (Thermo Electron Corp., now Thermo Scientific). Sunset Laboratories Inc. (referred to here as the Sunset EC/OC monitor) has developed a continuous device for measuring EC and OC concentrations in $PM_{2.5}$ on the basis of their off-line laboratory analysis instrument currently used in EPA's STN.[85] In this method, air sampled through a 2.5-μm sharp-cut cyclone is passed through a parallel plate CIF denuder[15] to remove gas-phase organic compounds that can be absorbed by quartz-fiber filter material. This denuder greatly reduces positive sampling filter artifacts.[86] Particles are then collected on a quartz-fiber filter inside the instrument for a user-defined period (usually 45 min), after which, the sample is analyzed using a thermal temperature protocol similar to the NIOSH method 5040.[84] The IMPROVE analysis protocol[87] also can be used. Analysis takes less than 15 min and then the instrument starts a new sampling cycle.

The Sunset EC/OC monitor, operating on a 2-hr cycle (1 hr for sample collection, 1 hr for analysis or idling), was evaluated in a field study in St. Louis.[88] Integrated filter-based and continuous samplers were collocated during the study and both employed parallel plate CIF denuders to reduce positive sampling artifacts.[15,89] The hourly OC concentrations from the continuous sampler were averaged to match the 24-hr filter-based samples and agreed well with the 24-hr integrated measurements (R^2 = 0.90, slope = 0.93). TC agreed slightly better. EC comparisons

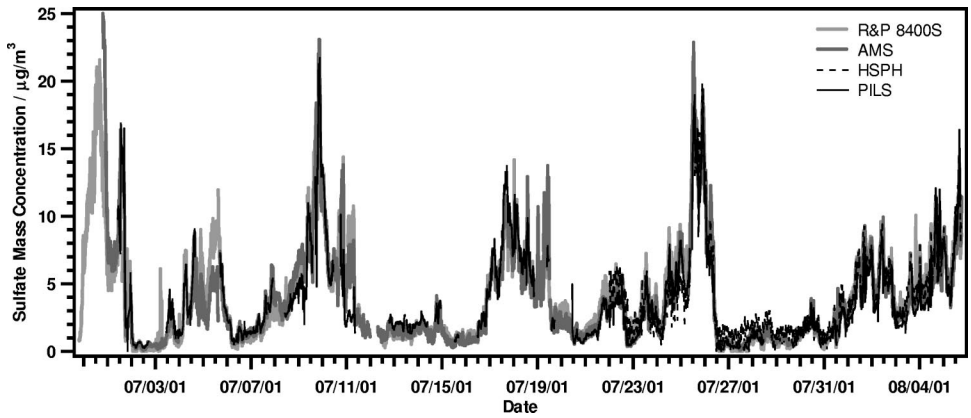

Figure 15. Particulate sulfate mass concentration time series of the AMS, the PILS, the R&P 8400S, and the HSPH continuous sulfate monitor for the whole PMTACS-NY 2001 campaign (adapted with permission from Drewnick et al.[76]). Copyright 2003 Elsevier, *Atmospheric Environment.*

to the integrated EC measurements had a lower R^2, although the slope was near 1. The lower R^2 value was most likely due to the very low ambient EC concentrations encountered at that sampling site. Results also indicated that a single instrument sampling every other hour yielded similar agreement with 24-hr time-integrated methods, implying that sampling EC every other hour is statistically representative of a 24 hr average under the conditions observed in their study.

Grover et al.[34] employed two continuous Sunset carbon analyzers; one in its normal configuration, as described above, and one modified to measure semi-volatile OC. In the latter instrument, a Teflon filter was placed upstream of the sampling inlet of the carbon monitor and a CIF filter replaced the quartz-fiber filter used for collecting PM. The CIF adsorbed semi-volatile organic material lost from the particles collected on the Teflon filter. The semi-volatile OC was detected by thermal evolution of the CIF in helium atmosphere. The PC-BOSS measurements, of both the nonvolatile and semi-volatile carbon components, were in good agreement with the sum of the carbon measurements made by the two Sunset instruments (R^2 = 0.93, slope = 0.90).

The Sunset EC/OC monitor also was tested recently by Arhami et al.[90] in Los Angeles. The authors verified that the use of the parallel plate CIF denuder effectively eliminated the positive artifact and that other artifacts were small and could be neglected for a sampling time of 45 min. The high precision of the instruments (R^2: OC = 0.98, EC = 0.97, slope of 1.01 ± 0.02, y-intercept of 0.12 ± 0.16 μg C/m^3) was demonstrated using two carbon Sunset analyzers sampling through a common sampling inlet. The authors also tested a fast mode of analysis (4 min instead of 15 min), which quickly determined TC by thermal evolution in a mixed helium and oxygen atmosphere and estimated EC on the basis of the optical measurement of BC obtained during the TOA analysis. OC was then determined by the difference of TC minus BC after conversion of BC to ambient concentrations. The analysis is faster and more sensitive because only total carbon is detected thermally resulting in an improved sampling time resolution. The method gave promising results, although its accuracy depended on the calibration of the optical measurements. In addition, the study showed that the instrument can be used to continuously measure the quasi-ultrafine component of ambient EC and OC by using the $PM_{0.25}$ (particles <0.25 μm in diameter) stage of a personal cascade impactor[91] upstream of the sampling inlet.

A comparison between the continuous R&P 5400 Ambient Particulate Carbon Monitor[92] and filter-based carbon measurements using a Reference Ambient Air Sampler (RAAS; Thermo Andersen) speciation sampler with thermal/optical reflectance (TOR) analysis for OC and EC was obtained at the Fresno Supersites Project.[87] The R&P 5400 operates differently than the Sunset monitor. In this monitor, particles collected for 30 min on an impaction surface are thermally evolved in clean air at 275 °C for OC and then at 750 °C for TC. No pyrolysis correction was made in this sampler. EC was determined by difference as described above.

The R&P 5400 carbon analyzer suffered instrument malfunctions and leakages, which resulted in a data capture of 60%. When the system was operating correctly, R^2 for TC between the 5400 and filter-based measurements ranged from 0.42 to 0.69, with similar correlations for OC and EC. On average, the R&P 5400 TC was 40–60% higher than TC measured on filters. Precisions with respect to filter samplers were approximately 70–80% of average carbon concentrations. The authors noted the missing pyrolysis correction in the R&P instrument and an analysis atmosphere of air for the R&P instrument instead of the helium and helium-oxygen mixture as in the Sunset analyzer among the possible causes for the relatively poor performance of the R&P 5400.

The R&P 5400 is being evaluated by EPA for possible deployment in EPA's National $PM_{2.5}$ Chemical Speciation Monitoring Network. In this comparison,[93] the R&P 5400 was compared with a Magee Scientific Aethalometer (Model AE-21) and to aerosol collected on quartz-fiber filters using a RAAS speciation monitor that operated the carbon channel at 7.3 min^{-1}. The filters were analyzed in the laboratory by thermal optical transmittance (TOT), using the STN protocol,[85] although OCX2 as described in the method is no longer applied to the data. Only moderate correlations were observed for TC and OC (r = 0.64 and 0.67, respectively) between the RAAS and R&P 5400. A significant underestimate by the R&P 5400 was observed relative to the RAAS TC and OC (64% and 78%, respectively). In part, the underestimate was due to a positive artifact associated with the quartz-fiber filter on the RAAS as well as the fact the R&P 5400 does not correct for charring. EC was overestimated by the R&P 5400 by 89%. The Aethalometer BC correlated well (r = 0.86) with the RAAS EC, but the Aethalometer overestimated RAAS EC by 30%. The R&P 5400 overestimated the Aethalometer BC by 17%.

Water-Soluble Organic Carbon (WSOC). Sullivan et al.[94] described a continuous method for the measurement of WSOC in ambient particles and its evaluation during the St. Louis Supersites Project. In this method, a PILS was combined with a Total Organic Carbon (TOC) analyzer (Model 800 Turbo Total Organic Carbon Analyzer, Sievers) and provided continuous 6-min integral measurements with a detection limit of 0.1 μg/m^3. Miyazaki et al.[95] compared the WSOC by PILS to 12-hr integrated filter measurements of WSOC. The methods agreed to within 12%. The WSOC measurements were compared with OC measurements and the ratio of WSOC to OC measured in summer and fall ranged from 0.40 to 0.80. The authors found that in certain periods this ratio was correlated to ozone, whereas in other periods it was not. They suggested that during the highly correlated periods with O_3, a major part of WSOC was associated with secondary organic aerosol formation, which is higher during photochemical activity when ozone concentrations are increased. Relationships with secondary organic aerosol (SOA) and oxygenated organic aerosols (OOA), which correlates with SOA, were further evaluated by Miyazaki et al.[95] and Kondo et al.,[96] respectively. This shows that the instrument may provide additional information about the sources and atmospheric processing of fine particulate

organic compounds soluble in water. Further improved methods and analysis techniques applied to the PILS-WSOC system yielded quantification of more refined speciation of different WSOC groups; i.e., acid, neutral, and basic functional groups.[97]

Absorption Methods for Measuring BC in Ambient Particles. Absorption methods are used to measure the dark chemical components of particles found in air, which is usually dominated by EC or BC, either also referred to as soot. Although BC and EC are similar, they are not necessarily the same and each is defined operationally by their measurement method. In general,[10] BC is strictly an optical measurement based on absorption of light at a given wavelength by the particles collected on a filter. Different detectors can be used to measure the optical absorption as described below. EC, on the other hand, is measured by the thermal oxidation and evolution of carbon from a filter followed by detection of the gas evolved (e.g., carbon dioxide). Some thermal methods include optical absorption to account for charring of the OC as it is heated. Thermal methods for OC and EC were described earlier in this paper.

Aethalometer. The continuous measurement of optical absorption or attenuation of particles collected on a filter is obtained by the Aethalometer[98] (Magee Scientific). The "classic" single-wavelength (880 nm) Aethalometer, AE-16, collects particles on a quartz-fiber filter tape, which is advanced when the transmission reaches a preset lower level. The absorption by particles is related to BC by an empirically defined calibration factor or absorption coefficient (m^2/g), which varies depending on the absorption wavelength and to some extent on the physical and chemical properties of the aerosol.[99–101] The commercially available single-wavelength Aethalometer uses an absorption coefficient value of 16.6 m^2/g for converting absorption to ambient concentrations of BC in $\mu g/m^3$. Dual wavelength (370 and 880 nm) and seven-wavelength (350, 470, 521, 590, 660, 880, and 950 nm) Aethalometers (AE-21 and AE-31, respectively) are now available and operate in a similar fashion to the single-wavelength instrument. Multiple wavelength instruments provide information about other carbonaceous components in air. For example, the 370 wavelength in the UV provides information about aromatic and PAH compounds associated with the particles collected on the filter.[99]

Recent results indicate that the Aethalometer overestimates BC concentrations on a fresh filter and underestimates BC concentrations on a loaded filter on the basis of comparisons with a PAS[100] and filters loaded with laboratory-generated soot and other compounds.[101] Additional details of the comparison with PAS are given in the next section. Factors that seem to influence the absorption or attenuation measurement of BC on filters include light scattering by the filter fibers and the subsequent increase in the optical path through the filter, as well as additional absorption by particles that can result because of the longer path length as light is scattered through the particle-laden filters. Weingartner et al.[101] have developed an empirical model to allow for correction of these factors that are associated with the filter-based absorption measurements.

In situ and filter-based carbon measurements were obtained at the Fresno Supersite over a period of several years. Comparisons of the methods used during 2000 have been reported.[87] During that time period, the 880-nm BC measurements of two Aethalometers (single- and seven-wavelength) were compared and were extremely well correlated ($R^2 = 1$).[87] The seven-wavelength instrument was on average approximately 9% (0.11 $\mu g/m^3$) lower than the single-wavelength instrument. The difference between the two instruments might have been a result of the seven-wavelength instrument having more frequent tape advances. Consequently, it also had more gaps in the data (10–20 min each time the tape was advanced). In Fresno, the average EC from filter-based measurements collected using quartz-fiber filters with TOR as the reference analytical method was from 25 to 31% higher than the single- and seven-wavelength Aethalometers, respectively. The reported EC and BC were well correlated ($R^2 > 0.89$). To achieve better agreement of the Aethalometer BC with TOR EC, the authors suggested a site-specific calibration factor (m^2/g) to convert light absorption to BC ($\mu g/m^3$) for the Aethalometer. The calibration factor used during this Fresno study was 19.2 m^2/g.

In Raleigh, NC, the AE-21 Aethalometer was compared with EC measured on quartz-fiber filters with TOT as the reference analytical method.[93] The Aethalometer reported 30% higher BC than EC ($R^2 = 0.86$), which is the opposite of what was reported in Fresno, CA. One likely difference is due to the EC analysis method, in which the TOR EC often reports higher values (as high as a factor of 2) than TOT EC.[102,103] The Aethalometer also was compared with the R&P 5400. The R&P 5400 EC was, on average, 17% greater than the Aethalometer BC, similar in direction to the Fresno, CA, results. However, without reference standards it is not possible to indicate which method provides the most accurate results for EC. This of course is further complicated by the several different methods that exist for determining EC as well as OC in PM collected on filters.

Jeong et al.[99] made continuous measurements of OC, EC, and $PM_{2.5}$ during summer 2002 in Rochester, NY, and Philadelphia, PA. In this case, the authors compared 2-hr integrated thermal EC (EC) and optical EC (BC-S), the latter using the Sunset Lab OC/EC analyzer's optical measurement usually used to correct for pyrolysis to optical BC (BC-A) obtained from a continuous two-wavelength Aethalometer. Venkatachari et al.[104] did a similar comparison in Flushing, NY, during January and early February 2004.

The 2-hr average EC and BC-S values were well correlated in Rochester ($R^2 = 0.95$) with a slope of 0.89 ± 0.02, whereas the correlation coefficient was 0.73 with a slope of 0.99 ± 0.07 in Philadelphia.[99] Comparing EC and BC-A, the correlation coefficients at both sites were 0.84 with a slope of 3.3 ± 0.2 in Rochester and 0.60 with a slope of 2.7 ± 0.1 in Philadelphia. In Flushing,[104] hourly averaged BC-S, EC, and BC-A were also well correlated with each other although slopes were again different from unity. These results suggest that the attenuation coefficients of optical EC analyses may vary and depend on the

sampling locations, in other words, on PM composition and atmospheric conditions.

In July 2002, high concentrations of wood smoke were transported to the site in Philadelphia from a Canadian forest fire located north of Quebec.[99] The proportionality between EC and BC-A decreased from 3.61 to 0.35, whereas there was no significant change of the correlation coefficient. Similar behavior was found with the comparison of EC and BC-S. Although EC and BC-S showed good agreement, the proportionality changed from 0.97 to 0.31 because of the influence of the forest fire. During the fire episode, there was a significant increase in the UV-absorbing organic compounds measured by the UV channel of the Aethalometer; this was indicative of oxygenated organic compounds. This illustrates one advantage of the seven-wavelength method compared with the single-wavelength instrument.

It is clear from these results that there needs to be careful definitions of the operational carbon fractions. It is suggested that the term "black carbon" be reserved for optically based measurements and the term "elemental carbon" be reserved for thermal or thermal-optical measurements, also indicated in the NARSTO PM Assessment by Fehsenfeld et al.[10] Even within each of these categories, it is essential to carefully define the measurement protocols because variations among the available protocols will produce differences in the measured OC and EC concentrations. In addition, it is critical that reference standards are developed for both OC and EC as measured by continuous and integrated-laboratory sampling methods.

Photoacoustic Methods. In situ continuous measurements of light absorption (B_{abs}) by aerosols are obtained directly by PAS.[105,106] In these systems, air, after having NO_2 removed, is drawn into an acoustic cell where it is illuminated by light at a specified wavelength to avoid interfering gases and is modulated at the resonant frequency of the cell. The electromagnetic energy absorbed by the particles (primarily soot or BC) heats the carrier gas, which expands and then contracts according to the modulation frequency of the light. The light source is usually a laser at a specific wavelength, such as 532 nm,[106] that is chosen to avoid absorption by other gas-phase species, such as oxygen or water. The change in pressure in the cell due to modulated heating and cooling of the particles causes a pressure variation that is effectively a sound wave with intensity measured by a microphone. Arnott et al.[106] report limits of detection for light absorption of 0.4 1/m or 40 ng/m^3 of BC in ambient air. Arnott et al.[106] indicate this improved limit of detection is achieved by a redesign of the system to greatly reduce absorption of the laser signal by the cell windows. The signal is now limited by acoustic and electronic noise.

As with the Aethalometer, absorption is converted into concentration by applying an absorption or absorptivity coefficient, which as discussed above varies because of the physical and chemical properties of the aerosol. Absorptivity coefficients are determined empirically by comparison to methods that measure EC or BC directly, such as the thermal-optical methods described above. However, because PAS measures the in situ absorption of particles in air, it avoids common interferences associated with collection of carbonaceous materials on filters. As well, the photoacoustic method can be calibrated using NO_2 gas[107] that cannot be achieved with filter-based methods such as the Aethalometer or thermal-optical methods. Therefore, PAS may currently be the best available technique for measuring particle absorption coefficients because it can be independently calibrated and avoids filter collection problems. However, although great progress has recently been made in understanding the method, additional operational and diagnostic evaluation is needed before it is suitable for routine regulatory monitoring because it has not yet been deployed under routine monitoring conditions.

McMurry[52] summarizes two studies comparing the photoacoustic method for measuring BC to filter-based thermal-optical methods and indicated agreement of absorption coefficients to within approximately 15%. Moosmüller et al.[108] also compared the PAS measurements of aerosol light absorption to filter-based methods (TOR) and to the Aethalometer. This comparison occurred during the winter in Brighton, CO, during the Northern Front Range Air Quality Study. The Aethalometer and PAS were well correlated ($R^2 \sim 0.9$) as shown in Figure 16, a and b, with slopes of the regression lines (representing absorption efficiency in m^2/g of aerosol) ranging from approximately 5 to 10 m^2/g for wavelengths of 685 and 532 nm. Time series of these data (Figure 16, c and d) show not only how well they track each other, although large differences are observed at times (single points having differences of a factor of 2), but also the large variations that occur over short time periods (hours) showing the influence of sources and meteorology on BC concentrations at the site. Similar correlations ($R^2 = 0.85$) were observed for comparisons to the filter-based TOR method with a lower absorption coefficient for EC of 3.6 m^2/g at 685 nm. These results are in the range of those obtained previously with absorption coefficients ranging from 2 to 17 m^2/g.[109,110] They also show the wavelength dependence of the absorption efficiency of aerosols. Data presented by Moosmüller et al.[108] over a range of wavelengths from 400 to 800 nm for different laboratory-generated and ambient aerosols also indicate a wavelength dependence on the absorption coefficient for absorbing aerosols of $\lambda^{-2.7}$. Arnott et al.[100,111] reported similar comparisons between the Aethalometer and the PAS method with a slope of 8.1 m^2/g in Big Bend in southeast Texas and 8.4 m^2/g in Reno, NV. Comparison with a particle soot absorption photometer (PSAP) during the Big Bend study yielded high correlations, but PSAP values were greater by 1.6. Arnott et al.[111] also examined the influence of RH on PAS measurements of aerosol light absorption and found that light absorption systematically decreased when RH increased above 70%.

Trace Elements

Methods are not currently available for the continuous measurement of trace elements in near real time in the field. Continuous samples for trace elements in particles less than 2.5 μm in diameter were obtained by the Semi-continuous Elements in Aerosol Sampler (SEAS).[112,113] In

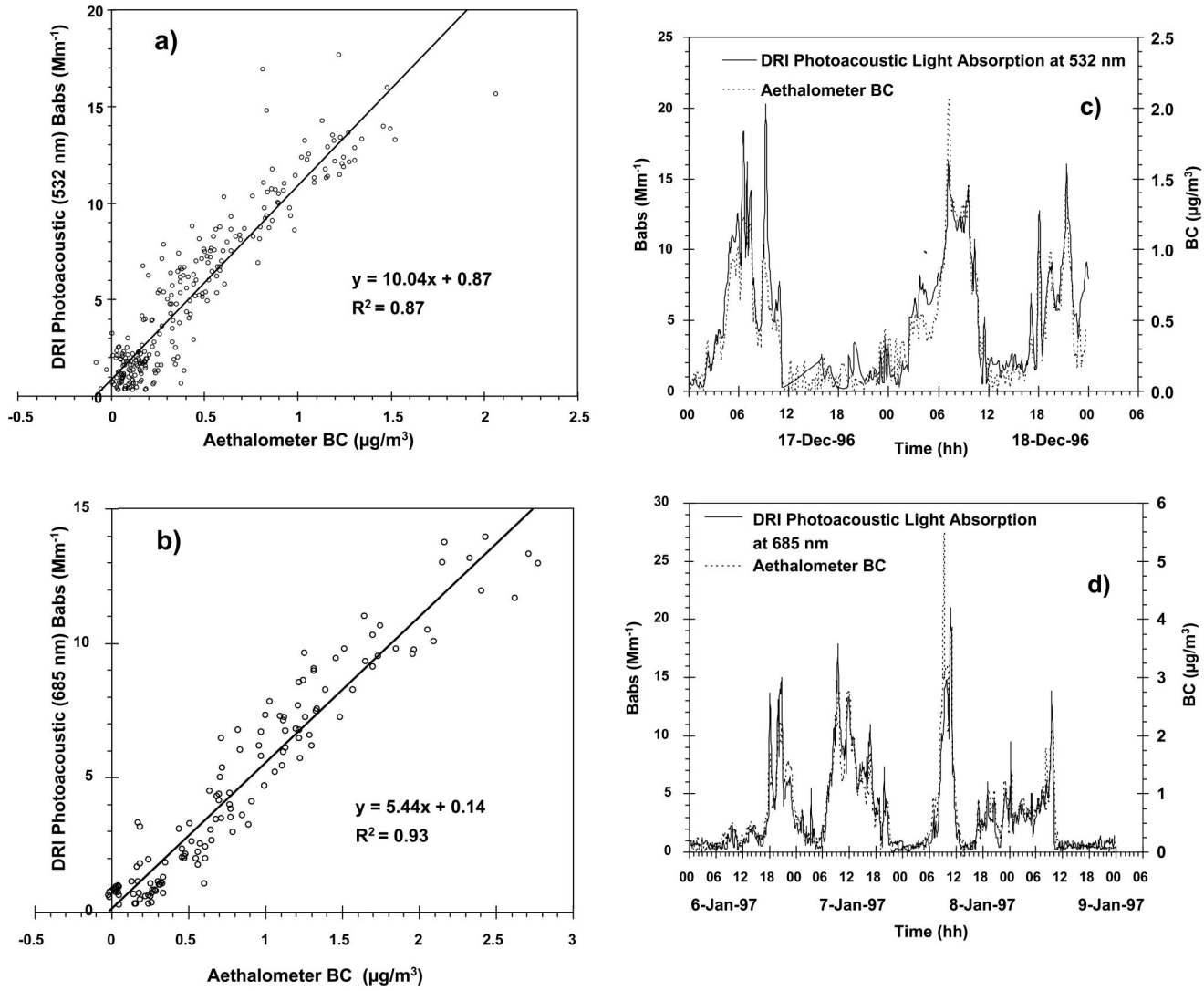

Figure 16. Comparison of Aethalometer and PAS at two wavelengths 532 nm and 685 nm. Data were collected at Brighton, CO, during the Northern Front Range Air Quality Study. (a and b) Correlation between Aethalometer and photoacoustic measurements at (a) at 532 nm for December 17 and 18, 1996, and (b) 685 nm for January 7, 1997. (c and d) Comparison of photoacoustic measurements of aerosol light absorption at (a) at 532 nm and (d) 685 nm and Aethalometer measurements of BC concentration. Adapted with permission from Moosmüller et al.[108] Reproduced/modified by permission of American Geophysical Union. Copyright 1998 American Geophysical Union.

this method, 30-min samples were collected automatically in vials in the field with subsequent analysis in the laboratory by graphite furnace atomic absorption spectroscopy (GFAAS) and/or inductively coupled plasma-MS (ICP-MS). In this way, 11 trace elements important for source apportionment were obtained with a 30-min time resolution. A second generation SEAS (SEAS-II) was deployed in the Supersites Program. A third generation SEAS is commercially available (OEI). The SEAS uses controlled condensational growth by direct steam injection to grow particles with aerodynamic diameters as small as 80 nm to approximately 3–4 μm. A virtual impactor concentrates the initial 90-L/min flow into 13 L/min and the droplets are then separated from the airstream by a real impactor. The liquid slurry is collected and returned to the laboratory for chemical analysis. The collection efficiency of the SEAS-II is estimated to be more than 80% for particles less than 1-μm AD.[114] A comparison between 24-hr average SEAS-II and X-ray fluorescence obtained from 24-hr STN filter samples indicated good agreement between the two methods for most elements, with agreement to within two standard deviations of the propagated analytical uncertainty (Figure 17).[115] Uncertainty was typically larger for X-ray fluorescence than for SEAS using GFAAS with Zeeman background correction. Figure 18 illustrates the high-time resolution (30-min data) results for 3 days in November 1999 obtained in College Park, MD.[113] Relatively wide variations in trace elements can be seen because of source impacts and meteorology. Application of these highly time-resolved measurements in the new Pseudo-Deterministic Receptor Model (PDRM)[116] indicates the advantages of having elemental data at high time resolution. PDRM is a hybrid receptor-Gaussian plume model that allows not only for the identification of specific sources but also for calculation of source emissions from those individual sources using meteorological dispersion factors and source-resolved ambient air concentrations.[114,116] The latter requires additional data (e.g.,

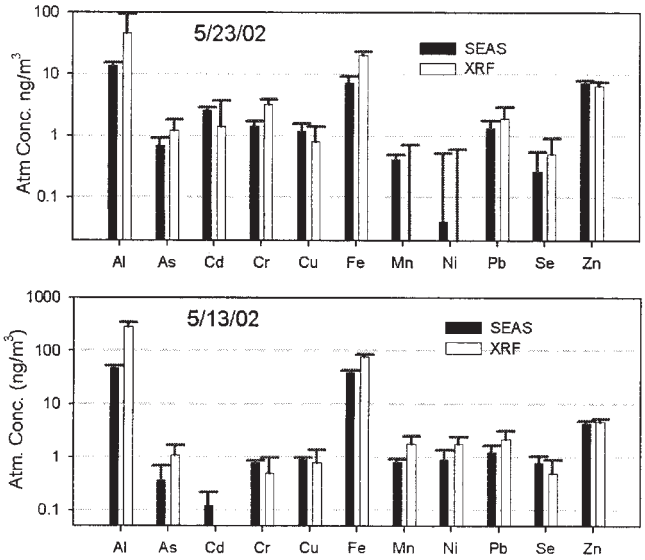

Figure 17. Atmospheric concentrations of metals measured simultaneously by 24-hr filter and SEAS methods (adapted with permission from Pancras et al.[115]). Copyright 2006 Elsevier, *Atmospheric Environment.*

meteorological data), and benefits from having measurements of other relevant gas-phase species like SO_2 and other indicator species; e.g., CO/NO_y for mobile sources and O_3 for photochemically aged air masses.

Particle Mass Spectrometers

Significant progress has taken place in the development and application of particle mass spectrometers over the last decade.[117,118] In particular, much progress has occurred since 1999 when, during the Atlanta Supersites Experiment,[5] four particle mass spectrometers were compared for the first time by Middlebrook et al.[119] (Figure 19). Before this time, no intercomparisons had occurred. In fact, this was the first field deployment for all the methods with the exception of the Aerosol Time-of-Flight MS (ATOFMS). What also made the Atlanta Supersites experiment even more valuable was the wide range of other continuous and filter-based methods available for comparison. The compared particle MS methods included National Oceanic and Atmospheric Administration's Particle Analysis by Laser Mass Spectrometry (PALMS), University of California-Riverside's ATOFMS, University of Delaware's Rapid Single-Particle Mass Spectrometer II (RSMS-II), and Aerodyne's Aerosol Mass Spectrometer (AMS) (as diagramed in Figure 19). Differences in operation and method among the instruments as well as a comparison of data are described by Middlebrook et al.[119] In general, the different single particle methods identified similar particle classifications with reasonable agreement among comparable size fractions, as illustrated in Table 3.

Since the 1999 Atlanta Supersites Project, single particle methods have advanced significantly, becoming dominant measurement methods in the research community, and likely representing the single greatest advance in PM measurement technologies over the last decade. Descriptions of the methods are beyond the scope of this paper. However, insights gained from particle mass spectrometers are described in a companion paper to this review[120] and two other recent reviews.[117,118] These papers show the extent of information being learned from application of these methods, most achieved just over the last few years.

SUMMARY AND RECOMMENDATIONS

Significant advances in the measurement of the chemical and physical properties of PM have occurred as an outcome of the Supersites Program and related studies over the last 5–7 yr. Results from these studies indicate that continuous monitoring methods often provide improved estimates of what is in the air as compared with current standard filter-based methods. Methods used to measure various physical properties of PM, not measured by filter-based methods, also have emerged or have been greatly improved. Of considerable importance is the near-real-time availability of these data, often at hourly time resolution or shorter. It is particularly encouraging that the integrity of these new methods has been established in multiple urban areas and in locations where PM consists of a large fraction of semi-volatile PM components. Application of continuous methods with greatly improved time resolution has already led to a more thorough understanding of atmospheric processes leading to PM accumulation in air and the linkages between PM sources and ambient concentrations of PM observed at receptor locations. Air quality managers can use this information to develop more cost-effective and efficient strategies for reducing PM to below the levels of the National Ambient Air Quality Standards (NAAQS) to protect public health and ecosystems from the adverse effects of PM.

The primary question addressed in this paper was, "Are there routine monitoring techniques that are at a stage of understanding and operational skill that should be instituted in routine monitoring networks so that we will have better information in a few years?" It is important to note that this was not a comprehensive review and that it was primarily based on results from the Supersites Program and related studies, mostly conducted within the United States during the last 5–7 yr. However, the recommendations below should provide user communities with sufficient guidance to assist with decision-making for near-term future monitoring. In the longer term, as new methods are developed and methods continue to be evaluated, the findings within will likely change but these recommendations represent the best guidance currently available.

Recommendations for methods that show the most promise, on the basis of the results from the Supersites Program and related studies, have been divided into those methods that should be considered for implementation into either routine monitoring networks (*Routine*) or into research networks (*Research*). However, most methods have only been evaluated in a limited number of locations and conditions, so virtually all methods require continued operational and diagnostic evaluation to better characterize the method and to quantify the analytical uncertainties associated with the measurement. A recommendation of *Routine* indicates it is commercially available and has shown significant reliability in tests, is operationally suitable to routine network operations, and

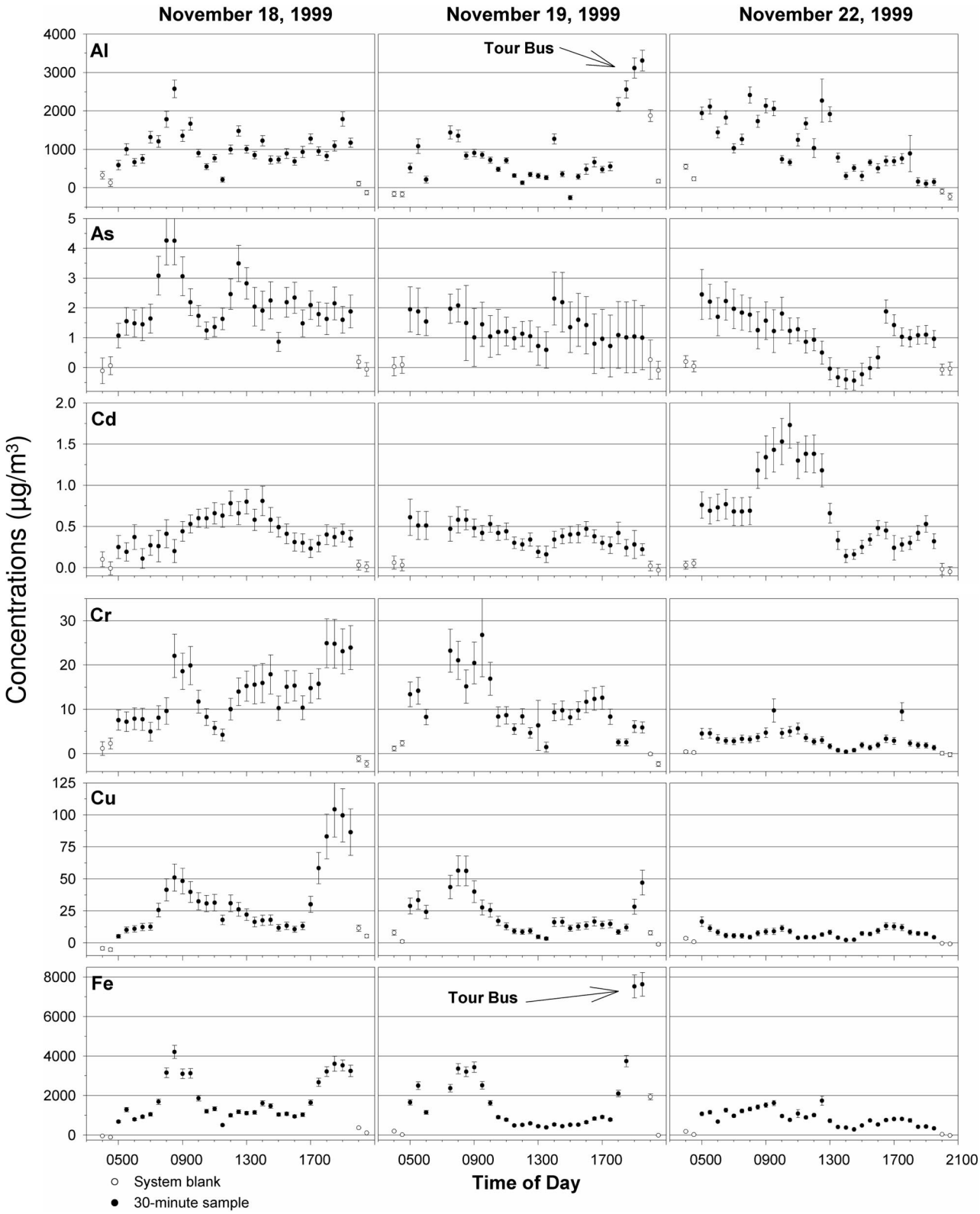

Figure 18. Ambient aerosol concentrations measured in College Park, MD, on November 18, 19, and 22, 1999. Each point represents one 30-min collection period. Solid symbols are 5-hr averages of the 30-min samples. The solid symbols in each of the plots are 5-hr averages. High concentrations of Fe at 7:00 p.m. coincided with a running tour bus parked 20 m from the sampling inlet (adapted with permission from Kidwell et al.[113]). Reprinted with permission. Copyright 2004 American Association for Aerosol Research.

further evaluations can occur under network conditions. A recommendation of *Research* indicates the method requires additional evaluations and testing under research conditions and/or may be technically difficult to operate under routine network conditions, perhaps requiring a highly skilled operator and considerable attention to

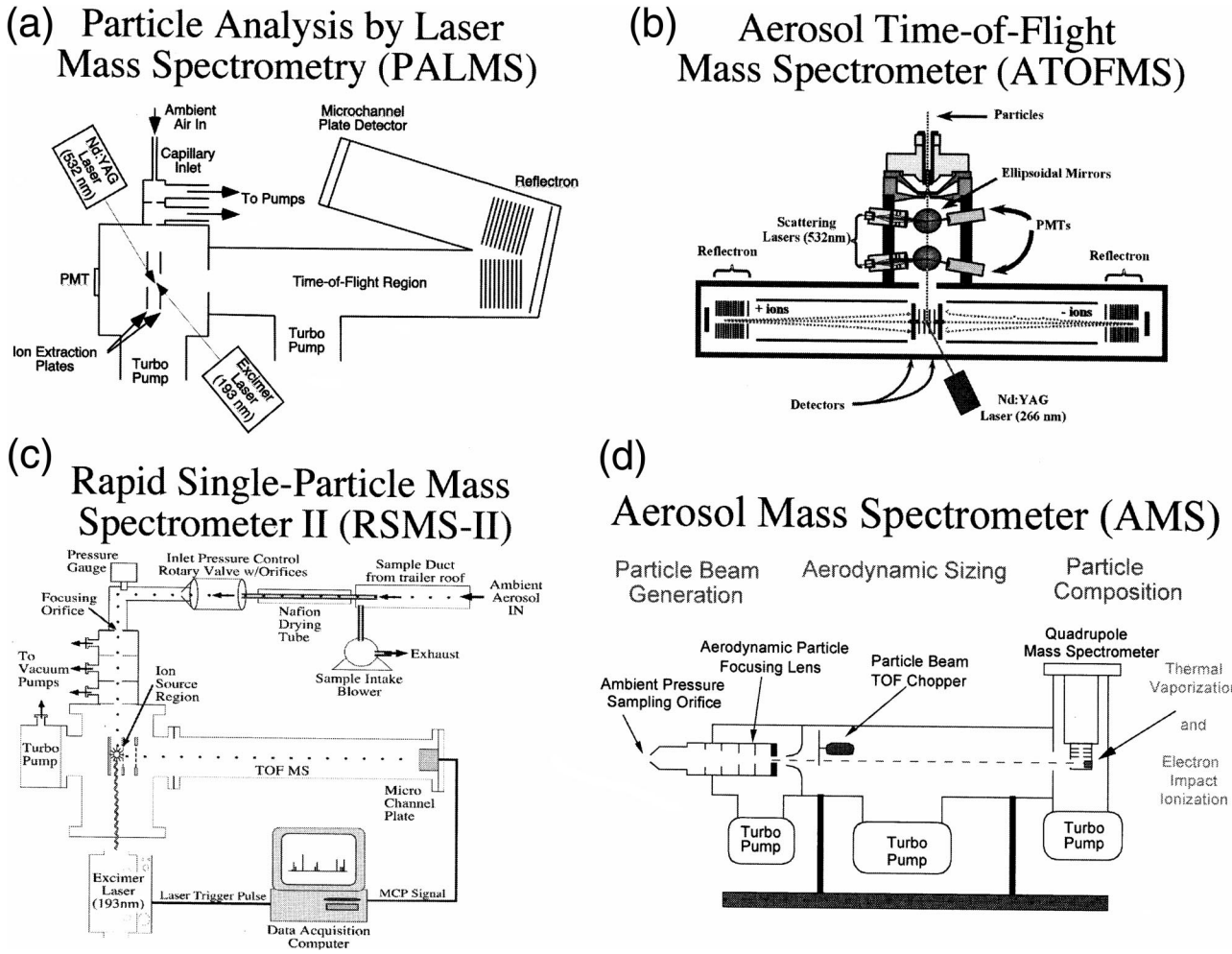

Figure 19. Schematic diagrams of the four particle mass spectrometers that operated during the Atlanta Supersite Project (from Middlebrook et al.[119]). (a) PALMS, (b) ATOFMS, (c) RSMS-II, and (d) (AMS). Reproduced/modified by permission of American Geophysical Union. Copyright 2003 American Geophysical Union.

maintain. In most cases, if the recommendation is *Routine*, then *Research* methods are not listed and other existing methods would fall under that category.

Mass and Physical Properties

$PM_{2.5}$ Mass. Results from the Supersites Program indicate that either the D-TEOM (no longer commercially available) or FDMS provide estimates of ambient $PM_{2.5}$ mass concentrations with reduced or eliminated sampling artifacts relative to other commercially available continuous methods (e.g., TEOM, SES TEOM, BAM, and CAMM) or routine filter-based methods. These conclusions were obtained in comparisons with methods designed to minimize sampling artifacts as well as methods that are known to lose semi-volatile material during sampling (e.g., heated TEOM or FRM). Concurrent measurements with the RAMS, PC-BOSS, Harvard Impactor, and other filter-based methods showed that the FDMS and D-TEOM efficiently collect the semi-volatile material not captured by monitors designed for such a purpose. Although evaluations have been limited to a couple of laboratory studies and field studies in only three or four locations, the field studies likely have been robust tests because the aerosol in the test locations

Table 3. Classification frequencies for all particles sampled during the entire study by the laser-based mass spectrometers.[a]

	RSMS-II 0.015–1.2 μm 15989 Spectra (%)[b]	PALMS 0.35–2.5 μm[c] 206131 Spectra (%)[b]	ATOFMS 0.2–2.5 μm 455444 Particles (%)[d]
Organic/sulfate mixtures	75	87	74
Sodium/potassium sulfate	7	7	6
Soot/hydrocarbon	3	3	5
Mineral	3	0.6	12
Total	88	97	97

Notes: From Middlebrook et al.[119] Reprinted/modified by permission of American Geophysical Union. Copyright 2003 American Geophysical Union. [a]Frequencies were not adjusted for particle transmission. [b]Only frequencies in the positive ion spectra are shown here. [c]The PALMS lower size limit of 0.35 μm is derived from the optical lower limit of 0.22 μm (see footnote a in Table 1 from Middlebrook et al.[119]—"optical lower limit (0.22 μm) was converted into aerodynamic diameter, d_a, by assuming the optical diameter equals the Stoke's diameter, d_s, and $d_a = d_s \times \mathrm{sqrt}(\rho_p C_c/\rho_0)$, where ρ_p is the particle bulk density = 1.5 g·cm^{-3} (P.H. McMurry, personal communication[126]), C_c is the Cunningham correction factor = 1.74 for d = 0.22 μm, and ρ_0 is the standard density = 1 g·cm^{-3} [Hinds[127]]. [d]Each ATOFMS particle had either a positive or negative spectrum or both.

typically contained relatively high concentrations of semi-volatile PM components.

Finally, the current FRM falls within the category of standard filter-based measurement methods and can potentially lose semi-volatile PM components during sampling. It is a regulatory standard to judge compliance with NAAQS, and not an analytical standard designed to determine the "true" accuracy of mass concentrations relative to what is actually in the air (NARSTO PM Assessment).[10] Its design was chosen initially to yield data comparable with the air quality data used in the health studies that provided the basis for the $PM_{2.5}$ standards.[1,121]

Recommendation: *Routine*—D-TEOM and FDMS.

PM_c Mass. Several instruments are under evaluation by EPA as potential reference or equivalent methods. These include the PM_c TEOM, PC BAM, and APS. In the first round of comparisons, all three showed significant differences, under some conditions, relative to the reference method (difference between PM_{10} and $PM_{2.5}$ FRM samplers). However, manufacturers have modified these samplers and they are currently undergoing additional evaluations. On the basis of their published performance evaluations, which were conducted under more carefully controlled conditions than the field tests, all three methods appear to be promising in providing reliable hourly coarse PM mass concentration data. However, the APS is not a direct measure of PM_c and assumptions to convert the measurement to ambient concentrations may result in significant uncertainties in the reported results because of the need to estimate particle density and shape factors under a wide variety of environmental and particle composition situations.

Recommendation: *Routine*—PM_c TEOM and PM_c BAM. Note: Implementation would not occur until EPA's evaluation is completed.

UF Mass. The available method is a prototype using existing instruments (BAM monitor preceded by a 150-nm cut point impactor) to directly measure UF PM mass in near real time. Comparisons to MOUDI and SMPS show good agreement with regression slopes and R^2 values close to 1. Use of this method in monitoring programs may become more important because recent data suggests UF PM mass may adversely affect human health and because UF mass does not seem to correlate with UF number concentration or with $PM_{2.5}$ mass, both of which can be measured routinely but apparently cannot be used as a surrogate for UF mass.

Recommendation: *Research*—Impactor followed by a continuous mass monitor, either BAM or TEOM.

Size Distributions and Number Concentration. Number concentration refers to the measurement of the total number of particles per unit volume within a given total size range and measured, for example, with a CPC. Distributions of particle size and concentration (number of particles per unit volume) can be measured over a series of sizes within a size range, for example, from a few nanometers to 10 μm using the combined SMPS-APS system. Measurements of particle number concentration and size distribution are important for better understanding the formation of aerosols by nucleation, condensation, coagulation, and the impact of PM on health. Several of these methods are well established and described in the literature.[52] Different applications of or modifications to these well-established methods have resulted in extended size ranges and in improved measurements with specified tolerances of several important and difficult to measure PM attributes, e.g., PBW and particle density.

Size Distribution. The combined SMPS, including the nano-SMPS, and APS appear to provide reliable size distribution concentration data from a few nanometers to 10 μm. The SMPS separates particles on the basis of particle mobility followed by counting single particles with a CPC. The size range is from a few nanometers to 800 nm. The APS counts single particles optically in the size range from 500 nm to approximately 20 μm, although counting efficiency degrades above 10 μm. Application of simple algorithms allows merging of the size distributions, with excellent agreement where the distributions overlap. Assumptions about particle density and shape allow conversion of the size distribution to mass concentration (UF, fine, and coarse). However, density varies with particle size and composition, and particle shape is difficult to measure, so these assumptions need to be confirmed. Furthermore, greater uncertainty is associated with the measurement of mass by this approach as opposed to direct measurement.

Recommendation: *Routine*—APS, SMPS, Nano-SMPS or a combination of two or all three depending on the desired size range.

Number Concentration. CPC, CNC, and other similar methods are readily available for obtaining number concentrations and are described in the literature.[52] In these methods, particles are typically grown by condensation with butanol or water followed by counting single particles optically. The lower limit has been extended to less than 10 nm. A CPC method based on growing the particles with water vapor (WCPC) rather than butanol was developed and consistent results were obtained between the two methods.

Recommendation: *Routine*—CPC, CNC, and others are already used in routine networks.
WCPC: Four models are currently commercially available, although additional evaluations are needed before full routine network operations are recommended. Note: Water is a safer chemical than butanol, which is combustible, has a strong odor, and could contaminate other concurrent measurements.

Density. Measurements of particle density are needed to convert measured physical properties (e.g., particle number) to mass. Although the components needed to measure density exist commercially (SMPS, DMA, APM, and ELPI), a commercial unit dedicated to density measurement is not yet available. Therefore, further development

and evaluation of practical continuous methods for density are needed to enable widespread applications, especially given the critical role that density plays in the different ways particles are measured in air (e.g., aerodynamic, mobility, and optical diameters).

Recommendation: *Research*—DMA-Aerosol particle mass analyzer.

Chemical Composition of Particles

Sulfate, Nitrate, and Ammonium. Several methods have been developed for continuous measurements of anion and cation species in aerosols. Sulfate and nitrate, the most abundant of these, are being routinely measured in research networks as well as being evaluated for use in national monitoring networks. Sulfate, nitrate, and other anions (light organic acids, e.g., formate, acetate, oxalate) and cations (NH_4^+, calcium, and magnesium) are measured directly by the IC-based methods, and sulfate and nitrate are measured indirectly by thermal-gas analysis methods. Results from the Supersites Program indicate that these methods provide useful data. However, because reference standards are not available, the thermal-gas methods appear to require calibration against daily average filter-based measurements, which can then be applied at hourly intervals. Acceptable correlations, but biased low by 10 to 20% relative to filters have been obtained for the Thermo 5020 sulfate analyzer. Better agreement was observed with the continuous methods that collect particles by condensation or humidification followed by IC analysis in near real time (e.g., PILS, SJAC, and PPS). Although similar performance to filter-based methods can be obtained for the ICVS method after calibration to 24-hr filter-based measurements, the method is nonlinear for both sulfate and nitrate with better agreement to filters at low concentrations, but low results compared with filters (20–40%) are reported at higher concentrations (e.g., NO_3 >2 $\mu g/m^3$).

Recommendation: *Routine*—IC-based methods for a range of anion (sulfate, nitrate, chloride, organic acids) and cation (ammonium, sodium, potassium, calcium, and magnesium) species.
Note: Operational evaluation of the latest commercial methods, which can be done on a limited basis within a routine monitoring network, is required before full-scale network operation is advised.

Elemental and Organic Carbon. Two methods (Sunset and R&P) are available commercially that measure OC and EC simultaneously. The Sunset monitor uses a method similar to the laboratory version used in EPA's Chemical Speciation Monitoring Network. Evaluations of the Sunset continuous instrument during the Supersites Program and other studies showed it to compare well in most cases to the STN filter-based measurements with excellent operational performance as well. However, the Sunset method still requires additional evaluation before full implementation in routine monitoring networks. In addition, if this method is employed in national monitoring networks, the temperature protocol will need to be changed to match the IMPROVE temperature protocol to allow for better consistency between continuous and filter-based methods. The latter is needed because in mid-2007 the STN protocol (sampling and analysis) for OC and EC was replaced by the IMPROVE protocol.[122] Although the R&P method also provides estimates of OC, EC, and TC, the reported concentrations are different.
Recommendation. *Routine:* Sunset method for OC, EC, and TC, especially if consistency with STN or IMPROVE is desired.

Trace Elements. Continuous data for trace elements with a 30-min time resolution have been obtained, although these data are not available in real time. Samples are collected in the field with subsequent analysis in the laboratory by appropriate methods (e.g., GFAAS and ICP-MS). Application of these data in source apportionment studies clearly indicates the importance of high time resolution data and emphasizes the need for a simple routine approach to measure trace elements continuously in the field.

Recommendation: *Research*—SEAS and continued need to develop field-based methods.

Particle Absorption/BC. The Aethalometer and PAS provide direct measures of the light absorbing carbon in aerosols as an absorption value (1/m). The absorption coefficient is dependent on the wavelength of light used to make the absorption measurements as well as a number of other factors, such as particle composition. Thus, location-specific coefficients are needed to obtain the most accurate results. The Aethalometer measurement is obtained after the PM is collected on a filter tape that advances over discrete time intervals whereas the PAS provides a continuous in situ measurement. In both methods, the light absorption value is converted to ambient concentration by applying an empirically obtained absorption or absorptivity coefficient in m^2/g. The measure in ambient concentration units is referred to as BC, which is related to but different from EC being measured thermally, albeit both are defined operationally. Because PAS measures the in situ absorption of particles in air, it avoids common interferences associated with collection of carbonaceous materials on filters, such as in the thermal or TOA methods and Aethalometer. PAS can also be calibrated by adding a known concentration of an absorbing gas, such as NO_2, directly into the absorption cell. PAS is not available commercially. The Aethalometer is robust and widely used in monitoring networks with relatively well-defined uncertainties, although recent comparisons to PAS are better defining the uncertainties and biases associated with the measurement of BC by the Aethalometer. One-, two-, or seven-wavelength Aethalometers are available commercially. The single-wavelength unit usually operates at 880 nm. Wavelengths closer to the UV (e.g., 350 nm) provide information about PAHs and other organic compounds that absorb in or near the UV. The Aethalometer and PAS are usually well correlated ($R^2 > 0.8$) with filter-based methods for EC but absolute comparisons depend on the absorption coefficient used to convert b_{abs} to BC.

Recommendation: *Routine*—Aethalometer and PAS.

Note: A commercial PAS unit needs to be developed and evaluated before routine operation.

WSOC. The method to measure WSOC (PILS-TOC) is new and not yet commercialized. There are no similar evaluated methods for comparison, but results indicate that WSOC correlates well with SOA during high ozone periods, thus providing a method possibly to track SOA in near real time. Confirmation of the relationship between WSOC and SOA is beginning to be observed in multiple locations as well as improvements to the method to allow of determination of acidic, neutral, and basic properties of WSOC.

Recommendation: *Research*—PILS-TOC analyzer with eventual commercialization.

Particle-Bound Water. Although PBW has been estimated previously, these data have been limited to a few particle sizes at any given time with results presented as growth factors or less hygroscopic and more hygroscopic. A new continuous method that provides growth factors and water content for the size range from a few nanometers to 10 μm AD has been developed. Evaluation of this method should continue so estimates of PBW can be integrated into estimates to close the mass balance using continuous data,[62] into performance evaluation of chemical transport and thermodynamic models, and for use in advance data analysis approaches.

Recommendation: *Research*—DAASS.

Particle Mass Spectrometers. Particle mass spectrometers measure the size and chemical composition of either single particles (single particle mass spectrometers [SPMS]) or groups of particles in a given size or size range (AMS). These methods are outside the scope of this paper because they require highly trained operators and significant attention to maintain in the field, and therefore are unlikely candidates for routine monitoring networks in the near future. However, numerous papers have been published as part of the Supersites Program describing these methods and their application to understanding atmospheric processes, chemistry, and source-receptor relationships. For a few examples describing the methods and insights gained from their application, refer to papers by Middlebrook et al.[119] and Zheng et al.[123,124] and recent reviews by Sullivan and Prather,[118] Canagaratna et al.,[117] and Wexler et al.[120] It is safe to say, however, that the particle mass spectrometers likely represent the single greatest advancement in PM methods technology in the last decade.

Recommendation: *Research*—Various approaches and instruments because of technical complexity of methods and operation and data processing. At least two methods are commercially available—ATOFMS and AMS.

KNOWLEDGE GAPS AND FUTURE NEEDS

Many uncertainties still exist in the measurement of PM, whether filter-based or continuous. Concerning the methods discussed here, continued evaluation and development is needed (even for many of the commercially available instruments) to understand better what these methods are measuring and how these methods compare with other methods. Specific additional needs include:

- Development of reference standards to obtain accuracy data and to help us understand sampling artifacts relative to what is present in the air. This is a complex issue for PM and few efforts are occurring to develop such standards.
- Continued efforts are needed to determine analytical characteristics (e.g., precision, bias, accuracy, interferences) of continuous methods to ensure we understand differences between the measured value and what is present in the ambient aerosol. This and the previous bullet extend to filter-based methods as well.
- Methods for the near-real-time measurements of trace elements are lacking, specifically methods useful for source apportionment and trace metals potentially responsible for adverse health effects.
- Continuous methods allow for a more accurate mass balance, and thus, an indirect assessment and evaluation into the uncertainties associated with converting OC, measured as $\mu C/m^3$, to OM. Efforts to understand these uncertainties should continue as well as efforts to understand other major uncertainties associated with the collection and analysis of OC.
- Continued efforts are needed to quantify single-particle methods and to understand better uncertainties associated with measurement of single particles versus the more widely used integrated methods.
- Development of continuous methods for organic species or classes of species are needed, although recent work using particle mass spectrometers and thermal desorption methods[125] are beginning to move forward along these lines. Much work is still needed because of the large number of organic compounds present in $PM_{2.5}$.

CLOSING REMARKS

A major accomplishment of the Supersites Program has been to develop and improve continuous and semicontinuous methods for PM mass and composition. The more highly time-resolved data provided by these methods have and will continue to improve our understanding of PM source-receptor relationships, atmospheric processes, and the accumulation of PM in air on urban and regional scales. The methods discussed here provide information that is critical for aerosol modeling and the development of effective emissions control strategies to reduce ambient concentrations of PM to below the levels mandated in the PM NAAQS, thus protecting public health and welfare. These methods also will benefit future health studies, particularly methods focusing on acute effects of PM, because these measurements provide better estimates of short-term exposure to PM species. Finally, although continuous and semicontinuous methods have improved, many require further testing before routine implementation in large-scale national networks can be expected.

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