Comparison of Integrated Filter and Semi-Continuous Measurements of $PM_{2.5}$ Nitrate, Sulfate, and Carbon Aerosols in the Speciation Trends Network (STN)

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1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) established the National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ gravimetric mass in 1997. A chemical Speciation Trends Network (STN) of 54 sites was established across the United States in support of the NAAQS to evaluate the chemical components of $PM_{2.5}$. Major components of $PM_{2.5}$ include nitrate (NO_3), sulfate (SO_4), elemental carbon (EC), and organic carbon (OC). At STN sites, approved speciation samplers are used to collect 24-hr filter-based measurements, nominally on every third day. Nitrate, sulfate, and carbon fractions are routinely analyzed, along with a suite of elements and $PM_{2.5}$ mass. Research Triangle Institute (RTI) in North Carolina performs all filter analyses for the STN. $PM_{2.5}$ mass is determined from Teflon® filters using a gravimetric method that is similar to the method used in the $PM_{2.5}$ mass attainment network. Elemental analysis is performed on the Teflon® filters (subsequent to gravimetric mass) by Energy-Dispersive X-Ray Fluorescence (EDXRF). The major inorganic ions of filter-based $PM_{2.5}$ STN samples are determined from nylon filters by ion chromatography (IC) following extraction in water. EC and OC fractions are collected using QMA-quartz filters that are analyzed by a thermal-optical transmittance (TOT) method that is a modified version of NIOSH 5040 (NIOSH, 1999).

Semi-continuous instruments have been developed to measure ambient aerosol concentrations of nitrate, sulfate, EC, and OC on a near real-time basis. At this time, no semi-continuous or continuous monitors have been developed for determination of elemental composition of $PM_{2.5}$ in ambient air. Collocated comparisons of the instruments with the standard methods used in the STN are needed to demonstrate their bias and precision. In the spring 2001, the EPA initiated a study to evaluate these monitors and their potential use in the routine speciation monitoring network. The semi-continuous monitors were collocated with STN samplers at five monitoring sites. Ideally, the quality of data from the semi-continuous monitors will be adequate to supplement speciation data collection; the data will have higher time resolution and be acquired more rapidly; and the monitors will require less maintenance. Proven continuous monitoring would eliminate transportation and laboratory analysis costs associated with filter-based samples and would benefit public outreach and air quality forecasting by increasing the timeliness of the data. Continuous-monitoring data may support more accurate source apportionment and help elucidate the processes leading to the occurrence of nitrate, sulfate, EC, and OC in $PM_{2.5}$.

Because the spatial requirements of the comparison study are geographically diverse, a wide range of environments was included in the study design. The participants in the study were the Arizona Department of Environmental Quality (Phoenix site); Illinois Environmental Protection Agency (Chicago site, operated by Cook County); Washington Department of Ecology (Seattle site); Indiana Department of Environmental Management (Indianapolis site); and Texas Council on Environmental Quality (Houston site). Although data were available from two sites in Illinois, only data from the Chicago site were analyzed here. Monitors have been collecting data for nearly three years at most of these sites.

2. OBJECTIVES

EPA contracted with Sonoma Technology, Inc. (STI) to conduct an analysis of the collocated filter-based and semi-continuous data collected during this study. Beyond the 54 STN sites, the EPA speciation network has an additional component of state and local-directed supplemental monitoring sites called SLAMS (State and Local Air Monitoring Stations). The SLAMS comprise a very dynamic network that is currently comprised of about 200 sites placed to meet state and local air monitoring needs. The goal is to determine if the commercially-available semi-continuous carbon, nitrate, and sulfate monitors used in this study are sufficiently robust to allow routine application in the speciation monitoring network.

Using filter-based samplers in the STN as the benchmark, the semi-continuous monitors were evaluated for comparability and predictability (see Section 4.4 for definitions). Monitors meeting comparability criteria would be useful for detecting spatial or temporal differences and would be acceptable for use in supplementing the data collected by the routine STN network. Comparable monitors would also be acceptable for use in the SLAMS network. Comparable monitors would not require and corrections or adjustments to the data. Criteria for predictability are the less stringent, but would allow calibration of the high time-resolution, semi-continuous data with the filter-based data, leading to more accurate representations of the diurnal variation that is known to exist for the major components of $PM_{2.5}$.

3. CONCLUSIONS AND RECOMMENDATIONS

The results of the comparisons between the semi-continuous nitrate, sulfate, and carbon data and collocated filter-based nitrate, sulfate, and carbon data from the STN network were reviewed. The comparisons were based on 24-hr average data from the semi-continuous monitors and 24-hr filter sampler data from the STN network. The results were then compared with the criteria for comparability and predictability, as discussed in Section 5.4. Table 3-1 summarizes whether the data from the monitors, operated at each of the five sites, met the comparability and predictability criteria.

Table 3-1. Summary of comparisons of semi-continuous nitrate, sulfate, and carbon monitor data with collocated filter-based STN data at the Phoenix (AZ), Chicago (IL), Indianapolis (IN), Deer Park (TX), and Seattle (WA) sites. Blank cells indicate that the comparison did not meet the criteria.

Instrument	Comparability (R^2, slope and intercept)					Comparability (R^2, ratio of means)					Predictability (r)				
	AZ	IL	IN	TX	WA	AZ	IL	IN	TX	WA	AZ	IL	IN	TX	WA
R&P 8400N[a]	NA	NA	NA	NA	NA		✓[e]				✓	✓	✓		[d]
Pre-moly[b]	NA	NA	NA	NA	NA			✓[e]			✓	✓	✓	✓	
Post-moly[c]	NA	NA	NA	NA	NA	✓		✓[g]			✓	✓	✓		[d]
R&P 8400S	NA	NA	NA	NA	NA	✓[f]			✓[f]				✓		✓
R&P 5400 EC															
R&P 5400 OC										[g]					✓
R&P 5400 TC										[g]			[d]		✓
Sunset EC	✓	✓	[e]	[e]	[d]	✓	[g]	[e]	[e]	[g]	✓	✓	[e]	[e]	✓
Sunset OC			[e]	[e]		[g]	[g]	[e]	[e]	✓	✓	✓	[e]	[e]	✓
Sunset TC			[e]	[e]		[g]	[g]	[e]	[e]	✓	✓	✓	[e]	[e]	✓

[a] Entire data set; both prior to and after converter replacement
[b] Only the R&P 8400N data subset prior to converter replacement
[c] Only the R&P 8400N data subset after converter replacement
[d] Close to meeting criteria
[e] No monitor installed
[f] Met ratio-of-means criteria, but not correlation criteria
[g] Met correlation, but not ratio-of-means criteria
NA Criteria did not apply

When evaluating comparability, neither the 8400N nor the 8400S provided results that consistently met both the ratio-of-means and the correlation comparability criteria suggested for this study. Only one 8400N monitor in Phoenix met both comparability criteria after converter

replacement. It is clear that more improvements and enhancements are required to improve comparability of these monitors with filter-based measurements. However, both the 8400N and 8400S did a better job at meeting the predictability (correlation) criterion. The 8400N monitors at four of five sites met the predictability criterion; and the fifth site was close to meeting it. The 8400S met predictability at two sites (Indianapolis and Seattle). These monitors largely do not provide data that are comparable to filter-based STN measurements; however, where monitors met the predictability criterion, the data may be adequate for adjustment using the filter-based STN measurements to more accurately represent diurnal patterns at these sites.

The comparability of the 5400 OCEC monitor, as compared to the filter-based STN carbon measurements, was poor. Predictability was also poor. The predictability criterion for OC was met at only one site (Seattle).

The Sunset carbon monitor did a better job at meeting, or came close to meeting, the ratio-of-means and correlation criteria for carbon. However, it met the slope and intercept comparability criteria on only one site. The Sunset carbon monitor met the predictability criterion at all five sites, indicating that adjustment of the data against STN filter-based measurements may be appropriate to more adequately represent diurnal patterns in speciation monitoring network.

3.1 R&P 8400N NITRATE MONITOR

Data from the R&P 8400N met the correlation and ratio-of-the-means comparability criteria at the Phoenix site, only for data after the converter was replaced. Data from Indianapolis and Chicago met the ratio-of-means criteria, but not the correlation criterion. Data from the other sites did not meet either of the comparability criteria. Data from the R&P 8400N met the predictability criteria at four of the five sites and were close at the fifth site.

Compared with the STN nitrate data, there was significant bias in the R&P 8400N data at all five sites; the bias was negative at four sites and positive at the Houston site. The nitrate response appears to be non-linear, with a stronger bias evident at higher ambient nitrate concentrations. The nitrate monitors seemed to have had consistently high conversion efficiencies and gas analyzer efficiencies, although there were some indications that problems with the gas analyzer converter efficiency could cause different results. The most time-consuming activity for the nitrate monitor was data acquisition and data processing; running aqueous standards and dealing with the flash strip failures were the next most time-consuming activities.

3.2 R&P 8400S SULFATE MONITOR

Data from the R&P 8400S at the Phoenix and Houston sites met the ratio-of-means criteria, but not the correlation criterion. The predictability criteria were met at only two of the five sites. When compared with the STN sulfate data, there was significant bias in the R&P 8400S data at all five sites; the bias was negative at four sites and positive at the Seattle site. The

sulfate monitors had significantly different conversion efficiencies at the various sites, although the gas analyzer efficiencies were consistently high. The most time-consuming activity for the sulfate monitor was data acquisition and data processing; running aqueous standards and dealing with the flash strip failures were the next most time-consuming activities.

3.3 R&P 5400 CARBON MONITOR

Of the EC, OC, and TC data from the R&P 5400, only the OC and TC data at the Seattle site met the predictability criteria while the TC data at the Indianapolis site almost met the predictability criteria. R&P 5400 EC, OC, and TC data did not meet the comparability criteria at any site. When compared with the STN carbon data, there was significant negative bias in the R&P 5400 TC, OC, and EC data at all five sites; regression slopes typically averaged 0.4 to 0.6. The most time-consuming activity for the 5400 carbon monitor was data acquisition and data processing; flow problems, along with oven and afterburner problems, were the most frequent and recurring operational issues.

3.4 SUNSET CARBON MONITOR

The results for the Sunset carbon monitor operated at three (Phoenix, Chicago, and Seattle) of the sites were significantly better. The EC data at Phoenix met the slope and intercept comparability criteria; the EC, OC, and TC data from all three sites either met or almost met the ratio-of-means and correlation comparability criteria; and EC, OC, and TC at all three sites met the predictability criteria. Compared with the STN TC and OC data, there was noticeable positive bias in the Sunset data at low concentrations, but little bias at higher concentrations. The most significant operational problems with the Sunset carbon monitor were failures with the associated laptop computer and differences in the version of analysis software used to calculate final concentrations.

4. SITE DESCRIPTIONS

4.1 CHICAGO, ILLINOIS

The Chicago Com Ed site is located in a trailer at the Commonwealth Edison (Com Ed) Maintenance facility, 7801 Lawndale Avenue, Chicago, Illinois. The AIRS Site ID is 170310076. The locational coordinates are latitude 41.885864 (41 deg 45 min 4.9 sec N) and longitude –87.625729 (87 deg 42 min 49.5 sec W). The site elevation is 186 m above mean sea level.

The Com Ed facility covers an area of several square blocks to the east of Lawndale Avenue. Residential areas are located immediately east, south, and west. Industrial areas, including large rail yards, are located 1 km to the northwest and 1.5 km to the east. Chicago Midway Airport is located 4 km to the northwest.

4.2 PHOENIX, ARIZONA

Phoenix is located in the central Arizona desert where many sources contribute to observed $PM_{2.5}$. It differs from the other locations in the study because most of its PM is generally in the coarse fraction ($PM_{10-2.5}$). The Phoenix data included in the this study were collected at the Phoenix JLG Supersite, AIRS Site ID 04-013-9997, located at 4530 N. 17th Avenue (latitude 33.502959, 33 deg 30 min 13.0 sec N and longitude –112.095785, 112 deg 5 min 42.0 sec W). The site is in a residential neighborhood about 1.5 km east of Interstate 17. The elevation is 346 m above mean sea level.

4.3 SEATTLE, WASHINGTON

The Seattle Beacon Hill site is located in a sampling trailer at the Beacon Hill Reservoir at Charleston Street and 15th Avenue South. The AIRS Site ID is 53-033-0080. The locational coordinates are latitude 47.569722 (47 deg 34 min 11 sec N) and longitude –122.312500 (122 degrees 18 min 45 sec W). The site elevation is 91 m above mean sea level. The Beacon Hill reservoir covers an area of approximately 50 acres and is located to the south and east of downtown Seattle. The site is adjacent to Jefferson Park and a golf course and is surrounded by mixed residential and light commercial development. The Duwamish industrial area and Interstate 5 are located approximately 1 km to the west of the site.

4.4 HOUSTON, TEXAS

The Houston Deer Park site used in this study is located at 4514-1/2 Durant St., Houston, Texas. The site is in a residential neighborhood, but the Houston Ship Channel and associated petrochemical and refining industries are a short distance to the north. The AIRS Site ID is 48-201-1039. The coordinates of the site are latitude 29.669722 (29 deg 40 min 11 sec N) and longitude –95.128611 (95 deg 07 min 43 sec W). The site is 6 m above mean sea level.

4.5 INDIANAPOLIS, INDIANA

The Indianapolis monitoring site is located in Washington Park, a public park adjacent to a police station parking lot to the west. It is surrounded by both commercial and residential properties, with mild traffic volume on the main road. The AIRS Site ID is 180970078. The locational coordinates are latitude 39.811097 (39 deg 48 min 39.9 sec N) and longitude –86.114469 (86 deg 6 min 52.1 sec W). The site elevation is 235 m above mean sea level.

5. INSTRUMENTATION

5.1 STN FILTER-BASED INSTRUMENTS

The every-third-day filter-based measurements at the five sites were made with speciation sampler types. The Spiral Ambient Speciation Sampler (SASS™; MetOne, Grants Pass, Oregon) were used at Phoenix and Indianapolis, and the Mass Aerosol Speciation Sampler (MASS 400 or MASS 450, URG, Chapel Hill, North Carolina) were used at Chicago, Houston, and Seattle.

5.1.1 MetOne SASS

Sites with MetOne SASS samplers hosted either a MetOne SASS or a MetOne SuperSASS. There are no significant operational differences between the two versions (the SuperSASS has additional channels for multiple-event sampling). Parallel channels allow simultaneous sampling, and each channel has a removable cartridge with a sharp-cut cyclone. One cartridge contains a Teflon filter for gravimetric analysis. A second cartridge contains a denuder to capture ammonia and nitric acid followed by a nylon filter. This sample filter is extracted and analyzed by IC for nitrate and sulfate. A third cartridge contains a quartz filter which is analyzed by thermal oxidation to determine OC and EC concentrations.

5.1.2 URG MASS400 and URG MASS450

The URG MASS400 (Mass Aerosol Speciation Sampler for Anions, Cations, and Trace Metals) is the filter-based sampler (with Teflon and Nylon filters) used for nitrate and sulfate measurements. The URG MASS450 (Mass Aerosol Speciation Sampler for Organic and Elemental Carbon and Semi-Volatile Organic Compounds) is the filter-based sampler (with a quartz filter) used for aerosol carbon measurements.

5.2 SEMI-CONTINUOUS MONITORS

Speciation monitors manufactured by Rupprecht and Patashnik (R&P, Inc., Albany, New York) deployed in this study include the R&P 5400 (carbon), R&P 8400N (nitrate), and R&P 8400S (sulfate) instruments. In mid-2004, a semi-continuous carbon monitor from Sunset Laboratory, Inc., Tigard, Oregon, was added at three of the five sites.

5.2.1 R&P 8400N Nitrate Monitor

A two-step process is used by the R&P 8400N Nitrate Monitor (8400N) to collect and analyze the aerosol sample. In this study, a 10-minute cycle time was used, with the first 8.75 minutes allotted to sample collection and the remaining time to analysis. In the collection step, ambient air is drawn through a system that includes a $PM_{2.5}$ sharp-cut cyclone, a carbon honeycomb denuder that removes interfering gases, and a Nafion humidifier that provides for

uptake of water by the particles and minimizes particle bounce from the NiChrome® collection strip. The air sample is maintained near ambient temperature by a sheath of ambient air surrounding the sample inlet line. During the analysis period, purified nitrogen is used to purge the collection cell; the purified nitrogen also acts as a carrier gas to the chemiluminescence oxides of nitrogen (NO_x) analyzer. A baseline reading is followed by the flash volatilization that catalytically reduces the nitrate to NO_x, which is carried to the high sensitivity gas analyzer for analysis. The difference between the integrated areas under the baseline and sample gas stream curves (adjusted for theoretical conversion efficiency) is combined with sampled volume to yield an ambient nitrate concentration.

Previous field evaluations of data from the prototype instrument and the commercialized version against various filter nitrate data have yielded inconsistent results. Intercomparisons between data from the prototype instrument and filter-based data in initial field tests gave favorable results (Stolzenburg and Hering, 2000; Liu et al., 2000; Hering and Stolzenburg, 1998). Following commercialization of the R&P instrument, data from field comparisons against filter-based data suggest that significant bias in nitrate concentrations exists compared to data from STN monitors (Hogrefe et al., 2004; Wittig et al., 2004; Harrison et al., 2004; Reid et al., 2005). Some researchers have found good data precision with the 8400N, allowing calibration of the high time-resolution data by the collocated filter data (Harrison et al., 2004; Wittig et al., 2004). Calibration of the data provides potential for additional temporal analyses but does not alleviate the equivalency requirement that would allow use of the semi-continuous monitors in place of STN monitors.

5.2.2 R&P 8400S Sulfate Monitor

The R&P 8400S Sulfate Monitor (8400S) follows a sampling protocol that parallels the R&P 8400N. The Pulse Generator component—the instrument that collects and flash volatilizes the sample—is identical to the 8400N except that platinum flash strips are used, a shorter flash duration (but a higher flash temperature) is used, and purified air is used as the carrier gas. A high sensitivity SO_2-pulsed UV fluorescence analyzer is used to measure the evolved gas.

Comparisons with filter-based sulfate data during a one-month study conducted at the Atlanta Supersite revealed that data from the 8400S and from measurements were "fairly well correlated" (Weber et al., 2003). Data from the 8400S were lumped with data from four other semi-continuous instruments and then regressed against the 24-hr filter-based data, yielding a slope of 1.15 and a correlation (r) of 0.92. Sample size for the 8400S was small (13 samples).

Drewnick et al. (2003) found high correlation ($r = 0.99$) between 8400S and STN filter-based measurements of sulfate, with a slope of 0.935. Sample size was small (7 samples).

5.2.3 Carbon

Thermo Optical Analysis (TOA) is routinely used for analysis of OC and EC from filter-based samples. It utilizes combustion in controlled atmospheres at selected temperatures, combined with light transmittance or reflectance to allow correction for pyrolyzed (charred) OC.

The gases produced in TOA are either converted to carbon dioxide (CO_2) and detected directly or converted to methane (CH_4) and detected by flame ionization.

OC and EC fractions are defined operationally by the method used. Changes in temperature regimes and dwell times, as well as the nature of the sample, can have significant effects on the OC/EC split (Schauer et al., 2003). Different thermal evolution protocols will yield different results; consistency in those protocols is needed to compare data sets. Thermal Optical Reflectance (TOR) is the method used in the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, while Thermal Optical Transmission (TOT) is the method used in the STN network. The IMPROVE TOR protocol uses a lower temperature protocol compared to STN TOT. Many other EC and OC analysis protocols are widely used, but generally the methods are insufficiently documented, making evaluations of their equivalence difficult.

R&P 5400 Monitor

The R&P 5400 carbon monitor (5400) measures OC and total carbon (TC) mass in $PM_{2.5}$. As used in this study, the monitor collects a sample for three hours, and analyzes the collected sample in about 20 minutes. The instrument has two separate sampling trains, allowing the collection and analysis of separate samples to occur in parallel. When sample collection ends on one train, sample collection begins on the second. The sample stream passes through a $PM_{2.5}$ size-selective inlet, and the PM collects on an impaction surface. At the end of the 3-hr sampling period, collection stops. In a closed system of ambient air, the chamber containing the sample is heated to two temperature plateaus in succession—340°C and 750°C. In the first plateau of 340°C (8 minutes long), the assumption is that all of the OC combusts in the presence of oxygen to form CO_2 and that no EC combusts. In the second temperature plateau of 750°C, all EC combusts to CO_2. A non-dispersive infrared sensor measures the CO_2 concentrations during these periods and based on the cumulative CO_2 concentration and sampled air volume, the ambient concentrations of OC and TC are calculated. The EC concentration is then determined by difference. There is no correction for pyrolysis in the 5400.

Measurements from the 5400 monitor have been compared with filter-based measurements in a few field studies. R&P 5400 TC measurements were not comparable to or predictable from collocated filter-based measurements, analyzed by TOR methods, at the Fresno Supersite (Watson and Chow, 2002), where frequent instrument problems led to low data recovery for the 5400. Average TC was 40-60% higher than filter-based TC. Correlation coefficients (r) between the 5400 and filter-based measurements for TC, OC, and EC were 0.46, 0.38, and 0.61, respectively.

In a comparison with samples collected with a filter-based Reference Ambient Aerosol Sampler (RAAS), analyzed by TOT at RTI (Rice, 2004), the 5400 underestimated TC and OC by 64% and 78%, respectively, while the EC component was overestimated by 89%. Correlation coefficients (r) for TC and OC were 0.64 and 0.67, respectively, and the correlation for EC was 0.37. Aside from the lack of pyrolysis correction in the 5400, a positive artifact associated with the filter-based measurements made without a denuder may have exacerbated the observed differences.

Comparisons conducted at the Atlanta Supersite showed very good agreement between data from the 5400 and from an *in situ* TOT method for TC and OC, with regression slopes and correlation coefficients close to 1.0 (Lim et al., 2003).

Sunset Carbon Monitor

In mid-2004, a Sunset Laboratory, Inc., Carbon Aerosol Analysis Field Instrument (Sunset) employing TOT was installed at three of the five sites: Chicago, Phoenix, and Seattle. This instrument is a field version of the Sunset laboratory-based analyzer, with the analysis section of the analyzer built and operated similarly to the laboratory-based analyzer described by Turpin et al. (1990). The monitor reports hourly concentrations of OC and EC, based on 47 minutes of sampling at a nominal flow rate of 8 lpm. The monitors at the three sites utilize a modified NIOSH 5040 protocol. Following sampling, the filter is heated in an oxygen-free, high-purity helium atmosphere to 600°C and then to 850°C, oxidizing OC to CO_2 that is then measured by a non-dispersive infrared detector. A red-light laser is used to monitor pyrolytic conversion of OC to EC. Following the oxygen-free heating, the oven is switched to a 2% oxygen/helium mixture and heated to 600°C and then to 850°C. During this phase, both original EC and pyrolyzed OC burn in the presence of oxygen to form CO_2. The point during the second heating cycle when the laser transmittance equals its beginning value is considered the split point—carbon measurements prior to this point are assigned to OC and those after to EC.

Bae et al. (2004) operated two collocated Sunset carbon monitors concurrently with integrated a 24-hr filter-based sampler at the St. Louis-Midwest Supersite throughout 2002; the sampler was built by Jamie Schauer at the University of Wisconsin, Madison, based on the Caltech organics sampler. The semi-continuous analyzers operated on alternate hours, employing a full hour of sampling instead of just 47 minutes so a truly continuous OCEC measurement was obtained. The slopes of the linear regressions of Sunset TC and OC against the filter-based measurements were 0.97 and 0.93, respectively, and exhibited correlation coefficients (r) of 0.94 and 0.95, respectively. EC exhibited a slope of 0.95 but a poorer correlation coefficients (r=0.60) attributed to very low EC levels at the sampling site (annual average 0.70 $\mu g/m^3$), with a large fraction of EC measurements near the detection limit.

5.3 DATA SET SUMMARY

Figure 5-1 graphically illustrates the deployment dates for the monitors at each of the five sites. In constructing 24-hr average data from the semi-continuous monitors, at least 75% data completeness was required. Hourly reported data for the Sunset carbon monitor required a minimum of 18 valid hourly averages per day. The R&P 5400 monitor reported 3-hr averages in this study, and five of the six daily samples (83%) served as the completeness criteria.

The 8400N and the 8400S report data as 10-minute averages, so determination of data completeness is less straightforward. The method for assessing completeness of these data differed between sites. For the Phoenix data, the nitrate measurements were assessed for data completeness by the daily averages based on the validity of 108 of the possible 144 daily 10-minute averages. In all other cases, hourly averages were calculated as an initial step and

accepted as valid if five of the six (83%) of the 10-minute periods were valid. This procedure was followed with a secondary calculation of the 24-hr average, requiring 18 (75%) or more valid hourly values.

Using the 10-minute nitrate data from the Phoenix site, a brief analysis was undertaken to determine the effect on regression statistics by these two alternative completeness methods. Results indicate minimal effects on the slopes, intercepts, and coefficients of determination for this particular data set (Table 5-1).

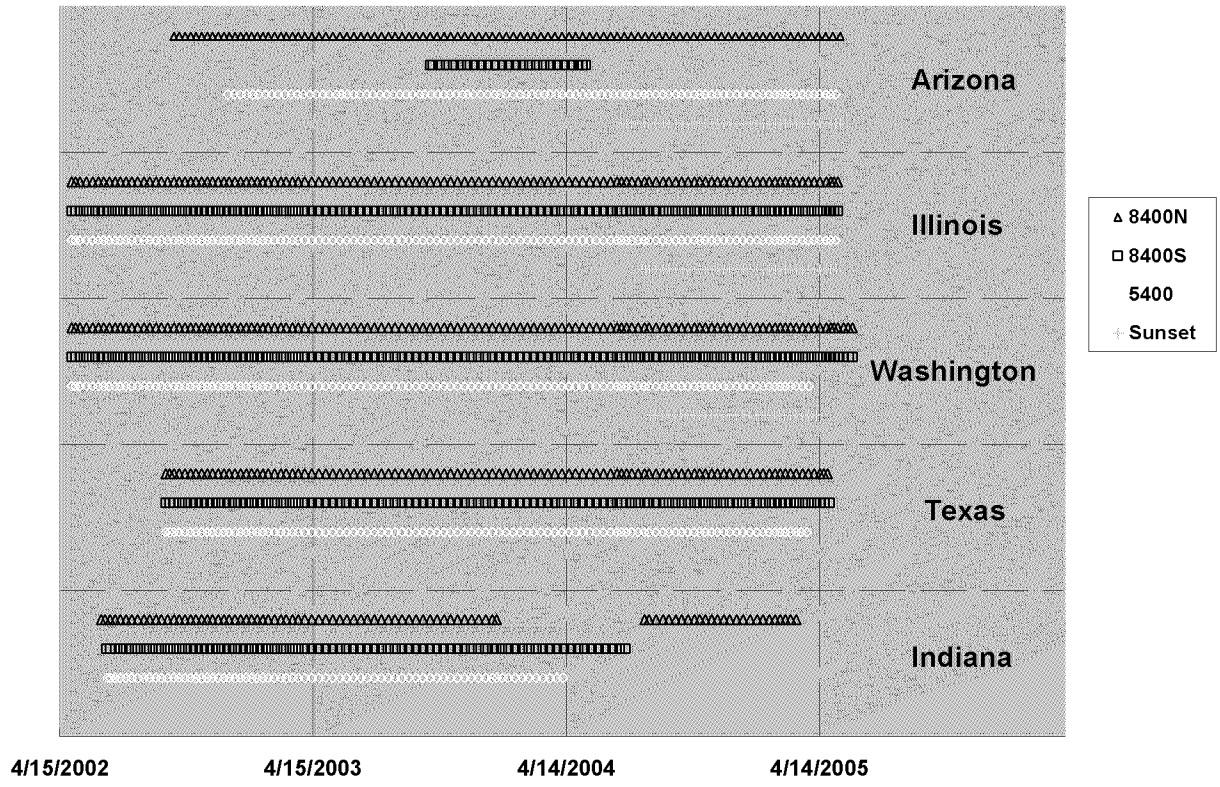

Figure 5-1. Range of deployment dates for each of the monitors in at the five sites in the study. Vertical lines denote yearly increments.

Table 5-1. Effect on regression statistics with two methods of data completeness evaluations for the 10-minute nitrate records.

Method	Number of Records	Slope	Intercept	R^2
Hourly (greater than or equal to 5 of 6 10-min averages), then daily (greater than or equal to 18 hourly averages)	895	0.7853	0.3449	0.8742
10-minute (greater than or equal to 108 of 144)	903	0.7846	0.343	0.8735

5.4 STATISTICAL APPROACH

Formal evaluations of comparability and predictability between the semi-continuous monitors and the STN monitors are based on ordinary least squares linear regressions. Average y/x ratios and y-minus-x differences, with associated standard deviations, are presented to supplement the regression statistics. The criteria used to decide whether the semi-continuous monitors are sufficiently robust to be used to supplement STN and SLAMS monitors is based on comparability and predictability. Below, we present criteria for comparability and predictability; the results for the speciated monitors in this study are compared against these criteria in Sections 5 and 6.

5.4.1 Comparability

The criteria for comparability are less stringent than those, for example, used in $PM_{2.5}$ mass equivalence, but the precisions involved are still sufficient to discern concentration differences in space and time. There are two sources of criteria for comparability, the criteria defined for STN samplers by the Expert Panel (Koutrakis, 1999), and the results obtained from evaluation of several speciation samplers in the Four-City Study (Solomon et al., 2000). Comparability is achieved when data from a monitor collocated with an STN monitor meet the following criteria:

Nitrate criteria

- Squared correlation (r2) greater than or equal to 0.90
- The ratio of the means of 1 ± 0.1 for nitrate (Koutrakis, 1999). The Four-City Study (Solomon et al., 2000), where a number of commercially-available speciation samplers were field-tested, suggested that the ratio-of-means criteria be 1 ± 0.15 for nitrate. This is the criteria used in this study to determine comparability for nitrate, since it reflects method performance in a field application.

Sulfate criteria

- Squared correlation (r2) greater than or equal to 0.95
- The ratio of the means of 1 ± 0.05 for sulfate.
- The Four-City Study report did not suggest an alternative criterion for sulfate.

Carbon criteria

- The Expert Panel did not provide criteria for carbon; however, the Four-City Study report suggested that the ratio-of-means criteria be 1 ± 0.15 for organic and elemental carbon.
- Definitions for comparability used for evaluation of in situ carbon measurements have been suggested by Watson and Chow, 2002. The criteria for comparability were 1) a slope that was 1 ± 3 standard errors; and 2) intercept equal to 0 ± 3 standard errors; and 3) a correlation (r) > 0.9. Both the ratio-of-means criteria and those proposed by Watson and Chow, 2002 will be used to assess comparability for carbon.

There is no federal reference method (FRM) for speciation sampling; therefore, the STN samplers are used as the reference for evaluating collocated semi-continuous speciation samplers. Note that the collocated STN data for the most commonly used sampler (the MetOne SASS) meet both the Expert Panel and Four-City Study criteria above (see Section

5.1). In addition, data from collocated STN and IMPROVE samplers are similar for nitrate and sulfate; thus, these criteria seem reasonable for an assessment of comparability.

5.4.2 Predictability

Predictability criteria are typically based on a minimum correlation coefficient (r) between two measured variables. Watson and Chow suggest a criterion for correlation of 0.9. The Data Quality Objectives (DQOs) for assessing the relationship between $PM_{2.5}$ FRM and continuous $PM_{2.5}$ measurements provided a range of squared correlations (R^2) from 0.73 to 0.84, depending on the acceptable amount of decision error (U.S. EPA, 2002). Therefore, a correlation of 0.9 seems to be a reasonable criterion for predictability in this study. The slope may deviate substantially from unity and the intercept may also deviate from zero. Predictability is of interest here, particularly with respect to accurately portraying highly time-resolved diurnal variability. Nitrate, sulfate, and carbon fractions in ambient air are susceptible to substantial diurnal variability from local sources. In cases where the high time-resolution, semi-continuous monitors exhibit substantial bias but good precision, benchmark filter-based data may be used to calibrate and adjust the high time-resolution data to more accurately portray these diurnal patterns.

6. PREVIOUS PRECISION AND COMPARISON RESULTS FOR STN SAMPLERS

In this section, we present STN collocated results and comparison results of data from the STN urban and IMPROVE (Interagency Monitoring of PROtected Visual Environments) rural networks. The purpose of presenting these results is to provide a context and examples of how well speciation data from filter-based STN samplers might be expected to compare with data from collocated STN filter-based samplers where the sampling and analysis protocols are the same and collocated IMPROVE samplers that use different sampling procedures, and in the case of carbon, different analysis methods.

6.1 PRECISION ESTIMATES FOR DATA FROM COLLOCATED STN SAMPLES

The EPA has performed collocated sampling within the STN network (Rice, 2005). Statistics for collocated samples for nitrate, sulfate, and carbon species are shown in Table 6-1. Detailed statistics for the MetOne sampler, which is the most-used, are also shown in Table 6-1; the slope and intercept results are from Deming regressions. The regression coefficients are quite high (r) greater than 0.92 for all these species, with slopes very near one and intercepts very near zero.

Table 6-1. Collocated precision and regression estimates for component species in the STN network for 2002-2004.

Sampler Type	Parameter	Number	Regression Slope	Intercept Slope	Ratio of Mean	Correlation (r)	STN/STN % CV
MetOne	Nitrate	1048	.985 ± .01	−.052 ± .05	.977	.99	12.3
	Sulfate	1047	1.019 ± .01	−.094 ± .02	.990	.99	10.6
	OC	1042	.970 ± .01	.016 ± .09	.973	.92	15.5
	EC	1041	1.009 ± .01	−.016 ± .01	.994	.95	17.0
	TC	1041	0.981 ± .01	−.039 ± .09	.984	.93	16.2

6.2 RESULTS FOR DATA FROM COLLOCATED STN AND IMPROVE

STN filter-based data are being used to evaluate the composition of $PM_{2.5}$ throughout the United States. Publicly available STN and IMPROVE data from collocated samplers at three locations (Seattle, Washington; Phoenix, Arizona; and Washington, DC) were obtained from EPA's Air Quality System (AQS), and regressions of IMPROVE data on STN data were conducted for nitrate, sulfate, EC, OC, and TC. A summary of the regression results is given in Table 6-2.

In general, we used data for January 2002 through May 2004. However, sometimes either the STN or IMPROVE data are missing; thus, the records are shorter. For the

Washington, DC, site, we used carbon data from January 2, 2002 through May 30, 2004, and ion data from January 2, 2002, through November 14, 2003. For the Seattle site, we used carbon and ion data from May 2, 2002, through May 30, 2004. For the Phoenix site, we used carbon data from December 13, 2002, through May 30, 2004, and ion data from August 12, 2002, through May 30, 2004 (see Hyslop et al., 2004).

Correlation coefficients (r) of the nitrate and sulfate data from the two networks exceeded 0.97 at all three sites; the Seattle location showed a slight positive bias for both particle-phase ions, and the Washington location a negative bias for nitrate. These results for nitrate using the MetOne sampler and for sulfate using the MetOne and Anderson samplers are quite similar to the collocated results shown in Table 6-1.

Carbon analysis methods differ between the two networks; thus, these comparisons are not as good as those for collocated STN comparisons shown in Table 6-1. IMPROVE uses a lower temperature protocol than STN. IMPROVE uses TOR for char correction, while STN uses TOT. The Seattle comparison results indicate less OC and TC bias than do the results from the other two sites. The URG sampler at the Seattle site has a nominal flow rate of 16.7 LPM, while the MetOne and Andersen samplers have flow rates of 6.7 and 7.3 LPM respectively. The IMPROVE sampler has a nominal flow rate of 22.8 LPM. The bias at the Phoenix and Washington sites is likely due to the increased magnitude of the difference in sampling flow rates for the MetOne and Andersen samplers and resulting difference in filter face velocity. Correlations for the EC component were substantially lower than for OC and TC.

Table 6-2. Summary of regression results between IMPROVE and STN filter-based data. Data are from the AQS.

Observable	Location	Sampler		Ordinary Least Squares			
		y	x	Regression Slope ± Standard Error	Intercept ± Standard Error	Correlation (r) (Pearsons)	Number of Pairs
Nitrate	Phoenix, AZ	Improve	MetOne	0.965 ± 0.01	0.02 ± 0.02	0.99	196
	Seattle, WA	Improve	URG	1.34 ± 0.02	-0.05 ± 0.02	0.98	206
	Washington, DC	Improve	Anderson	0.873 ± 0.02	-0.01 ± 0.04	0.97	175
Sulfate	Phoenix, AZ	Improve	MetOne	0.979 ± 0.02	0.04 ± 0.02	0.98	82
	Seattle, WA	Improve	URG	1.101 ± 0.01	-0.04 ± 0.02	0.99	205
	Washington, DC	Improve	Anderson	0.999 ± 0.02	0.20 ± 0.11	0.98	175
TC	Phoenix, AZ	Improve	MetOne	0.86 ± 0.02	-1.36 ± 0.16	0.96	158
	Seattle, WA	Improve	URG	1.1 ± 0.02	-0.32 ± 0.09	0.96	215
	Washington, DC	Improve	Anderson	0.69 ± 0.02	-0.14 ± 0.12	0.90	220
OC	Phoenix, AZ	Improve	MetOne	0.872 ± 0.03	-1.5 ± 0.2	0.94	158
	Seattle, WA	Improve	URG	1.15 ± 0.03	-0.41 ± 0.1	0.94	215
	Washington, DC	Improve	Anderson	0.657 ± 0.02	-0.23 ± 0.11	0.90	220
EC	Phoenix, AZ	Improve	MetOne	0.751 ± 0.04	0.18 ± 0.05	0.85	158
	Seattle, WA	Improve	URG	0.756 ± 0.05	0.15 ± 0.04	0.70	215
	Washington, DC	Improve	Anderson	0.665 ± 0.06	0.25 ± 0.04	0.63	220

7. RESULTS

The EPA's NAREL (National Air and Radiation Environmental Laboratory) provides quality assurance support to the EPA speciation networks. One of NAREL's tasks is to support the semi-continuous speciation study by preparing performance evaluation (PE) samples, which provide an estimate of the monitor bias. The PE samples are single-blind, meaning the operator knows that the sample is a PE, but does not have the known concentration. When the PE samples are analyzed in replicate, an estimate of within-monitor precision can obtained. This section provides the precision results from the PE samples and summarizes the comparisons between the semi-continuous and filter-based results (Section 7.1); detailed discussions of the comparison results for nitrate (Section 7.2), sulfate (Section 7.3), and carbon (Section 7.4) are also provided.

7.1 PRECISION ESTIMATES

This section provides the results of replicate, blind PE samples for the R&P nitrate and sulfate monitors and for the Sunset carbon monitor (Section 7.1.1); no precision estimates are provided for the R&P carbon monitor because this monitor's collection and analysis system is closed; therefore, no PE sample can be introduced into the system and there is no way to easily introduce a sample through the inlet. Section 7.1.2 provides precision estimates and detailed statistics for the collocated semi-continuous and STN comparisons.

7.1.1 Single- (Within-) Sampler Precision Estimates

Collocation of semi-continuous instruments would provide the most robust method of determining measurement precision because it includes the error contribution of all sampling (e.g., flow rate) and analytical system components. No collocated semi-continuous instruments were operated at the STN sites during this study. However, replicate blind PE samples can provide estimates of single-sampler precision; these results are presented as coefficient of variation (CV). Such estimates do not completely characterize the total measurement system precision because they omit field errors, such as those associated with flow rate. In addition, error unrelated to the sampling system may be introduced through differences in site-operator techniques in administering the PE.

To date, there have been five PE tests for the nitrate and sulfate monitors, and two PE tests for the Sunset carbon monitor. Replicate measurements were made at multiple levels of deposited nitrate and sulfate mass. Similarly, for the Sunset carbon monitor, replicate samples of filter punches were taken from sucrose-spiked filters and filters from STN ambient samplers. NAREL provided blind aqueous standards for nitrate and sulfate and carbon filter punches for the PE tests. The results are used here only for estimates of precision. Evaluation of the PE results, including a discussion of bias as well as precision, is presented elsewhere (Taylor, 2005).

Within-sampler precision estimates (CV) for the R&P 8400N (Table 7-1) and 8400S (Table 7-2) are based on available data from PE4 (fall 2004) and PE5 (spring 2005) that were conducted at all five sites (Taylor, 2005). Precision estimates for the Sunset carbon monitors

(Table 7-3) are based on the PE1 of fall 2004 and PE2 of spring 2005 at three sites (Taylor, 2005). No precision estimates are provided for the R&P 5400 carbon monitor.

For the Sunset monitor, CVs are presented from ambient samples only—sucrose-spiked filters have very high CVs for EC because of the absence of any EC in these spiked samples. Measurements of low-level chemical species such as EC are more likely to show large relative variability compared to $PM_{2.5}$ measurements. The Sunset within-sampler precisions averaged 2% for OC and TC (Table 7-3). The EC precision of 8% was inflated by the high CV (28%) in Phoenix for PE 2. If the suspect data underlying the 28% CV are eliminated, the CV for EC drops to 4%.

The average CV for nitrate, including all sites over all levels of deposited nitrate mass, was 5.2% in both PE4 and PE5 (Table 7-1). The average CV for sulfate was 10.7% in PE4 and 5.1% in PE5 (Table 6-2); overall average is 8.3%. There were no Phoenix PE data for sulfate, and a sulfate PE was not conducted at the Indianapolis site in spring 2005.

Table 7-1. Coefficients of variation of measured nitrate mass for the 8400N PE4 (fall 2004) and PE5 (spring 2005) of nitrate aqueous standards. The overall mean CV is 5.2%. (Data courtesy of NAREL.)

Site	Mass Deposited (ng)								
	10	20	30	100	200	250	300	400	
	CV (%)								Average
Phoenix PE 4	1.4%	–	2.9%	13.8%	–	1.1%	–	9.0%	5.6%
Chicago PE 4	4.2%	–	1.0%	2.6%	–	0.6%	–	1.3%	1.9%
Indianapolis PE 4	9.7%	–	5.1%	5.5%	–	8.2%	–	6.3%	6.9%
Houston PE 4	5.0%	–	4.8%	3.2%	–	7.0%	–	6.3%	5.3%
Seattle PE 4	1.8%	–	7.8%	1.9%	–	4.4%	–	15.3%	6.2%
Average PE 4	**4.4%**	**–**	**4.3%**	**5.4%**	**–**	**4.3%**	**–**	**7.6%**	**5.2%**
Phoenix PE 5	–	6.3%	–	3.2%	7.8%	–	3.4%	5.6%	5.3%
Chicago PE 5	–	3.2%	–	1.3%	0.8%	–	1.7%	2.2%	1.8%
Indianapolis PE 5	–	10.4%	–	1.2%	11.3%	–	2.0%	3.8%	5.8%
Houston PE 5	–	2.8%	–	6.1%	12.6%	–	10.3%	1.8%	6.7%
Seattle PE 5	–	7.8%	–	5.6%	9.3%	–	6.9%	2.1%	6.3%
Average PE 5	**–**	**6.1%**	**–**	**3.5%**	**8.3%**	**–**	**4.9%**	**3.1%**	**5.2%**
								Overall Average	**5.2%**

Table 7-2. Coefficients of variation of measured mass for the 8400S PE4 (fall 2004) and PE5 (spring 2005) of sulfate aqueous standards. The overall average CV is 8.3%. (Data courtesy of NAREL.)

Site	Mass Deposited (ng)									
	30	60	100	150	240	300	600	900	1200	
	CV (%)									Average
Phoenix PE 4	–	–	–	–	–	–	–	–	–	
Chicago PE 4	3.8%	–	8.1%	2.8%	–	5.6%	–	4.9%	2.5%	4.6%
Indianapolis PE 4	11.6%	–	29.9%	13.9%	–	30.6%	–	13.0%	4.1%	17.2%
Houston PE 4	15.5%	–	21.4%	20.3%	–	13.1%	–	8.4%	2.4%	13.5%
Seattle PE 4	12.1%	–	1.2%	11.8%	–	7.0%	–	5.5%	7.9%	7.6%
Average PE 4	**10.7%**		**15.1%**	**12.2%**		**14.1%**		**8.0%**	**4.2%**	**10.7%**
8400S PE 5										
Phoenix PE 5	–	–	–	–	–	–	–	–	–	
Chicago PE 5	–	4%	–	–	2%	–	2%	1%	2%	2.3%
Indianapolis PE 5	–	–	–	–	–	–	–	–	–	–
Houston PE 5	–	13%	–	–	8%	–	4%	2%	4%	6.2%
Seattle PE 5	–	6%	–	–	14%	–	3%	7%	2%	6.7%
Average PE 5		**7.8%**	**–**	**–**	**8.4%**	**–**	**3.2%**	**3.4%**	**2.6%**	**5.1%**
									Overall Average	**8.3%**

Table 7-3. Coefficients of variation for the Sunset blind PE1 (fall 2004) and PE2 (spring 2005) of EC, OC, and TC. The overall mean CV is 4%. The average CV for EC drops from 8% to 4% if the Phoenix PE 2 value is eliminated. (Data courtesy of NAREL.)

Sunset	CV (%)		
Site	EC	OC	TC
Phoenix PE 1	0%	1%	1%
Phoenix PE 2	28%	6%	4%
Chicago PE 1	5%	2%	1%
Chicago PE 2	2%	1%	1%
Seattle PE 1	6%	1%	0%
Seattle PE 2	6%	2%	2%
Average CV	8%	2%	2%

7.1.2 Between Sampler Precision Estimates

Regression statistics and precision estimates (σ), as the standard deviation of the paired differences, for the nitrate, sulfate, and carbon comparisons are shown in Table 7-4. The slopes and intercepts, and their standard errors, from the ordinary least squares regression are presented for each set of collocated measurements. The regressions utilized the semi-continuous monitor data as the *y* variable and the filter-based data as the *x* variable. Also, Pearsons correlation coefficients (r), the number of pairs in the comparison, the average y/x ratios and their standard deviations, the average of the paired differences (y – x), and the standard deviation of the paired differences are given. The distribution of the data pairs whose difference is less than 1σ, between 1 and 2σ, between 2 and 3σ, and greater than 3σ are also provided; the standard deviation of the paired differences is represented by σ. Representative scatter plots and regressions are presented in the discussions of the nitrate results (Section 7.2), sulfate results (Section 7.3), and carbon results (Section 7.4); scatter plots not shown in the text are shown in Appendix A. Also discussed in Sections 7.2 and 7.3 are the results of nitrate and sulfate aqueous standards tests and of gas analyzer tests; these tests are important components of quality control activities for the semi-continuous speciation monitors.

In the discussions in Sections 7.2 through 7.4, we compare the results shown in Table 7-4 with the criteria discussed in Section 5.4.

Table 7-4. Summary statistics for comparison of semi-continuous speciated $PM_{2.5}$ data with filter-based STN data.

Observable	Location	Sampler		Ordinary Least Squares							Distribution			
		y	x	Regression Slope ± Standard Error	Intercept ± Standard Error	Correlation (r) (Pearsons)	Number of Pairs	Average Ratio of y/x ± Standard Deviation	Avg Difference of y – x ($\mu g/m^3$)	S.D. of Avg Difference of y – x ($\mu g/m^3$)	<1σ	1σ – 2σ	2σ – 3σ	>3σ
NO_3 (all data)	Chicago, IL	R&P 8400N	URG	0.54 ± 0.01	0.53 ± 0.05	0.91	277	0.88 ± 0.27	-0.64	1.33	234	25	9	9
	Phoenix, AZ	R&P 8400N	MetOne	0.79 ± 0.02	0.34 ± 0.04	0.94	270	1.30 ± 0.80	0.05	0.63	223	33	9	5
	Indianapolis, IN	R&P 8400N	MetOne	0.59 ± 0.02	0.41 ± 0.08	0.90	178	0.82 ± 0.26	-0.74	1.21	137	25	10	6
	Houston, TX	R&P 8400N	URG	1.97 ± 0.07	0.34 ± 0.09	0.89	194	2.65 ± 1.75	1.28	1.19	117	49	15	13
	Seattle, WA	R&P 8400N	URG	0.85 ± 0.03	0.24 ± 0.03	0.87	297	1.26 ± 0.53	0.12	0.34	215	61	15	6
NO_3 ("Pre-moly")	Chicago, IL	R&P 8400N	URG	0.50 ± 0.02	0.54 ± 0.06	0.92	197	0.85 ± 0.25	-0.69	1.43	166	19	4	8
	Phoenix, AZ	R&P 8400N	MetOne	0.85 ± 0.02	0.34 ± 0.04	0.94	208	1.37 ± 0.86	0.16	0.56	175	23	4	6
	Indianapolis, IN	R&P 8400N	MetOne	0.62 ± 0.03	0.39 ± 0.10	0.90	126	0.85 ± 0.28	-0.61	1.15	101	15	4	6
	Houston, TX	R&P 8400N	URG	2.02 ± 0.09	0.32 ± 0.12	0.90	122	2.51 ± 0.95	1.33	1.19	71	33	9	9
	Seattle, WA	R&P 8400N	URG	0.81 ± 0.03	0.29 ± 0.03	0.87	203	1.31 ± 0.56	0.14	0.36	146	42	11	4
NO_3 ("Post-moly")	Chicago, IL	R&P 8400N	URG	0.67 ± 0.03	0.43 ± 0.10	0.94	80	0.97 ± 0.28	-0.48	1.01	63	11	3	3
	Phoenix, AZ	R&P 8400N	MetOne	0.65 ± 0.02	0.27 ± 0.04	0.98	62	1.05 ± 0.52	-0.34	0.68	43	15	3	1
	Indianapolis, IN	R&P 8400N	MetOne	0.52 ± 0.02	0.40 ± 0.10	0.95	52	0.73 ± 0.16	-1.05	1.31	36	11	3	2
	Houston, TX	R&P 8400N	URG	1.90 ± 0.12	0.37 ± 0.16	0.87	72	2.89 ± 2.59	1.20	1.19	46	16	6	4
	Seattle, WA	R&P 8400N	URG	0.96 ± 0.05	0.11 ± 0.05	0.89	94	1.16 ± 0.43	0.08	0.29	66	23	4	1
SO_4	Chicago, IL	R&P 8400S	URG	0.59 ± 0.02	0.78 ± 0.10	0.85	263	0.94 ± 0.31	-0.58	1.59	215	35	7	6
	Phoenix, AZ	R&P 8400S	MetOne	0.76 ± 0.10	0.18 ± 0.10	0.71	62	0.99 ± 0.33	-0.04	0.31	41	18	3	0
	Indianapolis, IN	R&P 8400S	MetOne	0.66 ± 0.03	0.50 ± 0.18	0.93	94	0.81 ± 0.19	-1.33	1.77	71	14	6	3
	Houston, TX	R&P 8400S	URG	0.81 ± 0.06	0.40 ± 0.23	0.74	175	0.96 ±0.45	-0.31	1.41	138	24	10	3
	Seattle, WA	R&P 8400S	URG	1.25 ± 0.03	0.24 ± 0.04	0.94	245	1.52 ± 0.27	0.55	0.41	108	92	26	19

Table 7-4. Summary statistics for comparison of semi-continuous speciated $PM_{2.5}$ data with filter-based STN data.

Observable	Location	Sampler		Ordinary Least Squares							Distribution			
		y	x	Regression Slope ± Standard Error	Intercept ± Standard Error	Correlation (r) (Pearsons)	Number of Pairs	Average Ratio of y/x ± Standard Deviation	Avg Difference of y – x ($\mu g/m^3$)	S.D. of Avg Difference of y – x ($\mu g/m^3$)	<1σ	1σ – 2σ	2σ – 3σ	>3σ
TC	Chicago, IL	R&P 5400	URG	0.53 ± 0.03	0.27 ± 0.11	0.78	270	0.61 ± 0.18	-1.48	0.99	81	125	43	21
	Phoenix, AZ	R&P 5400	MetOne	0.35 ± 0.02	0.95 ± 0.14	0.85	170	0.52 ± 0.18	-3.89	2.82	81	50	24	15
	Indianapolis, IN	R&P 5400	MetOne	0.51 ± 0.02	0.49 ± 0.13	0.89	142	0.63 ± 0.13	-2.07	1.34	44	65	21	12
	Houston, TX	R&P 5400	URG	0.46 ± 0.03	0.81 ± 0.11	0.75	155	0.83 ± 0.36	-0.71	0.94	96	40	17	2
	Seattle, WA	R&P 5400	URG	0.58 ± 0.01	0.47 ± 0.06	0.92	325	0.76 ± 0.24	-1.04	1.07	181	101	31	12
	Chicago, IL	Sunset Lab	URG	0.94 ± 0.04	0.80 ± 0.15	0.95	70	1.20 ± 0.23	0.56	0.54	30	32	6	2
	Phoenix, AZ	Sunset Lab	MetOne	0.76 ± 0.03	0.22 ± 0.19	0.95	91	0.81 ± 0.20	-1.23	1.19	44	37	7	3
	Seattle, WA	Sunset Lab	URG	0.91 ± 0.02	0.58 ± 0.09	0.98	74	1.15 ± 0.32	0.21	0.47	54	14	4	2
OC	Chicago, IL	R&P 5400	URG	0.54 ± 0.02	0.35 ± 0.08	0.80	270	0.67 ± 0.18	-1.05	0.80	114	105	30	21
	Phoenix, AZ	R&P 5400	MetOne	0.33 ± 0.02	0.72 ± 0.13	0.80	170	0.48 ± 0.17	-3.47	2.38	64	61	28	17
	Indianapolis, IN	R&P 5400	MetOne	0.50 ± 0.03	0.60 ± 0.13	0.86	142	0.66 ± 0.15	-1.71	1.27	60	55	18	9
	Houston, TX	R&P 5400	URG	0.47 ± 0.03	0.65 ± 0.10	0.73	155	0.81 ± 0.35	-0.65	0.88	100	38	14	3
	Seattle, WA	R&P 5400	URG	0.53 ± 0.02	0.57± 0.05	0.90	325	0.80 ± 0.27	-0.81	0.97	208	80	24	13
	Chicago, IL	Sunset Lab	URG	0.84 ± 0.04	0.87 ± 0.13	0.93	70	1.19 ± 0.26	0.39	0.51	39	23	7	1
	Phoenix, AZ	Sunset Lab	MetOne	0.68 ± 0.03	0.39 ± 0.20	0.91	91	0.78 ± 0.23	-1.26	1.23	45	35	8	3
	Seattle, WA	Sunset Lab	URG	0.79 ± 0.03	0.73 ± 0.11	0.96	74	1.14 ± 0.33	0.06	0.66	59	13	1	1
EC	Chicago, IL	R&P 5400	URG	0.31 ± 0.03	0.03 ± 0.03	0.49	270	0.37 ± 0.34	-0.42	0.31	97	119	37	17
	Phoenix, AZ	R&P 5400	MetOne	0.40 ± 0.02	0.28 ± 0.03	0.80	170	0.83 ± 0.75	-0.41	0.57	119	32	14	5
	Indianapolis, IN	R&P 5400	MetOne	0.39 ± 0.04	0.03 ± 0.03	0.65	142	0.45 ± 0.27	-0.36	0.25	51	59	23	9
	Houston, TX	R&P 5400	URG	0.29 ± 0.14	0.21 ± 0.06	0.16	155	0.99 ± 1.29	-0.07	0.35	132	15	5	3
	Seattle, WA	R&P 5400	URG	0.63 ± 0.02	0.02 ± 0.02	0.83	325	0.68 ± 0.30	-0.22	0.25	207	83	25	10
	Chicago, IL	Sunset Lab	URG	1.11 ± 0.04	0.09 ± 0.04	0.95	70	1.26 ± 0.29	0.17	0.17	41	19	7	3
	Phoenix, AZ	Sunset Lab	MetOne	1.04 ± 0.03	0.005 ± 0.03	0.97	91	1.05 ± 0.23	0.04	0.17	72	14	3	2
	Seattle, WA	Sunset Lab	URG	1.23 ± 0.06	-0.03 ± 0.06	0.92	74	1.24 ± 0.68	0.15	0.31	60	9	2	3

7.2 R&P 8400N NITRATE VERSUS STN FILTER-BASED NITRATE

7.2.1 Nitrate Data Corrections

Aqueous standard salt solutions of potassium nitrate (KNO_3) were used to evaluate the conversion efficiency of the 8400N at each site. Frequency of the tests ranged from monthly to quarterly. Replicate measurements were made at zero nitrate and four additional nitrate levels (nominally 20, 40, 60, and 80 ng applied nitrate). Slopes of the measured mass versus deposited mass were applied as corrections to the data, either as inputs in the 8400N setup under "Theoretical Conversion Factor", or during post-processing of the data. Zero and span audits of the NO analyzer were undertaken every few days (e.g., every three days at the Phoenix site). Average results for each site are shown in Table 7-5. The average theoretical conversion efficiency is the percent of the nitrate placed via the aqueous standard on the strip that is measured in the gas analyzer; we expect these efficiencies to be consistent across monitors (i.e., from site to site in this study). We also expect the efficiency to be close to 100%, thus demonstrating that all nitrate placed via the aqueous standard on the strip was volatilized and subsequently measured in the gas analyzer. The efficiencies for nitrate are generally high (87% to 96%) and fairly consistent among the sites.

Other corrections could potentially be applied to the semi-continuous 8400N nitrate data. Although none of the additional corrections discussed below have been applied to the data from this study, their potential to affect the summary statistics should be noted.

In the Pittsburgh Air Quality Study (PAQS), Wittig et al., 2004 applied a correction for instrument offset (18% on average), determined by sampling HEPA-filtered air (dynamic zero) during a series of 10-minute cycles, that was subtracted from the 8400N measurements. Bimonthly dynamic zero measurements were made during particulate nitrate measurements at the St. Louis-Midwest Supersite (Reid et al., 2005), but the data were not used to correct for instrument offset because of high variability in the blank values and uncertainty as to whether the dynamic zero values reflected a true blank measurement.

Corrections for sample flow drift may also be applied, based on measured sample flow rate and the flow rate indicated by the instrument. In PAQS (Wittig et al., 2004), flow drift corrections averaged –3% for nitrate. It is also possible to construct correction curves to account for reaction cell vacuum drift. The 8400N reaction cell vacuum set point is 5.0 in. Hg. Deviations from this set point can affect nitrate measurements through the instrument offset, conversion efficiency, and gas analyzer efficiency. During PAQS (Wittig et al., 2004), corrections for reaction cell vacuum drift averaged –1%.

Note: None of the additional corrections described above, were applied to the data from this five site study.

Table 7-5. Theoretical conversion efficiency from aqueous standards tests and gas analyzer efficiency from routine span audits.

	Nitrate			Sulfate		
	Aqueous Standards Tests		Gas Analyzer Audits	Aqueous Standards Tests		Gas Analyzer Audits
Location	Average Theoretical Conversion Efficiency ± St Dev (%)	Average Correlation Coefficient (r)	Average Analyzer Efficiency ± St Dev (%)	Average Theoretical Conversion Efficiency ± St Dev (%)	Average Correlation Coefficient (r)	Average Analyzer Efficiency ± St Dev (%)
Phoenix, AZ	96.1 ± 14.2	0.998	96.3 ± 2.9	215.2 ± 95.2	0.978	94.6 ± 16.8
Chicago, IL	94.4 ± 4.0	0.995	99.2 ± 1.3	63.3 ± 7.7	0.979	99.7 ± 0.8
Seattle, WA	96.1 ± 4.7	0.992	98.1 ± 2.1	50.3 ± 8.9	0.981	100.1 ± 3.5
Houston, TX	95.6 ± 13.1	0.996	N/A	64.9 ± 15.4	0.992	N/A
Indianapolis, IN	87.5 ± 10.9	0.958	N/A	83.4 ± 9.9	0.955	N/A

N/A = Data not available.

Applying all the corrections above during PAQS (Wittig et al., 2004) resulted in good correlations with filter-based measurements, but significant bias in 8400N measurements still existed.

The molybdenum catalyst in the NO_2 converters has a fixed lifetime (nominally one year) and exhibits decreased efficiency with time. Operators at each of the five sites returned the NO_x analyzer of the 8400N monitors to R&P during 2004 to have the converters evaluated and replaced. These converter changes occurred at different times of the year for each site, and the instruments were inoperable at differing time periods. As a consequence, the 8400N nitrate data were evaluated in three ways: pre-converter replacement, post-converter replacement, and all data combined. Replacement of the molybdenum converter increased the regression slopes for the data from the Chicago and Seattle monitors, while the slopes for the data from the Phoenix, Indianapolis, and Houston monitors decreased following converter replacement (Table 7-4).

From filter-based data, nitrate concentrations ranged up to 5 $\mu g/m^3$ in Seattle and Houston, 12 $\mu g/m^3$ in Indianapolis, 16$\mu g/m^3$ in Chicago, and to 18 $\mu g/m^3$ in Phoenix (see **Figures 7-1 to 7-4**, for example).

Data from the R&P 8400N met the correlation and ratio-of-means comparability criteria at the Phoenix site after converter replacement; data from the Illinois site met the ratio-of-means criteria in all cases, but not the correlation criteria; and data from the Indiana site met the ratio-of-means criteria after converter replacement, but not the correlation criteria. The other sites did not meet either of the comparability criteria. Data from the R&P 8400N met the predictability criteria at four of the five sites and were close at the fifth site. With the exception of the Houston 8400N, the semi-continuous monitors underestimated nitrate concentrations, as measured by the STN filter-based samplers, except at very low concentrations. Regression slopes ranged from

0.50 to 0.96, with associated standard errors of 0.01 to 0.05. All the data sets showed positive intercepts, suggesting a positive sampling artifact. The intercepts ranged from 0.11 to 0.54 $\mu g/m^3$, reflecting the manufacturer's stated instrument error of 0.4 $\mu g/m^3$. No dynamic zero data were available for correcting the nitrate data for instrument offset.

In Chicago (Figure 7-1), the 8400N averaged only 54% of the filter-based concentrations using all data. The average ratio of 8400N nitrate to filter-based nitrate was 0.88 ± 0.27, and the average difference (y – x) in concentration was –0.64 $\mu g/m^3$. The Chicago nitrate data is typical of the response observed at all sites except Houston.

In Phoenix and Seattle, the low slopes were coupled with high 8400N/STN (y/x) ratios. This is due to the preponderance of data at low concentrations and the positive intercepts. In Phoenix, even though the slope of 8400N versus STN indicated that the semi-continuous monitor was capturing only about 79% of the nitrate collected by the filters, the ratio of 8400N nitrate to filter-based nitrate was 1.3 ± 0.80, and the average concentration difference (y – x) was only 0.05 $\mu g/m^3$. Approximately 75% of the concentrations in Phoenix were less than 2 $\mu g/m^3$. These low concentrations combined with the positive intercept to yield a high ratio and low average difference.

In Seattle, about 80% of the filter-based nitrate concentrations were less than 1 $\mu g/m^3$, yielding an average y/x ratio of 1.26 ± 0.53 and an average concentration difference of 0.12 $\mu g/m^3$.

There was a substantial break in the time series of the Indianapolis nitrate data (Figure 5-1) so there are about one hundred fewer sample pairs than at the other sites.

The response of the Houston 8400N was atypical among the five sites (Figure 7-2), with results in the opposite direction. Slopes approached 2 for all data subsets, indicating a substantial overestimate of STN filter-based nitrate. Average y/x ratios were between 2.5 and 3.0 for the data subsets, and the average difference (y – x) exceeded 1.2 $\mu g/m^3$. This large discrepancy between the Houston site and the others is not explained, but raises additional concern about the true bias of the monitor compared to filter-based measurements.

The Seattle and Houston sites use URG samplers. For nitrate, the URG sampler uses a Teflon® and backup nylon filter for the collection and analysis of total nitrate. Non-volatile nitrate is collected on the front Teflon® filter and volatilized nitrate is collected on the backup nylon filter. Teflon filters are also used for gravimetric mass determinations and Energy-Dispersive X-Ray Fluorescence (EDXRF) for elemental analysis. The Teflon® filter is weighed first for mass, then subject to vacuum EDXRF, and finally extracted for ion analysis (including nitrate). The 4-City Study report (Solomon et al., 2002) noted that up to 40% of the nitrate collected on the Teflon filter can be lost due to vacuum XRF. Any losses on the Teflon® filter would affect the bias between the STN URG and 8400N at these sites.

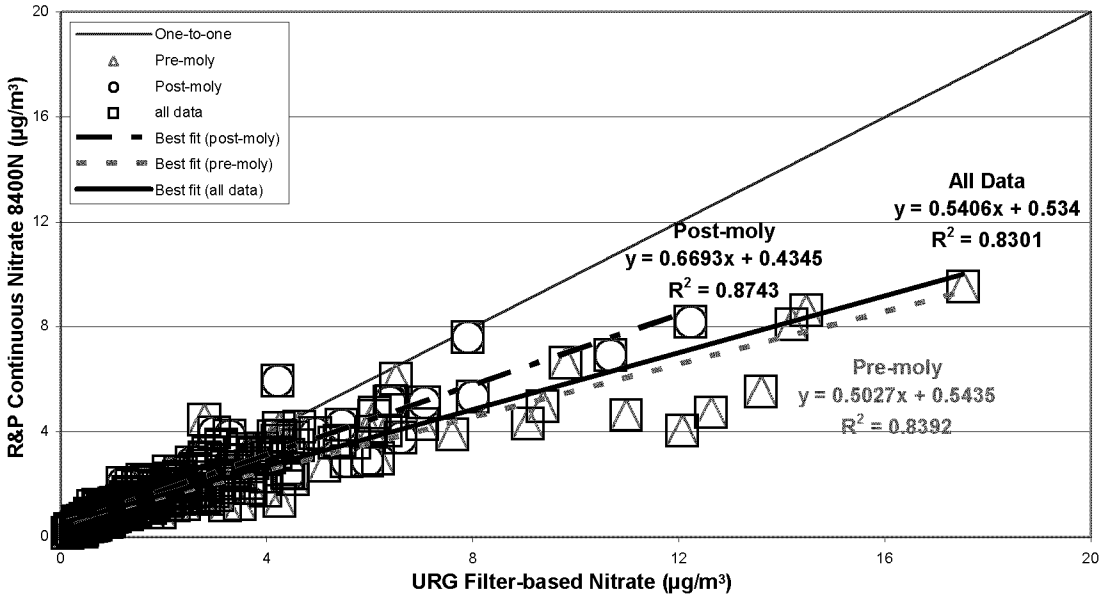

Figure 7-1. Twenty-four-hour average R&P 8400N $PM_{2.5}$ nitrate versus 24-hr integrated STN filter nitrate at Chicago, from May 2, 2002, to May 10, 2005.

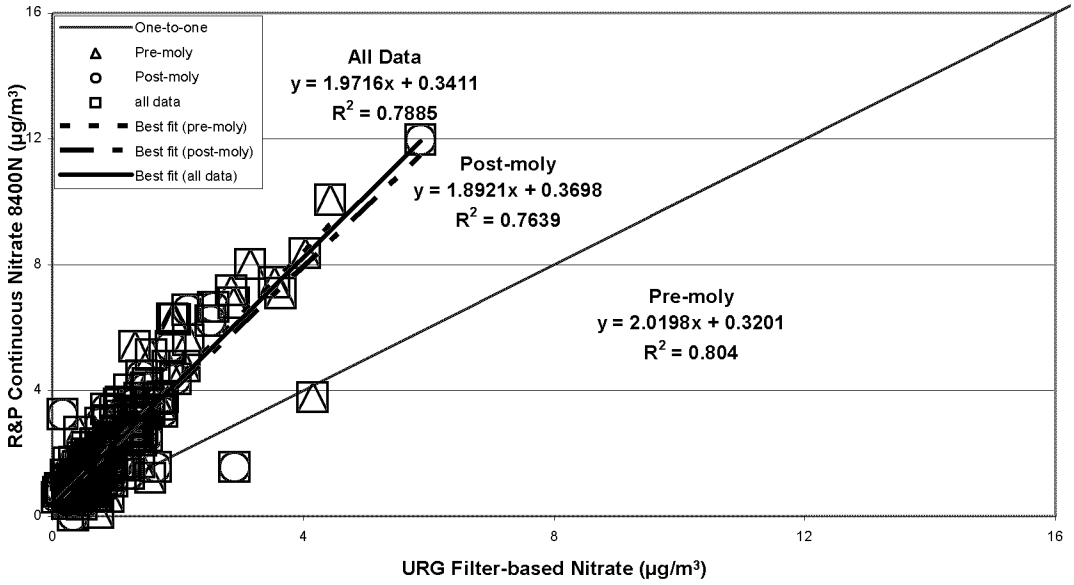

Figure 7-2. Twenty-four-hour average R&P 8400N $PM_{2.5}$ nitrate versus 24-hr integrated STN filter nitrate at Houston, from January 27, 2003, to April 13, 2005.

Although data from the R&P 8400N met both the correlation and ratio-of-means comparability criteria at only the Phoenix site, the R&P 8400N data did meet the predictability criteria at four of the five sites and were close at the fifth site. One benefit of this predictability is that the high time-resolution data may be calibrated by the filter data, yielding improved accuracy for examination of diurnal variability in nitrate concentrations. An example of this, using the nitrate data from Phoenix, is given in Figure 7-3, where the average diurnal nitrate

concentrations for wintertime (November through February) and summertime (March through October) nitrate data are adjusted, based on the filter data. Wintertime concentrations increased following adjustment while summertime concentrations decreased, reflecting the overestimation of nitrate by the 8400N at low ambient concentrations and the underestimation at higher concentrations at the Phoenix monitor.

Scatter plots and regressions for Phoenix, Seattle, and Indianapolis are included in Appendix A. With the exception of the atypical Houston data, the semi-continuous nitrate data reflect a non-linear component with respect to the filter-based data (Figure 7-4), where at low concentrations, the semi-continuous data exhibit minimal scatter and adhere more closely to the 1:1 line. At higher concentrations the semi-continuous data are noticeably lower than the filter-based nitrate. This pattern is similar to those reported by other researchers (Reid et al., 2005; Wittig et al., 2004). One of the postulated explanations for this pattern is a matrix effect between 8400N nitrate recovery and aerosol composition, where a deficiency of electron donors prevents complete reduction of nitrate to NO and NO_2 (Reid et al., 2005). An experiment utilizing CO-doped purge gas (increasing available electron donors) yielded a sustained 20% increase in nitrate concentration for the 8400N, although 8400N nitrate remained substantially lower than the filter-based measurements (Reid et al., 2005). Continued evaluations may lead to further performance enhancements and the potential for future comparability of the 8400N with STN filter-based methods.

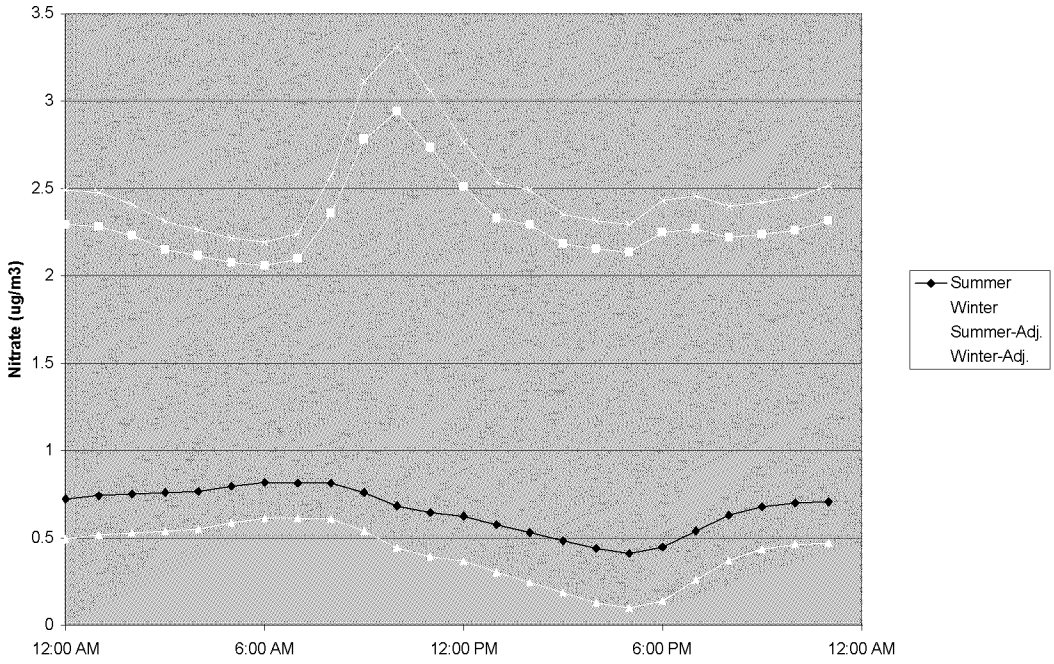

Figure 7-3. Average diurnal variability in R&P 8400N nitrate concentrations in Phoenix during the winter (November through February) and summer (March through October). Adjustments to the R&P 8400N data were made based on the regression of 8400N data with the filter data.

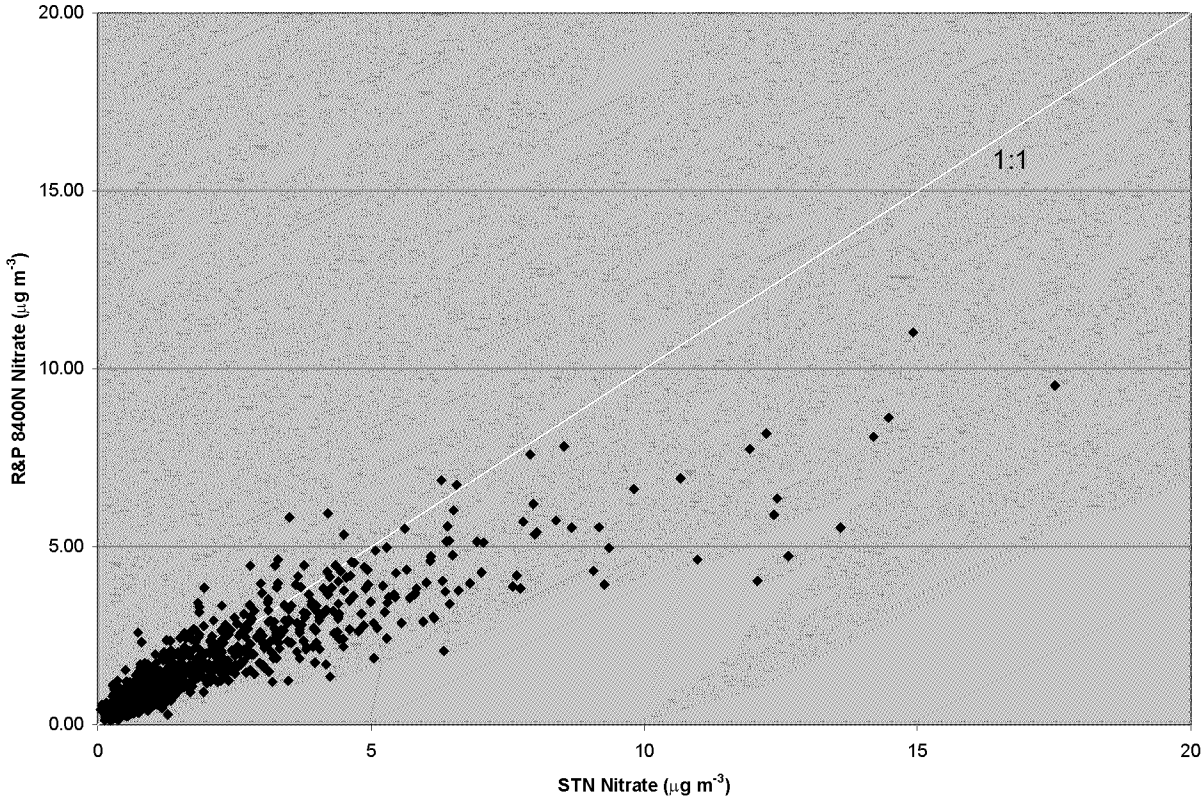

Figure 7-4. Nitrate data from Phoenix, Chicago, Seattle, and Indianapolis illustrating the typical non-linearity of the semi-continuous data relative to the STN filter-based data. Houston data are atypical and excluded.

7.3 R&P 8400S SULFATE VERSUS STN FILTER-BASED SULFATE

Aqueous standard salt solutions of ammonium sulfate (NH_4SO_4) were used to evaluate the conversion efficiency of the 8400S at each site. Frequency of the tests ranged from monthly to quarterly. Replicate measurements were made at zero nitrate and four additional nitrate levels (nominally 60, 120, 180, and 240 ng applied sulfate). Slopes of the measured mass versus deposited mass were applied as corrections to the data, either as inputs in the 8400S setup under "Theoretical Conversion Factor", or during post-processing of the data. Zero and span audits of the SO_2 analyzer were undertaken every few days (e.g., every three days at the Phoenix site). Average results for each site are shown in Table 7-5. These results for sulfate are significantly worse than those for nitrate; the theoretical conversion efficiencies are neither near 100%, nor consistent among the sites, varying from 50% to over 200%. However, the SO_2 gas analyzer efficiencies, as determined by aqueous standards, are quite high and close to 100%, as is expected.

The Phoenix and Seattle sites had substantially lower sulfate concentrations than did the more easterly cities of Houston, Chicago, and Indianapolis.

Only the Phoenix and Houston sites met the ratio-of-means criterion, but none of the data from the 8400S monitors met both comparability criteria at any of the five sites. Predictability criteria for sulfate were met at two of the five sites (Indianapolis and Seattle). The Phoenix sulfate monitor was operationally problematic. This analyzer was moved from Phoenix to Houston in June 2004, so the data comparison here with the Phoenix STN data involved only 62 data pairs covering the time period from September 2003 through May 2004 (Figure 5-1). Once the analyzer was moved to Houston, collocated 8400S measurements were made; however, at the time of this report, insufficient collocated data were available to analyze for precision estimates.

With the exception of data from the Seattle 8400S monitor, all sulfate regression slopes were less than or equal to 0.8 with positive intercepts (Table 7-4). No dynamic zero data were available to apply corrections for instrument offset. Although slopes were comparable between Chicago, Phoenix, and Indianapolis, the average difference between 8400S and STN sulfate data (y – x) was more negative for the more eastern cities because of the higher concentrations measured there. The scatter plot and regression for Chicago (**Figure 7-5**) were similar to those for Phoenix and Indianapolis.

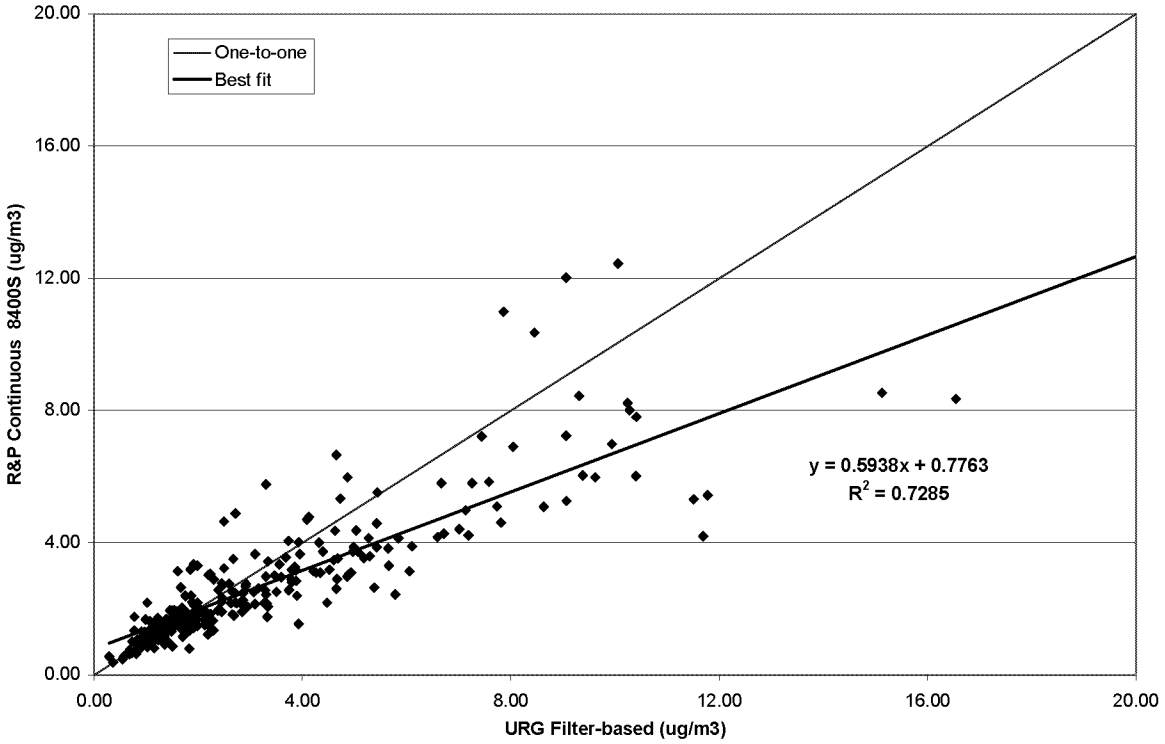

Figure 7-5. Twenty-four-hour average R&P 8400S $PM_{2.5}$ sulfate versus 24-hr integrated STN filter sulfate at Chicago, May 2, 2002 to May 10, 2005.

In contrast to the monitors at other sites, the Seattle 8400S sulfate monitor measured more sulfate than the STN filter-based sampler for all but 6 of the 245 data pairs, with a slope for the comparison of 1.25 ± 0.03 (**Figure 7-6**). All but a few measured concentrations in Seattle

were below 3 μg/m^3, and the linear fit at these low concentrations was very good. Both the Seattle (r = 0.94) and the Indianapolis (r = 0.92) sites met the predictability criteria.

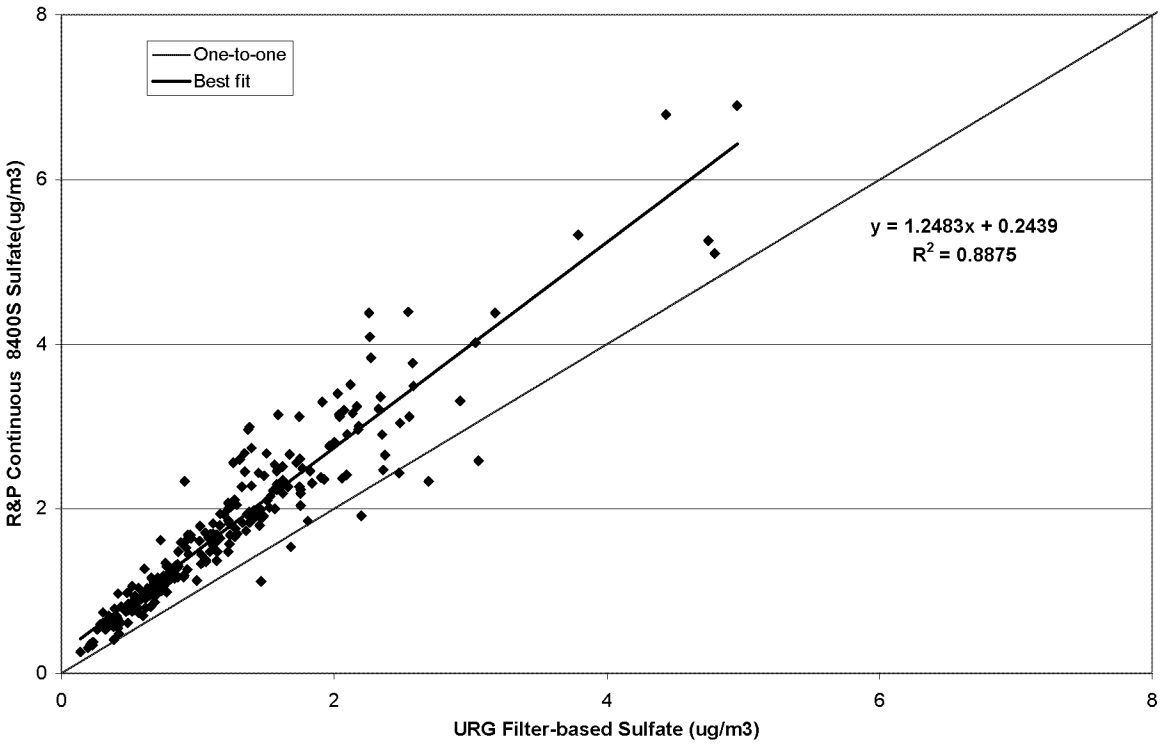

Figure 7-6. Twenty-four-hour average R&P 8400S $PM_{2.5}$ sulfate versus 24-hr integrated STN filter sulfate at Seattle, May 2, 2002 to February 3, 2005.

7.4 CARBON

That operationally defined measurements of aerosol TC, OC, and EC can yield highly variable results has been well documented. In a summary of comparison studies of filter methods to measure OC and EC, EC concentrations were found to differ by up to a factor of 7 among filter-based methods; factor of 2 differences were common (Watson et al., 2005). In the comparisons discussed in this report, the analytical methods differ substantially in such factors as the analysis atmosphere (e.g., ambient air versus pure helium), temperature regimes and dwell times, and correction for pyrolysis of OC. The STN method utilizing TOT is used as the benchmark, but the criteria for comparability or predictability must be viewed with the understanding that one analysis method is not necessarily better than another.

7.4.1 R&P 5400 Semi-Continuous Versus STN Filter-Based Carbon

There are substantial differences in analysis methods between the 5400 and the STN TOT procedure. The 5400 carbon analysis is undertaken in ambient air, while the TOT procedure uses pure helium for the OC step and a helium/oxygen mixture for the EC step. There is no correction for pyrolyzed OC (POC) in the 5400. Thus, any POC that is generated is potentially added to the EC fraction. Maximum temperatures differ (750°C in the 5400 and 920°C in STN TOT), and the OC versus EC split temperature is 600°C in TOT versus 275°C in the 5400. The TOT method converts the generated CO_2 to methane and measures it with a flame ionization detector (FID) while the 5400 employs a non-dispersive infrared (NDIR) detector. That results are dissimilar is not unexpected.

Of the EC, OC, and TC data from the R&P 5400 at the five sites, only OC and TC data from the Seattle site met the predictability criteria while the TC data from the Indianapolis site almost met the predictability criteria. No R&P 5400 EC, OC, and TC data met the comparability criteria at any site (see Table 7-4).

Slopes for TC ranged from 0.35 to 0.58, with correlation coefficients from 0.78 to 0.92. TC was underestimated over all concentration ranges, yielding average y/x ratios from 0.52 to 0.83, and average differences (y – x) from –0.71 to –3.89 $\mu g/m^{-3}$. **Figure 7-7** shows a typical regression for TC. Scatter plots of the 5400 versus STN TC for the other four sites are shown in Appendix A.

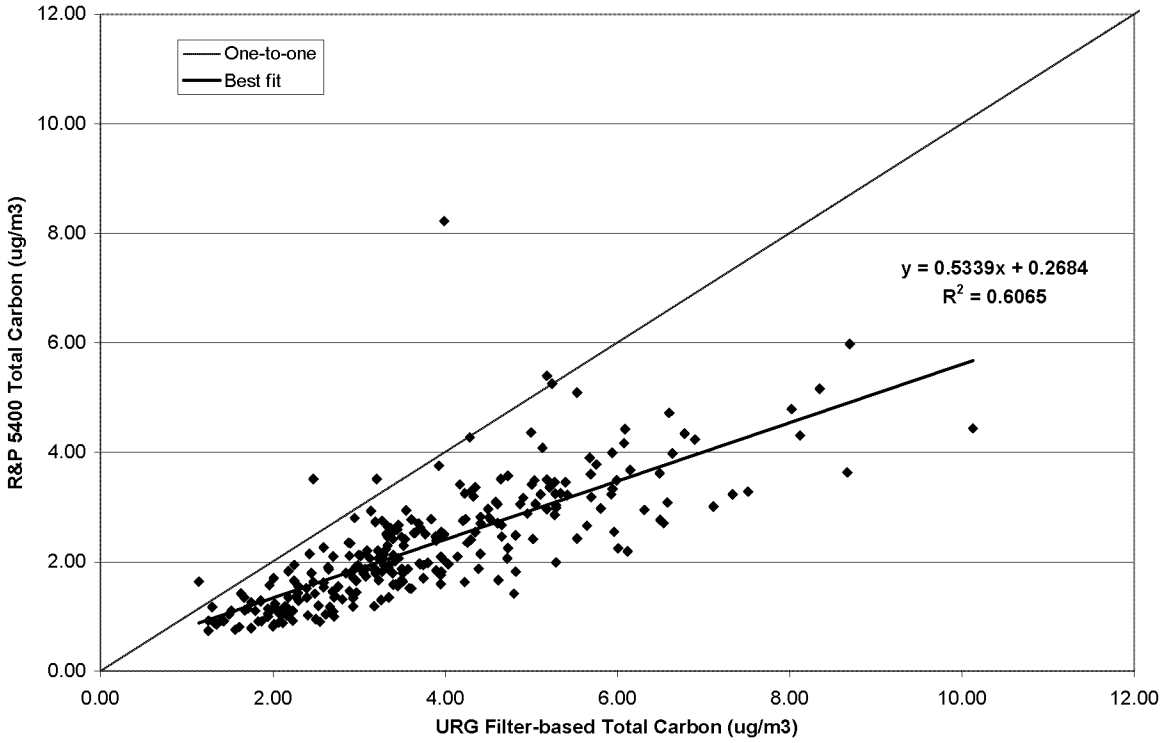

Figure 7-7. Twenty-four-hour average R&P 5400 $PM_{2.5}$ total carbon versus 24-hr integrated STN filter total carbon at Chicago, from May 2, 2002 to May 7, 2005.

Slopes for OC ranged from 0.33 to 0.54, with correlation coefficients from 0.73 to 0.90. OC was underestimated over all concentration ranges, yielding average y/x ratios from 0.48 to 0.81, and average differences (y – x) from –0.65 to –3.47 μg/m^3. **Figure 7-8** depicts the 5400-to-STN relationship for OC in Chicago. Plots for the other locations are shown in Appendix A.

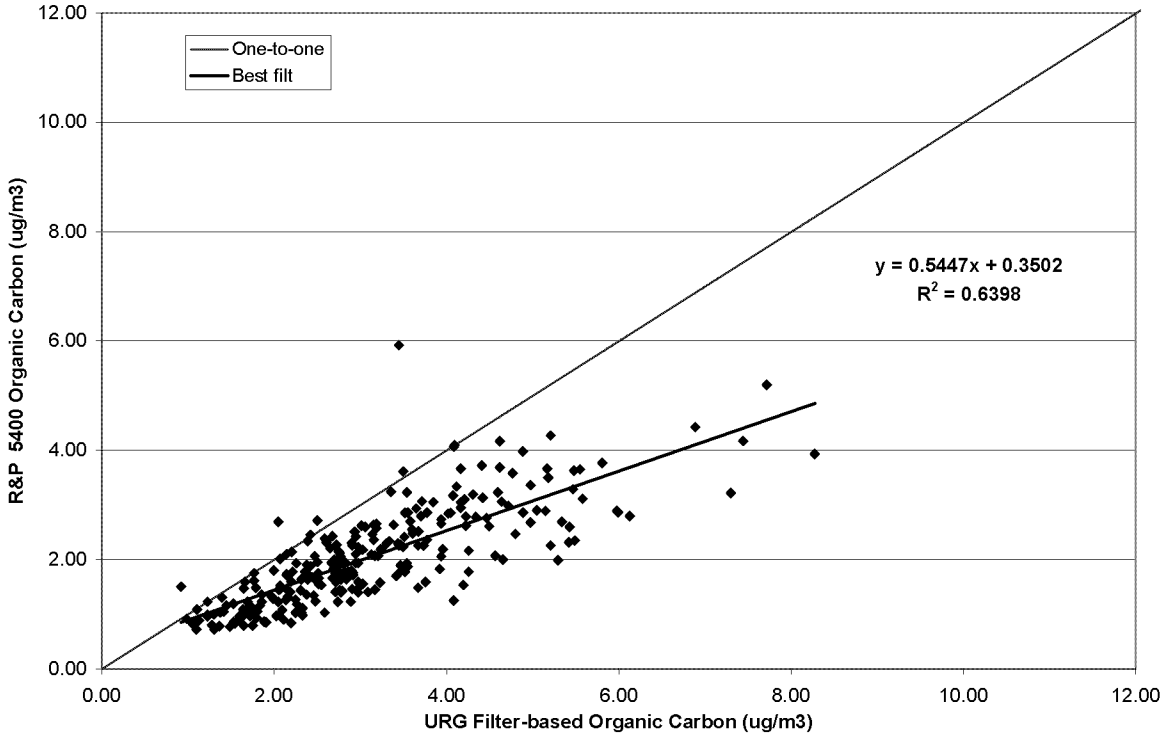

Figure 7-8. Twenty-four-hour average R&P 5400 $PM_{2.5}$ organic carbon versus 24-hr integrated STN filter organic carbon at Chicago, May 2, 2002 to May 7, 2005.

Slopes for EC ranged from 0.29 to 0.63, with correlation coefficients from 0.16 to 0.83. EC was underestimated over all concentration ranges, yielding average y/x ratios from 0.37 to 0.99, and average differences (y – x) from –0.07 to –0.42 μg/m^3. A typical regression plot, from Chicago, is shown in Figure 7-9.

In previous studies comparing data from the 5400 with filter-based aerosol carbon data, EC was overestimated by the 5400 (Watson and Chow, 2002; Rice, 2004). At the five STN sites included in the current analysis, the 5400 consistently underestimated the EC fraction, as reflected in the low slopes, the average y/x ratios all less than 1, and the consistently negative y-x differences.

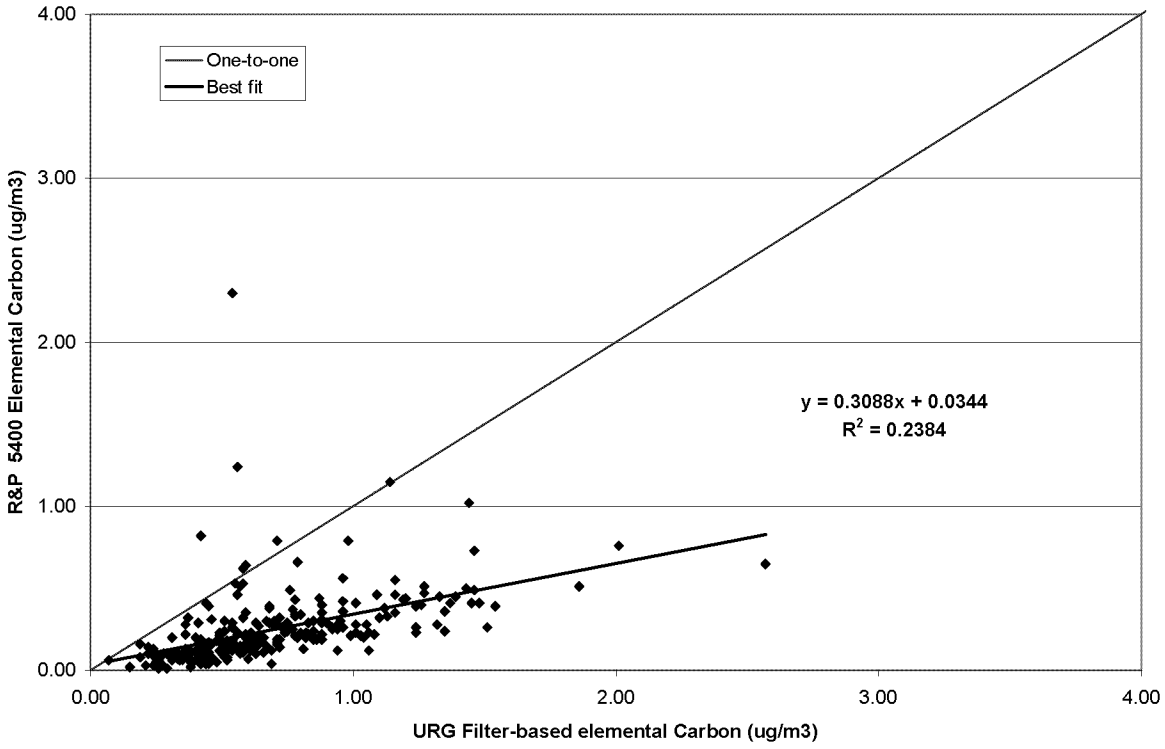

Figure 7-9. Twenty-four-hour average R&P 5400 $PM_{2.5}$ elemental carbon versus 24-hr integrated STN filter elemental carbon at Chicago, May 2, 2002 to May 7, 2005.

7.4.2 Sunset Semi-Continuous Versus STN Filter-Based Carbon

A Sunset Laboratory thermal-optical carbon monitor was added to the suite of instruments at the Chicago, Phoenix, and Seattle sites during 2004. The analysis method is similar to the STN TOT method—it uses a pure helium atmosphere for the OC step, followed by a helium/oxygen mixture for the EC step; maximum temperatures are similar (850ºC for the Sunset carbon monitor and 920ºC for STN TOT), and both methods have a light transmittance-based pyrolysis correction. The Sunset carbon monitor used in this comparison study use an NDIR to directly detect evolved CO_2. This method is similar to the laboratory-based STN analysis method.

The data sets for the Sunset comparisons are considerably smaller than the other data sets being evaluated here (70 to 90 pairs versus 150 to 300 pairs, see Table 7-1), but still sufficient for statistical analysis.

The results for the Sunset carbon monitor operated at three of the sites were significantly better than the results for the R&P 5400—the EC data at one site (Phoenix) met the slope and intercept comparability criteria; the EC, OC, and TC data from all three sites either met or almost met the ratio-of-means and correlation comparability criteria; and EC, OC, and TC at all three sites met the predictability criteria. The comparability evaluations between the Sunset and filter-

based OC and TC data offer some interesting results and point out the difficulty in assessing statistical equivalence and comparability.

Initial examination of the regression plots for Chicago (Figures 7-10 through 7-12) and Seattle (Figures 7-13 through 7-15) shows good agreement between the semi-continuous and filter-based data. The correlations are all greater than 0.90, and the regression slopes equal unity within 3 standard errors and/or average y/x ratios equal unity within 1 standard deviation (Table 7-1). However, the TC and OC intercepts differ from zero by more than 3 standard errors, making the Sunset data not comparable to filter-based data when intercept is a criterion (Table 7-1). How important is the intercept criterion? In the case of the Chicago Sunset TC, the slope is 0.91 and r = 0.98, and, as the regression plot (Figure 7-10) clearly demonstrates, the relationship over the range of measured concentrations is qualitatively good. However, under low ambient concentrations, an intercept of 0.80 ±0.15 imparts significant bias. This may indicate the need to determine a dynamic zero to adjust for background for the Sunset monitor. In addition, the Sunset monitor has an organic carbon gas-phase denuder and the STN does not. It is unclear how the denuder influences these results.

The Phoenix Sunset monitor met the correlation and ratio-of-means comparability criteria for OC and TC even though the low slopes for the Phoenix TC (**Figure 7-16**) and OC (**Figure 7-17**) were considerably outside the acceptable magnitude. Since OC is a major component of TC, OC concentrations dominated the TC slope, even though EC showed excellent agreement with the filter-based data (**Figure 7-18**).

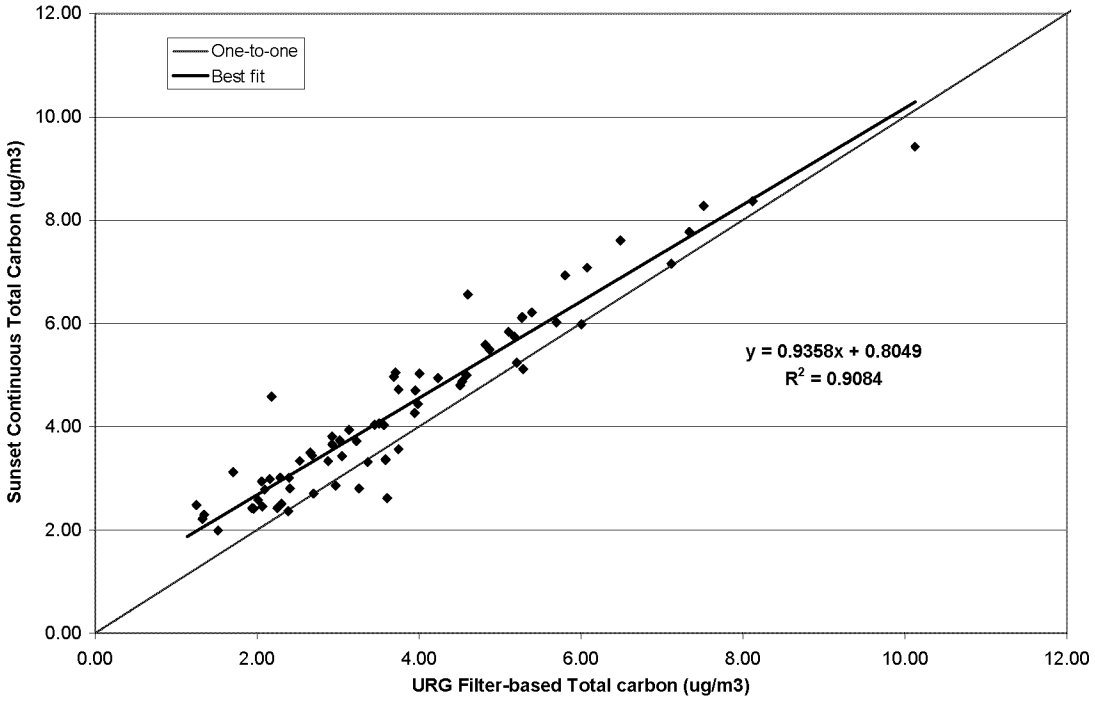

Figure 7-10. Twenty-four-hour average Sunset $PM_{2.5}$ total carbon versus 24-hr integrated STN filter total carbon at Chicago, August 1, 2004 to May 7, 2005.

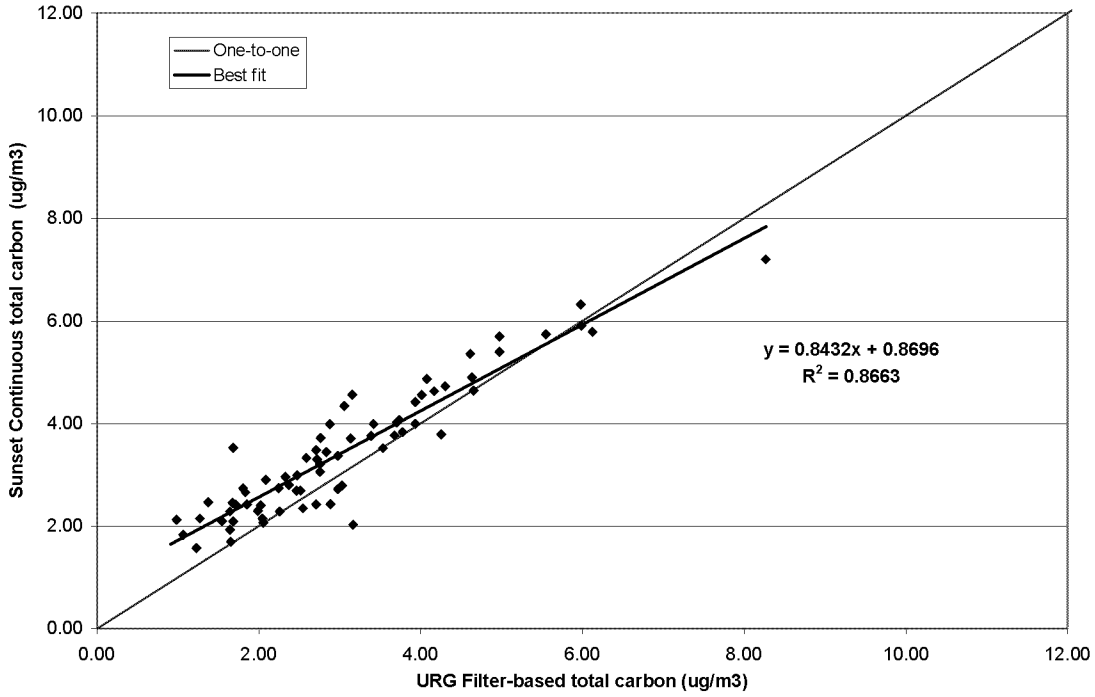

Figure 7-11. Twenty-four-hour average Sunset $PM_{2.5}$ organic carbon versus 24-hr integrated STN filter organic carbon at Chicago, August 1, 2004 to May 7, 2005.

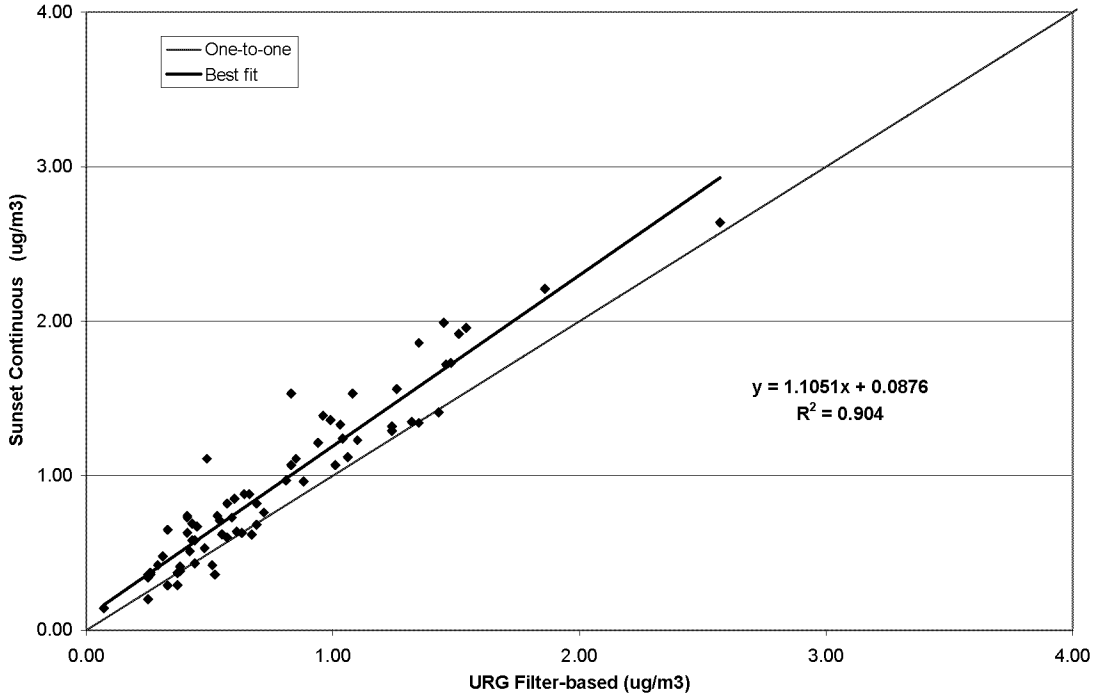

Figure 7-12. Twenty-four-hour average Sunset $PM_{2.5}$ elemental carbon versus 24-hr integrated STN filter elemental carbon at Chicago, August 1, 2004 to May 7, 2005.

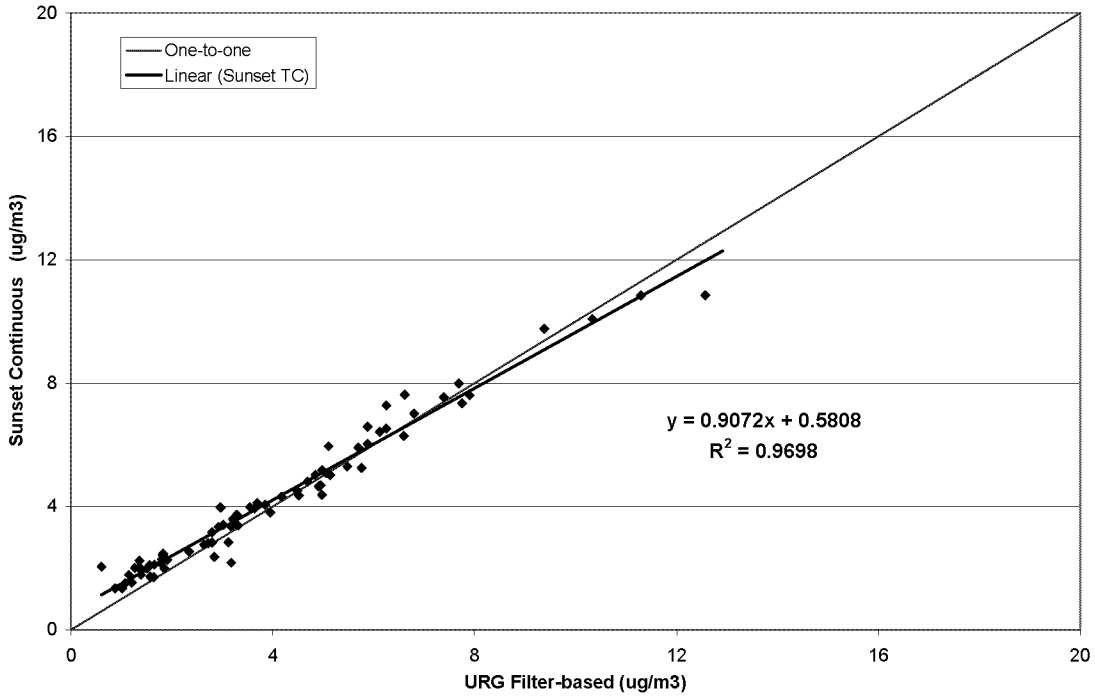

Figure 7-13. Twenty-four-hour average Sunset $PM_{2.5}$ total carbon versus 24-hr integrated STN filter total carbon at Seattle, August 13, 2004 to April 10, 2005.

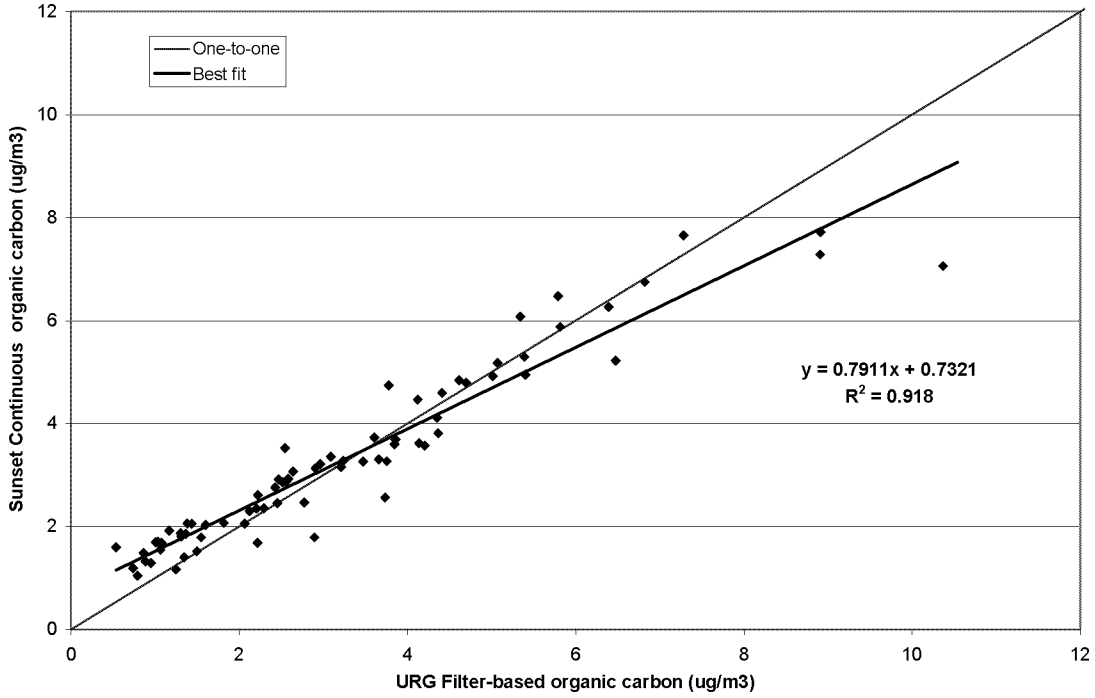

Figure 7-14. Twenty-four-hour average Sunset $PM_{2.5}$ organic carbon versus 24-hr integrated STN filter organic carbon at Seattle, August 13, 2004 to April 10, 2005.

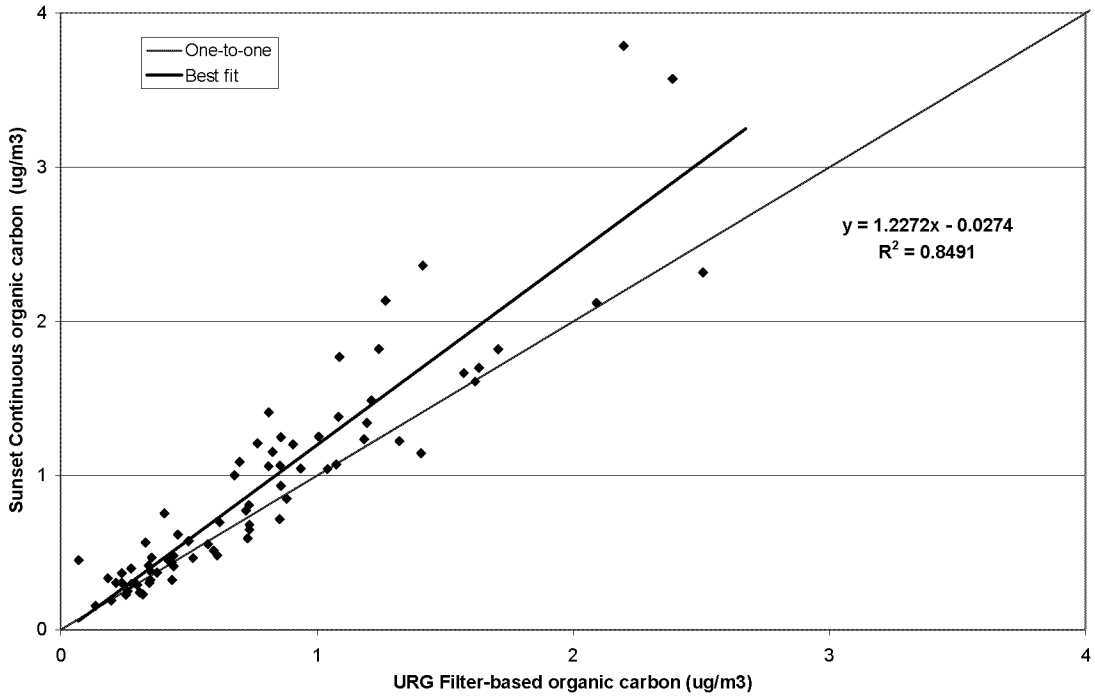

Figure 7-15. Twenty-four-hour average Sunset $PM_{2.5}$ elemental carbon versus 24-hr integrated STN filter elemental carbon at Seattle, August 13, 2004 to April 10, 2005.

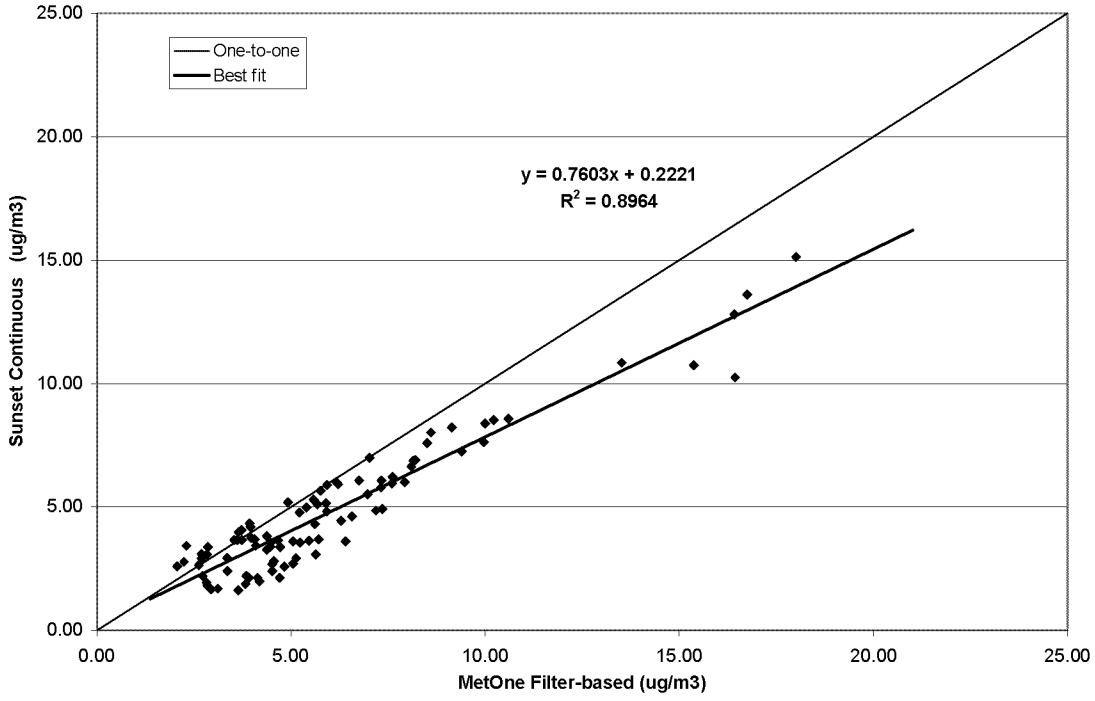

Figure 7-16. Twenty-four-hour average Sunset $PM_{2.5}$ total carbon versus 24-hr integrated STN filter total carbon at Phoenix, July 2, 2004 to May 13, 2005.

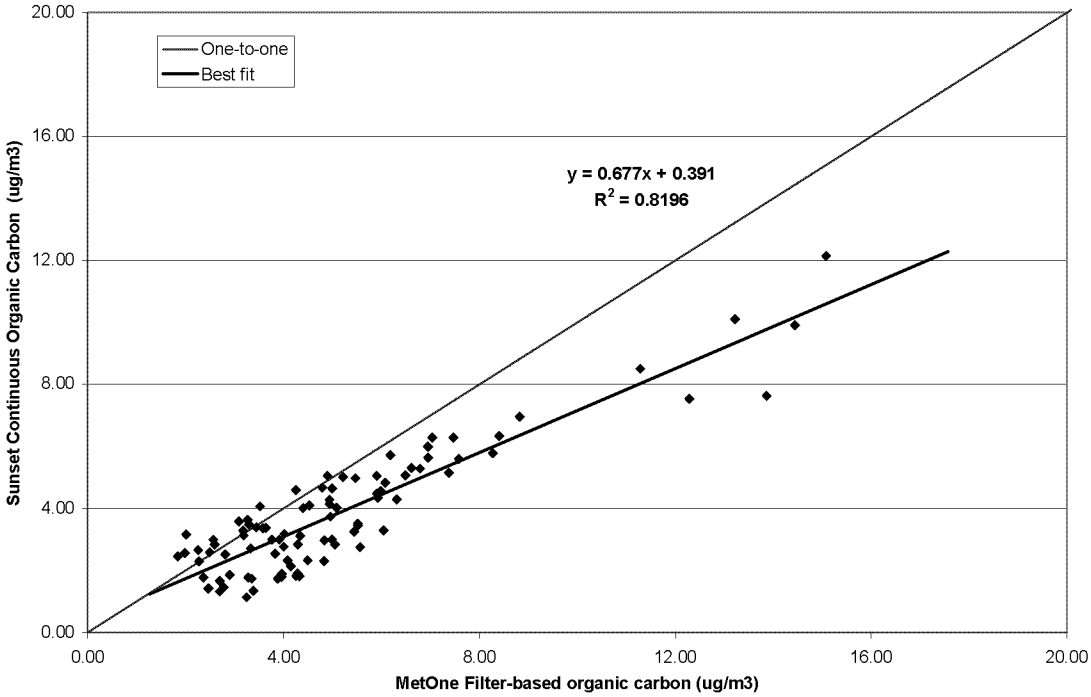

Figure 7-17. Twenty-four-hour average Sunset $PM_{2.5}$ organic carbon versus 24-hr integrated STN filter organic carbon at Phoenix, July 2, 2004 to May 13, 2005.

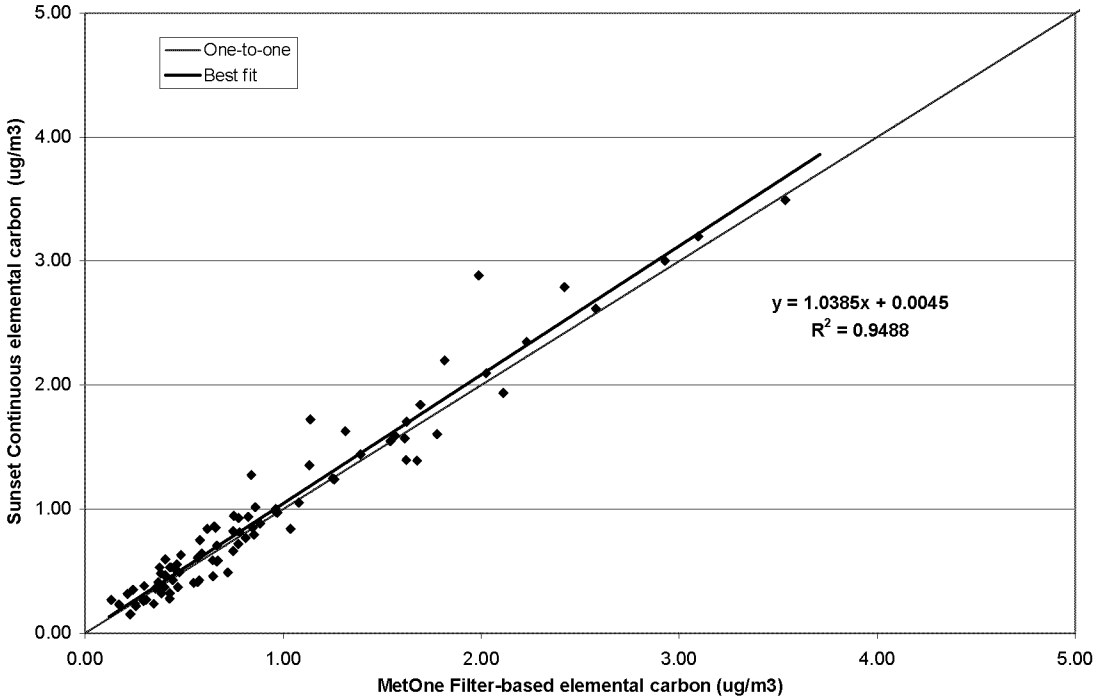

Figure 7-18. Twenty-four-hour average Sunset $PM_{2.5}$ elemental carbon versus 24-hr integrated STN filter elemental carbon at Phoenix, July 2, 2004 to May 13, 2005.

8. OPERATIONAL ISSUES

A desirable characteristic of semi-continuous speciation monitors is ease of maintenance. Site operators at the five locations were polled, and their comments about operational issues are qualitatively summarized here. Prior to the study, Standard Operating Procedures (SOPs), quality control (QC) checklists, and other assistance documents were jointly prepared by the study participants.

8.1 R&P 8400N AND 8400S

The 8400N and 8400S instruments have few operational differences beyond those mentioned in Section 5.2.2, so their operational characteristics are discussed together.

The general impression of the 8400 series operating manuals was that they were poorly written, lacked coherence, and, in some cases, contained erroneous information. Fortunately, the SOP and assistance documents were generally complete and well thought out. Site operators noted that the QC checklists should be continually updated as field experiences were discussed and evaluated during the field study. One example would be updating acceptable values for the nitrate flash duration range. Also mentioned was the importance of maintaining consistency in units between the nitrate and sulfate instrument QC checklists to avoid confusion for staff.

8.1.1 Distribution of Annual Hours

Site operators agreed that, as a very general estimate, about 400 hours were spent annually on each 8400 series monitor. Data acquisition and reduction alone are estimated to account for about 44% of all annual hours expended on these instruments, followed by aqueous standards tests at 14% of total hours. Most of these hours were within weekly or monthly visits, while PE tests dominated the hours attributed to quarterly tasks. Table 8-1 gives estimates of the proportion of annual hours allotted to specific tasks. Note that these estimates are for operations, maintenance, and data processing, and do not include reporting tasks.

8.1.2 Flash Strips

The 8400S exhibited more flash-strip-related problems than did the 8400N, apparently related to the washers that are used to hold the flash strip in place and the fact that the 8400S platinum strips are more delicate than the 8400N NiChrome® strips. The 8400S was originally supplied with round washers meant to hold the flash strips, but R&P replaced these round washers with square washers. Users reported that the jagged edges of the square washers apparently caused more strip failures. Both round and square washers are currently in use at the different sites. Some operators found no difference in the washers, while others strongly disliked the square ones. R&P was supposed to have distributed a flash strip installation guide tool to all operators. This tool was intended to hold the square washers in place while retaining nuts were tightened to avoid stressing the flash strip. One operator who received the tool stated that it was very helpful, but operators at some sites did not receive the tool. Site operators changed the

strips nominally once a month and reported that it was important to check the washers at every flash strip change for black marks or burning, and to replace them if they looked or felt bad. One site operator stated that constant strip-breaking on the 8400S (every 2–3 days) was a significant problem, and the instrument was eventually shut down because of this problem.

The posts on which the flash strips are mounted also tend to develop burrs or pits that can contribute to flash-strip failure, and these posts need to be sanded with a fine emery cloth.

If the flash duration of the 8400S is too short (less than 8 ms), the strips are prone to "burning up". A flash duration of between 10 and 16 ms will prolong the life of the 8400S flash strip.

Table 8-1. Percent of annual hours spent on operational and maintenance tasks for the R&P 8400 series monitors. The annual total for all tasks is estimated at 400 hours for each 8400N or 8400S monitor.

Maintenance Item or Task	Percent of Annual Hours
Carrier Gas	4.8
Calibration Gas	4.8
Water Reservoir	4.0
Flash strip	1.5
Flash duration	3.3
Carbon denuder maintenance	0.1
Sample flow rate	3.3
Orifice cleaning	1.5
Make-up flow and filter check	0.3
R-cell pressure adjustments	1.5
Zero and span drift	4.5
Manual analyzer audits	3.0
Cyclone maintenance	1.5
Field blanks	0.8
Leak checks	1.5
Flow checks	0.8
Ambient T and P verification	0.4
Aqueous standards	13.5
Performance evaluations (blind tests)	4.0
Data acquisition and reduction issues	43.5
Pump Maintenance/ Repair	1.3
Sample Line Replacement	0.5

8.1.3 Aqueous Standards

Testing against aqueous standards is time-consuming but necessary. The primary issues concerning aqueous standards for the 8400 series instruments are related to using varying volumes of the standard solution. One consequence is that for the larger volumes, there may not be adequate time for complete evaporation to occur, especially at lower temperatures. This issue was apparently a larger problem for the 8400S than for the 8400N. One suggested resolution of this problem was to use multiple concentrations of standards at one low volume (e.g., 0.2 µl SO_4, and 0.5 µl NO_3). R&P promised to provide standard solutions in multiple concentrations, but none of the site operators actually received these standards. PE solutions provided by NAREL for routine aqueous standards tests are being used at at least one site. Another suggestion for ensuring complete evaporation of the syringe-applied standard was to provide a heated flash cell (e.g., 35 to 50° C).

8.1.4 Water Reservoir and Hydration Tube

Some participants commented on problems with discoloration of the hydration tube. One participant attributed the discoloration to bacteria growing in the humidifier because the water was not bacteria-free. This operator has been using ultra-pure bacteria-free water to fill the hydration bottle. Others used distilled water. The true cause of this discoloration is undetermined. Another possibility is a reaction with the metal fittings, since the discoloration tends to be on either end of the hydration tube, near the metal "T" fittings. Discoloration of the hydration tube was commonly reported; but according to R&P, the ability of the permeation tubing to hydrate the sample air is not affected.

8.1.5 Orifice Cleaning

Although the 8400 series manuals recommend monthly intervals between sample orifice cleaning, site operators reported that weekly schedules (or at each site visit) are more apt to minimize flow rate problems.

8.1.6 Molybdenum Converter

The molybdenum converter in the 8400N instruments was evaluated and replaced during 2004. The efficiency of the "moly chips" that convert the nitrogen species to NO under high temperatures is reduced over time, and it is important to periodically check the conversion efficiency. There is some uncertainty about which nitrogen species should be used to check the converter efficiency. As discussed above, the effect of the converter replacement on the monitors' efficiencies, as measured by the periodic aqueous standards tests, varied among sites.

8.1.7 Data Screen Failures

Some sites experienced "data screen failures" due to failures in the backlight controller. R&P delivered an upgrade kit that involves the installation of a "piggy-back" board on the existing backlight controller.

8.1.8 Data Acquisition and Reduction

Methods of data acquisition and reduction for the semi-continuous monitors differed among sites. Some sites logged analog data and other sites logged digital data. All site operators indicated that viewing the data every day, often via remote access, was a valuable activity. The operators viewed the data to determine if the instrument was operating, and operating properly, to evaluate various instrument operating parameters that are provided on these new instruments using serial outputs and to identify major problems. The review and evaluation of important operational data from these monitors, such as flash duration, flow rate, and R-cell pressures, was valuable.

Several different systems were used to view the data on a daily basis. The Indiana site operator did a quick, daily review of the data through a special MeteoStar LEADS web site. The Texas operator performed his daily review via the Texas Commission on Environmental Quality (TCEQ) web site, which also uses MeteoStar LEADS, but the operator used an on-site PC to collect the data that were validated and used for reporting. The Illinois operators do not use the MeteoStar system. At the Phoenix site, an STI data acquisition system was used to collect the serial data. The data were then automatically screened against minimum validation criteria, plotted and made available on a web site and archived.

8.2 R&P 5400

Site operators agreed that, as a very general estimate, about 150 hours were spent annually on the R&P 5400 OCEC monitor. Data acquisition and reduction alone accounted for more than 50% of all annual hours spent on this instrument. Monthly and semi-annual checks and repairs of furnace lamps, afterburner lamps, and oven fuses combined to account for an additional 20% of annual hours. Table 8-2 shows estimates of the proportion of annual hours allotted to specific tasks. Note that these estimates are for operations, maintenance, and data processing but do not include subsequent reporting tasks.

Table 8-2. Percent of annual hours spent on operational and maintenance tasks for the R&P 5400 OCEC monitor. The annual total for all tasks are estimated at 150 hours for each 5400 monitor.

Maintenance Item or Task	Percent of Annual Hours
Flow audit	3.9
Collection path leak test	3.9
Analysis loop leak test	2.0
Licor calibrations	3.3
Furnace burners/afterburners fuses (monthly)	9.8
Inlet cleaning	11.8
Intake filters (cooling fans)	0.7
In-line filters	0.7
Data acquisition and reduction issues	52.3
Collector replacement	5.2
Furnace Lamp Checks/ Replacement (semi-annually)	10.5
Pump Maintenance/ Replacement	2.0

Flow problems, along with oven and afterburner problems, were the most frequent and recurring operational issues with the R&P 5400. It had been known that the sample flow through the collectors in the 5400 monitor tend to degrade over time, requiring replacement of the collectors, and this degradation was observed during the course of the Study. The collectors are expensive (~ $1,200 per pair), and it is recommended that both collectors be replaced whenever one of them starts to become clogged. Failure to reach set point temperatures was most frequently caused by blown fuses or burnt out oven lamps or afterburner lamps. The contact points for the lamps were also reported to have melted on occasion.

The 5400 monitor in Phoenix experienced leak problems. Although regular leak checks yielded apparently acceptable results, evidence exists that a leak may have existed and gone undetected for an extended period of time. The hypothesis is that the pressure sensor in the optical bench has a maximum range and that this range was being exceeded during the manual leak tests. The R&P recommendation is to achieve a pressure of about 1200 mb for this test. Empirically, it appears that the pressure sensor tops out at 1206 mb. If this pressure were to be exceeded, a pressure drop could be occurring during the leak test but would not be detected. On February 4, 2005, after both sides of the analyzer failed an analysis loop leak check while a manual leak check was passed, this hypothesis was tested. A manual leak check using a maximum pressure of 1180 mb was initiated, a pressure drop was noted immediately, and the leak was isolated at the septum/buffer tank by pinching off the line above the buffer tank. This action stopped the pressure drop, and the septum fittings were replaced. It is recommended that all manual leak checks use a maximum pressure of 1180 mb. The rated maximum pressure of the optical bench pressure sensor is not known.

In Phoenix, the replacement of some hardware in the Licor NDIR component in September 2004 caused false status codes during the auto-calibration procedure. R&P's

recommendation was to disable the auto-calibration and auto-leak check functions. This step increased the duties of the site operators because these checks had to be performed manually.

Some site operators felt that the data from the R&P 5400 were so disappointing that they did not want to waste their time discussing operational issues. Most of the above issues are based on comments in the Phoenix site log.

8.3 SUNSET CARBON MONITOR

Generally, site operator experiences with the Sunset OCEC analyzer have been good. The Sunset analyzer has no analog output, so users without serial datalogging capability are at a disadvantage. This characteristic combined with a failure in the laptop PC control system to cause massive (one month) data loss at the Chicago site, which apparently had only analog capabilities. A hard-drive failure in the laptop occurred one day before the month's data were due to be downloaded. A loss of six days' data occurred at the same site when the laptop locked up just after a Thursday visit by the site operator and was not rebooted until the next visit the following Tuesday. All site operators reported problems with the laptop computer at some point.

The burner coils in the Sunset have to be replaced periodically. The first report of burner failures came from Phoenix in August 2005, when both front and rear burners failed within a few weeks of each other.

Over the past year, the three Sunset monitors in the evaluation differed in their analysis software. All comparisons presented here have been based on a recalculation of the concentrations from the raw data, employing the most recent version of the analysis software. It will be important for the manufacturer to ensure that the deployed instruments have up-to-date versions of software and employ identical procedures.

Although the audit punches in the PE were easy to complete, the manual integration of the peaks was tedious. Modification of the software to enable the field results file to duplicate the post-calculated values would be helpful.

A few comments noted that the Sunset manual was inadequate to acquaint an operator with operation of the instrument. While covering the instrument setup routines fairly well, the manual offers minimal information on the theory of operation and data output interpretation. There are no schematics or illustrations. More clarification of and details about filter replacement procedures would be helpful. The inclusion of the NIOSH laboratory SOP in the manual is confusing because of differences between the laboratory and field instruments (FID versus NDIR, for example).

No sucrose spikes were ever applied by the site operators, except for those provided by NAREL for the PEs. This action would provide useful checks on the monitors' performance.

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APPENDIX A

SCATTER PLOTS AND REGRESSIONS FOR PHOENIX, SEATTLE, AND INDIANAPOLIS

A.1 NITRATE

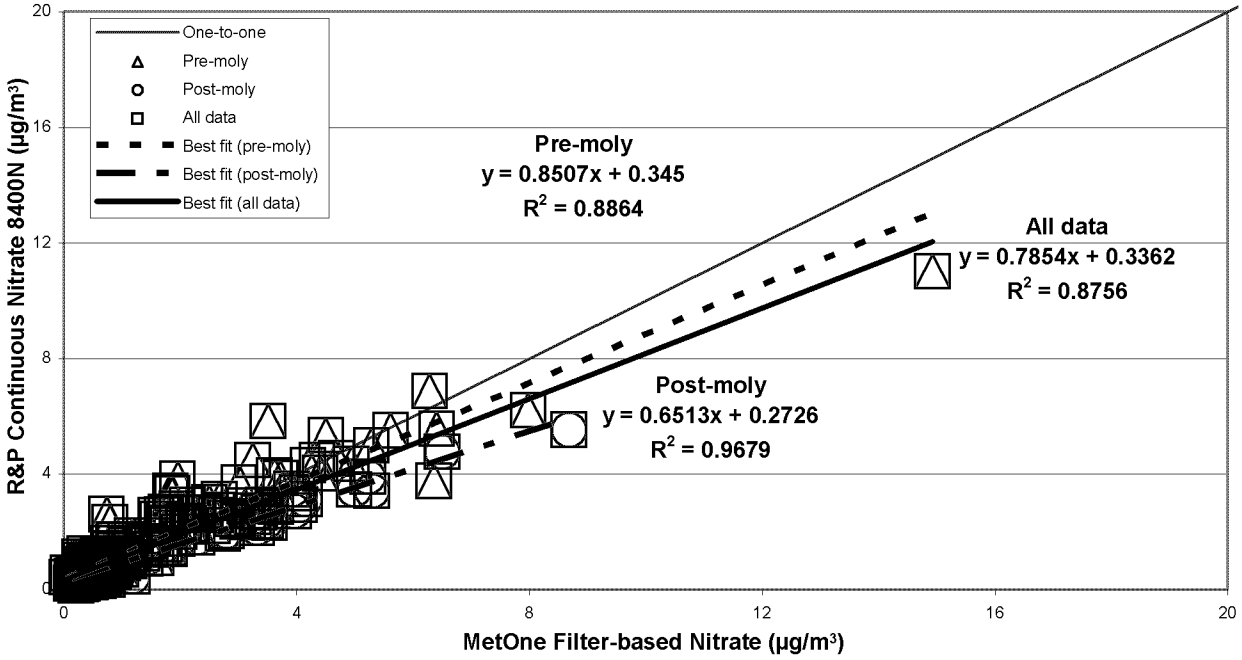

Figure A-1. Twenty-four-hour average R&P 8400N $PM_{2.5}$ nitrate versus 24-hr integrated STN filter nitrate at Phoenix, from September 26, 2002, to May 13, 2005.

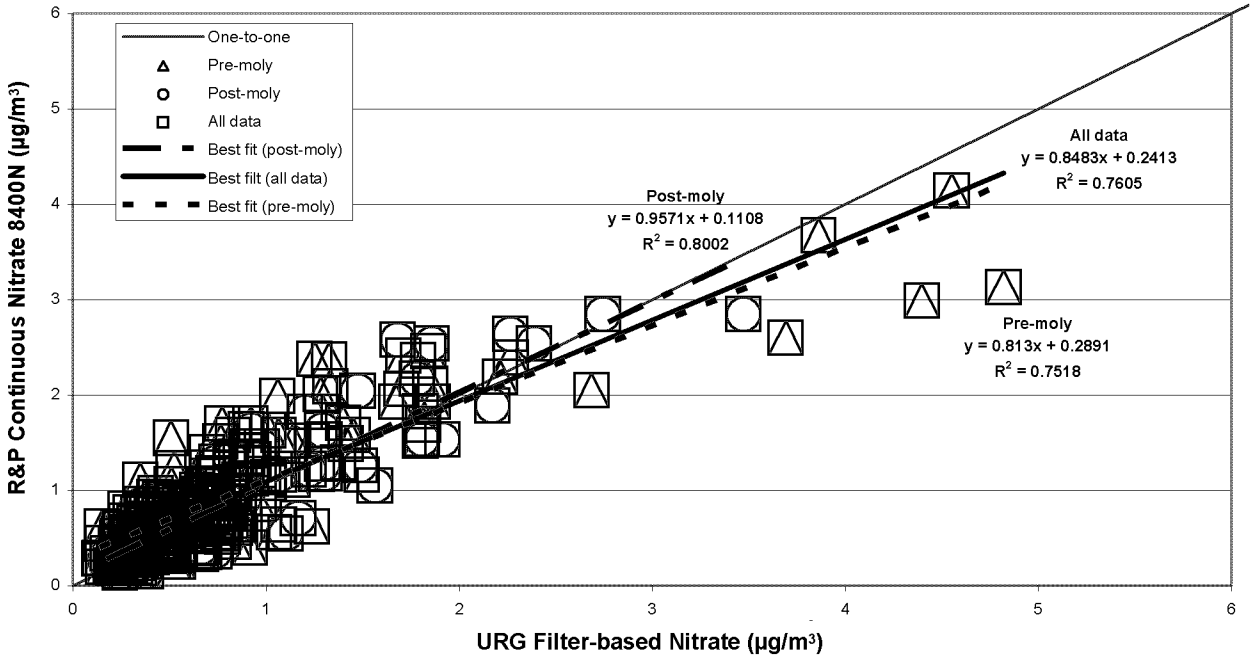

Figure A-2. Twenty-four-hour average R&P 8400N $PM_{2.5}$ nitrate versus 24-hr integrated STN filter nitrate at Seattle, from May 2, 2002, to April 14, 2005.

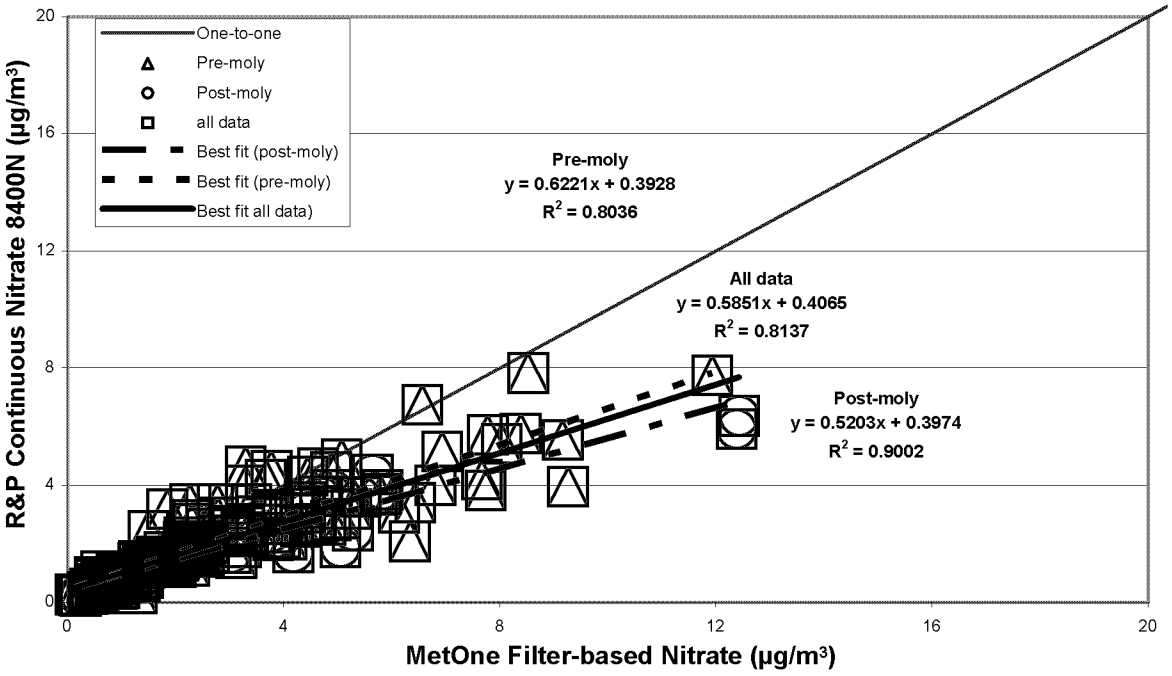

Figure A-3. Twenty-four-hour average R&P 8400N $PM_{2.5}$ nitrate versus 24-hr integrated STN filter nitrate at Indianapolis, from June 13, 2002, to March 11, 2005.

A.2 SULFATE

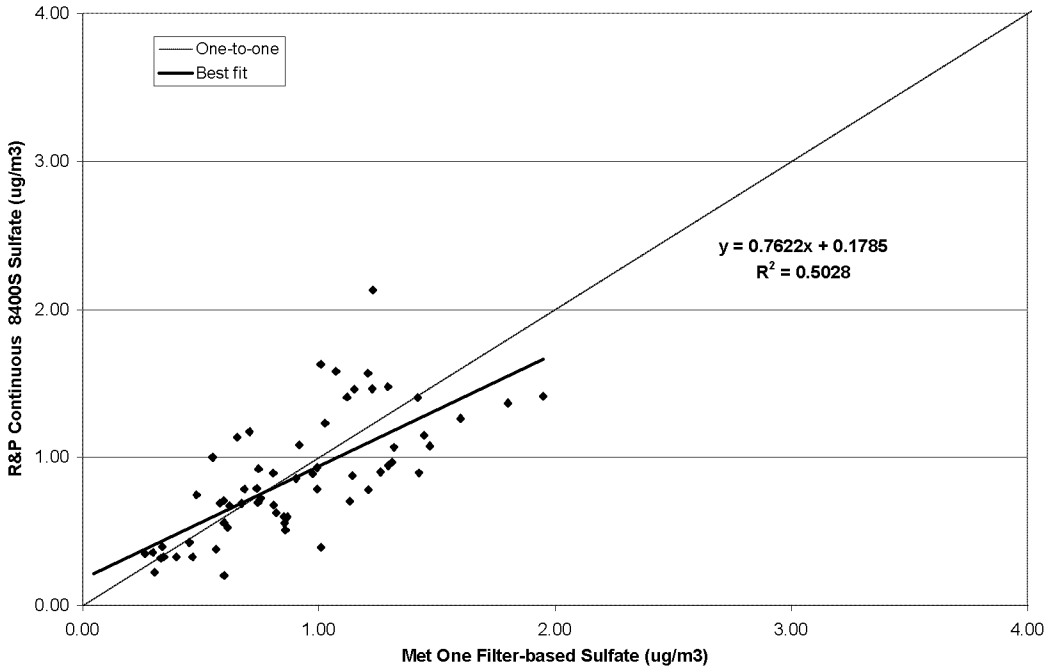

Figure A-4. Twenty-four-hour average R&P 8400S $PM_{2.5}$ sulfate versus 24-hr integrated STN filter sulfate at Phoenix, from September 30, 2003, to May 12, 2004.

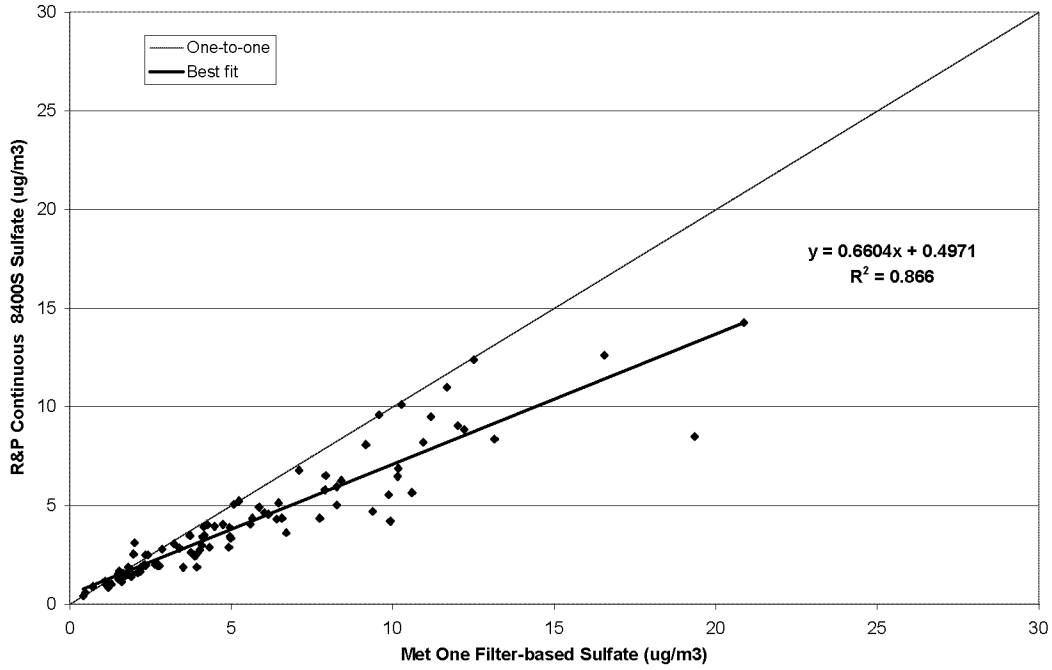

Figure A-5. Twenty-four-hour average R&P 8400S $PM_{2.5}$ sulfate versus 24-hr integrated STN filter sulfate at Indianapolis, from June 19, 2002, to July 8, 2004.

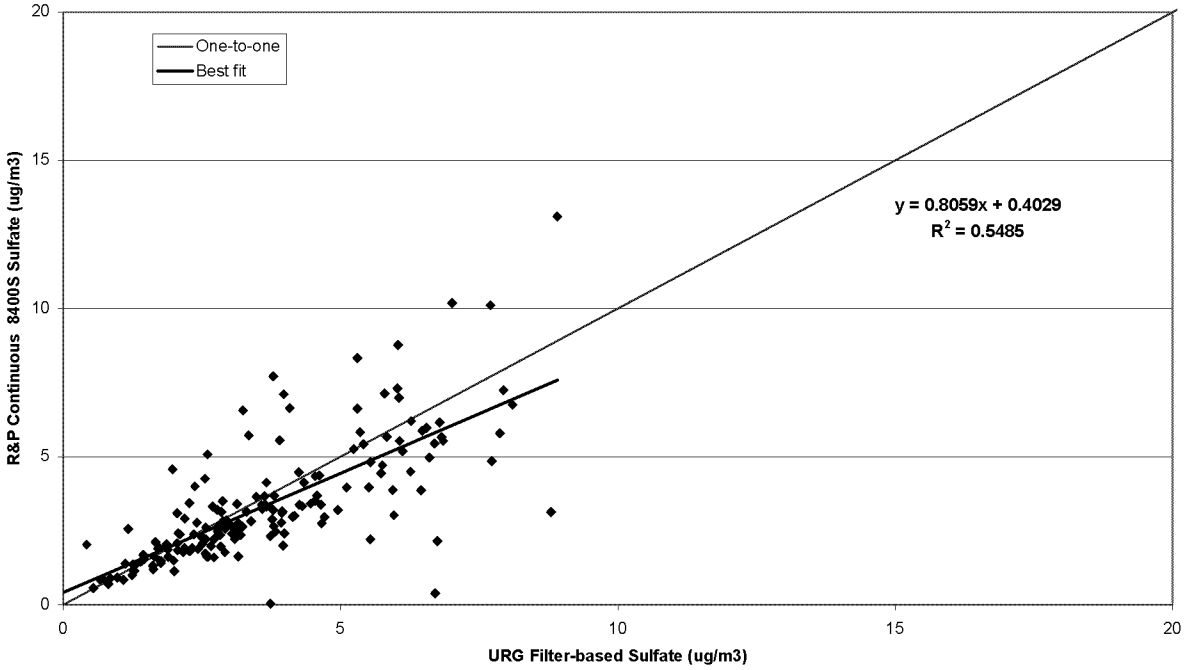

Figure A-6. Twenty-four-hour average R&P 8400S $PM_{2.5}$ sulfate versus 24-hr integrated STN filter sulfate at Houston, from January 27, 2003, to April 13, 2005.

A.3 R&P 5400 VERSUS STN CARBON

A.3.1 Total Carbon

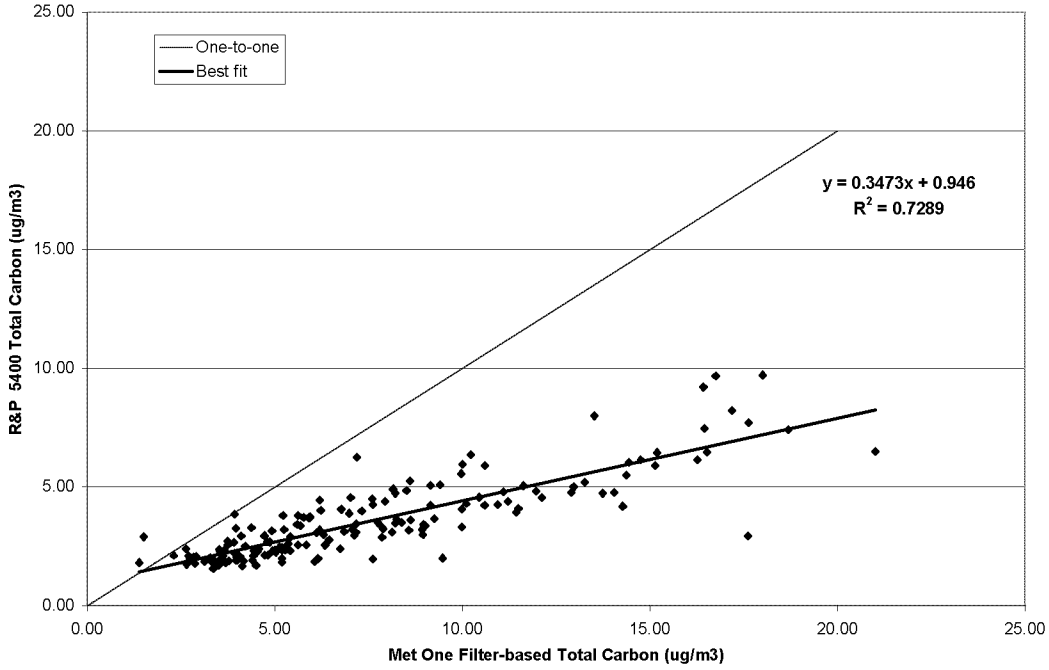

Figure A-7. Twenty-four-hour average R&P 5400 $PM_{2.5}$ total carbon versus 24-hr integrated STN filter total carbon at Phoenix, from December 13, 2002, to May 13, 2005.

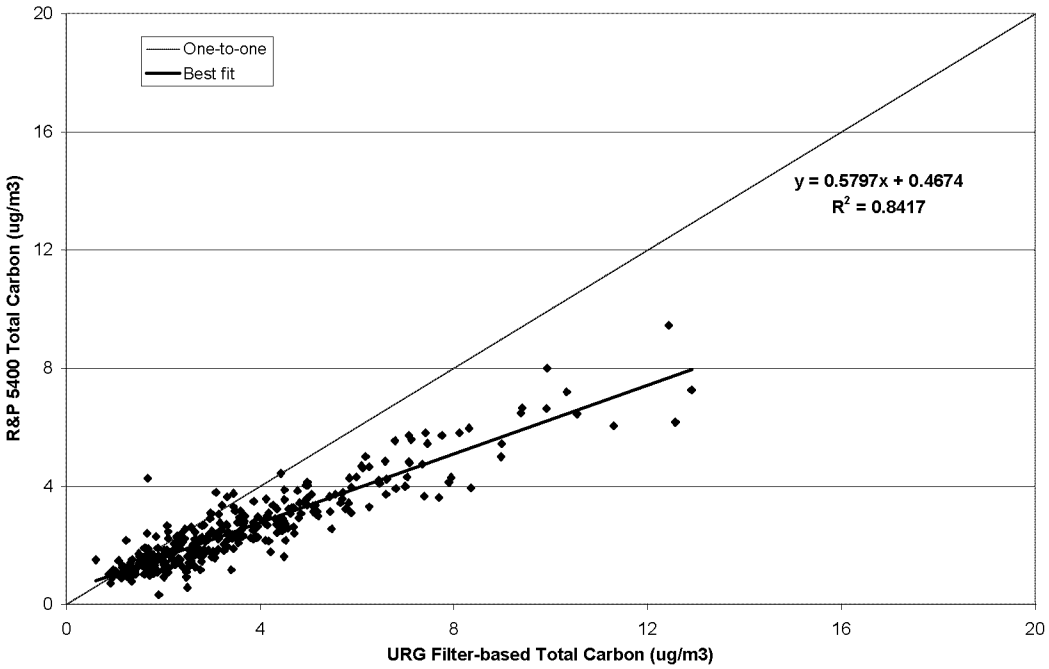

Figure A-8. Twenty-four-hour average R&P 5400 $PM_{2.5}$ total carbon versus 24-hr integrated STN filter total carbon at Seattle, from May 2, 2002, to March 29, 2005.

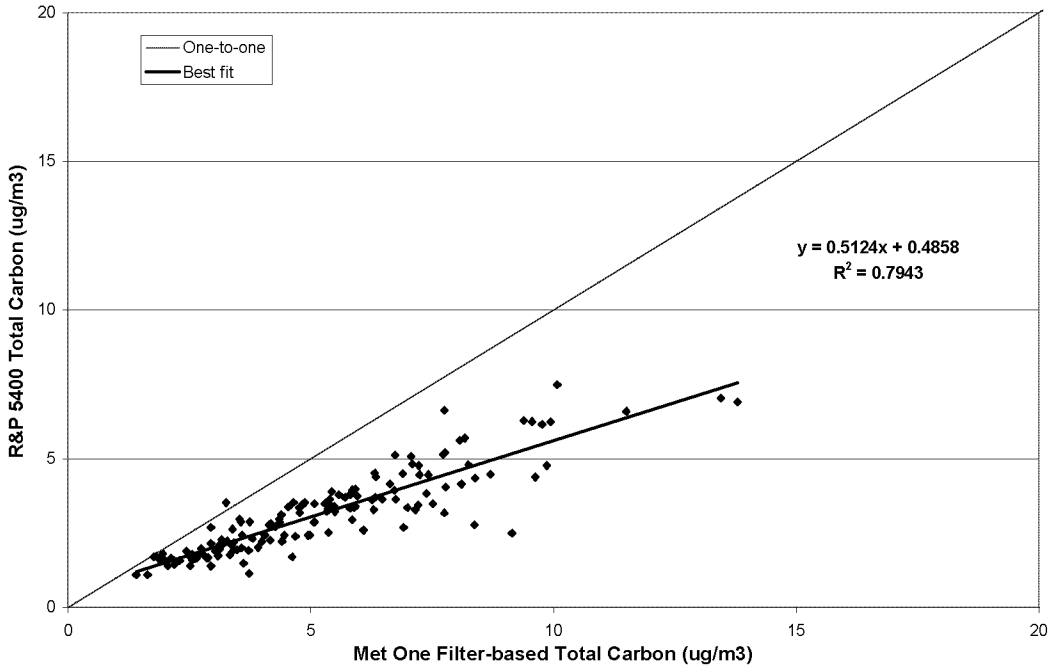

Figure A-9. Twenty-four-hour average R&P 5400 $PM_{2.5}$ total carbon versus 24-hr integrated STN filter total carbon at Indianapolis, from June 26, 2002, to April 9, 2004.

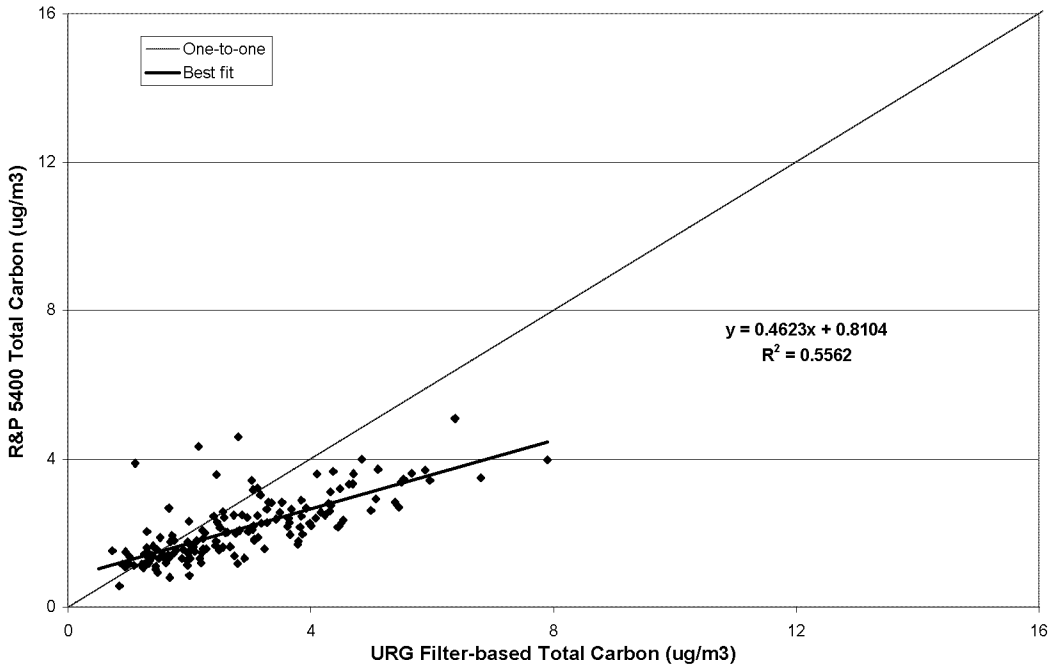

Figure A-10. Twenty-four-hour average R&P 5400 $PM_{2.5}$ total carbon versus 24-hr integrated STN filter total carbon at Houston, from January 24, 2003, to March 26, 2005.

A.3.2 Organic Carbon

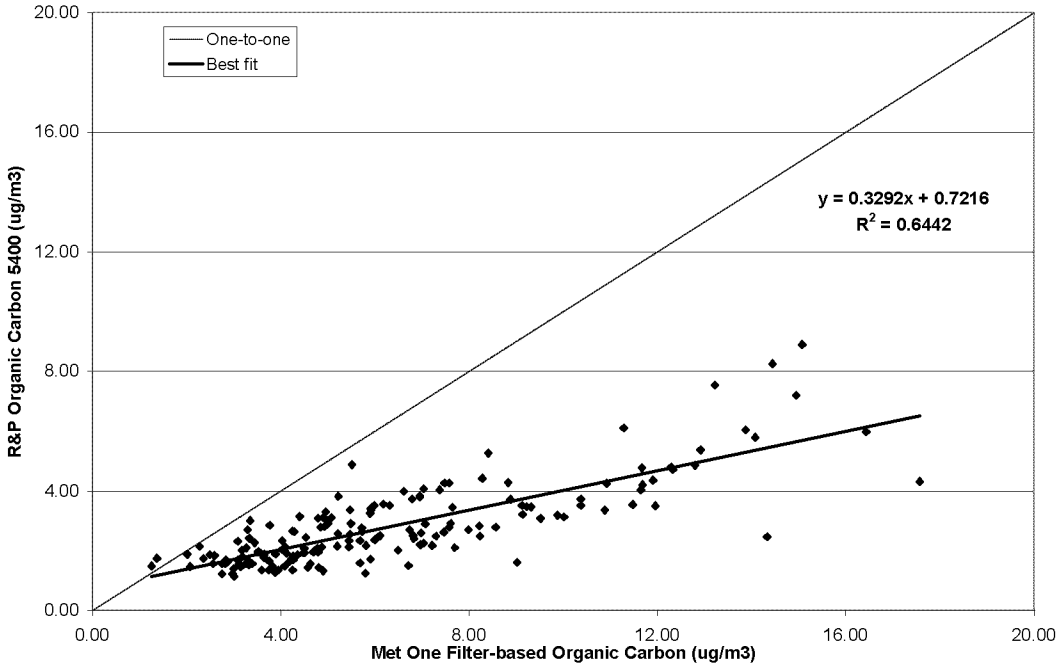

Figure A-11. Twenty-four-hour average R&P 5400 $PM_{2.5}$ organic carbon versus 24-hr integrated STN filter organic carbon at Phoenix, from December 13, 2002, to May 13, 2005.

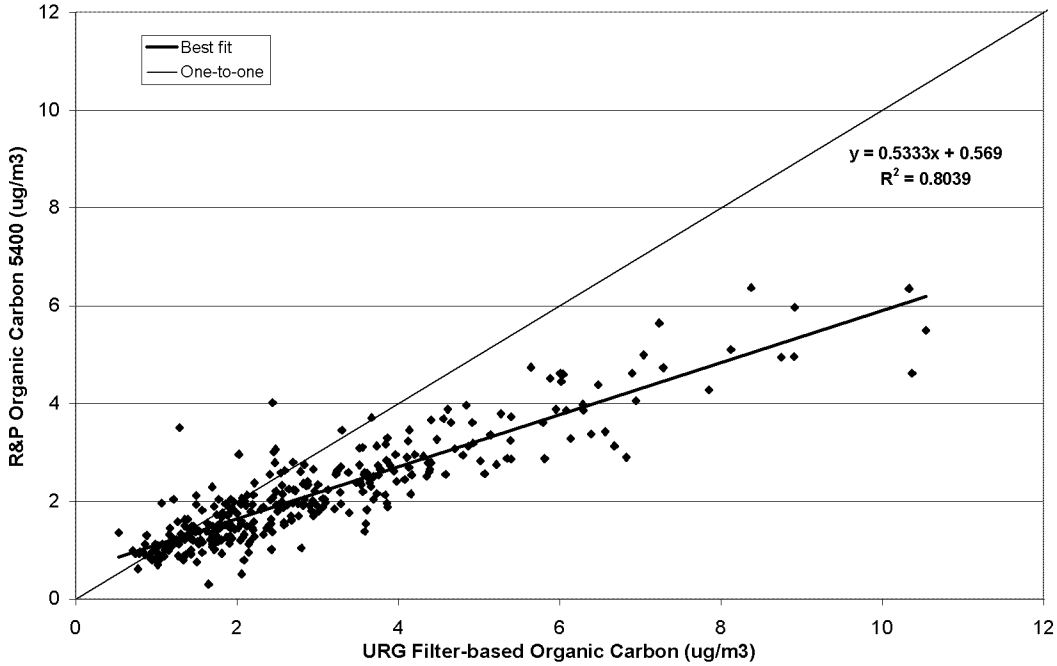

Figure A-12. Twenty-four-hour average R&P 5400 $PM_{2.5}$ organic carbon versus 24-hr integrated STN filter organic carbon at Seattle, from May 2, 2002, to March 29, 2005.

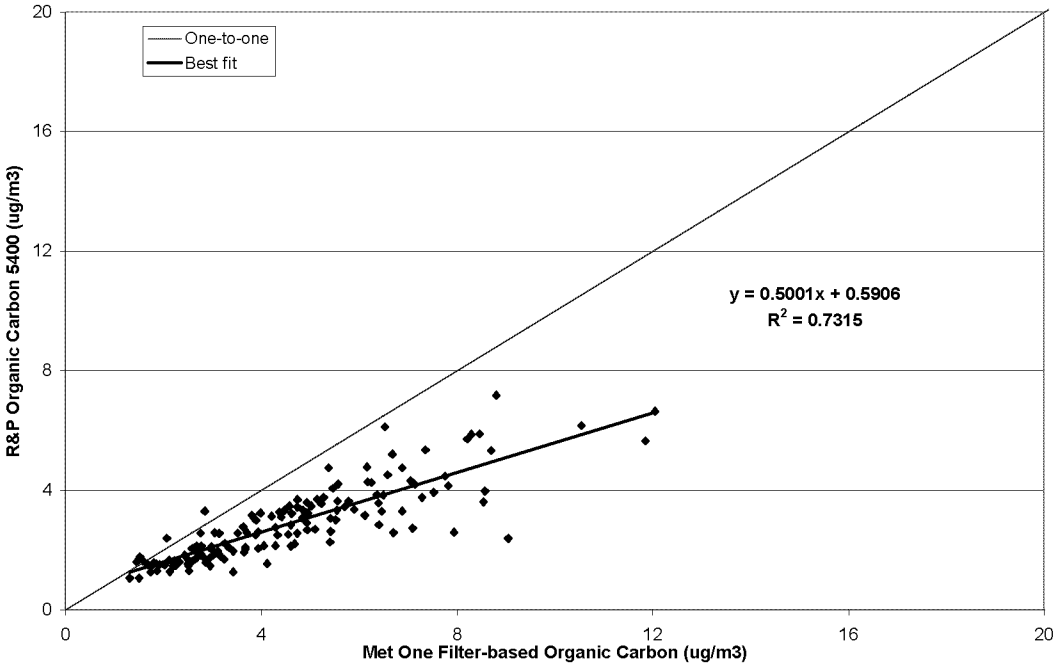

Figure A-13. Twenty-four-hour average R&P 5400 $PM_{2.5}$ organic carbon versus 24-hr integrated STN filter organic carbon at Indianapolis, from June 26, 2002, to April 9, 2004.

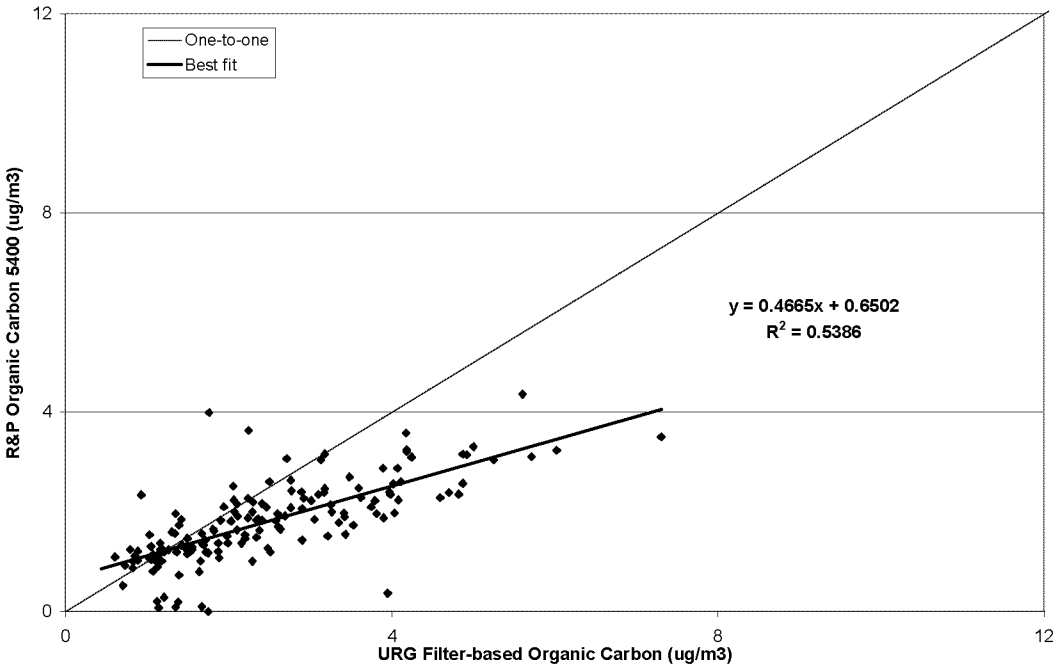

Figure A-14. Twenty-four-hour average R&P 5400 $PM_{2.5}$ organic carbon versus 24-hr integrated STN filter organic carbon at Houston, from January 24, 2003, to March 26, 2005.

A.3.3 Elemental Carbon

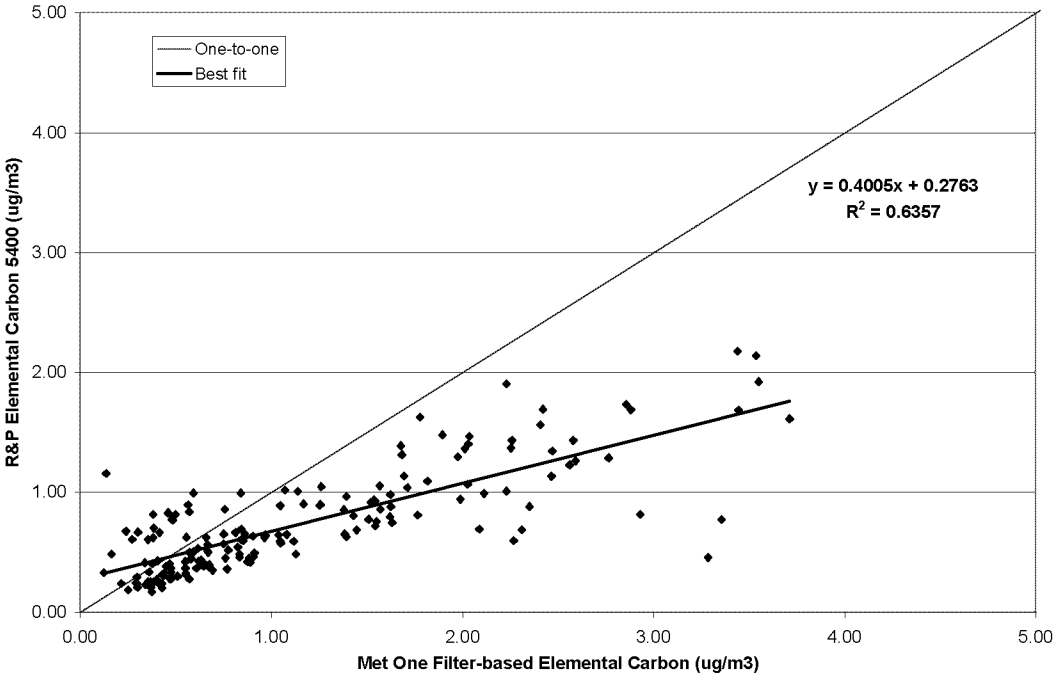

Figure A-15. Twenty-four-hour average R&P 5400 PM2.5 elemental carbon versus 24-hr integrated STN filter elemental carbon at Phoenix, from December 13, 2002, to May 13, 2005.

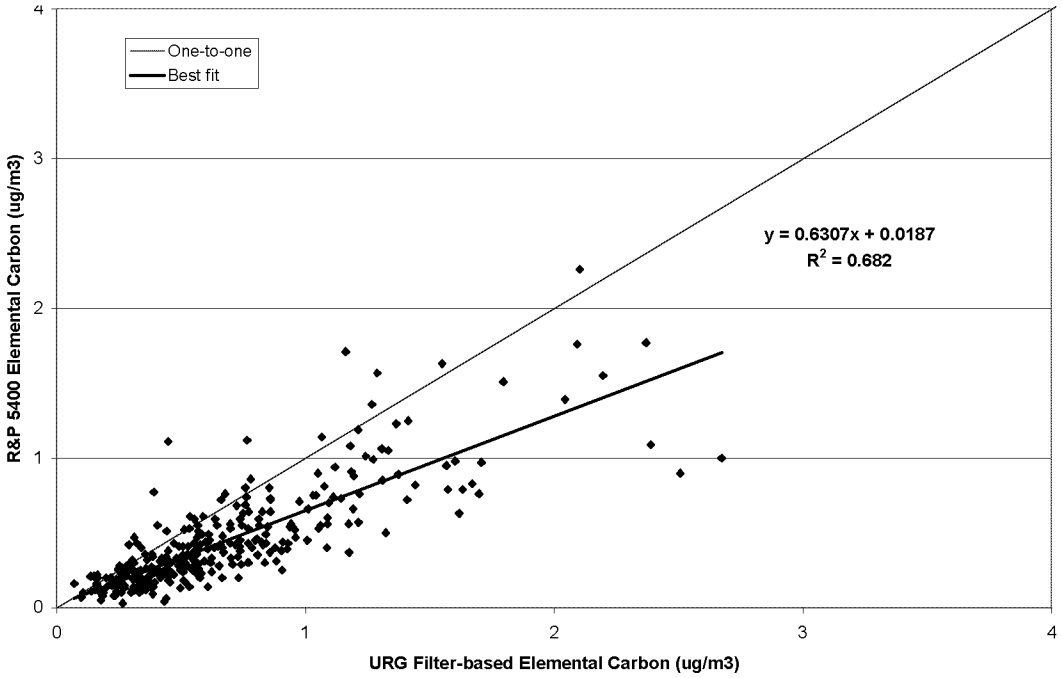

Figure A-16. Twenty-four-hour average R&P 5400 $PM_{2.5}$ elemental carbon versus 24-hr integrated STN filter elemental carbon at Seattle, from May 2, 2002, to March 29, 2005.

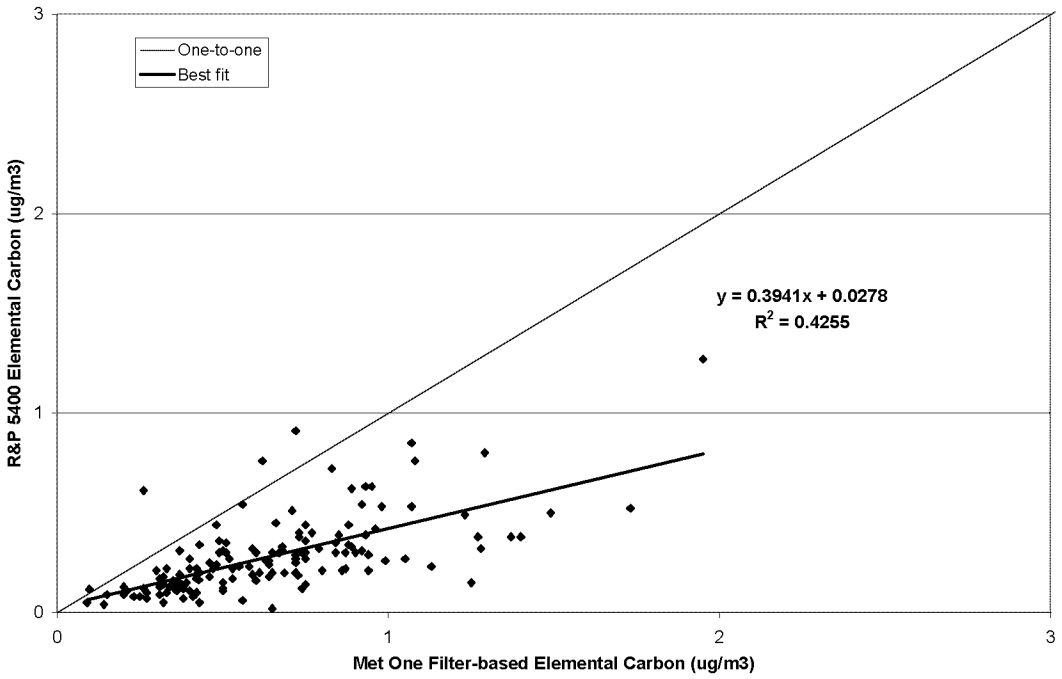

Figure A-17. Twenty-four-hour average R&P 5400 $PM_{2.5}$ elemental carbon versus 24-hr integrated STN filter elemental carbon at Indianapolis, from June 26, 2002, to April 9, 2004.

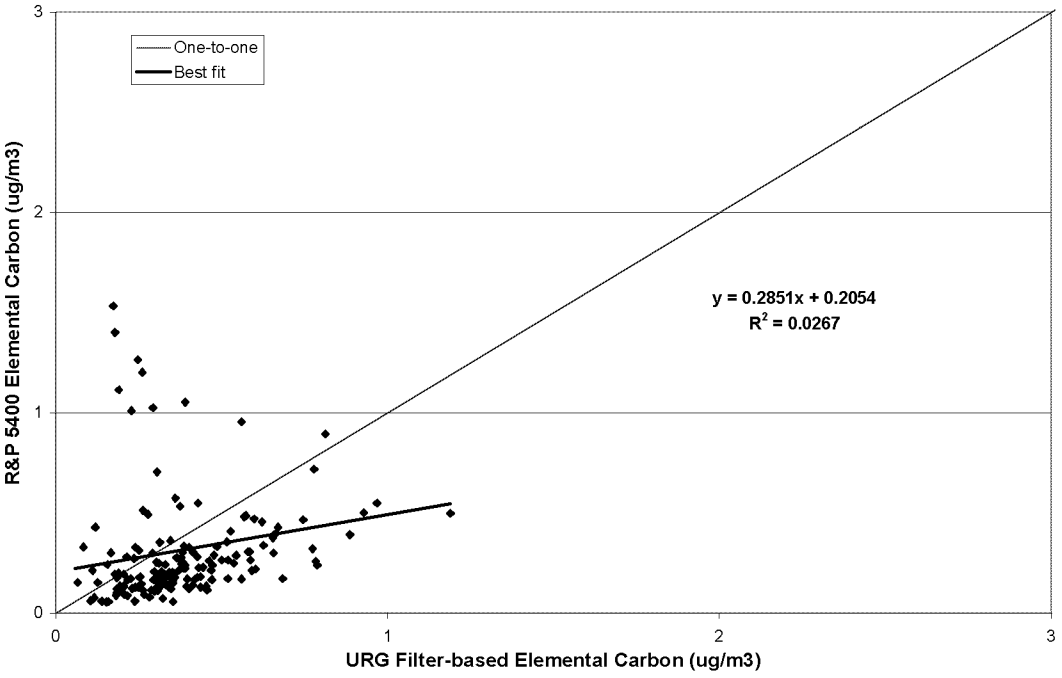

Figure A-18. Twenty-four-hour average R&P 5400 $PM_{2.5}$ elemental carbon versus 24-hr integrated STN filter elemental carbon at Houston, from January 24, 2003, to March 26, 2005.