QUALITY ASSURANCE FINAL REPORT

FOR THE

PITTSBURGH AIR QUALITY STUDY
PITTSBURGH SUPERSITE

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Quality Assurance Final Report

This report summarizes the quality of the measurement data sets and provides a context for interpretation of measurements collected during the Pittsburgh Air Quality Study (PAQS) Supersite. Data quality is evaluated using particular data quality indicators (DQIs), selected by the PAQS Quality Assurance Manager and Principal Investigators, and the findings of the technical system and performance audits conducted during the field campaign. Additional information about PAQS can be found in the Quality Assurance Program Plan (Khlystov et al., 2001), a publication which provides an overview of the PAQS measurements and preliminary scientific findings (Wittig et al., 2003a), and various publications focusing on measurements collected at the PAQS Supersite (Cabada et al., 2003a; 2003b; 2003c; Khlystov et al., 2001; 2003; Rees et al., 2003; Stanier et al., 2003a; 2003b; Subramanian et al., 2003; Takahama et al., 2003; Wittig et al., 2003b).

1. Technical System and Performance Audits

Data quality was assured by performing two types of audits of all instruments and systems used during PAQS. 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 few cases, the performance audits helped to diagnose instrument issues before the measurements were compromised. In even fewer cases, measurements were invalidated as a result of performance audit findings. In a 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 PAQS 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 PAQS 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 PAQS, are also listed in Table 1. A brief description of each indicator and the method of calculating the indicator at PAQS is presented next. The actual methodology for determining each indicator is stated in the individual SOPs and RPs. In a few instrances 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.

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

Observable	Method [1]	Group [2]	Resolution	Frequency	Period of Operation [3]	MDL [4] DQI and (DQO)	Precision [4] DQI and (DQO)	Accuracy [4] DQI and (DQO)	Completeness [4] DQI and (DQO)
Aerosol mass									
PM_{10} mass	Dichot sampler/Gravimetry	CMU	24 hr	Daily	7/1/01-7/1/02	1.2 µg/m^3 (2 µg/m^3)	1.43% (10%)	0.6% (10%)	86.6% (70%)
$PM_{2.5}$ mass	FRM sampler/Gravimetry	CMU	24 hr	Daily	7/1/01-7/1/02	0.9 µg/m^3 (2 µg/m^3)	1.43% (10%)	0.6% (10%)	92.5% (70%)
$PM_{2.5}$ mass	Dichot sampler/Gravimetry	CMU	24 hr	Daily	7/1/01-7/1/02	1.2 µg/m^3 (2 µg/m^3)	1.43% (10%)	0.6% (10%)	86.6% (70%)
$PM_{2.5}$ mass	R&P 1400a TEOM with SES	CMU	10 min	Continuous	7/1/01-7/1/02	0.65 µg/m^3 (1 µg/m^3)	2.2% (10%)	1.2% (10%)	94% (70%)
PM_x mass	MOUDI sampler/Gravimetry	CMU	24 hr	Daily	7/1/01-7/1/02 *	1.7 µg/m^3 (2 µg/m^{3}PS)	1.43% (10% PS)	0.6% (10% PS)	84% (70%)
PM_x mass	MOUDI sampler/Gravimetry	CMU	8 hr	3 per day	7/22-25/01, 7/31-8/3/01	1.5 µg/m^3 (2 µg/m^{3}PS)	1.43% (10% PS)	0.6% (10% PS)	100% (70%)
Aerosol size distribution									
Number, surface area, and volume distribution	TSI SMPS	CMU	10 min	Continuous	7/1/01-7/1/02	N/A	30% (30%)	20% size 30% count (N/A)	70% (70%)
Number, surface area, and volume distribution	TSI APS	CMU	10 min	Continuous	7/1/01-7/1/02	N/A	30% (30%)	10% size 30% count (N/A)	28% (70%)
Surface area distribution	Epiphaniometer	PSI	30 min	Semi-continuous	6/11/01-9/18/01	N/A	- (30%)	N/A	- (70%)
Aerosol Characteristics									
Light scattering	Optec NGN-3 nephelometer	CMU	10 min	Continuous	7/16/01-6/30/02	N/A	- (T/D)	- (T/D)	- (T/D)
Hygroscopicity	CMU DAASS	CMU	1 hr	Semi-continuous	7/1-8/31/01, 1/1-7/1/02	N/A	30% (T/D)	20% size 30% count (T/D)	70% (T/D)
Cloud condensation behavior	DH Associates M1 CCN	CMU	4 hr	Semi-continuous	9/01	N/A	- (T/D)	- (T/D)	- (T/D)

Observable	Method [1]	Group [2]	Resolution	Frequency	Period of Operation [3]	MDL [4] DQI and (DQO)	Precision [4] DQI and (DQO)	Accuracy [4] DQI and (DQO)	Completeness [4] DQI and (DQO)
Aerosol chemical composition									
PM_{10} inorganic ions	CMU Speciation sampler/ IC	CMU	24 hr	Daily	7/1/01-7/21/02	- (0.1 μg/m^3)	- (20%)	- (15%)	- (70%)
$PM_{2.5}$ inorganic ions	CMU Speciation sampler/ IC	CMU	24 hr	Daily	7/1/01-12/31/01	0.01-0.5 μg/m^3 (0.1 μg/m^3)	6.2-59.4% (20%)	-5.6 to +.1% (15%)	53-77% (70%)
$PM_{2.5}$ inorganic ions	CMU Speciation sampler/ IC	CMU	24 hr	Daily	1/1/02-7/21/02	0.02-0.37 μg/m^3 (0.1 μg/m^3)	6.3-42.1% (20%)	-1.9 to-5.7% (15%)	65-79% (70%)
$PM_{2.5}$ inorganic ions	CMU Speciation sampler/ IC	CMU	4-6 hr	5 per day	ESP01 Intensive	0.03-0.62 μg/m^3 (0.1 μg/m^3)	6.2-59.4% (20%)	-5.6 to +.1% (15%)	53-77% (70%)
$PM_{2.5}$ inorganic ions	BYU PC-BOSS	BYU	4-6 hr	5 per day	ESP01 Intensive	0.05 μg/m^3(SO_4) (T ?D)	8% (T/D)	8% (T/D)	77% (T/D)
PM_x inorganic ions	MOUDI sampler/IC	ADI	24 hr	Daily	7/1/01-7/1/02 *	0.01-0.67 μg/m^3 (0.1 μg/m^3 PS)	5% (20% PS)	- (20% PS)	78% (70%)
$PM_{2.5}$ nitrate	R&P 8400N (ICVC)	ADI	10 min	Semi-continuous	7/1/01-8/1/02	0.16 μg/m^3 (1.0 μg/m^3)	19.5% (10%)	3.1% (25%)	89% (85%)
$PM_{2.5}$ sulfate	R&P 8400S (ICVC)	CMU	10 min	Semi-continuous	7/1/01-9/1/02	0.96 μg/m^3 (1.0 μg/m^3)	20.9% (10%)	-8.1% (25%)	83% (85%)
$PM_{2.5}$ water soluble anions	CMU Steam sampler/IC	CMU	1-2 hrs	Semi-continuous	7/1/01-9/21/02	0.02-0.18 μg/m^3 (0.2 μg/m^3)	15% (10%)	-8% (20%)	87% (70%)
$PM_{2.5}$ water soluble cations	CMU Steam sampler/IC	CMU	1-2 hrs	Semi-continuous	7/1/01-9/21/02	0.17-0.19 μg/m^3 (0.2 μg/m^3)	15% (10%)	-17% (20%)	86% (70%)
$PM_{2.5}$ water soluble NH_4^+	CMU Steam sampler/OAD		10 min	Continuous	7/1/01-9/21/02	- (T/D)	- (T/D)	- (T/D)	- (T/D)
PM_{10} elements	Hi-Vol sampler/ICPMS	CMU	24 hr	Daily	7/12/01-8/02/02	- (0.1 μg/m^3)	- (20%)	- (20%)	- (70%)
$PM_{2.5}$ elements	Hi-Vol sampler/ICPMS	CMU	24 hr	Daily	7/11/01-9/30/02	- (0.1 μg/m^3)	- (20%)	- (20%)	- (70%)
$PM_{1.3}$ elements	UMD SEAS/GFAA	UMD	30 min	Semi-continuous	7/8-8/10/01, 3/29-4/17/02	0.12-7.2 ppb (T/D)	5-10% (T/D)	10-15% (T/D)	(70%)100% (T/D)
PM_x elements	MOUDI sampler/ICPMS	CMU	24 hr	Daily	ESP01, 02 Intensives *	- (0.1 μg/m^3 PS)	- (20% PS)	- (20% PS)	- (70%)

Observable	Method [1]	Group [2]	Resolution	Frequency	Period of Operation [3]	MDL [4] DQI and (DQO)	Precision [4] DQI and (DQO)	Accuracy [4] DQI and (DQO)	Completeness [4] DQI and (DQO)
Aerosol chemical composition									
$PM_{2.5}$ organic/elemental carbon	CMU TQQQ sampler/TOT	CMU	24 hr	Daily	7/1/01-7/31/02 *	0.17-0.53μgC/m^3 (0.5 μgC/m^3)	8% (30%)	2.3-5.7% (30%)	99% (70%)
$PM_{2.5}$ organic/elemental carbon	CMU TQQQ sampler/TOT	CMU	4-6 hr	5 per day	ESP01 Intensive	0.17-0.53μgC/m^3 (0.5 μgC/m^3)	8% (30%)	2.3-5.7% (30%)	99% (70%)
$PM_{2.5}$ organic/elemental carbon	CMU Denuder sampler/TOT	CMU	24 hr	6th day	7/1/01-6/1/02 *	0.3 μgC/m^3 (0.5 μgC/m^3)	2% (30%)	10% (30%)	75% (70%)
$PM_{2.5}$ organic/elemental carbon	CMU Denuder sampler/TOT	CMU	24 hr	Daily	ESP01, 02 Intensives	0.3 μgC/m^3 (0.5 μgC/m^3)	2% (30%)	10% (30%)	95% (70%)
$PM_{2.5}$ organic/elemental carbon	BYU PC-BOSS	BYU	4-6 hr	5 per day	7/9/01-7/29/01	0.05 μgC/m^3 (0.1 μgC/m^3)	8% (5%)	8% (5%)	77% (70%)
$PM_{2.5}$ organic/elemental carbon	SLCarbon (TOT) analyzer	RU	2-4 hr	Semi-continuous	7/1/01-9/1/02	- (0.3 μgC/m^3)	- (10%)	- (10%)	- (70%)
PM_x organic/elemental carbon	MOUDI/TOT	CMU	24 hr	Daily	ESP01, 02 Intensives *	.12-.21 μgC/m^3 (0.5 μgC/m^3PS)	8% (30% PS)	2.3-5.7% (30% PS)	66% (70%)
PM_x organic/elemental carbon	MOUDI/TOT	CMU	8 hr	3 per day	7/22-25/01, 7/31-8/3/01	- (0.5 μgC/m^3PS)	- (30% PS)	- (30% PS)	- (70%)
$PM_{2.5}$ speciated organics	Organic sampler/GC-MS	FIU	24 hr	6th day	7/1/01-7/1/02 *	- (T/D)	- (T/D)	- (T/D)	- (T/D)
$PM_{2.5}$ speciated organics	Organic sampler/GC-MS	FIU	24 hr	Daily	ESP01, 02 Intensives	- (T/D)	- (T/D)	- (T/D)	- (T/D)
PM_x speciated organics	LPI/FTIR	RU	24 hr	Daily	ESP01, 02 Intensives	- (T/D)	- (T/D)	- (T/D)	- (T/D)
$PM_{2.5}$ biological material	Epi-fluorescent microscopy with assays	UColo	24 hr	Daily	7/7/01-7/1/02	- (T/D)	- (T/D)	- (T/D)	- (T/D)
$PM_{2.5}$ fog composition	Collector/IC/TOC/pH	CSU	Per event	8 events	7/1/01-9/1/02	1.3-27.9μM (T/D)	0.5-6.7% (T/D)	1-19.6% (T/D)	100% (T/D)
$PM_{1.0}$ size resolved composition	Aerodyne Mass Spectrometer (AMS)	UCB, Aerodyne	5 min	Semi-continuous	9/6/02-9/21/02	- (T/D)	- (T/D)	- (T/D)	- (T/D)
Single Particle Chemical Composition									
Polar organics	RSMS-III	UCD,UD	10 min	Semi-continuous	9/20/01-10/1/02	- (T/D)	- (T/D)	- (T/D)	- (T/D)
Ion composition	RSMS-III	UCD,UD	10 min	Semi-continuous	9/20/01-10/1/02	- (T/D)	- (T/D)	- (T/D)	- (T/D)
Particle morphology	Nuclepore filter/SEM	RJL	24 hr	Daily	ESP01, 02 Intensives	- (T/D)	- (T/D)	- (T/D)	- (T/D)

Observable	Method [1]	Group [2]	Resolution	Frequency	Period of Operation [3]	MDL [4] DQI and (DQO)	Precision [4] DQI and (DQO)	Accuracy [4] DQI and (DQO)	Completeness [4] DQI and (DQO)
Gaseous Species									
Light (C_2-C_{12}) hydrocarbons	Canister/GC-FID	CMU	24 hr	3rd day	9/1/01-7/31/02 *	0.0-0.25 μg/m^3 (T/D)	33% (T/D)	20% (T/D)	65% (T/D)
Light (C_2-C_{12}) hydrocarbons	Canister/GC-FID	CMU	24 hr	Daily	ESP02 Intensive	- (T/D)	- (T/D)	- (T/D)	- (T/D)
Total peroxides	CSU Monitor	CSU	1 hr	Continuous	7/1/01-9/1/02	0.09 ppbv (0.2 ppbv)	2.8% (20%	-2.2% (20%)	94% (70%)
O_3	API 400A	CMU	10 min	Continuous	7/1/01-9/1/02	0.14 ppbv (0.6 ppbv)	1.7% (10%)	1.1% (10%)	95% (80%)
NO and NO_x	API 200A	CMU	10 min	Continuous	7/1/01-9/1/02	0..39 ppbv (0.4 ppbv)	2.3% (10%)	1.2% (10%)	90% (80%)
SO_2	API 100A	CMU	10 min	Continuous	7/1/01-9/1/02	0.34 ppbv (0.4 ppbv)	6.9% (10%)	-0.8% (10%)	94% (80%)
CO	API 300	CMU	10 min	Continuous	7/1/01-9/1/02	0.1 ppmv (0.4 ppmv)	1.1% (10%)	1.1% (10%)	94% (80%)
Inorganic gases	CMU Speciation sampler/ IC	CMU	24 hr	Daily	7/1/01-7/1/02 *	- (0.5 μg/m^3)	- (30%)	- (30%)	- (70%)
Inorganic gases	CMU Speciation sampler/ IC	CMU	4-6 hr	5 per day	ESP01 Intensive	- (0.5 μg/m^3)	- (30%)	- (30%)	- (70%)
Water soluble inorganic gases	CMU Steam sampler/ IC	CMU	1-2 hr	Semi-continuous	7/1/01-9/21/02	0.02-0.19 μg/m^3 (0.2 μg/m^3)	15% (10%)	86% (20%)	- (70%)

Observable	Method [1]	Group [2]	Resolution	Frequency	Period of Operation [3]	MDL [4] DQI and (DQO)	Precision [4] DQI and (DQO)	Accuracy [4] DQI and (DQO)	Completeness [4] DQI and (DQO)
Hydrocarbons	UC Online GC-FID/MS	UCB	1 hr	Semi-continuous	1/9-2/12, 7/10-8/10/02				
1-butene						1.0 ppt	2%	7%	96.5%
1-methylcyclopentene						0.7 ppt	2%	7%	99.2%
1-pentene						0.8 ppt	2%	7%	96.5%
2-methyl-1-butene						0.8 ppt	2%	7%	96.5%
2-methylpropene						1.0 ppt	2%	7%	96.5%
3-methyl-1-butene						0.8 ppt	2%	7%	96.5%
3-methylfuran						2.2 ppt	6%	8%	99.2%
acetone						47.3 ppt	4%	7%	96.1%
alpha pinene						1.1 ppt	13%	14%	96.0%
benzene						25.6 ppt	7%	9%	96.3%
butanol						27.6 ppt	6%	8%	99.1%
butane						1.0 ppt	2%	7%	96.5%
c-2-butene						1.0 ppt	2%	7%	96.5%
perchloroethylene						0.6 ppt	6%	9%	96.3%
c-2-pentene						0.8 ppt	2%	7%	99.2%
dichloromethane						33.9 ppt	12%	14%	99.2%
acetaldehyde						82.2 ppt	9%	11%	94.0%
acetonitrile						38.1 ppt	13%	14%	96.7%
chloroform						1.0 ppt	4%	7%	96.2%
cyclopentane						0.8 ppt	2%	7%	96.5%
cyclopentene						0.8 ppt	2%	7%	99.2%
dimethylsulfide						3.2 ppt	6%	8%	99.2%
ethylbenzene						1.6 ppt	6%	9%	96.3%
ethanol						15.7 ppt	15%	17%	90.8%
hexane						0.7 ppt	2%	7%	96.5%
isopropanol						22.8 ppt	13%	15%	91.1%
isobutane						1.0 ppt	2%	7%	96.5%
isopentane						0.8 ppt	2%	7%	96.5%
isoprene						0.8 ppt	2%	7%	99.2%
methacrolein						11.3 ppt	6%	8%	99.2%

Observable	Method [1]	Group [2]	Resolution	Frequency	Period of Operation [3]	MDL [4] DQI and (DQO)	Precision [4] DQI and (DQO)	Accuracy [4] DQI and (DQO)	Completeness [4] DQI and (DQO)
Hydrocarbons	UC Online GC-FID/MS	UCB	1 hr	Semi-continuous	1/9-2/12, 7/10-8/10/02				
methyl ethyl ketone						10.2 ppt	9%	11%	96.3%
methanol						372.9 ppt	15%	17%	88.0%
methylpentanes						0.7 ppt	2%	7%	96.5%
methyl-t-butyl ether						1.7 ppt	4%	7%	96.3%
methyl vinyl ketone						6.8 ppt	5%	8%	99.2%
m-xylene						5.3 ppt	6%	9%	96.3%
o-xylene						2.4 ppt	18%	20%	96.1%
pentanal						19.3 ppt	9%	11%	99.1%
pentane						0.8 ppt	2%	7%	96.5%
propane						1.4 ppt	2%	7%	96.5%
propene						1.3 ppt	2%	7%	96.5%
propyne						1.3 ppt	2%	7%	96.5%
p-xylene						3.4 ppt	6%	9%	96.3%
t-2-butene						1.0 ppt	2%	7%	96.5%
t-2-pentene						0.8 ppt	2%	7%	96.5%
toluene						22.3 ppt	4%	7%	96.5%

Observable	Method [1]	Group [2]	Resolution	Frequency	Period of Operation [3]	MDL [4] DQI and (DQO)	Precision [4] DQI and (DQO)	Accuracy [4] DQI and (DQO)	Completeness [4] DQI and (DQO)
Meteorology									
Wind speed	MetOne 014A	CMU	10 min	Continuous	7/1/01-9/1/02	0.5 m/s (N/A)	- (10%)	- (10%)	99% (80%)
Wind direction	MetOne 014A	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Temperature	Campbell HMP45C	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Relative Humidity	Campbell HMP45C	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Pressure	Campbell CS105	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Precipitation	MetOne 370	CMU	10 min	Continuous	7/1/01-9/1/02	0.254 mm (N/A)	- (10%)	- (10%)	99% (80%)
UV Radiation	Kipp&Zonen CUV3	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)
Solar Radiation	Kipp&Zonen CM3	CMU	10 min	Continuous	7/1/01-9/1/02	N/A	- (10%)	- (10%)	99% (80%)

1 Methods – ADI: Aerosol Dynamics Inc.; APS: Aerodynamic Particle Sizer; BYU: Brigham Young University; CMU: Carnegie Mellon University; CSU: Colorado State University; FRM: Federal Reference Method; FTIR: Fourier Transform Infrared Spectrometry; Grav: Gravimetry; IC: Ion Chromatography; ICPMS: Inductively Coupled Plasma Mass Spectrometry; ICVC: Integrated Collection and Vaporization Cell; LPI: Low Pressure Impactor; GC-FID: Gas Chromatography with Flame Ionization Spectroscopy; GC-MS: Gas Chromatography with Mass Spectroscopy; GFAA: Graphite Furnace with Atomic Absorption; OAD: Online Ammonium Detector; R&P: Rupprecht and Patashnick, Co.; RSMS: Rapid Single particle Mass Spectrometer; SEAS: Semi-continuous Environmental Aerosol Sampler; SEM: Scanning Electron Microscopy; SL: Sunset Labs; SMPS: Scanning Mobility Particle Sizer; TEOM with SES: Tapered Element Oscillating Microbalance with a Sample Equilibration System; TOC: Total Organic Carbon; TOT: Total Optical Transmittance; UCB: University of California at Berkeley; UCD: University of California at Davis.

2 Groups – ADI: Aerosol Dynamics, Inc.; BYU: Brigham Young University; CMU: Carnegie Mellon University; CSU: Colorado State University; FIU: Florida International University; PSI: Paul Scherrer Institute; RJL: R. J. Lee Instruments, RU: Rutgers University; UC: University of California at Berkeley; UCB: University of Colorado at Boulder; UCD: University of California at Davis; UD: University of Delaware; UMD: University of Maryland.

3 Period of operation – ESP01 Intensive: July 1, 2001 – August 3, 2001; ESP02 Intensive: January 1, 2002 – January 15, 2002; *: Except during periods when samples were collected at a higher time resolution as noted in the entry below.

4 Data quality indicators and (Data quality objectives); N/A: Not applicable; T/D: To be determined; Values for MOUDIs and LPIs are per substrate (stage or filter).

2.1 Minimum detection limit (MDL)

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

Equation 1 $MDL = t_{(n-1,\ 0.99)} \bullet s$

where s is the standard deviation of the replicate zero analyses, and t is the student's t-test value for a standard deviation estimate with n-1 degrees of freedom at a 99% confidence level. 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 gas monitors, the MDL accounts for all sampling and analytical procedures and therefore represents a detection limit that can be applied to ambient concentrations. For gas monitors, MDLs were based on the response of the instruments to purified air. MDLs for filter-based or canister-based instruments were determined from field and laboratory blank tests. At PAQS, approximately 10% of all substrates (filters or canisters) 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. However, because the analytical standards used to evaluate field blank and laboratory blank substrates for filter-based or canister-based measurements are prepared and used in the laboratory, the MDL is not an ambient MDL but instead an instrument MDL.

2.2 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 PAQS 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 between the replicate analyses and {x} is the mean of the replicate analyses.

Equation 2 $Precision\ (\%) = 100\ [2\ s] / \{x\}$

2.3 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:

Equation 3 $Accuracy\ (\%) = (100 * [S - \{x\}]) / S$

where S is the standard value of the authentic traceable standard and {x} is the mean of the instrument responses to the replicate analysis.

2.4 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.

Equation. 1 Completeness (%) = (N valid measurements/total N measurements) ● 100

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 2. Comparison of methods

Observable	Methods that will be compared [a]	Methods that will not be compared [a]
PM_{10} Mass	Dichot/Gravimetry v. MOUDI/Gravimetry	-
$PM_{2.5}$ Mass	FRM/Gravimetry v. Dichot/Gravimetry, MOUDI/Gravimetry, and TEOM with SES	-
$PM_{2.5}$ plus gas Ammonium	Speciation sampler/IC v. Steam sampler/IC	RSMS-III[1,2]
$PM_{2.5}$ Nitrate	Speciation sampler/IC v. ICVC[1], and PC BOSS[2]	RSMS-III[1,2]
$PM_{2.5}$ Sulfate	Speciation sampler/IC v. ICVC[1], PC BOSS[2], and Steam sampler/IC	RSMS-III[1,2]
$PM_{2.5}$ Carbon	TQQQ sampler/TOT v. Denuder sampler/TOT and TOT carbon analyzer[1]	ICVC[1,4], RSMS-III[1,2]
$PM_{2.5}$ Elements	-	Speciation Sampler/ICPMS[6] v. LIBS[1,2,4], RSMS-III[1,2], SEAS/GFAA[1,2]
$PM_{2.5}$ Polar Organics	-	Detailed Speciation/GC-FID v. LPI/FTIR[2], RSMS-III[1,2]
Particle sizing	MOUDI/Gravimetry v. APS[3] and SMPS[3]	RSMS-III[1,2], Epiphaniometer[4]
VOCs	Canister/GC-FID v. On-line GC-FID/MS	-

[a] 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
6: Measurement analysis not completed at the time the QAFR was written.

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 already been performed by several PAQS investigators (Cabada et al., 2003a; 2003c; Rees et al., 2003; Stanier et al., 2003a; Subramanian et al., 2003; Wittig et al., 2003b).

Figure 1. Comparison of aerosol mass measurements (Cabada et al., 2003c): a) 24-hour Dichot PM_{10} mass v. 24-hour MOUDI PM_{10} mass, b) 24-hour FRM $PM_{2.5}$ mass v. 24-hour average of 5-min TEOM $PM_{2.5}$ mass, c) 24-hour FRM $PM_{2.5}$ mass v. 24-hour Dichot $PM_{2.5}$ mass, and d) 24-hour FRM $PM_{2.5}$ mass v. 24-hour MOUDI $PM_{2.5}$ mass. Also shown are the 1:1 lines (dashed lines).

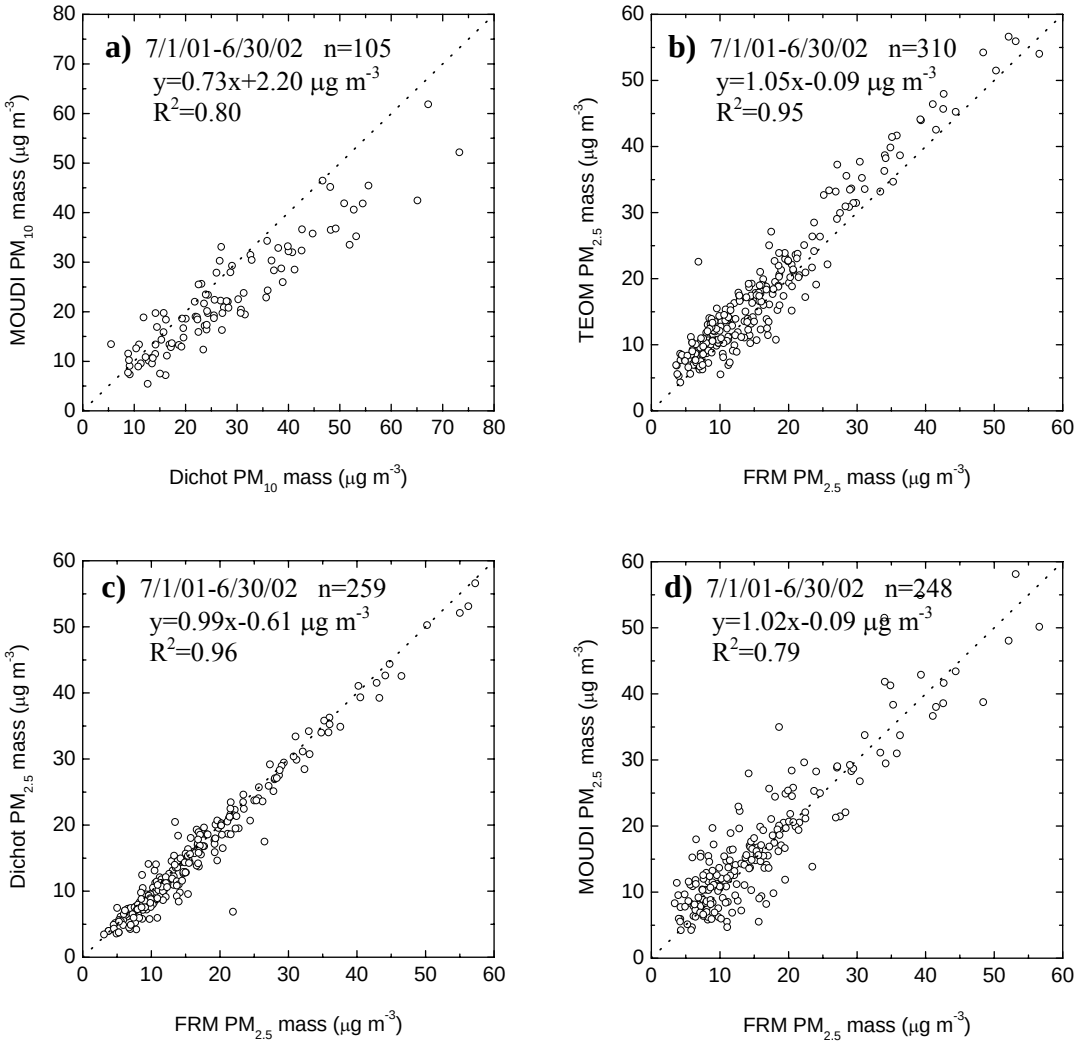


Figure 2. Comparison of $PM_{2.5}$ plus gas ammonium measurements: a) 24-hour average of July 2001 4-hour and 6-hour speciation sampler and 24-hour speciation sampler for remaining months v. 24-hour average of 1-hour or 2-hour steam sampler. Also shown is the 1:1 line (dashed line).

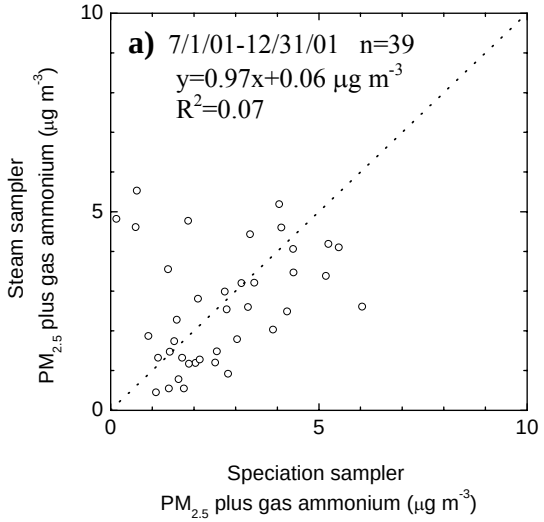


Figure 3. Comparison of $PM_{2.5}$ nitrate measurements (Wittig et al., 2003a): a) 24-hour average of July 2001 4-hour and 6-hour speciation sampler and 24-hour speciation sampler for remaining months v. 24-hour average of 1-hour R&P 8400N and b) 24-hour average of July 2001 4-hour and 6-hour speciation sampler v. 24-hour PCBOSS. Also shown are the 1:1 lines (dashed lines).

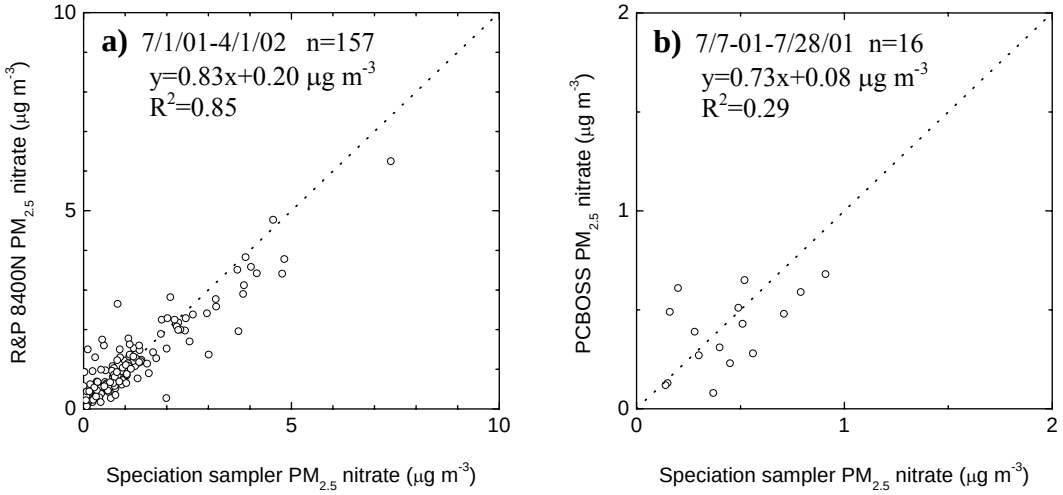


Figure 4. Comparison of $PM_{2.5}$ sulfate measurements (Wittig et al., 2003a): a) 24-hour average of July 2001 4-hour and 6-hour speciation sampler and 24-hour speciation sampler for remaining months v. 24-hour average of 1-hour or 2-hour steam sampler/IC, b) 24-hour average of July 2001 4-hour and 6-hour speciation sampler and 24-hour speciation sampler for remaining months v. 24-hour average of 1-hour R&P 8400N, and c) 24-hour average of July 2001 4-hour and 6-hour speciation sampler v. 24-hour PCBOSS. Also shown are the 1:1 lines (dashed lines).

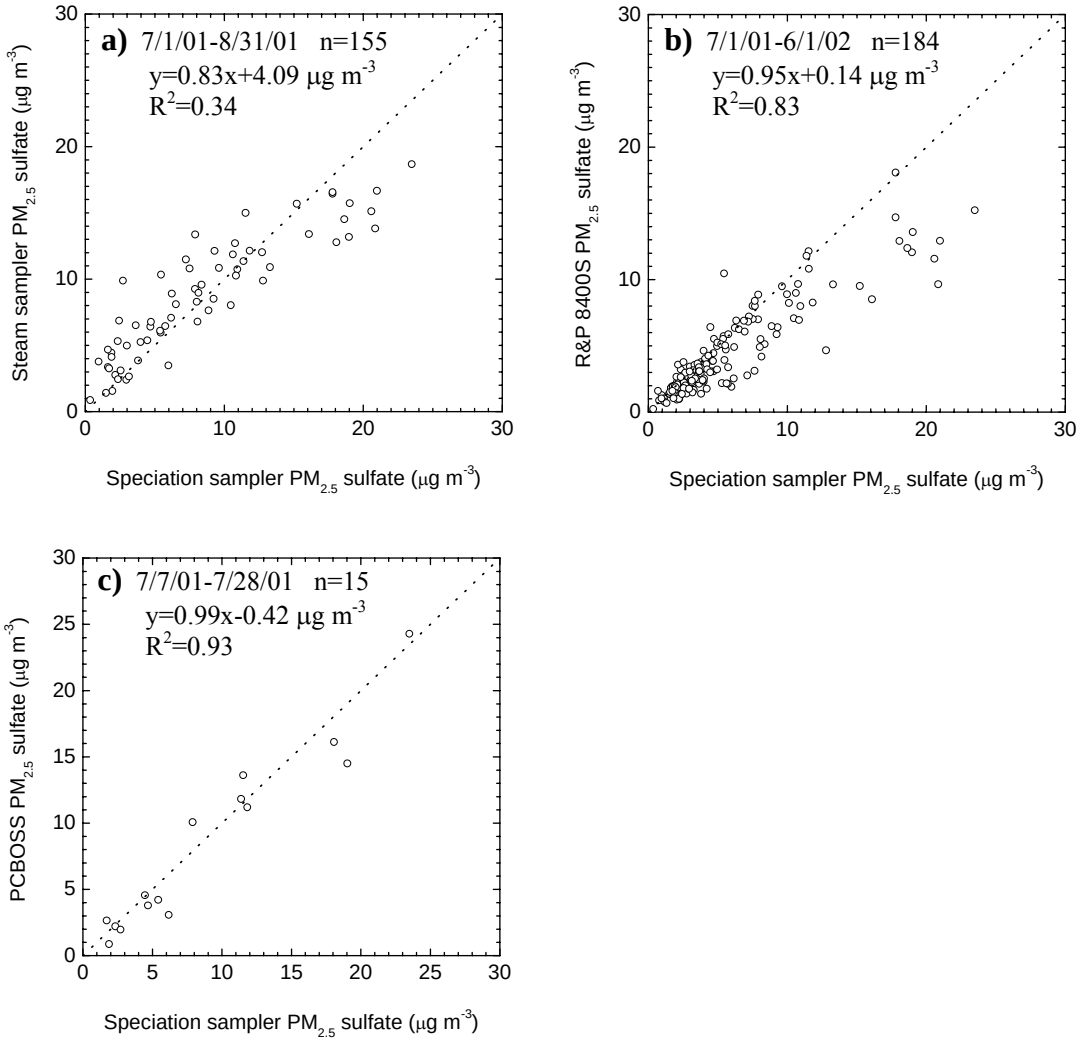


Figure 5. Comparison of $PM_{2.5}$ organic carbon measurements: a) 24-hour TQQQ sampler v. 1-in-6 day 24-hour Denuder sampler, b) 24-hour TQQQ sampler v. 24-hour average of 2-hour to 4-hour TOT carbon analyzer. Also shown are the 1:1 lines (dashed lines).

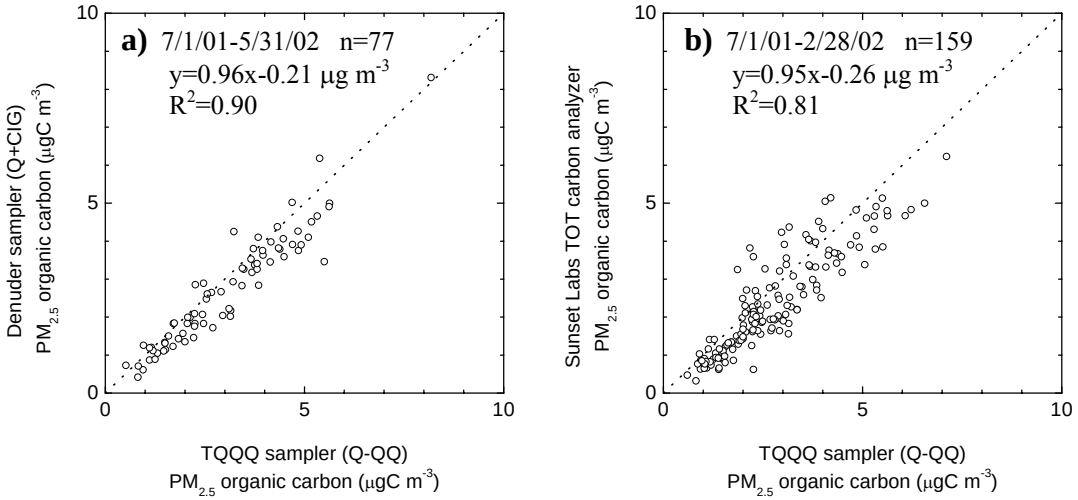


Figure 6. Comparison of $PM_{2.5}$ elemental carbon measurements: a) 24-hour TQQQ sampler v. 24-hour Denuder sampler, b) 24-hour TQQQ sampler v. 24-hour average of 2-hour to 4-hour TOT carbon analyzer. Also shown are the 1:1 lines (dashed lines).

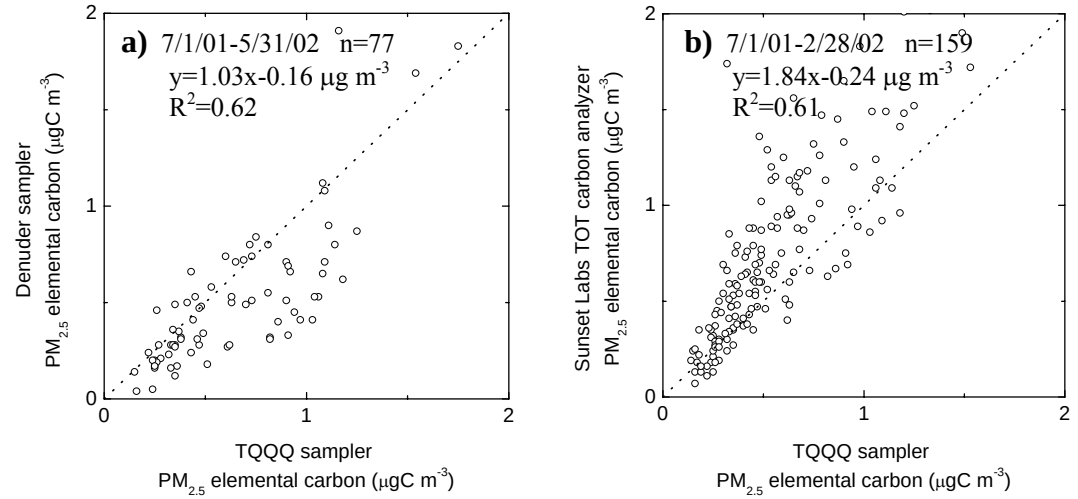


Figure 7. Comparison of the geometric mean of the aerosol diameter: 24-hour MOUDI sampler v. 24-hour average of 5-minute SMPS measurements. Also shown is the 1:1 line (dashed line).

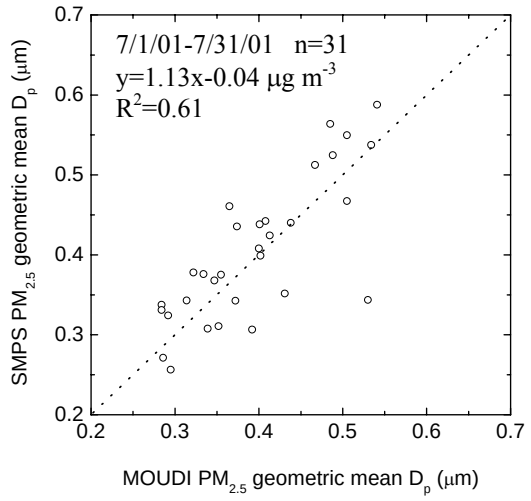
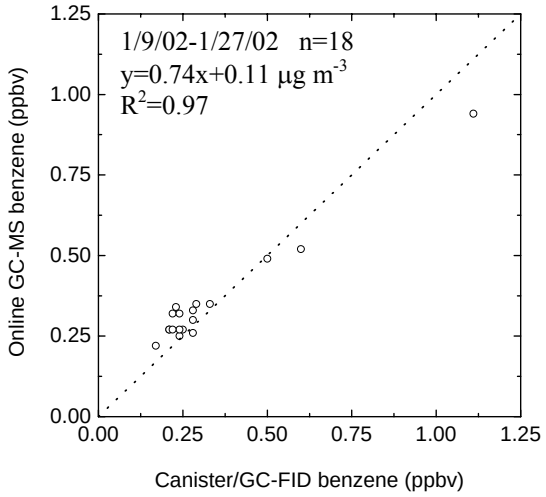


Figure 8. Comparison of gas-phase benzene measurements: 24-hour Canister sample with GC-FID analysis v. 24-hour average of 1-hour Online GC-MS measurements. Also shown is the 1:1 line (dashed line).



Overall, the select methods compare reasonably. In a few instances, best estimate data sets were produced to address the QA concerns of these methods ($PM_{2.5}$ 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 is located in Schenley Park in the Oakland district of Pittsburgh. The site is on top of a grassy hill adjacent to the CMU campus, several hundred meters from the nearest heavily traveled street (Forbes Avenue), and fifty meters past the end of a dead end street on campus. There are no major sources within several hundred meters of the site. Schenley Park extends more than a kilometer

to the south and west, the predominant upwind directions. The exposure of the surrounding environs represents both an 'urban' and 'neighborhood' scale for particle monitoring.

2.7 Data Quality Objectives Not Met During PAQs

In a few instances, the data quality objectives were not met at PAQS. Typically, these instances were associated with newly developed instrumentation that did not perform as well as expected, and are summarized in Table 3. When possible, best estimate data sets were produced to address the QA concerns of these measurements ($PM_{2.5}$ 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 3. Observables for which the DQI did not meet the DQO at PAQS.

Observable	**Method**	**Issue**
Number, surface area, and volume distribution	TSI APS	Data completeness - The instrument broke during fall of 2001 and was not repaired and returned by the manufacturer until March of 2002.
PM_{10}, $PM_{2.5}$, and PM_x mass	FRM, Dichot, and MOUDI samplers/ Gravimetry	MDL – Table 1 shows the MDL DQO as 2 $\mu g/m^3$ for FRM, Dichot and MOUDI samplers. The DQOs for these instruments were erroneously reported as 0.2 $\mu g/m^3$ in the QAPP.
$PM_{2.5}$ nitrate and sulfate	R&P 8400N/S (ICVC)	Precision - The DQOs were overly optimistic, given the fact that these instruments were newly commercialized. In actuality, the instruments were less precise than expected. However, a rigorous quality control plan allowed these issues to be tracked over the course of the study (Wittig et al., 2003b).
$PM_{2.5}$ sulfate	R&P 8400S (ICVC)	Data completeness - The instrument experienced more frequent malfunctions than expected (typically strip breakage) as well as a fatal error a month before the end of the study.
PM_{10} and $PM_{2.5}$ elements	Hi-Vol sampler/ICPMS	MDL, precision, accuracy, data completeness - measurements were not finalized by the time this report was compiled.
$PM_{2.5}$ water soluble NH_4^+	CMU Steam sampler/OAD	MDL, precision, accuracy, data completeness - measurements were not finalized by the time this report was compiled.
PM_{10} and $PM_{2.5}$ inorganic ions	CMU Speciation sampler/IC	MDL, precision, accuracy, data completeness - PM_{10} measurements were not finalized by the time this report was compiled. Precision - NH_3 gas was present in extremely low concentrations so the DQO was not achieved. Completeness – $PM_{2.5}$ sampler malfunction as well as loss or destruction of samples prior to analysis were responsible for recovery levels below DQOs for all species, except SO_4 which met the DQO.

Observable	Method	Issue
Size segregated chemistry: inorganic ions, EC/OC	MOUDI/IC,TOT	MDL – Calcium had a high MDL due to instrument problems; all other inorganic ions achieved the DQO. Accuracy – No accuracy was determined for the inorganic analyses due to lack of an absolute standard. Completeness – Instrument problems for the EC/OC analyses resulted in 66% completeness, below the 70% target DQO.
PM2.5 total carbon	ADI Carbon analyzer (ICVC)	MDL, precision, accuracy, data completeness – Data will not be submitted due to instrument difficulties.
Light hydrocarbons (C1-C12)	Canister/GC-FID	MDL, precision, accuracy, data completeness – Measurements for ESP02 Intensive (sampling once daily) not yet finalized by the time this report was compiled.
Meteorology	All methods	MDL, precision, accuracy - The standard operating procedures (and manufacturer recommended procedures) did not allow these DQIs to be calculated.

3. Conclusions

- A majority of the data quality indicators showed the PAQS central site instruments performed as expected or better.
- In a few instances, PAQS central site instruments could not be evaluated because the data were not finalized by the time this report was produced ($PM_{2.5}$ water soluble NH_4^+ using the CMU Steam sampler/IC and PM_{10} and $PM_{2.5}$ elements using the Hi-Vol sampler/ICPMS).
- 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 to address the QA concerns of these measurements ($PM_{2.5}$ sulfate, nitrate, and ammonium).

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Wittig, B., Takahama, S., Khlystov, A., Pandis, S. N., Hering, S., Kirby, B., Davidson, C., 2003b. Semi-continuous $PM_{2.5}$ inorganic composition measurements during the Pittsburgh Air Quality Study. Submitted to Atmospheric Environment.

A1.1 Meteorology measurements

A1.1.1 CMU meteorology sensors; Audited with Wei Tang on 2/12/2002

Performance summary:

- No checks were appropriate.

Performance observations:

- Temperature, Relative humidity, Pressure, and Radiation sensors will need to be recalibrated at the factory before the end of the study. Wei should arrange this ahead of time to minimize the measurement-loss.

Performance issues and recommendations:

- The leveling of the CM3 Pyranometer and CUV3 UV Radiometer, and orientation of the 014A Wind Speed Sensor are to be checked on a monthly basis, according to the SOP. These checks have not been rigorously performed since the initial installation. They should be rigorously checked this month to be sure there is no change in leveling or orientation. If no changes are observed, the frequency of this QC activity can be changed to semiannual. If changes are observed, this activity needs to be performed on schedule and the prior data needs to be reprocessed and flagged.

  Response (March 6, 2002):

  I have performed the tasks mentioned in the audit report with the met station. It seemed that leveling of the CM3 Pyranometer and CUV3 UV Radiometer has been fine after all kinds of weather conditions. We can changed the frequency of leveling check from monthly to semiannual. However, the wind direction sensor's orientation needs to be checked more rigorously from monthly to weekly. I have added an addendum in the SOP to address the problem. The wind direction data will have to be reprocessed and flagged. Please flag the data between 5pm-6:30pm on March 6, during which I did the check.

SOP recommendations:

- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have an impact on the measurements.
- Check that the SOP states the minimum frequency of each QC activity.

  Response (March 6, 2002):

  SOP is completed.

A1.2 Particle sizing measurements

A1.2.1 CMU SMPS/APS instruments; Audit with Charlie Stanier on 2/11/2002

Performance summary:

- Flow checks: All checks were performed with Charlie using Gilibrator

Component	Target flow	Actual flow	Acceptable?
NDMA	7.01 LPM	7.54 LPM	No, 7.6% high
LDMA	3.2 LPM	3.27 LPM	Yes
Inlet	2.5 LPM	2.45 LPM	Yes

- Leak tests: All checks were performed with Charlie using a HEPA filter at the inlet

Component	Target counts	Actual counts	Acceptable?
NDMA	0 particle/cc	0 particle/cc	Yes
LDMA	0 particle/cc	1 particle/cc	Yes

Performance observations:

- Labview sometimes freezes, stopping data acquisition. However, it has worked fine for the past 1.5 months. Charlie checks for this on a daily basis.
- Compressor has needed to be replaced a few times since July intensive. There are usually warning signs well before the compressor dies, so this is not a serious QA problem.

Performance issues and recommendations:

- Investigate reason for NDMA flow rate discrepancy with indicated value. This discrepancy is surprising since the unit was calibrated only a week earlier. Account for flow rate discrepancy in calculating particle sizes for data obtained in the past week.

  Response (March 6, 2002):

  Have continued to have unpredictable flow problems with the NDMA sheath system, probably due to a deteriorating sheath blower, which failed on 3/5/02 (this was not identified as the root cause until 3/5/02). A replacement blower was ordered 3/4/02. The following actions were taken to troubleshoot sheath flow performance:
  - *2/12/02. Sheath air system not reaching 7.0 LPM setpoint. Diffusion dryer removed from system to reduce pressure drop.*
  - *2/13/02. Blower currents required to obtain 7.0 LPM noted in log to compare against previous (and anticipated future checks).*
  - *2/15/02. Replaced PD-200T Nafion dryer in sheath air loop with a brand new dryer. Negligible change in pressure drop. Visual inspection showed old dryer had little or no fouling.*
  - *2/15/02. Sheath flow rate checked at blower (usual procedure) giving 6.99-7.02 LPM and flow check inline at classifier, giving 7.10-7.11 LPM. Based on this information, no changes to data or blower calibration done (as recommended based on 2/11 test and audit). However, data quality statement for February will note that NDMA sheath flow is more variable than previous months, running 7.0 ± 0.6 LPM.*
  - *3/3/02. Blowers nearly at 100% capacity to reach 7.0 LPM flow during dry scans.*
  - *3/4/02. Replacement blower ordered.*
  - *3/5/02. Sheath blower failed.*
  - *3/6/02. System put online without drying system (for lower pressure drop). Operating on bypass blower only with bypass flow rate. Flow checked with Gilibrator = 7.0 ± 0.2 LPM. (bypass blower alone is inherently more noisy than usual "dual blower" control due to differential pressure control rather than mass flow meter).*
  - *Plan to restore system to original performance as of 3/6/02, by installing a new sheath blower and larger fittings on diffusion dryer to lower pressure drop.*
- Computer clock slowly loses time, necessitating occasional updates. The computer clock time should be checked against naval time weekly. A criterion for time accuracy of less than 5 mins off is recommended, since the time resolution of the measurements is 7 mins.

  Response (March 6, 2002):

  Computer clock being inspected every 2 days. Adjusted if out of sync by 2 min or more.
- Laser on CPC 3010 has had a noisy signal on occasion. Since the last repair, the laser noise has not been checked. Check the laser for noise multiple times in next month to establish that this problem is fully resolved.

  Response (March 6, 2002)

  Checked several times. Operating well. Noise level < 1% of value prior to repair.

- Instrument ran out of butanol yesterday. This is most likely due to increased consumption during high concentration episodes (as experienced over the weekend). When particle concentrations are high, butanol levels should be checked more frequently than usual.

  Response (March 6, 2002):

  Butanol being filled once per two days. Butanol bottle being left attached to CPC longer to allow saturator block to absorb more butanol.
- Instruments were calibrated with PSL at the beginning of the Supersite sampling, but not since then. Determine whether calibration with PSL is necessary every six months, as written in SOP. If it is, perform the required calibrations. If not, justify why not.

  Response (March 6, 2002):

  PSL calibration will be performed in March or April of 2000.

SOP recommendations:

- Integrate a current system flow diagram into the SOP.
- Clarify the numerical criteria for 'negligible' leaks, 'satisfactory' flow rates, and 'acceptable' computer clock time error. Include frequencies of various QC activities.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

  Response (March 6, 2002):

  All SOP recommendations are in the process of being written.

A1.2.2 CMU SMPS/APS instruments; Follow-up Audit with Charlie Stanier on 8/6/2002

Performance summary:

- Flow checks: All checks were performed with Charlie using Gilibrator

Component	Target flow	Actual flow	Acceptable?
NDMA (amb RH)	7.01 LPM	7.17 LPM	Yes
NDMA (dry)	7.01 LPM	7.16 LPM	Yes
LDMA	3.2 LPM	not performed	---
Inlet	2.5 LPM	not performed	---

- Leak tests: All checks were performed with Charlie using a HEPA filter at the inlet

Component	Target counts	Actual counts	Acceptable?
NDMA	0 particle/cc	0 particle/cc	Yes
LDMA	0 particle/cc	<1 particle/cc	Yes
APS	0 particle/cc	0 particle/cc	Yes

- LDMA Ambient RH channel showed 4 particles for entire scan, Dry channel showed 11 particles for entire scan. These values correspond to <1 particle/cc.
- PSL checks using ammonium sulfate were performed by Charlie on a separate date:
  - LDMA sizing 155 nm PSL at 151-157 nm in both ambient and dry modes.
  - NDMA and LDMA sizing of monodisperse ammonium sulfate agrees to within ± 4%.
  - NDMA and LDMA counting agrees to within about 10%.
  - LDMA counting agrees to within about 10% of stand-alone CPC.
  - APS counting and sizing agrees with LDMA to within about 20%, after APS recalibrated to PSL and monodisperse ammonium sulfate. Note: APS redeployed after major factory upgrade on 5/6/02. Factory calibration used from 5/6/02 – 6/12/02. However, PSL checks on 6/12/02 showed APS was giving 1.60 – 1.71 μm response for PSL when 2.06 μm response was expected.

Performance observations:

- The small number of particle counts during the leak tests show that leakage is negligible – normally, the full-scale response is about 1000 particles for a full scan on the LDMA (compared with 4 particles and 11 particles, above), and about 30 particles/cc on the NDMA (compared with 0 particles, above). The APS records about 900 particles per 30 second scan (compared with 0 particles, above).
- The flow problems in the February 11, 2002 audit appear to have been resolved.
- There were 11 software/data acquisition problems since February 2002, typically resulting in large (3-9 hour) gaps in the measurements.
- PSL experiments showed excellent sizing of LDMA, NDMA, and acceptable sizing of APS.

Performance issues and recommendations:

- None

A1.2.3 CMU MOUDI sampler; Audited with Sarah Rees on 2/12/2002

Performance summary:

- No checks were performed on the MOUDIs at the time of the audit because an adaptor was not available for checks of MOUDI B at the inlet and because MOUDI C was not at the site.
- Sarah will perform checks on the MOUDIs in the Mech E Lab and report her results.

Component	Target flow	Actual flow	Acceptable?
MOUDI B	30 LPM at 21 in H_2O	24 LPM at 21 in H_2O	No
MOUDI C	30 LPM at 21 in H_2O	29.6 LPM at 21 in H_2O	Yes

Performance observations:

- MOUDI B is operating below the setpoint, and cannot be used until the problem is rectified.

Performance issues and recommendations:

- MOUDI B should be repaired before being used for field sampling again. Flows and pressures should be checked through the physical inlet before the sampler is considered to be online again.
  Response (March 7, 2002):
  After checking the pump and ensuring there were no leaks in the system, it was discovered that a considerable amount of dirt had built up in the nozzle plates of the upper stages. These plates were cleaned; since then MOUDI B has ran at setpoint.
- MOUDI C should be used for sampling until MOUDI B is back online. Flows and pressures should be checked through the physical inlet before the sampler is considered to be online.
- The rain hat on MOUDI shelter is rusty and should be replaced within a week.

SOP recommendations:

- The changes in pressure drop across the lower stages of the MOUDI are indicators of potential problems, but this was not realized until August. The SOP should include an Addendum regarding how the changes in flow rates were used to diagnose problems beginning in August.
- Include an Addendum in the original SOP describing and dating any other procedural or data quality objective changes that have had an impact on the measurements.
  Response (March 7, 2002):
  SOP will be updated to include checking for dirt accumulation in the upper nozzle plates.

A1.2.4 CMU MOUDI sampler; Follow-up Audit with Sarah Rees on 9/11/2002

Performance summary:

- Flow/leak checks: Checks were performed by Sarah at the site.

Component	Target flow/vacuum	Actual flow/vacuum	Acceptable?
MOUDI	30 LPM at 21 in H_2O	30 LPM at 21 in H_2O	Yes

Performance observations:

- None.

Performance issues and recommendations:

- None.

A1.3 PM mass measurements

A1.3.1 CMU microbalance; Audited with Sarah Rees on 2/11/2002

Performance summary:

- Weight checks: Check was performed with Sarah using a typical reference weight

Component	Target weight	Actual weight	Acceptable?
Typical ref	100,000 μg	99,997 μg	Yes

Performance observations:

- Detailed calibration of the microbalance is performed every three months. These calibrations use pristine reference weights that are kept sealed except during these quarterly calibrations. This is a good QC practice.
- Every Dichot sample, FRM sample, and set of MOUDI filters has one field blank. There is also a lab blank run during the same weighing period. This is a good QC practice.
- A reference weight is used at the beginning of each day's weighing period; weight must be within 3 micrograms of the correct weight. This is a reasonable objective.
- Duplicate weighing of blank filters must be within 15 micrograms of each other. This replicate requirement is much smaller than a typical sample weight, which is on the order of 100 micrograms. This is a reasonable objective.

Performance issues and recommendations:

- The weighing chamber is cleaned once per week. There have been particles observed in the chamber, believed to be coming off the rubber gloves. Check occurrence of particles in the weighing chamber to determine if weekly cleaning is sufficient. Increase the frequency of the glove box cleaning as needed.
- The Automatic Humidity Control is no longer used as of approximately two months ago. Rather, desiccant is placed in the weighing chamber, and this appears to keep humidity at a constant level. Confirm that the desiccant is able to maintain the relative humidity of the box at a constant value within desired tolerances.

SOP recommendations:

- Check if SOPs for instruments that require weighing include a discussion of the blanks. Reference these other SOPs in the Weighing SOP.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements, such as Automatic Humidity Control.

  Response (March 7, 2002):

  The microbalance SOP has been checked and updated to reflect all current procedures. The technician responsible for microbalance operation has been reminded to clean the glove box weekly and ensure that no dirt accumulates.

A1.3.2 CMU Dichot sampler; Audited with Sarah Rees on 2/12/2002

Performance summary:

- Leak checks: Check was performed with Sarah using duct tape to seal the inlet.

Component	Target	Actual time	Acceptable?
Leak at inlet	25 in Hg vacuum held for >55 sec	25 in Hg vacuum held for > 60 sec	No

- Flow rate checks: Check was performed with Sarah using the Gilibrator and the audit cap.

Component	Target	Actual flow	Acceptable?
Flow at inlet	14.83 LPM	10.75 LPM (5-pt avg)	No, 27.5% low
	14.83 LPM	12.37 LPM (5-pt avg)	No, 16.6% low

Performance observations:

- The Dichot was offline because it shut itself off when rain froze in the filter. If this becomes a chronic problem, a strategy for keeping the filters dry should be developed.

Performance issues and recommendations:

- When the sampler was checked for leaks, a small leak was detected. This leak should be repaired and the sampler put online when it passes the leak check.
- The sampler failed the flow audit. It is unclear whether the small leak caused such a high degree of instability in the flow control of the sampler. The sampler experienced freezing in the lines the day before. Possibly this could explain the erratic and erroneous behavior of the sampler. This problem should be further investigated and resolved as soon as possible. Recent data collected with the Dichot should be inspected, corrected if possible, and flagged for sampler malfunction. The flow check should be repeated after the leak is repaired. If the sampler demonstrates flow stability, the sampler flow meter should be calibrated before the sampler is put back online.

Response (March 7, 2002):

The source of the leak was the o-rings surrounding the Dichot filter cartridges. These o-rings have warped over time, possibly due to accumulation of ice in the filter cartridge area. The leak has been corrected, and the Dichot rotameters recalibrated. The accumulation of ice in the Dichot will be minimized to prevent this problem in the future.

- Cyclones need to be cleaned and o-rings should be inspected quarterly at minimum.

SOP recommendations:

- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.3.3 CMU Dichot sampler; Follow-up Audit with Sarah Rees on 9/11/2002

Performance summary:

- Leak checks: Check was performed with Sarah using duct tape to seal the inlet.

Component	Target	Actual	Acceptable?
Leak at inlet	25 in Hg vacuum held for >60 sec	25 in Hg vacuum held for <50 sec	No

- Flow rate checks: Check was performed with Sarah using the Gilibrator and the audit cap.

Component	Target	Actual flow	Acceptable?
Flow at inlet	16.7 LPM	16.3 LPM (5-pt avg)	Yes

Performance observations:

- The Dichot has not been used for over a month. At the beginning of it's last week of use, the sampler was operating properly, as indicated by the flow and leak checks. So, the leak caught during this audit, most likely developed after it's final period of use.

Performance issues and recommendations:

- Repair the leak for future use.

Response (September 24, 2002):

The source of the leak was the o-rings surrounding the Dichot filter cartridges. The leak has been corrected, and the Dichot rotameters recalibrated.

A1.3.4 CMU FRM sampler; Audited with Sarah Rees on 2/12/2002

Performance summary:

- No physical tests were conducted but procedures and most recent results were reviewed.
- Sarah will perform checks during midnight filter change and report her results.
- Leak checks: Check was performed by Sarah at filter change.

Component	Target vacuum	Actual vacuum	Acceptable?
Internal	25 in Hg vacuum held for >60 sec	25 in Hg vacuum held for >60 sec	Yes
External	25 in Hg vacuum held for >60 sec	25 in Hg vacuum held for >60 sec	Yes

- Flow rate checks: Check was performed by Sarah using the Gilibrator at filter change.

Component	Target flow	Actual flow	Acceptable?
Flow at inlet	16.7 LPM	16.6 LPM	Yes

Performance observations:

- The FRM was not tested during the official audit because a sample was being collected and the threat of contamination was high.

Performance issues and recommendations:

- Cyclones need to be cleaned and o-rings should be inspected quarterly at minimum.

SOP recommendations:

- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

Response (March 7, 2002):

The SOP has been reviewed and updated to reflect current operating practices.

A1.3.5 CMU FRM sampler; Follow-up Audit with Sarah Rees on 9/11/2002

Performance summary:

- Leak checks (vacuum held for >60 sec): Check was performed by Sarah at filter change.

Component	Target vacuum	Actual vacuum	Acceptable?
External	<8.5 mmHg vacuum	5 mmHg vacuum	Yes

- Flow rate checks: Check was performed by Sarah using the Gilibrator at filter change.

Component	Target flow	Actual flow	Acceptable?
Flow at inlet	16.7 LPM	16.6 LPM	Yes

Performance observations:

- None.

Performance issues and recommendations:

- None.

A1.3.6 CMU R&P TEOM monitor; Audited with Darrell Stern on 2/15/2002

Performance summary:

- Mass calibration: Check was performed with Darrell using Allegheny Health standard.

Component	Target K_0	Actual K	Acceptable?
Filter element	13573	13669	Yes

- Flow rate checks: Check was performed with Darrell using the Gilibrator at the inlet.

Component	Target flow	Actual flow	Acceptable?
Flow at inlet	16.67 LPM	16.76 LPM	Yes

Performance observations:

- In general, the TEOM has been stable and reliable over the sampling period. Occasional divergences where the mass is very high and then very low have been observed when dramatic changes in the climate occur. The manufacturer asserts that the high positive values and high negative values average out to zero. Current practice is to remove these divergences from the data set and flag the time periods.
- On a quarterly basis, a blank is run at the physical inlet at the cyclone using a HEPA filter. Mass calibrations are also checked at a single point on a quarterly basis.

Performance issues and recommendations:

- Flow checks were only made sporadically from July 2001 to February 2002 because of issues with the Gilibrator. Now that the Gilibrator is repaired, more frequent flow measurements should be made.
  Response (March 6, 2002):
  Flow measurements will be made on a quarterly basis from this point on.
- It is unclear if the instrument sensitivity varies as a function of RH or ambient gas or PM components. While it is outside of the scope of this audit to evaluate differences in sensitivity, any tests that elucidated this issue would be very valuable.
  Response (March 6, 2002):
  Relative humidity at the filter will be recorded in the data set to help elucidate this issue. Possible studies to evaluate changes in instrument response with changing ambient aerosol content will be considered.

SOP recommendations:

- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.3.7 CMU R&P TEOM monitor; Follow-up Audit with Darrell Stern on 8/19/2002

Performance summary:

- Mass calibration: Check was performed with Darrell using Allegheny Health standard.

Component	Target K_0	Actual K	Acceptable?
Filter element	13573	13627	Yes

- Flow rate checks: Check was performed with Darrell using the Gilibrator at the inlet.

Component	Target flow	Actual flow	Acceptable?
Flow at inlet	16.67 LPM	16.25 LPM	Yes
Zero flow	0 LPM	0.16 LPM	Yes

Performance observations:

- None.

Performance issues and recommendations:

- None.

A1.4 PM inorganics measurements

A1.4.1 CMU ion chromatograph; Audited with Satoshi Takahama on 2/14/2002

Performance summary:

- No physical tests were conducted but procedures and most recent results were reviewed.
- Standard preparation and IC loading were observed by the QA Manager. The IC standard checks were reasonable and demonstrated good laboratory practice.

Performance observations:

- A water blank and a Dionex reference standard are run with every set of standards used for a full calibration. A "check standard" is run at intervals between full calibrations to determine if the IC response is within tolerable limits. This is a good QC practice.
- Fresh standards are made from stock solution monthly. This is a good QC practice.
- A set of standards are run on the IC at the same time as the check standards. While this is good QC practice, it is not necessary to calibrate the system and challenge it with an unknown every time standards are performed. If time needs to be saved, this practice can be performed less frequently than the standards.
  Response (March 6, 2002):
  The retention time shifts slightly each time the eluent solution is replaced. Therefore, it is more convenient to run calibration standards each time the eluent is remade. It is also convenient to group sets of samples with their calibration standards to allow the software to identify peaks automatically. Note that the peak identifying mechanism in the software requires that samples with similar retention times be grouped together, and each group requires its own calibration curve(s). While it may not be absolutely necessary to run verification standards repeatedly once the accuracy of newly prepared calibration standards have been established, eliminating the analysis of verification standards will only shorten a 3600-minute run by 30 minutes. The time gained by eliminating this additional QC check will not make a significant difference.
- All sample cartridge activities are performed under a flow hood. This is a good practice.

Performance issues and recommendations:

- Address the Whatman filter problem. One possible solution is to not analyze the steam samples with this IC and to reduce the sample volume and the effects of the methanol loading as a result. Then the backlog of Whatman filters can be reduced and eventually run in near real-time. This smaller sample volume cannot be used for steam samples because of the low concentrations of inorganics collected using the steam sampler.
  Response (March 6, 2002):
  Whatman filters are currently stored in the freezer for analysis at a later date (undetermined).
- Consider determining the frequency of running standards based on the number of samples run rather than elapsed time. Whichever way is chosen, be sure it can be justified.
  Response (March 6, 2002):
  When calibration standards are run is based on how quickly the eluent is consumed, which is in most cases related to the number of samples run- I mentioned to Beth that this was done once every 2½ days to give an idea of how often it is done, but the time elapsed is actually not the governing factor.
- Sample cartridges are cleaned using Kimwipes. Evaluate whether lint from the Kimwipes is obstructing flow through the screens. Consider rinsing the screens under pressure.
  Response (March 6, 2002):
  Kimwipes are classified as having "low lint" content- one suggestion Beth had was to look for other wipes, but Kimwipes are marketed in the same category as other clean room wipes. Using compressed air has not yet been investigated.
- Regularly check the integrity of the o-rings in the sample canisters for drying and cracking. Consider whether the o-rings should be lubricated with vacuum grease.
  Response (March 6, 2002):
  So far leak checks have not pointed to O-ring degradation as a major concern. Applying grease is undesirable for two reasons- 1) potential contamination of the filters and 2) additional time required for cleaning. The idea of greasing O-rings is not being entertained at the moment, but O-rings will be inspected quarterly and replaced if there is visible degradation, or if leak tests indicate O-ring failure.

SOP recommendations:

- Use an Addendum to describe and date when there is a change of procedure that affects the measurement, such as using NaOH to extract the Nylasorb filters.
  Response (March 6, 2002):
  An addendum has been added and is currently being modified.

- Check to ensure the SOP reflects the types of activities, the quality objectives of each activity, and the frequency of each activity, such as the calibration with standards.
- Check to ensure the SOP contains detailed instrument and solution information, considering that differences in these can have dramatic effects on the success of the analysis. Include distilled procedural information when it is integral to the success of the analysis.
  Response (March 6, 2002):
  In progress.

A1.4.2 CMU inorganic sampler; Audited with Satoshi Takahama on 2/12/2002

Performance summary:

- Flow checks: All checks were performed with Satoshi using the Gilibrator at the inlet.

Line	Pressure	Target flow	Actual flow	Acceptable?
N line	-69 psi	7.7 LPM	7.15 LPM	No, 7.14% low
D line	-66 psi	7.7 LPM	7.33 LPM	Yes
P line	-53 psi	7.7 LPM	7.39 LPM	Yes
S line	6 in-H_2O	N/A	9.13 LPM	N/A

- Leak tests: Check was performed with Satoshi using the flow adaptor at the inlet.

Line	Initial Pressure	Final Pressure	Elapsed time	Acceptable?
Inlet	-12 psi	-11 psi	5 sec	Yes

Performance observations:

- The leak test showed a serious leak, which was a result of the denuders not being screwed into the coupler. There was also insufficient Teflon tape on the denuder screw threads. Once the leak was fixed, the flow rate was acceptable.
- Any checks on the sampler require substantial rerouting of the flows. Are the flow checks measuring the flow through the lines during normal sampling?
- All three lines have a flow set point of 7.7 LPM. Does this allow for a $PM_{2.5}$ size cut?

Performance issues and recommendations:

- Check communications to ensure that all personnel changing filters are knowledgeable in the procedures, and provide home phone numbers for everyone in the group.
- Although there have been no problems with the pumps and o-rings to date, they should be checked on a bimonthly basis, at least, for wear. Check vacuum pumps visually for carbon particles, which would indicate that further inspection of the carbon vanes inside the pump is needed. Integrate these checks into the current QC activities and SOP.
- URG slip fittings and the denuders should be checked on a bimonthly basis for proper assembly (i.e. that they are supported reasonably and leak-free).
- Replace the outlet strip that was damaged by heat.
- Cyclones need to be cleaned quarterly at minimum.

SOP recommendations:

- Add QC procedures to SOP: pump checks, fittings checks, denuder change checks.
- Include frequency of making each type of QC measurement, and indicate criteria for successful leak tests and successful flow rate tests. QC criteria such as “regularly”, “adequate”, and “to be determined” should be numerically defined.
- If the samplers are extremely stable over time such that leak tests and flow rate tests are needed only at infrequent intervals, specify this interval in the SOP and explain that the interval was chosen due to observed stability in the samplers.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.4.3 CMU inorganic sampler; Follow-up Audit with Satoshi Takahama on 8/1/2002

Performance summary:

- Flow checks: All checks were performed with Satoshi using the Gilibrator at the inlet.

Line	Pressure	Target flow	Actual flow	Acceptable?
N line	-96 psi (-25 psi)*	7.7 LPM	7.26 LPM	Yes, 5.7% low
D line	-92 psi (-25 psi)*	7.7 LPM	6.73 LPM	No, 12.6% low
P line	-73 psi (-20 psi)*	7.7 LPM	6.97 LPM	No, 9.5% low
S line	7 in-H_2O	N/A	9.42 LPM	N/A

- Leak tests: Check was performed with Satoshi using the flow adaptor at the inlet.

Line	Initial Pressure	Final Pressure	Elapsed time	Acceptable?
Inlet	-7 in-H_2O	0 in-H_2O	> 30 sec	Yes

Performance observations:

- The D and P lines showed flow rates that were below the target values of 7.7 LPM each. Flow rates have been measured once per week since the February audit with the Gilibrator, and these flow rates have been relatively stable. Note that the dp cutpoint will also be affected by the lower flowrate.
- The leak test was satisfactory, with the pressure drop moving only very slowly toward zero when the pump was shut off.

Performance issues and recommendations:

- The stability of the flowrates measured each week with the Gilibrator should be quantified by determining the amount of change in flowrate of each line from week-to-week. These flowrates should be used in the calculations of airborne concentrations. The changes in flowrates should also be used to estimate the uncertainty in the estimated flowrate through the project.
- The uncertainties in the particle diameter cutoffs of the PM10 inlet and PM2.5 cyclone should be estimated due to the low flowrates.

A1.4.4 CMU steam sampler; Audit with Andrey Khlystov on 2/14/2002

Performance summary:

- Flow rate check: Performed at the inlet with Andrey using the Gilibrator.

Component	Target Flow Rate	Actual Flow Rate	Acceptable?
Inlet cyclone	16.7 LPM	17.34 LPM	Yes

Performance observations:

- The steam sampler collects three types of samples: (1) 2-hour 5-ml sample in plastic vials for IC analysis, (2) 2-hour 7-10 ml sample in plastic vials for archival, and (3) 0.2-ml/min for real-time ammonia analysis through a counter-flow conductivity cell. The plastic vials have replaced glass vials due to contamination issues.
- A 7-point calibration is performed on the ammonia conductivity cell.
  Response (March 6, 2002):
  The 7-point calibration is done once a week. Preliminary results indicated that the calibration does not change substantially from week to week unless there is some malfunction of the detector. We are currently evaluating the whole period of measurements (6 months) to quantify stability of the calibration and to find the optimum calibration schedule.
- Handling blanks are collected by placing deionized water in a plastic vial, as a sample would be collected. These blanks do not reflect possible contamination in the inlet, steam sampler glassware, or tubing. Sampling blanks are not collected because the entire system would have to be offline during the blank collection.
- The tubing is replaced every 3 months. It was last replaced in December.
- The flow rate check was 4% high. This is less than the 5% criteria most would consider acceptable. However, the flow was adjusted 3 hours before the audit. The flows were readjusted to 16.74 LPM after the audit. Because there was no clear explanation for the flow drift, Andrey should monitor the flows frequently until they stabilize.

Performance issues and recommendations:

- The frequency of running the 7-point calibration should be established, and criteria for calibration checks versus calibrations should be determined.
- The archive sample vial was overflowing during the audit because the flow rate through the ammonia sampler was restricted to 0.1 ml/min by tubing that had degraded. This will affect the accuracy of the archived sample, in the event that it is used for reanalysis. More frequent tubing replacements should be considered.
  Response (March 6, 2002):
  The reason for the fast tube degradation was found to be accumulation of insoluble particles in the entrance of the ammonium detector. This placed the tubing under extra strain leading to its degradation. From now on the detector will be cleaned every 3 months instead of every 6 months.
- There is no method of checking the integrity of the entire sampling line for leaks or particle accumulation. A good QC check would be to semiannually run a blank at the physical inlet at the cyclone. This could be done using a HEPA filter and denuder at the inlet, or by using a source of pressurized particle-free and denuded air from a pump that is fed into the physical inlet.
  Response (March 6, 2002):
  These tests are planned in spring this year, when a second sampler will be ready, such that no major data loss will occur.

- It is unclear if the steam sampler glassware and lines need to be periodically cleaned for buildup of residue. The need for regular cleaning should be assessed.
  Response (March 6, 2002):
  The sample transfer lines are replaced regularly to avoid it being blocked by accumulated insoluble material. There is no indication so far (in the past 8 months) that there is accumulation of insoluble material on the glass parts of the sampler (they are constantly washed by condensing steam). Accumulation of the insoluble material as such is not deemed incremental to the performance of the sampler: the sampler measures only water soluble content. It is also unlikely that accumulation of insoluble material will increase the retention of water soluble material in timescales comparable to the current sampling frequency (1-2 hours). Measurements during periods of very low concentrations also suggest that there is no problem with residual contamination. Concentrations as low as 0.1 $\mu g/m^3$ were measured with the sampler, which is it's detection limit. This suggests that even if there is any contamination / retention, it is below the detection limit of the instrument and is thus insignificant. The glass walls of the sampler are constantly washed by condensing steam. Manual washing would have the same effect as that of condensing steam, thus will not bring any improvement. The only improvement can be done by washing in an ultrasonic bath. This, however, may compromise the integrity of the sampler and should be avoided. For these reasons we conclude that washing of the glass parts of the sampler is not necessary.

SOP recommendations:

- The SOP should be completed. It should mention the frequency of calibrating the ammonia analyzer, and the calibration acceptability criteria.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.
  Response (March 6, 2002):
  The SOP is being finalized.

A1.4.5 CMU steam sampler; Follow-up Audit with Andrey Khlystov on 7/29/2002

Performance summary:

- Flow rate check: Performed at the inlet with Andrey using the Gilibrator.

Component	Target Flow Rate	Actual Flow Rate	Acceptable?
Inlet cyclone for #1	16.7 LPM	16.90 LPM	Yes
Inlet cyclone for #2	16.7 LPM	15.27 LPM	Yes

Performance observations:

- On July 10, 2002, a second steam sampler was set up. The new steam sampler (#2) incorporated an inlet line without a denuder, while the original steam sampler (#1) incorporated a denuder to remove gaseous species. Based on very limited data, it appears that sampler 1 records consistently lower sulfate concentrations than sampler 2, as expected. However, the ADI continuous sulfate monitor, which measures only sulfate aerosol, agrees with sampler 2 rather than sampler 1. The reasons for the anomalous results are unknown. Tests will be conducted shortly to compare the two steam samplers under identical conditions.
- Although within an acceptable range, the flow rate for sampler 2 was increased to reach a value close to 16.7 LPM. The final value measured with the Gilibrator was 16.80 LPM.
- A 7-point calibration was performed on the ammonia conductivity cell. Results are forthcoming. This calibration has been performed once per week as desired.

Performance issues and recommendations:

- Continue to characterize the performance of the two samplers relative to each-other.

A1.4.6 ADI R&P nitrate and sulfate monitors; Audited with Carly Jerla on 2/15/2002

Performance summary:

- Flow checks: All checks were performed using the Gilibrator.

Component	Target flow	Measured flow	Acceptable?
Nitrate	1.14 LPM	1.09 LPM	Yes
Sulfate	1.04 LPM	1.07 LPM	Yes

- Leak tests: All checks were performed using a HEPA filter after the cyclone.

Component	Target conc	Measured conc	Acceptable?
Nitrate	0 $\mu g/m^3$	0.3 $\mu g/m^3$	Yes
Sulfate	0 $\mu g/m^3$	0.67 $\mu g/m^3$	Yes

Performance observations:

- None

Performance issues and recommendations:

- The instruments have had regular problems with the pumps. The nitrate pump failures are preceded by a graduate increase in the gas monitor reaction cell vacuum, but there is no good warning for the sulfate pump failure. Therefore the sulfate pump should be inspected on a bimonthly basis, at minimum.
  Response (March 6, 2002):
  The pump will be inspected on a bimonthly basis and this change in operations will be appended to the SOP.
- Calibrations drift within +/-15% on both instruments. The reason for calibration drifts should be investigated.
  Response (March 6, 2002):
  The change in response to aqueous calibration standards was evaluated. Because the calibration drifts in both directions (high and low) and because the R&P instruments are newly commercialized, a wider range of response at a single calibration point is considered to be acceptable. Change in calibration response will be tracked biweekly.
- Flow checks were only made sporadically from July 2001 to February 2002 because of issues with the Gilibrator. Now that the Gilibrator is repaired, more frequent flow measurements should be made.
  Response (March 6, 2002):
  Flow measurements will be made on a monthly basis from this point on.
- There is no method of checking the integrity of the entire sampling line for leaks or particle accumulation. A good QC check would be to semiannually run a blank at the physical inlet at the cyclone. This could be done using a HEPA filter at the physical inlet.
  Response (March 6, 2002):
  This system integrity test will be performed on a quarterly basis and reflected in the SOP.
- It is unclear if the instrument sensitivity varies as a function of the PM components. While it is outside of the scope of this audit to evaluate differences in sensitivity, any tests that elucidated this issue would be very valuable.
  Response (March 6, 2002):
  This evaluation is not within the goal of this project.

SOP recommendations:

- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.4.7 R&P nitrate and sulfate monitors; Follow-up Audit with Lisa Branden on 7/31/2002

Performance summary:

- Flow checks: All checks were performed using the Gilibrator.

Component	Target flow	Measured flow	Acceptable?
Nitrate	0.81 LPM	0.99 LPM	No
Sulfate	1.27 LPM	0.94 LPM	No

- Leak tests: All checks were performed using a HEPA filter after the cyclone.

Component	Target conc	Measured conc	Acceptable?
Nitrate	0 $\mu g/m^3$	0.23 $\mu g/m^3$	Yes
Sulfate	0 $\mu g/m^3$	0.27 $\mu g/m^3$	Yes

Performance observations:

- Nitrate instrument broke (irreparably) on August 1st.
- The stability of the instrument calibrations was investigated over a two-week period. The results of these experiments are as follows:

	Nitrate	Sulfate
Average slope (aqueous standards) =	1.16 +/- 0.09	1.46 +/- 0.15
Average intercept (zero-filter) =	0.15 +/- 0.07	0.35 +/- 0.32

Performance issues and recommendations:

- Recalibrate nitrate and sulfate instrument flow meters.

A1.5 PM metals measurements

A1.5.1 CMU Hi-Vol sampler; Audit with Natalie Anderson on 2/11/2002

Performance summary:

- Flow and leak checks: All checks were performed with Natalie using a clean "blank" filter and a magnahelic gauge

Component	Target pressure	Actual pressure	Acceptable?
Flow at inlet	____	2.7 psia	Yes - within 3%
Leak at inlet	____	_____	Yes

Performance observations:

- Leak test is somewhat primitive – merely putting tape over holes and listening for a whistling sound. There is not much that can be done to address this observation.

Performance issues and recommendations:

- Black particles were observed on the filter – this has been a problem for the past few weeks. Gasket material is suspected. Check gaskets in the inlet of each Hi-Volt. Collect and analyze each type of gasket material for metals to assess whether contamination is an issue.
  Response (March 7, 2002):
  The problem with large particles on the filters has been solved. The gaskets both on the cartridges and in the sampling box have been replaced and now the filters look fine.
- Calibration of flow is performed using a pressure tap – but this can account for pressure drop on filters loaded with particles only up to about 37 psia. Actual pressure drops on polluted days can be over 50 psia. Do a multipoint calibration up to 37 psia to determine if converting pressure to flow rate is accurate up to that loading. Extrapolation errors for higher loadings.
  Response (March 7, 2002):
  Calibration of both the PM10 and PM2.5 Hi-Voles was conducted today with reasonable results. Both flow rates are within 4.3% of the original calibration curves. It should be within 3%, but the filters today are quite loaded--both were showing around 40-45" H2O pressure drop, which is much higher than usual. Once the filter gets really loaded (like above a 35" H2O pressure drop) the flow rate measurement deviates from the original calibration curves slightly more. On days with high pressure drops it may become necessary for the person removing the filter to use the Vari-flo orifice to check the flow rate. Otherwise, we will just have to flag those days since the flow rate calculation may not be as accurate. But since polluted days are of interest, it's probably a good idea to know, by using the Vari-flo orifice, just how far off the flow calculation is.
- Cyclones need to be cleaned and o-rings should be inspected quarterly at minimum.

SOP recommendations:

- Include criteria for 'acceptable' flow rate measurements, including those at high loadings.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.5.2 CMU Hi-Vol sampler; Follow-up Audit with Natalie Anderson on 8/6/2002

Performance summary:

- Flow and leak checks: All checks were performed with Natalie using a clean "blank" filter and a magnahelic gauge.

Component	Magnahelic/flow	Orifice pressure/flow	Acceptable?
Flow at inlet	23.3" H2O, 1.271m^3/min	2.9"H2O, 1.137m^3/min	Yes (<1%)

Performance observations:

- It appears that the problems discussed in the February 11, 2002 audit have been resolved. Since particle loadings throughout 2002 have been sufficiently low that the magnahelic gauge has been below 50, calibrations for high loading conditions have not been necessary.

Performance issues and recommendations:

- Since there were days when no circular chart paper was used, care should be taken to ensure that the samplers were running during the entire 24 hour period using the elapsed time meters.
- The PM2.5 sampler elapsed time meter stopped working several weeks ago, and the only elapsed time meter available was on the PM10 Hi-Vol. Furthermore, the PM2.5 motor began to fail a few weeks ago. It is necessary to ensure that accurate time periods of sampling can be determined. Filters where the time of sampling is unknown should be discarded.

A1.6 PM organics measurements

A1.6.1 CMU EC/OC analyzer; Audited with Juan Cabada on 2/13/2002

Performance summary:

- No physical tests were conducted but procedures and most recent results were reviewed.

Performance observations:

- Once per month, a 5-point calibration is conducted by injecting varying amounts of a 4% methane-in-helium mixture into the analyzer. Amounts are 0.5, 1.0, 1.5, 2.0, and 2.5 cc of the mixture. The instrument response has been observed to be linear. Actual filter samples can have less than 10% of the carbon in the minimum calibration point (0.5 cc).
- At the beginning of every analysis day, three injections of methane-in-helium are applied at different points in the instrument cycle. The responses are used to check the flow and instrument response.

Performance issues and recommendations:

- An assumption is that all components of OC evolve at the same rate as the methane standard. Judy Chow at DRI uses many different compounds to test this assumption and has found good results; more recently, Juan has been using sucrose as a one-point check on this assumption. Judy Chow's data should be used to verify the validity of the results.
  Response (March 6, 2002):
  DRI instrument calibrates using CH4, CO2, sucrose and KH, and reports a shifts in calibrations between 1% and 3%. Another way to check for the evolution of the peaks is to check the thermogram and the correction to pyrolysis using the laser signal monitoring of the sample.
- The three-injection instrument check should also serve as a calibration check because the internal instrument standard is used to normalize the concentrations of OC and EC for each sample. The internal standard area count should be inspected at the beginning of each analysis day to confirm the stability and consistency of the instrument. When outside of the acceptable response range of 5%, the data should be flagged and the instrument should be repaired and/or recalibrated.
  Response (March 6, 2002):
  Data will be flagged when this occurs. So far the instrument has had a very stable response to this test.
- Some procedures described in the SOP have never been applied. If the procedures are shown to be unnecessary, they can be deleted from the SOP. If the procedures are necessary, they should be performed at the frequency stated in the SOP.
  Response (March 6, 2002):
  The SOP has been modified to comply with all the procedures that are actually taking place for the operation of the instrument.
- A Sunset Laboratory representative does quarterly maintenance on the instrument. Otherwise, the instrument is only maintained in the event of a failure. The Sunset Laboratory manual should be consulted to determine if regular maintenance is needed. Any specified maintenance should be performed and worked into the normal activities.
  Response (March 6, 2002):
  No special maintenance is mentioned in the manual.

SOP recommendations:

- In the event that some procedures are deleted, the SOP should be modified so that it is an accurate account of the activities, including leak checks and regular maintenance.
  Response (March 6, 2002):
  That has been done in the new SOP.
- Numerical criteria for success should be given in the SOP, as opposed to merely stating the criteria qualitatively.
  Response (March 6, 2002):
  Done.
- The EC/OC SOP is not in standard NARSTO format. This SOP will be revised to be in the proper format as soon as possible.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.6.2 CMU speciation sampler; Audit with R Subramanian on 2/14/2002

Performance summary:

- Flow calibration: Performed at the inlet with RS using a water manometer.

Magnahelic Reading	Manometer Reading	R^2 Acceptable?
60 in H_2O	6.4 in H_2O	Yes
50	5.4	
40	4.35	
30	3.2	
20	2.05	
10	0.9	

Performance observations:

- A leak test was attempted by plugging the orifice. As expected, the magnahelic did indeed read zero. However, this was not deemed to be a rigorous test, since only a very large leak would have resulted in a nonzero magnahelic reading.
- The cyclone on the speciation sampler was designed to be PM_{10} at 28 LPM. The manufacturer calibrated the cyclone up to 110 LPM, which is only a $PM_{3.1}$ size cut. The $PM_{2.5}$ flow setpoint has been obtained by extrapolation to 145 LPM. This means that there is uncertainty in the cut point even if the flow is measured with high accuracy.

Performance issues and recommendations:

- The flow though the venturi is normally set to 20 in H_2O. It is not clear why the calibration should be conducted up to 60 in H_2O, given that the set point is only 20 inches. Focusing the calibration points at the lower end of the magnahelic range may be more useful for assessing the effect of flow drift during filter loading.
  Response (March 7, 2002):
  The sampler is designed for flows up to 280 lpm, and turning the voltage control to give low flows (without using the valve) leads to very unstable readings on the magnehelic. Hence, for better control, the blower voltage has to be set to a higher flow, and the valve has to be used to bring the flow down to the required value. Now, as per the calibration procedure of the sampler, readings have to be taken at five different positions of the valve, including full-open. Hence, though the magnehelic is set to 20" during normal operation, the calibration is carried out starting from a higher reading. A further observation is that the manometer used to calibrate the sampler shows a limited range of readings compared to the magnehelic gauge on the sampler (0 – 6" H2O, approx). If we calibrate the sampler over a smaller range of flows close to the target flow, the readings on the manometer may not be very distinguishable from one other. In any case, since the calibration procedure needs a very high regression coefficient for an acceptable calibration, the flow calculation should be very acceptable over the entire range tested.
- The criteria for acceptability and reasonable drift in flow calibrations should be assessed because drift will indicate problems with the pump and/or sampler. This criteria as well as the frequency of conducting the calibration should be determined:

Date	Slope	Intercept	R^2
2/14/02	30.5	–0.217	>0.999
10/4/01	26.2	+0.629	>0.999

  Response (March 7, 2002):
  The frequency of calibration is set as per the manual (this information will also be included in the SOP). Beyond the requirement of the correlation coefficient being more than 0.990, acceptability criteria are not specified by the manufacturer. I will try to check this. The sampler does have a dry gas meter, from which a measure of the flow rate can be obtained (it has been observed that the set flow and the dry gas meter flow do not always match – there is some difference). I could track the dry gas meter flow to make sure the flows (and sampler) are functioning properly.
- It is not easy to perform a leak test on the speciation sampler. A more sensitive pressure gauge would be needed, and it is probably not worth the effort.
- Cyclones need to be cleaned and o-rings should be inspected quarterly at minimum.
  Response (March 12, 2002):
  The group analyzing the samples has not specified any frequency for cleaning the sampler; I can check with them if any repeated cleaning is required, and whether it affects the results. Cleaning the sampler or any of the parts is a very labor-intensive, time-consuming process, and I would like to keep it to a minimum as far as possible, provided, of course, that the data are not compromised.

SOP recommendations:

- State the criteria for and the frequency of conducting the flow calibrations and checks.

Response (March 7, 2002):
I will do that by March 10, 2002.

- Address the issues associated with the fact that the $PM_{2.5}$ cut point of the cyclone is based on an extrapolation of the flow/cut point relationship.
  Response (March 7, 2002):
  I am not sure how to do this, but I will try.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.
  Response (March 7, 2002):
  This is already included in the SOP.

A1.6.3 CMU speciation sampler; Follow-up Audit with R. Subramanian on 7/29/2002

Performance summary:

- Calibrations were not performed during this audit because they had been performed on July 13, 2002 by Prakash Rao, an undergraduate working with Subu. The results were as follows:
- Flow calibration on July 13, 2002:

Magnahelic Reading	Manometer Reading	Actual Flow through Orifice
54 in H_2O	5.6 in H_2O	0.243 m^3/min
40	4.3	0.213
30	3.1	0.181
20	2.0	0.146
10	0.75	0.090

Performance observations (see second bullet under Performance Observations in 6.2.1 above):

- These values give a slope of 26.631 and a y-intercept of 0.596, with an r^2 of 0.998 (to 3 sig figs). The actual flow rate at 20 in H_2O was 0.146 m^3/min, or 146 LPM, very close to the target of 145 LPM.
- The problem of using a cyclone that was never calibrated at the flow rate used (145 LPM) was discussed during this audit. The manufacturer of the cyclone, URG, provided a graph showing the particle diameter cutoff as a function of flow rate. The calculated cutoff at the highest flow rate used by URG, 110 LPM, was 3.12 μm. In a phone conversation with URG, R. Subramanian spoke with a URG technical rep who stated that he had calculated a flow rate of 145 LPM in order to achieve a cutoff of 2.5 μm, as desired. Although this value has never been independently determined, the use of the cyclone in the speciation sampler does not require an accurate PM cutoff. Work with the EC/OC analyses during this Supersite campaign has shown that most of the organic carbon is below 2.5 μm. Thus a cutoff larger than this value would not introduce much more organic aerosol into the sampler. A smaller value than 2.5 μm is unlikely as the curve provided by URG was approaching an asymptote only a small amount below 3.12 μm.
- The calibration has been performed every 3 months as recommended in the previous audit. A wide range from 10 to 50 in H_2O has been used in the calibrations despite the fact that there is only a single set point at 20 in H_2O. This has been done to provide enough range to read the manometer accurately. Given the linearity of the response of the manometer to this range of magnahelic readings, the highly linear results suggest an accurate calibration.

Performance issues and recommendations:

- None.

A1.6.4 CMU Denuder sampler; Audit with R Subramanian on 2/14/2002

Performance summary:

- Flow calibration: Performed at the inlet with RS using the Gilibrator.

Component	Target Flow	Rotameter Flow	Actual Flow	Acceptable?
AC denuder	16.7 LPM	16.80 LPM	16.10 LPM	Yes
Dynamic blank	16.7	17.29	16.19	Yes

Performance observations:

- The denuder rotameter flows are calibrated using the Gilibrator once every 6-7 runs.
- No leak test is done if the Gilibrator and the rotameter agree to within 10%.

Performance issues and recommendations:

- It would be valuable to work out a way to do a simple leak test without the need for detailed measurements to find out if there is a leak. This was attempted, but was not successful.
- Cyclones need to be cleaned and o-rings should be inspected quarterly at minimum.

SOP recommendations:

- If a leak test can be worked out, the procedures and criteria for passing should be described in the SOP.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.6.5 CMU Denuder sampler; Follow-up Audit with R Subramanian on 7/29/2002

Performance summary:

- Calibrations were not performed during this audit because they had been performed on the previous day.
- Flow calibration: Performed at the inlet by P. Rao using the Gilibrator.

Component	Target Flow	Rotameter Flow	Actual Flow	Acceptable?
Line 1	16.7 LPM	16.93 LPM	15.69 LPM	Yes
Line 2	16.7	17.17	15.99	Yes

Performance observations:

- Line 2 is no longer being used for dynamic blanks. This is because all of the previous tests have shown no positive artifact, and Line 2 was needed for comparison runs. Currently, Line 1 is being used for variable length runs while Line 2 is being used for simultaneous 24 hour runs. The first set of runs employed Line 1 for successive 8 hour samples. The second set, currently underway, employs Line 1 for a 48 hour run while Line 2 has two successive 24 hour runs.

Performance issues and recommendations:

- The flow check on both lines was within +/-10% of the setpoint, as desired.

A1.6.6 CMU organic TQQQ sampler; Audit with R Subramanian on 12/20/2001

Performance summary:

- Flow check: Performed at the inlet with RS using the Gilibrator.

Component	Target Flow	Rotameter Setting	Actual Flow	Acceptable?
TQ line	16.7 LPM	66	15.36 LPM	Yes
QQ line	16.7	50	15.19	Yes

- Leak check: Performed with RS using the flow audit adaptor.

Component	Target Pressure	Actual Pressure	Acceptable?
Sampler	Drop by < 5 in H_2O in 1 sec	Drop by < 5 in H_2O in 1 sec	Yes

Performance observations:

- None

Performance issues and recommendations:

- The flow check on both lines was within +/-10% of the setpoint. However, they were close to the limit. Another flow check should be performed within 3 months because the sampler was close to failing the audit.
- The method of leak determination is not rigorous. A gage that displays in Hg would be more useful for this test. It would be valuable to improve the leak test method.
- Cyclones need to be cleaned and o-rings should be inspected quarterly at minimum.

SOP recommendations:

- If an improved leak test can be worked out, the procedures and criteria for passing should be described in the SOP.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.6.7 CMU organic TQQQ sampler; Follow-up Audit with R. Subramanian on 7/29/2001

Performance summary:

- Calibrations were not performed during this audit because they had been performed on the previous day.
- Flow check: Performed at the inlet by P. Rao using the Gilibrator.

Component	Target Flow	Rotameter Setting	Actual Flow	Acceptable?
TQ line	16.7 LPM	63 (flow = 16.41)	15.35 LPM	Yes
QQ line	16.7	62.5 (flow = 16.20)	14.98	Yes

Performance observations:

- None

Performance issues and recommendations:

- The flow check on both lines was within +/-10% of the setpoint, as desired.

A1.6.8 Rutgers EC/OC analyzer; Audited with Juan Cabada on 2/13/2002

Performance summary:

- No physical tests were conducted but procedures and most recent results were reviewed.

Performance observations:

- A 5-point calibration similar to that conducted monthly for the CMU instrument is conducted by injecting varying amounts of a methane-in-helium mixture into the analyzer. The amounts of the mixture injected are the same as with the CMU analyzer, namely 0.5, 1.0, 1.5, 2.0, and 2.5 cc of the mixture. However, the mixture in this case is only 2% methane rather than 4%. This calibration has been conducted only twice, in July and in October.
- Similar to the CMU instrument, three injections of methane-in-helium are applied at different points in the instrument cycle for the Rutgers analyzer.
- The quartz filter inside the oven is changed twice per week.

Performance issues and recommendations:

- It is difficult to determine if the calibrations and checks are satisfactory, since there are no criteria for success of these tests. These criteria should be determined.
  Response (March 6, 2002):
  The actual numbers for comparison are included in the latest SOP obtained from Rutgers.
- There is no frequency for the 5-point calibration given. Thus it is impossible to say whether the two calibrations performed in July and October are sufficient. The success and stability of the OCEC analyzer should be evaluated to determine if the current frequency of these tests is acceptable. If the current frequency is acceptable, a regular schedule should be implemented. If the current frequency is found to be unacceptable, a more frequent schedule should be implemented.
  Response (March 6, 2002):
  Performance of instrument is very stable along the time for these kinds of calibrations. Rutgers has updated the frequency of other tests to check this calibration.
- The dynamic blanks are taken once monthly, not weekly as written in the SOP. The need for weekly dynamic blanks should be assessed and the activities adjusted accordingly.
  Response (March 6, 2002):
  Dynamic blanks are taken weekly as of 02/21/02.

SOP recommendations:

- The SOP is missing many important details, such as the frequency of testing and the criteria for success of each test. These should be detailed in the SOP.
- The SOP should be modified to state the actual frequency of procedures, including but not limited to the dynamic blank.
  Response (March 6, 2002):
  Rutgers just send an addendum to its SOP modifying some procedures and frequency of tests.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.
  Response (March 6, 2002):
  I will get in contact with Rutgers to clarify this point.

A1.6.9 Rutgers EC/OC analyzer; Follow-up Audit with Juan Cabada on 8/1/2002

Performance summary:

- No physical tests were conducted but most recent results were reviewed.
- 3 peak calibration

He	He/Ox	Cal	Acceptable?
179130	174555	176486	Yes

- Instrument blank

OC (µg/m2)	EC (µg/m2)	TC (µg/m2)	Acceptable?
0.07	0.00	0.07	Yes

- Dynamic blank: 0.66 — Yes
- Flow check at inlet before denuder and after manifold

Indicated (LPM)	Measured (LPM)	Acceptable?
8.9	9.11	Yes, 2.4% low

Performance observations:

- None.

Performance issues and recommendations:

- None.

A1.6.10 ADI carbon monitor; Audited with Carly Jerla on 2/15/2002

Performance summary:

- Flow checks: All checks were performed using the Gilibrator.

Component	Target flow	Measured flow	Acceptable?
Instrument	1.04 LPM	1.12 LPM	Yes

- Leak tests: All checks were performed using a HEPA filter after the cyclone.

Component	Target conc	Measured conc	Acceptable?
Instrument	0 $\mu g/m^3$	0.21 $\mu g/m^3$	Yes

Performance observations:

- The instrument had flow balance issues from August 2001 to December 2001. Susanne Hering corrected the balance issue on Dec 13, 2001. All data before that date should be considered to be invalid.

Performance issues and recommendations:

- The flow balance issues should be assessed bimonthly to evaluate if the problem developed gradually or was the result of an improper installation.
  Response (March 6, 2002):
  The flow balance will be investigated on a bimonthly basis. This change in activity will be appended to the SOP.
- Flow checks were only made sporadically from July 2001 to February 2002 because of issues with the Gilibrator. Now that the Gilibrator is repaired, more frequent flow measurements should be made.
  Response (March 6, 2002):
  Flow measurements will be made on a monthly basis from this point on.
- There is no method of checking the integrity of the entire sampling line for leaks or particle accumulation. A good QC check would be to semiannually run a blank at the physical inlet at the cyclone. This could be done using a HEPA filter at the physical inlet.
  Response (March 6, 2002):
  This system integrity test will be performed on a quarterly basis. This change in activity will be appended to the SOP.
- It is unclear if the instrument sensitivity varies as a function of the organic PM components. While it is outside of the scope of this audit to evaluate differences in sensitivity, any tests that elucidated this issue would be very valuable.
  Response (March 6, 2002):
  Studies to evaluate changes in instrument response with changing ambient aerosol content will be considered.

SOP recommendations:

- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.6.11 ADI carbon monitor; Follow-up Audit with Lisa Branden on 7/31/2002

Performance summary:

- Flow checks: All checks were performed using the Gilibrator.

Component	Target flow	Measured flow	Acceptable?
Instrument	0.92 LPM	0.82 LPM	Yes

- Leak tests: All checks were performed using a HEPA filter after the cyclone.

Component	Target conc	Measured conc	Acceptable?
Instrument	0 $\mu g/m^3$	4.88 $\mu g/m^3$	Yes

Performance observations:

- The stability of the instrument calibration was investigated over a two-week period. The results of this experiment are as follows:
  Average slope (aqueous standards) = 1.42 +/- 0.48
  Average intercept (zero-filter) = 1.95 +/- 0.63

Performance issues and recommendations:

- None.

A1.7 Gas species measurements

A1.7.1 CMU volatile organic compound analysis; Audited with Juan Cabada on 2/13/2002

Performance summary:

- No checks were performed because no internal or external standards were available.

Performance observations:

- In the absence of an internal standard, frequently occurring compounds have been used to establish retention time drift. Frequently occurring compounds should be identified at the beginning and end of the chromatogram to assess if drift distortion is an issue. This is a good practice and should be consistently performed until internal standards are available.
- Two types of blanks are performed to test the system. An instrument blank is run before each set of analyses to identify the presence of a leak in the analysis system. A canister blank is run every 20 canisters to test the cleaning effectiveness. These are good QC practices that should be performed on a consistent basis.
- An external standard has been ordered and will be available in the next month.

Performance issues and recommendations:

- The gas chromatograph used to analyze the VOCs has not been maintained since July 2001. This may or may not be a problem. The GC manual should be consulted to determine if regular maintenance is needed and should be performed and worked into the normal activities.
  Response (March 6, 2002):
  I will check the GC manuals to check for any special maintenance that has to performed.
- Internal and external calibration standards should be acquired.
- An internal standard should be used at the beginning of each day of analysis at minimum to establish area count normalization and retention time drift. If resources permit, an internal standard should be run with each analysis cycle.
  Response (March 6, 2002):
  UCb standards will be used.
- An external standard calibration/calibration check should be performed on a quarterly schedule at minimum. The internal standard should be run with the external standard during these quarterly calibrations/calibration checks.
  Response (March 6, 2002):
  As soon as we get the new standards this procedure will be established.

SOP recommendations:

- There is no SOP yet written for the VOC analysis.
- Regular maintenance on the gas chromatograph should be discussed in the SOP.
- Canister blanks and instrument blanks should be discussed in the SOP, including the procedures for obtaining them, the frequency of collecting and running them, and success criteria.
  Response (March 6, 2002):
  SOP will be written in the next month.

A1.7.2 CMU volatile organic compound sampler; Audited with Juan Cabada on 2/13/2002

Performance summary:

- A flow rate check on a 6-liter canister was performed with Juan using the Gilibrator.

Component	Target Flow Rate	Actual Flow Rate	Acceptable?
Flow at 27 in Hg	3.5 cc/min	1.57 cc/min (2-pt avg)	No
Flow at 22.8 in Hg	3.5 cc/min	6.0 cc/min (1-pt)	No
Flow at 12 in Hg	3.5 cc/min	6.27 cc/min (3-pt avg)	No

  Response (March 6, 2002):
  An experiment was performed after the audit and cans are fully filled in 16 hrs.

Performance observations:

- The flow tests suggest that the sampling is not occurring at the desired rate of 6 liters per 24 hours, equivalent to 3.5 cc/min. If sampling is occurring faster, the canister will be filled in much less than 24 hours, so the concentrations measured will not be true 24-hour averages.
  Response (March 6, 2002):
  They are actually 16 hr averages.
- Canisters are cleaned by purging with nitrogen gas from the head space of a liquid nitrogen dewar. There is both a canister blank and an instrument blank taken.

Performance issues and recommendations:

- A test should be performed to assess the sampling rate into an evacuated canister. The results of this test should be compared to the earlier test.
  Response (March 6, 2002):
  This will be done periodically and included in the SOP
- In the event that prior 24 hour samples were collected in less than 18 hours, numerical adjustments to the measurements are likely to be necessary.
  Response (March 6, 2002):
  OK.
- In the event that the inlet is not working to factory specification, the inlet should be cleaned and reevaluated. This will require a cleaning procedure to be developed. A second test of the sampling flow rate with time should be considered to determine if a problem with the inlet resolved by cleaning will correct the off-target flows into the canister.
- In the event that the inlet cannot be repaired by cleaning, the inlet should be returned to the vendor for repairs.
  Response (March 6, 2002):
  Working on this.

SOP recommendations:

- There is no SOP yet written for the VOC sampling. This SOP needs to be written in time for inclusion with the VOC data.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.7.3 CMU API gas monitors; Audited with Darrell Stern on 2/15/2002

Performance summary:

- Flow check: Performed using the Gilibrator at the instrument inlet.

Component	Target flow	Measured flow	Acceptable?
CO Monitor	740 ccm	735 ccm	Yes
SO_2 Monitor	622 ccm	649 ccm	Yes
Ozone Monitor	700 ccm	678 ccm	Yes
NO/NO_x Monitor	476 ccm	475 ccm	Yes

- Calibration check: Performed using 0.1 grade pressurized air and ACHD calibrators at the instrument inlet.

Component	Target conc	Measured conc	Acceptable?
CO Monitor	0 ppm	0 ppm	Yes
	10.2 ppm	10.3 ppm	
SO_2 Monitor	0 ppb	0 ppb	Yes
	203 ppb	199 ppb	
Ozone Monitor	0 ppb	0 ppb	Yes
	201 ppb	202 ppb	
NO Monitor	0 ppb	0 ppb	Yes
	406 ppb	433 ppb	
NO_x Monitor	0 ppb	0 ppb	Yes
	406 ppb	438 ppb	

Performance observations:

- At the beginning of the study, contamination of the filter holder was a persistent issue, especially for the ozone monitor. This has not been a problem in recent months because of the increase in QC during the filter changing procedure.
- The instrument calibration is checked biweekly. A 4-point calibration is performed quarterly.

Performance issues and recommendations:

- Flow checks were only made sporadically from July 2001 to February 2002 because of issues with the Gilibrator. Upon repair, more frequent flow measurements should be made.
  Response (March 6, 2002):
  Flow measurements will be made on a quarterly basis from this point on.
- The NO/NO_x monitor experienced a major failure in late November. This monitor should continue to be closely watched for repeat problems. The NO/NOx calibration audit was acceptable but near failing. The instrument response has drifted since it came back from repair, consistent with the type of repair that was performed (i.e. cleaning the optical window). When the instrument response stabilizes, the instrument should be recalibrated.

Response (March 6, 2002):
The instrument has been watched since its repair in December 2001. By the first week of March 2002, the instrument was found to be stable and was recalibrated.

SOP recommendations:

- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.7.4 CMU API gas monitors; Follow-up Audit with Darrell Stern on 7/22/2002

Performance summary:

- Calibration check: Performed using 0.1 grade pressurized air and ACHD calibrators at the instrument inlet.

Component	Target conc	Measured conc	Acceptable?
CO Monitor	0 ppm	0 ppm	Yes
	46.3 ppm	46.5 ppm	
SO_2 Monitor	0 ppb	0 ppb	Yes
	305 ppb	301 ppb	
Ozone Monitor	0 ppb	0 ppb	Yes
	255 ppb	255 ppb	
NO Monitor	0 ppb	0 ppb	Yes
	406 ppb	411 ppb	
NO_x Monitor	0 ppb	0 ppb	Yes
	406 ppb	412 ppb	

Performance observations:

- None.

Performance issues and recommendations:

- None.

A1.7.5 CSU peroxide monitor; Audited with Sam Byun on 2/12/2002

Performance summary:

- No physical tests were performed because all checks are automated and reviewed by CSU. Sam is not responsible for making maintenance decisions based on his findings.
- The only checks that are typically done are controlled using a single button on the computer, so there was no real procedural check to be done.

Performance observations:

- Once every two days, three standard solutions are made, and ammonia is added to ensure the pH is at the desired value.
- The data from the automated flow check and peroxide sensor calibration are sent to Taehyoung at Colorado State University.
- Minor plumbing problems in the instrument are fixed by Sam; all other malfunctions require contact with Taehyoung or Jeff Collett for directions on how to fix the problem.

Performance issues and recommendations:

- A physical flow check should probably be performed at the inlet at some frequency. CSU should develop a method for this audit and determine the frequency.
- The technician should be given some guidance as to how to interpret the calibration results. Currently the results are emailed to CSU on a weekly basis and interpreted by CSU researchers. This lag of a week could result in substantial data loss from the instrument.

SOP recommendations:

- The SOP should include the procedure and diagnostics for and frequency of flow audits at the inlet.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.

A1.8 Fog measurements

A1.8.1 CSU fog collector; Audited with Sam Byun on 2/12/2002

Performance summary:

- No physical tests are needed.

Performance observations:

- Data from the Fog Collector are sent to Jeff Collett at Colorado State University every week, even if there has not been any fog. If there has been fog, Sam weighs the amount of fogwater and checks its pH.
- A laser beam is continually focused on a sensor. If a fog event begins, the light becomes attenuated and sampling starts. This "Particle Volume Monitor" is calibrated every week.

Performance issues and recommendations:

- None

SOP recommendations:

- The SOP is not in standard NARSTO format. The SOP should be revised to be in this format in time for the Level 2 validation.
- Include an Addendum in the original SOP describing and dating any procedural or data quality objective changes that have had an impact on the measurements.