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Comparison of integrated samplers for mass and composition during the 1999 Atlanta Supersites project

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[1] The first of the U.S. Environmental Protection Agency's (EPA) Particulate Matter (PM) Supersites projects was established in Atlanta, GA, during the summer of 1999 in conjunction with the Southern Oxidants Study. The short-term primary focus was a one month intensive field campaign to evaluate advanced PM measurement methods for measuring PM mass and the chemical and physical properties of PM. Long-term objectives are being met through coordination and cooperation with existing programs in Atlanta and the southeastern United States. Three categories of PM instruments were deployed during August 1999: time-integrated or discrete filter-based methods like those used in EPA's PM2.5 Chemical Speciation Network; continuous or semicontinuous species specific methods, most of which are still in development; and single particle mass spectrometers, the most advanced methods looking at the chemical composition of single particles. The focus of this paper is on comparison of the discrete filter-based methods. Samples were collected by 12 discrete filter-based samplers on an every other day basis during the study period at the Jefferson Street Southeastern Aerosol Research and Characterization (SEARCH) study site. Samples were analyzed for PM2.5 mass, sulfate, nitrate, ammonium, organic carbon, elemental carbon, and trace elements, the latter by XRF. Samplers used a variety of filters; denuder-filter combinations in the case of nitrate and organic carbon, particle size fractionating devices, and flow rates. Ambient concentrations for most species were sufficiently above detection limits for testing comparability among samplers, with nitrate being the most notable exception for the major components having an average reported value of 0.5 $\mu g/m^3$. Several trace species, e.g., As and Pb, also were often below limits of detection of the analysis method. Results indicate that real differences exist among the samplers tested for most species, with sulfate and ammonium being the exceptions, under the conditions tested. Differences are due to sampler design, and in the case of elemental carbon, also due to the use of different chemical analysis methods. Comparability among most of the samplers for a given species was: mass (±20%); sulfate (±10%); nitrate (±30–35%); ammonium (±10–15%); organic carbon either with or without denuders (±20%) or including samplers both with and without denuders (±35–45%); elemental carbon (±20 to ±200%, the latter if different analysis methods are used); and minor and trace elements (±20–30%). A net organic carbon-sampling artifact on quartz-fiber filters was estimated from the comparison of denuded versus undenuded samples and is in the range of 1–4 $\mu g/m^3$. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0394 Atmospheric Composition and Structure: Instruments and techniques; *KEYWORDS:* chemical speciation, Atlanta Supersites project, filter sampling, comparison study, integrated samplers, PM2.5

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1. Introduction

[2] Historically, the chemical composition of ambient atmospheric particulate matter (PM) has been obtained by collecting particles on filters by filtration over a specified time period, typically 24-hrs, with subsequent gravimetric and chemical analysis in the laboratory [*Chow*, 1995, *U.S. Environmental Protection Agency* (*EPA*), 2001]. The major chemical components of the collected aerosol include sulfate, nitrate, ammonium, organic material, which is composed of hundreds of organic compounds, elemental carbon, and geologic material (e.g., oxides of aluminum, iron, silicon, calcium, and titanium) [*Solomon et al.*, 1989; *Rogge et al.*, 1993; *Chow*, 1995; *Chow et al.*, 1996; *Schauer and Cass*, 2000, and references within; *Clarke et al.*, 1999; *EPA*, 2001; *Tolocka et al.*, 2001; *Turpin et al.*, 2000]. Particle composition varies with, for example, location (source influence and meteorology), age of the aerosol, and particle size. Many different sampling systems have been designed over the years for collecting particulate matter on filters for subsequent chemical analysis in the laboratory. Chemical analysis includes bulk analysis [*Solomon et al.*, 2001], and single particle analysis [*Fletcher et al.*, 2001]. *Chow* [1995], *Chow and Watson* [1999] and *Mark* [1998] summarize integrating particulate matter sampling methods for mass and chemical composition and characteristics of sampler components, including size-selective inlets, filter media and holders, and flow measurement, control, and pumps, along with a summary of several sampler configurations. *Mark* [1998] also includes particle size measurement methods (i.e., impactors) that allow for subsequent chemical analysis of the collected material. Stable species, such as sulfate and minor and trace elements (e.g., Fe, Ca, Si, Pb, etc.) are collected with minimal bias on Teflon (PTFE membrane) filters if proper inlets, transport tubes, and flow control are used in the sampler [*Chow*, 1995]. Particle acidity and labile species such as ammonium nitrate and semivolatile organic compounds are more difficult and require specialized sampling protocols, typically using denuders and reactive collection substrates [*Appel*, 1993; *Turpin et al.*, 1994; *Chow*, 1995].

[3] Recently, the U.S. Environmental Protection Agency (EPA) has established three interlaced networks to provide different levels of information in space, time, and aerosol composition [*EPA*, 1998a, 1998b]. The first network consists of about 1100 PM2.5 Federal Reference Method mass monitors [*Code of Federal Regulations* (*CFR*), 1997], sited to estimate population exposure. The PM2.5 FRM network provides 24-hour integrated PM2.5 mass data, typically on a one in three or one in six day schedule, although several hundred sites are using continuous mass methods. Annual average and 24-hour mass values are used to determine compliance with the National Ambient Air Quality Standard for Particulate Matter [*CFR*, 1997]. The second network, the U.S. EPA National PM2.5 Chemical Speciation Network (referred to below as the Chemical Speciation Network) [*EPA*, 1997], consists of up to 300 chemical speciation monitors, 54 of which are part of the U.S. EPA's long-term NAMS (National Air Monitoring Stations) network for measuring trends in atmospheric pollutants (e.g., ozone, CO, SO_2, PM2.5, PM10) and the remainder part of the SLAMS (State and Local Air Monitoring Stations) network. The chemical speciation monitors provide 24-hour integrated chemical composition data, typically on a one in three or on a one in six day schedule. This network is not used for compliance but to assist states with the development of equitable and efficient State Implementation Plans. The components measured include PM2.5 mass, nitrate, sulfate, ammonium, chloride, sodium, and potassium ions, organic carbon (OC), elemental carbon (EC), and trace elements (Na-Pb). Size-selective inlets, particle fractionators, and denuder/filter-based methods are used in these samplers [*EPA*, 1999]. Samplers developed for use in the Chemical Speciation Network have been compared recently during the winter at four locations throughout the U.S. [*Solomon et al.*, 2000] (herein referred to as the Four City Study).

[4] The third network consists of eight Supersites projects that together compose the U.S. EPA's PM Supersites Program [*Albritton and Greenbaum*, 1998; *EPA*, 1998a]. Each project consists of one or more highly instrumented sites that are coordinated with active air quality monitoring and health effects related studies. The Supersites Program is designed to provide (1) detailed information on the spatial and temporal nature of PM and on atmospheric processes, and thus to provide States with additional data for developing cost-effective emissions management strategies for lowering concentrations of PM2.5 in ambient air; (2) support to health effects related programs; and (3) an evaluation of advanced monitoring methods for their potential transition to routine monitoring networks. The Atlanta Supersites project is the first PM Supersites project to be established and along with the Fresno Supersites project comprises phase 1 of the PM Supersites Program. The main objective of the Atlanta Supersites project is to evaluate and compare advanced methods for determining the chemical and physical properties of the atmospheric aerosol (PM and PM precursor species) [*Solomon et al.*, 2003]. Information gained about the methods tested is then applied to the phase 2 Supersites projects. Thus the Atlanta Supersites project provides an ideal opportunity for a comparison of the Chemical Speciation Network samplers under summertime conditions, as well as inclusion of other speciation samplers that have been developed as research tools or to support the larger speciation network. The speciation samplers also provide an independent reference for comparison of the more advanced semicontinuous methods [*Weber et al.*, 2003]. The chemical speciation samplers operated in Atlanta are described in the experimental section.

[5] To advise on the development of the Chemical Speciation Network, and on the development of chemical speciation samplers, EPA established an outside independent panel of experts (Expert Panel). The panel generally recommended the approaches employed currently in the speciation network [*Koutrakis*, 1998; *EPA*, 1999]. These

Table 1. Performance Criteria Recommended by EPA's Expert Chemical Speciation Panel [*Koutrakis*, 1999] or From the Four City Study Results [*Solomon et al.*, 2000][a]

	Expert Panel	Four City Study		
Species	Ratio 1 ± 0.1	Ratio 1 ± 0.1	Ratio 1 ± 0.15	Ratio 1 ± >0.15
		Correlation Coefficients (r)		
Mass	≥0.9	≥0.9		
SO_4^{2-} or S	≥0.95	≥0.95		
	Ratio 1 ± 0.05			
NO_3^-	≥0.9		≥0.9	
NH_4^+	≥0.9	≥0.9		
OC			≥0.85	≥0.85)[b]
EC			≥0.85	≥(0.85)[b]
Trace elements			≥0.85	

[a]Criteria are ratio of test sampler to relative reference value and regression coefficient (r) of the test sampler regressed against the relative reference. Expert Panel did not provide criteria for OC, EC, or trace elements.
[b]May be a more realistic expectation.

include determining mass by gravimetric analysis and elements by energy dispersive x-ray fluorescence (XRF) both from PM collected on a Teflon filter, ions (sulfate, nitrate, ammonium, potassium, and sodium) by ion chromatography (IC) analysis after aqueous extraction of PM collected on a Teflon or nylon filter (current protocol uses nylon), fine particle nitrate by IC analysis after extraction of PM collected on a reactive filter (nylon or carbonate impregnated paper) that is preceded by a denuder designed to efficiently remove acidic gases (a denuder coated with MgO or sodium carbonate, or a multichannel carbon impregnated filter denuder), and organic and elemental carbon by thermal optical transmission on prebaked quartz-fiber filters that are not preceded with a denuder, thus exposing this collection media to organic gases that could result in a positive artifact [*Turpin et al.*, 1994; *McDow and Huntzicker*, 1990; *Tolocka et al.*, 2001].

[6] The Expert Panel also recommended criteria by which to judge agreement among the samplers [*Koutrakis*, 1999]. Performance criteria suggested by the Expert Panel for mass, sulfate, nitrate, and ammonium are given in Table 1. Performance criteria for OC and EC were not recommended due to the poor understanding of how to collect OC with minimal bias, nor were they recommended for trace elements.

[7] Performance criteria also can be suggested from the precision data and regression analysis results for the chemical speciation samplers evaluated in the Four City Study [*Solomon et al.*, 2000]. Results from this study suggest that the performance criteria established by the Expert Panel are, in general, reasonable. Criteria suggested from the Four City Study results also are given in Table 1, not only for mass, sulfate, nitrate, and ammonium, but for OC, EC, and the trace elements as well.

[8] Whichever criteria are used, they require definition of a relative reference for comparison since reference standards do not exist for determining accuracy or bias for mass or the chemical components of mass. Thus this study provides for a test of sampler comparability or equivalency among samplers, rather than a determination of bias from a known value. As briefly discussed later in this paper and more thoroughly by *Solomon et al.* [2003], the relative reference for this study was obtained by averaging data collected for each species across all samplers on a daily basis and for the study period, in this case 15 sampling periods. In the design of this program, the FRM also was established as an appropriate alternate relative reference for stable species, such as sulfate, elemental carbon, and trace elements, since these should be collected with minimal bias. While the FRM also could serve as an alternate relative reference for mass, since it is the reference method by which regulatory attainment data are collected [*CFR*, 1997], there is potential for negative artifacts due to the loss of semivolatile species from the Teflon filter. Therefore the primary relative reference is used for mass comparisons among the samplers. For organic carbon, the Versatile Air Pollution Sampler (VAPS) (URG, Durham, NC) is considered an alternate relative reference since the VAPS uses an XAD denuder that has been shown to reduce positive sampling artifacts, at least under the conditions tested [*Gundel et al.*, 1998; *Solomon et al.*, 2000]. An alternate relative reference was not established for nitrate. In this paper, the criteria given in Table 1 are used to judge compatibility among the samplers against the study period relative reference, the FRM for stable species, and the VAPS for OC.

2. Experimental

2.1. Location and Schedule

[9] The Atlanta Supersites project was located at the Georgia Power Company facility on Jefferson St., approximately 4 km NW of downtown Atlanta. This site has been used for about two years to support the SEARCH (Southeastern Aerosol Research and Characterization) and ARIES (Aerosol Research Inhalation Epidemiological Study) programs sponsored by EPRI and southeastern utilities. The site was located in a mixed commercial-residential neighborhood within approximately 200 m of a bus maintenance yard and several warehouse facilities, and approximately 200 m and 40 m, respectively of Jefferson and Ashby streets. Additional details are given by *Solomon et al.* [2003]. Located at the north end of the site were two approximately 20 m long platforms (Figures 1 and 2), on which most of the integrated samplers were located as well as two continuous mass samplers. A MOUDI (Micro Orifice Uniform Deposit Impactor, Model numbers 100 and 110, 30 Lpm, MSP Corporation, Minneapolis, MN) was located in a trailer south of the platform operated by the University of Miami (UMiami), while the Georgia Institute of Technology (GIT) chemical speciation sampler was located on the roof of the GIT trailer (see Figure 1). To evaluate spatial continuity across the platforms two FRM samplers were located diametrically from each other on the two platforms

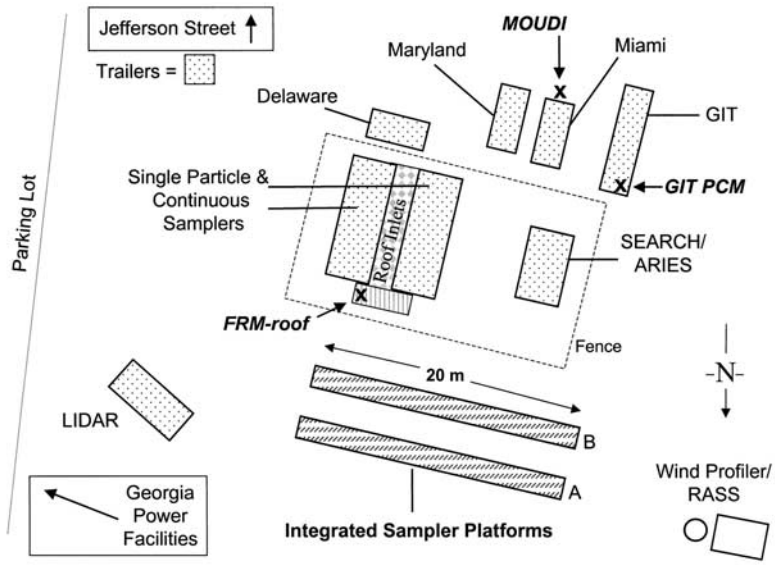


Figure 1. Schematic diagram of the intensive monitoring site during the 1999 Atlanta Supersites project.

(Figures 1a, spaces A and R). To evaluate vertical representativeness of the samplers on the platforms with the continuous sampler inlets protruding from the roof of the trailers, a third FRM was located on the roof between the two main trailers.

[10] Most of the time-integrated or discrete PM samplers were operated for 24-hour sampling periods from 7 AM to 7 AM local time. Two samplers, the MOUDI (UMiami) and the Atmospheric Research & Analysis, Inc. (ARA) Particle Composition Monitor, were operated for 12-hour sampling periods (7 AM to 7 PM and 7 PM to 7 AM), which were averaged to the appropriate 24-hour period to match the other discrete samplers. Samples were collected on an alternate day schedule from 3 August 1999 through 1 September 1999; thus 15 sample sets were collected.

2.2. Instrumentation

[11] Twelve different discrete (12-hour or 24-hour time integrated) chemical speciation samplers were operated during the Atlanta Supersites project, although not all samplers collected samples for the full suite of chemical components. General characteristics of the samplers are given in Table 2. The experimental protocol and design of each sampler are illustrated schematically in Figure 3. All

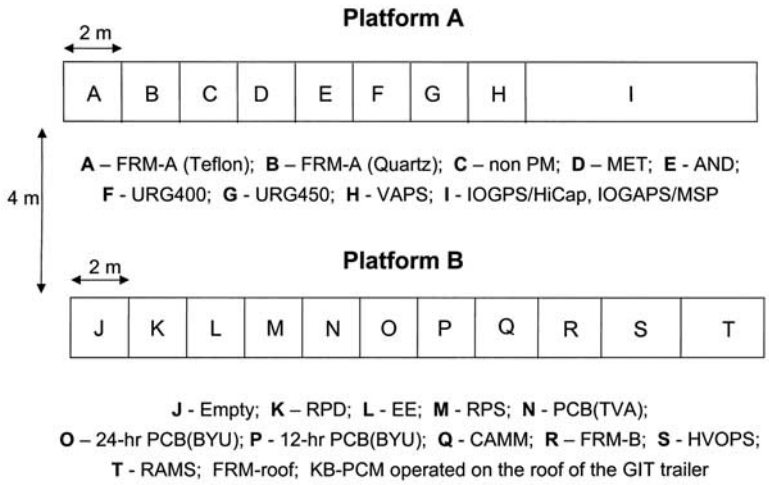


Figure 2. Location of discrete samplers on sampling platforms located north of the trailers housing continuous samplers and single particle mass spectrometers.

Table 2. General Characteristics of Discrete Samplers Used During the Atlanta Supersites Experiment

Sampler	Operator[a]	Manufacturer/Model	Inlet Type/Cutpoint, μm/Flow Rate	Species Measured[b]	Nitrate: Denuder/Filter Type	Organic Carbon: Denuder/Filter Type/ OC-EC Method
FRM A, B, C[c]	EPA[d]	*FRM A*: R&P/2000 *FRM B*: AND/RAAS2.5-100 *FRM C*: BGI/PQ 200	WINS[e]/2.5/16.7 Lpm	*FRM A*: major components *FRM B and C*: mass and XRF elements	none/Teflon	none/quartz-fiber (preheated)/TOT
AND	EPA[d]	Andersen: RAAS2.5/400	Cyclone/2.5/24 Lpm	mass and major components	MgO annular/nylon	none/quartz-fiber (preheated)/TOT
MET	EPA[d]	MetOne/SASS	Cyclone/2.5/6.7 Lpm	mass and major components	MgO annular/nylon	none/quartz-fiber (preheated)/TOT
URG	EPA[d]	URG/MASS 400 & 450	WINS/2.5/16.7 Lpm	mass and major components	Na_2CO_3 annular/Na_2CO_3 impregnated	none/quartz-fiber (preheated)/TOT
RPS	R&P/EPA	R&P/Partisol 2300 Chemical Speciation Sampler	Harvard Impactor/2.5/10 Lpm	mass and major components	honeycomb Na_2CO_3/nylon	none/quartz-fiber (preheated)/TOT
RPD	EPA	R&P/Partisol 2025 Sequential Air Sampler (Dichotomous)	Virtual Impactor/2.5/15 Lpm	mass and XRF elements	not applicable	not applicable
VAPS	EPA[d]	URG/VAPS	Virtual Impactor/2.5/15 Lpm	nitrate, OC, EC, and Ions	Na_2CO_3 impregnated/ polycarbonate filter	XAD annular/quartz-fiber (preheated)/TOT
KB	GIT	URG/custom	Cyclone/2.5/16.7 Lpm	mass, ions, OC, and EC	Na_2CO_3 annular/Na_2CO_3 impregnated	XAD annular/quartz-fiber (preheated)/TOT
EE	ARA	ARA/custom	WINS/2.5/16.7 Lpm	mass and major components	Na_2CO_3, citric acid/nylon filter	CIF/quartz-fiber (preheated)/TOR
PCB(TVA)	TVA	BYU/custom	Cyclone/2.5/105 Lpm	mass, ions, OC, and EC	BOSS CIF/Teflon-Nylon Filter Pack	BOSS CIF/Quartz-CIF Filter Pack/TOR
PCB(BYU)	BYU	BYU/custom	Cyclone/2.3/150 Lpm	mass, ions, OC, and EC	BOSS CIF/Teflon-nylon filter pack	BOSS CIF/Teflon-nylon filter pack/ TPV[f]
MOUDI	UMiami	MSP Corp./Model 100	Cyclone/2.5/30 Lpm	ions, OC, and EC	no denuder/TFE film impaction and quartz final filter	no denuder/Al Foil impaction and quartz-fiber final filter/TOR

[a]Abbreviations are as follows: RTI, Research Triangle Institute; R&P, Rupprecht & Patashnick, Co., EPA, U.S. EPA; ORD, National Exposure Research Laboratory; GIT, Georgia Institute of Technology; TVA, Tennessee Valley Authority; BYU, Brigham Young University; ARA, Atmospheric Research & Analysis, Inc.; UMiami, University of Miami.

[b]Major components include sulfate, nitrate, ammonium, organic carbon, elemental carbon, and trace elements by XRF (S, Si, K, Ca, Mn, Fe, Cu, Zn, Pb, and As).

[c]FRM A was located on platform A, furthest from the trailers; FRM B was located on platform B, nearest the trailers; FRM C was located on the roof between the two main trailers at the end nearest the platforms.

[d]These samplers were included in EPA's initial evaluation of the Chemical Speciation Samplers [*Solomon et al.*, 2000] designated for use in EPA's PM2.5 National Chemical Speciation Network [*EPA*, 1999].

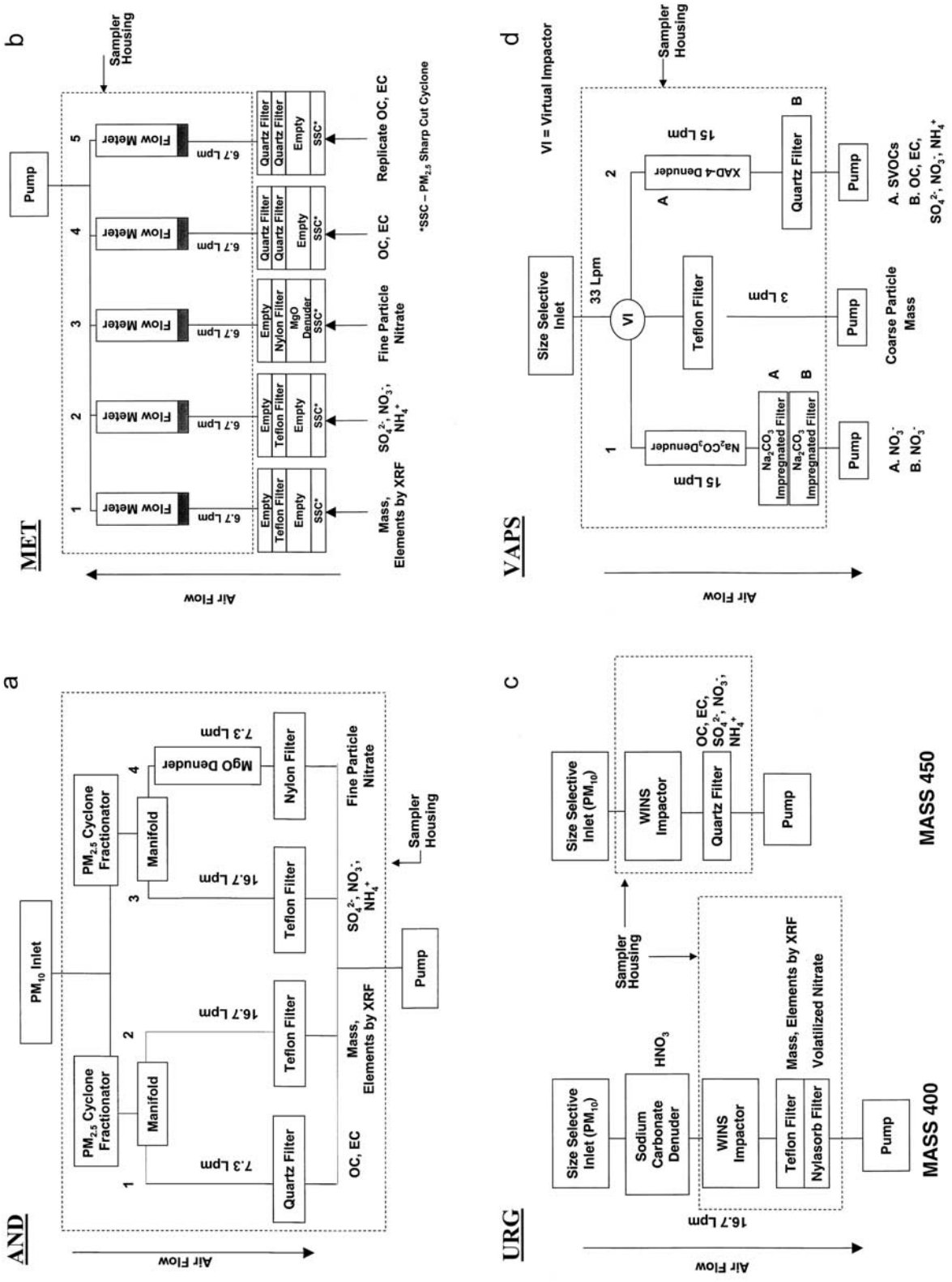
[e]WINS is the official impactor designed and approved for use by EPA in the PM2.5 FRM.

[f]Temperature Programmed Volatilization (TPV), see description of PC-BOSS in text for more detail.

discrete samplers employed the collection of particulate matter on filters appropriate for subsequent chemical analysis [*Chow*, 1995; *Solomon et al.*, 2001]. In general, all groups reported concentration values for mass, sulfate, nitrate, ammonium, organic carbon, and elemental carbon. The samplers operated by EPA and ARA also reported concentration values for trace elements by XRF. Those used in the database include S, Si, K, Ca, Mn, Fe, Cu, Zn, Pb, and As. Of these, the main focus will be on those typically associated with coarse particles (crustal related elements: Si, Ca, and Fe) as these provide relative information for comparison of a sampler's collection efficiency (slope and cutpoint, the latter being the 50% collection efficiency for particles of a specified diameter).

[12] Except for the FRM PM2.5 sampler and the MOUDI, all chemical speciation samplers used a denuder to remove acidic gases upstream of a reactive filter (nylon, Na_2CO_3, or carbon impregnated) for the collection of aerosol nitrate. The Versatile Air Pollution Sampler (VAPS), PC-BOSS, and PCM samplers used either XAD-4 coated annular denuders or multichannel carbon impregnated filter (CIF, Schleicher and Schuell, Keene, NH) denuders to remove organic gases prior to collection of particulate organic carbon on filters. The other samplers did not use denuders upstream of the filters designated for the collection of organic carbon. A brief summary of each sampling systems is given below.

[13] Several different laboratories were used in this study for determining the chemical composition of PM collected on the various filters. However, an evaluation of interlaboratory variability was not performed since most of the methods were similar and differences were expected to be small compared to differences in the collection methods, with the exception of methods used for OC and EC as described below. *Solomon et al.* [2001] reviews the chemical analysis methods used in this study. Mass was deter-


a
AND
Air Flow
PM10 Inlet
PM2.5 Cyclone Fractionator
PM2.5 Cyclone Fractionator
Manifold
Manifold
MgO Denuder
Quartz Filter
Teflon Filter
Teflon Filter
Nylon Filter
7.3 Lpm
16.7 Lpm
16.7 Lpm
7.3 Lpm
OC, EC
Mass, Elements by XRF
SO4 2-, NO3-, NH4+
Fine Particle Nitrate
Pump
Sampler Housing
b
MET
Air Flow
Pump
Sampler Housing
Flow Meter
6.7 Lpm
Empty
Teflon Filter
Nylon Filter
MgO Denuder
Quartz Filter
SSC*
Mass, Elements by XRF
SO4 2-, NO3-, NH4+
Fine Particle Nitrate
OC, EC
Replicate OC, EC
*SSC – PM2.5 Sharp Cut Cyclone
c
URG
Air Flow
Size Selective Inlet (PM10)
Sodium Carbonate Denuder
HNO3
WINS Impactor
Teflon Filter
Nylasorb Filter
Pump
Sampler Housing
16.7 Lpm
Mass, Elements by XRF
Volatilized Nitrate
MASS 400
Size Selective Inlet (PM10)
WINS Impactor
Quartz Filter
Pump
OC, EC, SO4 2-, NO3-, NH4+
MASS 450
d
VAPS
Air Flow
VI = Virtual Impactor
Size Selective Inlet
33 Lpm
VI
Na2CO3Denuder
Na2CO3 Impregnated Filter
Teflon Filter
XAD-4 Denuder
Quartz Filter
Pump
15 Lpm
3 Lpm
A. NO3-
B. NO3-
Coarse Particle Mass
A. SVOCs
B. OC, EC, SO4 2-, NO3-, NH4+

mined by gravimetric analysis; sulfate, nitrate, and ammonium by ion chromatography; and elements were determined by XRF, or ICP-MS. Organic and elemental carbon were determined by one of three methods: thermal optical transmittance (TOT; NIOSH Method 5040 protocol) [*Birch and Cary*, 1996; *Birch*, 1998], thermal optical reflectance (TOR; IMPROVE protocol) [*Chow et al.*, 1993], and temperature programmed volatilization (TPV) [*Ellis and Novakov*, 1982; *Tang et al.*, 1994]. These three methods provide fairly consistent (±10–20%) results for TC (sum of OC and EC), but different results for OC and EC [*Chow et al.*, 2001; G. A. Norris et al., Comparison of particulate organic and elemental carbon measurements made with the IMPROVE and NIOSH Method 5040 Protocols, submitted to *Aerosol Science and Technology*, 2002, hereinafter referred to as Norris et al., submitted manuscript, 2002]. Therefore, for these two species, sampler biases also may be confounded with analytical method biases.

[14] Specifically for the samplers operated by EPA (see Table 2), mass and trace element loadings were determined in the PM collected on Teflon filters (Teflo 47 mm, 2.0 μm, Pall Corporation, Gelman Laboratory, Ann Arbor, MI) by gravimetric analysis or by energy dispersive X-ray fluorescence (XRF), respectively. Anion and cation species were determined in the PM collected on Teflon (Teflo 47 mm, 2.0 μm, Pall Corporation, Gelman Laboratory, Ann Arbor, MI), nylon (Nylasorb 47 mm, 1.0 μm, Pall Corporation, Gelman Laboratory, Ann Arbor, MI), or quartz-fiber (47 mm diameter, 2500 QAT-UP-47, Pall-Gelman, Ann Arbor, MI) filters. Teflon filters were extracted in water after being wet with a small amount of ethanol and nylon filters were extracted in IC eluent. Organic and elemental carbon were determined in the PM collected on quartz-fiber filters (47 mm diameter, 2500 QAT-UP-47, Pall-Gelman, Ann Arbor, MI) by thermal-optical transmittance (TOT) using the National Institute for Occupational Safety and Health (NIOSH) Method 5040 protocol.

2.2.1. AND: Reference Ambient Air Sampler (RAAS) Developed by Andersen Instruments

[15] A schematic flow diagram of the Andersen RAAS as operated in Atlanta is shown in Figure 3a. It consists of a size-selective inlet followed by two PM2.5 cyclones in parallel, the outlets of which are connected to separate sampling manifolds. These cyclones remove particles greater than 2.5 micrometers with a 50% collection efficiency, when operated at 24 Lpm. The flow is then split in each manifold into two channels (maximum of three for at total of up to six channels). Of the four channels used in this study, the first channel (labeled 1 in Figure 3a) is used to estimate atmospheric concentrations of particulate organic and elemental carbon (OC and EC) and analyzed as described above. The flow rate in this channel is 7.3 Lpm. In the second channel (labeled 2 in Figure 3a), particulate matter is collected on a Teflon filter for the determination of mass and trace elements (Na-Pb) and analyzed as described above. The flow rate through this channel is 16.7 Lpm. In the third channel (labeled 3 in Figure 3a), particulate matter also is collected on a Teflon filter and analyzed for sulfate, nitrate, and ammonium ion concentrations. The last channel (labeled 4 in Figure 3a) is used to obtain a nearly unbiased estimate of fine particle nitrate by removing acidic gases (e.g., HNO_3) from the air stream using a diffusion denuder coated with MgO and collecting aerosol nitrate on a reactive Nylasorb (nylon) backup filter. In all instances where a denuder is used in this study for the collection of fine particle nitrate, its use assumes that the denuder is efficient for removing HNO_3 and other acidic gases that might be collected on the nylon filter and analyzed as nitrate and that the nylon filter does not efficiently collect NO_2, which might be converted subsequently to nitrate. In all channels, critical orifices control the flow while flow rates are monitored using electronic mass flow sensors. All internal components before the filter holders or denuders are Teflon coated and no grease or oil is used in the sampler's design. The system also monitors continuously relative humidity (RH), barometric pressure (BP), orifice pressure (OP), ambient temperature (T), manifold temperature (MT), meter temperature (MeT), and cabinet temperature (CT). Data can be downloaded through a RS-232C serial port, which allows for two-way remote communication [*Andersen Instruments*, 1999].

2.2.2. MET: Spiral Ambient Speciation Sampler (SASS) Developed by MetOne

[16] A schematic flow diagram for the MetOne SASS sampler as used in Atlanta is presented in Figure 3b. The SASS has five separate channels, operated through a common controller and pump. Each channel contains a sharp cut cyclone (SCC: BGI, Incorporated, Waltham, MA) designed to give a 2.5 μm cutpoint (50% collection efficiency) with a slope and cutpoint similar to the FRM when operated at 6.7 Lpm [*Peters et al.*, 2001a; *MetOne*, 1999]. The first channel (labeled 1 in Figure 3b) collects particulate matter on a

Figure 3. (opposite) Experimental protocol for: (a) thermo Andersen Reference Ambient Air Sampler (RAAS) (AND); (b) experimental protocol for the MetOne Spiral Ambient Speciation Sampler (SASS) (MET); (c) experimental protocol for the URG Mass Aerosol Speciation Sampler (MASS) (URG); (d) experimental protocol for the University Research Glassware Versatile Air Pollution Sampler (VAPS); (e) experimental protocol for the Rupprecht & Patashnick Co., Inc., Chemical Speciation Sampler (RPS); (f) experimental protocol for the Rupprecht & Patashnick Co., Inc., Dichotomous Partisol Model 2025 Sequential Air Sampler (RPD); (g) experimental protocol for the PM2.5 Federal Reference Method (FRM); (h) experimental protocol for the Brigham Young University Particle Concentrator-Brigham Young University Organic Sampling System (PC BOSS) [PCB(BYU)]; (i) experimental protocol for the Tennessee Valley AuthorityParticle Concentrator-Brigham Young University Organic Sampling System (PC BOSS) [PCB(TVA)]; (j) experimental protocol for the Georgia Institute of Technology Particle Composition Monitor (KB); (k) experimental protocol for the Atmospheric Research & Analysis, Inc. Particle Composition Monitor (EE); and (l) experimental protocol for the University of Miami Micro-Orifice Uniform Deposit Impactor (MOUDI).

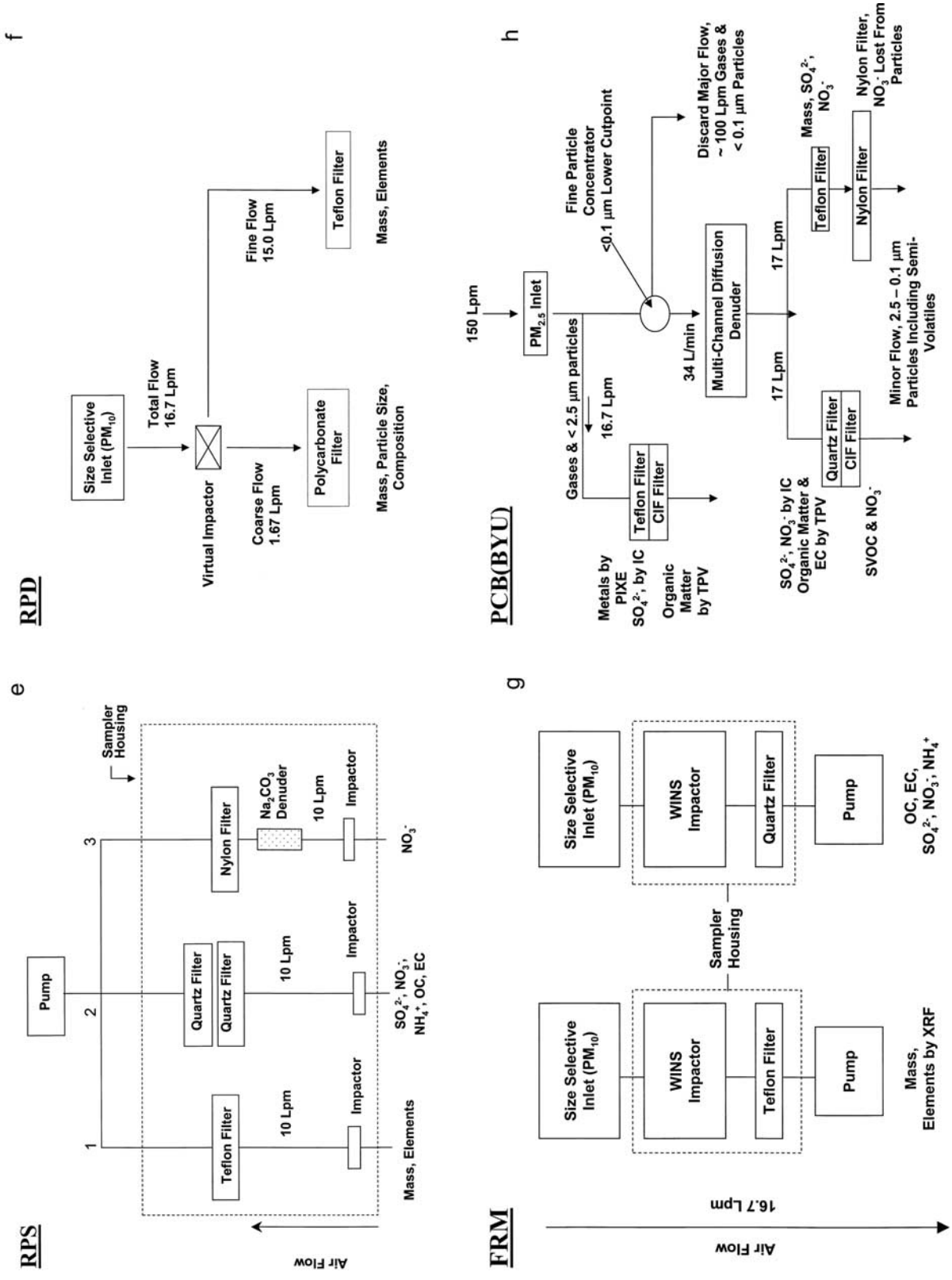


Figure 3. (continued)

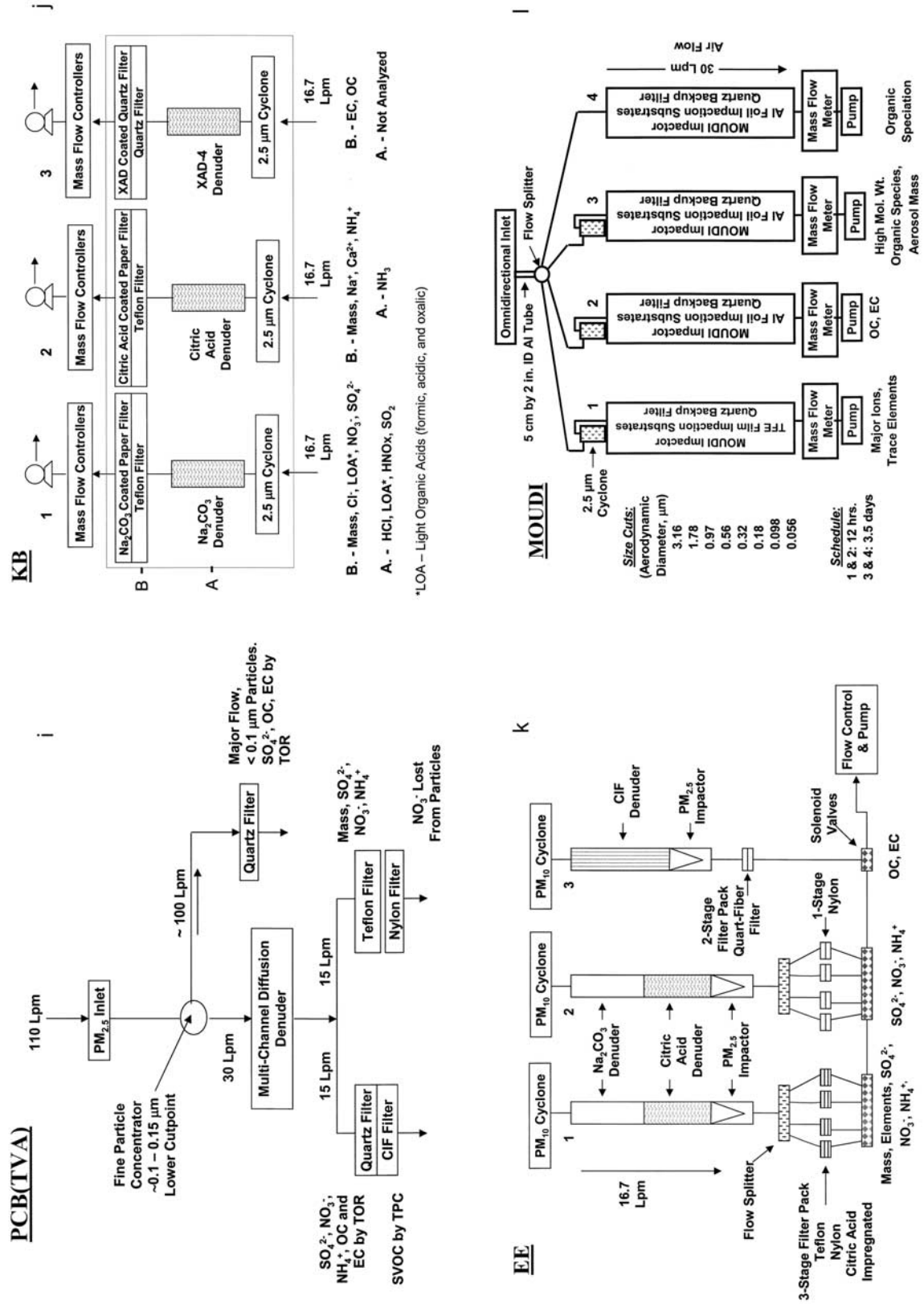


Figure 3. (continued)

Teflon filter that is analyzed for atmospheric concentrations of PM2.5 mass and trace elements. The second channel (labeled 2 in Figure 3b) also collects particulate matter on a Teflon filter that is analyzed for sulfate, nitrate, and ammonium ion concentrations as described above. A MgO coated aluminum honeycomb diffusion denuder is located behind the SCC in the third channel (labeled 3 in Figure 3b). This denuder removes acidic gases (e.g., HNO_3) from the sampled air stream. The MgO denuder is followed by a nylon filter that is analyzed for nitrate as described above. As in the AND sampler, this denuder/reactive filter pair is used to obtain a nearly unbiased estimate of aerosol nitrate with the same assumptions given above. The fourth channel (labeled 4 in Figure 3b) contains two baked quartz-fiber filters located behind the SCC. The first quartz-fiber filter is analyzed for OC and EC, while the second quartz-fiber filter is archived. The fifth channel (labeled 5 in Figure 3b) also contains two baked quartz-fiber filters as a replicate set to channel 4. This set of quartz-fiber filters is archived for future use. The flow rate through each channel is nominally 6.7 Lpm and is controlled by a critical orifice. The flow rate in this instrument is monitored using electronic mass flow sensors. The instrument also monitors continuously for meteorological variables similar to the AND.

2.2.3. URG: Mass Aerosol Speciation Sampler (MASS) Developed by University Research Glassware

[17] The URG MASS sampler as operated in Atlanta is shown in Figure 3c. This sampler consists of two modules (URG MASS 400 and MASS 450), each with an FRM PM10 size-selective inlet and a WINS impactor [*Peters et al.*, 2001b] to allow for the collection of PM2.5 aerosol. The MASS 400 is equipped with a Na_2CO_3 denuder located after the PM10 size-selective inlet but before the WINS impactor to avoid possible contamination from the denuder coating onto the subsequent filter. This denuder is used to remove acidic gases much like the MgO denuders discussed above. Particles less than 2.5 μm are collected on the top filter of a dual filter pack, which is an inert Teflon filter that is analyzed for PM2.5 mass and trace elements. The backup nylon filter efficiently collects nitrate that may have vaporized from the front Teflon filter during sampling. Thus the sum of nitrate measured on the Teflon and nylon filters provides a nearly bias free estimate of fine particle nitrate. This assumes the denuder is efficient for HNO_3 and that the nylon filter does not collect NO_2. The MASS 450 contains a single prebaked quartz-fiber filter. This filter is split in half with OC and EC determined from one half and sulfate, nitrate, and ammonium ions determined on the other half. The flow rate through each module is nominally 16.7 Lpm. Flow is monitored using a dry gas meter with a feed back loop to the controller to adjust for variations in flow rate as particles are collected on the filter. This system also monitors continuously for meteorological variables similar to the AND.

2.2.4. VAPS: Versatile Air Pollution Sampler Developed by University Research Glassware

[18] The VAPS sampler as used in Atlanta is shown in Figure 3d. PM2.5 is obtained using a size-selective impactor to remove particles greater than about PM10, followed by a virtual impactor with a PM2.5 cutpoint. Total flow through the sampler is 33 Lpm. The coarse particles follow the minor flow (3 Lpm) and are collected on a Teflon filter from which coarse (PM10–PM2.5) particle mass is obtained by gravimetric analysis. The fine (PM2.5) particle flow (30 Lpm) is split evenly between two channels. One channel (labeled 1 in Figure 3d) contains an annular diffusion denuder coated with Na_2CO_3 followed by a filter pack containing two Na_2CO_3 impregnated filters in series, both of which were analyzed separately for nitrate, the top for particulate nitrate and the bottom for artifact nitrate. The Na_2CO_3 denuder is extracted and analyzed by IC for nitrate to give an estimate of ambient nitric acid concentrations. The second channel (labeled 2 in Figure 3d), contains an XAD-4 coated annular denuder, designed specifically for the VAPS (L. Gundel, personal communication, 1998) to remove gas-phase semivolatile organic compounds that might be collected by the quartz-fiber filter that follows the denuder [*Gundel et al.*, 1998; *Lane et al.*, 2000]. The aerosol collected on the quartz-fiber filter is analyzed for OC and EC. The VAPS is used in this study as an alternate relative reference for OC, since OC is collected with less bias in this sampler using the XAD-4 coated denuder than those which do not use a denuder to remove potential interfering organic gases [*Gundel et al.*, 1998; *Lane et al.*, 2000; *Solomon et al.*, 2000; L. Gundel, personal communication, 1998].

2.2.5. RPS: R&P Chemical Speciation Sampler Developed by Rupprecht & Patashnick Co., Inc.

[19] The Rupprecht & Patashnick Co., Inc. (R&P) Partisol Model 2300 Chemical Speciation Sampler (RPS) as employed in Atlanta is illustrated schematically in Figure 3e. This sampler consists of three sampling modules (ChemComb™ cartridges) connected to a single vacuum pump. The sampler contains four individual mass flow controllers that actively maintain a user-selectable constant volumetric sampling flow rate, and it can be operated either in a single-event or sequential mode. Following this field program, a new family of enhanced performance PM2.5 size-selective inlets was developed for the ChemComb cartridge at sample flow rates of 10 and 16.7 Lpm [*Demokritou et al.*, 2001]. Total flow through the system used in Atlanta is 30 Lpm and the flow rate through each module is 10 Lpm. An impactor is located at the front of each module that hangs in a downward direction with air being pulled up through the modules. A single Teflon filter is located behind the impactor in channel 1. This filter is analyzed for mass and trace elements as described above. Two quartz-fiber filters in series are located in channel 2. The top quartz-fiber filter is analyzed for sulfate, nitrate, and ammonium ions and for OC and EC. The third channel includes a Na_2CO_3 coated honeycomb denuder to remove acid gases followed by a nylon filter, which is analyzed for nitrate. As described above, nitrate measured in this manner likely minimizes sampling artifacts for the collection of aerosol nitrate. The RPS incorporates sensors to measure continuously the barometric pressure and ambient temperature. Runtime statistical data could be viewed on the integrated display panel or downloaded through the standard RS-232 serial port using RPCOMM or RPDATA communications software.

2.2.6. RPD: R&P Dichotomous Partisol Model 2025 Sequential Air Sampler Developed by Rupprecht & Patashnick Co., Inc.

[20] The R&P automated dichotomous sampler as used in Atlanta is schematically shown in Figure 3f. In this sampler, PM2.5 is obtained using a PM10 size-selective inlet in

conjunction with a virtual impactor that has a 2.5 μm cutpoint. Total flow is 16.7 Lpm, which is split into major (15 Lpm) and minor flows (1.67 Lpm) by the virtual impactor. Coarse particles and a small fraction of fine particles follow the minor flow and are collected on a polycarbonate filter for subsequent analysis by scanning electron microscopy with XRF to obtain information on the chemical composition of single particles. Fine particles (<PM2.5 μm) follow the major flow and are collected on a Teflon filter, which is analyzed for PM2.5 mass and trace elements. Mass flow controllers maintain the flows. This is an automated system so filter cassettes containing several sampling periods can be loaded at once on both the fine and coarse portions of the sampler, thus minimizing labor for changing filters. For this study, filters were removed after each sampling period, to be consistent with the other samplers.

2.2.7. FRM: Federal Reference Method

[21] The experimental design of the two FRM samplers as used in Atlanta is schematically illustrated in Figure 3g. Two FRM samplers are used to obtain a chemical characterization of the collected aerosol in a manner similar to the other samplers. One FRM uses a Teflon filter from which PM2.5 mass and trace element (Na-Pb) loadings are obtained. The second FRM uses a prebaked quartz-fiber filter that is split in half with one half being analyzed for OC and EC and the other half for sulfate, nitrate, and ammonium ions. As mentioned above, the FRM is the reference method for PM2.5 mass and should provide a suitable reference for nonvolatile species, such as sulfate, elemental carbon, and many of the trace elements determined by XRF. The semivolatile species, such as ammonium nitrate and some of the organic species are collected with less bias by the VAPS sampler; thus the VAPS will provide a reference for organic carbon.

2.2.8. PC BOSS (PC-BYU) and PC BOSS (PC-TVA): Particle Concentrator-Brigham Young University Organic Sampling System

[22] Figure 3h shows the schematic of the PC-BOSS (PCB) used in Atlanta and operated by Brigham Young University [PCB(BYU)] during the Atlanta Supersites project. A similar system, illustrated in Figure 3i, was operated by the Tennessee Valley Authority [PCB(TVA)] and differences between the two approaches are described below. The inlet to the BYU sampler is a Bendix cyclone [*Chan and Lippmann*, 1977] with a particle cutpoint of 2.3 μm aerodynamic diameter (AD) at an inlet flow rate of 150 Lpm. After the inlet, 16 Lpm are diverted to the side flow manifold that holds a single filter pack containing a Teflon filter and a carbon-impregnated cellulose filter in series. Sulfate collected on the Teflon filter is used to evaluate the particle concentrator efficiency and organic material collected on the CIF backup filter is used to evaluate denuder efficiency [*Modey et al.*, 2001]. The remainder of the sampled air stream enters a virtual-impactor particle concentrator. *Ding et al.* [2002] and *Sioutas et al.* [1994] describe the design and evaluation of the particle concentrator. The particle concentrator separates 75% of the gas-phase material into the major flow leaving particles larger than the virtual impactor cutpoint (about 0.1 μm) along with a significantly reduced fraction of the gas-phase material in the minor flow.

[23] The minor flow air containing concentrated fine particles (0.01 μm to 2.3 μm AD) enters the BOSS CIF diffusion denuder [*Eatough et al.*, 1993], which removes gas-phase species with an efficiency that is expected to exceed 99% [*Ding et al.*, 2002; *Lewtas et al.*, 2001] since most of the gas-phase species are removed in the particle concentrator. As a result, positive sampling artifacts from the collection of gas-phase compounds by quartz-fiber filters after the denuder are expected to be negligible.

[24] The denuder is followed by two parallel filter packs. One filter pack contains a 47-mm quartz-fiber filter (Pall Corporation, Gelman Laboratory, Ann Arbor, MI) followed by a 47-mm carbon impregnated filter (Schleicher and Schuell, Keene, NH). This combination of filters is used to determine fine particulate carbonaceous material, sulfate, and stable nitrate on the quartz-fiber front filter. Semivolatile nitrate and organic material lost from the particles collected on the quartz-fiber filter are trapped on the sorbent CIF backup filter. The other parallel filter pack contains a Teflon filter (Tefluor, 47 mm, 2 μm pore size, Whatman, Clifton, NJ) followed by a nylon filter (Nylasorb 47 mm, 1 μm, Pall Corporation, Gelman Laboratory, Ann Arbor, MI). The Teflon filter is used to determine mass, sulfate, and stable nitrate, whereas the nylon filter is used to determine nitrate lost from particles during sampling. Particulate matter nitrate reported in this paper for the PCB(BYU) sampler is an average of nitrate measured by both filter packs, including the backup filters. With this combination of techniques, negative sampling artifacts are greatly minimized.

[25] TVA also operated a PC-BOSS sampler [PCB(TVA)] on the 24-hour, every other day schedule. A schematic and experimental protocol for the TVA sampler as used in Atlanta is shown schematically in Figure 3i. There are several major differences between the BYU and TVA PC-BOSS systems as deployed at the Atlanta Supersites project and illustrated in Figures 3h and 3i. PCB(TVA) uses the same Bendix cyclone operating at an inlet flow rate of about 105 Lpm (monitored every 10 min during sampling period by the data logging system), compared to 150 Lpm for the PCB(BYU). The slope of the cyclone cutoff curve was not directly verified, but is estimated to be about 2.9 μm based on data from *Chan and Lippmann* [1977]. As shown in Figure 3i, the TVA sampler does not use a side stream flow behind the inlet to collect PM2.5 for analysis of PM2.5 mass and components, but collects PM in the major flow. Results from sulfate analyses of this quartz-fiber filter (prefired Pall Tissue quartz 2500QAT-UP, Pall Gelman, Ann Harbor, MI) are used to evaluate the efficiency of collection of fine particle mass in the minor flow stream by the particle concentrator, i.e., to correct for loss of <0.15 μm particles via the major flow. Denuder efficiency was not directly evaluated in this study for PCB(TVA). The lower size cut of the particle concentrator is in the range of 0.1 to 0.15 μm rather than <0.1 μm due to the different total flow rates employed. Nitrate reported by the PCB(TVA) sampler is based on the Teflon-nylon filter pack (Teflon, PTFE with PP ring, 47 mm, 2, Whatman, Clifton, NJ; nylon, Nylasorb, 47 mm, 1 μm, Pall Gelman, Ann Harbor, MI), as nitrate is not measured on the backup CIF filter. Finally, the denuder flow in the PCB(TVA) is controlled by down stream mass flow controllers at 30.0 ± 0.2 Lpm with 15.0 Lpm for each

of the two filter packs collecting PM in the minor flow, compared with a total of 34 Lpm with 17 Lpm for each filter pack in the BYU system.

[26] Differences also exist between the analytical methods employed by both groups. For the PCB(BYU), sulfate and nitrate analysis is by ion chromatography of either aqueous extracts for Teflon and quartz-fiber filters or IC eluent extracts for CIF and nylon filters [*Ding et al.*, 2002]. Quartz-fiber and CIF filters collected by the PCB(BYU) are analyzed for carbonaceous material by thermal desorption of the collected materials using temperature programmed volatilization (TPV). This method is somewhat different than TOT referenced above or thermal optical reflectance (TOR) referenced below. In this case, the CIF filters are heated from 50°C to about 300°C at a ramp rate of 10°C/min in a stream of nitrogen. The quartz-fiber filters are heated from 50°C to 800°C at a ramp rate of 28°C/min in a stream of N_2/O_2 (70:30% v/v). Soot (EC) is estimated from the high temperature peak (usually above 450°C) on the thermogram obtained from the quartz-fiber filter analysis [*Ellis and Novakov*, 1982]. There is no correction for pyrolysis as it is expected to be minimal by this method. However, because of the presence of high concentrations of secondary organic material, which evolves at a temperature just below that for soot, the precision for EC is about 30–50%.

[27] In the minor flow streams of the PCB(TVA), mass is determined on the Teflon front filter by gravimetric analysis. Sulfate and nitrate concentrations are measured on the front filter of the quartz-fiber/CIF filter and Teflon/nylon filter packs by IC, while ammonium is determined on the same filters by automated colorimetry (AC) using the indophenol blue method. PCB(BYU) did not determine ammonium ion on any of their filters. Organic and elemental carbon are obtained on the PCB(TVA) quartz-fiber filter using thermal optical reflectance (TOR) [*Chow et al.*, 1993], while, SVOCs are determined on the PCB(TVA) CIF filters by BYU using TPV. Nitrate is not determined on the CIF filter as is done with the PCB(BYU); however, nylon filters are extracted with IC eluent and nitrate is determined in the extract by IC.

[28] A quartz-fiber filter is used to collect particles from the major flow of the PCB(TVA) and is monitored continuously by a mass flow meter. Sulfate is determined by IC in the extract after determination of OC and EC by TOR. The concentration of sulfate is used to estimate the fraction of mass that was not collected in the minor flow stream. Reported mass, ionic concentrations, and OC/EC are obtained by summing the major and minor flow concentrations, which are calculated based on the total flow entering the sampler (≈105 Lpm). (Note, the OC value from this filter is not free of positive OC artifact from absorption of gaseous semivolatile organic compounds as is the case with the minor flow quartz-fiber filter.)

2.2.9. KB and EE: Particle Composition Monitors From Georgia Tech and ARA

[29] The Particle Composition Monitor used in this study by the Georgia Institute of Technology (GIT, KB) is illustrated schematically in Figure 3j. Atmospheric Research and Analysis (ARA, Inc., EE) operated a similar system and differences between the two approaches are described below. The KB sampler consists of three modules, located in a single temperature controlled shelter that is kept at approximately 4°C above ambient temperature. The flow rate through each module is 16.7 Lpm and each module has a standard URG Teflon coated cyclone with a 2.5 μm cutpoint to allow for the collection of PM2.5. In the GIT version (KB) [*Baumann et al.*, 2001], channel 1 uses a pair of in series annular denuders coated with Na_2CO_3 to remove acidic gases, followed by a filter pack containing a Teflon filter (unringed Zeflour™, 47 mm diameter, 2 μm pore-size, Gelman Laboratories, Ann Arbor, MI) followed by a Na_2CO_3 impregnated paper filter (Whatman 41, 47 mm diameter, Maidstone, England). Mass is determined gravimetrically on the Teflon filter, after which the filter is extracted in water and analyzed for chloride, nitrate, sulfate, and light organic acids (LOA; formic, acetic, and oxalic acids) by IC. The denuders are extracted and the extracts are analyzed by IC to determine gas-phase concentrations of HCl, HNO_2, HNO_3, SO_2, and LOA.

[30] The cyclone in channel 2 is followed by two annular denuders, in series, each coated with citric acid to remove ammonia gas followed by a filter pack containing a Teflon filter followed by a citric acid impregnated paper filter. Mass again is determined by gravimetric analysis of the Teflon filter (replicate of channel 1) and cation concentrations (Na^+, Ca^{2+}, NH_4^+) are obtained by IC after aqueous extraction of the Teflon filter. The denuders are extracted and analyzed by IC for NH_4^+ to obtain gas-phase concentrations of ammonia. The third channel collects PM2.5 on a quartz-fiber filter (Pallflex #2500, 47 mm diameter, 1 μm pore-size, Gelman) preceded by an XAD-4 coated annular denuder [*Gundel et al.*, 1998; *Lane et al.*, 2000], similar to the one used in the VAPS. The XAD-4 coated annular denuder removes gas-phase organic species (either volatile or semivolatile organic species) to minimize positive artifacts on the quartz-fiber filter. The quartz-fiber filter is followed by an XAD-4 impregnated quartz-fiber filter [*Baumann et al.*, 2003; J. Z. Zhao et al., manuscript in preparation, 2001] used to estimate the fraction of semivolatile organic species volatilized from the particles collected on the front filter. Results from *Lewtas et al.* [2001] indicate negligible collection of VOC on quartz-fiber filters placed downstream of and XAD-4 denuder. The front quartz-fiber filter is analyzed for OC and EC by TOT as described above. The backup XAD-4 coated quartz-fiber filter undergoes a modified analysis that is significantly different than conventional TOT analysis. In this case, O_2 is not introduced into the system and EC is not measured, since EC is efficiently collected on the front quartz-fiber filter. The maximum oven temperature for this analysis is 176°C in pure He atmosphere. Field blanks are collected for each XAD-4 coated quartz-fiber filter. Detection limits and precision based on collocated sampling are given by *Baumann et al.* [2001].

[31] The ARA PCM (EE) consists of three modules located in a single housing that is not temperature controlled. The flow rate is 16.7 Lpm using a dedicated mass flow controller and pump for each module. Each module has its own PM10 cyclone inlet, which is followed by denuders as described below and then by a WINS PM2.5 impactor. Modules 1 and 2 each have a Na_2CO_3 coated annular denuder followed by a citric acid coated annular

denuder to remove acidic and basic gases, respectively. Following the denuders in Module 1 is a three-stage filter pack containing, in order of airflow, Teflon, nylon, and citric acid impregnated paper filters. Mass, ions, and elements are determined on the Teflon filter, while volatilized nitrate and ammonium are determined on the nylon and citric acid impregnated filters, respectively. Mass is determined gravimetrically according to the FRM procedure [*CFR*, 1997], particulate nitrate and sulfate by IC, ammonium by automated colorimetry (AC), and elements by XRF. Module 2 denuders are followed by a nylon filter for the determination of particulate nitrate and sulfate by IC and ammonium by AC. Module 3 has a PM10 cyclone inlet followed by a BYU design CIF denuder followed by a WINS impactor. The CIF denuder removes a fraction of the gas-phase organic compounds that might appear as a positive artifact. The denuder is followed by a two-stage filter pack containing two quartz-fiber filters in series. Both filters are analyzed for OC and EC by TOR, the latter or backup filter collecting quartz-adsorbable semivolatile organic gases volatilized from the particles collected on the front quartz-fiber filter and/or organic gases not removed by the denuder.

[32] It should be noted, that the ARA 12-hour (7 AM to 7 PM; 7 PM to 7 AM) sampling schedule employed during the Atlanta Supersites project is different from the one used for the ARIES and SEARCH studies (24-hours midnight to midnight), and therefore results from the ARA PCM may not be strictly applicable to those studies.

2.2.10. MOUDI: Micro Orifice Uniform Deposit Impactor

[33] Figure 3l shows the MOUDI sampling system as operated in Atlanta by the University of Miami (UMiami). Four MOUDI samplers were employed during the study. Two operated on a 12-hour sampling schedule with stop times at 0600 and 1800 EST. Samples collected by these MOUDIs are analyzed for major ions and trace elements (MOUDI 1 in Figure 3l) and for OC and EC (MOUDI 2 in Figure 3l). The other two MOUDI samplers operated on a 3.5 day schedule collecting samples for organic aerosol speciation (MOUDI 4 in Figure 3l) and for high molecular weight organic species and aerosol mass (MOUDI 3 in Figure 3l). Samples were restarted as soon as substrate changeovers were complete. For the MOUDI samplers, only the ions, OC, and EC 12-hour results, averaged to the appropriate 24-hour values, are discussed in this paper.

[34] The intake of the MOUDI sampling line was at about 13 m above ground level. The inlet consists of an omnidirectional Liu-Pui type intake scaled to the total system flow rate of 120 Lpm [*Liu et al.*, 1983]. The inlet is mounted on the top of a 10-m section of 5-cm ID aluminum tubing attached to a flow splitter mounted on the top of a 2-m plastic storage container. The airflow is ducted from the flow splitter to four 2.5 μm diameter cutpoint cyclones that are each followed by the MOUDI Model 100 impactors and mass flow meters (MKS Model 0558A-050LSV). Each MOUDI has eight stages with aerodynamic diameter cutpoints of 3.16, 1.78, 0.97, 0.56, 0.32, 0.18, 0.098, and 0.056 μm at the nominal flow rate of 30 Lpm. For each of the MOUDI samplers, a blank is taken for each type of substrate for each sampling period with an extra set taken during removal of the last sample. Blanks are handled and analyzed in the same manner as samples.

Table 3. Chemical Characteristics of PM2.5 Mass and Composition at the Jefferson Street Site During the August 1999 Atlanta Supersites Project

Species	Average[a]	Standard Deviation[b]	Maximum[c]	Minimum[c]
		μg/m³		
Mass	31.3	8.4	47.2	16.0
SO_4^{2-}	10.6	4.1	18.5	2.7
NO_3^-	0.5	0.08	0.70	0.36
NH_4^+	3.6	1.3	6.1	1.1
OC	7.8	1.8	10.3	3.8
EC	1.0	0.25	1.42	0.71
		ng/m³		
S	4240	1530	7120	1110
Si	213	93	395	69
K	65.5	19.1	111	33.9
Ca	83.2	50.3	234	18.7
Mn	2.9	0.9	4.1	1.0
Fe	145	44	201	45
Cu	4.4	3.7	15.3	1.26
Zn	17.1	9.5	46.2	6.6
Pb	5.8	4.1	19.0	2.1
As	1.5	0.39	2.42	1.00

[a]This is the relative reference value for the study period as described in the text.
[b]Standard deviation of study period relative reference values.
[c]Maximum and minimum of the daily relative reference values as described in the text.

[35] MOUDI 1 (Figure 3l) is used for measurements of major ions and trace elements. Filter substrates for this sampler include 37-mm diameter, 2-mil thick, FEP Teflon impaction substrates and 37-mm diameter quartz-fiber final filters that are prewashed, dried, and stored in glass bottles with Teflon-lined screw caps until used. After collection, the filters are split in half, with half being analyzed for major anions (Cl^-, NO_3^-, and SO_4^{2-}) by IC and NH_4^+ by automated colorimetry, while the other half is analyzed for trace elements by ICP-MS.

[36] MOUDI 2 (Figure 3l) uses Al foil and quartz-fiber filter substrates that are heated overnight at 500°C in air to reduce blank values for OC and EC prior to use. After collection the substrates are analyzed by a modified TOR analysis suitable for use with the Al substrates.

[37] Substrates in MOUDI 3 are analyzed for mass and medium-to-high molecular weight organic compounds, while substrates in MOUDI 4 are analyzed for speciated organic compounds. Because substantial amounts of materials are necessary for these analyses, the substrates are only changed every 3.5 days. However, the samplers are turned on and off to coincide with the timing of the 12-hour MOUDI samples. Hence each 3.5 day MOUDI 3 sample is equivalent to the sum of seven of the 12-hour MOUDI samples. As with MOUDI 2, the Al and quartz-fiber substrates are heated overnight at 500°C prior to use. After sampling, the substrates in MOUDI 3 are post-weighed for mass and analyzed for high molecular weight organic species by Soxhlet extraction in methanol, evaporation under N_2, with dissolution in methylene chloride followed by GC/MS analysis (A. Cook, Georgia Tech Research Institute, personal communication, 2001). The substrates in MOUDI 4 are analyzed for speciated organic compounds by solvent extraction (DCM:Acetone:Hexane 2:3:5 by vol-

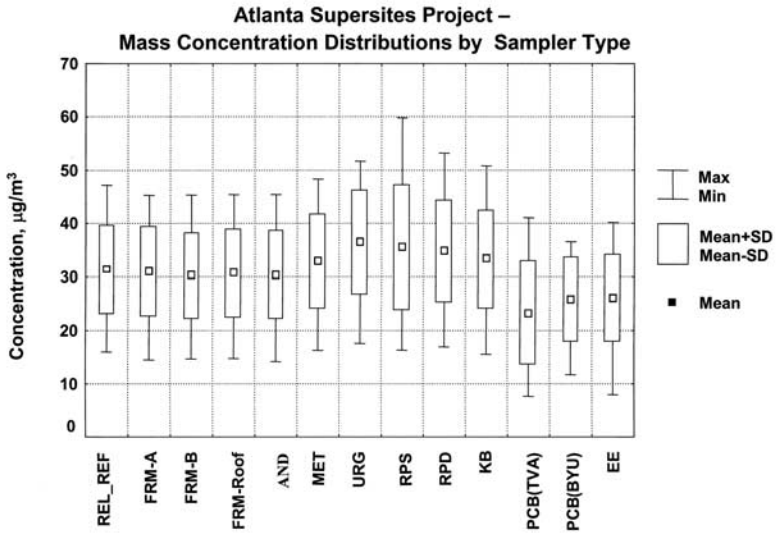


Figure 4. Mass frequency distribution given as box plots for discrete samplers. FRM-A, FRM-B, and FRM-roof provide an estimate of spatial representativeness within the sampling site for PM2.5 mass and trace elements.

ume) followed by GC/MS [*Tremblay et al.*, 2000], similar to the method of *Schauer et al.* [1996].

2.3. Quality Assurance/Quality Control

[38] Each group was responsible for its own quality control. EPA Region 4 in conjunction with EPA Office of Air Quality Planning and Standards (OAQPS) also conducted system and performance audits on most discrete samplers prior to the first day of sampling and the remaining samplers during the first few days of the study. Results of these audits are given in the final audit report for the study [*Mikel*, 2002]. Audit results for the discrete samplers are essentially all within a few percent of the expected value for flow, ambient temperature and pressure, and filter temperature. Overall, results from this study will provide equivalence or comparability of samplers among those evaluated. Detection limits, an estimate of field blanks, and precision estimates based on collocated sampling at Rubidoux, CA, for the AND, MET, URG and FRM samplers are given by *Solomon et al.* [2000] based on wintertime measurements during EPA's initial evaluation of these samplers.

3. Results

3.1. Composition of Atlanta's Fine Particulate Matter

[39] Summary statistics for mass, major species, and a trace element are presented in Table 3. Average values were calculated across all integrated samplers for a given species and for the study period. This average also is considered the relative reference value [*Solomon et al.*, 2003] and represents one approach for comparing data among the samplers since reference standards do not exist for the chemical components of PM2.5. Average PM2.5 mass at the Jefferson Street site for the month of August 1999 was about 31 $\mu g/m^3$ or about twice the annual average PM2.5 standard of 15 $\mu g/m^3$ or about half of the 24-hour average PM2.5 standard of 65 $\mu g/m^3$ [*CFR*, 1997]. Sulfate and organic material (organic carbon multiplied by 1.4 to account for hydrogen and oxygen when collected in an urban environment) [*Turpin et al.*, 2000] each accounted for about 34 to 35% of the mass, while nitrate accounted for less than 2% of the mass, as is typical for east coast cities during the summer [*EPA*, 2001]. Ammonium ion, primarily associated with sulfate, accounted for about 12% of the mass. Elemental carbon and an estimate of crustal material (sum of Fe, Si, and Ca after converting to their oxides [*Solomon et al.*, 1989; *Eldred et al.*, 1998] each accounted for about 3% of the PM2.5 mass. Overall, this simple mass balance accounted for nearly 90% of the mass, the remainder most likely being water and unaccounted for trace elements. This reasonable mass balance suggests that the composition data represent the mass collected on the filter to within about 10% or so, although there may be compensating errors. *Butler et al.* [2003] more thoroughly examine the spatial and temporal composition of PM2.5 mass and chemical composition within and around Atlanta from March 1999 to February 2000.

3.2. Within Site Spatial Representativeness

[40] Three FRM samplers were operated to evaluate spatial representativeness across the platforms and in the vertical direction to the height of the inlets above the trailers. One FRM was located on platform A, furthest from the trailers, a second diametrically opposed was located on platform B, while the third was located on the roof of the trailer adjacent to platform B (see Figures 1 and 2). The ratio of the average of each sampler to the mean among the average of the samplers (i.e., the relative reference value) ranged from 0.99 to 1.1 for mass with a coefficient of variation of the daily average standard deviation to the mean among the samplers of 2%. For Ca, Fe, Si, and an estimate of crustal material (sum of these three elements) the ratio was typically within 5%, but did not exceed 8%, while the coefficient of variation ranged from 12% for Ca to 7% for Fe. Frequency distributions as box plots for PM2.5 mass for each of the integrated samplers are illustrated in Figure 4. The first bar

Table 4. Study Period Averages for Mass and Chemical Components for Time-Integrated Samplers[a]

Species	REL REF[b]	FRM-A	FRM-B	AND	MET	URG	RPS	RPD	EE	VAPS	KB	PCB (TVA)	PCB (BYU)	MOUDI (Without AF)[c]	MOUDI (With AF)
								μg/m³							
Mass	**31.3**	30.9	30.2	30.3	32.9	***36.5***	***35.4***	34.8	***26.0***	–	33.3	***23.2***	**25.8**	–	–
SO_4^{2-}	**10.6**	10.7	–	10.7	10.8	11.1	10.3	–	10.1	9.8	10.8	***9.0***	11.0	**9.2**	–
NO_3^-	**0.51**	***0.22***	–	0.58	***0.61***	0.50	***0.62***	–	***0.8***	***0.71***	***0.62***	***0.33***	**0.35**	**0.16**	–
NH_4^+	**3.6**	3.4	–	3.5	3.7	3.9	3.6	–	4.0	3.3	3.7	***3.0***	–	3.2	–
OC	**7.8**	8.5	–	***9.2***	***9.3***	8.1	***10.5***	–	***6.1***	***6.3***	7.6	***5.3***	**5.1**	**3.8**	6.8
EC[d]	**1.04**	***0.73****	–	0.89*	***0.86****	***0.77****	0.89*	–	***2.0+***	***0.79****	***0.80****	***1.5+***	**2.6+**	**1.4+**	–
								ng/m³							
S	**4240**	4340	4140	4140	4120	4270	4480	4220	–						
Si	**213**	193	***178***	217	***177***	***182***	***362***	202	***119***						
K	**65.5**	60.5	58.3	65.7	58.1	59.1	***94.8***	64.5	***35.3***						
Ca	**83.2**	73.0	71.3	88.9	70.9	***68.8***	***139***	80.1	78.4						
Mn	**2.9**	2.6	2.6	3.0	3.2	2.7	3.3	3.1	2.7						
Fe	**145**	130	***122***	152	125	***122***	***229***	147	***95***						
Cu	**4.4**	4.1	***6.7***	4.3	3.9	***3.1***	4.5	3.9	***3.5***						
Zn	**17.1**	16.8	18.8	16.7	14.7	16.9	19.6	17.1	***20.3***						
Pb	**5.8**	6.2	5.7	5.9	5.1	5.3	6.3	5.9	***4.5***						
As	**1.5**	1.3	1.4	1.4	*2.1*	1.5	1.6	1.3	–						

[a]Missing data (about 7% of the data collected overall) were estimated by regression of the daily values versus the relative reference data and then back calculating the missing values, with the exception of organic carbon where daily values were regressed against the OC values obtained by the VAPS sampler. Therefore n = 15 for all averages. Italic and bolded values exceed performance criteria based on the Four-City Study results and specified in Table 1; although from a practical standpoint, not all values exceeding the performance criteria should be considered different from the relative reference, but that depends on investigators objectives for the data.

[b]REL REF, relative reference; values and criteria are defined in the text.

[c]AF, after filter located after all stages in the MOUDI.

[d]EC determined by TOT with the NIOSH protocol (*) or TOR by the IMPROVE protocol(+).

represents the relative reference data calculated as described above and by *Solomon et al.* [2003]. The next three bars represent the three FRM samplers that were used to determine spatial representativeness within the site. As illustrated in Figure 4 and based on the ratio and coefficient of variation data, little difference existed among these three FRM samplers for PM2.5 mass and for crustal related species (not shown) suggesting little spatial variability existed within the site for these species. Other fine particle species, such as sulfate, nitrate, OC, and EC are expected to show similar results, i.e., little spatial variability within the site.

3.3. Comparison Among Samplers

3.3.1. Mass Frequency Distributions

[41] The frequency distributions shown in Figure 4 represent the temporal variability for mass observed by each sampler during the study period. Mass was not determined on the 12-hour MOUDI or the VAPS. On average, several samplers reported observed mass values slightly higher (>10%) than the relative reference value (URG, RPS, RPD), while several others reported mass values slight lower (<10%) than the relative reference value (PCB-TVA, PCB-BYU, EE). These differences are due likely to the different designs of the samplers and this will be explored further throughout the remainder of this paper.

[42] In the box plots, different size boxes (mean ± one standard deviation, maximum, minimum) suggest that the different samplers obtained slightly different frequency distributions. For example, the RPS has the largest box indicating the greatest variability for observed mass during the study period, while the PCB(BYU) had the least variability. Differences in the maximum and minimum 24-hour average values also indicate variability among the samplers. The highest 24-hour mass was observed by the RPS at about 60 μg/m^3, whereas the calculated maximum relative reference value was about 47 μg/m^3. Further testing of the inlet by R&P after the study indicted that the inlet did not have the expected collection efficiency performance and has been redesigned [*Demokritou et al.*, 2001; M. Meyer, R&P, personal communication, 2001]. The FRM and the previously evaluated EPA samplers' maximum 24-hour mass values observed during the study period ranged from about 45 μg/m^3 (AND and MET) to about 52 μg/m^3 (URG). The URG sampler also was slightly higher than the AND in the Four City Study [*Solomon et al.*, 2000]. The RPD also is slightly higher and uses a PM2.5 virtual impactor with a cutpoint at 2.5 μm, but it has a less steep slope than some of the other PM2.5 separators [*Loo and Cork*, 1988; *Peters et al.*, 2001a].

[43] PCB(TVA) and the EE had the lowest daily average mass values at just under 8 μg/m^3, while the calculated relative reference was at about 16 μg/m^3. The other PC-BOSS sampler (PCB-BYU) also was at the lower end at about 12 μg/m^3. As well, the mean and 24-hour average maximum values for these three samplers were lower than the others indicating that the observed mass values obtained by these samplers resulted in a different distribution of PM2.5 mass than with the other collocated samplers. The two PC-BOSS samplers had CIF denuders before the Teflon filter that was weighed for mass, while the EE had two denuders in series, a Na_2CO_3 to remove acidic gases and a citric acid coated denuder to remove ammonia. It is possible that these denuder combinations affected the collected mass by causing an increase in loss of semivolatile species. However, the URG and KB samplers had sodium carbonate-coated denuders in front of the Teflon filters that were weighed for mass and their observed mass concentrations are slightly above the relative reference value. It is possible

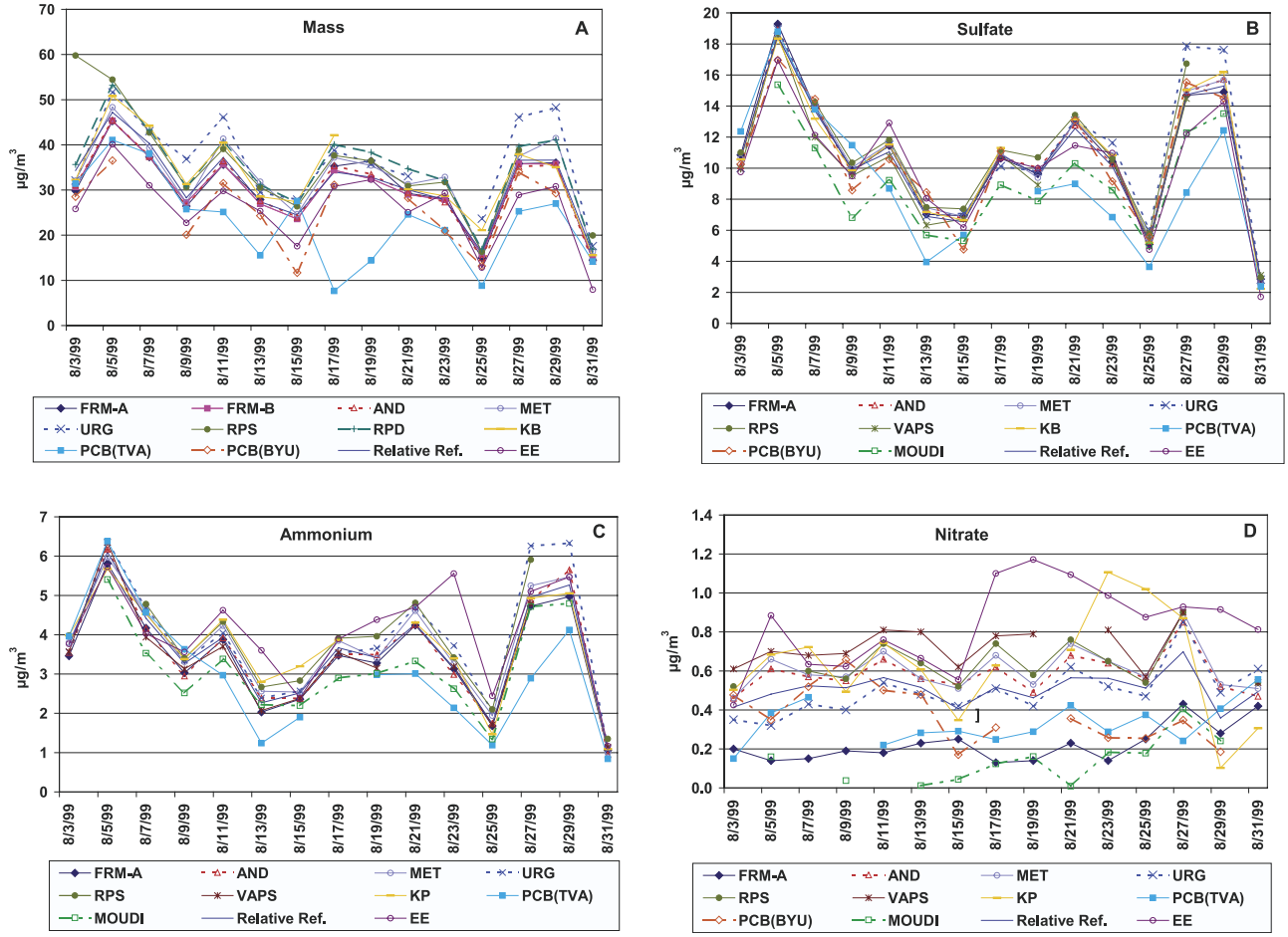


Figure 5. Comparison of discrete samplers for major and minor components: (a) mass; (b) sulfate; (c) ammonium; (d) nitrate; (e) elemental carbon; (f) organic carbon; and (g) silicon.

that the inlet collection efficiency of URG and KB samplers offset the loss of semivolatile species; for example, EE uses a WINS PM2.5 impactor (geometric standard deviation of 1.18; *Peters et al.*, 2001b), while KB used a PM2.5 cyclone (50% collection efficiency at 2.5 µm, slope = $(D_{16}/D_{84})^{0.5}$ = 1.45) [*Baumann et al.*, 2003]. *Finn et al.* [2001] reported recently possible contamination of down stream filters due to the use of coatings that small amounts of contain glycerol (e.g., Na_3CO_3 coated diffusion denuders) and this also may have contributed to the higher mass values for the KB and URG samplers.

3.3.2. Study Period Averages for Mass and Chemical Components

[44] Study period average data for all samplers are presented in Table 4 for mass, sulfate, nitrate, ammonium, OC, EC, and 10 trace elements commonly observed by XRF, although trace elements were not measured on all samplers. Sulfur is included as one of the 10 trace elements, which, when multiplied by 3 is typically equal to sulfate within a few percent. Even though data capture was high (>93% overall), missing values were random based typically on sampler problems during collection. Therefore pairwise comparisons across means were reduced to around 10 or less samples over the study period, noting that only one or two samples were missing from any one sampler. To improve confidence, since only 15 sample sets were collected during the month, missing data were calculated based on regression analysis against the relative reference. Therefore, in Table 4, each mean value consists of 15 data points. Italic and bolded values in the table exceed the performance criteria given in Table 1, although in some cases, the differences are small from a practical standpoint.

3.3.3. Time Series Analysis

[45] Figures 5a–5g present time series plots for mass, sulfate, ammonium, nitrate, OC, EC, and silicon. These species represent the major components of mass, with silicon representing crustal material in the collected sample and also providing evidence of possible penetration of large particles into the sampler. Also plotted on these figures is the relative reference value for that species. Missing values have not been back calculated for the data presented in these figures.

[46] In general, the concentrations of species from one day to the next tend to track each other; although there are exceptions. Sulfate and ammonium concentrations obtained by the different samplers have the least scatter on a daily basis among the samplers reporting these species, as might be expected since ammonium sulfate is primarily fine particle (<1.0 µm) (i.e., typically not affected by the PM2.5 collection efficiency characteristics) and is nonvolatile. The most scatter was observed for organic carbon and nitrate, as might be expected since these are semivolatile species and depend strongly on the collection method

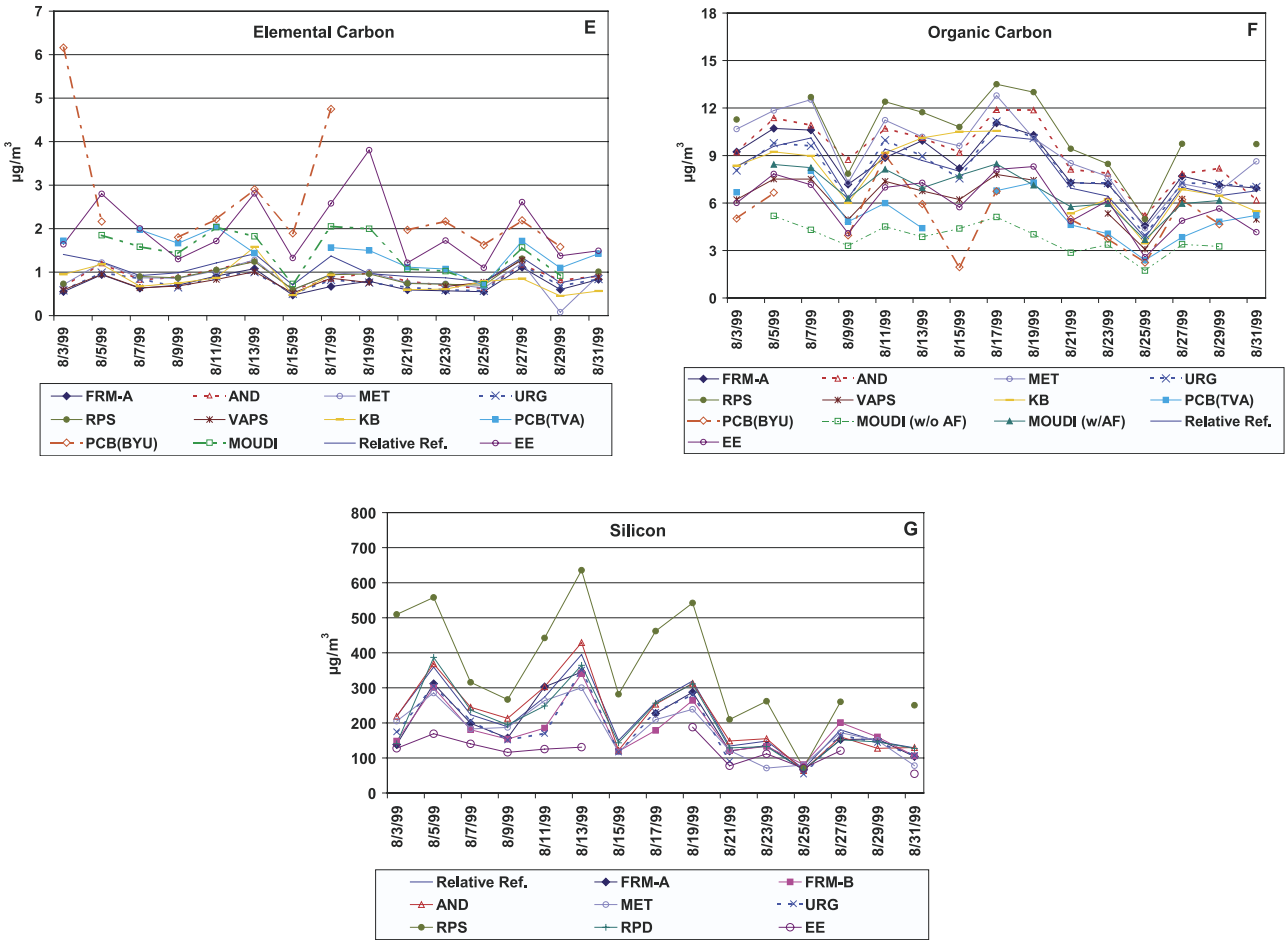


Figure 5. (continued)

employed. Elemental carbon concentrations reported by the samplers appear to be in two groups. One group is around 1 µg/m^3 and the other is about double that value. The group of samplers reporting higher values used TOR or TPV analysis, while the lower group used TOT. Recent intercomparisons between TOR and TOT also indicate this factor of about two bias between the methods for determination of EC in urban particulate matter samples [*Chow et al.*, 2001; Norris et al., submitted manuscript, 2002]. Crustal related elements, using silicon as a surrogate, tend to group together with the exception of two samplers, RPS, which is high, and EE, which is low. For RPS this discrepancy is likely due to

Table 5a. Correlation Coefficients (r): Test Sampler to Relative Reference[a]

	REL_REF	FRM_A	FRM_B	AND	MET	URG	RPS	RPD	VAPS	KB	EE	PCB (TVA)	PCB (BYU)	MOUDI (Without AF*)	MOUDI (With AF)
MASS	1.00	0.97	0.99	0.99	0.97	0.93	***0.86***	0.99		0.96	0.93	***0.68***	***0.90***		
SO_4^{2-}	1.00	1.00		1.00	1.00	0.98	0.99		0.99	1.00	0.96	***0.88***	0.96	0.99	
NO_3^-	1.00	***0.24***		***0.85***	***0.86***	***0.72***	***0.87***		***0.67***	***0.71***	***0.29***	***−0.10***	***0.26***	***0.36***	
NH_4^+	1.00	1.00		0.99	0.99	0.97	0.99		0.99	0.98	***0.85***	***0.88***		0.98	
OC	1.00	0.95		0.93	0.94	0.97	0.99		0.97	0.88	0.91	0.88	***0.70***	0.87*	0.91
EC	1.00	***0.60***		***0.56***	***0.64***	***0.59***	0.89		***0.52***	***0.76***	***0.48***	***0.56***	***0.70***	***0.79***	
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00							
Si	1.00	0.96	0.94	0.99	0.94	0.97	0.95	0.97			***0.80***				
K	1.00	0.98	0.99	0.99	0.96	0.98	0.98	0.99			***0.39***				
Ca	1.00	0.98	0.96	1.00	0.98	0.98	0.97	0.98			***0.04***				
Fe	1.00	0.94	0.97	0.99	0.98	0.95	0.97	0.92			***0.70***				
Zn	1.00	0.94	0.89	0.99	0.96	0.99	0.97	0.91			***0.18***				
Mn	1.00	***0.70***	0.82	0.89	***0.67***	***0.67***	0.84	**0.69**			***−0.14***				
Cu	1.00	0.90	***0.72***	0.95	0.92	0.91	0.92	0.95			***0.70***				
Pb	1.00	0.96	0.99	0.94	0.82	0.96	0.89	0.95			0.85				
As	1.00	***0.46***	***0.65***	0.80	***0.15***	***0.71***	***0.52***	**0.24**							

[a]Relative reference values and criteria are defined in the text. Italic and bolded values exceed performance criteria based on the Four City Study results and specified in Table 1.

Table 5b. Correlation Coefficients (r): Test Sampler Relative to FRM or VAPS for OC[a]

	FRM_A	REL_REF	FRM_B	AND	MET	URG	RPS	RPD	VAPS	KB	EE	PCB (TVA)	PCB (BYU)	MOUDI (Without AF)	MOUDI (With AF)
MASS	1.00	0.97	0.99	0.99	0.98	0.91	***0.77***	0.99		0.96	0.97	***0.60***	0.94		
SO_4^{2-}	1.00	1.00		1.00	1.00	0.97	0.99		0.99	0.99	0.96	***0.88***	0.95	0.98	
NO_3^-	1.00	***0.24***		***0.20***	***0.19***	***0.70***	***0.21***		***−0.15***	***−0.26***	***−0.07***	***0.29***	***−0.25***	***0.53***	
NH_4^+	1.00	1.00		0.99	0.99	0.97	0.99		0.99	0.97	***0.86***	***0.87***		0.97	
OC	1.00	0.95		0.94	0.93	0.94	0.95		0.95	0.88	0.93	***0.84***	***0.64***	0.89[b]	0.90
EC	1.00	***0.60***		0.96	***0.79***	0.93	0.98		0.89	***0.65***	***0.60***	***0.42***	***−0.09***	***0.69***	
S	1.00	1.00	1.00	1.00	1.00	0.99	1.00	0.99							
Si	1.00	0.96	0.90	0.96	0.92	0.90	0.87	0.95			***0.76***				
K	1.00	0.98	0.97	0.99	0.94	0.96	0.94	0.97			***0.36***				
Ca	1.00	0.98	0.91	0.98	0.97	0.97	0.95	0.96			***0.02***				
Fe	1.00	0.94	0.89	0.95	0.95	0.84	0.89	0.81			***0.58***				
Zn	1.00	0.94	***0.75***	0.92	0.93	0.95	0.92	0.84			***0.31***				
Mn	1.00	0.70	***0.43***	***0.77***	***0.22***	***0.38***	***0.73***	***0.47***			***−0.21***				
Cu	1.00	0.90	***0.38***	0.89	0.88	0.94	0.82	0.91			***0.58***				
Pb	1.00	0.96	0.94	0.89	0.82	0.90	***0.77***	0.92			0.89				
As	1.00	***0.46***	***0.34***	***0.23***	***−0.30***	***0.17***	***0.12***	***0.01***							

[a]Relative reference values and criteria are defined in the text. Italic and bolded values exceed performance criteria based on the Four City Study results and specified in Table 1.
[b]AF refers to the after filter located after all stages in the MOUDI.

differences in inlet collection efficiency performance (slope and cutpoint), which has been subsequently corrected by modifying the geometry of the impactor [*Demokritou et al.*, 2001; M. Meyer, R&P, personal communication, 2001]. For EE the difference is possibly due to the system design with the extra denuders or due to differences in the analytical performance between the XRF methods employed by the two groups, noting that the same XRF laboratory was used for all EPA samplers, whereas ARA used a different laboratory. However, for the ARA elemental data there is no consistent pattern with some elements being significantly lower than the relative reference (i.e., Fe, K, Fe, S; measured but not reported in the database) (E. Edgerton, ARA Inc., personal communication, 2001), while others are close to or higher than the relative reference (i.e., Zn, Ca, Mn, Pb, Cu). Additional evaluations will be needed to fully understand these differences.

3.3.4. Correlation Analysis

[47] Pearson correlation coefficients (r) are given in Table 5 for the test sampler versus the relative reference values and for the test samplers relative to the FRM, except for OC, which is relative to the VAPS OC. Correlation coefficients exceeding the performance criteria given in Table 1 are in boldface and italic type.

4. Discussion

[48] A series of discrete or time-integrated filter-based chemical speciation samplers were collocated and compared during the 1999 Atlanta Supersites project. General characteristics of the samplers are given in Table 2 and experimental designs are given schematically in Figure 3 and discussed above. Three of the samplers listed in Table 2 (AND, MET, URG) are included in EPA's national procurement for use in EPA's National PM2.5 Chemical Speciation Network. These three samplers, along with the VAPS (used as a historical reference), were evaluated previously at four locations (Rubidoux, CA; Phoenix, AZ; Philadelphia, PA; and Raleigh, NC) under wintertime conditions [*Solomon et al.*, 2000]. Thus, in contrast, this study represents a summertime comparison for these samplers. As well, many of the operational and performance problems noted with the samplers during the earlier evaluation were corrected by the vendors, so this evaluation should see improvements in the operation and performance of these samplers. The RPS is an additional commercial sampler for possible use in EPA's National PM2.5 Chemical Speciation Network and this study represents its first independent evaluation against other similar type samplers. Several research grade speciation samplers [EE, KB, PCB(TVA), PCB(BYU)] also were included in this comparison since these have been used in a number of long-term studies (over two years) (EE and KB PCM samplers), including the SEARCH, ARIES, and the Southern Center for the Integrated Study of Secondary Aerosols (SCISSAP), or are designed to collect PM2.5 mass and its components, particularly organic material, with minimal bias [*Eatough et al.*, 1999; *Lewtas et al.*, 2001].

4.1. Sampler Comparisons

[49] Examination of Figures 3a–3l indicates differences among the design of the samplers, not only for collecting the semivolatile species but for mass and ions as well. The sampling trains for mass and each of the chemical components of interest are summarized in Table 6. General differences include the type of denuder (sodium carbonate coated, MgO coated, CIF), the location of the denuder (before or after the fine particle separator), the type of filter material (Teflon, nylon, quartz-fiber, carbonate impregnated, CIF), the type of particle separator (i.e., the collection efficiency of the separator, slope and cutpoint, impactor, cyclone, or virtual impactor), flow rate, sample handling and storage procedures, and the analysis method, the latter especially for organic and elemental carbon (see last column of Table 2 for OC-EC method). Samples collected on the EPA samplers (FRM, AND, MET, URG, RPS, RPD, and VAPS) were analyzed by the same laboratory, while the other groups used laboratories of their choosing. Analysis methods used by each group are described above.

4.1.1. Mass

[50] The performance criteria established in this study for mass is a ratio of 1 ± 0.1 and a linear regression coefficient of ≥0.9. Study period averages (Table 4) for mass are

Table 6. Summary of Sampling Trains for Mass and Chemical Components[a]

Sampler	Mass and Elements	SO_4^{2-}, NO_3^-, NH_4^+	Fine Particle Nitrate[b]	OC and EC
AND	PM10 inlet/PM2.5 cyclone/manifold/ **Teflon**	PM10 inlet/PM2.5 cyclone/manifold/**Teflon**	PM10 inlet/PM2.5 cyclone/manifold/ MgO denuder/**Nylon**	PM10 inlet/PM2.5 cyclone/manifold/ **quartz-fiber**
MET	PM2.5 sharp cut cyclone/**Teflon**	PM2.5 sharp cut cyclone/**Teflon**	PM2.5 sharp cut cyclone/ MgO honeycomb denuder/**nylon**	PM2.5 sharp cut cyclone/**quartz-fiber**
URG	PM10 size-selective inlet/carbonate annular denuder/WINS PM2.5 impactor/**Teflon**/nylon	PM10 size-selective inlet/WINS PM2.5 impactor/**quartz-fiber**	PM10 size-selective inlet/carbonate annular denuder/WINS PM2.5 impactor/**Teflon/nNylon**	PM10 size-selective inlet/WINS PM2.5 impactor/**quartz-fiber**
VAPS	NM[c]	PM10 size-selective inlet/ PM2.5 virtual impactor/ XAD denuder/**quartz-fiber**	PM10 size-selective inlet/carbonate annular denuder/**carbonate impregnated paper**/ carbonate impregnated paper	PM10 size-selective inlet/ PM2.5 virtual impactor/ XAD denuder/**quartz-fiber**
RPS	PM2.5 Harvard impactor/**Teflon**	PM2.5 Harvard impactor/ **quartz-fiber**/quartz-fiber	PM2.5 Harvard impactor/ carbonate annular denuder/**nylon**	PM2.5 Harvard impactor/ **quartz-fiber**/quartz-fiber
RPD	PM10 size-selective inlet/PM2.5 virtural impactor/**Teflon**			
FRM	PM10 size-selective Inlet/WINS PM2.5 impactor/**Teflon**	PM10 size-selective inlet/ WINS PM2.5 impactor/ **quartz-fiber**	[NM]	PM10 size-selective inlet/ WINS PM2.5 impactor/ **quartz-fiber**
PC-BOSS (BYU)	PM10 inlet/fine particle concentrator/multichannel CIF denuder/**Teflon**[d]/nylon	PM10 inlet/fine particle concentrator/multichannel CIF denuder/**Teflon** (sulfate, nitrate)/nylon	PM10 inlet/fine particle concentrator/multichannel CIF denuder/**Teflon/nylon**	PM10 inlet/fine particle concentrator/multichannel CIF denuder/**quartz-fiber**/ CIF filter
PC-BOSS (TVA)	PM10 inlet/fine particle concentrator/multichannel CIF denuder/**Teflon**[d]/nylon	PM10 inlet/fine particle concentrator/multichannel CIF denuder/**Teflon**/nylon	PM10 inlet/fine particle concentrator/multichannel CIF denuder/**Teflon/nylon**	PM10 inlet/fine particle concentrator/multichannel CIF denuder/**quartz-fiber**/ CIF filter
KB (PCM)	PM2.5 cyclone/carbonate denuder/**Teflon**[d]/carbonate impregnated paper	PM2.5 cyclone/carbonate denuder (anions), citric acid denuder (cations)/ **Teflon**/citric acid impregnated paper	PM2.5 cyclone/carbonate denuder/**Teflon/carbonate impregnated paper**	PM2.5 cyclone/XAD denuder/**quartz-fiber**/XAD coated quartz-fiber
EE (PCM)	PM10 cyclone/carbonate denuder/citrate denuder/ PM2.5 impactor/**Teflon**/ nylon/citrate impregnated paper	PM10 cyclone/carbonate denuder/citrate denuder/ PM2.5 impactor/**Teflon**/ nylon/citrate impregnated paper	PM10 cyclone/carbonate denuder/citrate denuder/ PM2.5 impactor/**nylon**	PM10 cyclone/CIF denuder/ PM2.5 impactor/ **quartz-fiber/quartz-fiber**
MOUDI	size-selective inlet/ PM2.5 cyclone/**Teflon film (elements only)**/ quartz-fiber backup	size-selective inlet/PM2.5 cyclone/**Teflon film**/ quartz-fiber backup	[NM]	size-selective inlet/PM2.5 cyclone/**Al film**/ quartz-fiber backup

[a]Bold entries indicate the filter(s) where the identified species is measured.
[b]Fine particle nitrate is nitrate collected using a denuder to remove interfering gases (e.g., HNO3) followed by a reactive filter so positive and negative sampling artifacts are minimized.
[c]NM, Not measured by the sampler.
[d]Elements not determined.

within 10% of the relative reference for the FRM, AND, MET, and KB samplers, meeting the predetermined criteria, and within 20% for URG, RPS, and RPD, which are high relative to the relative reference and EE and PCB(BYU), which are low relative to the relative reference. Only the PCB(TVA) sampler exceeded 20% and is low relative to the relative reference. On average, all samplers are well correlated with the relative reference ($r \geq 0.9$; Table 5) except the PCB(TVA), which appears out of phase with the other samplers on 15–21 August 1999 (Figure 5a), although sulfate compares well on these days (Figure 5b). This figure also illustrates the systematic nature of the bias reported for mass concentrations among samplers, with samplers biased high, typically having high mass concentrations every day, and those biased low typically having low mass concentrations. Figure 5a also shows that while the mass reported by the samplers may agree to within 20% of the relative reference on average for the study, poorer agreement is observed on a daily basis, with daily variability ranging from about 15–20 $\mu g/m^3$ or about 50% or more of the relative reference. Since all groups followed similar procedures for gravimetric analysis (FRM procedure) [*CFR*, 1997] and sample handling and storage, the variability observed among the samplers is most likely due to differences in the designs of the samplers.

[51] With regards to the EPA samplers, the FRM, AND, and MET report results that are consistent with each other, not differing on average by more than about 5% compared to the relative reference. The URG sampler, as in the Four City Study [*Solomon et al.*, 2000], is still biased slightly

high (>10%), even though it uses the FRM inlet and a WINS PM2.5 FRM impactor. Essentially, the only difference between this sampler and the FRM is a sodium carbonate coated annular denuder located between the inlet and the WINS to help ensure that particle losses from the denuder would be removed by the WINS (see Figures 3c and 3g). These differences are not likely due to the inlet or impactor, since the same issue has been observed in two different studies (winter and summer) and there is no evidence for large particle penetration based on the consistency of the trace element (e.g., Si, Fe, Ca) data with the FRM. It is possible that the glycerol used in the sodium carbonate coated denuder is contaminating the filter [*Finn et al.*, 2001] resulting in higher mass than expected relative to the FRM. Additional study is required to confirm this. RPS and RPD are likely high due to less efficient inlets than the others. This is qualitatively confirmed by examination of the crustal material components (Si, Fe, Ca), which are typically observed mostly in the coarse particle fraction of the aerosol (>PM2.5) and are high relative to the other samplers. As well, the RPD uses a virtual impactor, similar to the VAPS, which was shown in the Four City Study to allow a greater fraction of large particle penetration than the other EPA sampler inlets. Post study testing also showed that the RPS inlet was not performing as expected and the inlet has been replaced subsequently with an impactor that has an improved collection efficiency (slope, cutpoint, and particle bounce) [*Demokritou et al.*, 2001; M. Meyer, R&P, personal communication, 2001].

[52] Three samplers (EE, PCB-TVA, PCB-BYU) were low compared to the relative reference for mass. The two PC-BOSS systems use a particle concentration (see Figures 3h and 3i), which discards from the PM2.5 measurement, particles less than about 0.1 μm aerodynamic diameter. However, corrections for the particle concentrator collection efficiency are made using either the sample collected after the PM2.5 inlet (PCB-BYU) or the sample collected in the major flow stream from the particle concentrator (PCB-TVA). In Atlanta, this correction efficiency was obtained using sulfate and assumes all species have the same collection efficiency as sulfate. Previous studies have shown that the concentrator efficiency is comparable for sulfate, soot, and nonvolatile organic material and that the use of sulfate alone should introduce an error of no more than 5% in the other calculated species [*Pang et al.*, 2001; *Lewtas et al.*, 2001; *Eatough et al.*, 1999; *Ding et al.*, 2002]. However, the particle concentrator data are low, which may in part be explained by the following two reasons. In Atlanta, over a 13-month period including August 1999, *Woo et al.* [2001] have shown that particles in the range from 10 to 100 nm could account for on average about 17% of the particles by volume. Assuming a density of 1.6 g/cm^3 [*McMurry et al.*, 2001] (also measurements made in Atlanta), this could account for up to 10% of the mass. Thus part of the difference may be due to incomplete correction resulting in lower mass values for the PC-BOSS samplers. These samplers also use a CIF denuder upstream of the Teflon filter used for mass determination (see Figures 3h and 3i and Table 6). The use of the denuder prior to the Teflon filter might enhance volatilization of the semivolatile components from that filter, thus resulting in a lower reported mass. EE has a pair of denuders (citric acid coated and sodium carbonate coated) upstream of the Teflon filter, thus also having potential for enhanced volatilization. These samplers, however, are designed to collect volatile material using backup filters and addition of the volatile components (nitrate, ammonium, and OC) measured on these backup filters more than accounts for the differences in mass [*Modey et al.*, 2001]. However, the URG and KB samplers also have a denuder (sodium carbonate) upstream of the Teflon filter used for mass determination. It is possible that inlet collection efficiencies overcompensated for the enhanced loss of semivolatile material from the Teflon filter, but this cannot be determined from the data collected in this study, since KB did not measure trace elements. As well, KB indicated high readings at the beginning of the study and modified their filter equilibration procedure during the study (longer post equilibration times) and for the later part of the study there was better agreement between KB and the relative reference. Therefore water (a semivolatile component of PM, which should not be neglected) also can play a significant role in how well these samplers can agree.

4.1.2. Sulfate

[53] The performance criteria established in this study for sulfate is a ratio of 1 ± 0.1 and a regression coefficient (r) of ≥0.95. Study period averages (Table 4) for sulfate are within 10% for all samplers but the PCB(TVA) and the MOUDI samplers, which are biased low to the relative reference by about 15%. On average, all the EPA samplers agreed to better than 5% except the VAPS, which was low by about 8%. Pearson correlation coefficients (r; Table 5) were all ≥0.95, except for the PCB(TVA) sampler, which has a correlation of 0.88. The excellent agreement among samplers for sulfate is illustrated in Figure 5b. However, this figure also illustrates that while the sulfate reported by the samplers may agree to within 10% of the relative reference on average, more variability is observed on a daily basis among the samplers, with daily variability ranging from about 2–6 μg/m^3 on low and high sulfate concentration days, respectively, or about 50% or more of the relative reference.

[54] On average, sulfate concentrations reported by the samplers are in good agreement with each other, suggesting that all the samplers collect fine particles (<1.0 μm AD) with little bias. The consistently slightly low values reported by the PCB(TVA) and the MOUDI during the middle of the study may be due to a variety of factors, including, for example, biases in the calibration of flow rates among the samplers even though they all passed the performance audits (±10%) [*Mikel*, 2002], the use of the particle concentrator for the PCB(TVA) system, and the ability of individual stages of the MOUDI to be analyzed and summed to get total fine particle sulfate. In fact, the PCB(TVA) agreed well and was slightly high to the relative reference during the first four days of the study, while the MOUDI agreed well with the relative reference on the last three days of the study. Lower values observed at the end of the study for PM2.5 mass and ions obtained by the PCB(TVA) may have been due to limitations in the prototype design, such as leaks in the system or some other reason, however, the data are considered valid and have been submitted to the final data archive (Tennessee Valley Authority, R. Tanner, personal communication, 2001).

[55] Sulfate is often estimated from sulfur determined by XRF by multiplying sulfur by the molar ratio of sulfate to sulfur of 3. In this study, the ratio of XRF S*3/sulfate had a mean ratio of 1.19 ± 0.03 with a correlation coefficient (r) of 0.95. This ratio was determined from EPA samplers (FRM, AND, MET, URG, and RPS), where sulfur was measured by XRF and sulfate by IC. To remove possible day-to-day biases, the ratio was calculated for each sampler for the study period and then averaged across the five samplers. The average ratio of XRF sulfur*3 to IC sulfate in the Four City Study was within a few percent of 1 overall and at each of the cities where samplers were evaluated [*Solomon et al.*, 2000]. The same analytical laboratory and field operators were used for this and the Four City Study. Review of the data and quality control/quality assurance results obtained during analysis of the Atlanta study indicated no apparent problem with either analysis method. These results therefore suggest that in Atlanta during the Supersites project there may have been other sulfur containing compounds present in the collected PM besides sulfate that were measured by XRF but not IC. While not quantitative, *Lee et al.* [2003] observed hydroxymethanesulfonate (HMS) in about 10% their negative ion spectra of their single particle mass spectrometer method, suggesting the presence of nonsulfur sulfate in Atlanta during the study period. Additional investigation and quantification are needed to verify these findings.

4.1.3. Ammonium

[56] On average during the study period, sulfate was the most abundant species comprising approximately 34% of the mass measured on a Teflon filter, while nitrate accounted for less than 2% of the mass. Therefore the ammonium ion was predominantly associated with sulfate (slope of NH_4^+:SO_4^{2-} of 0.32; r = 0.97) and comparison results for ammonium tend to mimic those of sulfate. The performance criteria established in this study for ammonium are a ratio of 1 ± 0.1 and a regression coefficient (r) of ≥0.9. Study period averages (Table 4) for ammonium are within 10% for all samplers except the PCB(TVA) and the MOUDI samplers, which are biased low to the relative reference by about 17% and 11%, respectively. The former likely due to the prototype nature of the sampler, as noted above for the PCB(TVA) sulfate results, however, the data are considered valid and have been included in the final data archive. Correlation coefficients (r) are given in Table 5 and are all greater than 0.9 except for PCB(TVA), which has a coefficient of 0.88. Daily results are illustrated in Figure 5c and mimic closely those of sulfate, as expected, with the PCB(TVA) and MOUDI results biased low relative to the other samplers and relative reference.

4.1.4. Nitrate

[57] Nitrate concentrations observed during the Atlanta Supersites project were low, with a study period average of about 0.5 $\mu g/m^3$, which is approaching the limit of detection for the nitrate analysis by IC (~0.1 to 0.2 $\mu g/m^3$ assuming the FRM). Therefore interpretation of results for nitrate needs to consider the greater analytical uncertainty at these low levels. As well, an alternate relative reference is not available for nitrate, since the VAPS was operated with two sodium carbonate impregnated filters in series to evaluate possible nitrate artifacts at the anticipated low levels expected in Atlanta.

[58] The performance criteria established in this study for nitrate is a ratio of 1 ± 0.15 and a regression coefficient of ≥0.9. Only the URG sampler met these criteria for the ratio (Table 4) and none of the samplers met the criteria for the correlation coefficient (Table 5). The other EPA chemical speciation samplers, and KB, were within about 25% of the relative reference value and correlation coefficients were typically around or greater than 0.7 for these samplers. The other samplers exceeded a ratio of 30%. Within a given day, there is considerable variability and scatter among the samplers for reported nitrate concentrations; however, there are consistent trends in bias as observed in Figure 5d. Qualitatively, the VAPS, MET, AND, EE, and RPS are clustered above the relative reference value (see Figure 5d and Table 4), although EE deviates much higher during the second half of the study, while the FRM, MOUDI, and PCB(TVA) samplers are below the relative reference value for nitrate. This would be expected for the FRM and MOUDI since neither use a denuder or reactive filter to collect nitrate while minimizing losses due to volatilization. Greater variability is observed with KB and PCB(BYU) samplers with part of the study having nitrate values above and part below the relative reference value (Figure 5d).

[59] Examination of Table 6 indicates that the sampling trains for the collection for particulate nitrate in these samplers vary considerably, and differences in observed nitrate concentrations are likely due in part to these differences. For example, four of the samplers (AND, MET, VAPS, and RPS) measure nitrate directly on a reactive filter located behind a denuder. However, differences exist here as well, as given in Table 6. These samplers tend to report slightly higher nitrate levels as mentioned above. The URG, PCB(TVA), PCB(BYU), EE, and KB use filter packs behind one or two denuders, and except for the EE and URG samplers, tend to report nitrate concentrations below the relative reference. As mentioned above, the MOUDI and FRM use neither denuders nor reactive filters and the effect of this is illustrated in Table 4 and Figure 5d where they report consistently low nitrate values relative to the relative reference and other samplers.

[60] Results from the Four City Study [*Solomon et al.*, 2000] suggested a small positive artifact for nitrate when using carbonate-impregnated filters. To examine the cause of this artifact (e.g., due to the collection and subsequent oxidation of other nitrogen oxides, such as HONO and NO_2 on carbonate impregnated filters), the VAPS sampler was operated as shown in Figure 3d with a sodium carbonate coated annular denuder and two sodium carbonate impregnated cellulose filters in series after the denuder. On the average, the nitrate concentrations observed on the VAPS were 0.72 $\mu g/m^3$ and 0.23 $\mu g/m^3$ on the front and backup sodium carbonate impregnated filters, respectively. The average difference between the two was 0.49 ± 0.10. This value is approximately equal to the relative reference value and is within one standard deviation of the EPA speciation monitors. Therefore it is possible that the use of sodium carbonate filters for collecting aerosol nitrate may result in a value that is positively biased, but only by a few tenths of a $\mu g/m^3$, which would only be of concern when nitrate values drop below 1 to 2 $\mu g/m^3$. While these concentrations are typical for the east coast U.S. during the summer, the impact of this artifact is small in practical terms.

[61] From these data it is clear that the design of the sampler impacts the reported particulate nitrate concentrations and differences are likely due to whether a denuder is used or not, the type of coating on the denuder, the type of reactive backup filter, whether nitrate is measured directly using a single filter or by filter pack that uses two filters, flow rate, or chemical analysis method.

4.1.5. Elemental Carbon

[62] Elemental carbon, like sulfate, is typically fine particle and is stable. The performance criteria established in this study for EC is a ratio of 1 ± 0.15 and a regression coefficient of ≥0.85. Study period averages (Table 4) for EC fall primarily within two groups, those where the test sampler (test sampler/relative reference) is less than and within 15–30% of the relative reference and those greater than and within 40–90% of the relative reference value. The PCB(BYU) has a ratio of 140% for EC. In all cases, except the MOUDI, EC is determined from a pretreated quartz-fiber filter followed by analysis using TOT, TOR, or TPV. MOUDI samples are collected using Al foil disks and analyzed by TOR. The major difference for the reported values of EC among the samplers is due to the analysis method with TOT reporting lower EC values than TOR. Norris et al. (submitted manuscript, 2002) and *Chow et al.* [2001] report a factor of 2 difference between these two methods (TOR > TOT) for samples collected in a typical urban area. The methods use slightly different temperature programs in the analysis of OC resulting in a difference in the reported EC for the same filter. The consistency of this is observed in Table 4 and Figure 5e. As indicated in Table 2, the EPA samplers and KB use TOT for analysis of EC on quartz-fiber filters while EE, PCB(TVA), and the MOUDI use TOR. BYU was the only group to use temperature program volatilization and the PCB(BYU) has the largest reported difference for EC, exceeding 140% on average (test sampler/relative reference).

4.1.6. Organic Carbon

[63] Besides mass and particle bound water, organic carbon (OC) is the most difficult major species to measure in atmospheric particulate matter. First, OC is a surrogate for the sum of all particulate organic compounds found in air; thus it is composed of hundreds of compounds, some of which are semivolatile and are partitioned between the gas and solid (droplet and particle) phases. Second, the difficulty to overcome sampling artifacts (positive and negative) has resulted in a lack of suitable methods to collect OC without considerable bias. Positive artifacts result from adsorption of SVOC on quartz-fiber filter media that is required for the determination of OC and EC by thermal methods, whereas negative artifacts are due to the loss of SVOC from particles collected on the filter due to changes in the equilibrium gas-phase concentrations and pressure drop across the filters. Third, current methods to measure OC as a single species are compromised by lack of reference standards with which to establish a common basis for comparison of the several, but different chemical analysis methods commonly in use today. In this study, three methods to measure OC alone were employed and each defines OC in an operational sense, separating OC, EC, and carbonate carbon; the latter if present is not likely to exceed 5% of the total carbon measured. Finally, the instruments used to measure OC do not measure these surrogates (OC, EC, CC) directly rather they measure only carbon. Adjustment factors are then applied, such as multiplying OC by 1.4 to account for hydrogen, oxygen, and other elements. A recent review suggests 1.4 may be suitable in some urban areas, but in rural areas conversion factors up to 2 or more may be more appropriate due to the higher oxygen content of the organic compounds in the aged aerosol [*Turpin and Lim*, 2001].

[64] The performance criteria established in this study for OC is a ratio of 1 ± 0.15 and a regression coefficient of ≥0.85 (Table 1); although, due to the uncertainty in collection and analysis, Table 1 also indicates that these criteria may be too stringent. Study period averages (Table 4) for OC show considerable variability ranging from 3.8 $\mu g/m^3$ to 10.5 $\mu g/m^3$. The relative reference value is 7.8 $\mu g/m^3$ and for the VAPS, the alternate reference is 6.3 $\mu g/m^3$, lower than the relative reference as expected since it uses a denuder to remove some of the positive artifact. The FRM, URG, KB, and MOUDI including the after filter met the ratio criteria for OC, relative to the relative reference value. The EPA samplers that did not use a denuder to remove gas-phase organic species tend to be grouped together and are higher than the relative reference value ranging from about 5–35% (test sampler/relative reference). Samplers that used a denuder (XAD-4 coated or CIF) to remove gas-phase organic species prior to collection of particles on a quartz-fiber filter were biased low compared to the relative reference by about 20–35%. On an absolute basis, the difference on average between the two groups is 3 $\mu g/m^3$ (average of 9.26 for nondenuded and 6.24 for denuded, based on averaging the data presented in Table 4). These results suggest that the denuders are removing a significant fraction of the quartz-adsorbing gas-phase organic compounds prior to the collection filter and on average the net organic artifact observed under the conditions of this study is about 3 $\mu g/m^3$. This value is within the range reported by *Solomon et al.* [2000] for the Four City Study and by *Kim et al.* [2001] for five locations in the South Coast Air Basin, including Rubidoux, CA, one of the cities in the Four City Study. However, no information is available from these analyses regarding negative artifacts, which are likely enhanced due the use of denuders since gas-phase material is removed by denuders prior to collection on the filter, partially shifting the partition of semivolatile species from the aerosol phase to the gas phase. *Modey et al.* [2001] report that during the Atlanta Supersites project on average for the 15 sampling periods, 40% of the fine particle organic material and 82% of the nitrate were measured on the backup filters collected by the PCB(BYU) sampler. In this study, most samplers measured total particulate nitrate directly using denuders and reactive filters (FRM and MOUDI were the exceptions), whereas, OC results reported in this paper are only for OC measured on the front quartz-fiber filter without the subtraction of OC measured on a backup filter even if measured.

[65] Daily variability for organic carbon among the samplers is large, as can be seen in Figure 5f. On any given day the spread in the data is close to the average for that day. As discussed above, part of this variability is due to the use of denuders in some samplers but not in others. For samplers that do not use a denuder, part of the variability also is due likely to the differences in face velocity through the quartz-fiber filter [*McDow and Huntzicker*, 1990; *Solomon et al.*, 2000]. With the exception of RPS, the samplers that do not

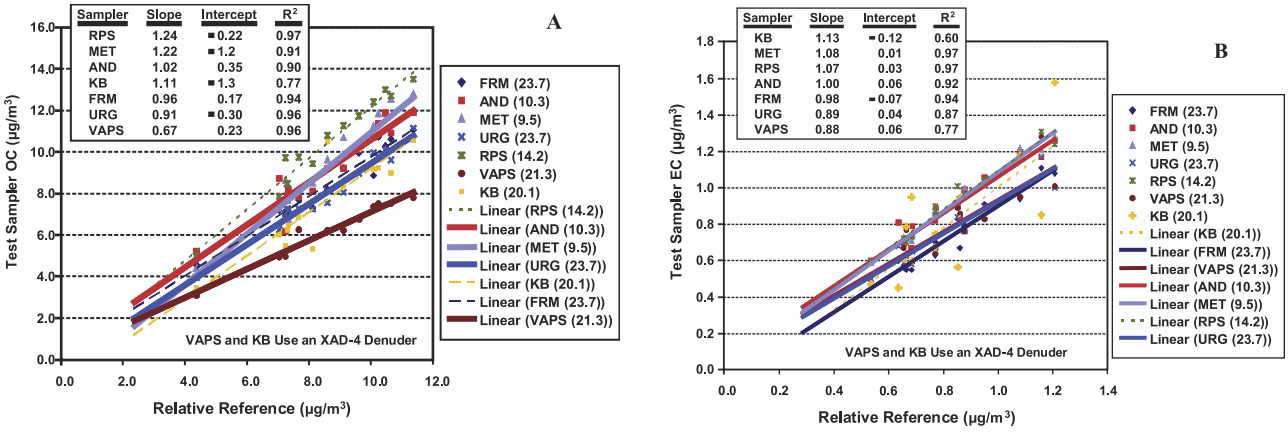


Figure 6. Effect of face velocity across quartz-fiber filters located in the various discrete chemical speciation samplers: (a) organic carbon and (b) elemental carbon.

use denuders seem to follow the trend (Figure 6a), where higher OC is observed on the samplers with the lowest flow rate, which is consistent with previous results suggesting that residence time within the filter material is an important variable. The same trend is not observed in EC (Figure 6b). The higher RPS values may be due to the less efficient collection efficiency of the RPS sampler that was noted above in the discussion on mass. On the other hand, while there is considerable variability among the samplers on a daily basis, they do tend to track each other closely, with regression coefficients of greater than the criteria specified in Table 1 for most samplers. Only PCB(BYU) does not meet the regression criteria, which may be the result of removing the positive artifact from the regression analysis, noting that the positive artifact observed with the other samplers likely increases correlation among those samplers, and its absence, as with the PCB(BYU), would result in lower correlation coefficients.

[66] An estimate of the net artifact due to adsorption of gas-phase organic species by the quartz-fiber filters and loss of semivolatile species from particles during sampling is given in Table 7. These results were obtained by linear regression analysis of the FRM PM2.5 mass (*x* axis) versus organic carbon collected on quartz-fiber filters with and without denuders. Mass is collected on an inert Teflon filter and would not suffer from positive sampling artifacts, while the use of denuders should remove most of the positive artifact when using quartz-fiber filters [*Gundel et al.*, 1998; *Tolocka et al.*, 2001; *Solomon et al.*, 2000]. Thus the comparison of OC collected on a Teflon filter to that collected on a quartz-fiber filter with an efficient denuder should yield a ratio of 1. Negative artifacts are not accounted for by this approach, and it is assumed that loss of OC from particles collected on a Teflon filter is similar to that of a quartz-fiber filter, both either denuded or undenuded. It also is assumed that at zero PM2.5 mass there should be zero OC measured on a filter and greater values would suggest a net positive artifact, while negative values would suggest a negative sampling artifact. Thus examination of the y-intercept provides at least qualitative information on OC artifacts during this study. In the Four City Study, the VAPS was used as the reference and it essentially had a zero intercept. In this study, the intercept of the VAPS is about 2.1 $\mu g/m^3$ and it has nearly the highest OC of the samplers that use an organic denuder. The differences in artifact for the VAPS samplers between the two studies may be due to the collection efficiency of the XAD-4 denuder under different environmental conditions (winter versus summer) or OC concentrations. The net OC artifact, based on the above analysis, is given in Table 7 relative to the OC reported by the VAPS and the PCB(BYU) samplers, the latter which has the lowest OC values in this study. The maximum net artifact observed ranged from about 2–4 $\mu g/m^3$ relative to the VAPS and PCB(BYU) samplers respectively. This is similar to the estimates obtained during the Four City Study [*Tolocka et al.*, 2001; *Solomon et al.*, 2000]. It also is interesting to note that the VAPS has the lowest OC of the samplers that used TOT to determined OC and EC and that the OC artifact for all samplers that used TOR is lower than the VAPS. This might be expected since TOR OC results are typically lower than TOT OC results, while EC results are reverse, thus providing a mass balance for total carbon [*Chow et al.*, 2001; Norris et al., submitted manuscript, 2002]. These results suggest a bias due to the analysis method as well as bias due to the collection methods.

4.1.7. Trace Elements

[67] Ten trace elements were reported in this study, but only for the EPA samplers and EE. The performance

Table 7. Estimate of Net OC Artifact Relative to OC Collected by the VAPS and PCB(BYU) Samplers

Sampler	Slope[a]	Intercept[b]	r	Artifact-VAPS[c]	Artifact-BYU[d]
MET	0.17	3.90	0.60	1.82	3.93
FRM	0.16	3.46	0.72	1.38	3.49
RPS	0.24	3.42	0.74	1.33	3.45
AND	0.19	3.14	0.79	1.05	3.16
URG	0.16	3.13	0.72	1.04	3.16
KB	0.17	2.35	0.67	0.26	2.38
VAPS[e]	**0.14**	**2.09**	**0.86**	**0.00**	2.11
MOUDI	0.15	1.85	0.81	−0.24	1.88
PCB(TVA)	0.12	1.78	0.57	−0.31	1.81
EE	0.15	1.24	0.76	−0.85	1.27
PCB(BYU)[e]	**0.17**	**−0.03**	**0.73**	**−2.11**	**0.00**

[a]Based on regression of FRM mass (x-axis) versus OC reported by the test sampler (y-axis).
[b]The intercept is an estimate of OC artifact, since at zero mass there should be zero OC.
[c]Test sampler minus VAPS.
[d]Test sampler minus PCB(BYU).
[e]Reference samplers. VAPS used in Four City Study; PCB(BYU) appeared to have the smallest potential artifact.

criteria established for trace elements by XRF is a ratio of 1 ± 0.15 and a regression coefficient of ≥0.85. These criteria are likely too lenient for sulfur, which was considered with sulfate earlier, and too stringent for low concentration species, like As and Pb, but reasonable for the rest. Study period averages (Table 4) for elements are within 15% for all elements measured on samples collected by the FRM-A, AND, and RPD samplers and typically within 20% for FRM-B, MET, and URG. Only the RPS and EE samplers exceeded 20% for multiple elements, with RPS reporting values higher than the relative reference value and EE reporting lower values. Minor elements, such as Si, K, Ca, and Fe are all highly correlated with the relative reference and FRM values, except EE (Table 5). In general, correlations are around 0.7 or higher for Zn, Mn, Cu, and Pb, but somewhat lower for As, which is only around 1 to 2 ng/m^3. Daily variability is illustrated in Figure 5g using silicon as an example. Most of the samplers cluster close to the relative reference, although RPS and EE clearly stand out from the rest. Within a given day, variability for most of the samplers for Si is around 100 ng/m^3 or about half the average value on any given day. Other elements show similar variability among the samplers.

[68] Of the ten elements reported, silicon, calcium, and iron are primarily associated with soil dust and particles greater than 2.5 aerodynamic diameters. A small portion of these elements is found in the PM2.5 fraction due to the cutpoint of the samplers not being ideal and because some of the particles are less than 2.5 μm. For these reasons, these species tend to be good indicators of the collection efficiency performance of PM2.5 size fractionators. On average, the reported concentrations for these three species were high on RPS by about 40% and low on EE by about 45%. These results suggest that either the cutpoint or the slope of the collection efficiency curve is different from the other samplers, RPS allowing more coarse particles to penetrate the sampler and EE excluding fine particles close to the cutpoint. The mass values mimic these findings as well. The RPS inlet (size fractionator) has already been replaced with one that has a sharper cutpoint. Other reasons for the low values for EE may include differences due to laboratory bias (e.g., calibration errors) between the two XRF units, as sulfur also was low compared to the relative reference for sulfur (E. Edgerton, ARA, personal communication, 2001) or a lower than expected flow rate for the one module where mass and elements were measured. However, not all trace elements were low. The exclusion of fine particles close to the cutpoint explains both the low mass and low values for Si, Ca, and Fe, but it does not explain the low values for sulfur, which may be due to a calibration error since sulfate reported by EE compared well to the relative reference for sulfate.

4.2. FRM Comparability

[69] While the FRM has been considered in the discussion above, it is important to indicate specifically how the FRM and the EPA speciation samplers compare, since the speciation samplers have been designed to minimize sampling artifacts due to volatilization of semivolatile species, particularly ammonium nitrate. For mass, there was no difference between the FRM, AND, and MET, while the URG and RPS samplers were slightly higher. All samplers operated with Teflon filters but had different designs as indicated in Table 6. The RPS was high as mentioned above due to the poorer than expected collection efficiency performance of the impactor employed. Reasons for the high values reported by the URG sampler in this study and in the Four City Study [*Solomon et al.*, 2000] have not been specifically identified, but it may be due to contamination from the glycerol associated with the Na_2CO_3 coating in the denuder located in front of the collection filter [*Finn et al.*, 2001]. No bias was observed between sulfate reported using the EPA speciation samplers and the FRM; however, the FRM value was low by about a factor of 3 for nitrate. This is expected since the speciation samplers use denuders and reactive filters to collect nitrate, while the FRM collects PM for mass measurements on a Teflon filter without the use of a denuder, and therefore would be impacted by negative artifacts due to volatilization of ammonium nitrate. On the average, OC measured on a quartz-fiber filter collected by the FRM was in the ballpark with the EPA speciation samplers, but it was high relative to samplers using denuders to remove gas-phase organic compounds. Results from this study and the Four City Study suggest that denuders reduce the overall positive sampling artifact for OC; however, nothing can be indicated about negative artifacts and significant questions remain. Elemental carbon results of the FRM to the EPA speciation samplers also were in good agreement as they all used the TOT for determining EC loadings on filters. Elements measured on samples collected by the EPA speciation samplers also agreed well (except RPS as discussed earlier) with the FRM as expected since they all used fractionators with similar collection efficiency performance. Therefore, relative to the EPA speciation samplers, the FRM performs well for stable species and for OC, since the EPA speciation samplers do not use denuders to remove gas-phase organic compounds. Major differences exist between the FRM and EPA speciation samplers for nitrate, since the speciation samplers use denuders and reactive filters to minimize biases in nitrate sampling.

5. Summary and Conclusions

[70] The Atlanta Supersites project provided a unique opportunity for comparison of time-integrated filter-based measurements for PM2.5 mass and its chemical components. Ten collocated samplers operated for periods of 24 hours every other day for the month of August and two additional samplers operated on two 12-hour periods that were averaged to overlap the 24 hour samples. These samples were then analyzed subsequently for mass by gravimetric analysis, sulfate, nitrate, and ammonium ion by chromatography, organic and elemental carbon by one of three thermal or thermal-optical methods, and for minor and trace elements by XRF. Of the samplers tested, four (AND, MET, URG, and RPS) are candidates for use in EPA's National PM2.5 Chemical Speciation Network, which is currently being implemented. Three of the four were evaluated previously in EPA's Four City Study comparing commercially available chemical speciation samplers and results obtained here are compared to that study as well. Several other groups participated in the study to evaluate

their samplers, used currently in research networks, against the EPA samplers and other methods being evaluated during the study (e.g., the continuous species specific methods).

[71] Overall comparability among the samplers for PM2.5 mass was in the range from an overestimate of about a 15% for mass to an underestimate of about 35%. Mass values reported by most of these samplers agreed to within ±20%. Excellent comparability was observed for sulfate among the samplers, with most samplers meeting or exceeding the desired comparability criteria given in Table 1. Overall comparability among the samplers for sulfate and ammonium ranged from an overestimate of less than 10% to an underestimate of about 20%. Sulfate and ammonium values reported by most of these samplers agreed to within ±10%. More variability was observed among the samplers for fine particle nitrate and organic carbon. Most samplers agreed to within about ±30–35% for nitrate; however, ambient nitrate concentrations were low and there likely would be better agreement at higher concentrations. Samplers not using denuders agreed with each other to within about 20%, while ones using denuders also agreed to within about 20%. Overall sampler agreement for OC was about ±35–45% if there is no separation among samplers based on the use of denuders. Elemental carbon agreed poorly among the samplers, with one set biased high by about 28% on average compared to the relative reference and the other biased low by about 41% on average. Within each group variability is about 20%. Differences for EC between the two groups, basically a factor of about 2, are due to the use of different analysis methods and not necessarily due to sampler performance, although variability within each group is due to sampler characteristics. Good agreement was observed among trace elements for most samplers. For the 10 elements reported, most samplers tended to agree to within ±20–30%.

[72] There is no doubt that real differences exist among the samplers for their collection performance for most of the species reported. The most significant differences exist for organic carbon and nitrate, which are semivolatile and the most difficult to collect. Overall, except for EC, differences are likely due to the design of the samplers as illustrated in Figures 3a–3l and Table 6 and include differences in (1) inlet collection efficiency (slope and cutpoint), (2) enhanced volatilization from the Teflon or quartz-fiber filter when located behind a denuder, (3) face velocity effects for OC, (4) whether a denuder and reactive filter is used for semivolatile species, and (5) the need to correct species concentrations for ultrafine particles (less than 0.1–0.15 μm) removed due to the use of the particle concentrator. In the case of EC, most of the difference among all methods is due likely to the use of two similar, but different analytical methods. In source areas, where an ultrafine particles may be important, like Atlanta, discarding this fraction could be significant and correction difficult. Depending on aerosol composition, the differences among the samplers described in this paper may have significant implications for understanding aerosol composition, chemistry, and for determining suitable emissions management strategies.

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