



## TECHNICAL MEMORANDUM

**TO:** Solomon Ricks / OAQPS  
**FROM:** Eric Boswell / NAREL  
**AUTHOR:** Jewell Smiley / NAREL  
**DATE:** February 23, 2006  
**SUBJECT:** Performance Evaluation of R&P 8400N, 8400S, and Sunset Carbon Air Monitors

### Introduction

EPA has completed another round of performance testing for the R&P 8400N [nitrate], the R&P 8400S [sulfate], and the Sunset [carbon] semi-continuous monitors. The R&P units are designed to capture PM<sub>2.5</sub> from the ambient air and provide measurements of nitrate and sulfate every ten minutes. The Sunset carbon units are also designed to capture PM<sub>2.5</sub> from the ambient air and provide measurements of organic carbon (OC) and elemental carbon (EC) every hour. As with previous testing, split single-blind aqueous spike solutions were used to evaluate the nitrate and sulfate monitors, and split single-blind filter segments were used to evaluate the carbon monitors. Results were received from field sites located in or near Phoenix, Chicago, Indianapolis, Houston, and Seattle. Seattle was not able to fully participate in this study due to operational problems coupled with moving their instruments to a new location. This is the sixth PE study performed by EPA for the R&P 8400 series monitors over the course of approximately three years and the third PE study for the semi-continuous Sunset instruments over the course of approximately one year.

### Experimental Design

Each site operator received an equivalent set of performance evaluation (PE) samples with detailed instructions for analyzing and reporting all of the samples. Five blind spike solutions covering a wide range of concentrations were analyzed in triplicate by each nitrate and each sulfate instrument.

Each carbon instrument analyzed three different filter samples in duplicate. Each set of filters included a blank filter, a filter spiked with sucrose, and a filter loaded with fine particulate matter (PM<sub>2.5</sub>). Operators for the nitrate and sulfate instruments were instructed to analyze the local blank water and the local calibration standard along with the PE test solutions. This requirement served to help document the instrument performance immediately before the PE solutions were analyzed. Operators for the carbon instruments were instructed to submit raw data files for the PE filters. The raw data files were used at a later time to re-calculate the analytical results and reconstruct thermograms which were inspected to help evaluate instrument performance.

All of the PE samples for this study were prepared at the National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. Five nitrate spike solutions and five sulfate spike solutions were prepared and tested for accuracy at NAREL using a Dionex DX500 Ion Chromatograph (IC). After all of the PE solutions were verified using the IC, portions of each solution were placed into clean labeled screw-cap vials for shipment to the field operators. Each site operator received a set of five nitrate PE solutions labeled N1-10-05 through N5-10-05 and a set of five sulfate PE solutions labeled S1-10-05 through S5-10-05.

The concentration of nitrate and sulfate present in each PE solution is listed in Table 3 and Table 5 respectively, at the end of this report. One of the nitrate spike solutions, N3-10-05, was prepared using a mixture of four nitrate salts, but all of the other solutions were prepared from the same salts and chemicals that are present in the local calibration solutions used at each field site. Four of the five nitrate PE solutions were prepared using potassium nitrate and 18 mega-ohm laboratory water

which was passed through a 0.2- $\mu$ m membrane filter immediately before use. Sulfate PE solutions were prepared by dissolving ammonium sulfate and oxalic acid into the same laboratory water previously described. The oxalic acid was added to each sulfate solution at a rate of 4 mg of carbon (from the oxalic acid) per 3 mg of sulfate (from the ammonium sulfate). The N3-10-05 spike solution was prepared from the following mixture of four salts.

|                 |                   |
|-----------------|-------------------|
| 250 ng/ $\mu$ L | ammonium nitrate  |
| 50 ng/ $\mu$ L  | calcium nitrate   |
| 50 ng/ $\mu$ L  | potassium nitrate |
| 50 ng/ $\mu$ L  | sodium nitrate    |
| <hr/>           |                   |
| 400 ng/ $\mu$ L | Total nitrate     |

A mixture of salts was used for one of the PE solutions to continue investigating the effect of sample matrix upon instrument response.

A new syringe was provided to each site operator with instructions to use the new syringe for all spiking during this study. Normally each instrument is calibrated by injecting different volumes of one [local] spike solution to establish the calibration range. For this study five PE solutions were provided for each instrument to establish a calibration range using only one spike volume. The purpose for using only one spike volume was to keep the amount of water deposited onto the flash strip constant for all spikes. The new syringe was used to deliver one spike volume for all solutions described in this report. The site operator was instructed to perform a manual audit of the pulse analyzer before starting the aqueous spikes. Audit results from the 8400N and the 8400S are presented in Table 2 and Table 4 respectively, at the end of this report.

The Sunset field instruments have been programmed to collect PM<sub>2.5</sub> from the ambient air onto a quartz fiber filter for a period of forty-seven minutes after which time the filter is heated and purged for approximately thirteen minutes to determine the OC and EC present in the sample. The same quartz collection filter can be used repeatedly to collect many samples over several days, but periodically it is replaced by the operator due to non-volatile residues that gradually accumulate. Each PE filter was analyzed at the field site by replacing the collection filter with a PE filter after which time it is heated and purged to determine the OC and EC present on the PE filter.

Several PE filters were prepared at NAREL for this study. All of the samples were prepared by using a quartz fiber substrate which was purchased from Gelman as circular filters having a 47-mm diameter. A large batch of the new filters was cleaned by heating to 500 EC inside a muffled furnace for at least two hours after which the filters were placed into sealed Petri dishes and stored at freezer temperature until needed. Two of the filters in the batch were analyzed for EC and OC residues using a Sunset laboratory instrument set up to perform the Thermal Optical Transmittance (TOT) analytical method approved for the Speciation Trends Network (STN method). The STN method performed at NAREL is similar to the field method but includes some fundamental differences in the software and hardware configuration. Results from the two test filters showed less than 0.2  $\mu$ gC/cm<sup>2</sup>, so the batch of filters was declared sufficiently clean for use.

Several of the clean 47-mm filters were assembled into canisters which were used to collect PM<sub>2.5</sub> from the Montgomery air. Collocated Super SASS units were programmed to load the filters with a lengthy 163-hour collection event. The long collection time was necessary to get the amount of captured EC high enough for the study. After the collection event was completed, the loaded filters were recovered from the canisters and placed individually into labeled Petri slides and stored at freezer temperature until needed. To gain confidence in the quality of filter replication, a small punched segment was removed from each of the loaded filters and analyzed using the STN method.

Good precision was observed for the measured EC and OC with relative standard deviations at 11% and 2.5% respectively.

This study was designed to submit small circular punches of the quartz filter to the field sites so that each test sample could be installed into the instrument with minimum effort from the operator. Each circular punch must have a 16-mm diameter to fit properly into the field instrument. A circular punch device was used to cut 16-mm circles from the larger 47-mm quartz filters. A large number of the blank 16-mm quartz circles were required for this study. Some of them were analyzed directly as a test sample. Some of them were spiked with an aqueous solution of sucrose. The sucrose spikes were allowed to air dry for about thirty minutes before they were packaged for shipment. Therefore it was not possible for the field operator to visually see a difference between the blank test samples and the test samples spiked with sucrose. Each field site was supplied with four Petri slides as described in Table 1.

**Table 1. Components of the Sample Kit Submitted To Each Field Site**

| Petri Slide Count   | Petri Label  | Description of the Petri Slide Contents                              |
|---|--------------|--|
| First   | C1-10-05     | Test sample replicates (four blank quartz circles)                   |
| Second  | C2-10-05     | Test sample replicates (four circles spiked with sucrose)            |
| Third   | C3-10-05     | Test sample replicates (four circles loaded with PM <sub>2.5</sub> ) |
| Fourth  | Blank quartz | twelve designated blank quartz circles **                            |
| <b>** each test sample must be mounted into the instrument with a designated blank circle</b> |              |  |

This study required the operator to temporarily interrupt the automated analysis of ambient air at his site, remove the collection filter from his instrument, and then use his instrument to analyze the test samples listed in Table 1. Table 1 shows each site receiving twelve test samples and twelve designated blank circles. A designated blank circle was available for each test sample provided to the site. The operator was instructed to mount a designated blank circle into the instrument along with each test sample. This procedure was necessary to maintain normal behavior of the transmitted laser signal. The laser normally shines through the collection filter. The collection filter, which was temporarily removed from the instrument, is actually two filters mounted together for extra strength. Since each PE sample will be a replacement for the collection filter, the PE sample should be doubly thick as well.

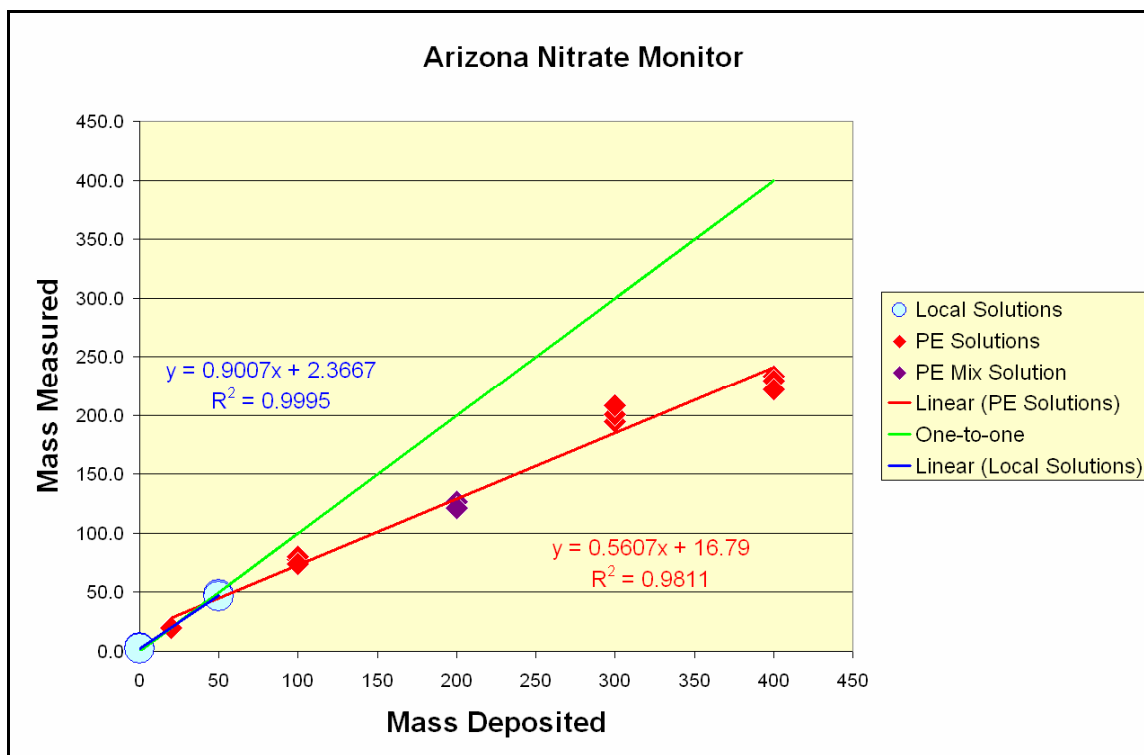
### **Analysis of the Blind Aqueous Nitrate Spike Solutions**

Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, 0.5 µL. The analysis began with the local blank water followed by analysis of the local 100 ng/µL nitrate standard. The study continued by running the five blind solutions identified simply as N1-10-05 through N5-10-05. The results reported from the sites are included in Table 3 at the end of this report along with the previously undisclosed concentration of each PE solution. An extra column of “Re-calculated Results” has also been added to Table 3. Results from each site were re-calculated from a calibration curve based upon the four potassium nitrate PE solutions analyzed at that site. By re-calculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis. This is our way of normalizing the data to hopefully, achieve better agreement from all the sites.

Results from a single site are presented as a scatter plot in Figure 1 through Figure 4. The mass

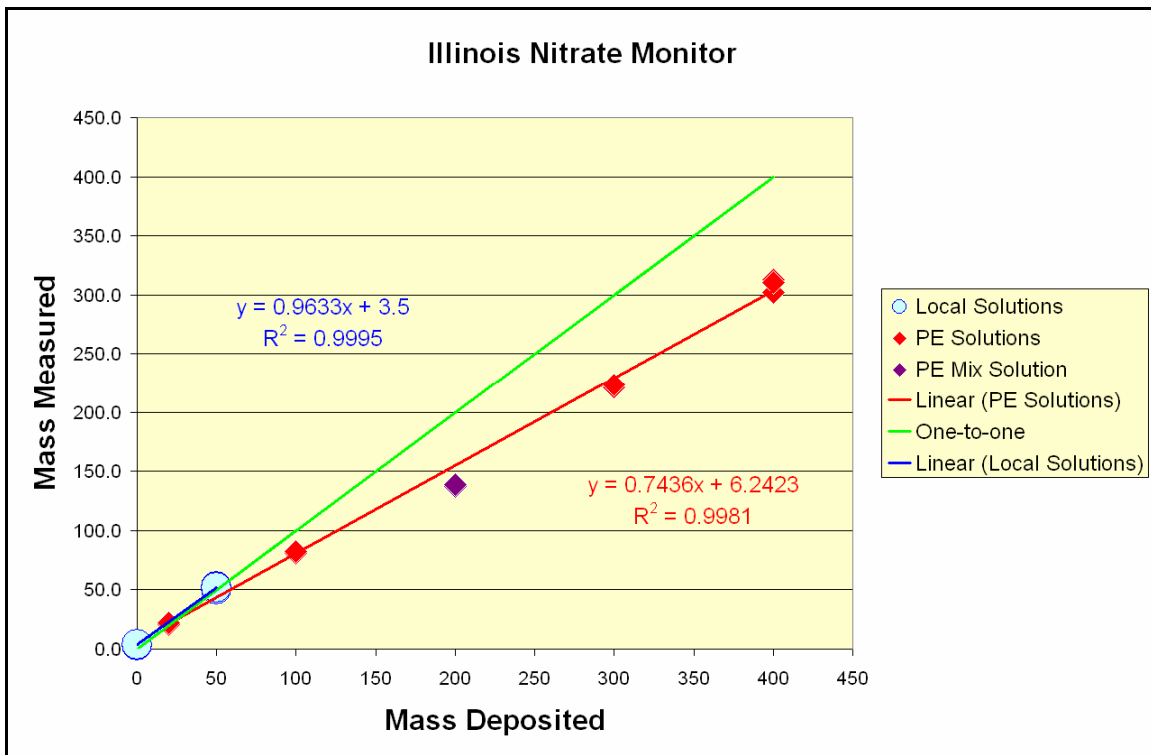
measured versus the mass deposited is plotted for each spike. Results from the potassium nitrate PE solutions are colored red in the plots, and results from the local blank water and local 100 ng/μL solution are presented in blue. Results from the “PE Mix Solution” (sample N3-10-05) are colored violet in the plots. Each plot also shows a green “One-to-One” line which represents perfect agreement between the mass measured and the mass deposited. These figures do not show a dramatic difference in instrument response for the “PE Mix Solution” that was observed in the last study.

**Figure 1**



The “PE Mix Solution” supplied for our last study was not exactly the same solution used for this study. The previous “PE Mix Solution” contained an equal mass of nitrate and sulfate which made the previous spike solution about twice as salty. Results from the previous study showed a dramatically reduced instrument response for the “PE Mix Solution”.

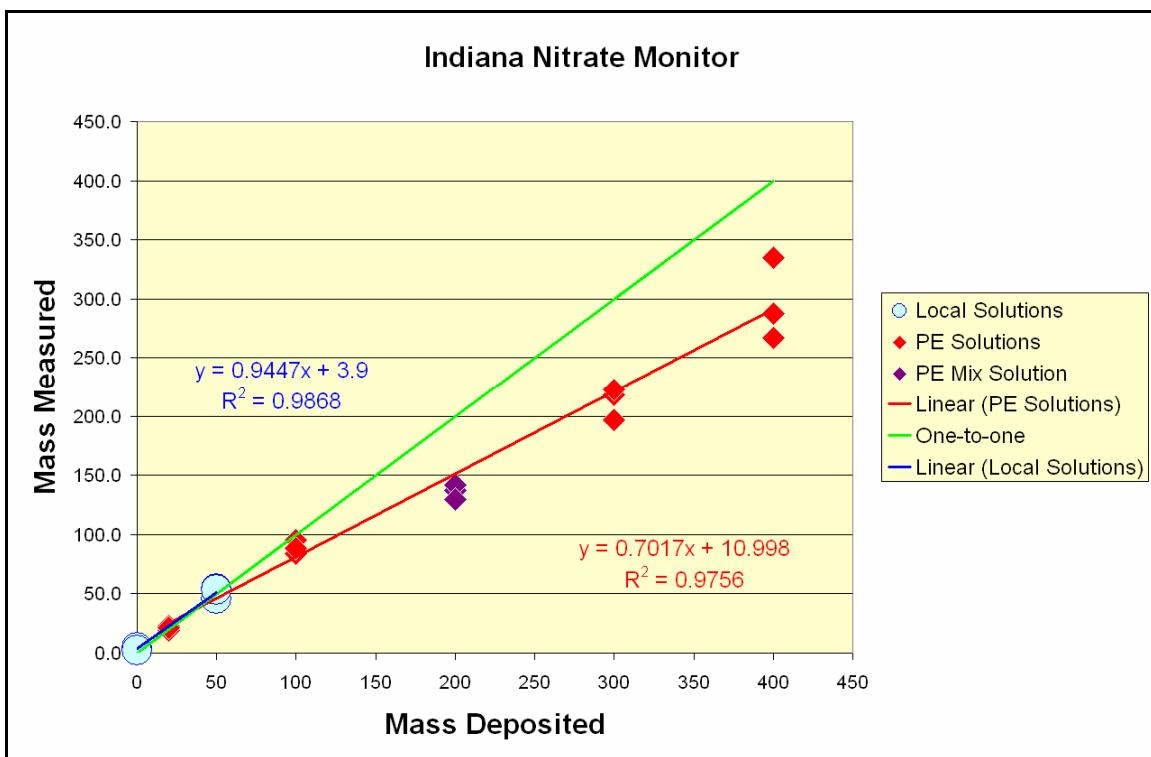
Reasonably good precision was observed for the nitrate spikes shown in Figure 1. A linear regression was performed using the results from the local solutions and also using the results from the four PE solutions shown in red. The regression equations in Figure 1 show a significantly larger slope for the local solutions (0.9007) than for the PE solutions (0.5607). This may indicate that the local calibration standard is more concentrated than the nominal 100 ng/μL. We have seen evidence in previous studies that the local nitrate calibration standard at most of the field sites is too concentrated.

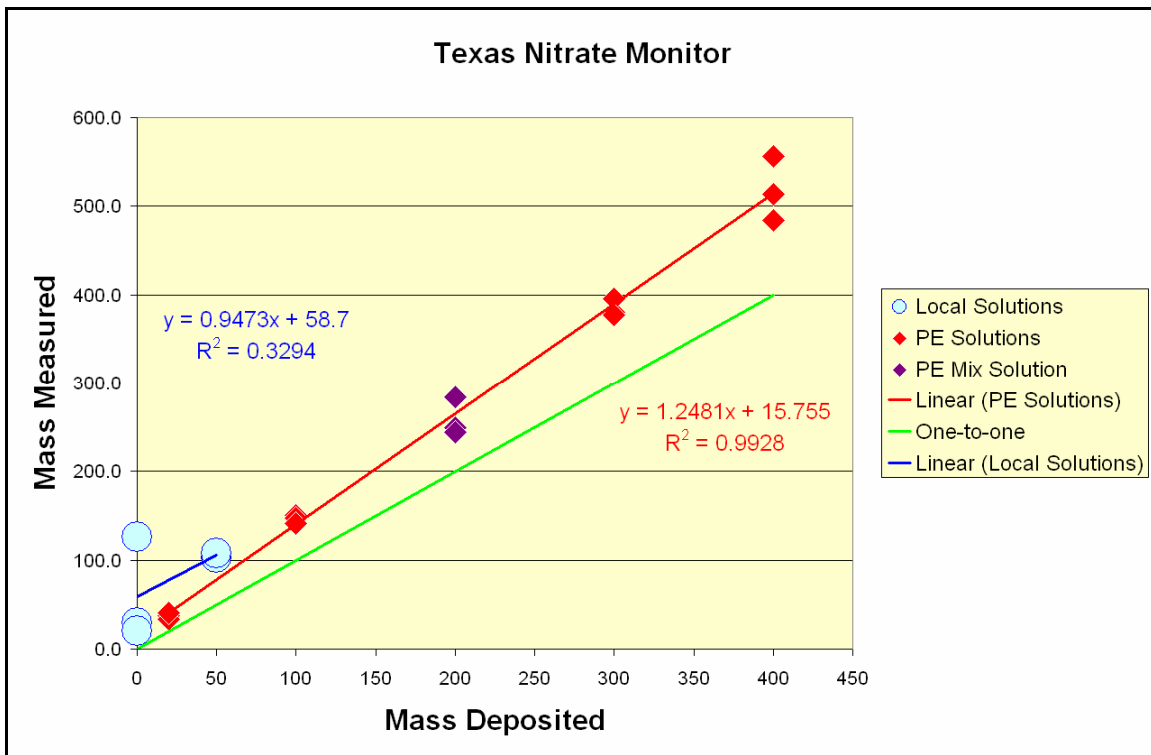


**Figure 2**

Excellent precision was observed for the nitrate spikes shown in Figure 2, and good precision was observed for the spikes shown in Figure 3.

**Figure 3**

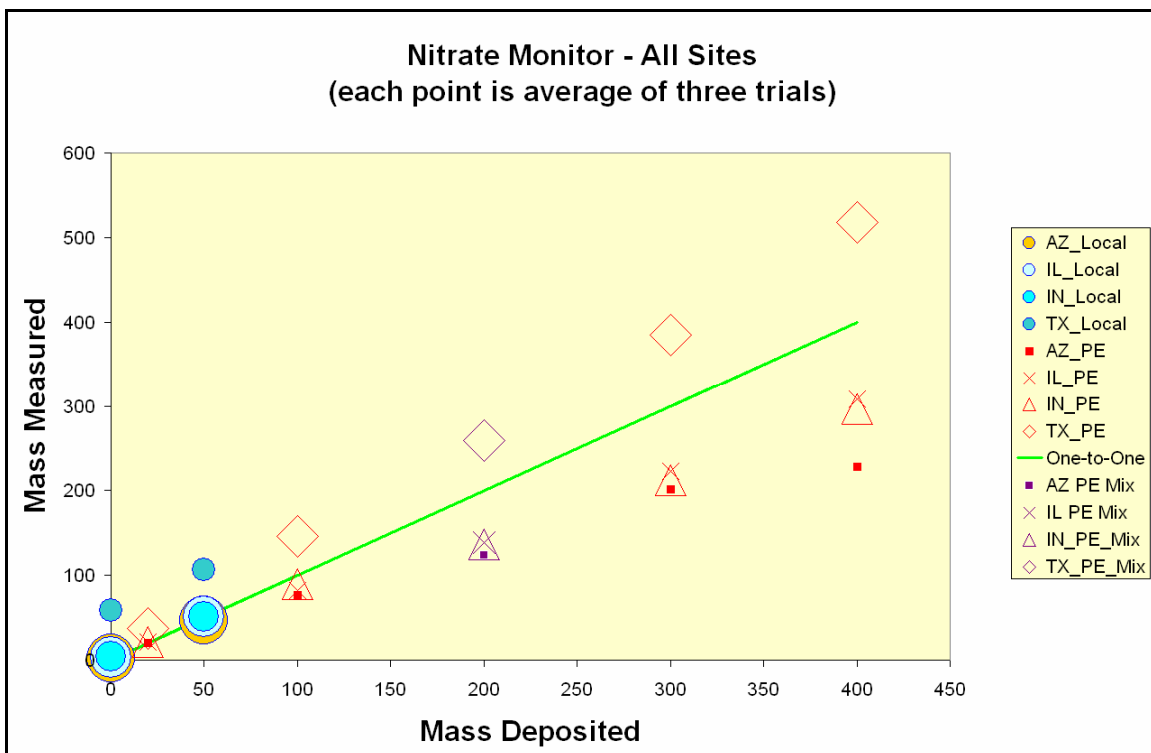




**Figure 4**

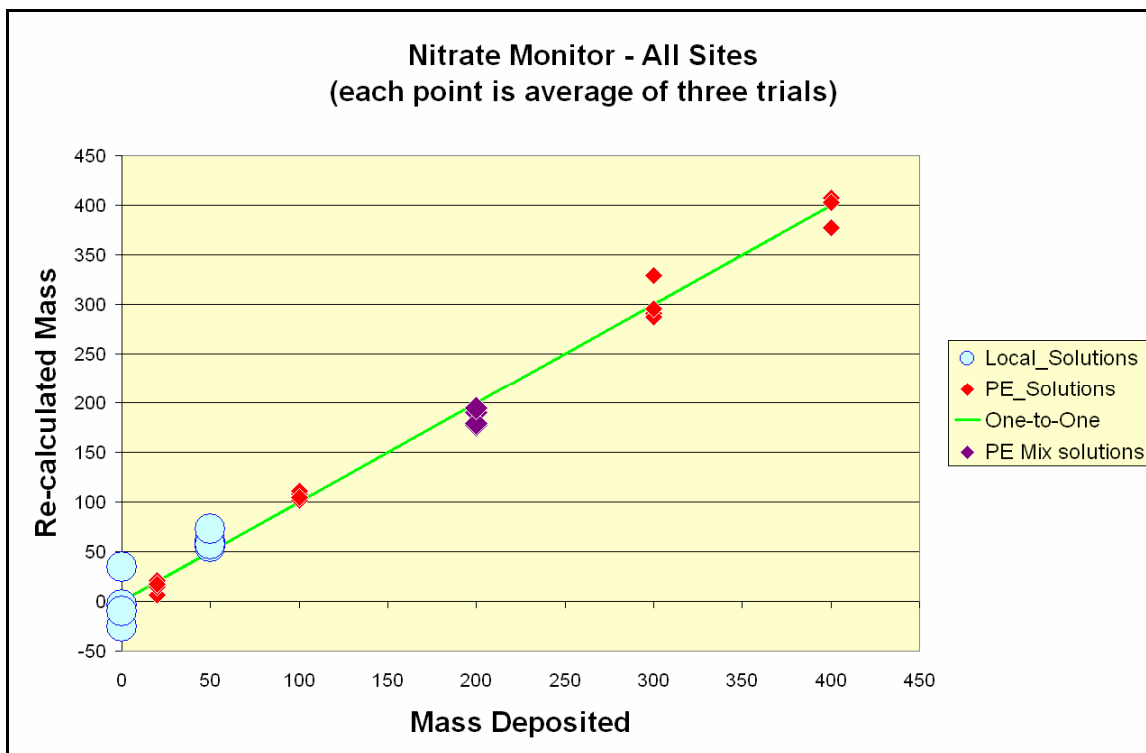
The results shown in Figure 4 are unusual for two reasons. One result from the triple analysis of the local blank water was higher than the calibration standard. Furthermore, the results for all of the samples, both local solutions and all of the PE solutions, are higher than the true values. Results from all of the sites are presented together in Figure 5. To simplify the plot, each point represents

**Figure 5**



an average result from three separate spikes of the same aqueous solution. Figure 6 shows re-calculated mass from all of the sites. A linear calibration curve based upon analysis of the four PE solutions themselves was generated for each instrument, and new results were calculated. Based upon the new results from the calibration curves, all sites report about the same value for each PE solution. Those results from all of the aqueous solutions that do not lie on the One-to-One line indicate less than perfect precision.

**Figure 6**



### Analysis of the Blind Aqueous Sulfate Spike Solutions

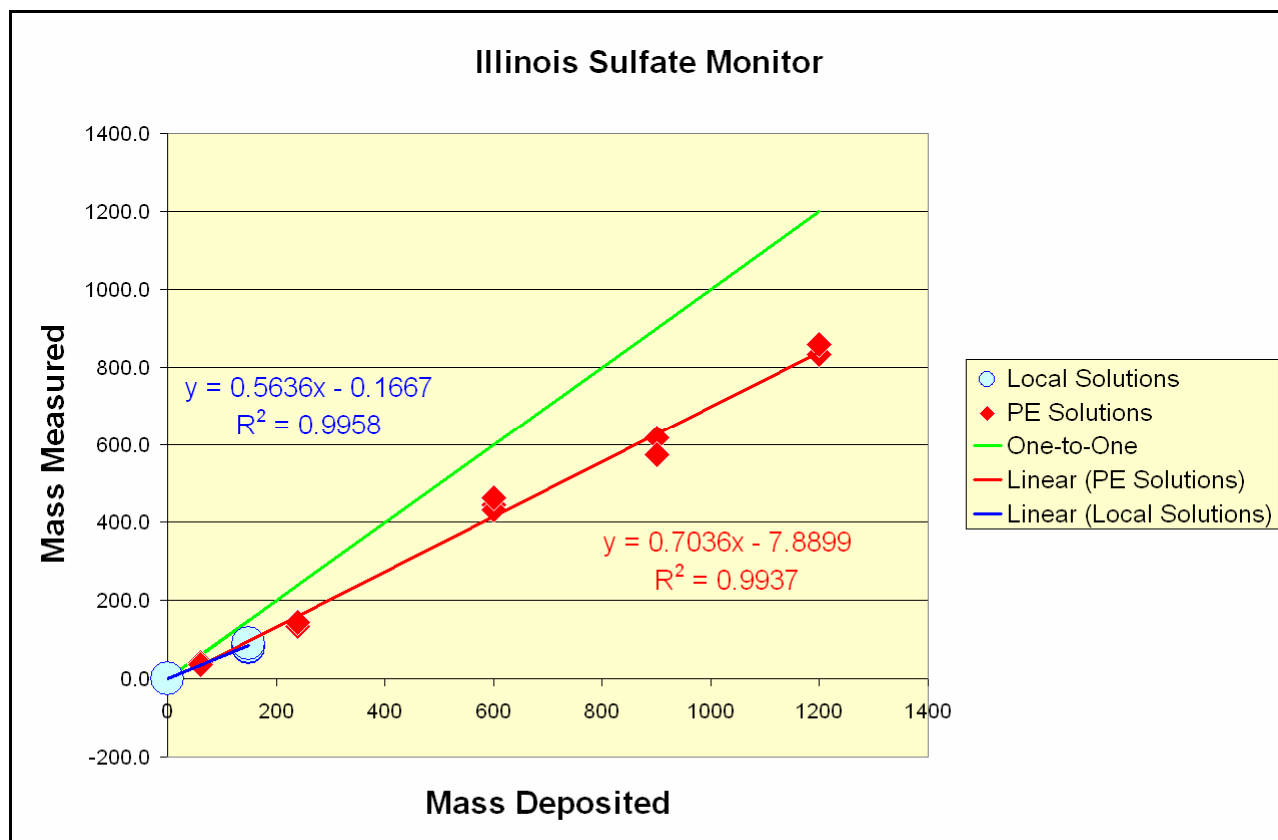
Results were received from three R&P 8400S monitors for this study. One unit was located at the Chicago site and two units were collocated in Houston. Arizona's sulfate monitor was relocated to Houston's Deer Park, Texas site several months ago, and it is identified as Texas Sulfate Monitor#2 in this report. The sulfate and the nitrate instruments at Seattle did not participate in this study for reasons explained earlier in this report.

Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, 0.5  $\mu\text{L}$ . The analysis began with the local blank water followed by analysis of the local 300 ng/ $\mu\text{L}$  sulfate standard. The study continued by running the five blind solutions identified simply as S1-10-05 through S5-10-05. The results reported from the sites are included in Table 5 at the end of this report along with the previously undisclosed concentration of each PE solution. An extra column of "Re-calculated Results" has also been added to Table 5. Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site. By re-calculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis. This is our way of normalizing the data to hopefully, achieve better agreement from all the sites.

Results from a single site are presented as a scatter plot in Figure 7 through Figure 9. The mass

measured versus the mass deposited is plotted for each spike. Results from the PE solutions are colored red in the plots, and results from the local blank water and local 300 ng/μL solution are presented in blue. Each plot also shows a green “One-to-One” line which represents perfect agreement between the mass measured and the mass deposited.

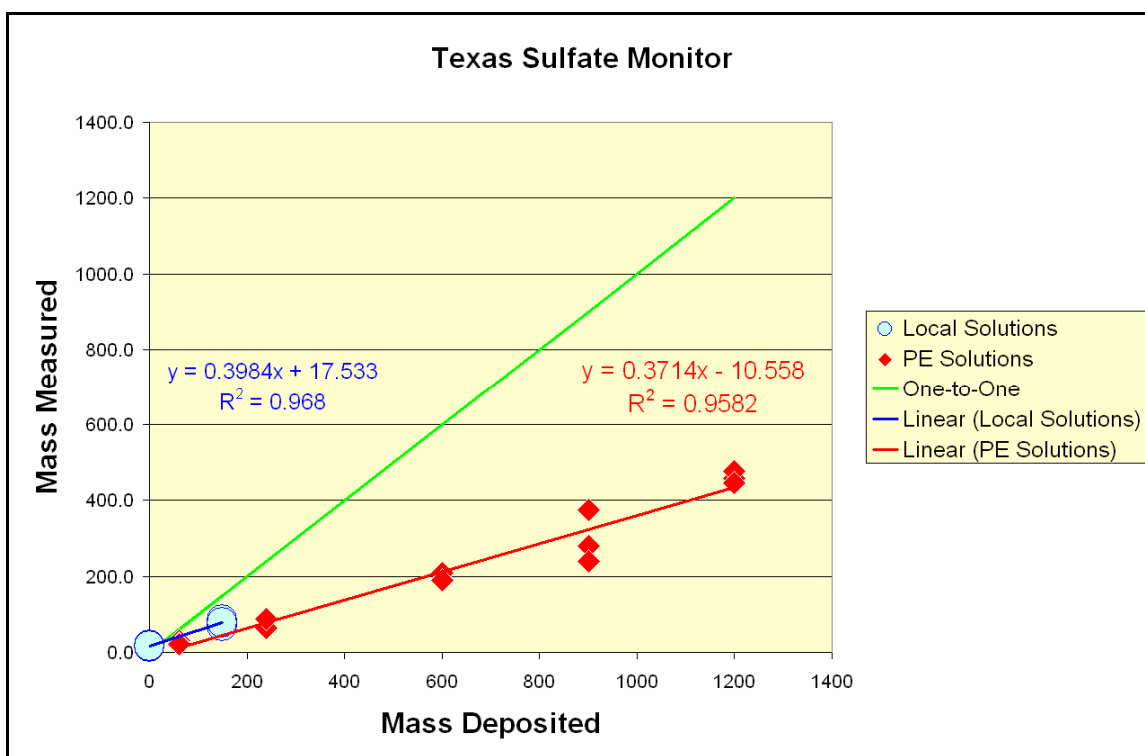
**Figure 7**



Good precision was observed for the sulfate spikes shown in Figure 7. A linear regression was performed using the results from the local solutions and also using the results from the five PE solutions shown in red. Both regressions shown in Figure 7 show similar slopes and intercepts with very good correlation.

The results shown in Figure 8 have a problem. The results in Figure 8 give the appearance of a sudden shift in the zero (or possibly the span) after the local solutions were analyzed but before the PE solutions were analyzed. Since the operator did not know the concentration of sulfate in the PE samples, he was unaware of the decline in instrument response after the local solutions were analyzed.

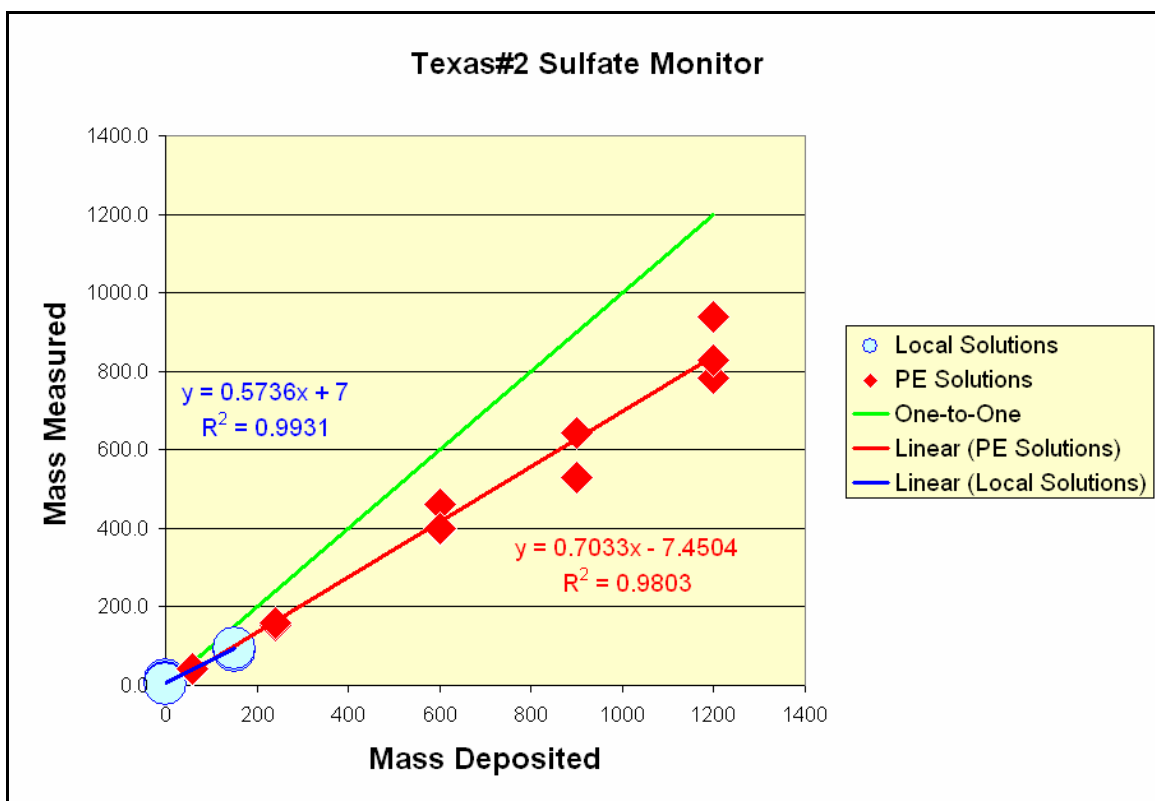


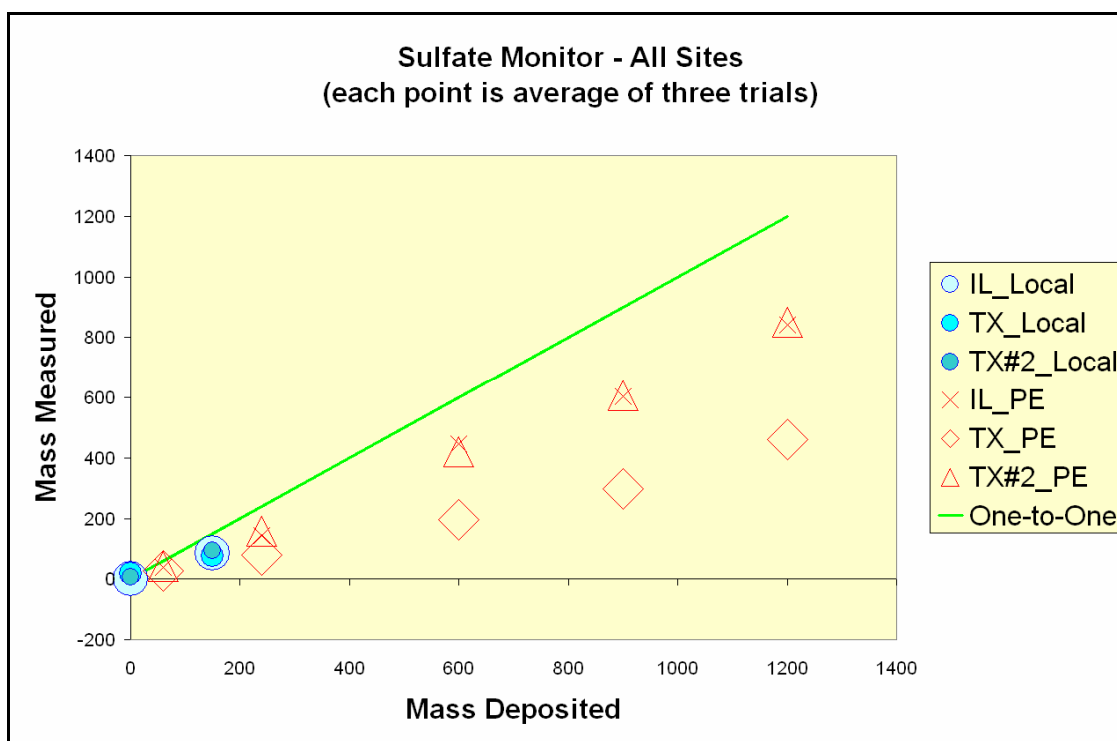


**Figure 8**

Reasonably good precision was observed for the sulfate spikes shown in Figure 9.

**Figure 9**

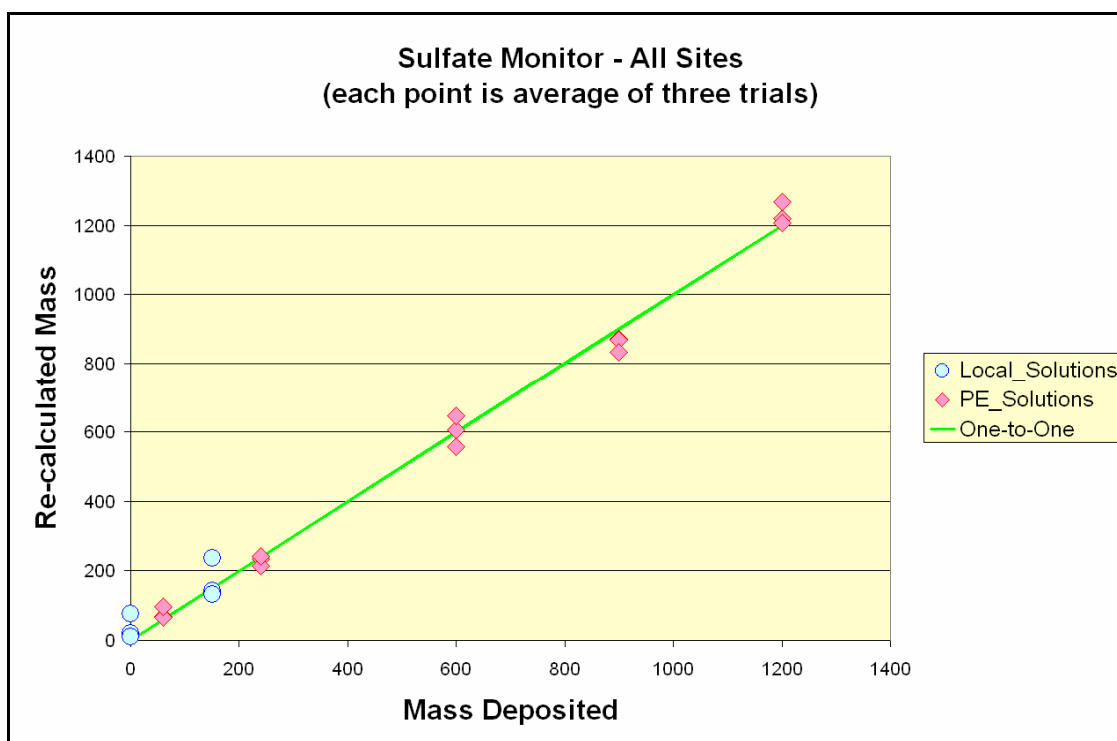




**Figure 10**

Results from all three instruments are shown in Figure 10. Figure 11 shows re-calculated mass from all of the sites. A linear calibration curve based upon analysis of the five PE solutions themselves was generated for each instrument, and new results were calculated. Results in Figure 11 that do not lie on the One-to-One line indicate less than perfect precision. The two points most noticeably above the One-to-One line are local solutions shown previously in Figure 8.

**Figure 11**



## Analysis of the Blind Quartz Filters for Organic Carbon and Elemental Carbon

Sunset carbon results were received from Phoenix, Chicago, and Seattle. Detailed instructions for analyzing the PE samples were provided to the site operators. As stated earlier, the normal automated analysis of ambient air was halted, and the collection filter was removed from the instrument. This study was designed to replace the collection filter with one of the test samples, and then run the instrument through the analysis cycle. There was concern that results from the blank test samples might be high. High blank values can be caused by shipping and handling, but the greatest concern was for opening the instrument's oven every time a new test sample was installed. Because of this concern, the sucrose spike level was relatively high, and the PM<sub>2.5</sub> test sample was loaded with a relatively high level of OC.

Figure 12 shows the total carbon (TC) results for the sucrose spikes and the PM<sub>2.5</sub> test samples presented as a bar graph. TC is simply the sum of the EC and the OC for this study. The results are expressed as micrograms of carbon released from the test sample. Results determined at NAREL are shown along with the results reported from the three field sites. It is important to understand that the results reported for NAREL were determined using the STN analytical method since NAREL does not have a field instrument. Figure 12 also includes the sucrose spike level as well as the uncertainty of measurements performed at NAREL. The results from Chicago and Seattle look very good, but there seems to be a slightly high bias in the results from Arizona. Good duplicate precision was observed for all of the sites.

Figure 12

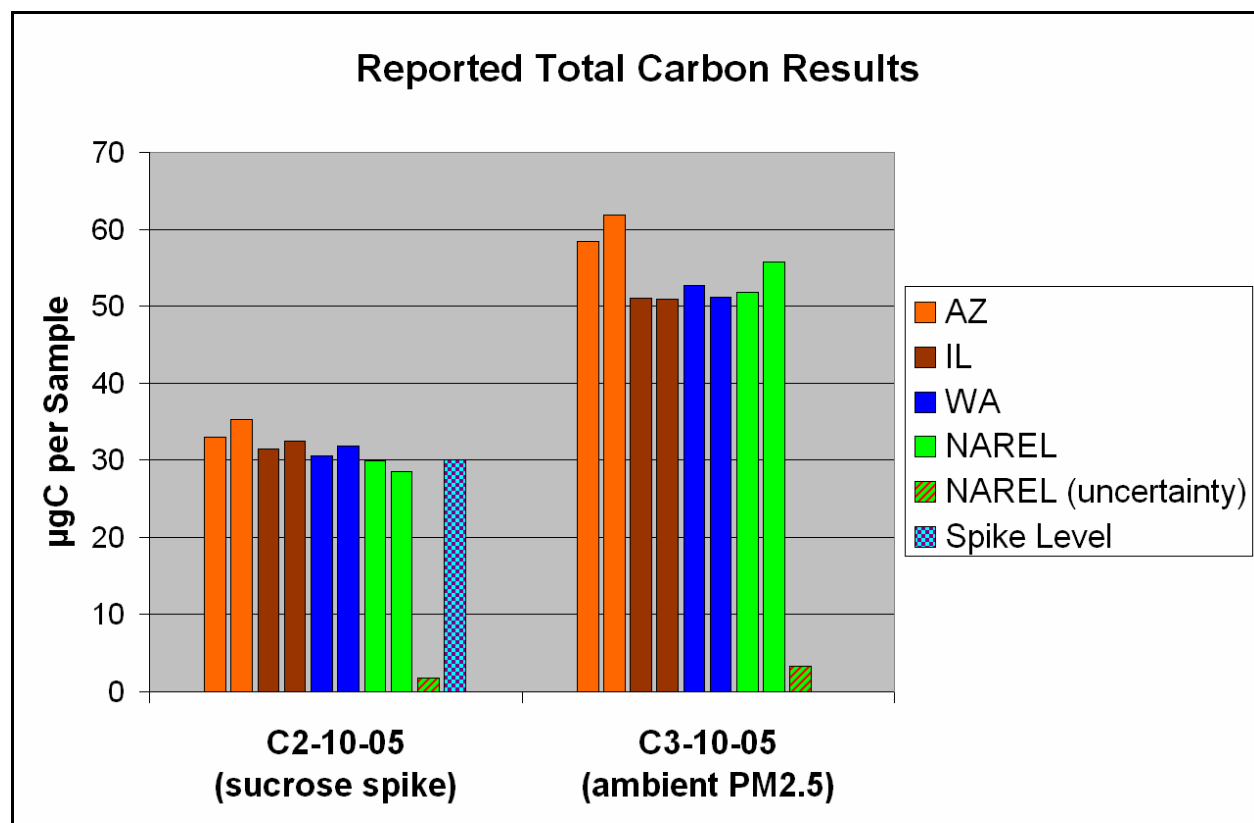
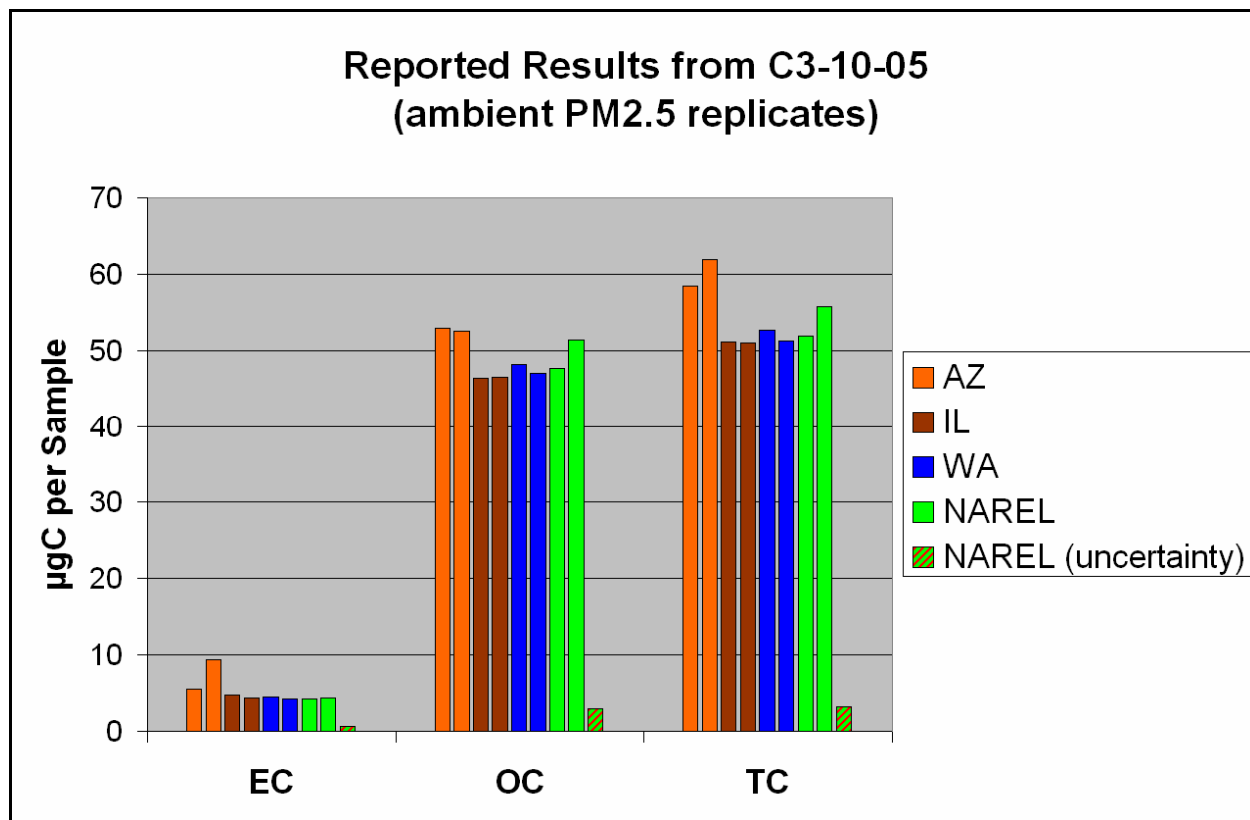


Figure 13 includes the EC and OC values along with the TC for the ambient PM<sub>2.5</sub> test sample. The sucrose spike sample is not presented in Figure 13 because all sites reported essentially zero EC for the sucrose test sample. That is good because sucrose does not contain EC, and therefore the OC should be equal to the TC.

**Figure 13**



All of the results reported from the sites and determined at NAREL are available in Table 6 at the end of this report. Results from the blank test circles were not presented in Figure 12 nor in Figure 13, but the blank results are included in Table 6.

The raw data files along with the calculated result files were submitted to NAREL so that they could be examined for anomalies. After examining these files, it was noted that the Phoenix site is using a slightly different version of software to perform the calculations. Results from all three sites were re-calculated at NAREL using a recent version of the calculation software (RTCalc407.exe) provided by Sunset. The re-calculated results are presented along with the original results in Figure 14 and Figure 15. The re-calculated results from Phoenix show very small difference from the original results reported. All of the re-calculated values including those presented in Figure 14 and Figure 15 are shown in Table 7 at the end of this report.

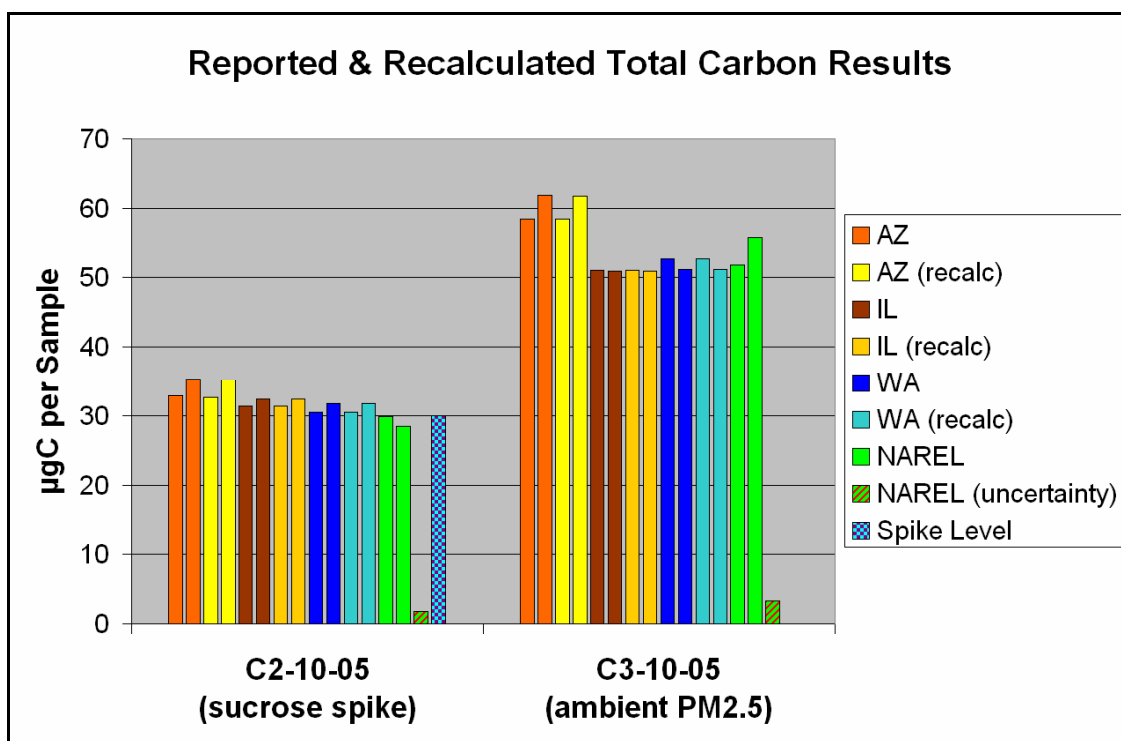
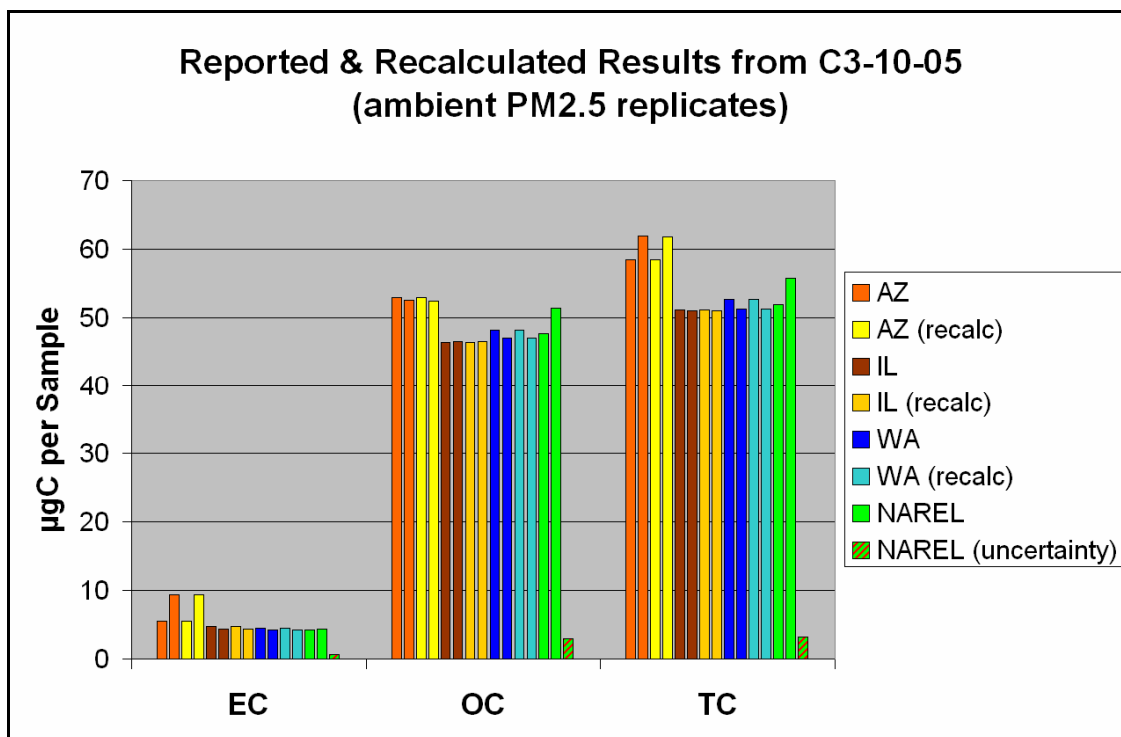


Figure 14

Figure 15



## Conclusions

This PE study included the R&P 8400 series nitrate and sulfate analyzers as well as the Sunset carbon analyzer. These monitors are designed to operate unattended at remote field sites for many hours as they collect PM<sub>2.5</sub> from the ambient air and provide measurement data for nitrate, sulfate, OC/EC. This study was not designed to evaluate the overall performance of the monitors since the overall performance includes both sample collection and sample analysis. This study was designed, however, to evaluate the accuracy and precision of the sample analysis. This study, similar to previous studies, used single-blind spike solutions to evaluate the R&P units, and the Sunset units were able to analyze blind quartz filter segments prepared at NAREL. In all cases the PE results reported from the field were compared to an expected value.

As in previous studies, both the R&P nitrate and sulfate analyzers continued to show reasonably good precision and linear response over a wide the range of concentration. Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site. By re-calculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis. The normalized data indicate that all sites report about the same value for each PE solution, and good accuracy can be achieved over a wide calibration range for aqueous spikes.

One of the nitrate test solutions contained four different nitrate salts. The salt mixture was included in this study to continue learning about the effect of sample matrix on instrument response. The results presented in Figure 1 through Figure 6 do not show the depressed instrument response which was observed in the previous study. The only difference between this study and the previous study was to remove the 400 ng/μL of sulfate (from ammonium sulfate) that was present in the previous salt mixture. This cut the salinity of the solution by approximately half. By changing the composition of the solution in this manner, the 0.5-μL spike performed by the operator may have been less difficult to evaporate before it was thermally desorbed. Of course, there are many other explanations that may be valid.

Previous studies revealed that all of the sites were not using the exact same version of the Sunset software. That discovery was made by re-calculating raw data submitted to NAREL by the site operators. Since the initial discovery, new software has been installed at two of the three sites. For this study, the original results from Chicago and Seattle match the re-calculated values exactly, and the original results from Phoenix were only slightly different from re-calculated values. The Sunset carbon analyzer continues to demonstrate good accuracy and precision for the PE samples analyzed during this study.

**Table 2. Evaluation of the 8400N Pulse Analyzer**

| Site  | Audit Date | Audit Time | *** Span Gas Conc. (ppb) | Steady State Check (ppb) | Flow Balance Check (ppb) | Line Purge (ppb) | NOx Pulse Read (ppb*s) | Age of Flash Strip (days) |
|---|------------|------------|--------------------------|--------------------------|--------------------------|------------------|------------------------|---------------------------|
| Arizona   | 12-Jan-06  | 4:42 PM    | 4500                     | 4495.5                   | 3899.6                   | -0.9             | 2747.4                 | 2                         |
| Illinois  | 13-Dec-05  | 8:00 AM    | 4830                     | 4840.7                   | 4254.7                   | 0.6              | 2915.4                 | 8                         |
| Indiana   | 08-Nov-05  | 12:20 PM   | 5100                     | 4909.7                   | 4303.8                   | 0.8              | 3142.5                 | 7                         |
| Texas   | 29-Dec-05  | 10:45 AM   | 5593                     | 5163.7                   | 4339.3                   | 1.0              | 3170.6                 | 8                         |
| Washington  | -----      | -----      | -----                    | -----                    | -----                    | -----            | -----                  | -----                     |
| *** Span gas concentration as labeled on the bottle (should be approximately 5000 ppb). |            |            |                          |                          |                          |                  |                        |                           |

**Table 3. Aqueous Nitrate Standards**

| Site    | Sample ID          | Volume Deposited (μL) | Mass Deposited (ng) | Baseline (ppb*s) | Corrected Pulse (ppb*s) | Measured Mass (ng) | Analyzer Flow (L/min) | Re-calculated Mass*** (ng) |
|---------|--------------------|-----------------------|---------------------|------------------|-------------------------|--------------------|-----------------------|----------------------------|
| Arizona | Local blank water  | 0.5                   | 0                   | 14.2             | 58.1                    | 2.1                | 0.84                  | -24.0                      |
| Arizona | Local blank water  | 0.5                   | 0                   | 13.9             | 75                      | 2.7                | 0.84                  | -23.0                      |
| Arizona | Local blank water  | 0.5                   | 0                   | 8.3              | 63.5                    | 2.3                | 0.84                  | -23.7                      |
| Arizona | Local 100ng/μL std | 0.5                   | 50                  | 15.5             | 1348.3                  | 47.9               | 0.84                  | 57.6                       |
| Arizona | Local 100ng/μL std | 0.5                   | 50                  | 10               | 1346.8                  | 47.8               | 0.84                  | 57.4                       |
| Arizona | Local 100ng/μL std | 0.5                   | 50                  | -1.9             | 1310.5                  | 46.5               | 0.84                  | 55.1                       |
| Arizona | N1-10-05           | 0.5                   | 20                  | 22.5             | 562.1                   | 20                 | 0.84                  | 7.9                        |
| Arizona | N1-10-05           | 0.5                   | 20                  | 15               | 584.7                   | 20.8               | 0.84                  | 9.3                        |
| Arizona | N1-10-05           | 0.5                   | 20                  | 17.9             | 569.4                   | 20.2               | 0.84                  | 8.2                        |
| Arizona | N2-10-05           | 0.5                   | 100                 | 19.8             | 2195                    | 78                 | 0.84                  | 111.3                      |
| Arizona | N2-10-05           | 0.5                   | 100                 | 8                | 2245.9                  | 79.8               | 0.84                  | 114.5                      |
| Arizona | N2-10-05           | 0.5                   | 100                 | 22.6             | 2076.6                  | 73.8               | 0.84                  | 103.8                      |

**Table 3. Aqueous Nitrate Standards**

| Site     | Sample ID          | Volume Deposited (μL) | Mass Deposited (ng) | Baseline (ppb*s) | Corrected Pulse (ppb*s) | Measured Mass (ng) | Analyzer Flow (L/min) | Re-calculated Mass*** (ng) |
|----------|--------------------|-----------------------|---------------------|------------------|-------------------------|--------------------|-----------------------|----------------------------|
| Arizona  | N3-10-05           | 0.5                   | 200                 | 13.4             | 3411.7                  | 121.2              | 0.84                  | 188.3                      |
| Arizona  | N3-10-05           | 0.5                   | 200                 | 17.2             | 3573.7                  | 126.9              | 0.84                  | 198.5                      |
| Arizona  | N3-10-05           | 0.5                   | 200                 | 24.4             | 3415.1                  | 121.3              | 0.84                  | 188.5                      |
| Arizona  | N4-10-05           | 0.5                   | 300                 | 15.3             | 5485.3                  | 194.8              | 0.84                  | 319.5                      |
| Arizona  | N4-10-05           | 0.5                   | 300                 | 24.9             | 5647.1                  | 200.6              | 0.84                  | 329.9                      |
| Arizona  | N4-10-05           | 0.5                   | 300                 | 14.3             | 5853.2                  | 207.9              | 0.84                  | 342.9                      |
| Arizona  | N5-10-05           | 0.5                   | 400                 | 12.3             | 6569                    | 233.3              | 0.84                  | 388.2                      |
| Arizona  | N5-10-05           | 0.5                   | 400                 | 10               | 6471.6                  | 229.9              | 0.84                  | 382.1                      |
| Arizona  | N5-10-05           | 0.5                   | 400                 | 9                | 6238.3                  | 221.6              | 0.84                  | 367.3                      |
| Illinois | Local blank water  | 0.5                   | 0                   | 11               | 97.7                    | 3.5                | 0.86                  | 1.0                        |
| Illinois | Local blank water  | 0.5                   | 0                   | 11               | 91.8                    | 3.3                | 0.86                  | 0.7                        |
| Illinois | Local blank water  | 0.5                   | 0                   | 9.3              | 101.7                   | 3.7                | 0.86                  | 1.2                        |
| Illinois | Local 100ng/μL std | 0.5                   | 50                  | 10.5             | 1403.4                  | 50.7               | 0.86                  | 64.4                       |
| Illinois | Local 100ng/μL std | 0.5                   | 50                  | 8.3              | 1451.3                  | 52.4               | 0.86                  | 66.7                       |
| Illinois | Local 100ng/μL std | 0.5                   | 50                  | 11.1             | 1436.5                  | 51.9               | 0.86                  | 66.0                       |
| Illinois | N1-10-05           | 0.5                   | 20                  | 12.8             | 627.5                   | 22.7               | 0.86                  | 26.8                       |
| Illinois | N1-10-05           | 0.5                   | 20                  | 9.4              | 573.6                   | 20.7               | 0.86                  | 24.1                       |
| Illinois | N1-10-05           | 0.5                   | 20                  | 8.7              | 609.5                   | 22                 | 0.86                  | 25.8                       |
| Illinois | N2-10-05           | 0.5                   | 100                 | 6                | 2228.6                  | 80.5               | 0.86                  | 104.4                      |
| Illinois | N2-10-05           | 0.5                   | 100                 | 5.8              | 2306                    | 83.3               | 0.86                  | 108.2                      |
| Illinois | N2-10-05           | 0.5                   | 100                 | 11.4             | 2274.3                  | 82.2               | 0.86                  | 106.7                      |
| Illinois | N3-10-05           | 0.5                   | 200                 | 12.3             | 3850.4                  | 139.1              | 0.86                  | 183.1                      |
| Illinois | N3-10-05           | 0.5                   | 200                 | 11               | 3793.7                  | 137.1              | 0.86                  | 180.5                      |
| Illinois | N3-10-05           | 0.5                   | 200                 | 9                | 3842.8                  | 138.9              | 0.86                  | 182.9                      |
| Illinois | N4-10-05           | 0.5                   | 300                 | 9.3              | 6157.8                  | 222.5              | 0.86                  | 295.2                      |
| Illinois | N4-10-05           | 0.5                   | 300                 | 6                | 6126.7                  | 221.4              | 0.86                  | 293.7                      |
| Illinois | N4-10-05           | 0.5                   | 300                 | 12.2             | 6190.1                  | 223.7              | 0.86                  | 296.8                      |



**Table 3. Aqueous Nitrate Standards**

| Site     | Sample ID          | Volume Deposited (μL) | Mass Deposited (ng) | Baseline (ppb*s) | Corrected Pulse (ppb*s) | Measured Mass (ng) | Analyzer Flow (L/min) | Re-calculated Mass*** (ng) |
|----------|--------------------|-----------------------|---------------------|------------------|-------------------------|--------------------|-----------------------|----------------------------|
| Illinois | N5-10-05           | 0.5                   | 400                 | 9                | 8662                    | 313                | 0.86                  | 416.8                      |
| Illinois | N5-10-05           | 0.5                   | 400                 | 8.9              | 8355.5                  | 302                | 0.86                  | 402.0                      |
| Illinois | N5-10-05           | 0.5                   | 400                 | 11.4             | 8583.2                  | 310.2              | 0.86                  | 413.0                      |
| Indiana  | Local blank water  | 0.5                   | 0                   | -629.8           | 128.8                   | 4.5                | 0.83                  | -4.8                       |
| Indiana  | Local blank water  | 0.5                   | 0                   | -677             | 135.2                   | 4.8                | 0.83                  | -4.4                       |
| Indiana  | Local blank water  | 0.5                   | 0                   | -681.3           | 67.7                    | 2.4                | 0.83                  | -7.8                       |
| Indiana  | Local 100ng/μL std | 0.5                   | 50                  | -697.4           | 1302.5                  | 45.9               | 0.83                  | 54.1                       |
| Indiana  | Local 100ng/μL std | 0.5                   | 50                  | -651.6           | 1537.9                  | 54.2               | 0.83                  | 66.0                       |
| Indiana  | Local 100ng/μL std | 0.5                   | 50                  | -676.1           | 1513                    | 53.3               | 0.83                  | 64.7                       |
| Indiana  | N1-10-05           | 0.5                   | 20                  | -691.8           | 539.4                   | 19                 | 0.83                  | 15.8                       |
| Indiana  | N1-10-05           | 0.5                   | 20                  | -745.6           | 657.3                   | 23.2               | 0.83                  | 21.8                       |
| Indiana  | N1-10-05           | 0.5                   | 20                  | -699.1           | 598.9                   | 21.1               | 0.83                  | 18.8                       |
| Indiana  | N2-10-05           | 0.5                   | 100                 | -733.6           | 2705.6                  | 95.3               | 0.83                  | 124.5                      |
| Indiana  | N2-10-05           | 0.5                   | 100                 | -653             | 2375                    | 83.7               | 0.83                  | 108.0                      |
| Indiana  | N2-10-05           | 0.5                   | 100                 | -680.3           | 2509.6                  | 88.4               | 0.83                  | 114.7                      |
| Indiana  | N3-10-05           | 0.5                   | 200                 | -675.5           | 3904.5                  | 137.6              | 0.83                  | 184.7                      |
| Indiana  | N3-10-05           | 0.5                   | 200                 | -678.3           | 4014.9                  | 141.5              | 0.83                  | 190.3                      |
| Indiana  | N3-10-05           | 0.5                   | 200                 | -700.9           | 3689.9                  | 130                | 0.83                  | 173.9                      |
| Indiana  | N4-10-05           | 0.5                   | 300                 | -681.2           | 5592.4                  | 197.1              | 0.83                  | 269.4                      |
| Indiana  | N4-10-05           | 0.5                   | 300                 | -681.5           | 6186.2                  | 218                | 0.83                  | 299.2                      |
| Indiana  | N4-10-05           | 0.5                   | 300                 | -644.6           | 6316                    | 222.6              | 0.83                  | 305.7                      |
| Indiana  | N5-10-05           | 0.5                   | 400                 | -701.4           | 7581.2                  | 267.1              | 0.83                  | 369.1                      |
| Indiana  | N5-10-05           | 0.5                   | 400                 | -683.3           | 9503.4                  | 334.9              | 0.83                  | 465.6                      |
| Indiana  | N5-10-05           | 0.5                   | 400                 | -697.2           | 8168.2                  | 287.8              | 0.83                  | 398.6                      |
| Texas    | Local blank water  | 0.5                   | 0                   | 36.9             | 3262.9                  | 126                | 0.91                  | 89.4                       |
| Texas    | Local blank water  | 0.5                   | 0                   | -1               | 762.9                   | 29.5               | 0.91                  | 12.1                       |
| Texas    | Local blank water  | 0.5                   | 0                   | 55.9             | 533.8                   | 20.6               | 0.91                  | 5.0                        |

**Table 3. Aqueous Nitrate Standards**

| Site  | Sample ID          | Volume Deposited (μL) | Mass Deposited (ng) | Baseline (ppb*s) | Corrected Pulse (ppb*s) | Measured Mass (ng) | Analyzer Flow (L/min) | Re-calculated Mass*** (ng) |
|-------|--------------------|-----------------------|---------------------|------------------|-------------------------|--------------------|-----------------------|----------------------------|
| Texas | Local 100ng/μL std | 0.5                   | 50                  | -5.6             | 2660.2                  | 102.7              | 0.91                  | 70.7                       |
| Texas | Local 100ng/μL std | 0.5                   | 50                  | 4                | 2782.6                  | 107.5              | 0.91                  | 74.6                       |
| Texas | Local 100ng/μL std | 0.5                   | 50                  | 10.4             | 2797                    | 108                | 0.91                  | 75.0                       |
| Texas | N1-10-05           | 0.5                   | 20                  | 24.8             | 978.2                   | 37.8               | 0.91                  | 18.7                       |
| Texas | N1-10-05           | 0.5                   | 20                  | 28.6             | 880                     | 34                 | 0.91                  | 15.7                       |
| Texas | N1-10-05           | 0.5                   | 20                  | 4.6              | 1064.4                  | 41.1               | 0.91                  | 21.4                       |
| Texas | N2-10-05           | 0.5                   | 100                 | -4.2             | 3886                    | 150.1              | 0.91                  | 108.7                      |
| Texas | N2-10-05           | 0.5                   | 100                 | -11              | 3822                    | 147.6              | 0.91                  | 106.7                      |
| Texas | N2-10-05           | 0.5                   | 100                 | -1.2             | 3663.9                  | 141.5              | 0.91                  | 101.8                      |
| Texas | N3-10-05           | 0.5                   | 200                 | 9.8              | 6441.9                  | 248.8              | 0.91                  | 187.7                      |
| Texas | N3-10-05           | 0.5                   | 200                 | 5.6              | 7354                    | 284                | 0.91                  | 215.9                      |
| Texas | N3-10-05           | 0.5                   | 200                 | -9.2             | 6320.8                  | 244.1              | 0.91                  | 184.0                      |
| Texas | N4-10-05           | 0.5                   | 300                 | 55               | 9856.5                  | 380.6              | 0.91                  | 293.3                      |
| Texas | N4-10-05           | 0.5                   | 300                 | 21.6             | 10233.3                 | 395.2              | 0.91                  | 305.0                      |
| Texas | N4-10-05           | 0.5                   | 300                 | -15.6            | 9772.6                  | 377.4              | 0.91                  | 290.8                      |
| Texas | N5-10-05           | 0.5                   | 400                 | 11.6             | 14397.2                 | 556                | 0.91                  | 433.8                      |
| Texas | N5-10-05           | 0.5                   | 400                 | -4               | 13310.6                 | 514                | 0.91                  | 400.2                      |
| Texas | N5-10-05           | 0.5                   | 400                 | -13              | 12534.9                 | 484.1              | 0.91                  | 376.2                      |

\*\*\* Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site.

**Table 4. Evaluation of the 8400S Pulse Analyzer**

| Site  | Audit Date | Audit Time | *** Span Gas Conc. (ppb) | Steady State Check (ppb) | Flow Balance Check (ppb) | Line Purge (ppb) | Age of Flash Strip (days) |
|---|------------|------------|--------------------------|--------------------------|--------------------------|------------------|---------------------------|
| Illinois  | 13-Dec-05  | 8:00 AM    | 700                      | 696.4                    | 599.8                    | -0.1             | 1                         |
| Texas   | 29-Dec-05  | 10:10 AM   | 923                      | 907.4                    | 777.8                    | 7.5              | 8                         |
| Texas#2   | 29-Dec-05  | 10:10 AM   | 923                      | 929.5                    | 828.7                    | 3.6              | 8                         |
| Washington  | -----      | -----      | -----                    | -----                    | -----                    | -----            | -----                     |
| *** Span gas concentration as labeled on the bottle (should be approximately 1000 ppb). |            |            |                          |                          |                          |                  |                           |

**Table 5. Aqueous Sulfate Standards**

| Site     | Sample ID          | Volume Deposited (μL) | Mass Deposited (ng) | Baseline (ppb*s) | Corrected Pulse (ppb*s) | Measured Mass (ng) | Analyzer μLow (L/min) | Re-calculated Mass*** |
|----------|--------------------|-----------------------|---------------------|------------------|-------------------------|--------------------|-----------------------|-----------------------|
| Illinois | Local blank water  | 0.5                   | 0                   | 21.2             | 1.1                     | 0.1                | 1.07                  | 11.4                  |
| Illinois | Local blank water  | 0.5                   | 0                   | 13.2             | -5.5                    | -0.4               | 1.07                  | 10.6                  |
| Illinois | Local blank water  | 0.5                   | 0                   | 17               | -3.4                    | -0.2               | 1.07                  | 10.9                  |
| Illinois | Local 300ng/μL std | 0.5                   | 150                 | 11.6             | 1143.5                  | 80.3               | 1.07                  | 125.3                 |
| Illinois | Local 300ng/μL std | 0.5                   | 150                 | 1.2              | 1185                    | 83.2               | 1.07                  | 129.5                 |
| Illinois | Local 300ng/μL std | 0.5                   | 150                 | -3.8             | 1276                    | 89.6               | 1.07                  | 138.6                 |
| Illinois | S1-10-05           | 0.5                   | 60                  | 21.4             | 569.8                   | 40                 | 1.07                  | 68.1                  |
| Illinois | S1-10-05           | 0.5                   | 60                  | -16.1            | 594                     | 41.7               | 1.07                  | 70.5                  |
| Illinois | S1-10-05           | 0.5                   | 60                  | -26              | 514.2                   | 36.1               | 1.07                  | 62.5                  |
| Illinois | S2-10-05           | 0.5                   | 240                 | 4                | 1917.7                  | 134.7              | 1.07                  | 202.6                 |
| Illinois | S2-10-05           | 0.5                   | 240                 | -6.4             | 2082.7                  | 146.3              | 1.07                  | 219.1                 |
| Illinois | S2-10-05           | 0.5                   | 240                 | -33.4            | 2061.3                  | 144.8              | 1.07                  | 217.0                 |

**Table 5. Aqueous Sulfate Standards**

| Site     | Sample ID          | Volume Deposited (μL) | Mass Deposited (ng) | Baseline (ppb*s) | Corrected Pulse (ppb*s) | Measured Mass (ng) | Analyzer μLow (L/min) | Re-calculated Mass*** |
|----------|--------------------|-----------------------|---------------------|------------------|-------------------------|--------------------|-----------------------|-----------------------|
| Illinois | S3-10-05           | 0.5                   | 600                 | -4.2             | 6345.6                  | 445.6              | 1.07                  | 644.5                 |
| Illinois | S3-10-05           | 0.5                   | 600                 | -12.6            | 6163.4                  | 432.8              | 1.07                  | 626.3                 |
| Illinois | S3-10-05           | 0.5                   | 600                 | -6.2             | 6578.7                  | 462                | 1.07                  | 667.8                 |
| Illinois | S4-10-05           | 0.5                   | 900                 | -25              | 8790.1                  | 617.3              | 1.07                  | 888.5                 |
| Illinois | S4-10-05           | 0.5                   | 900                 | -2.7             | 8787.1                  | 617.1              | 1.07                  | 888.2                 |
| Illinois | S4-10-05           | 0.5                   | 900                 | -24.6            | 8164.4                  | 573.3              | 1.07                  | 826.0                 |
| Illinois | S5-10-05           | 0.5                   | 1200                | -21.5            | 11863.6                 | 833.1              | 1.07                  | 1195.2                |
| Illinois | S5-10-05           | 0.5                   | 1200                | -12              | 11854.2                 | 832.5              | 1.07                  | 1194.3                |
| Illinois | S5-10-05           | 0.5                   | 1200                | -4.4             | 12204.8                 | 857.1              | 1.07                  | 1229.3                |
| Texas    | Local blank water  | 0.5                   | 0                   | 204.8            | 169.4                   | 15                 | 1.35                  | 68.8                  |
| Texas    | Local blank water  | 0.5                   | 0                   | 171.2            | 226.1                   | 20                 | 1.35                  | 82.3                  |
| Texas    | Local blank water  | 0.5                   | 0                   | 8                | 199.5                   | 17.6               | 1.35                  | 75.8                  |
| Texas    | Local 300ng/μL std | 0.5                   | 150                 | 97.8             | 768.4                   | 67.9               | 1.35                  | 211.3                 |
| Texas    | Local 300ng/μL std | 0.5                   | 150                 | 15               | 973.2                   | 86                 | 1.35                  | 260.0                 |
| Texas    | Local 300ng/μL std | 0.5                   | 150                 | 46.1             | 882.3                   | 78                 | 1.35                  | 238.5                 |
| Texas    | S1-10-05           | 0.5                   | 60                  | 43.2             | 349                     | 30.8               | 1.35                  | 111.4                 |
| Texas    | S1-10-05           | 0.5                   | 60                  | 75               | 276.4                   | 24.4               | 1.35                  | 94.1                  |
| Texas    | S1-10-05           | 0.5                   | 60                  | 81.6             | 250.9                   | 22.2               | 1.35                  | 88.2                  |
| Texas    | S2-10-05           | 0.5                   | 240                 | 65               | 716.7                   | 63.3               | 1.35                  | 198.9                 |
| Texas    | S2-10-05           | 0.5                   | 240                 | 89.9             | 989.7                   | 87.5               | 1.35                  | 264.0                 |
| Texas    | S2-10-05           | 0.5                   | 240                 | 1                | 984.6                   | 87                 | 1.35                  | 262.7                 |
| Texas    | S3-10-05           | 0.5                   | 600                 | 62.6             | 2182                    | 192.8              | 1.35                  | 547.6                 |
| Texas    | S3-10-05           | 0.5                   | 600                 | 60.8             | 2354.5                  | 208.1              | 1.35                  | 588.8                 |
| Texas    | S3-10-05           | 0.5                   | 600                 | 26.4             | 2143.9                  | 189.5              | 1.35                  | 538.7                 |
| Texas    | S4-10-05           | 0.5                   | 900                 | -36.6            | 3178                    | 280.9              | 1.35                  | 784.8                 |
| Texas    | S4-10-05           | 0.5                   | 900                 | 69.6             | 2722                    | 240.6              | 1.35                  | 676.3                 |

**Table 5. Aqueous Sulfate Standards**

| Site    | Sample ID          | Volume Deposited (μL) | Mass Deposited (ng) | Baseline (ppb*s) | Corrected Pulse (ppb*s) | Measured Mass (ng) | Analyzer μLow (L/min) | Re-calculated Mass*** |
|---------|--------------------|-----------------------|---------------------|------------------|-------------------------|--------------------|-----------------------|-----------------------|
| Texas   | S4-10-05           | 0.5                   | 900                 | -64.8            | 4244.8                  | 375.1              | 1.35                  | 1038.5                |
| Texas   | S5-10-05           | 0.5                   | 1200                | 102.2            | 5175.5                  | 457.4              | 1.35                  | 1260.1                |
| Texas   | S5-10-05           | 0.5                   | 1200                | 13.4             | 5402.5                  | 477.5              | 1.35                  | 1314.2                |
| Texas   | S5-10-05           | 0.5                   | 1200                | 20.2             | 5055.2                  | 446.8              | 1.35                  | 1231.6                |
| Texas#2 | Local blank water  | 0.5                   | 0                   | 66.4             | 128.9                   | 12.6               | 1.5                   | 28.5                  |
| Texas#2 | Local blank water  | 0.5                   | 0                   | 44               | 60.5                    | 5.9                | 1.5                   | 19.0                  |
| Texas#2 | Local blank water  | 0.5                   | 0                   | 45.5             | 25.5                    | 2.5                | 1.5                   | 14.1                  |
| Texas#2 | Local 300ng/μL std | 0.5                   | 150                 | 31.4             | 909.6                   | 89.1               | 1.5                   | 137.3                 |
| Texas#2 | Local 300ng/μL std | 0.5                   | 150                 | 32.4             | 963                     | 94.3               | 1.5                   | 144.7                 |
| Texas#2 | Local 300ng/μL std | 0.5                   | 150                 | 34.4             | 976.9                   | 95.7               | 1.5                   | 146.7                 |
| Texas#2 | S1-10-05           | 0.5                   | 60                  | 51               | 434.2                   | 42.5               | 1.5                   | 71.0                  |
| Texas#2 | S1-10-05           | 0.5                   | 60                  | 41.8             | 398.3                   | 39                 | 1.5                   | 66.1                  |
| Texas#2 | S1-10-05           | 0.5                   | 60                  | 51.2             | 420.2                   | 41.2               | 1.5                   | 69.2                  |
| Texas#2 | S2-10-05           | 0.5                   | 240                 | 30.6             | 1571.2                  | 153.9              | 1.5                   | 229.4                 |
| Texas#2 | S2-10-05           | 0.5                   | 240                 | 41               | 1625.6                  | 159.2              | 1.5                   | 237.0                 |
| Texas#2 | S2-10-05           | 0.5                   | 240                 | 47.1             | 1623.6                  | 159                | 1.5                   | 236.7                 |
| Texas#2 | S3-10-05           | 0.5                   | 600                 | 44               | 4031.8                  | 394.9              | 1.5                   | 572.1                 |
| Texas#2 | S3-10-05           | 0.5                   | 600                 | 28.7             | 4725                    | 462.8              | 1.5                   | 668.7                 |
| Texas#2 | S3-10-05           | 0.5                   | 600                 | 50.6             | 4088.1                  | 400.4              | 1.5                   | 580.0                 |
| Texas#2 | S4-10-05           | 0.5                   | 900                 | 38.9             | 6560.9                  | 642.7              | 1.5                   | 924.5                 |
| Texas#2 | S4-10-05           | 0.5                   | 900                 | 33.4             | 6556.2                  | 642.2              | 1.5                   | 923.8                 |
| Texas#2 | S4-10-05           | 0.5                   | 900                 | 55.2             | 5412.9                  | 530.2              | 1.5                   | 764.5                 |
| Texas#2 | S5-10-05           | 0.5                   | 1200                | 41.2             | 9573.7                  | 937.8              | 1.5                   | 1344.1                |
| Texas#2 | S5-10-05           | 0.5                   | 1200                | 44.2             | 7990.2                  | 782.7              | 1.5                   | 1123.6                |
| Texas#2 | S5-10-05           | 0.5                   | 1200                | 31               | 8463.2                  | 829                | 1.5                   | 1189.4                |

**\*\*\* Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site.**

**Table 6. Reported Results**

| Sample ID | Sample Description   | AZ Results (µg/sample) |       |       | IL Results (µg/sample) |       |       | WA Results (µg/sample) |       |       | NAREL Results – STN Method* (µg/sample) |       |              |
|-----------|----------------------|------------------------|-------|-------|------------------------|-------|-------|------------------------|-------|-------|---|-------|--------------|
|           |                      | EC                     | OC    | TC    | EC                     | OC    | TC    | EC                     | OC    | TC    | EC                                      | OC    | TC           |
| C1        | blank filter         | 0.24                   | 4.90  | 5.14  | 0.00                   | 1.70  | 1.70  | 0.11                   | 1.58  | 1.70  | 0.00                                    | 0.34  | 0.34 ± 0.62  |
| C1 dup    | blank filter         | 0.16                   | 4.53  | 4.69  | 0.00                   | 1.38  | 1.38  | 0.00                   | 1.57  | 1.57  | 0.00                                    | 0.11  | 0.11 ± 0.61  |
| C2        | 30 µgC sucrose spike | 0.07                   | 32.79 | 32.86 | 0.00                   | 31.33 | 31.33 | 0.00                   | 30.50 | 30.50 | 0.00                                    | 29.86 | 29.86 ± 1.79 |
| C2 dup    | 30 µgC sucrose spike | 0.06                   | 35.28 | 35.34 | 0.00                   | 32.40 | 32.39 | 0.06                   | 31.75 | 31.80 | 0.00                                    | 28.52 | 28.52 ± 1.73 |
| C3        | ambient PM2.5        | 5.53                   | 52.93 | 58.46 | 4.71                   | 46.36 | 51.06 | 4.54                   | 48.17 | 52.71 | 4.19                                    | 47.70 | 51.89 ± 3.19 |
| C3 dup    | ambient PM2.5        | 9.39                   | 52.49 | 61.88 | 4.42                   | 46.56 | 50.98 | 4.20                   | 46.99 | 51.19 | 4.37                                    | 51.36 | 55.73 ± 3.39 |

*\*NAREL results were determined using the filter based method that is approved for the Speciation Trends Network.*

**Table 7. Re-calculated Field Results**

| Sample ID | Sample Description   | AZ Results (µg/sample) |       |       | IL Results (µg/sample) |       |       | WA Results (µg/sample) |       |       |
|-----------|----------------------|------------------------|-------|-------|------------------------|-------|-------|------------------------|-------|-------|
|           |                      | EC                     | OC    | TC    | EC                     | OC    | TC    | EC                     | OC    | TC    |
| C1        | blank filter         | 0.25                   | 4.87  | 5.12  | 0.00                   | 1.70  | 1.70  | 0.11                   | 1.58  | 1.70  |
| C1 dup    | blank filter         | 0.14                   | 4.46  | 4.60  | 0.00                   | 1.38  | 1.38  | 0.00                   | 1.57  | 1.57  |
| C2        | 30 µgC sucrose spike | 0.06                   | 32.49 | 32.56 | 0.00                   | 31.33 | 31.33 | 0.00                   | 30.50 | 30.50 |
| C2 dup    | 30 µgC sucrose spike | 0.05                   | 35.27 | 35.32 | 0.00                   | 32.40 | 32.39 | 0.06                   | 31.75 | 31.80 |
| C3        | ambient PM2.5        | 5.49                   | 52.65 | 58.14 | 4.71                   | 46.36 | 51.06 | 4.54                   | 48.17 | 52.71 |
| C3 dup    | ambient PM2.5        | 9.30                   | 52.01 | 61.31 | 4.42                   | 46.56 | 50.98 | 4.20                   | 46.99 | 51.19 |