

**QUALITY ASSURANCE FINAL REPORT**

**FOR THE**

**BALTIMORE SUPERSITE PROJECT**

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**Draft**

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## Quality Assurance Final Report

### 1. Introduction

This report summarizes the quality of the measurement data sets and provides a context for interpretation of the data collected during the Baltimore Supersite (BSS). Data quality is evaluated using specific data quality indicators (DQIs) selected by the BSS Quality Assurance Manager and Principal Investigators, and the findings of the technical system and performance audits conducted during the field campaign. Additional information about BSS can be found in the Quality Assurance Program Plan (Ondov., 2002), a publication which provides an overview of the BSS measurements and preliminary scientific findings (Ondov et al., 2006a), and various publications focusing on measurements collected at the BSS Supersite (Ondov et al., 2006b and references therein; see also the Baltimore Supersite Bibliography, section 4.1.2).

In the BSS project, data from all of the instruments operated by the University of Maryland were captured to the site server computer and uploaded to the BSS database machine for storage. The stored data, including all recorded instrument parameters, were then loaded into the BSS SQL relational database for inspection and further processing. After loading, an instrument parameter flagging application was run to flag the data as good, bad, or correctable based on the values of instrument parameters and status codes, according to protocols that had been established. The data are then flagged using an operator log flagging application. This process allowed flagging of data which appeared to be valid based on instrument parameters, but which the operators know to be invalid, e.g., when filters or flow monitoring devices are temporarily placed on inlets for calibration or auditing purposes. As necessary, calibration corrections (i.e., span gas audit corrections and conversion efficiency factors) and recalculations are applied. Some of these arose from faulty or inappropriate algorithms inherent to the manufacturer's software/instrument control system. For example, atmospheric concentrations reported by our R&P instruments (i.e., R&P TEOM, R&P 8400N, R&P 8400S, and R&P 2100 ) are referenced to 25°C, not ambient temperature as prescribed by EPA. Likewise the TEOM PM<sub>2.5</sub> reported data after multiplying by 1.03 and adding 3 µg/m<sup>3</sup>. We elected to implement recalculations, audit and efficiency corrections, and adjustments to ambient temperature by building database applications run by the Data Manger because of the likelihood that some corrections might change once the entire data sets were examined and because implementation of such changes could be centrally managed more easily and rigorously documented in this manner.

Our goal was to produce Level II data as required by EPA for the NARSTO archive. Level II data protocol required that data are checked for "reasonableness" (including mass balance and out-of-range considerations) and comparison with reference methods. Out of range values are flagged by the instrument parameter flagging function. Mass balance checks require comparison with reference methods. In this study, reference methods for PM<sub>2.5</sub> mass and component species (Sulfate, Nitrate, EC, OC) are the 24-hr FRM PM<sub>2.5</sub> and Speciation Monitor data. PAMS (ozone precursor gases) and O<sub>3</sub>, CO, Nox, NO, and NO<sub>2</sub> were provided by MDE using an on-line FRM GC-FID and FRM monitors. Quality assurance data are available through MDE for these measurements and are not reported herein..

### 1. Technical System and Performance Audits

Data quality was assured by performing two types of audits of all instruments and systems used during BSS. A single technical system audit of all sample custody forms, logs and standard operating procedures was performed at the beginning of the study. The intent of this audit was to refine the forms and procedures to be used for the duration of the study. Two performance audits

were also performed during the field campaign to evaluate the performance of the field instruments by external personnel (who were not normally responsible for the instruments) using external standards (which were not normally used to evaluate the instrument performance). Audit findings were immediately communicated to and discussed with the investigators. In one case, the performance audits helped to diagnose an instrument issue before the measurements were compromised. In this particular case, some TEOM measurements were invalidated as a result of performance audit findings. In the majority of cases, the audits confirmed the stable performance of the instruments. Appendix 1 of this report presents the technical system and performance audit findings and the responses of the investigators to issues raised during the audits.

## 2. Data Quality Indicators

The Data Quality Indicators (DQI) used to evaluate the BSS data set include precision, accuracy, minimum detection limits (MDLs) and completeness. When appropriate, measurement comparability was also evaluated. Measurement representativeness was evaluated for the site as a whole.

A list of all the measurements collected during the BSS field campaign and the actual DQI values for a majority of the indicators are presented first in Table 1. Data quality objectives (DQOs), determined when possible for each instrument and system prior to use during BSS, are also listed in Table 1. A brief description of each indicator and the method of calculating the indicator at BSS is presented next. The actual methodology for determining each indicator is stated in the individual SOPs and RPs. In a few instances typically associated with newly developed instruments, the DQI was greater than the DQO. In these cases, the possible explanation for the discrepancy between the DQIs and DQOs is presented as well. In one particular case, i.e, that for the prototype Harvard Sulfate monitor, operational problems encountered are largely irrelevant owing to subsequent development and commercialization of this instrument. Thus, whereas we have published detailed comparisons against reference methods for TEOM, nitrate, ECOC, and SEAS results, a comparison for the prototype sulfate monitor has not been published, elsewhere, and is, instead, included in full detail in this document.

### 2.1 Minimum detection limit (MDL)

Analytical procedures and sampling equipment impose specific constraints on the determination of detection limits. The MDL is defined as a statistically determined value above which the reported concentration can be differentiated from the blank or equivalent instrumental back-ground signal, and was calculated for a majority of measurements using Equation 1.

$$MDL = \frac{S_m - \overline{S_{bk}}}{m} \quad (1)$$

where  $S_m = \overline{S_{bk}} - 2 s_{bk}$

where  $S_m$  is the analytical signal,  $s_{bk}$  is the standard deviation of the blank or background signal, and  $m$  is the slope of the calibration curve. Measurement results below MDLs of the instrument were reported as measured and to the level of precision of the instrument, but flagged accordingly. For continuous monitors, the MDL accounts for all sampling and analytical procedures and therefore

represents a detection limit that can be applied to ambient concentrations. All gas monitors were operated by MDE using Federal Reference Methods. MDLs for filter-based measurements were determined from field and laboratory blank tests. At BSS, approximately 10% of all substrates (filters) handled were field or laboratory blanks. The field blank was a substrate that underwent all the preparation, transportation, storage, and analysis activities as and with the sample substrate. A laboratory blank was a substrate that underwent the preparation and analysis activities as and with the sample substrate.

## 2.2 Precision and Accuracy

**2.2.1 Precision.** Precision is a measure of the repeatability of results or of the agreement among individual measurements of the same parameter under the same prescribed conditions. The number of replicate analyses needed to properly assess the precision of each instrument was independently determined by each BSS investigator.

Precision of analytical instruments was evaluated by repeated analysis of independent traceable standards that were separate from the standards used for instrument calibration. Precision of continuous gas monitors was evaluated using purified air. Precision of semi-continuous aerosol instruments was evaluated, when possible, by using artificially generated analytes. When possible, precision of filter-based methods was assessed by running collocated samplers. For each series of replicate analyses, the precision was calculated using Equation 2, where  $s$  is the standard deviation,  $\sigma$ , between the replicate analyses and  $\bar{x}$  is the mean of the replicate analyses.

$$\sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (2)$$

**2.2.2. Accuracy.** Accuracy (bias) is the closeness of a measurement to a reference value, and reflects the systematic distortion of a measurement process. To the extent possible, accuracy was determined from replicate analyses of authentic, traceable standards that were not used in the calibration of the instrument. For each instrument tested, multiple challenge data points were collected. The accuracy of the instrument was determined by:

$$bias = \bar{x} - S_i$$

where  $\bar{x}$  is the population mean of replicate measures of the determined quantity and  $S_i$  the standard value of the authentic traceable standard for measured parameter  $i$ .

**Table 1.** Observable Resolution, Frequency, Period of Operation, Data Quality Objectives (DQO) and Indicators (DQI) at the BSS Supersite.

Observable	Method <sup>1</sup>	Group <sup>2</sup>	Resolution	Frequency	Period of Operation	MDL <sup>4</sup> DQI and (DQO)	Precision <sup>4</sup> DQI and (DQO)	Accuracy <sup>4</sup> DQI and (DQO)	Completeness <sup>4</sup> DQI and (DQO)
<i>Aerosol mass</i>									
PM <sub>10</sub> mass	STN sampler/Gravimetry (Met One SASS)	JHU/MDE	24 hr	3 <sup>rd</sup> day Daily	2/15/02 – 11/30/02 7/1 – 8/15/02; 11/1-30/02	7.2 µg/m <sup>3</sup> (2 µg/m <sup>3</sup> )	- (10%)	- (10%)	97% (70%)
PM <sub>2.5</sub> mass	FRM sampler/Gravimetry	JHU/MDE	24 hr	3 <sup>rd</sup> day Daily	2/15/02 – 11/30/02 7/1 – 8/15/02; 11/1-30/02	2.0 µg/m <sup>3</sup> (2 µg/m <sup>3</sup> )	- (10%)	infinite (infinite %)	>90% (70%)
PM <sub>2.5</sub> mass	R&P 1400a TEOM with SES	UMCP	30 min	Continuous	5/20/01-6/14/01; 7/1/01-6/14/01; 3/21/02-12/15/02	0.25 µg/m <sup>3</sup> (1 µg/m <sup>3</sup> )	4% (10%)	3.1% (10%)	<50%(70%) 63% (70%) 96%(70%)
<i>Aerosol size distribution</i>									
Number, surface area, and volume distribution	TSI SMPS 3081/3010	UMCP	5 min	Continuous	5/18/01-6/14/2001 6/15/2001-9/14.2001 2/09/02-11/30/2002	3 cm <sup>-3</sup> Δlog dp <sup>-1</sup>	30% (30%)	20% size 30% count (N/A)	86% (70%) 90% (70%) 99% (70%)
Number, surface area, and volume distribution	TSI APS 3321	UMCP	5 min	Continuous	5/21/01-6/14/01 6/15/01-9/14/01 2/09/02-1/30/02	<b>N/A</b>	30% (30%)	10% size 30% count (N/A)	<b>96% (70%)</b> 95% (70%) 98% (70%)
<i>Aerosol Characteristics</i>									
Light scattering	RS M903 nephelometer	CU	5 min	Continuous	5/16/01-6/15/01 5/18/02-11/30/02	N/A	-	0.001 km <sup>-1</sup>	91% (70%) 87% (70%)
Vertical profile	JHU 2000 LIDAR	JHU	5-30 min	Daylight hours	2001:5/22-25,2,28. 6/5-14, 7/3.4, 8/14-16 2002: 7/15-18,20-23,27-29, 8/2-14, 9/5	300 m	100 m	<b>T/D</b>	995%
Cytokines	SEAS/Eliza: TNF-a, IL-6, IL-8, MCP-1	UMAB	30-min	Continuous Selected samples	7/16-19/02; 11/19-29/02	8.9-28 pg/m <sup>3</sup>	4.2-9.0 (15%)	<b>2-10% (20%)</b>	100% (70%)

Observable	Method <sup>1</sup>	Group <sup>2</sup>	Resolution	Frequency	Period of Operation <sup>3</sup>	MDL <sup>4</sup> DQI and (DQO)	Precision <sup>4</sup> DQI and (DQO)	Accuracy <sup>4</sup> DQI and (DQO)	Completeness <sup>4,6</sup> DQI and (DQO)
<i>Aerosol chemical composition</i>									
PM <sub>2.5</sub> inorganic ions	STN sampler/ IC	JHU/MDE	24 hr	Daily	5/19/01-6/15/01	0.08 nitrate, 0.12 sulfate (µg/m <sup>3</sup> )	- (20%)	- (20%)	100% (70%)
PM <sub>2.5</sub> nitrate	R&P 8400N	UMCP	10 min	continuous	6/27/01-9/14/01-11/30/02	0.24 µg/m <sup>3</sup>	8.7% (20%)	9.1% (20%)	61% (70%)
PM <sub>2.5</sub> sulfate	Prototype Harvard R&P 8400NS	UMCP	30 min	continuous	2/10/02-12/10/02	0.4-1.1 µg/m <sup>3</sup>	7% (20%)	10% (20%)	93% (70%)
		UMCP	10 min	continuous	2/14/02-11/30/02 7/2/01-9/15/01	1.0 µg/m <sup>3</sup>	- (20%)	-, (20%)	61% (70%)
PM <sub>2.5</sub> elements	Speciation Sampler/XRF	JHU/MDE	24 hr	Daily, or 1 in 3	2/8-11/30/2002	(10-200 ng/m <sup>3</sup> )	- (20%)	- (20%)	0-3% <sup>5</sup> (70%) Fe, Zn (99, 34%)
PM <sub>2.1</sub> elements	UMD SEAS/GFAA	UMCP	30 min	Continuous	6/5-1-/01; 8/27-29/01 9/6-10/01; 7/6-9, 17-21/02; 11/19-22, 24-26/02	0.02-7.1 ng/m <sup>3</sup>	variable (20%)	variable (20%)	80% (70%)
PM <sub>0-10</sub> elements	UCD DRUM-SXRF	UCD	3 hr	Mutli-day	4/1-12/02; 8/14-10/28/02	(T/D)	(20%)	(T/D)	T/D (70%)
PM <sub>2.5</sub> organic/elemental carbon	STN Sampler/TOT	JHU/MDE	24 hr	Daily, 1 in 3	2/15/02 – 11/30/02 7/1 – 8/15/02; 11/1-30/02	0.17-0.53 µgC/m <sup>3</sup> (0.5 µgC/m <sup>3</sup> )	8% (20%)	2.3-5.7% (20%)	99% (70%)
PM <sub>2.5</sub> organic/elemental carbon	Sunset Labs ECOC	UMCP	1- hr	24 per day	2/14/02-11/30/02	0.4 µg total C/m <sup>3</sup> (0.5 µgC/m <sup>3</sup> )	8% (20%) EC 4% (15%) OC	<11.5% EC (20%) <22 % OC (20%)	85% (70%)
PM organic/eemental carbon	R&P 5400	UMCP	1-hr	24 per day	8/1/02-9/14/02	0.52 µg total C/m <sup>3</sup> (0.5 µgC/m <sup>3</sup> )	5% Total C (20%)	23-40% bias TC ((20%)	90% (70%)
PM <sub>2.5</sub> speciated organic compounds	Organic sampler/GC-MS	FIU	3 hr	Daily	7/17-22, 24; 8/4-12; 11/7-9,14-16,19-22,24-25/02; 2/20,21,23,24/03	-(T/D)	-(T/D)	-(T/D)	-(T/D)
<i>Single Particle Chemical Composition</i>									
Ion composition	RSMS-III	UCD,UD	10 min	Continuous	3/20/02-12/1/02	-(T/D)	-(T/D)	- (T/D)	99% (50%)

Observable	Method <sup>1</sup>	Group <sup>2</sup>	Resolution	Frequency	Period of Operation <sup>3</sup>	MDL <sup>4</sup> DQI and (DQO)	Precision <sup>4</sup> DQI and (DQO)	Accuracy <sup>4</sup> DQI and (DQO)	Completeness <sup>4,6</sup> DQI and (DQO)
<i>Meteorology</i>									
Wind speed	RM Young 3001	JHU	1 sec	Continuous	All	0.2 m/s (0.5 m/s)	-	0.5 m/s (10%)	98% (90%)
Wind direction	Met One 024A	JHU	1 sec	Continuous		N/A	3°, (3°)	1.5° (5°)	98% (90%)
Temperature	Vaisala HMP45AC	JHU	1 sec	Continuous		240 K	0.5° (10%)	0.3 K (10%)	98% (90%)
Relative Humidity	Vaisala HMP45C	JHU	1 sec	Continuous		0%	- (10%)	2% (10%)	98% (90%)
Pressure	Vaisala PTB101B	JHU	5 min	Continuous		600 mbar	- (10%)	- (10%)	98% (90%)
Precipitation	Davis 7842 Tipping bucket	JHU	5 min	Continuous		0.2 mm	- , (10%)	2% (10%)	99.7% (90%)
	Campbel Sci. TE25	JHU	5 min	Continuous		0.1 mm	- , (10%)	1% (10%)	- (90%)
u,v,w	3-D Sonic anemometer (CSAT3)	JHU	10 Hz	Continuous	see text	N/A	- , (10%)	0.04 m/s (10%)	99.3%, (90%)
Solar Radiation	Eppley Pyranometer PSP	JHU	1 sec	Continuous	All	N/A	- , (4%)	- , (4%)	98% (90%)

1. Methods – CSAT3: Campbell Scientific 3-D sonic anemometer; FRM: Federal Reference Method; FTIR: Grav: Gravimetry; IC: Ion Chromatography; ICVC: Integrated Collection and Vaporization Cell; DRUM Impactor; GC-FID: Gas Chromatography with Flame Ionization Spectroscopy; GC-MS: Gas Chromatography with Mass Spectroscopy; GFAA: Graphite Furnace with Atomic Absorption; RS: Radiance Research; R&P: Rupprecht and Patashnick, Co.; RSMS: Rapid Single particle Mass Spectrometer; SEAS: Semi-continuous Environmental Aerosol Sampler; SL: Sunset Labs; SMPS: Scanning Mobility Particle Sizer; STN: Speciation Trends Network; TEOM with SES: Tapered Element Oscillating Microbalance with a Sample Equilibration System; TOC: Total Organic Carbon; TOT: Thermal Optical Transmittance; UCD: University of California at Davis.
2. Groups – FIU: Florida International University; JHU: Johns-Hopkins University; MDE: Maryland Department of Environment; UCD: University of California, Davis; UD: University of Delaware; UMCP: University of Maryland, College Park; UMAB: University of Maryland, Baltimore.
3. Period of operation – Met instruments were operated during all measurement periods, except as specified in the text.
4. Data quality indicators and (Data quality objectives); N/A: Not applicable; T/D: To be determined.
5. Percentage of all elements reported in all samples.
6. See text for additional details.
7. SEAS statistics are those for samples selected for analysis.

### 2.2.3 Completeness

Completeness of a measurement data set indicates the percentage of the scheduled sample collections or measurements that resulted in ambient observations that were valid and met the data quality objectives established in the QAPP. Completeness was calculated using Equation 4, where N represents the number of measurements.

$$\text{Completeness (\%)} = (\text{N valid measurements} / \text{total N measurements}) \cdot 100 \quad (4)$$

### 2.2.4 Operational Experience and Figures of Merit for Individual Instruments.

FRM and STN measurements. The detection limit of the FRM (40CFR50 Appendix L) is estimated to be  $2 \mu\text{g}/\text{m}^3$ , based on mass changes in field blanks in conjunction with the  $24 \text{ m}^3$  nominal total air sample volume specified for the 24 hr sample. Average detection limits for STN PM<sub>2.5</sub> major constituents are as follows (Presnell et al., 2005): ( $7.2 \mu\text{g}/\text{m}^3$ ), nitrate ( $0.084 \mu\text{g}/\text{m}^3$ ), sulfate ( $0.12 \mu\text{g}/\text{m}^3$ ), total carbon ( $2.353 \mu\text{g}/\text{m}^3$ ), EC ( $2.353 \mu\text{g}/\text{m}^3$ ), OC ( $2.353 \mu\text{g}/\text{m}^3$ ). Average detection limits for STN-XRF elements (Presnell et al., 2005), in  $\text{ng}/\text{m}^3$ , are as follows: Al (195), As (23) Cd (109), Cr (19.8), Cu (22), Fe (22.8), Pb (49), Mn (21), Ni (16.5), Se (27.8), Zn (22.6).

**TEOM.** The Ponca St. TEOM was operated with an inlet filter installed for several days to evaluate the level of instrument noise. Because of rain, we were unable to obtain valid data before having to return the TEOM to MDE. A frequency distribution analysis of negative TEOM 30-min concentration values suggest that values  $< -0.3$  may be considered to be outside the normal instrument noise. The negative data were flagged accordingly. FMC TEOM data required ambient temperature correction and correction for PM<sub>10</sub> transformation that was automatically applied by the manufacturer's algorithm.

We corrected the data to undo the manufacturer's algorithm, which transformed all data to what we understand is an estimate of the PM<sub>10</sub> concentration and we corrected the instrument start times for various periods due to errors in the manufacturer's software and clock drift problems. All data were temperature and pressure corrected to reflect ambient outdoor conditions at the time of measurement. The TEOM PM<sub>2.5</sub> have been compared with speciation sampler PM<sub>2.5</sub> data, which they well agree.

**Accuracy** of the TEOM was evaluated relative to integral 24-hour FRM and STN PM<sub>2.5</sub> mass determinations available from March 27<sup>th</sup> - May 23<sup>rd</sup> and July 4<sup>th</sup> and November 30<sup>th</sup>, 2002 (Park et al., 2006). Relative to the FRM PM<sub>2.5</sub> monitor, the slope and intercept of the correlation curve was  $1.03 \pm 0.042$  and  $0.31 \pm 0.80 \mu\text{g}/\text{m}^3$ , respectively, indicating an average bias of +3% (i.e., TEOM measurements were 3% greater than FRM values); and average **precision** of 4% (expressed as one standard deviation of the calibration slope). Based on frequency change for The **detection limit** is reported to be  $0.25 \mu\text{g}/\text{m}^3$ , based on the instrument sensitivity factor and detectable frequency change over 30 minutes.

**Completeness:** 96% of attempted measurements were successfully acquired and determined valid at Ponca St., i.e., substantially more than the target value of 70%. Condensation problems plagued TEOM measurements at FMC, where only about 50% of the measurements sought were valid. These problems were solved by the time measurements (using MDE's TEOM) were initiated at Clifton Park, but data acquisition was interrupted owing to a lightning strike, resulting in a valid data acquisition 63%, i.e., slightly less than the anticipate frequency of 70%.

**TSI SMPS and APS.** **Detection limits** of the SMPS as reported by the manufacturer is 3 particles

$\text{cm}^{-3} (\text{d log dp})^{-1}$ . Precision and accuracy figures reported in Table 1 are those derived from extensive study by (Steiner et al., ) for essentially identical instruments. These are as follows: Precision and accuracy by count: both 30% for both instruments: by size, 20 and 10%, respectively, for the SMPS and APS. The SMPS required more maintenance than expected owing to abrasion of the inlet impactor orifice, which had to be replaced on three occasions during the study, nevertheless, 86% and 90% completeness was achieved at FMC and Clifton Park, respectively, and >95% at Ponca St. The Level II validations included comparison of APS and SMPS data to determine if the counts match appropriately in the 0.4/0.5  $\mu\text{m}$  region of the spectra where both instruments report data. Additionally, integrated PM<sub>2.5</sub> particle volume distributions were computed and compared with TEOM mass distributions to determine if the inferred particle density (generally this should be about 1.9 gm/cc for accumulation aerosol up to about 0.5  $\mu\text{m}$ ; as low as 1 g/cc for droplet modes near 0.8  $\mu\text{m}$ , and near 2.5 for coarse mode particles).

**Nephelometer (RS M903).** Neither the **detection limit** nor **precision** are available for this instrument. However Accuracy as reported by the manufacturer was 0.001 km<sup>-1</sup>. The nephelometer was available and operated at FMC and Ponca St. Completeness was 87 and 91% , respectively. On 24<sup>th</sup> February, 2002, a routine check revealed a very low flow rate through the nephelometers. As a result the data for this period were flagged accordingly.

**LIDAR.** Lidar data was used to determine the Atmospheric Boundary Layer height and provide graphic images of relative particle concentration as a function of altitude, directly over the Baltimore Supersites (FMC, Clifton Park, Ponca St.). **Completeness:** The LIDAR was successfully operated on 16 days at FMC (May 22-25, 27,28; June 5-14<sup>th</sup>, 2001); 5 days (July 3-4; August 14-16, 2001) at Clifton Park; and 25 days (July 15-18,20-23, 27-29; August 2-14; and September 5, 2002) at Ponca St., for a total of 46 days of operation. This represents a **completeness** of 85% of the planned 52 weekly measurements for this instrument. LASER power supply failures plagued early deployment of the JHU 3-color LIDAR. After deployment at FMC, the JHU LIDAR system was relocated to the Clifton Park site on June 30<sup>th</sup> and operated there on the 3<sup>rd</sup> and 4<sup>th</sup> of June, after which, technical difficulties prevented continuation of its operation. The power supply failed and had to be sent to the manufacturer for repair. Data collection was resumed with a fully functional system on August 14 2001 and operated until August 16, 2001. Both Lasers broke on September 13, 2001, and the Lidar was non operational for the weekly sampling. The lasers were sent to BigSkyLaser for Repair and were returned in December, 2001. However, sampling could not be restarted in December due to low temperatures because the electronics malfunction for temperatures lower than 5° C. Subsequently, the instrument was replaced with a single-wavelength, non eye-safe. The **minimum altitude** at which LIDAR signals could be detected was 300 m and the resolution (figure of **precision**) was 100 m. **Accuracy** has not been established for this instrument. Use of the non-eye-safe LIDAR required manual operation with a spotter and the instrument could not be operated in rain, snow, or heavy fog. As a result far fewer measurements were attempted than had been planned. All Lidar and meteorological data from all three BSS sites (FMC, Clifton, and Ponca St.) were processed and quality assured. Lidar images have been combined to produce a single image for each day that the Lidar was operated, each with consistent scaling.

**CYTOKINE ASSAYS:** In vitro test procedures for measuring the bioactivity of SEAS samples included cytotoxicity (measured by alamar blue reduction), endotoxin concentration, and alterations

in cytokine release (MCP-1 and IL-8 for A549 cell assays and TNF $\alpha$  and IL-6 for RAW264.7 cell assays). Limits of detection range from 8.9 to 28 pg. Completeness: 100% of the target number of 276 assays were successfully completed on SEAS samples collected at the three Baltimore Supersite sampling locations. Additional studies were conducted using standard PM samples (NIST 1648 and NIST interim PM2.5), lipopolysaccharide (LPS) and one metal ion, zinc (Zn) to support interpretation of the results. Accuracy and precision figures (Table 1 and below) are those provided by the manufacturer of the ELISA assay kits. A coefficient of variation of <10% is adequate for the intended use of the data.

	Accuracy (based on recovery)	Precision	(CV%)
TNF $\alpha$	$\pm$ 98%	62.2 $\pm$ 5.6 pg/ml	9.0
IL-6	$\pm$ 110%	30.0 $\pm$ 2.0 pg/ml	7.0
MCP-1	$\pm$ 96%	78.2 $\pm$ 3.3 pg/ml	4.2
IL-8	$\pm$ 98%	115 $\pm$ 5.3 pg/ml	4.6

**RSMSIII.** Over the aerodynamic particle range (45-1250 nm), the fraction of particles entering the mass spectrometer inlet that were subsequently analyzed decreases with size, ranging from  $1 \times 10^{-4}$  at 770 nm to  $4 \times 10^{-6}$  at 45 nm. For RSMSIII, the most applicable "**detection limit**" is defined as the number concentration frequency required to obtain a representative sample in a reasonable amount of time, i.e.,  $\sim 10^4$  particles/cc (dN/dlogdp). **Precision and accuracy** figures of merit are not applicable because RSMS III is not a quantitative instrument. However, our expectation from previous laboratory studies is that the uncertainty in particle classification is less than 10% of the total. This is, if 100 particles were assigned to a class, then less than 10% were "incorrectly" assigned. For most classes, the incorrect classification rate is likely to be much smaller. We regard a classification error of <10% to be adequate to provide useful results. This contention is supported by successful development of nitrate and sulfate concentrations using RSMSIII and SMPS/APS data as described by Lake et al, 2004; and Tolocka et al.(2004a). Less than 1% of the of 381,000 particles analyzed were "invalid" meaning that in the end they could not be processed. Many others (5-10%?) were flagged initially (e.g. for mass calibration problems, etc.) but they were corrected and validated one by one. RSMS obtained data for 75% of the possible time periods (i.e. 2-hour intervals) between March and December 2002. We regard this as highly successful for a research grade instrument of this type. Our initial objective was at least 50%; however, our evaluation of the Baltimore Supersite deployment suggests that we can routinely achieve 70% **completeness**.

**Meteorological Instruments.** Meteorological data were sampled continuously during the entire time period. Meteorological data acquisition was halted on 2/28/2003 at midnight, coinciding with the official end of the BSS experiment. However, sporadic data is available after that date. Plots of 5 minute averages are available online at <http://www.jhu.edu/~dogee/mbp/supersite2001/>. Missing data periods are as follows: Rain gauge: 1/29/2003 19:20 – 1/30/2003 23:30; Sonic anemometer: 1/29/2003 19:20 – 1/30/2003 05:20. Variables affected during these periods were rain and derived parameters as follows: Velocities u,v,w [m/s], potential temperature [ $^{\circ}$  C] @ 20 Hz; friction velocity  $u_*$  [m/s], Monin Obukhov Length L [m], sensible heat flux H [W/m $^2$ ]. With respect to data quality all sensors operated within errors specified by the manufacturer (Table 1). Data completeness was typically 98% for all met instruments except for the 3-D sonic anemometer (3-DSA), for which completeness was only 51% between April 15<sup>th</sup> and July 15<sup>th</sup> 2002, largely because the instrument was unavailable for use from June 4<sup>th</sup> to August 4<sup>th</sup>, 2002. Minor amounts of 3-DSA data were lost

due to power failure, storm, or operational errors. Solar radiation, mean wind speeds, temperature and humidity showed the expected diurnal variations. Moreover, turbulence parameters such as atmospheric stability and friction velocity are computed and show the expected elevated turbulence levels at daytime. The turbulence sensor (3d sonic anemometer) does not collect data when its emitting or receiving surfaces are wet. Precipitation in the form of snow cannot be measured by the rain gage. Meteorological summaries and descriptions were prepared for periods when PM or its constituents showed interesting or significant excursions. To assure high data quality, the cup anemometers were calibrated on 6/5/2002 in the JHU wind tunnel. The sonic anemometer as well as the vaisala temperature humidity probe was calibrated in June by the manufacturer.

**ECOC.** ECOC was determined at Clifton Park with the R&P5400. 90% of attempted measurements were achieved, however, EC/OC discriminations are deemed unreliable and only total aerosol particle carbon is reported. Instrument detection limit was estimated to be  $0.52 \text{ ug/m}^3$ , determined as twice the standard deviation of 60 blank measurements reported for the NewYork Supersite (Ventachari et al., 2006). Precision has been evaluated from measurements with two, co-located R&P5400 instruments (<http://www.rpco.com/products/ambprod/amb5400/54tuxy.gi>) and is shown to be ~5%. Bias (**accuracy**) of total carbon measurements as estimated by comparison with STN filter-based measurements was  $-23 \pm 58\%$  (Ventachari et al., 2006) in New York City, and  $-40\%$  in Chicago (Homolya et al., undated web document). In New York, where extensive comparisons with STN filter determinations were made, concluded that the methods are simply not comparable. Correlation is good in some instances but extremely poor in other instances. We believe that measurements at Ponca St. were subject to a minimum bias of ~20% owing to the high sampling cutpoint ( $\sim 0.15 \text{ }\mu\text{m}$ ) and relatively high (50 C) sampling temperature. At Clifton Park there were too few STN measurements made to allow meaningful comparison of the two methods. For all of these reasons, no corrections were applied to R&P ECOC data and we declined to publish them.

The then-new Sunset Labs ECOC instrument was deployed at Ponca St. Measured concentration values were based on a final definitive calibration constant ( $13.6 \text{ ug C/ unit of integral area}$ ) from Sunset labs. Reanalysis of 300 raw ECOC data sets required reanalysis due to instrument problems. Data capture efficiency for the Sunset Labs instrument was 93.8% at Ponca st.; 85.3% of 5556 measurements were flagged as valid. Samples were flagged invalid because of filter replacement, maintenance, filter blow-outs during sampling, and power failure. Thermally and optically derived EC agreed well (slope=0.98 and  $R^2=0.95$ ) during our 9.5-month study period at Ponca St., though the optically derived EC measurements contained more structure at low concentrations, indicating a lower measurement error by this method. Thermal OC blank for the instrument was estimated to be  $\sim 0.5\text{-}1.0 \text{ }\mu\text{g C m}^{-3}$ . The **detection limit** for total carbon (TC, defined as 3 standard deviations of blank values) was  $\sim 0.40 \text{ }\mu\text{g total C m}^{-3}$  for the 1-h operation cycle. As a measure of **accuracy**, Sunset EC and OC data by our protocol were typically 11.5% and 22% < 24-h RTI EC and OC data, respectively (Park et al., 2005b). This is largely the result of differences in operational protocols, required to permit 1-hr time resolution. Measurement **precision** is estimated to be ~8% for EC and 4% for OC.

**SEAS (Pancras et al., 2005, 2006).** **Completeness:** 15,450 30-min samples were collected at the 3 Baltimore supersite monitoring locations for elemental analyses and 12,930 samples were co-collected for cytokine assays. Additionally, 2,657 were collected in Pittsburgh, 14,400 in St. Louis,

and 2,200 in Tampa (Pancras et al., 2550, 2006a,b). Frequency of sampling success was >90 % (Pancras et al., 2006). A total numbers of samples analyzed were: 1,904 (Ponca St.), 292 (Clifton Park), and 227 (FMC). Of these,  $\geq 93\%$  of all measured concentrations of all elements were flagged valid, above the detection limit and had uncertainties (precision)  $\leq 50\%$ . Uncertainties were within target DQOs for 30 minute measurements of 20% in at least 70% of the samples on which analyses were performed except as follows: Cd, 42%; Ni 52%; As and Se, 66%. However, such incidences generally correspond to background levels, i.e., in the absence of plumes from major sources. And, this compares favorably to the overall performance of the STN-XRF measurement detection rate of only 30%.

**Blank evaluation and detection limits.** Laboratory tests were made to assess SEAS system “blank” levels for elements determined by GFAAZ. A High Efficiency Particulate (HEPA) filter capsule was connected at the inlet of SEASII for system-blank sampling. As the system became free of particles, volume of blank sample was negligibly small at the target RH at which SEAS is operated. Therefore, homogenous nucleation of water droplets was forced in SEAS II by raising target RH value. Above a certain saturation ratio ( $>3.0$ ), the system-blank volume was considerable, ranging between 2 and 6 ml, but with less control on sample production rate. The ultimate use of this system blank data was initially not realized, as the excess volume needed to be accounted for in the concentration calculations.

Analysis of >100 field system-blank samples from all sites revealed that elements such as As, Se, Cd, and Pb, were mostly at or below the instrument detection limits of the analytical platform (GFAASZ) employed for the metals determination in the slurry sample. It is known that these metals are predominately found in ultrafine particles, and therefore readily solubilized in the nucleation stage itself and transported efficiently to the collection assembly. However, concentrations of Ni, Al, Fe, Zn and Cr in field blanks were significant, ranging 2-20 times of laboratory system-blanks. The field system-blank concentrations of these metals decreased gradually as the number of successive blanks increased. This observation suggested that a small fraction of water-insoluble particles, presumably silicates, got retained in the VI and drain solenoid valve paths of SEAS II. Over a period of continuous operation, the accumulated particles at the drain valve resulted this 1mm-id valve fail. Blanks performed immediately after the replacement with new valves had concentrations similar to laboratory system blanks. It was concluded that when a HEPA filter capsule was connected for field blanks, steam condensing on the inlet impactor contaminated the system. Thus, the field system-blank samples collected in all sites are, therefore, not useful in defining detection limits. Instead, they are simply a product of system cleaning. As a result, ambient concentrations of elements determined by SEAS II were corrected using carefully controlled laboratory blanks determined on the SEAS II. The solenoid valves in SEAS II are now replaced with large-bore ball valves.

The **detection limit** of metals by SEAS II was calculated from the laboratory system-blanks produced by Target RH method. Four successive samples were collected, weighed separately, and then combined as a single sample and analyzed. Minimum detection limits (in  $\text{ng}/\text{m}^3$ ) obtainable by SEAS II are as follows: Al, 1.9, As 0.004, Cd, 0.015; Cr, 0.019; Cu, 0.53; Fe, 0.24; Mn, 0.07; Ni, 0.084; Pb, 0.15; Se, 0.002; and Zn, 3.6. Variability in the MDLs arises mainly from sample collection volume. **Precision** is highly variable and, depending on the signal strength relative to the detection limit, ranges from 50% at the detection limit to 5 to 7% at slurry concentrations in the 10's of ppb range. **Accuracy** of GFAAZ relative to NIST certified values of SRUM 1640 and the contemporary urban PM interim NIST reference material was excellent as were comparisons of total acid digestion vs. direct slurry analysis by GFAAZ (Pancras et al., 2005).

A **comparison** of SEAS-GFAAZ with STN-filter-XR results are shown in Figure 6, wherein “error bars” represent analysis precision, expressed as one standard deviation ( $\sigma$ ) derived from propagated uncertainties (SEAS-GFAAZ) or as propagated from counting statistics and measurement uncertainties (XRF). As shown, good precision was obtained by both methods for Al, Fe, Cr, and Zn in at least one of the samples; however, uncertainties in the XRF measurements were typically larger than those derived for GFAAZ. This is especially true for Cd, which was not routinely detected by XRF. For all but Al and Fe, concentrations measured by the two methods were well within  $2\sigma$ . Concentrations of Al, Fe, and Cr, which are often associated with supermicrometer dust particles, are generally lower as determined by SEAS-GFAAZ. This is due in part to the larger cut-off size of the R&P inlet (2.5 vs 1.25  $\mu\text{m}$ ) and the fact that insoluble dust particles are inefficiently transferred to the collection vials in SEAS-II (Ondov et al 2005). Generally, efficiency is high when Al and Fe concentrations are not dominated by dust. This typically occurred when dust particle (i.e., particles larger than 1  $\mu\text{m}$ ) were elevated (as evidenced by simultaneous measurements made with an Aerodynamic Particle Sizer (TSI)). This problem was traced to retention in a Teflon solenoid valve between the virtual impactor and impinger which is used to purge the sample to the fraction collector using compressed air. This valve has since been replaced with a Teflon ball valve in which the aerosol makes far less contact with the inside walls of the valve. These comparisons are limited because the STN-XRF detection limits were uniformly greater (i.e., poorer) than SEAS-GFAAZ, which resulted in 70% non-detects in 24-hr STN samples collected at the Baltimore Supersite.

**SEQUENTIAL ORGANIC SAMPLER DATA:** For the summer intensive sampling period of 2002, a total of 139 filter/PUF samples were extracted and their extracts (278 separate filter and PUF extracts) processed on the GC/MS. In total, more than 500 mass spectrometric chromatograms have been generated, not counting standard GC/MS runs. For the November intensive, a total of 136 filter and PUF pairs were extracted, including 17 field and transport blanks. 25 samples were collected in February 2003, when we conducted a mini-intensive to obtain true Winter data.

**R&P 8400N NITRATE MONITOR (see Harrison et al., 2004):** Nitrate content of airborne particles were measured at 10-min intervals at the Baltimore Supersite, Ponca St. location in east Baltimore from February 14 through November 30, 2002, using the R&P 8400N semicontinuous nitrate monitor to determine its contribution to fine-particle aerosol mass concentrations. Comparison with 24-hr filter based nitrate measurements made concurrently using the U.S. Environmental Protection Agency’s Speciation monitoring and analysis protocol, revealed a discrepancy of 33% between the 24-hr averages derived from the two methods for most of the 9.5 month study period after all corrections, including conversion efficiency measured with pipetted  $\text{KNO}_3$  standards, span-gas audit results, and Reaction Cell Pressure deviations. This result suggests that the 8400N conversion efficiency for nitrate in Baltimore was 68%. The uncertainties (**precision**) in individual 10-min measurements, estimated from measured parameters, averaged 8.7% and ranged from 6.3 to 23%, excluding uncertainty encompassing dissociation losses. Uncertainties in 24-hr averages of the 10-min measurements were generally larger (median of 9.1%) owing to added uncertainty associated with missing/invalid values. The **detection limit** for 24-hr averaged concentrations, (defined as the value where the measured concentration is twice its uncertainty) was typically 0.17  $\mu\text{g}/\text{m}^3$  during the study. The value for the 10-min measurements was typically 0.24  $\mu\text{g}/\text{m}^3$  (also after slope correction to achieve agreement with 24-hr speciation measurements). Regression slopes were statistically equivalent for all months except February and October (an

outlier not understood) averaged 1.33 and intercepts were generally small and insignificant. Good agreement between the 24-hr data sets was achieved after the mean regression slope were applied to the 10-minute data, for these months. In February, when flat flash strips were used and instrument compartment (Tcomp) - outdoor ambient temperature differences were often severe, i.e., conditions favoring loss of ammonium nitrate by dissociation equilibrium, the regression slope was statistically larger than the average for the remaining months, and unlike that for the other months, the intercept was positive and significant. A nonlinear least squares model incorporating terms to account for dissociation losses was used to investigate the potential error in 10-minute nitrate measurements at Ponca St. in an effort to determine the level of confidence in which short-term excursions in nitrate concentrations may be reliably identified. Results suggest that the largest errors in measured nitrate concentrations resulting from dissociation losses occur when concentrations are near the detection limit, instrument-outdoor temperature differences were large, and ambient RH low (<40%), i.e., conditions which most frequently and severely occurred in February and March. In February, dissociation losses as large as  $1.65 \mu\text{g}/\text{m}^3$  (100 % of the slope-corrected measured value) may have occurred and such losses were predicted to be >30% in 63.5% of the 10-min measurements for that month. However, model predictions for the other months, when new ridged-flash strips were used, suggest that dissociation losses were much less significant with values at most being 57% of the slope-corrected measurement and <15% in 72% of the 10-min measurement (87% were <30%). For the other months, predicted losses were <15% for >95% of the measurements. Our experience suggests that the semicontinuous monitor can produce reliable 10-minute concentrations when instrument-outdoor differences are kept small, an independent measurement is used to correct the data, and are improved when grooved flash strips are used.

**PROTOTYPE HARVARD SULFATE MONITOR (Park et al., 2006a; Ondov et al., BSS 15<sup>th</sup> quarterly Progress report):** The semi-continuous Harvard Sulfate monitor was used for all sulfate measurements made at the Ponca St. site.

**Principle of operation.** The basic principle of operation is that sulfate is reduced to  $\text{SO}_2$  in the presence of stainless steel at elevated temperature, and the eluent is detected with a commercial  $\text{SO}_2$  analyzer. In the prototype instrument, air is aspirated by a pump located in the analyzer at approximately  $0.55 \text{ L min}^{-1}$ , first passing through a  $2.5 \mu\text{m}$  cut. The air stream is then denuded of ambient  $\text{SO}_2$  (an interference) *via* a sodium carbonate coated annular glass denuder, and of  $\text{NO}_x$  (the sum of nitrogen dioxide ( $\text{NO}_2$ ) and nitrous oxide ( $\text{NO}$ )) by a carbon denuder (optional: see Section 2.3.2 below). The sample is then passed through the converter (a 1.8 m  $1/8$ " o.d. resistively heated stainless steel tube), before detection of the eluent  $\text{SO}_2$  by a TEI 43CTL trace level  $\text{SO}_2$  analyzer (Thermo Electron Instruments, Franklin, MA, USA). To back out the false-positive analyzer response to gas phase compounds that may also form  $\text{SO}_2$  in the heated zone, the airstream is alternated on a 20 minute cycle between 14 minutes of unfiltered air, and 6 minutes of HEPA filtered air (*via* a separate  $0.8 \text{ L min}^{-1}$  intake located next to the main intake, with the excess flow escaping through a vent). A solenoid valve is used to switch between filtered (*i.e.* zero) and unfiltered (*i.e.* sample) air streams. The sulfate concentration is, therefore, proportional to the response of the analyzer to unfiltered air minus the response of the analyzer to filtered air. The output voltage of the analyzer and a voltage corresponding to the solenoid position were logged to a computer as 15 second averages using a model 6034E PCI PC ADC card (National Instruments Co.). The custom written logging software (OSL, Whitehouse Station, NJ, USA) automatically converted Volts to  $\text{SO}_2$

/ ppbV by application of a 50 multiplier (as dictated by the user-defined settings on the analyzer), and started a new file at midnight each day.

**Limitations of the Method.** Laboratory measurements at Harvard School of Public Health (HSPH) showed that 100 % conversion of ammonium sulfate aerosols occurred at temperatures exceeding 1000 °C. 1 mole of  $(\text{NH}_4)_2\text{SO}_4$  aerosol is, therefore, converted to one mole of  $\text{SO}_2$ . For the prototype instrument employed in this study, conversion was achieved using a standard converter (Thermo Electron Instruments, Franklin, MA, USA) that was initially designed to convert  $\text{NO}_2$  to  $\text{NO}$ . Efficiency of conversion was expected to drop over time as the converter becomes exhausted (Mark Davey, HSPH, personal communication).

As supplied, the TEI 43CTL trace level  $\text{SO}_2$  analyzer is optimized to be highly sensitive to  $\text{SO}_2$ , but has a rejection ratio for  $\text{NO}$  of only 40:1. During the 11 month operation of the sulfate instrument, maximum non-averaged ambient  $\text{NO}_x$  (The sum of  $\text{NO}$  and  $\text{NO}_2$ ) concentrations occasionally exceeded 1 part per million by volume (ppmV). As discussed above,  $\text{NO}_2$  will be converted to  $\text{NO}$  in the converter; therefore, at such high ambient  $\text{NO}_x$  concentrations the interference of  $\text{NO}$  on the analyzer will be significant. As such, the analyzer was modified by replacing the bandpass filter to have an  $\text{NO}$  rejection ratio of 400:1, but which reduced  $\text{SO}_2$  sensitivity approximately 3-fold. To increase the sulfate detection limit, the instrument was modified on 15 May 2002 by refitting the original bandpass filter in the analyzer and employing a honeycomb carbon denuder (MAST, UK) to remove  $\text{NO}_x$  from the sample stream. When utilized, the carbon denuder was positioned after the sodium carbonate denuder as  $\text{SO}_2$  had been shown to poison the carbon denuder (Eric Edgerton, personal communication).

As oxygen is present, we assume that ammonia ( $\text{NH}_3$ ) and other gas phase nitrogen containing compounds are oxidized to  $\text{NO}$  or  $\text{NO}_2$  and that any  $\text{NO}_2$  formed diffuses to the wall of the converter, where it is converted to  $\text{NO}$ . As with gas phase sulfur containing compounds, this false-positive response was backed out by alternating between filtered and unfiltered air (Section 2.3.1). Ammonia is also produced by the thermal decomposition of both  $\text{NH}_4\text{SO}_4$  and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) aerosols. As 1 mole of ammonium sulfate aerosol will form one mole of  $\text{NO}$ , this will increase the apparent conversion efficiency of the method. One mole of  $\text{NH}_4\text{NO}_3$  aerosol will actually be converted to 2 molecules of  $\text{NO}$  in the converter, and therefore, cause an interference to sulfate measurements. Nitric acid will be removed by the sodium carbonate denuder. Problems due to  $\text{NO}$  interference were more pronounced when the analyzer had only a 40:1 rejection ratio to  $\text{NO}$  (*i.e.* after 15 May 2002).

**Data Reduction and Calculation of Measured Sulfate Concentrations.** The daily raw 15 second data files (including the date/time, analyzer output ( $\text{SO}_2$  / ppbV), and solenoid position), were imported in to a SQL database (Microsoft, Inc.). A database application (OSL, Whitehouse Station, NJ) was written to calculate sulfate concentrations from the raw data-stream. Large lots of data were processed in a single program run to minimize analysis losses for samples at the beginning and end of the record set.

**Calculation of Net  $\text{SO}_2$  Concentration ( $\text{SO}_{2\text{net}}$ ).** The 15 second data-stream was reduced to discreet 20 minute data by calculating the net response of the analyzer to  $\text{SO}_2$  ( $\text{SO}_{2\text{net}}$ ) upon switching between filtered and un-filtered air. As the solenoid position changes, the instrument displays a finite response time due largely to its internal flow path volume that imparts a delay between the time the

switching valve is activated and the time SO<sub>2</sub> is detected. Further, the time required to achieve background signal conditions is variable as it depends on the ambient sulfate concentration. To deal with these conditions, we constructed the program to first define the start of the sample and background averaging intervals using predetermined offset values and then find the midpoint record for each interval. A half-width parameter is then used to control the number of records to be included on either side of the midpoint interval. Use of these parameters allows one to achieve analysis without precise knowledge of the true lag time for each set of sampling and background records.

The solenoid voltage switches between a low (not necessarily zero) voltage and a high voltage (about 1.7 V) when switching from sampling to background mode and visa versa. As both high and low voltages drifted, suitable threshold voltages were applied before analyzing the data.

Accounting for the response time and solenoid voltage thresholds, the program automatically calculates the average SO<sub>2</sub> (ppbV) for each sampling and background interval. A single background value is then computed as the average of the background intervals immediately before and after the sampling interval, and this is subtracted from the average for the sampling period. Standard deviations are calculated for each interval and propagated to produce a measure of uncertainty in the net result.

**Data Flagging.** Once the raw data-stream was reduced to discrete 20 minute data, they were manually flagged using database applications on the basis of the information from the operator's log. Specifically, the data was flagged void or questionable due to: auditing, calibrating, power outage, excessive NO<sub>x</sub> interference, instrument switched off before 20 min sample completed, the analyzer had an electrical fault, a leak was noticed as part of the audit, or either the zero-air flow or oven temperature were out .

**Calculation of Measured Sulfate Concentrations (Sulfate<sub>measured</sub>).** The analytical equation used to calculate the measured sulfate concentration is shown below.

$$\text{Sulfate}_{\text{measured}} = \text{AF}_i \left( (1170.6 * \text{SO}_{2\text{net}} * (\text{P}_{\text{amb}}/\text{T}_{\text{amb}})) - (3.10 * \xi_{\text{nitrate}} * [\text{Nitrate}] / \text{R}_{\text{NO}}) \right)$$

Where:

**Sulfate<sub>measured</sub>** is the measured sulfate concentration (in µgm<sup>-3</sup>) before correcting to filter samples.

**AF<sub>i</sub>** is a dimensionless audit factor to account for analyzer drift.

**1170.6** is a constant (with the units µg K m<sup>-3</sup> atm<sup>-1</sup> ppbV<sup>-1</sup>), and is calculated as: Molecular weight of sulfate (96 g mole<sup>-1</sup>) divided by R (0.082058 L atm mole<sup>-1</sup> K<sup>-1</sup>) and includes conversions for µg to g, L to m<sup>3</sup> and ppbV to parts by volume.

**P<sub>amb</sub>** is the ambient pressure in atmospheres.

**T<sub>amb</sub>** is the ambient outdoor temperature in K.

**ξ<sub>nitrate</sub>** is the efficiency of ammonium nitrate to NO conversion relative to the conversion efficiency of sulfate to SO<sub>2</sub> (dimensionless)

**3.10** is a dimensionless constant, and is calculated as the product of the 'moles of NO produced per mole of NH<sub>4</sub>NO<sub>3</sub> (2)' and the 'molecular weight of Sulfate (96 g mole<sup>-1</sup>)' divided by the 'molecular weight of Nitrate (62 g mole<sup>-1</sup>)'.

**[Nitrate]** is the measured ammonium nitrate concentration in µg m<sup>-3</sup>.

$R_{NO}$  is the dimensionless rejection ratio of the analyzer to NO (*i.e.* either 400 or 40).

Ambient temperature and pressure were obtained from a meteorological station sited at the Supersite. In cases where these data were missing, information from other instruments was inserted. If no other data were available, a pressure of 1 atmosphere and an interpolated value of the temperature were used.

**Correction for drift in analyzer span ( $AF_i$ ).** Audit factors,  $AF_i$ , were calculated as the ratio of the calibration gas (typically 470 ppbV) to the  $SO_2$  (ppbV) indicated on the analyzer at the time of the calibration or audit. Values of  $AF_i$  were calculated for those specific date and times when the analyzer span was audited or calibrated. Values of  $AF_i$  were then linearly interpolated to the date and time of each individual sulfate data record using an Excel Visual Basic macro (Microsoft Inc.). The analyzer was observed to drift by up to 4.3 % over extended periods of time.

**Correction for Nitrate interference.** Corrections due to the false positive response of nitrate aerosols were made with ambient  $NH_4NO_3$  concentrations measured using an R&P8400N ambient particulate nitrate monitor (Rupprecht and Patashnick, Albany, New York, USA) after they were corrected to the 24-hr integrated Speciation Nitrate measurements. As  $NH_4NO_3$  is far less stable at 800 °C than is  $NH_4SO_4$ , it is likely that the conversion efficiency of  $NH_4NO_3$  is higher than that of  $NH_4SO_4$ , and so we assumed that the efficiency of conversion efficiency for  $NH_4NO_3$  ( $\xi_{nitrate}$ ) is 1. Correction for NO interference from Nitrate-containing aerosol particles was made using a database application (OSL, Whitehouse Station, NJ), employed subsequent to the program that calculated the sulfate concentration.

**Correction for ambient  $NO_x$ .** Prior to the installation of the carbon denuder on the 16 May 2002, any ambient  $NO_x$  will be converted to NO, and detected by the analyzer. For this period, the analyzer had been modified to reject NO at a ratio of 400:1. At this rejection ratio, provided  $NO_x$  concentrations are relatively constant over the 20 minute sampling period, there should be little increase in the sulfate detection limit. However, as explained above, maximum NO concentrations occasionally exceeded 1 ppmV, and these events typically lasted on the order of seconds.  $NO_x$  was measured at the Supersite as 10 minute averages, which is longer than the 6 minute blank cycle employed in the semi-continuous sulfate instrument. As such, it was not possible to subtract  $NO_x$  interferences from the raw semi-continuous sulfate data-stream; however, periods of significant contamination were flagged as void.

**Efficiency Corrections.** As there was no provision for direct calibration with a known concentration of sulfate aerosol or for injection of known amounts of mass, this instrument required calibration against 24-hr speciation sulfate concentrations. Comparisons between 24-hr integrated MetOne and averages of the corresponding Harvard sulfate data are shown in Figure 1.

Note that prior to May 15, 2002, when a carbon MAST denuder was installed, sulfate signals were barely detectable above the background signal for most of the data, hence, are largely unusable. This was in large part due to interference by nitrogen oxides, which was eliminated by the MAST denuder. Prior to this date, the apparent conversion efficiency declined from a high of about 82% to a low of about 3%. After the denuder was installed, the apparent efficiency increased to about 50% from about June 1<sup>st</sup> until the middle of July, but was highly variable. Afterwards, the apparent efficiency declined to an average of about 35%, but was again highly variable. The stainless-steel converter tubing was replaced on 31 October 2002. Afterwards, the conversion efficiency (average of about 38%) was less variable for approximately 3 weeks, but was lower than measured in June and July.

The conversion efficiency of the unit is clearly temperature dependent. As mentioned above, the original prototype system was operated at 1000°C, at which the conversion efficiency for ammonium sulfate was reported to be 100%. However, owing to the physical limitations, we operated the converter (Thermo Electron Inc.) at 800 °C, at which an ammonium nitrate conversion efficiency of 75% was expected. Tests performed in the development of the original prototype showed that the conversion efficiency for sulfate in the form of sulfuric acid was about 25% less than that for ammonium sulfate. Also, metal sulfates were found to be undetectable (David Harrison, private communication). As shown in Figure 1, higher conversion efficiencies were observed in warm months (May through August) than in cold months (Oct ~ Nov). Ammonia emissions are greater in summer than in colder months and are highly variable. Lower ammonia emissions would favor ammonium hydrogen sulfate formation, which can be viewed as a mixture of ammonium sulfate and sulfuric acid. Its possible, therefore, that the highly variable conversion efficiency is the result of variations in aerosol acidity and alkaline dust content.

As indicated in Figure 1, the apparent efficiency varied somewhat less within each month than it did from month-to-month, especially after May 15<sup>th</sup>. Therefore, we chose to correct the Harvard Monitor data using monthly efficiency correction factors.

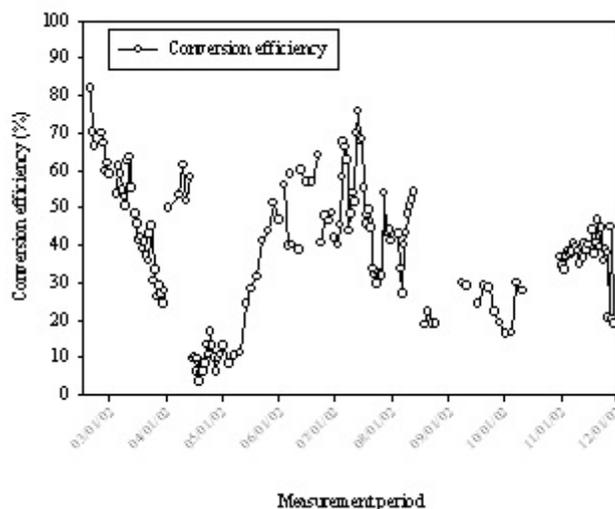


Figure 1. Conversion Efficiency of the prototype Harvard Sulfate Monitor (Ondov et al., BSS 15<sup>th</sup> quarterly progress report)

Table 2. Regression relationship between 24-hr MetOne and Harvard sulfate data in 2002

	Regression analysis	R <sup>2</sup>	
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Month			
May	$Y = (1.876 \ 0.298) X + (2.376 \ 0.952)$	0.929	
June	$Y = (1.596 \ 0.069) X + (0.732 \ 0.313)$	0.993	
July	$Y = (1.571 \ 0.099) X + (1.395 \ 0.554)$	0.901	
August	$Y = (1.950 \ 0.072) X + (0.943 \ 0.291)$	0.976	
September	$Y = (1.217 \ 0.838) X + (1.776 \ 2.256)$	0.680	
October	$Y = (3.334 \ 0.175) X + (0.995 \ 0.351)$	0.992	
November	$Y = (2.213 \ 0.152) X + (0.558 \ 0.207)$	0.886	

Y ( g/m<sup>3</sup>): 24-hr MetOne sulfate; X (( g/m<sup>3</sup>): 24-hr Harvard sulfate

Note that for the September data, regression analysis was not statistically significant, so the regression result was not applied to the sulfate data. Rather an average efficiency factor was used for correcting the September data.

## 2.5 Comparability

Comparability refers to how confidently one data set can be compared with another. Ideally, two instruments that measure the same observable should be statistically comparable. The existence of several overlapping techniques will allow the intercomparison of existing measurement approaches and also the evaluation of new and emerging approaches. Table 2 presents a list of observables for which multiple measurement methods were used.

Table 3. Comparison of methods

Observable	Methods that will be compared <sup>a</sup>	Methods that will not be compared <sup>a</sup>
PM <sub>2.5</sub> Mass	FRM/Gravimetry v. STN/Gravimetry, and TEOM	-
PM <sub>2.5</sub> Nitrate	STN sampler/IC v. R&P 8400N <sup>1</sup>	RSMS-III <sup>1,2</sup>
PM <sub>2.5</sub> Sulfate	STN sampler/IC v. prototype Harvard monitor <sup>1</sup>	RSMS-III <sup>1,2</sup>
PM <sub>2.5</sub> EC	STN sampler/TOA v. SL TOA carbon analyzer <sup>1</sup>	RSMS-III <sup>1,2</sup> RSMS-III <sup>1,2</sup>
PM <sub>2.5</sub> OC	STN sampler/TOA v. SL TOA carbon	

	analyzer <sup>1</sup>	
PM <sub>2.5</sub> Elements	STN sampler/XRF v. SEAS-GFAAZ	RSMS-III <sup>1,2</sup>
PM <sub>2.5</sub> Organics	None	RSMS-III <sup>1,2</sup>
Particle sizing	STN Sampler/Gravimetry v. APS and SMPS	RSMS-III <sup>1,2</sup>
Aerosol scatting parameters	Nephelometer v Mie theory/SMPS-APS	-

- <sup>a</sup> 1: State-of-the-art measurement method  
2: Measurement method that is not quantitative  
3: Measurements only collected during intensive study periods (July 2001 and possibly January 2002)  
4: Limited availability of measurements due to excessive instrument malfunction  
5: At overlapping region only

In this report, comparisons between measurement methods were performed only for data that met the precision, accuracy and completeness data quality objectives. These select comparisons are presented in the figures that follow, as are the major axis regression statistics (assuming a linear relationship) used to gage comparability. Comparability was not determined for state-of-the-art measurement methods that were not quantitative; when only one method was used to measure a particular observable; and if there was limited overlap of the particular observable due to excessive malfunction of an instrument. More detailed comparisons and instrument evaluations have been performed by several BSS investigators (Adam et al., 2004; Harrison et al. 200 ; Park et al., 2005 ecoc; Park et al., 2006a; Lee et al., 200X ; Pancras et al., 2005; Pancras et al., 2006; Tolocka et al., 200x nitrate, various BSS quarterly progress reports and the BSS final project report).

**2.5.1 Comparison of TEOM Semicontinuous and FRM and STN-Filter PM2.5 mass measurements at Ponca St.**

### Comparison of FRM and TEOM PM<sub>2.5</sub> mass

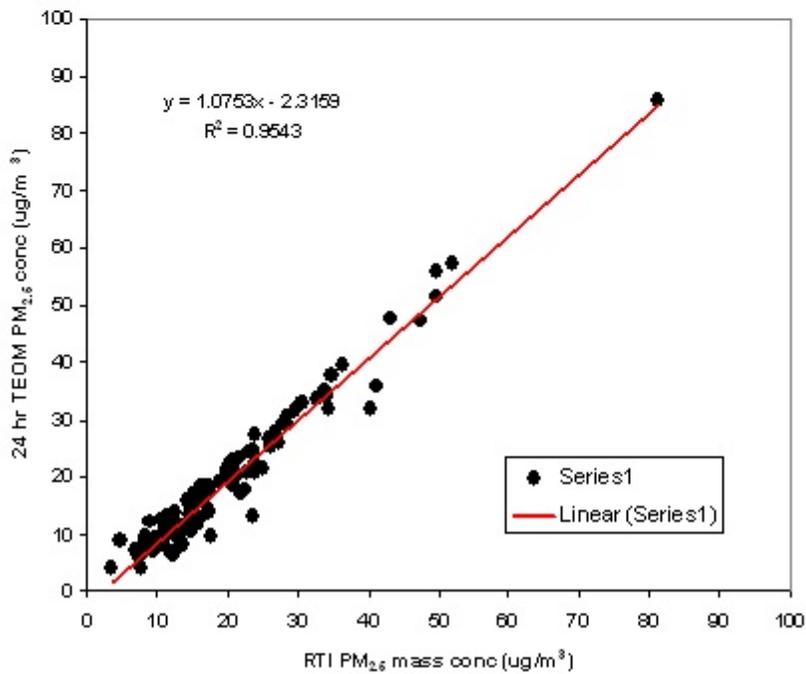
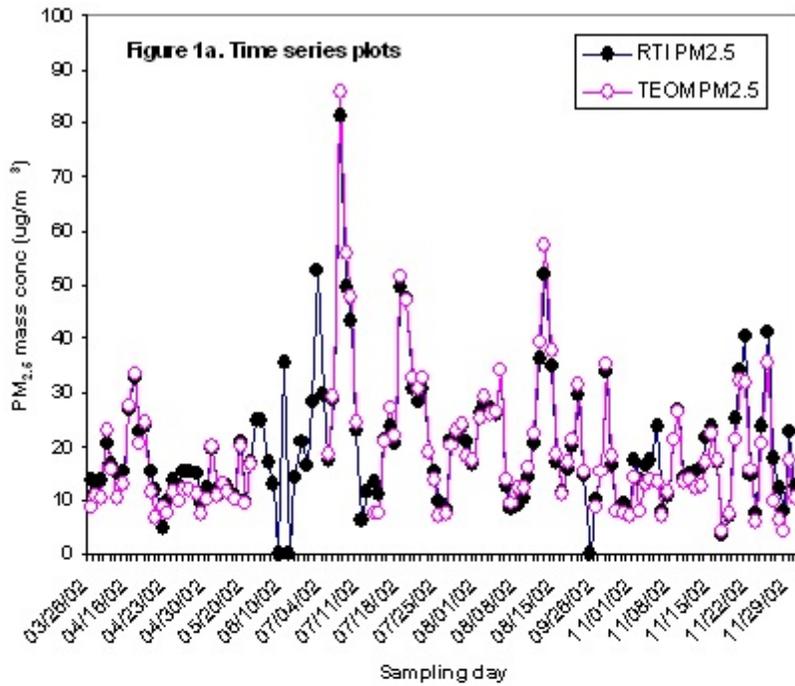


Figure 3. TEOM PM<sub>2.5</sub> mass concentrations compared to the mass concentrations measured by the STN sampler at Ponca Street.

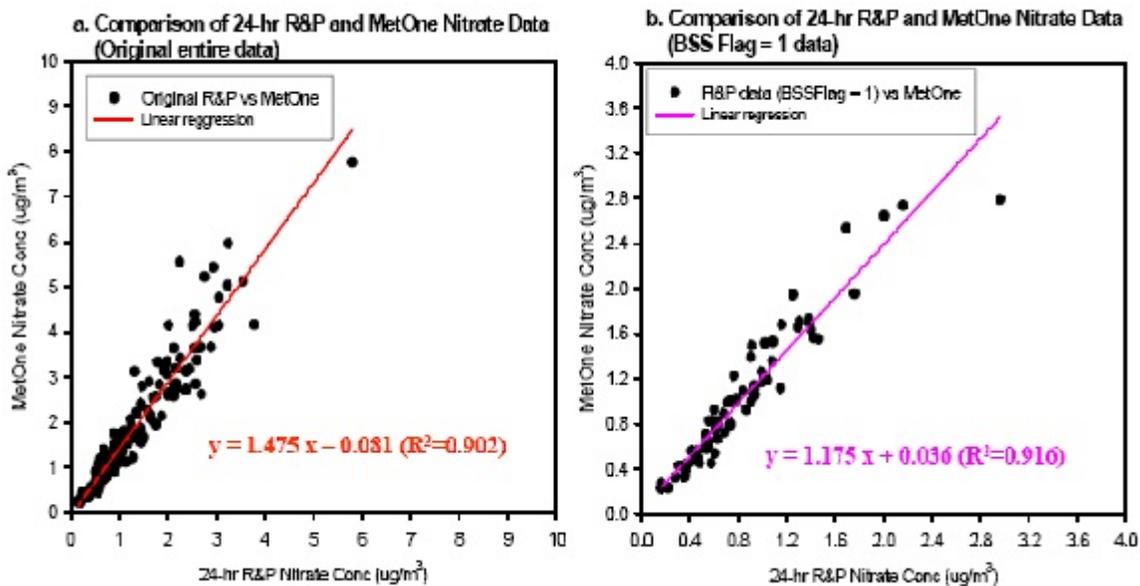


Figure 4. Comparison of R&P nitrate and Met-One Nitrate data (before correction of the latter) Harrison et al., 2004; also: BSS Prog report 12

### 2.5.3. Comparison of Semicontinuous ECOC and STN filter-based measurements at Ponca St.

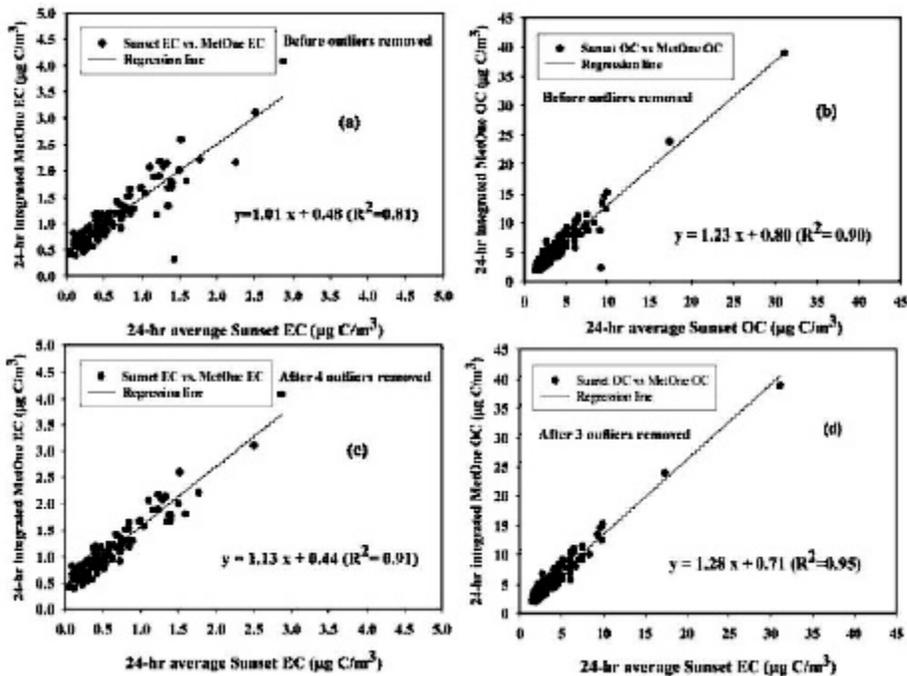


Figure 5. Comparison of 24-hr averages of 1-hr EC and OC measurements made with the Sunset Labs Carbon Monitor with integrated 24-hr STN filter-based measurements at the Baltimore Supersite at Ponca St., in East Baltimore in 2002.

**2.5.4. Comparison of Elements in fine particles via semi-continuous SEAS-GFAAZ with STN Filter-XRF measurements at Ponca St. (Pancras et al., 2005; Pancras et al., 2006).**

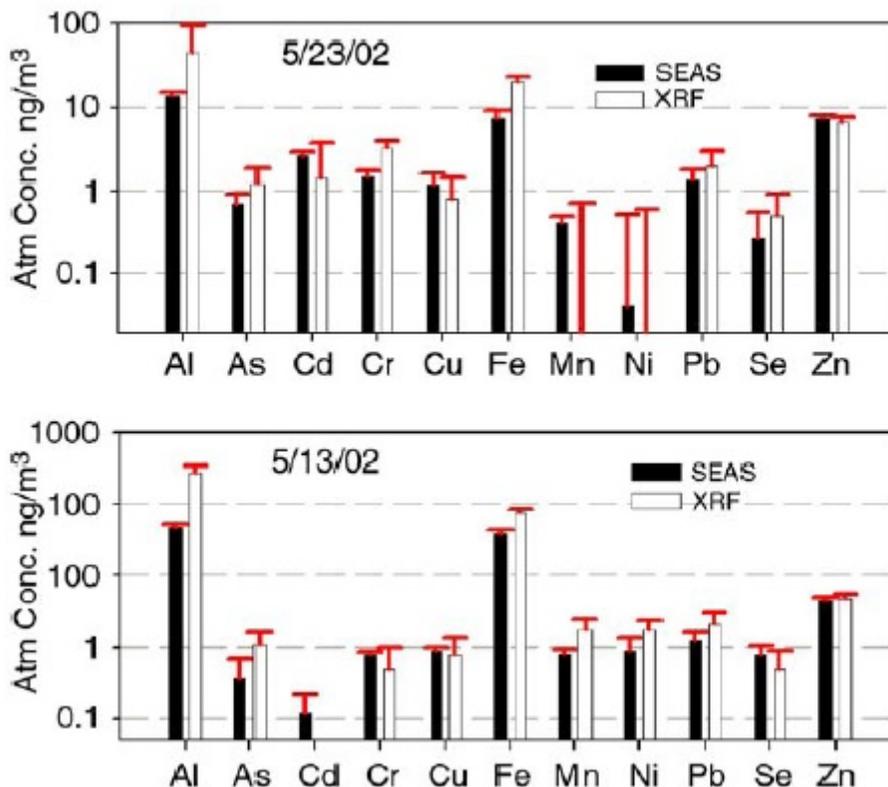


Figure 6. Atmospheric fine particle concentrations of 11 elements measured simultaneously by SEAS-GFAAZ and STN-Filter-XRF methods (Pancras et al., 2006).

**2.5.5. Comparison of semicontinuous PM2.5 sulfate and STN filter based measurements at Ponca St. (Ondov et al., Baltimore Supersite Progress Report 15).**

Analysis of the data collected after May 15<sup>th</sup> 2002, showed that for all of months the reference speciation sulfate concentrations were highly correlated with the Harvard Monitor values (see Table 1), i.e.,  $R^2 > 0.89$  for all months except September. Ideally, the conversion efficiencies would simply be the inverse of the slopes listed in Table 4. However the offsets are fairly large, i.e., in the range of 1 to 2  $\mu\text{g}/\text{m}^3$  so that the full regression equation is required to correct the data. Prior to May 16<sup>th</sup>, variability was less. STN sulfate measurements for October are deemed to be unreliable.

Table 4. Regression relationships between the MetOne and Harvard sulfate data in 2002.

Month	Regression Analysis	R <sup>2</sup>	Remarks
May	Y=(1.876±0.298X + (2.376±0.952)	0.929	
June	Y=(1.596±0.069X + (0.732±0.313)	0.993	
July	Y=(1.571±0.099X + (1.395±0.554)	0.901	
August	Y=(1.950±0.072X + (0.943±0.291)	0.976	
September	Y=(1.217±0.838X + (1.776±2.256)	0.680	
October	Y=(3.334±0.175X + (0.995±0.351)	0.992	
November	Y=(2.213±0.152X + (0.558±0.207)	0.886	

Y ( $\mu\text{g}/\text{m}^3$ ): 24-hour MetOne sulfate; X ( $\mu\text{g}/\text{m}^3$ ):24-hr Harvard sulfate

Note that for the September data, the regression analysis was not statistically significant, so the regression result was not applied to the sulfate data. An average efficiency value was used to correct the September data.

**2.5.6. Aerosol Extinction.** Highly resolved spatial and temporal lidar backscatter data obtained during the Baltimore Supersite study were analyzed with a near end approach to determine vertical profiles of the aerosol extinction coefficient during a period (4-12 July 2002) encompassing smoke fumigation from the Canadian forest fires (Figure 7). The approach takes into account the aerosol scattering measured at ground level, obtained with a nephelometer at 0.530  $\mu\text{m}$ , the ground level particle size distribution measurements (with SMPS and APS) and the calculated refractive index to determine the boundary condition using Mie theory. In addition to the vertical profile of the aerosol extinction

coefficient, we compare the aerosol scattering coefficient at ground level, measured by the nephelometer, with related parameters, specifically derived mass concentration and the mass scattering coefficient. The index of refraction is chosen such that the measured and computed

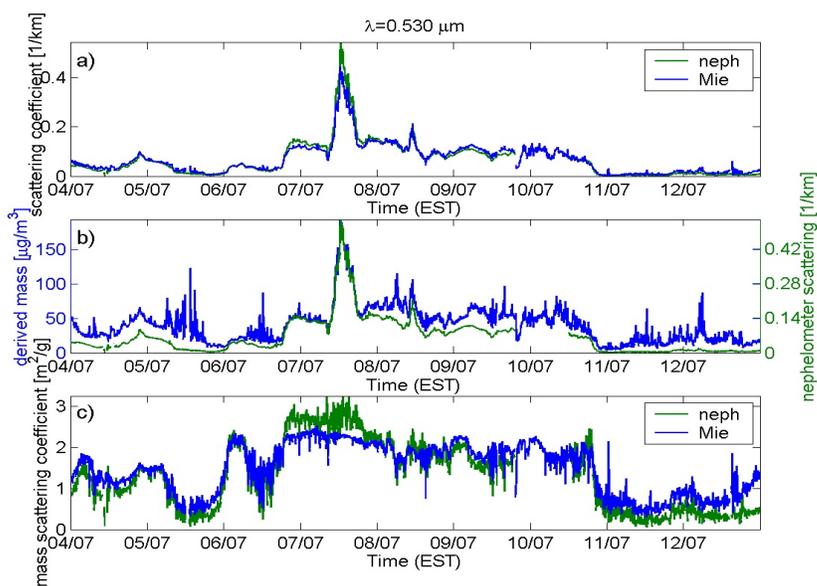


Figure 7. Temporal variation of the aerosol scattering coefficient as measured by nephelometer and computed by Mie theory (a), of the derived mass (b) and of the mass scattering coefficient (c). Tick marks on the time axis correspond to midnight.

scattering coefficients match (such that the correlation coefficient between measured and computed aerosol scattering at 0.530  $\mu\text{m}$  is  $R = 0.98$ ). The chosen index of refraction for aerosol is 1.5-0.47i, which is typical for soot. The measured aerosol scattering coefficient by nephelometer at 0.530  $\mu\text{m}$  ranged from  $\sigma_p=0.002 \text{ km}^{-1}$  to  $\sigma_p=0.541 \text{ km}^{-1}$ , whereas the aerosol extinction coefficient computed with Mie theory (based on size distributions and refractive index) at 0.530  $\mu\text{m}$  ranges from  $\kappa_p=0.010 \text{ km}^{-1}$  to  $\kappa_p=1.050 \text{ km}^{-1}$ . The derived mass concentration is defined as the average density (here  $1 \text{ gm}^{-3}$  corresponding to soot) multiplied with volume size distribution (derived from particle number distribution measured with SMPS and APS). It was between  $3.96 \mu\text{g m}^{-3}$  and  $194.00 \mu\text{g m}^{-3}$ . The mass scattering coefficient is defined as the ratio between scattering coefficient and mass derived and it was between  $0.058 \text{ m}^2\text{g}^{-1}$  and  $3.260 \text{ m}^2\text{g}^{-1}$ . A discrepancy between mass scattering calculated using measured and computed scattering exists as the measured and computed scattering do not match perfectly. The mean and standard deviation of the two can be seen in Table 5.

The period analyzed was divided into three sub intervals corresponding to the periods before, during and after the haze event. Table 5 shows the mean and standard deviation for measured (nephelometer) and computed (Mie theory) aerosol scattering, computed (Mie theory) aerosol extinction coefficient, derived mass and mass scattering coefficient (using measured and computed scattering coefficient) for the 3 periods. The main remark is the increasing of the optical parameters during the second period (period of the haze event due to the Canadian forest fires).

The optical parameters as recorded or computed at ground level were compared with other studies done in similar conditions (e.g. Carrico, C. M., M. H. Bergin, J. Xu, K. Baumann, H. Maring, Urban aerosol radiative properties: Measurements during the 1999 Atlanta Supersite Experiment, *J. Geophys. Res.*, 108(D7)8422, doi:10.1029/2001JD001222, 2003 ; Hoff, R. M., H. A. Wiebe, L. Guise-Bagley, Lidar, nephelometer, and in situ aerosol experiments in southern Ontario, *J. Geophys. Res.*, 101(D14), 19199-19209, 1996). We did not find published studies about recent Canadian forest fire (July 2002), analyzed in this paper with which to compare the results. High values of the aerosol extinction coefficient are obtained on vertical profiles during the haze due to Canadian forest fire (reaching sometimes values from 0.4 to 0.7  $\text{km}^{-1}$ ).

Table 5. Mean and standard deviation for measured (nephelometer) and computed (Mie theory) aerosol scattering, computed (Mie theory) aerosol extinction coefficient, derived mass and mass scattering coefficient (using measured and computed scattering coefficient)

		4 July 00:00 EST – 6 July 18:00 EST	6 July 18:05 EST – 10 July 21:00 EST	10 July 21:05 EST – 12 July 23:55 EST
Measured aerosol scattering $\sigma_p$ [ $\text{km}^{-1}$ ] (nephelometer)	Mean	0.032	0.126	0.006
	Standard deviation	0.019	0.080	0.003
Computed aerosol scattering $\sigma_p$ [ $\text{km}^{-1}$ ] (Mie theory)	Mean	0.039	0.126	0.013
	Standard deviation	0.020	0.066	0.007
Computed aerosol extinction $\kappa_p$ [ $\text{km}^{-1}$ ] (Mie theory)	Mean	0.107	0.306	0.047
	Standard deviation	0.049	0.146	0.027
Derived mass M [ $\text{mg m}^{-3}$ ]	Mean	30.1	59.6	17.3
	Standard deviation	14.5	27.0	9.83
Mass scattering $\sigma_p/M$ [ $\text{m}^2\text{g}^{-1}$ ] – nephelometer	Mean	1.1	2.05	0.365
	Standard deviation	0.533	0.495	0.147
Mass scattering $\sigma_p/M$ [ $\text{m}^2\text{g}^{-1}$ ] – Mie theory	Mean	1.34	2.08	0.762
	Standard deviation	0.470	0.270	0.248

Overall, the select methods compare reasonably. In a few instances, best estimate data sets were produced to address the QA concerns of these methods (PM<sub>2.5</sub> sulfate, nitrate, and ammonium).

## 2.6 Representativeness

Representativeness expresses how closely a sample reflects the characteristics of the surrounding environment and can be quantified in terms of a spatial scale for monitoring. The main monitoring site was located at Ponca St., 7 km east of downtown Baltimore's inner central inner harbor. Representativeness relative to the FMC, Clifton Park, and various MDE monitoring stations is discussed in Ondov et al., 2006. Ponca St. is heavily influenced by traffic during easterly and southerly winds. During westerly winds, air is advected across downtown Baltimore with only normal city streets upwind for 14 km (i.e., distance to western edge of downtown Baltimore City). Traffic on I895 and I95, combined is <300,000 vehicles per day, i.e., actually less than Rte 395, the main traffic conduit into Baltimore City, which typically supports >400,000 vehicles/day. Ponca is, therefore, appropriately representative of both east Baltimore residential areas and of exposures from motor vehicle emissions on scales of 50 m to >14 km, depending on wind direction. The most recent results of the Supersites and PM centers, indicate strongly that this range of scales is critically important in assessing health effects of urban aerosol PM. The exposure of the surrounding

environs represents both an ‘urban’ and ‘neighborhood’ scale for particle monitoring. Concentrations of PM2.5, its major constituents, and 11 elements determined by SEAS are shown in Figure 8

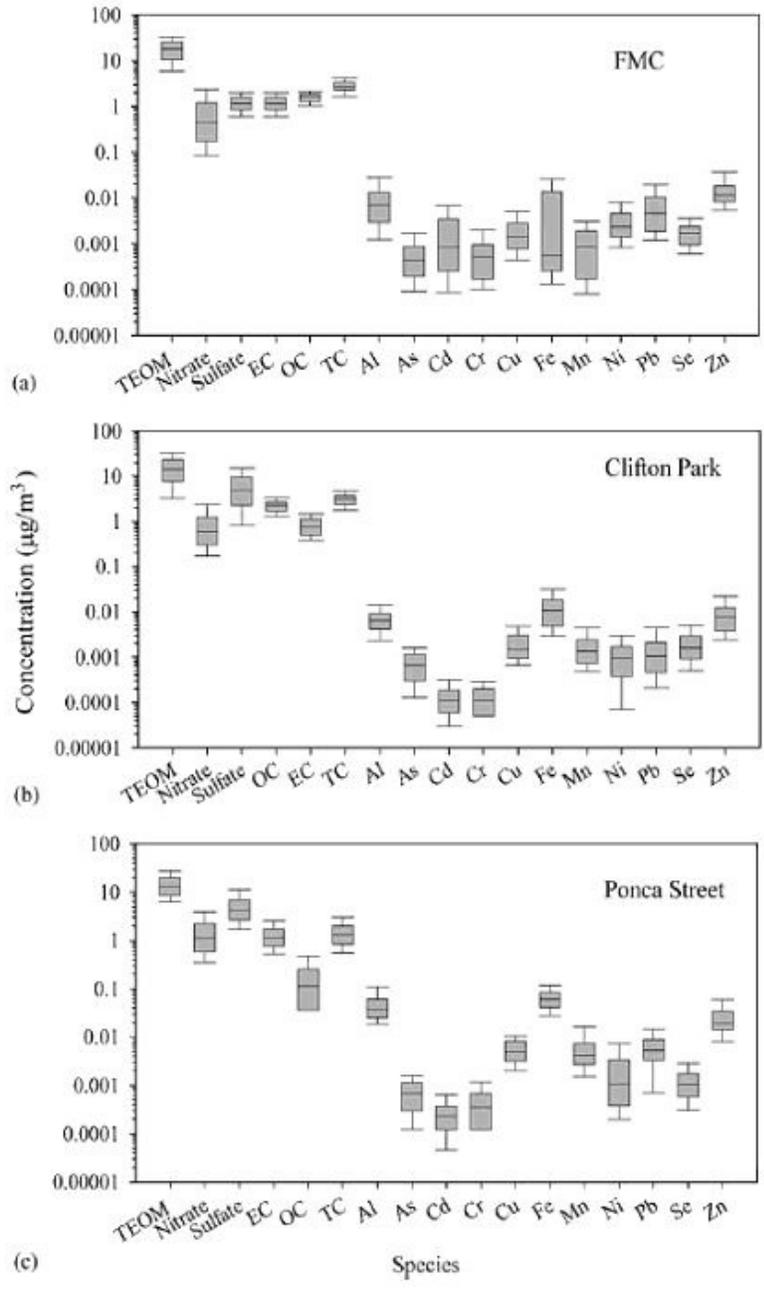


Figure 8. Comparison of concentrations of PM2.5 (TEOM), nitrate, Sulfate, EC, OC, and 11 elements in aerosol particles measured at the three Baltimore Supersite monitoring locations.

## 2.7 Data Quality Objectives Not Met During BSS

In a few instances, the data quality objectives were not met at BSS. Typically, these instances were associated with newly developed instrumentation that did not perform as well as expected, and are summarized in Table 5. When possible, best estimate data sets were produced to address the QA concerns of these measurements (PM<sub>2.5</sub> sulfate, nitrate, and ammonium). In addition, several sets of data were not completely analyzed by the time this report was completed. These are marked with a dash in Table 1.

**Table 6.** Observables for which the DQI did not meet the DQO at BSS or for which substantive issues warrant .

Observable	Method	Issue
Sulfate	Harvard Prototype	Data completeness - plagued by poor conversion efficiency. This is largely irrelevant as a vastly improved new generation commercial model is now available.
Elements	STN-XRF	Data completeness/MDL: 70% of elemental measurements returned for Ponca St. were non-detects.
PM <sub>2.5</sub> nitrate	R&P 8400N (ICVC)	Accuracy. Measurements against 24-hr STN values were ~30% low over the course of the study. They could be adjusted to agree more closely with 24-hr average STN values, but the validity of individual 10-min 8400N measurements is highly uncertain (Harrison et al., 2004).
PM1.2 elements	SEAS-GFAAZ	Accuracy: Transmission efficiency for crustal elements (most notably, Al, Fe, and Ca) was quite low (in some cases 35-35%) due to losses in the Teflon solenoid valve. This problem is now largely solved. Unforeseen difficulties with a glass inlet pipe led to invalidation of much of the samples collected with one of the co-located SEAS during the November 2002 intensive campaign.
PM size distributions	SMPS	Maintenance: The inlet impactor had to be changed much more frequently than we had expected due to abrasion of its orifice, which if left in service would have corrupted the sampling flow rate and shifted the size distribution midpoints. Nonetheless, this was otherwise an highly-reliable instrument.
Size segregated Elements	DRUM-SXRF	Accuracy: We had difficulty achieving the proper flow rate with the unit's critical orifice. Completeness: we received analyses for only 1 Drum impactor sample.

**Table 6.** Observables for which the DQI did not meet the DQO at BSS or for which substantive issues warrant .

<b>Observable</b>	<b>Method</b>	<b>Issue</b>
ECOC	Sunset Labs	Completeness: We had some difficulties maintaining ignition of the unit's hydrogen flame ionization detector. Otherwise this instrument was highly effective.
Meteorology	All methods	MDL, precision, accuracy - The standard operating procedures (and manufacturer recommended procedures) did not allow these DQIs to be calculated. However, agreement between various wind speed, wind direction, temperature, pressure, and RH measurements was generally quite good.

### 3. Conclusions

- A majority of the data quality indicators showed the BSS central site instruments performed as expected or better.
- Most data quality objectives that were not met were associated with newly developed instrumentation that did not perform as well as expected. When possible, best estimate data sets were produced by correlation against STN filter-based methods to address the QA concerns of these measurements (sulfate and nitrate) .

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## APPENDICES

### Audit Reports

Quality Assurance Audit  
July 16, 2001

On July 16, 2001, a quality assurance audit was conducted at the Baltimore Supersite. The major objectives were to check on flow rates and temperature measurements. At this time, it was not possible to audit the single particle mass spectrometer, the high volume, sequential organic sampler, or the two SEAS. The first two instrument as well as the second SEAS are not yet on site and the on-site SEAS was not operating as it was waiting for parts.

There are several initial general issues that need to be raised. There were manuals available at the site, but none of the SOPs were readily available. In general, it is good to have short, checklist type procedures at each instrument that makes it easy to both operate the system as well as identify and act on any indicators of potential problems are observed.

For example, on July 15, there was an entry on the SMPS log indicating a low  $\Delta P$  across the impactor. This results should have triggered a cleaning of the impactor. When making the flow measurements on July 16, it was found that the impactor was clogged. Thus, the quality of all of the data from at least Sunday to the time of the cleaning on Monday must be considered as suspect and clearly cannot be validated. Thus, it is strongly recommended that SOPs be placed near the instruments and checklists with the obvious indicators of potential quality problems and corrective actions to be taken to mitigate the problem.

It is very important that the kind of flow checks made this day be made on a regular basis (weekly). The flow check on the TEOM found that the major flow in the system was being misreported by the instrument. In this case, the TEOM was delivered to the site by MDE, but it was not initially checked for its performance. During the audit, it was found that at the inlet to the mass flow controller, the flow rate as found to be less than 2 lpm when the front panel indicated a flow of 13.3 lpm. Further tests were done directly at the entrance to the flow controller for the bypass flow. A piece of tubing was connected to permit the connections to the Gilibrator flow meter. Constricting the tubing did cause the flow rate to go to close to zero (0.1 lpm). Thus, there is clearly something defective in the mass flow controller for the bypass flow. Since it cannot be documented that the flow meter has ever functioned on site, all of the TEOM data must be considered unreliable.

We found that the flow rates on sulfate and nitrate monitors were correct. However, the flow through the OC/EC/TC monitor appeared to be low by 1 LPM compared to the nominal flow rate reported by the instrument.

The SMPS and the APS flow tests showed good agreement between the audit value with the nominal settings. With the CSAS, there is currently no way to determine if there is flow through the unit. It is recommended that some type of low pressure drop flow indicator be used to ascertain that flow is occurring in the system.

The speciation samplers are being maintained by the JHU group and they were in the process of performing the calibration audits during the visit. It was clear that they had well established procedures. We need to obtain appropriate copies of their calibration sheets, but it appears that this

part of the system is being properly attended to.

In this audit visit, we failed to check the performance of the FRM PM<sub>2.5</sub> sampler. This check should be done as soon as possible.

At this point the only documentation is in a series of notebooks. There is no procedure for routine copying of logs and notebooks to assure that there are duplicate copies in different locations so that it is less likely that critical information is lost. It is strongly recommended that a process being instituted as soon as possible to copy the logbooks and log sheets to maintain a complete record of the sampling operations.

In the next audit, it will be important that the laboratory analyses also be audited. Thus, visits to Dr. Ondov's lab at the University of Maryland at College Park and Dr. Squibb's lab at the University of Maryland at Baltimore will be needed. It will not be possible to visit Florida International University, but we will need to work out a procedure by which their procedures can be reviewed.

Quality Assurance Audit  
March 8, 2002

On March 8, 2002, a second quality assurance audit was conducted at the Baltimore Supersite. The primary objectives were to check on flow rates and temperature measurements. At this time, it was not possible to audit the single particle mass spectrometer, the high volume, sequential organic sampler, or the two SEAS. The mass spectrometer was not yet on site and the remaining systems were still being constructed and put into service.

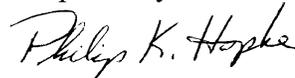
This audit found the situation to be much better than last July. Manuals and the SOPs were readily available. In general, it is still a good idea to have short, checklist type procedures at each instrument that makes it easy to both operate the system as well as identify and act on any indicators of potential problems are observed. It is recommended that such checklist instructions be developed. In addition, there need to be new SOPs developed since there has been a change in several of the instruments. The R&P sulfate analyzer has been replaced with a HSPH-design system and the R&P EC/OC instrument has been replaced with a Sunset Laboratories unit. There also needs to be an SOP for the Met Tower instruments. These should be completed as soon as possible and submitted to the QA manager for approval.

Examination of the notebooks found that for the limited time that the various instruments had been running, appropriate flow checks and calibrations had been performed. Unfortunately we had a failure of the audit flow device and it has subsequently been returned to the manufacturer for repair and recalibration. Thus, we could only make measurements with the site's Gilibrator 2 so we did not have a fully independent flow check. Flow checks on the APS and the SMPS found that the flow rates were within their proper specifications. There was a bent nozzle in the APS that will need to be replaced. The lack of the higher flow device precluded full testing of the complete suite of instruments.

There were some safety considerations that were brought to the attention of the site personnel. Particularly there were several unsecured compressed gas tanks. I was told there was insufficient room for them. However, they could have been laid on their side or secured in other ways until appropriate restraints were acquired. There remains some concern about personnel on the roof of the trailer since there are no railings. It may be useful to consider some type of temporary railings around the roof to provide some measure of security for personnel that have to perform tasks on the roof.

In this audit, we still have not examined the laboratory analyses processes. Visits to Dr. Ondov's lab at the University of Maryland at College Park and Dr. Squibb's lab at the University of Maryland at Baltimore will be needed. It will not be possible to visit Florida International University, but we will need to work out a procedure by which their procedures can be reviewed. We should plan to do these audits in June or July of this year.

Respectfully submitted,



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