St. Louis – Midwest Fine Particulate Matter Supersite

QUALITY ASSURANCE FINAL REPORT

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Washington University in St. Louis

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St. Louis – Midwest Particulate Matter (PM) Supersite
Quality Assurance Final Report

Washington University in St. Louis
Jay R. Turner, Principal Investigator

1. Introduction

The overall goal of the St. Louis - Midwest Supersite was conduct aerosol physical and chemical measurements needed by the health effects community, the atmospheric science community and the regulatory community to properly assess the impact of particulate matter exposure on human health and to develop control strategies to mitigate these effects. Metropolitan St. Louis is a major population center (2.5 million) well isolated from other urban centers of even moderate size, and is impacted by both distant and local sources. Local industry includes manufacturing, refining, and chemical plants. St. Louis is climatologically representative of the country's eastern interior, affected by a wide range of synoptic weather patterns and free of localized influences from the Great Lakes, Ocean, Gulf, and mountains. It accordingly provides an ideal environment for studying the sources, transport, and properties of ambient particles.

The St. Louis - Midwest Supersite commenced detailed measurements of ambient particulate matter (PM) in the St. Louis area in April 2001 with some measurements sustained through March 2005. This four-year measurement program was funded by various organizations. A cooperative agreement between USEPA OAQPS/ORD and Washington University established the foundation for the program (including infrastructure) and supported one year of measurements (April 2001 – May 2002). A grant through USEPA Region VII, with contributions from USEPA, Missouri DNR, CENRAP and LADCO/MRPO, permitted a majority of the initial measurement platform to be sustained through at least May 2003. Subsequently, LADCO/MPRO funded a skeletal suite of measurements through March 2005. Portions of the measurement program were also funded by the Electric Power Research Institute (EPRI).

The lead institution for the St. Louis Supersite was Washington University in St. Louis (Jay Turner, PI). The following groups were formally involved in the measurement program.

- Washington University in St. Louis (Jay Turner group)
- Desert Research Institute (Judith Chow and John Watson group)
- Georgia Institute of Technology (Rodney Weber group)
- Harvard School of Public Health (Petros Koutrakis group)
- University of Maryland – College Park (John Ondov group)
- University of Minnesota (Peter McMurry group)
- University of Wisconsin – Madison (James Schauer group)

Additional collaborators in the St. Louis – Midwest Supersite Consortium included (affiliations at the time of their core involvement with the consortium):

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- George Allen, Harvard School of Public Health
- Alan Hansen and Tina Bahadori, EPRI
- Rudolf Husar, Bret Schichtel and Warren White, Washington University

There were three primary objectives for this monitoring program:

1. Implement and evaluate highly time-resolved particle measurement techniques.
2. Characterize spatial and temporal (from minutes up to 24 hours) patterns of a large spectrum of particle physical and chemical properties in the St. Louis metropolitan area.
3. Investigate particle health effects through integration with allied epidemiological and toxicological studies.

This report summarizes the quality assurance metrics used to document measurement quality. Emphasis is placed on measurements during the time period April 2001 through June 2002, although data collected in subsequent phases of the measurement program is also used where appropriate to document the data quality. Data quality indicators included precision, bias, accuracy, detectability, completeness, representativeness, and comparability. These metrics are defined, including equations where appropriate, in the St. Louis – Midwest Supersite Quality Assurance Project Plan (QAPP) available at http://www.epa.gov/ttn/amtic/stlouis.html.

The following independent audits were conducted by DRI staff during the measurement period: systems audit by John Watson and Judith Chow; and performance audits by Matt Gonzi and John Bower (December 2001), and M. Gonzi and Dale Crow (October 2002). Audit results were transmitted to the project PI who in turn worked with the respective measurement teams to address any issues identified during the audits. Corrective actions were taken as warranted.

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2. Data Completeness

The data completeness MQO was 75% for all species and all measurements. Table 2-1 summarizes data completeness for this study.

Table 2-1. Summary of data completeness by measurement method.

Parameter	Method	Resolution	Period	Completeness
Aerosol Physical Properties				
$PM_{1.0}$ mass	cyclone / gravimetric	24-hour	04/13/01-06/30/02	94.1 %
$PM_{2.5}$ mass[(a)]	HI / gravimetric	24-hour	04/13/01-06/30/02	99.1 %
PM_{10} mass	HI / gravimetric	24-hour	04/13/01-06/30/02	98.2 %
$PM_{2.5}$ mass	CAMMS	1-hour	04/15/01-06/30/02	92.3 %
size distributions	UMN / PSD system	5-minute	04/01/01-04/30/02	76.0 %
Aerosol Chemical Properties				
$PM_{2.1}$ sulfate	HEADS / IC	24-hour	04/13/01-06/30/02	97.1 %
$PM_{2.1}$ nitrate	HEADS / IC	24-hour	04/13/01-06/30/02	98.4 %
$PM_{2.1}$ ammonium	HEADS / IC	24-hour	04/13/01-06/30/02	94.8 %
$PM_{2.5}$ sulfate	PILS - IC	1-hour	06/22/01-04/30/02	74.5 %
$PM_{2.5}$ nitrate	PILS - IC	1-hour	06/22/01-04/30/02	73.8 %
$PM_{2.5}$ nitrate	R&P 8400N	1-hour	02/05/02-06/30/02	75.4 %
$PM_{2.5}$ EC	UWM / TOT	24-hour	04/11/01-06/30/02	95.7 %
$PM_{2.5}$ OC	UWM / TOT	24-hour	04/11/01-06/30/02	97.3 %
$PM_{2.5}$ EC	Sunset Field ECOC	1-hour	04/12/01-06/30/02	70.0 %
$PM_{2.5}$ OC	Sunset Field ECOC	1-hour	04/12/01-06/30/02	70.0 %
$PM_{2.5}$ BC & UV-C	Aethalometer	5-minute	04/11/01-06/30/02	95.7 %
Gases				
SO_2	HEADS denuder	24-hour	04/13/01-06/30/02	98.0 %
HNO_2	HEADS denuder	24-hour	04/13/01-06/30/02	98.0 %
HNO_3	HEADS denuder	24-hour	04/13/01-06/30/02	98.0 %
NH_3	HEADS denuder	24-hour	04/13/01-06/30/02	96.8 %
SO_2	IEPA analyzer	1-hour	04/15/01-06/30/02	98.8 %
CO	IEPA analyzer	1-hour	04/15/01-06/30/02	97.3 %
NO/NO_x	IEPA analyzer	1-hour	04/15/01-06/30/02	95.5 %
O_3	IEPA analyzer	1-hour	04/15/01-06/30/02	98.9 %
Meteorology				
Wind Speed	see description of each sensor in the report text	5-minute	05/08/01-06/30/02	99.8%
Wind Direction		5-minute	05/08/01-06/30/02	99.8%
Temperature @ 10m		5-minute	05/08/01-06/30/02	94.3%
Temperature @ 2m		5-minute	05/08/01-06/30/02	97.6%
Relative Humidity		5-minute	05/08/01-06/30/02	99.8%
Solar Radiation		5-minute	05/08/01-06/30/02	99.8%
Barometric Pressure		5-minute	05/08/01-06/30/02	100.0%
Precipitation		5-minute	05/08/01-06/30/02	100.0%

(a) $PM_{2.5}$ "A" channel only; a second channel "B" was collected each day which could be used to impute void records for "A" channel data.

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3. Aerosol Physical Properties

PM Gravimetric Mass (integrated)

Daily 24-hour integrated particulate matter mass measurements were conducted for PM_1 (PM_{10} standard inlet followed by a PM_1 cyclone), $PM_{2.5}$ (Harvard Impactor, HI) and PM_{10} (Harvard Impactor). Gravimetric analysis was performed by the Koutrakis group at the Harvard School of Public Health. Data completeness is summarized in Table 2-1. Data completeness corresponds to measurements conducted on the core site platform.

Detection Limits. Table 3-1 summarizes the field blanks data collected during the measurement program. In each case, the filter was deployed identical to an ambient sample (including pre- and post-sampling flow checks and the standard field latency between setup and takedown). Mean field blank masses were statistically indistinguishable from zero (95% CL) and thus no field blank correction was applied to the gravimetric mass data. The last column of Table 3-1 lists MDL concentration values based on three times the standard deviation of the field blank data and operation at the setpoint flowrate.

Precision. The movable measurement platform (satellite site shelter) was periodically deployed at the core site for collocated measurements with the results summarized in Table 3-2. These metrics are based on all data. Including only those concentration values exceeding ten times the MDL reported in Table 3-1 yields collocated precision of 1.0 $\mu g/m^3$ (4.6%) for $PM_{1.0}$ (N = 3) and 2.0 $\mu g/m^3$ (9.5%) for $PM_{2.5}$ (N = 10). All concentration values were greater than ten times the MDL for the collocated PM_{10} data set. In addition to the completely independent measurements, two $PM_{2.5}$ samples were collected in parallel on most days. The last row of Table 3-2 shows the collated precision for those measurements which shared the same pump and timer but had independent flow control elements. This measurement captures a subset of the overall collocated variability.

Bias and Comparability. One quality check for the PM gravimetric mass data is to test whether $PM_{1.0} < PM_{2.5} < PM_{10}$ mass within the measurement uncertainty. Figure 3-1 shows scatter plots for $PM_{1.0}$ and $PM_{2.5}$ (Fig. 3-1a), and $PM_{2.5}$ and PM_{10} mass (Fig. 3-1b). There were four cases where $PM_{1.0}$ exceeded $PM_{2.5}$ (by 0.5, 0.7, 0.8, and 1.0 $\mu g/m^3$), and one case where $PM_{2.5}$ exceeded PM_{10} (by 0.2 $\mu g/m^3$). Assuming the 0.5 $\mu g/m^3$ absolute precision estimated from $PM_{2.5}$ samplers from the same sampling system (last row of Figure 3-2), these cases can be explained by measurement error.

In addition to the above Supersite platform measurements, the Illinois EPA (IEPA) operated a full suite of NAAQS compliance monitors, including a $PM_{2.5}$ FRM, at the 13th & Tudor (East St. Louis) at the monitoring site which shared the same physical footprint as the Supersite. The IEPA and Supersite $PM_{2.5}$ gravimetric mass measurements were independently conducted at all levels (different field staff, audit devices, handling and storage facilities, and gravimetric mass analytical laboratories). IEPA samplers and continuous analyzers were included in the systems and performance audits conducted by DRI.

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Comparability between the IEPA FRM and Supersite Harvard Impactor (HI) gravimetric mass measurements are shown in Figure 3-2a for the period 4/14/01 through 3/31/2003 and excluding one value at (95.7, 88.8). A reduced major axis regression yielded:

$$FRM_{IEPA} = (0.92 \pm 0.05) \times HI + (-0.8 \pm 0.7\ \mu g / m^3)$$

The FRM and HI measurements are comparable with the HI biased high. This bias likely arises from differences in samplers, including but not limited to the impactor cutpoint curves (collection efficiency as a function of aerodynamic diameter). There are several outliers in Figure 3-2a which in most cases have been identified as anomalous values for the FRM measurement (based on comparisons to other onsite measurements including semicontinuous $PM_{2.5}$ mass, and comparisons to St. Louis area network-wide FRM data).

IEPA $PM_{2.5}$ FRM data quality is demonstrated by comparison to additional FRM measurements conducted at the East St. Louis site by the Turner group (WUSTL) in support of a field evaluation of the Thermo $PM_{2.5}$ SHARP mass monitor (Hill *et al.* 2006). Figure 3-2b shows the collocated $PM_{2.5}$ FRM gravimetric mass data for calendar year 2005. The collocated precision was 1.3 μg/m^3. There are three outliers – 6/15/05 (IEPA=7, WUSTL =11), 10/1/05 (IEPA=23, WUSTL=14), 12/6/05 (IEPA=13, WUSTL=18). Based on comparisons to the onsite $PM_{2.5}$ continuous mass monitors and other FRM measurements in the STL area, it appears the 6/15/05 outlier is WUSTL biased high, the 10/1/05 outlier is IEPA biased high, and the 12/6/05 outlier is IEPA biased low. After removing these three outliers the collocated precision for the CY2005 data is 0.8 μg/m^3. This comparison is a robust determination of the measurement precision given that IEPA and WUSTL conducted completely independent measurements.

Table 3-1. Field blanks data for PM mass measurements, 4/13/2001-6/30/2002.

Parameter	Method	N	Mean ± Std Dev (μg)	Nominal Blank Concentration[(a)] (μg/m^3)	MDL (μg/m^3)
$PM_{1.0}$ mass	cyclone	29	-5.3 ± 16.2	-0.2	2.0
$PM_{2.5}$ mass	HI	54	2.5 ± 7.0	+0.2	1.5
PM_{10} mass	HI	30	3.4 ± 4.5	+0.2	0.9

(a) Nominal concentrations based on 24 hours of sampling at the setpoint flow rates (16.7 LPM for cyclone, 10 LPM for HI).

Table 3-2. Collocated 24-hour integrated PM mass measurements, 4/13/2001-6/30/2002.

Parameter	Method	Collocated N	Absolute Precision (μg/m^3)	Mean Conc. (μg/m^3)	Relative Precision
$PM_{1.0}$ mass[(a)]	cyclone	31	1.18	11.25	10.5 %
$PM_{2.5}$ mass[(a)]	HI	32	1.26	14.26	8.8 %
PM_{10} mass[(a)]	HI	33	1.69	26.92	6.3 %
$PM_{2.5}$ mass[(b)]	HI	396	0.51	17.17	3.0 %

(a) Collocated $PM_{2.5}$ measurements with completely independent sampling systems.
(b) Parallel $PM_{2.5}$ measurements using the same pump and timer but different flow control elements.

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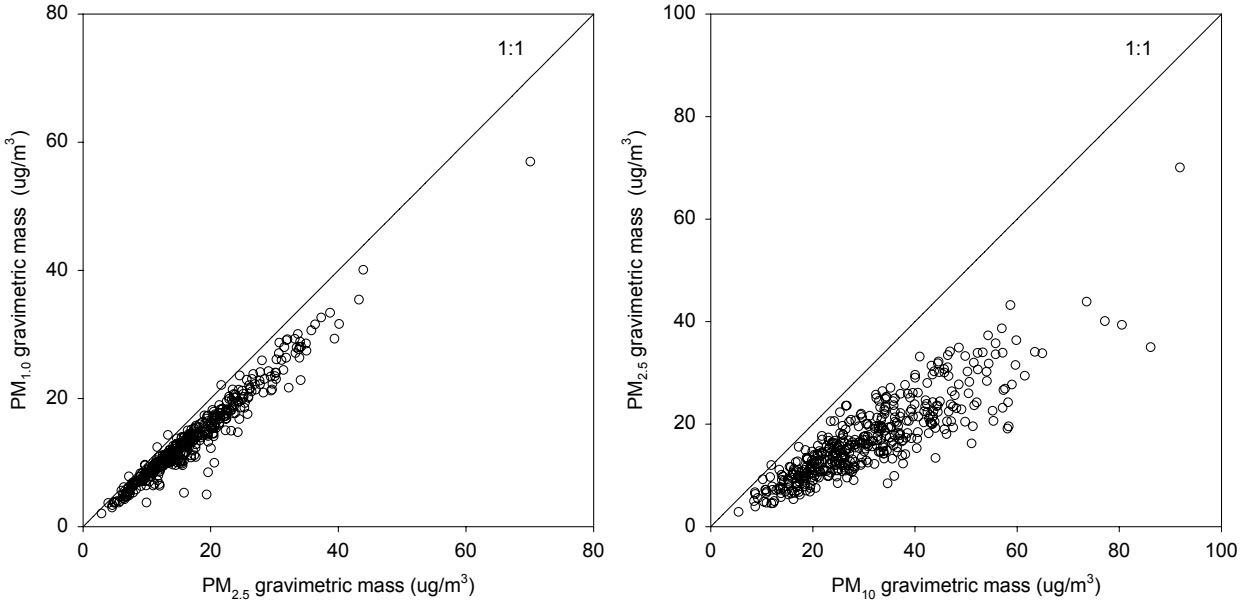

Figure 3-1. Comparisons between PM gravimetric mass measurements: (a) $PM_{1.0}$ versus $PM_{2.5}$; and (b) $PM_{2.5}$ versus PM_{10}, for the samplers summarized in Table 3-1 and the period 4/13/01-6/30/02.

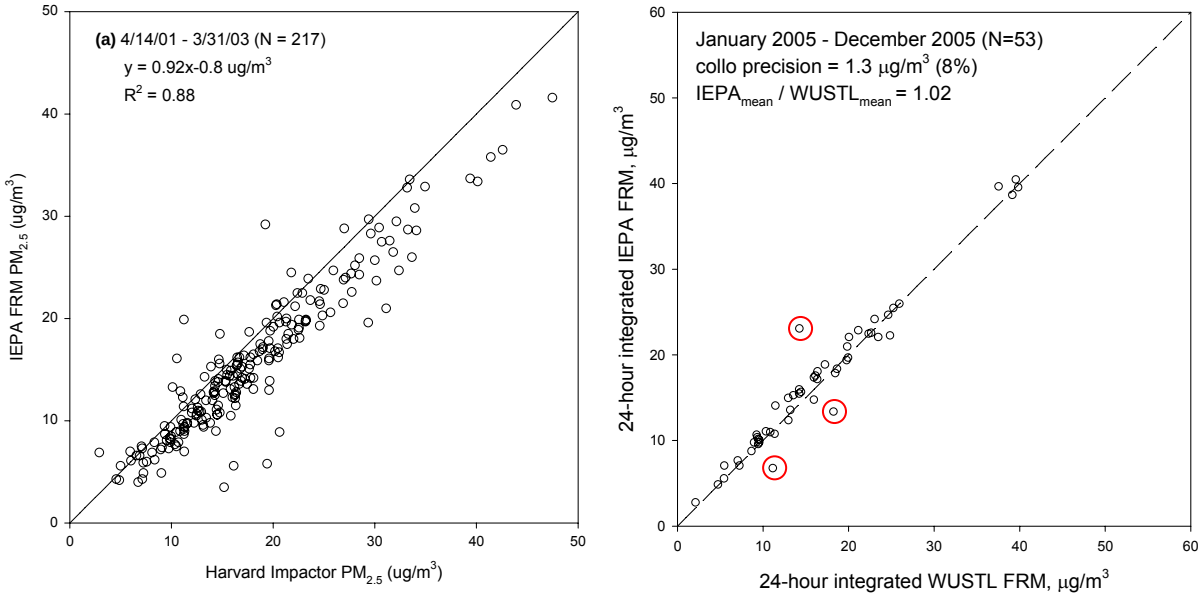

Figure 3-2. 24-hour integrated $PM_{2.5}$ mass concentration measured by: (a) FRM operated by IEPA and Harvard Impactors operated by WUSTL; and FRM operated by IEPA and FRM operated by WUSTL. The 1:1 line is also shown (solid diagonal line).

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$PM_{2.5}$ Mass by CAMMS (semicontinuous)

Semicontinuous $PM_{2.5}$ mass concentrations were measured using the Anderson Continuous Aerosol Mass Measurement System (CAMMS) and validated at 1-hour resolution. Persistent hardware problems required the units be replaced during the study. The units and their respective measurement periods were: #121 (4/29/01-10/4/01); #123 (4/15/01-8/15/01); and #135 (10/16/01-6/30/02). The primary data sampler data stream is #123 and #135, while #121 is the collocated sampler data. Data completeness is summarized in Table 2-1.

Detection Limits. Dynamic zero measurements were periodically performed by placing a HEPA filter on the inlet. The MDL, defined as three times the standard deviation of these zero air measurements, was 4.5μg/m^3.

Precision. Collocated precision results for units #121 and #123 are summarized in Table 3-3. A portion of this dispersion is due to a bias between the instruments. Transforming the hourly data for #123 using a constrained linear least squares regression of #123 on #121 (slope 0.881) yields a collocated precision of 2.9 μg/m^3 (13.0%).

Bias and Comparability. $PM_{2.5}$ mass can be compared be compared between the 24-hour integrated gravimetric mass measurement (HI) and the 24-hour average of the 1-hour semicontinuous mass measurement (CAMMS). Figure 3-3 shows the 24-hour CAMMS and HI data for the period 4/14/01 through 6/30/2002, including only those days with at least 22 valid CAMMS 1-hour average mass concentrations (7/4/2001 was excluded because one CAMMS hour was invalid and this dramatically affected the 24-hour average due to microscale impacts from fireworks). A reduced major axis regression yielded:

$$CAMMS = (0.96 \pm 0.04) \times HI + (0.9 \pm 0.8\ \mu g / m^3)$$

Table 3-3. Collocated 1-hour average $PM_{2.5}$ mass measurements, 4/29/01-8/15/01.

Parameter	Method	Collocated N	Absolute Precision (μg/m^3)	Mean Conc. (μg/m^3)	Relative Precision
$PM_{2.5}$ mass[(a)]	CAMMS #121 & #123	1,838	3.3	20.9	15.7 %
$PM_{2.5}$ mass[(a,b)]	CAMMS #121 & #123	36	4.0	54.6	7.3%

(a) All data excluding three hours exceeding 100 μg/m^3.
(b) Also excludes data less than ten times the MDL estimated from dynamic zero data (4.5 μg/m^3).

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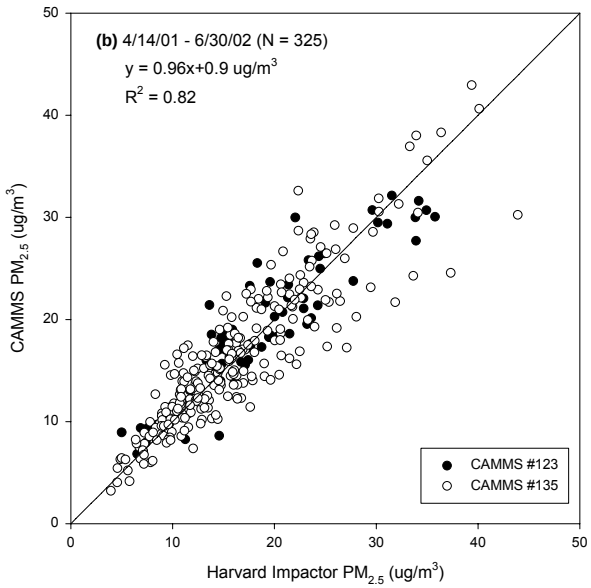

Figure 3-3. 24-hour $PM_{2.5}$ mass concentration measured by CAMMS (semicontinuous) and Harvard Impactors (integrated sampling with offline gravimetric analysis). The 1:1 line is also shown (solid diagonal line).

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Particle Size Distributions (semicontinuous)

Particle size distributions (PSD) over the size range 3 nm – 2 μm were measured at 5-minute time resolution. Data was obtained using a battery of instruments, including a nano-SMPS, regular-SMPS and an optical particle counter (OPC). A second optical particle counter was initially used to extend the size distributions up to 10 μm. However, there were repeated failures of this unit and thus the data was validated and reported for the three instruments covering the range 3 nm – 2 μm. The instruments and measurement conditions are described in detail by Shi (2003) and summarized by Shi *et al.* (2007) with the former dedicating an entire chapter to quality assurance for the PSD data.

As reported in Table 2-1, data completeness for the first 13 months (April 2001 – April 2002) was 76.0%. A more-detailed breakdown of the data completeness is (Shi, 2003):

- 53.6% - data valid (no flags)
- 22.5% - data flagged/suspect
- 3.9% - data invalid
- 12.5% - no data
- 7.5% - data invalid (hourly OPC calibration for 10 of the 60 minutes)

A primary data quality metric for the PSD measurements was the particle number concentration measured by two instruments for overlapping size ranges. The nano- and regular-SMPS overlap for sizes 30-40 μm while the regular-SMPS and OPC overlap for sizes 0.1-0.4 μm. Consult Shi (2003) for details.

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4. Aerosol Chemical Properties

$PM_{2.1}$ Major Ions by HEADS (integrated)

$PM_{2.1}$ major ions (sulfate, nitrate, ammonium) were sampled using the Harvard-EPA Annular Denuder System (HEADS) which included a sodium carbonate denuder, citric acid denuder and a filter pack with a Teflon filter followed by a Nylon filter. The filters were extracted by the Koutrakis group (Harvard School of Public Health) and analyzed using ion chromatography by the Chow group (Desert Research Institute). Sulfate was determined from the Teflon filter, nitrate from the Teflon and Nylon filters, and ammonium was measured on the Teflon filter with reconstructed ammonium calculated assuming all nitrate on the Nylon filter was ammonium nitrate that volatilized off the Teflon filter.

Detection Limits. Effective MDL values, estimated as three times the standard deviation of 29 field blanks, are 0.18 (nitrate), 0.94 (sulfate) , and 0.01 $\mu g/m^3$ (ammonium). The MDL for sulfate is significantly influenced by one value and its removal reduced the sulfate MDL from 0.94 to 0.20 $\mu g/m^3$, which is consistent with the MDL for nitrate. This revised MDL was used in subsequent data analysis. Ambient concentration values were not blank-corrected.

Precision. Table 4-1 summarizes the collocated precision. For each species the collocated precision, expressed as a relative value, was consistent when using all data or only those days with concentration values exceeding ten times the estimated MDL.

Bias and Comparability. A deployment of the movable measurement (satellite) platform August-December 2002 in Reserve, KS, provided an opportunity to conduct collocated measurements with the IMPROVE protocol measurements at SAFO1. Figure 4-1a shows the IMPROVE and HEADS sulfate data. A reduced major axis regression yielded:

$$HEADS_{SO4} = (1.04 \pm 0.05) \times IMPROVE_{SO4} + (-0.09 \pm 0.15\ \mu g/m^3)$$

The slope is statistically indistinguishable from unity and the intercept is statistically indistinguishable from zero (95% CL). The collocated precision for all data is 0.20 $\mu g/m^3$ (9.4%), which is essentially the same precision obtained for collocated HEADS samplers deployed at East St. Louis (Table 4-1). Figure 4-1b shows the IMPROVE and HEADS nitrate data excluding the highest-concentration record of (HEADS=6.06 $\mu g/m^3$; IMPROVE = 8.68 $\mu g/m^3$). A reduced major axis regression yielded:

$$HEADS_{NO3} = (1.02 \pm 0.06) \times IMPROVE_{NO3} + (0.01 \pm 0.13\ \mu g/m^3)$$

The slope is statistically indistinguishable from unity and the intercept is statistically indistinguishable from zero (95% CL). The collocated precision for all data is 0.15 $\mu g/m^3$ (8.3%), which is close to the precision obtained for collocated HEADS samplers deployed at East St. Louis (Table 4-1).

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Table 4-1. Collocated 24-hour integrated $PM_{2.1}$ ion measurements, 04/13/01-6/30/02.[(a)]

Parameter	Method	Collocated N	Absolute Precision ($\mu g/m^3$)	Mean Conc. ($\mu g/m^3$)	Relative Precision
$PM_{2.1}$ sulfate	HEADS / IC	29 20	0.31 0.33	2.94 3.61	10.5 % 9.2 %
$PM_{2.1}$ nitrate	HEADS / IC	29 18	0.21 0.25	2.23 3.13	9.2 % 7.8 %
$PM_{2.1}$ ammonium (Teflon filter only)	HEADS / IC	29 29	0.14 0.14	1.04 1.04	13.5 % 13.5 %

(a) The first value includes all collocated data, and the second value is for data exceeding ten times the estimated MDL only.

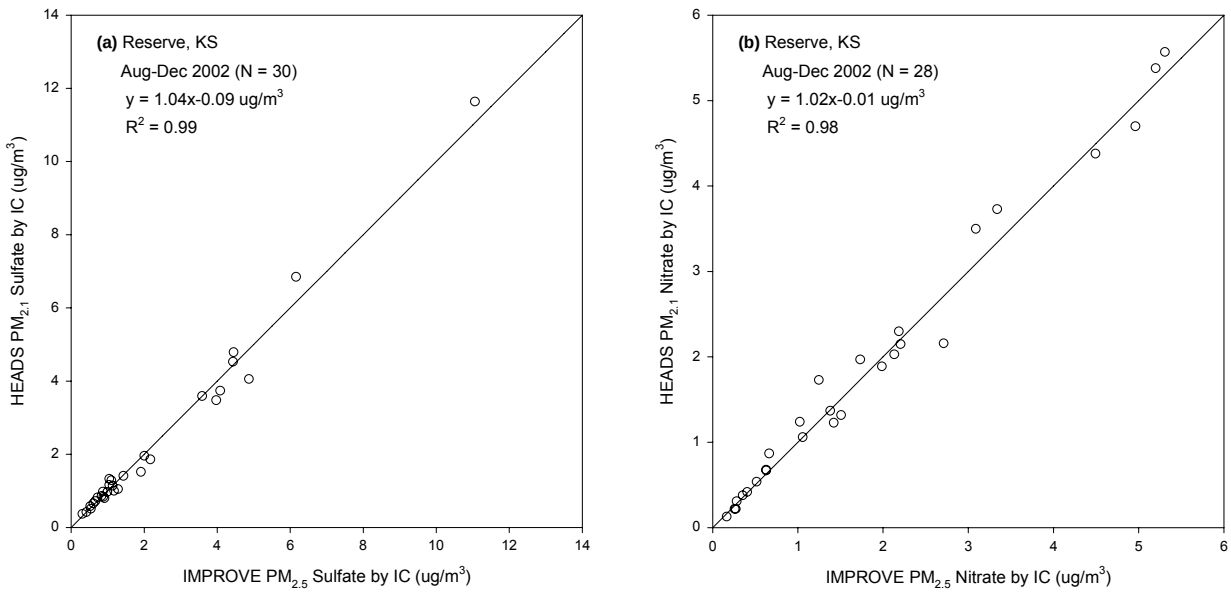

Figure 4-1. Comparisons between HEADS and IMPROVE fine PM ions measured at the Reserve, KS (SAFO1) IMPROVE protocol site: (a) sulfate; and (b) nitrate. The 1:1 line is also shown (solid diagonal line).

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$PM_{2.5}$ Nitrate by R&P 8400N (semicontinuous)

$PM_{2.5}$ nitrate measurements using the R&P 8400N commenced in February 2002 and continued through March 2005. Reid (2005) describes in detail the instrument operation, data validation, and quality assurance measures for these nitrate measurements. Raw concentration data was collected at 10-minute time resolution and was validated at 1-hour time resolution.

Detection Limits. As described by Reid (2005), the instrument response to particle-free air (a "dynamic zero" test) was routinely measured by placing a Teflon filter mounted in a Teflon filter housing in the sample line immediately upstream of the denuder. Dynamic zero testing was performed during the bimonthly (twice a month) maintenance with at least three 10-minute cycles run with the Teflon filter installed. Standard deviations for the study-mean dynamic zero tests were in the range 0.2-0.3 $\mu g/m^3$ for the three instruments deployed over the period February 2002 through July 2005, corresponding to an MDL of 0.6-0.9 $\mu g/m^3$. For semicontinuous instruments, dynamic zero tests have been used both to estimate method detection limits (from the standard deviation of the replicated measurements) and estimate an offset to be applied to the data. For the R&P 8400N, however, the interpretation of dynamic zero tests is not clear. Harrison *et al.* (2004) conducted dynamic zero tests with a HEPA filter at the inlet of an 8400N. They postulate that nitric acid and ammonia were likely adsorbed by the HEPA filter and the observed response resulted from these precursor gases desorbing from the denuder into the ammonia- and nitric acid-free sample stream (presumably to form ammonium nitrate). Thus, in terms of the ambient $PM_{2.5}$ data, the dynamic zero response might provide insights into a positive bias from sharp decreases in ambient concentrations of the precursor gases which would promote denuder off gassing. This scenario assumes that ammonium nitrate formation from denuder off gassing is both thermodynamically and kinetically favorable. While this is a plausible interpretation of dynamic zero testing, more work is needed to determine whether this is correct. In the interim, the estimated MDL of 0.6-0.9 $\mu g/m^3$ should be used with caution. For example, this may be an upper bound since the dynamic zero response exhibited seasonal behavior (Reid, 2005) and the standard deviations used to estimate the MDL include such variation

Precision. Six weeks of collocated data was collected in January-February 2005 to quantify the collocated precision in the measurements (Figure 4-2). The units showed excellent agreement, and the scatter provides insights into the collocated precision of the 8400N measurements at hourly resolution. Deming's regression was performed on the data using on the data using record-specific uncertainties of the form $\sigma_i = a + b \times C_i$, with $a = 0.30$ $\mu g/m^3$ and $b = 0.05$; C_i is the hourly-averaged nitrate concentration in $\mu g/m^3$. The regression coefficients are reported in Figure 4-2.

Bias and Comparability. Measurements were conducted in rural Reserve, KS from September 2002 – December 2002 (Figure 4-2) and in East St. Louis, IL (Figure 4-3) during the remainder of this 16-month interval. Nitrate measurements by the R&P 8400N at East St. Louis were continued though March 2005. Substrate-based nitrate sampling was performed using HEADS in East St. Louis and a composite of HEADS and IMPROVE in Reserve; as previously demonstrated there was excellent agreement for collocated HEADS and IMPROVE samples. The 8400N nitrate recovery with respect to filter nitrate was similar for both sites. Excellent recoveries were observed below ~2 $\mu g/m^3$ (albeit with more scatter at the urban East St. Louis

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site compared to the rural Reserve site). Above approximately 2 μg/m^3, the 8400N recovery decreased and exhibited greater variability with increasing filter nitrate. The overall behavior is inadequately represented by a linear fit; therefore, box plots for the relative and absolute differences in 8400N nitrate with respect to filter nitrate are presented in Figures 4-3 and 4-4. The data for these box plots were stratified by quartiles for the filter nitrate concentration. An explanation for the observed low and variable nitrate recoveries has been described by Reid (2005) and Reid *et al.* (2005).

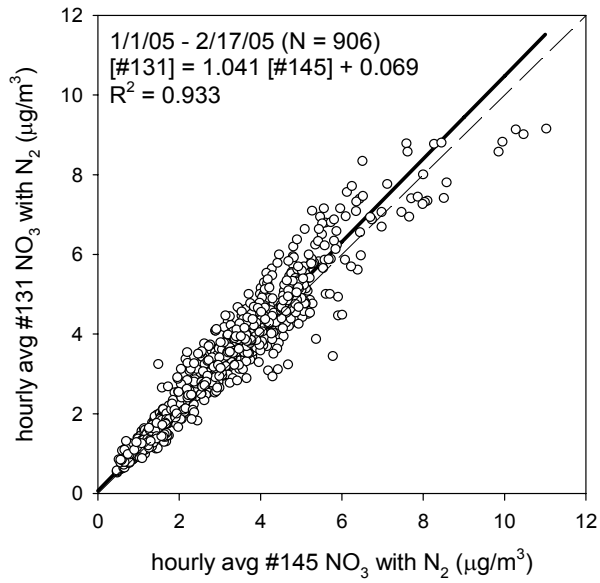

Figure 4-2. Hourly average nitrate for collocated R&P 8400 units. This work was conducted in January-February 2005 as part of a study to examine the effect doping the N_2 carrier gas with electron donors to improve conversion efficiency. From Reid (2005).

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Figure 4-3. Fine PM nitrate measurements conducted at Reserve, KS (September 2002 – December 2002; N = 86): (a) daily-average R&P 8400N nitrate versus daily-integrated filter nitrate; (b) daily-average R&P 8400N nitrate recovery with respect to daily-integrated filter nitrate, stratified by quartiles for filter nitrate; and (c) daily-average R&P 8400N nitrate minus daily-integrated filter nitrate, stratified by quartiles for filter nitrate. For the box plots, whiskers represent 10th and 90th percentiles. From Reid (2005).

Reserve, Kansas

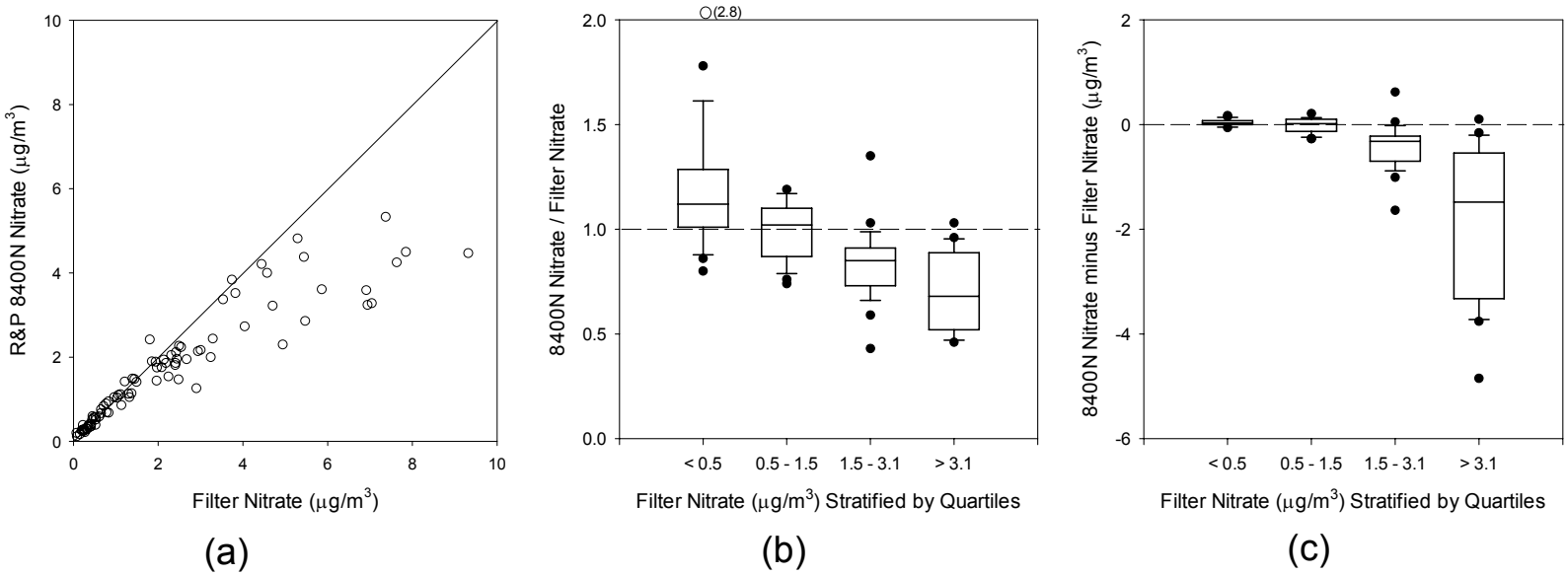

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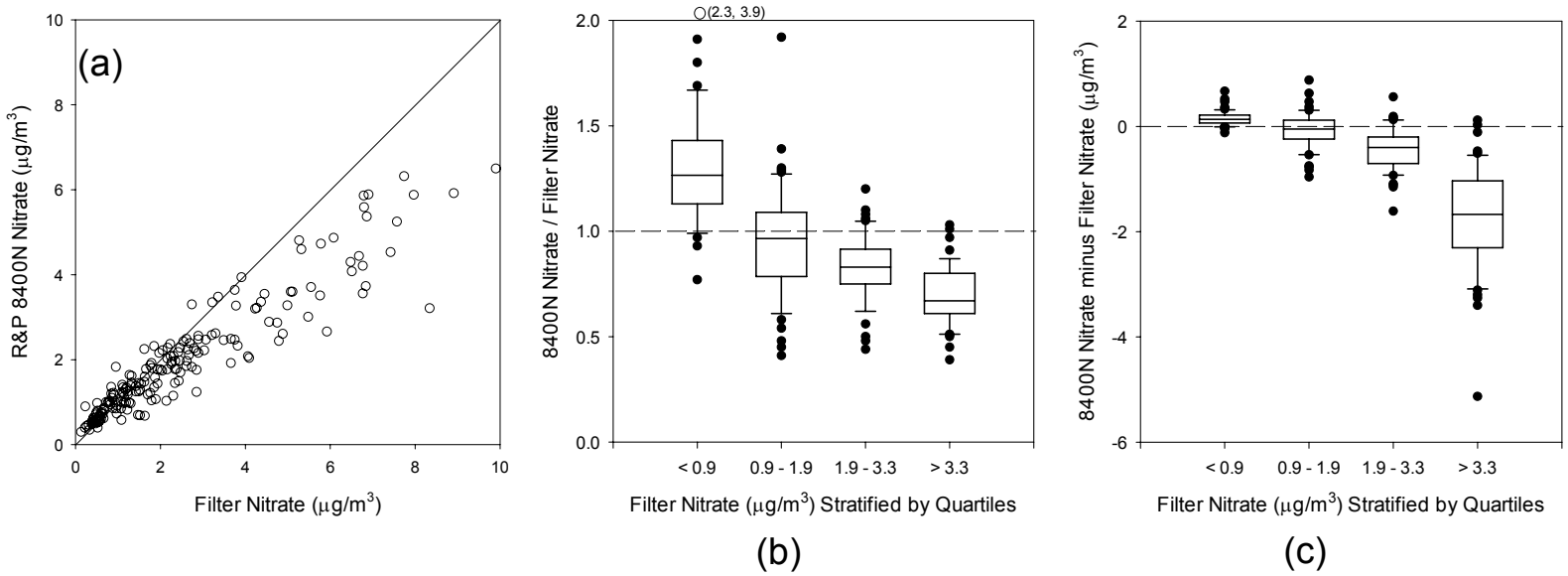
Figure 4-4. Fine PM nitrate measurements conducted at East St. Louis, IL (February 2002 – May 2003; N = 191): (a) daily-average R&P 8400N nitrate versus daily-integrated filter nitrate; (b) daily-average R&P 8400N nitrate recovery with respect to daily-integrated filter nitrate, stratified by quartiles for filter nitrate; and (c) daily-average R&P 8400N nitrate minus daily-integrated filter nitrate, stratified by quartiles for filter nitrate. For the box plots, whiskers represent 10th and 90th percentiles. From Reid (2005).

East St. Louis, IL



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$PM_{2.5}$ Sulfate and Nitrate by PILS-IC (semicontinuous)

$PM_{2.5}$ sulfate and nitrate measurements using the Georgia Tech / BNL Particle-into-Liquid Sampler (PILS) commenced in May 2001 and continued through March 2005. Yu (2005) describes in detail the instrument operation, data validation, and quality assurance measures for the PILS measurements. Raw concentration data was collected at 15-minute time resolution and was validated at 1-hour time resolution.

Detection Limits. Yu (2005) presents the method used to estimate detection limits for the PILS-IC sulfate and nitrate data. Table 4-2 reports the reliable range of results for both sulfate and nitrate as defined by the lower limit of detection (LLD) and by the lower and upper limit of quantification (LLQ, ULQ). The lower limit of detection was estimated from the lowest calibration standard concentration with an IC detector response (analyte peak) signal-to-noise ratio greater than three. The baseline noise of a chromatogram is affected by the hardware and operating conditions of the IC (column type, eluant composition and concentration, solution (including water) quality, degree of internal IC temperature fluctuation, whether or not the eluant is degassed, and whether or not a suppressor is used). The lower limit of quantification (LLQ) was the lowest concentration within the linear range, just as the upper limit of quantification (ULQ) was determined by the highest concentration within the linear range. For sulfate, the LLD did not correspond to the LLQ because although chromatogram peaks were clearly distinguishable from the baseline at the lowest concentration standard, concentrations below Level 2 did were nonlinear (i.e., the Milli-Q and Level 1 standards were typically above the regression line generated from the calibration data). Orsini *et al*. (2003) documented that past field studies have also witnessed detectable sulfate and nitrate peaks during blank runs, possibly attributable to DI water (sulfate) and background NO_x entering through ineffective denuders (nitrate).

Table 4-2. Detection limits (reliable ranges) for sulfate and nitrate by PILS-IC.

	Sulfate ($\mu g/m^3$)			Nitrate ($\mu g/m^3$)	
	LLD	LLQ	ULQ	LLD/LLQ	ULQ
Sample loops	0.03	0.33	33	0.02	22
Concentrator pre-columns	0.05	0.53	53	0.04	35

Reported values are not true method detection and quantifiable limits, but rather are operational definitions based on the calibrations standards corresponding to an IC conductivity signal-to-noise ratio greater than three (LLD) and the calibration standards denoting the linear range (or at the extreme values of the calibration standard concentration range if linear to that concentration).

Precision. Precision estimates for PILS-IC, based on both propagation of precision for the intrinsic measured parameters and from collocated measurements, have been reported elsewhere (Orsini *et al.* 2003). In contrast to that relatively short duration study with stable operating conditions, the East St. Louis deployment focused on sustained, routine measurements during which additional sources of imprecision can surface. Numerous factors influencing PILS-IC measurement precision are described by Ryszkiewicz (2005; Chapter 5), which focused on a newer-generation version of PILS compared to the version deployed for the 2001-2002 measurement program. We have not fully assessed how the factors identified by Ryszkiewicz

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(2005) affect the quantitative precision estimates for the earlier generation measurements and rely upon bias and comparability metrics to document the data quality.

Bias and Comparability. A major barrier to collecting high quality PILS sulfate data was a positive bias from SO_2 plumes breaking through the upstream denuder. Figure 4-5 shows the 24-hour PILS sulfate and HEADS sulfate after first screening to remove all hours with ambient SO_2 mixing ratios exceeding 10 ppbv and then rolling up the hourly PILS data to 24-hour averages. Only those days with 21-or-more valid hours of PILS sulfate data were retained for the comparison (N=119). PILS sulfate was biased about 12% low with respect to HEADS sulfate (the intercept was statistically indistinguishable from zero at the 95% CL). Figure 4-6 shows the 24-hour PILS nitrate and HEADS nitrate for days with 21-or-more valid hours of PILS nitrate data (N=136). An examination of the identified outliers is presented by Yu (2005). Excluding these outliers from the regression, PILS nitrate was biased about 14% low with respect to HEADS nitrate (the intercept was statistically indistinguishable from zero at the 95% CL). Similar bias for both sulfate and nitrate suggests the source of the bias is not species-specific but resides in some aspect of the measurements that affect all anions. Ryszkiewicz (2006) presented a detailed analysis of measurement uncertainties and error in the St. Louis – Midwest Supersite PILS measurements for sulfate and nitrate.

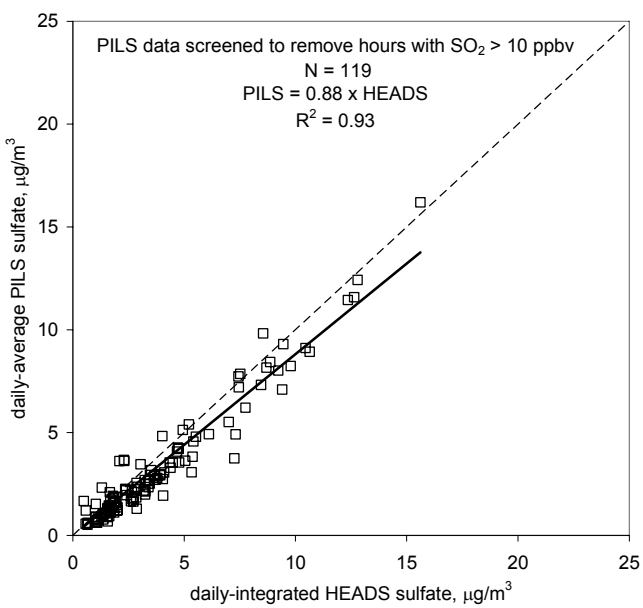

Figure 4-5. Scatter plot of daily-average PILS sulfate versus daily-integrated HEADS sulfate. PILS sulfate was screened to remove all hours coincident with SO_2 > 10 ppbv and subsequently rolled-up to daily-averages. From Yu (2005).

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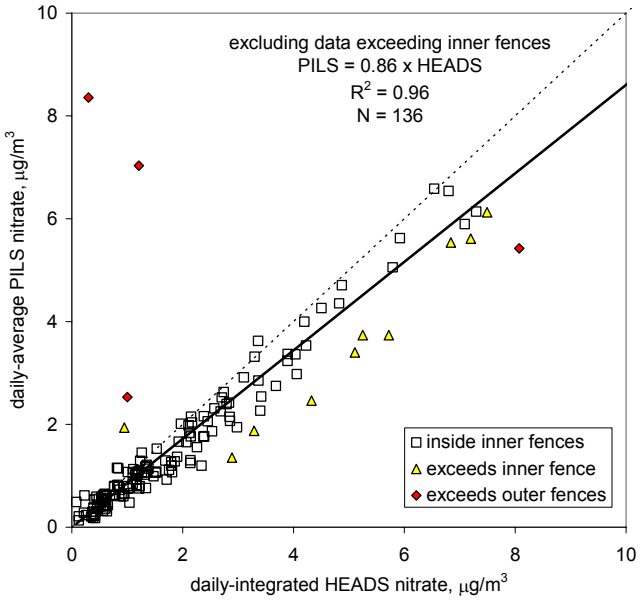

Figure 4-6. Scatter plot of daily-average PILS nitrate versus daily-integrated HEADS nitrate. A nonparametric analysis of the distribution of paired concentration differences revealed four points exceeding the outer fence criteria (red diamonds) and an additional ten points exceeding the inner fence criteria (yellow triangles); these fourteen points were excluded from the regression. From Yu (2005).

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$PM_{2.5}$ Elemental Carbon and Organic Carbon (integrated)

Daily 24-hour integrated $PM_{2.5}$ elemental carbon (EC) and organic carbon (OC) measurements were conducted using custom samplers with offline thermal/optical analysis by the Schauer group (University of Wisconsin – Madison) using the ACE-ASIA protocol which conforms to NIOSH 5040. Details of the field sampling and laboratory analysis, including a comprehensive presentation of the CY2002 data quality indicators, are provided by Bae *et al.* (2004).

Detection Limits. Field blanks were periodically collected by briefly placing a filter in the sampling train in the absence of flow. EC and OC blank corrections were derived for each calendar year and applied to the respective ambient data. For the period 7/1/01 – 6/30/03 there were 76 field blanks with concentrations 0.14 ± 0.10 $\mu g/m^3$ for TC, 0.10 ± 0.06 $\mu g/m^3$ for OC, and 0.04 ± 0.05 $\mu g/m^3$ for EC (assuming the setpoint flow rate of 12 LPM for 24 hours). Using three times the standard deviation as the MDL yields detection limits of 0.30 $\mu g/m^3$ for TC, 0.18 $\mu g/m^3$ for OC, and 0.15 $\mu g/m^3$ for EC.

Precision. Bae *et al. (*2004) present the methodology used to estimate the sample-specific precision based on a propagation of uncertainties for the chemical analysis (as reported by the laboratory Sunset OCEC analyzer) and the field blank correction. For concentration values exceeding ten times the MDL, the precision based on the reported uncertainties was 9.4% C.V. for OC (N = 369) and 12.8 % C.V. for EC (N = 25). The EC precision modestly exceeds the 10% DQO, and it is noted that less than 6% of the samples exceeded ten times the estimated MDL.

Collocated carbon sampling was not formally programmed. Eleven collocated samples were collected in 2001, however, with the results presented in Table 4-3 for samples exceeding ten times the above MDL values. Note the EC precision estimate is not robust because it is based on only one sample pair.

Table 4-3. Collocated 24-hour integrated $PM_{2.5}$ carbon measurements.[(a)]

Parameter	Method	Collocated N and N (Conc > 10×MDL)	Absolute Precision ($\mu g/m^3$)	Mean Conc. ($\mu g/m^3$)	Relative Precision
TC	UWM / ACE-ASIA	11 (7)	0.31	4.09	7.5 %
OC	UWM / ACE-ASIA	11 (9)	0.36	3.06	11.9 %
EC	UWM / ACE-ASIA	11 (1)	0.40	1.83	22.0 %

(a) Precision reported for samples with concentrations exceeding tens times the MDL.

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$PM_{2.5}$ Elemental Carbon and Organic Carbon (semicontinuous)

Semicontinuous $PM_{2.5}$ elemental carbon (EC) and organic carbon (OC) measurements were conducted using two Sunset Laboratory field ECOC analyzers with staggered sampling and analysis times to provide a continuous data stream of hourly average concentrations. Online thermal/optical analysis followed the ACE-ASIA protocol which conforms to NIOSH 5040. Measurement details, including a comprehensive presentation of the CY2002 data quality indicators, are provided by Bae *et al.* (2004).

Bias and Comparability. Bae *et al.* (2004) present a detailed comparison of the semicontinuous and integrated ECOC data. For CY2002 data, an ordinary least squares regression of the 24-hour average semicontinuous carbon (only days with at least 20 hours of valid semicontinuous carbon data) on the 24-hour integrated sampler carbon yielded:

$$SEMI_{TC} = (0.97 \pm 0.02) \times INTEGRATED_{TC} + (0.93 \pm 0.11\ \mu g/m^3) \qquad R^2 = 0.89$$
$$SEMI_{OC} = (0.93 \pm 0.02) \times INTEGRATED_{OC} + (0.94 \pm 0.09\ \mu g/m^3) \qquad R^2 = 0.90$$
$$SEMI_{EC} = (0.95 \pm 0.05) \times INTEGRATED_{TC} + (0.09 \pm 0.04\ \mu g/m^3) \qquad R^2 = 0.60$$

The data was not blank-corrected for these comparisons and the regression intercepts are estimates of the blank corrections for the semicontinuous data. Scatter plots for these comparisons are presented by Bae *et al.* (2004).

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$PM_{2.5}$ Aethalometer® Carbon Measurements (semicontinuous)

$PM_{2.5}$ Aethalometer black carbon (BC) and UV-absorbing carbon (UV-C) data was collected on both the core and satellite platforms and validated at 5-minute resolution. Aethalometer (Magee Scientific AE-21, also marketed as the Andersen AE-21) response depends on the mass of absorbing and scattering aerosol deposited on the filter tape through which the light transmittance is measured. This loading-dependent response is manifested as high imprecision for collocated measurements. Efforts to characterize this artifact in the St. Louis data are presented by Goodwin (2005).

Precision. Collocated data was collected and analyzed for the period 4/11/01-6/30/01. To remove the loading-dependent artifact from the collocated instrument comparisons, the data was censored to retain only those 5-minute records with attenuation difference less than 5 units between the instruments. Furthermore, only those records with arithmetic mean concentration greater than ten times the MDL were retained, where the MDL value is assumed to be 0.050 $\mu g/m^3$ and is based on three times the standard deviation of dynamic blank measurements. The results are summarized in Table 4-4. There is an improvement in the collocated precision when the data is censored to include only those records with similar attenuation for both instruments; with a four-fold worse precision when including all data. The difference between these two collocated precision values demonstrates the error introduced by the loading-dependent effect, and will typically vary by location and time of year. While it should be not be interpreted as a representative measurement error, it will be present in the data unless appropriate methodologies are used to compensate for the loading effect. For this reason, record-specific attenuation (ATN) values have been reported along with the mass concentration values for the data set submitted to the NARSTO database.

Table 4-4. Collocated 5-minute $PM_{2.5}$ Aethalometer BC measurements.

Parameter	Method	Collocated N	Absolute Precision ($\mu g/m^3$)	Mean Conc. ($\mu g/m^3$)	Relative Precision
BC[a,b]	Andersen AE-16	15,338	0.313	1.232	25.4 %
BC[a,c]	Andersen AE-16	1,042	0.249	1.353	18.4 %

(a) Collocated data records 4/11/01-6/30/01 with average concentration greater than ten times the MDL of 0.050 $\mu g/m^3$.
(b) Includes all records with rms difference less than 10 $\mu g/m^3$ (excludes 12 records, 0.08% of total).
(c) Includes only those records with attenuation difference of less than 5 units between the collocated instruments.

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$PM_{2.5}$ Elements by XRF (integrated)

Elemental analysis by XRF was performed by DRI on the $PM_{2.5}$ Teflon filter samples collected using Harvard Impactors.

Detection Limits. Table 4-5 summarizes the DRI-reported MDL values and laboratory blank instrument detection limits (IDL) observed in this study. Sodium and magnesium concentration data are reported as qualitative only.

Precision. In 2006 a subset of samples were reanalyzed by DRI using a newly-commissioned XRF instrument which replaced the XRF instrument used for the first two years of St. Louis – Midwest Supersite samples. This analysis provides a stringent test for the analysis methods contribution to collocated precision since different instruments were used. The last four columns of Table 4-5 report the comparisons for samples with the first analysis concentration at least ten times the DRI-reported MDL. Twenty-three of the forty reported elements had no concentration values exceed this threshold. Relative precision was better than 10% for all elements with at least five concentration values above the threshold.

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Table 4-5. XRF analysis Minimum Detection Limit (MDL) and Instrument Detection Limit (IDL) estimates, and replicate analysis of the same filter samples by a *different* XRF instrument than used for the St. Louis – Midwest Supersite samples.

				Replicate Analysis (All Data)				Replicate Analysis (Conc>10xMDL)			
Element	MDL[a] (µg/m^3)	IDL[b] (µg/m^3)	MDL[c] (µg/m^3)	N	Conc (µg/m^3)	Prec (µg/m^3)	Rel Prec	N	Conc (µg/m^3)	Prec (µg/m^3)	Rel Prec
Sodium (Na)	0.0385	0.4063	0.4154	26	0.1461	0.1217	83%	0			
Magnesium (Mg)	0.0140	0.0523	0.0819	26	0.0316	0.0261	82%	0			
Aluminum (Al)	0.0056	0.0238	0.0289	26	0.0431	0.0167	39%	0			
Silicon (Si)	0.0035	0.0463	0.0248	26	0.0992	0.0080	8%	22	0.1127	0.0083	7.3%
Phosphorus (P)	0.0031	0.0075	0.0065	26	0.0487	0.0508	104%	1	0.3275	0.0831	25.4%
Sulfur (S)	0.0028	0.0069	0.0444	26	1.4216	0.0985	7%	26	1.4216	0.0985	6.9%
Chlorine (Cl)	0.0056	0.0061	0.0040	26	0.0233	0.0399	171%	4	0.0889	0.0996	112.0%
Patassium (K)	0.0034	0.0044	0.0039	26	0.0666	0.0029	4%	26	0.0666	0.0029	4.4%
Calcium (Ca)	0.0026	0.0083	0.0055	26	0.1102	0.0030	3%	25	0.1141	0.0031	2.7%
Titanium (Ti)	0.0016	0.0010	< 0.0001	26	0.0034	0.0022	63%	0			
Vanadium (V)	0.0014	< 0.0001	< 0.0001	26	0.0009	0.0011	113%	0			
Chromium (Cr)	0.0010	0.0003	0.0008	26	0.0007	0.0005	66%	1	0.0089	0.0008	9.3%
Manganese (Mn)	0.0009	0.0010	0.0002	26	0.0050	0.0012	25%	6	0.0132	0.0012	9.2%
Iron (Fe)	0.0008	0.0002	0.0071	26	0.1163	0.0106	9%	26	0.1163	0.0106	9.1%
Cobalt (Co)	0.0005	0.0005	0.0006	26	0.0005	0.0009	172%	0			
Nickel (Ni)	0.0005	0.0002	0.0002	26	0.0003	0.0004	130%	0			
Copper (Cu)	0.0006	0.0002	0.0015	26	0.0543	0.0052	10%	19	0.0737	0.0060	8.2%
Zinc (Zn)	0.0006	0.0020	0.0040	26	0.0405	0.0015	4%	26	0.0405	0.0015	3.8%
Gallium (Ga)	0.0010	0.0031	0.0015	26	0.0005	0.0008	168%	0			
Arsenic (As)	0.0009	0.0001	0.0008	26	0.0029	0.0018	64%	0			
Selenium (Se)	0.0007	0.0008	0.0007	26	0.0007	0.0009	126%	1	0.0015	0.0021	141.4%
Bromine (Br)	0.0006	0.0003	0.0005	26	0.0040	0.0015	37%	13	0.0060	0.0016	27.0%
Rubidium (Rb)	0.0006	0.0004	0.0005	26	0.0002	0.0003	139%	0			
Strontium (Sr)	0.0006	0.0006	0.0007	26	0.0008	0.0009	123%	0			
Yttrium (Y)	0.0007	0.0006	0.0005	26	0.0002	0.0003	148%	0			
Zerconium (Zr)	0.0009	0.0008	0.0008	26	0.0006	0.0008	125%	0			
Molybdenum (Mo)	0.0015	0.0010	0.0014	26	0.0007	0.0009	132%	0			
Palladium (Pd)	0.0062	0.0016	0.0021	26	0.0004	0.0006	151%	0			
Silver (Ag)	0.0067	0.0006	0.0022	26	0.0013	0.0012	92%	1	0.0120	0.0033	27.3%
Cadmium (Cd)	0.0067	0.0034	0.0012	26	0.0020	0.0025	126%	0			
Indium (In)	0.0072	0.0030	0.0014	26	0.0008	0.0013	167%	0			
Tin (Sn)	0.0094	0.0034	0.0058	26	0.0064	0.0031	48%	1	0.1104	0.0108	9.7%
Antimony (Sb)	0.0100	0.0022	0.0024	26	0.0019	0.0021	114%	0			
Barium (Ba)	0.0290	0.0228	0.0260	26	0.0052	0.0090	172%	0			
Lanthanum (La)	0.0346	0.0324	0.0341	26	0.0029	0.0069	239%	0			
Gold (Au)	0.0017	0.0037	0.0017	26	0.0006	0.0012	194%	0			
Mercury (Hg)	0.0014	0.0004	0.0005	26	0.0010	0.0015	142%	1	0.0107	0.0020	18.8%
Thallium (Tl)	0.0014	0.0005	0.0006	26	0.0003	0.0008	285%	0			
Lead (Pb)	0.0016	0.0010	0.0015	26	0.0302	0.0025	8%	16	0.0471	0.0029	6.1%
Uranium (U)	0.0013	0.0009	0.0008	26	0.0002	0.0003	228%	0			

(a) MDL reported by Desert Research Institute
(b) IDL as three times the standard deviation of ten laboratory blanks
(c) MDL as three times the standard deviation of thirteen field blanks (Reserve, KS)

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5. Meteorology

Table 5-1 summarizes the meteorological measurements validated at 5-minute time resolution for the period 5/8/01-6/30/02. Parameters marked with an asterisk (*) were continuously measured (1 second frequency except barometric pressure and precipitation) with averaging to 5-minute intervals and calculations of 5-minute standard deviations performed by the datalogger.

Table 5-1. Meteorological parameters validated at 5-minute resolution.

Parameter	Units	Sensor (all Climatronics)
scalar mean wind speed at 10m*	m/s	102083-G0-H0 anemometer
vector wind speed at 10m	m/s	
standard deviation of wind speed at 10m	m/s	
unit vector wind direction at 10m*	°N	102083-G0-H0 wind vane
resultant vector wind direction at 10m	°N	
Yamartino standard deviation of wind direction at 10m	deg	
Campbell sigma-theta at 10m	deg	
temperature at 10 m*	°C	100093 thermocouple
standard deviation of temperature at 10m	°C	
temperature at 2m*	°C	
standard deviation of temperature at 2m	°C	
temperature at 2m minus temperature at 10m	°C	
standard deviation of temperature at 2m minus temperature at 10m	°C	
relative humidity*	%	102425 lithium chloride sensor
standard deviation of relative humidity	%	
solar radiation*	W/m^2	CM3 102318 pyranometer
standard deviation of solar radiation	W/m^2	
barometric pressure*	hPa	102270-G3 barometer
standard deviation of barometric pressure	hPa	
total period precipitation*	mm	100097-1-G0 tipping bucket
maximum wind gust at 10m	m/s	102083-G0-H0 anemometer
time of maximum wind gust at 10m	hh:mm CST	
wind direction of maximum wind gust at 10m	°N	102083-G0-H0 wind vane

Solar Radiation

Solar radiation was measured using a Climatronics CM3 102318 pyranometer and validated at 5-minute time resolution. The manufacturer-reported zero offset is less 15 W/m^2 at 200 W/m^2 thermal radiation. Using October – December 2002 hourly data, the average of the reported hourly standard deviation in solar radiation is 0.4 W/m^2 for hours with negative solar radiation reported (nighttime conditions). Using three times this metric as a crude estimate for the MDL, the solar radiation MDL would be 1.2 W/m^2.

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A DRI site audit in October 2002 included collocation of a continuously measuring Eppley Precision Spectral Pyranometer (PSP) which was installed near the site sensor with an exposure as close to that of the site sensor as possible. Nighttime data (1700 through 0500 CST) were excluded from the comparison since the sensors read zero within the measurement precision. Figure 5-1a shows the collocated hourly data. A reduced major axis regression yielded:

$$Audit = (1.01 \pm 0.02) \times Site + (9.7 \pm 7.3 \ \ W/m^2)$$

The slope us statistically indistinguishable form unity (95% CL) and the intercept is nearly zero compared to the typical range of daytime solar radiation. Collocated precision was 11.0 W/m^2 (2.8%) for the 23 hours of daytime collocated data, which is less than the manufacturer-reported maximum zero offset of 15.0 W/m^2 at 200 W/m^2 thermal radiation.

Barometric Pressure

Barometric pressure was measured using a Climatronics 102270-G3 barometer and validated at 5-minute time resolution. The manufacturer-reported accuracy is less than ±0.1%. A DRI site audit in October 2002 included collocation of a continuously measuring Vaisala PBT101B Transducer. Figure 5-1b shows the collocated hourly data. A reduced major axis regression yielded:

$$Audit = (0.98 \pm 0.02) \times Site + (23 \pm 14 \ \ mb)$$

The slope us statistically indistinguishable form unity (95% CL) and the intercept is nearly zero compared to the typical range of barometric pressure. Collocated precision was 1.6 mb (0.16%) for the 63 hours of collocated data, which is close to the manufacturer-reported accuracy of less than ±0.1%.

Temperature

Ambient temperature was measured using aspirated Climatronics 100093 thermocouples at 2m and 10m. The manufacturer-reported accuracy is ±0.15°C. A DRI site audit in October 2002 included collocation of a continuously measuring, aspirated Campbell 107 Thermistor near the 2m site sensor. Figure 5-1c shows the collocated hourly data. A reduced major axis regression yielded:

$$Audit = (0.93 \pm 0.02) \times Site + (1.3 \pm 0.2 \ ^{o}C)$$

The regression parameters are misleading; Figure 5-1c demonstrates a slope of nearly unity above 5°C while the site probe response was biased low below this temperature. The bias at low temperature arises during high RH conditions with moisture penetrating the signal cables. This behavior periodically occurred despite the cable being replaced several times. Data was screened for anomalously low temperatures at high RH (specifically, above 85% RH) and the affected records were voided. In addition, during very stagnant conditions warm air exhausted from two nearby 6 hp blowers used for the high-volume toxicological samplers caused a mild heating of the 2m temperature sensor. Data was screened for such conditions and the affected records were voided. These two factors account for the relatively low data completeness for temperature

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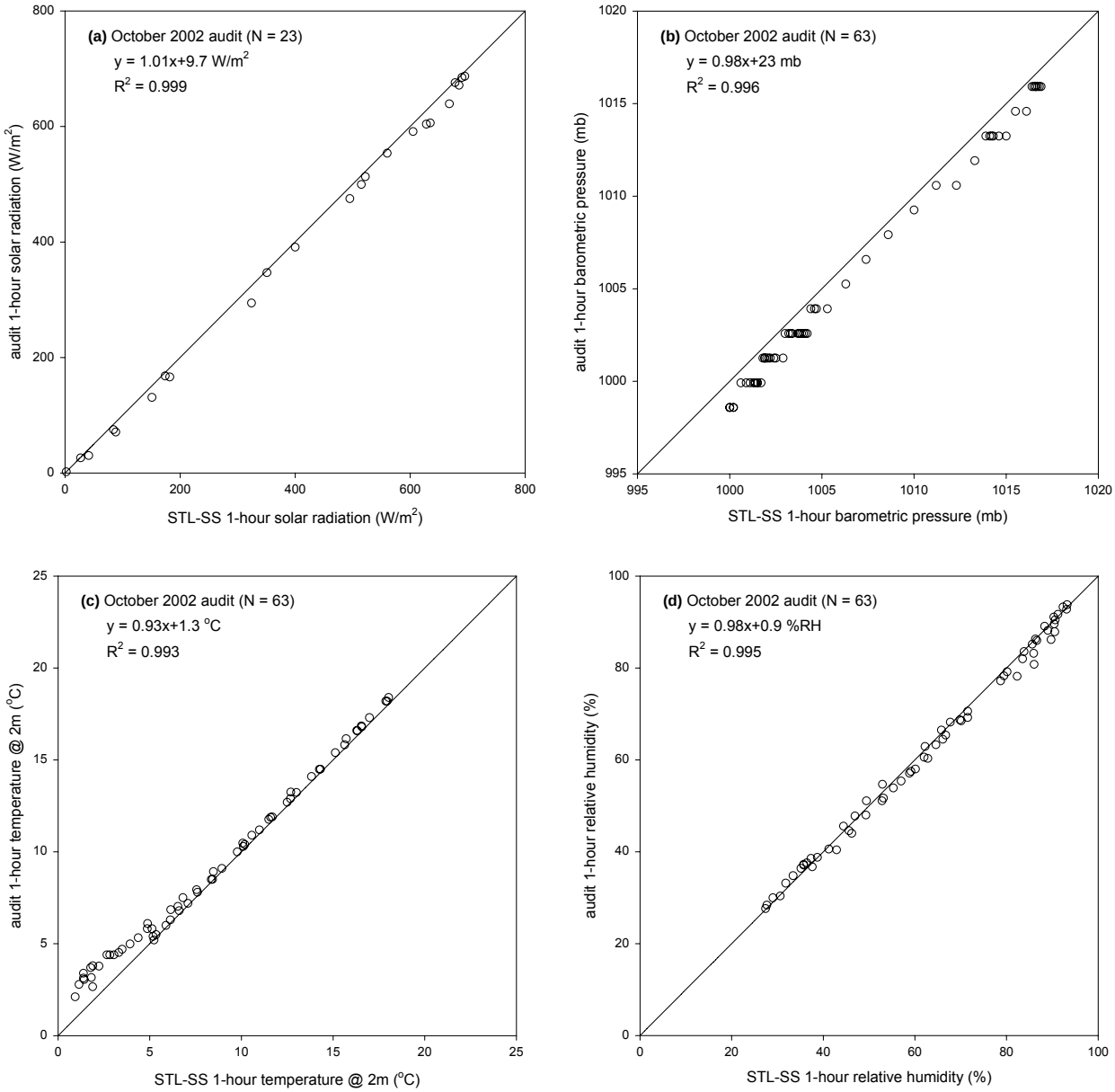

Figure 5-1. Collocated meteorology sensor performance for the October 2002 audit conducted by DRI: (a) solar radiation; (b) barometric pressure; (c) temperature; and (d) relative humidity.

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(94.3% at 2m, 97.6% at 10m) compared to all other meteorological parameters for which completeness ≥ 99.8% was achieved. For 2m site temperatures above 5°C, a reduced major axis regression yielded (N = 44; R^2 = 0.998):

$$Audit = (1.00 \pm 0.01) \times Site + (0.3 \pm 0.1\ ^{o}C)$$

Collocated precision was 0.6°C (6.8%) for all 63 hours of collocated data and 0.2°C (2.1%) for the 44 hours with the site temperature above 5°C, with the latter being close to the manufacturer-reported accuracy of ±0.15°C.

Relative Humidity

Relative humidity was measured using an aspirated Climatronics 102425 lithium chloride sensor. The manufacturer-reported accuracy is less than ±3% RH in the range 10-90% RH. A DRI site audit in October 2002 included collocation of a continuously measuring Vaisala HMP35C sensor. Figure 5-1d shows the collocated hourly data. A reduced major axis regression yielded:

$$Audit = (0.98 \pm 0.02) \times Site + (0.8 \pm 1.1\ \%RH)$$

The regression slope is statistically indistinguishable from unity and the intercept is statistically indistinguishable from zero (95% CL). Collocated precision was 1.1% RH (1.8% relative precision) for the 63 hours of collocated data, meeting the manufacturer-reported accuracy of less than ±3% RH.

Wind Speed

Wind speed was measured using a Climatronics 102083-G0-H0 (Wind Mark III series) anemometer at 10m. The manufacturer-reported accuracy is ±0.11 m/s or 1.5% with starting threshold less than 0.45 m/s. A DRI site audit in October 2002 included an evaluation of the sensor's starting threshold using a torque wheel at a torque of 0.3 g/cm. The sensor shaft was turned at five constant speeds (0-1000 RPM) and the site sensor speed was regressed on the torque wheel speed using an ordinary linear least squares regression yielding (R^2 = 1.000):

$$Site = (0.99) \times Audit + (0.09\ mph)$$

An additional check was performed by comparing the hourly-average wind speeds between the Supersite in East St. Louis and an IEPA site in Edwardsville, IL (both measurements at 10m). Data was screened to focus on advective conditions with 1,418 hours at Edwardsville exceeding 4 m/s for the period 5/8/2001-6/30/2002. A reduced major axis regression yielded (R^2 = 0.693):

$$WS_{Edwardsville} = (1.00 \pm 0.03) \times WS_{Supersite} + (0.1 \pm 0.1\ m/s)$$

For advective conditions, there is excellent agreement between the 10m wind speeds measured at these two sites separated by ~30 km.

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Wind Direction

Wind direction was measured using a Climatronics 102083-G0-H0 (Wind Mark III series) wind vane at 10m. The manufacturer-reported accuracy is ±3° with starting threshold less than 0.45 m/s. A DRI site audit in October 2002 included an measurement of the magnetic bearing of the sensor cross arm with a Brunton Pocket Transit, converted to true bearings using the magnetic declination for the site. The sensor vane was placed parallel to and perpendicular to the cross arm in two orientations each and the readings from the site data computer were recorded. The audit directions were adjusted for the cross arm bearings and compared to the site readings. Measurements were performed at the four major directions (E, S, W, N) and in each case the difference between the site sensor bearing and the audit sensor bearing was no more than 1 degree (average difference 0.5 degrees), meeting the manufacturer-reported accuracy of less than ±3°.

Precipitation

Precipitation was measured using a Climatronics 100097-1-G0 tipping bucket. The manufacturer-reported accuracy is ±1% up to 5.1 cm/hr and ±5% up to 25 cm/hr.

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6. Gases

PM Precursors by HEADS

PM precursor gases (SO_2, HNO_2, HNO_3, NH_3) were sampled using the Harvard-EPA Annular Denuder System (HEADS) which included a sodium carbonate denuder, citric acid denuder and a filter pack with a Teflon filter followed by a Nylon filter. The denuders were extracted by the Koutrakis group (Harvard School of Public Health) and analyzed using ion chromatography by the Chow group (Desert Research Institute). Acid gases were measured from the sodium carbonate denuder extracts, and ammonia was measured from the citric acid denuder extracts.

Minimum Detection Limits. There were 29 field blanks for the acid gases and 28 field blanks for ammonia. Effective MDL values, estimated as three times the standard deviation of the field blanks and reported as $\mu g/m^3$, were 0.52 for SO_2, 0.08 for HNO_2, 0.04 for HNO_3, and 0.33 for NH_3. Ambient mixing ratios for these species were not blank-corrected.

Collocated Precision. Table 6-1 summarizes the collocated precision. Only one NH_3 mixing ratio exceeded ten times the estimated MDL.

Table 6-1. Collocated 24-hour integrated HEADS denuder gases, 04/13/01-6/30/02.[(a)]

Parameter	Method	Collocated N	Absolute Precision ($\mu g/m^3$)	Mean Conc. ($\mu g/m^3$)	Relative Precision
Denuder SO_2	HEADS / IC	31 30	5.76 5.85	28.4 29.3	20.2 % 20.0 %
Denuder HNO_2	HEADS / IC	31 23	0.38 0.44	1.70 2.10	22.3 % 20.8 %
Denuder HNO_3	HEADS / IC	31 15	0.20 0.27	1.27 1.98	15.4 % 13.8 %
Denuder NH_3	HEADS / IC	30 01	0.37 N/A	1.72 N/A	21.6 % N/A

(a) The first value includes all collocated data, and the second value is for data exceeding ten times the estimated MDL only.

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Criteria Gases

Criteria gases (CO, NO/NO_x, O_3 and SO_2) were measured by Illinois EPA (IEPA) at their compliance monitoring site adjacent to the Supersite footprint. These data were validated at 1-hour time resolution by IEPA and are available from the USEPA AIRS/AQS data system. In addition to the routine compliance monitoring audit program, these gas analyzers were audited by DRI as part of the St. Louis – Midwest Supersite measurement program. Table 6-2 summarizes the October 2002 audit results. The arithmetic mean deviation (averaged over the five non-zero calibration points) was within ±10% for each of the gases.

Table 6-2. DRI audit of IEPA criteria gas monitors (October 2002).

Parameter	Analyzer	Concentration Range (# values)	Slope[(a)]	Intercept[(a)]	R^2
CO	Thermo 48	0 – 40 ppmv (6)	0.998	0.1 ppmv	1.00
NO NO_x	API 200A	0 – 427 ppbv (6)	0.916 0.901	-1.8 ppbv 0.1 ppbv	1.00
O_3	Dasibi 1008-RS	0 – 419 ppbv (6)	1.000	-0.1 ppbv	1.00
SO_2	Dasibi 4108	0 – 422 ppbv (6)	0.935	0.1 ppbv	1.00
(a) Unconstrained ordinary linear least squares regression of site instrument on audit instrument.					

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7. Summary

The St. Louis – Midwest Supersite measurement program included both conventional and emerging measurement methods for PM physical and chemical properties, relevant gases, and meteorology. The following measurements stated in the QAPP were abandoned, data not reported, or not addressed in this Quality Assurance Final Report for reasons indicated:

- *Particle Size Distributions 2 - 10 μm*… several hardware failures leading to the unit being offline for very large portions of the study period and the data was not submitted to NARSTO.
- *Integral Moment Measurement System*… design flaws and hardware failures leading to low data completeness and questionable data quality.
- *MedVol Dichotomous sampler*… data not available at the time this report was prepared.
- *High Volume Toxicological Sampler (ChemVol)*... no accepted approach for performing flow audits at the time of this study.
- *Semicontinuous Nitrate (Harvard method)*...a unit suitable for routine field measurements was not ready in time for this study. Thus, we deployed a PILS-IC (starting June 2001) and also R&P 8400N (starting February 2002).
- *Organic Speciation*... 24-hour integrated $PM_{2.5}$ samples were collected daily using a custom sampler built by the University of Wisconsin-Madison. 1-in-6 day samples were extracted and analyzed by GCMS for 112 organic compounds (Bae, 2005). Recently a full two years of daily samples have been analyzed for 41 organic species by thermal desorption-GCMS. There is extensive overlap between the analyte lists for these two analytical methods. Quality assurance, includes a detailed assessment of comparability between the analytical methods, is described by Sheesley *et al.* (2007).

Data completeness exceeded the 75% target for all parameters except PILS sulfate and nitrate (74%) and semicontinuous ECOC (70%). In both cases, data completeness was close to the target despite hardware issues associated with sustained, routine operation of emerging methods (the Sunset Labs Field ECOC Analyzers were serial number 001 and 002). All data quality indicators could not be assessed for all measurements due to the nature of the samplers or instruments. Most measurements met the 10% precision target and substantial detail is provided in this reported to qualify the reasons why certain measurements did not meet this target (e.g. optical saturation artifacts in Aethalometer black carbon measurements). Comparability between measurements was also qualitatively demonstrated through scatter plots and quantitatively assessed by regressions.

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