TECHNICAL MEMORANDUM

TO: Jim Homolya / OAQPS

FROM: Michael S. Clark / NAREL

COPY: Dr. John Griggs / NAREL

DATE: September 5, 2003

SUBJECT: Third Quarterly Performance Evaluation of R&P 8400 Ambient Air Monitors

Executive Summary

A third quarterly Performance Evaluation (PE) study has been completed. Five sites located in different states are currently operating at least one of the 8400 series ambient air monitors manufactured by R&P. The 8400N and the 8400S units are designed to capture $PM_{2.5}$ from the ambient air and provide measurements of nitrate and sulfate respectively, every ten minutes. Aqueous spike solutions have been used again to evaluate performance of these semi-continuous monitors. Five blind spikes covering a wide range of concentrations were analyzed in triplicate by each instrument. In addition to the blind spikes, four additional nitrate solutions were provided to each site. The four extra solutions were carefully prepared using a variety of nitrate salts while maintaining the nitrate concentration at 100 ng/µL to match the local calibration solution. All of the sites were given the same set of test solutions. The operators were instructed to analyze the local blank water and the local calibration standard along with the test solutions.

The blind spike solutions were evaluated by preparing scatter plots for each monitor showing the mass of analyte reported versus the mass of analyte spiked into the instrument. A linear response was evident for most of the monitors. However, poor precision was observed in some of the spike data which makes the shape of the response curve less certain. To further examine the data generated from the blind spike solutions, a linear calibration curve based upon analysis of the 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, and good accuracy can be achieved over a wide calibration range for aqueous spikes. It is worth stating that an aqueous spike is not a captured ambient air deposit. However, the aqueous spike may be the most valuable single method to evaluate instrument performance, and it provides a basis for adjusting the raw data output from the pulse analyzer.

This study has included four extra nitrate solutions delivered to each site. As stated above, the extra solutions were carefully prepared to maintain the nitrate concentration at 100 ng/µL, but each solution was prepared using a different salt: ammonium nitrate, calcium nitrate, potassium nitrate, and sodium nitrate. The site operator was instructed to perform duplicate spikes of the extra nitrate solutions immediately following spikes of the blind PE solutions. All of the site operators agreed to perform these extra spikes to briefly observe the result of changing the salt used for calibration. After all, ambient air samples are not restricted to one form of nitrate. Similar results were produced

at all five sites. Within a reasonable margin of measurement error as indicated by duplicate spikes, all four of the salts produced the same instrument response.

The two previous PE studies have indicated a possible error in the local nitrate solutions. Based upon analysis of the PE solutions at all sites, the local nitrate solutions appeared to be slightly more concentrated than the accepted value of 100 ng/µL. Each site operator has submitted a small portion of the local nitrate solution and the local sulfate solution to NAREL for evaluation using Ion Chromatography (IC). Results of the IC analysis confirms earlier suspicions. The local nitrate solutions submitted from all of the sites are 106% to 111% of the stated 100 ng/µL concentration value, and the local sulfate solutions are 99% to 105% of the stated 300 ng/µL concentration value. The IC determinations are not likely to contain more than a 3% error.

Experimental Design

Blind aqueous spike solutions were prepared at the National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. All PE solutions were prepared from the same salts and chemicals that are present in the local calibration solutions used at each field site. Nitrate PE solutions were prepared using KNO_3 and 18 mega-ohm laboratory water which was passed through a 0.2-µm membrane filter immediately before use. Sulfate PE solutions were prepared by dissolving NH_4SO_4 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 NH_4SO_4). All PE solutions were analyzed using a Dionex DX500 Ion Chromatograph configured for the analysis of anions. All PE solutions were verified to be within 5 % of the nominal concentration of nitrate and sulfate before they were shipped to the site operator. The concentration of nitrate and sulfate present in each PE solution is listed in Table 2 and Table 4 respectively, at the end of this report.

Four extra nitrate solutions were prepared at NAREL for this study. The extra solutions were carefully prepared using different nitrate salts but keeping the nitrate concentration constant at 100 ng/µL. The following four salts were dissolved separately using 18 mega-ohm laboratory water to prepare the four test solutions: NH_4NO_3, $Ca(NO_3)_2 \cdot 4H_2O$, KNO_3, and $NaNO_3$. The actual nitrate concentration in all of the solutions was confirmed by IC analysis before they were shipped to the field sites along with the blind PE solutions.

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, including the extra salt solutions.

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 1 and Table 3 respectively, at the end of this report.

Each of the field sites were supplied with two clean pre-labeled vials with instructions for shipping a small amount of the local nitrate and sulfate calibration solution to NAREL for subsequent IC analysis. Site operators were also asked to complete a form which provided NAREL with historical information regarding the local calibration solutions.

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, 0.8 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 N1-05-03 through N5-05-03. The results reported from the sites are included in Table 2 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 2. 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 1 through Figure 5. 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 100 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.

Good precision was observed for the nitrate spikes shown in Figure 1.

Figure 1

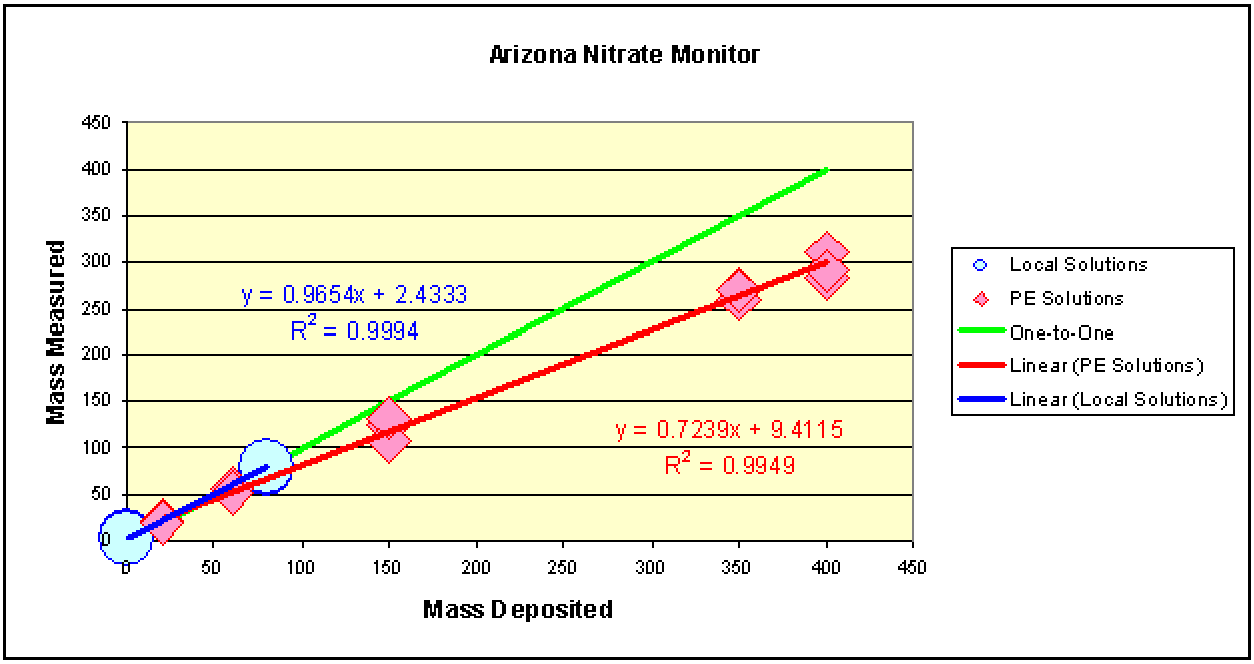
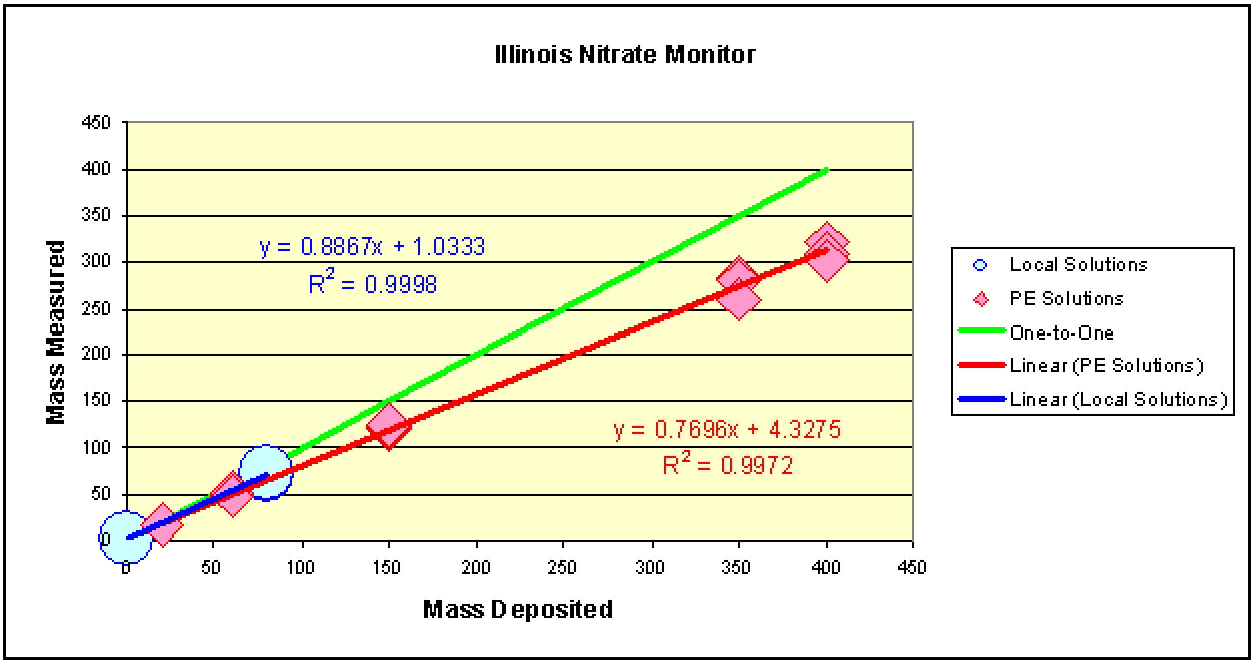


Figure 2



Good precision was observed for the nitrate spikes shown in Figure 2, but poor precision was observed for the high-level spikes shown in Figure 3.

Figure 3

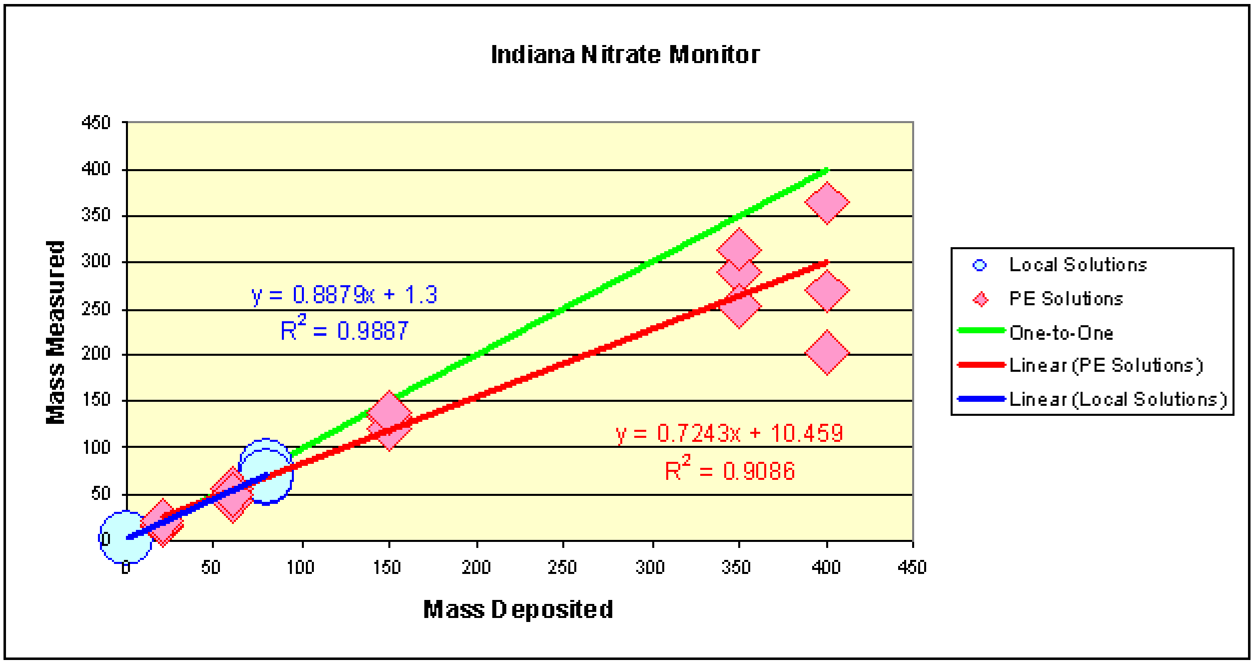
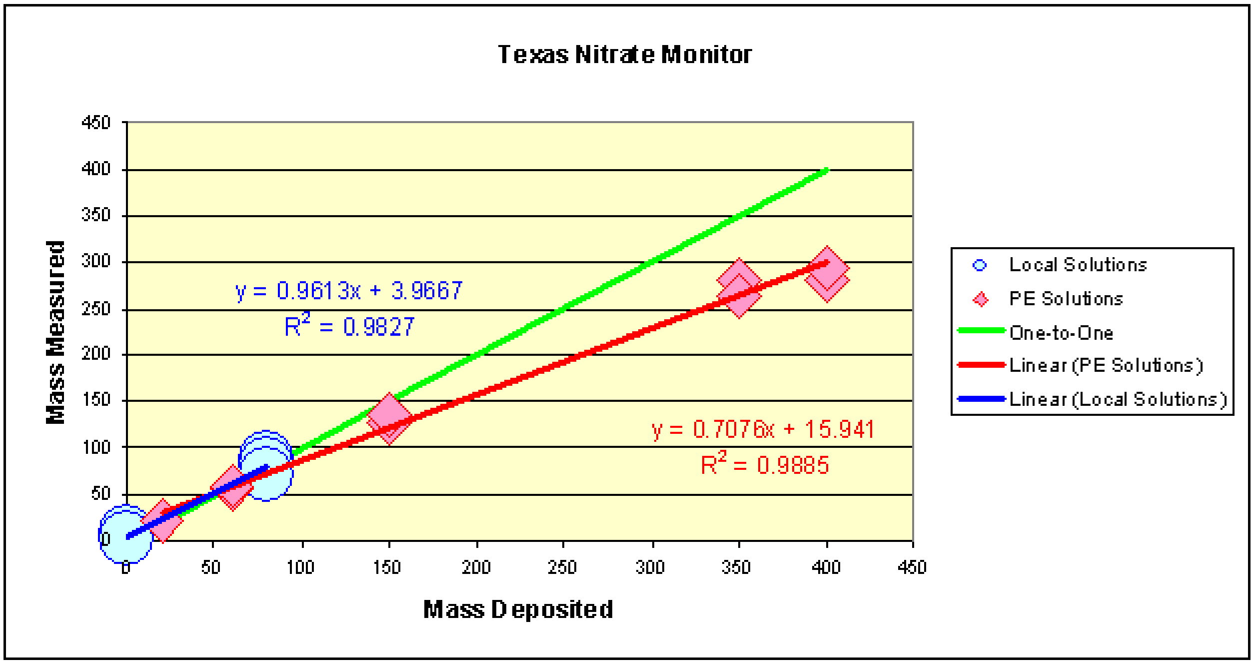


Figure 4



Good precision was observed for the nitrate spikes shown in Figure 4, but one of the high-level spike results shown in Figure 5 appears to be an outlier. Notice also, that the regression lines in Figure 5 have unusually large slope values.

Figure 5

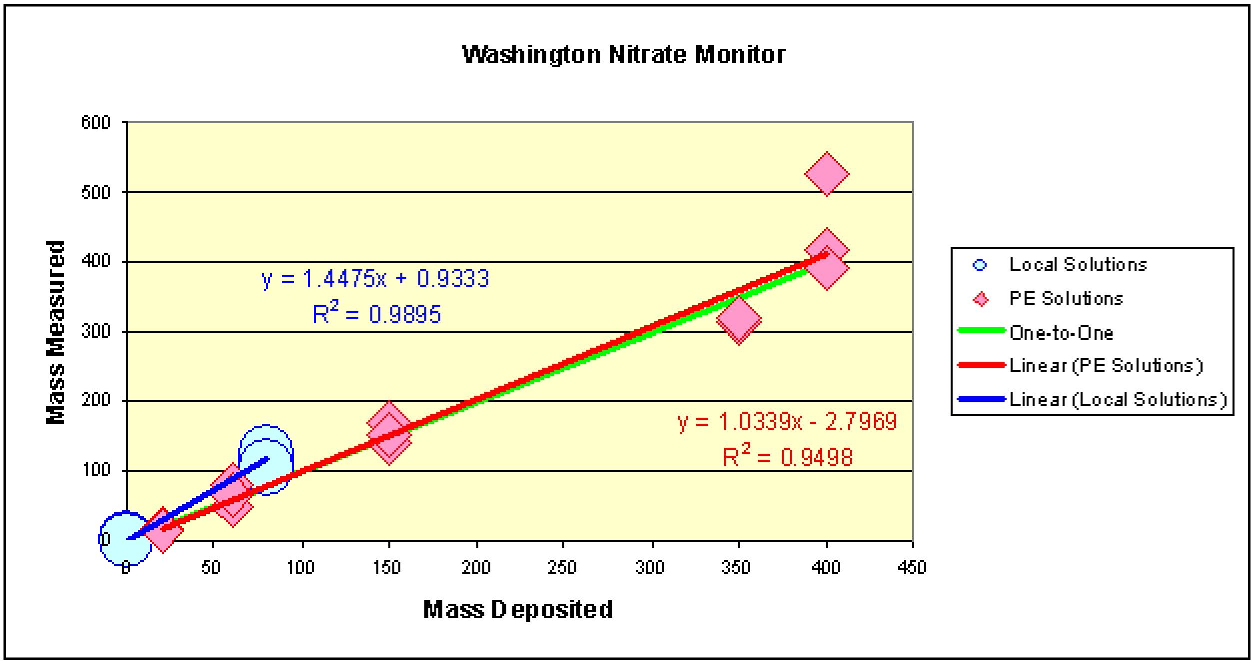


Figure 6

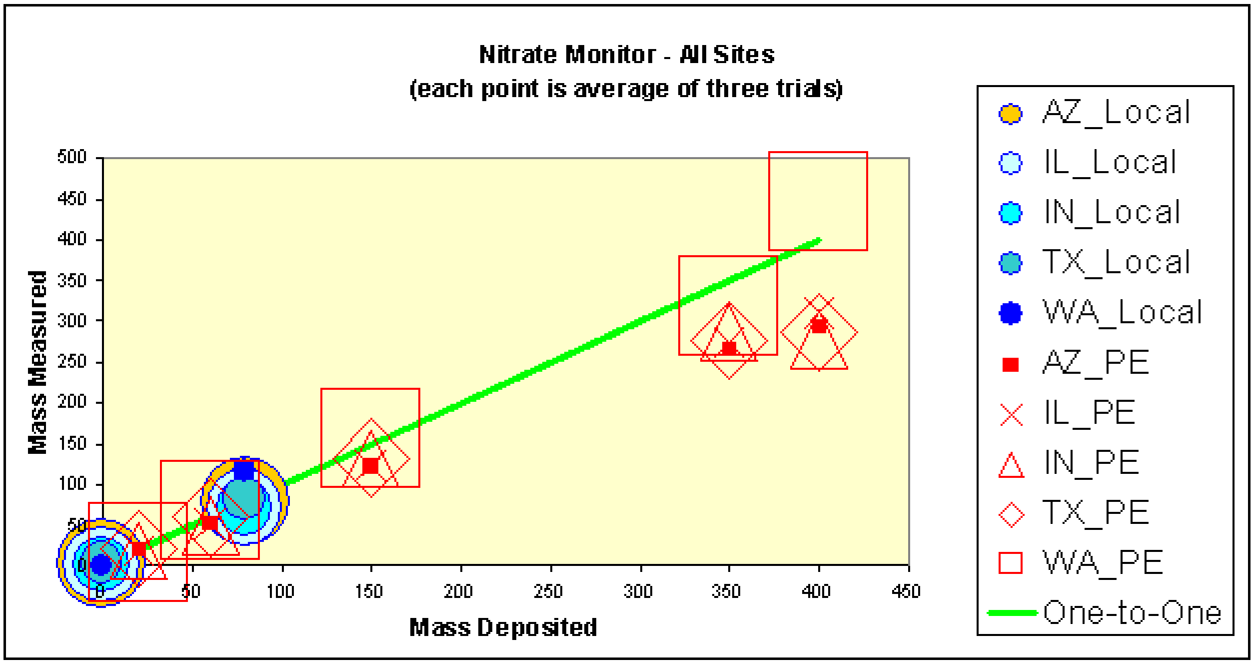


Figure 6 contains results from all five sites. To simplify the graph, each point represents an average result from three replicate spikes of the same spike solution. Each site is represented by a different symbol as shown in the plot legend. Figure 7 shows re-calculated mass from all of the sites. The results shown in Figure 6 were re-calculated from a calibration curve established at each instrument by analysis of the PE solutions themselves. If the calibration curve at each instrument had been

Figure 7

perfect, all of the re-calculated data points from the blind PE solutions would fall exactly on the green One-to-One line.

Analysis of the Blind Aqueous Sulfate Spike Solutions

The Arizona site did not operate a sulfate monitor during the period of this study, and therefore only four sites reported sulfate results. Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, 0.4 µL. The analysis began with the local blank water followed by analysis of the local 300 ng/µL sulfate standard. The study continued by running the five *blind* solutions identified simply as S1-05-03 through S5-05-03. The results reported from the sites are included in Table 4 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 4. 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 8 through Figure 11. 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 8

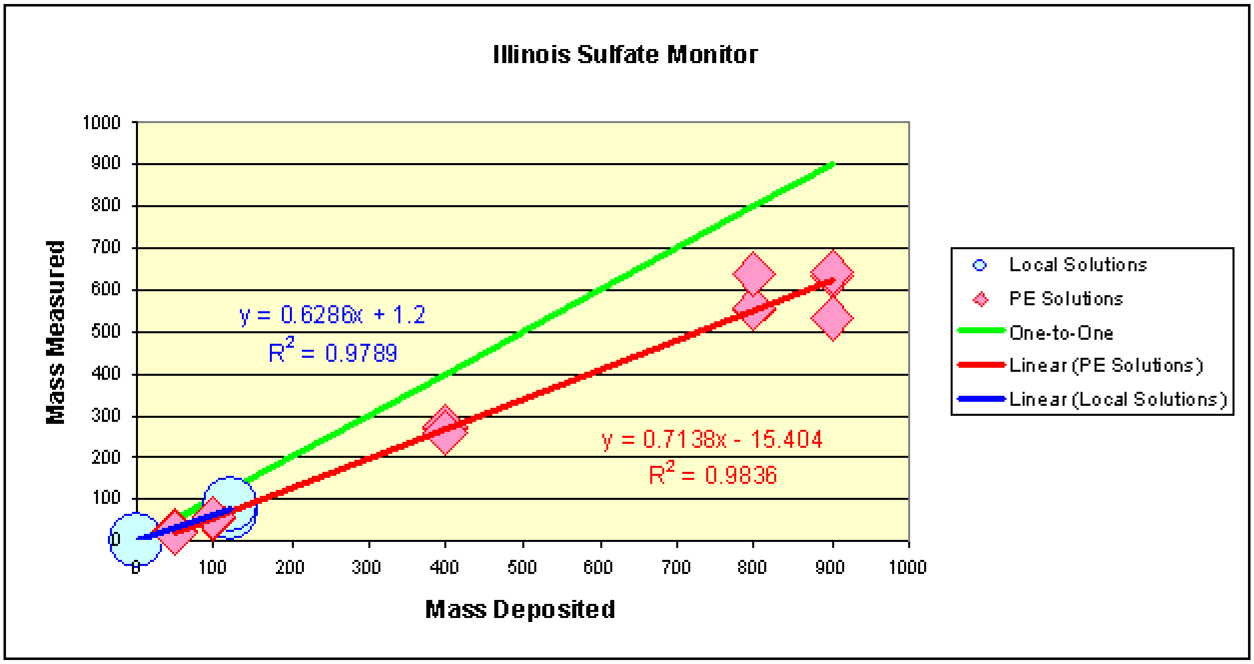


Figure 9

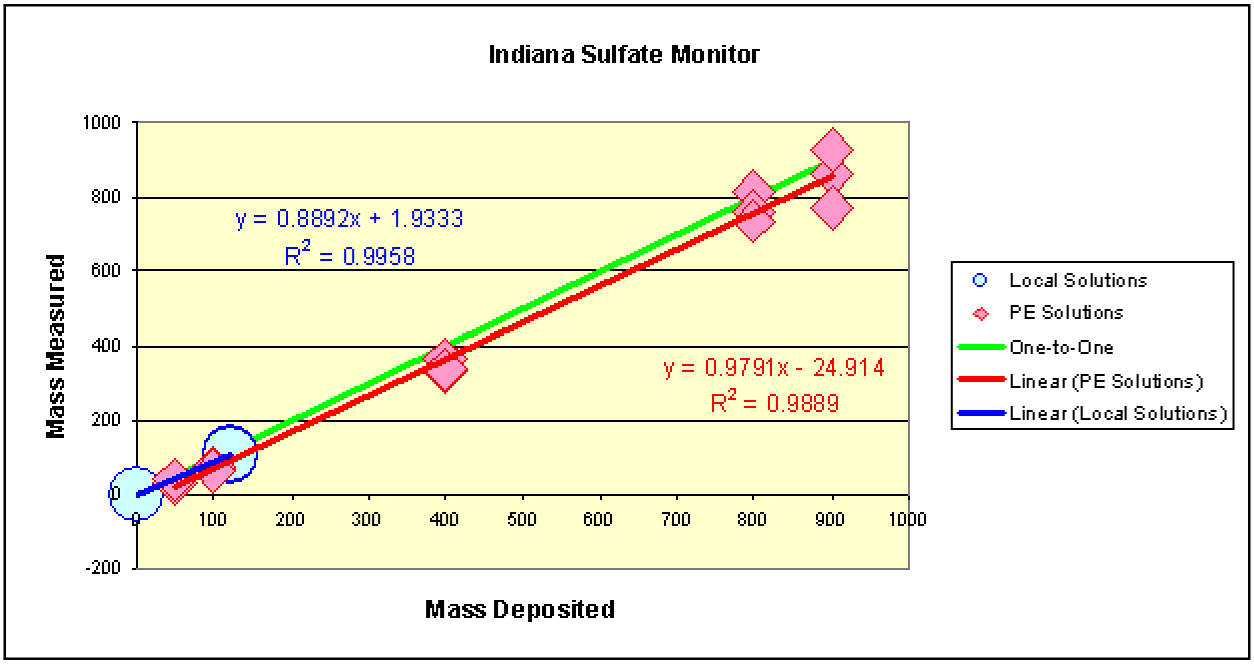


Figure 10

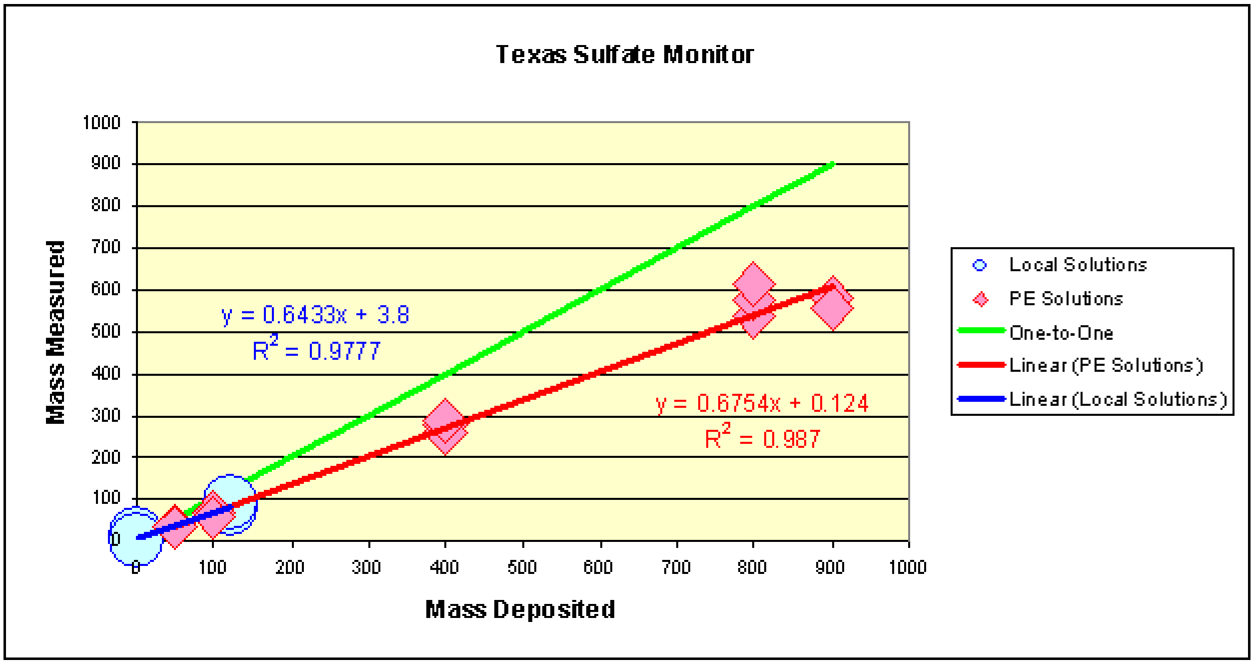


Figure 11

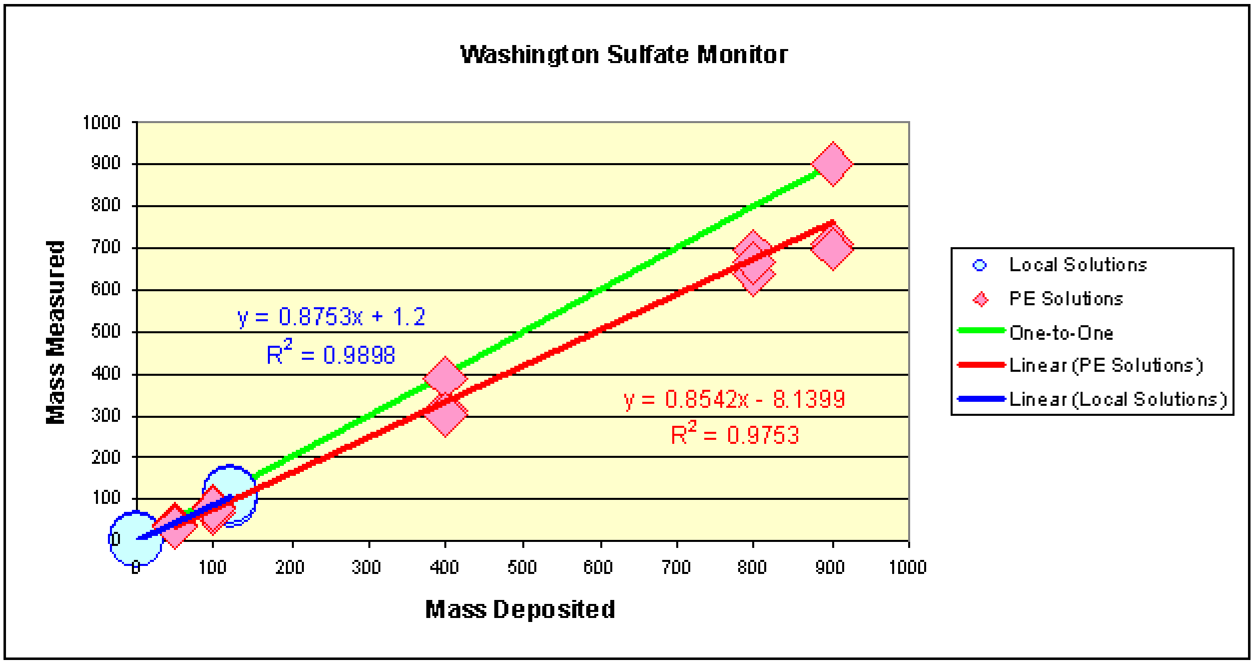


Figure 12 contains results from all four sites. To simplify the graph, each point represents an average result from three replicate spikes of the same spike solution. Each site is represented by a different symbol as shown in the plot legend.

Figure 12

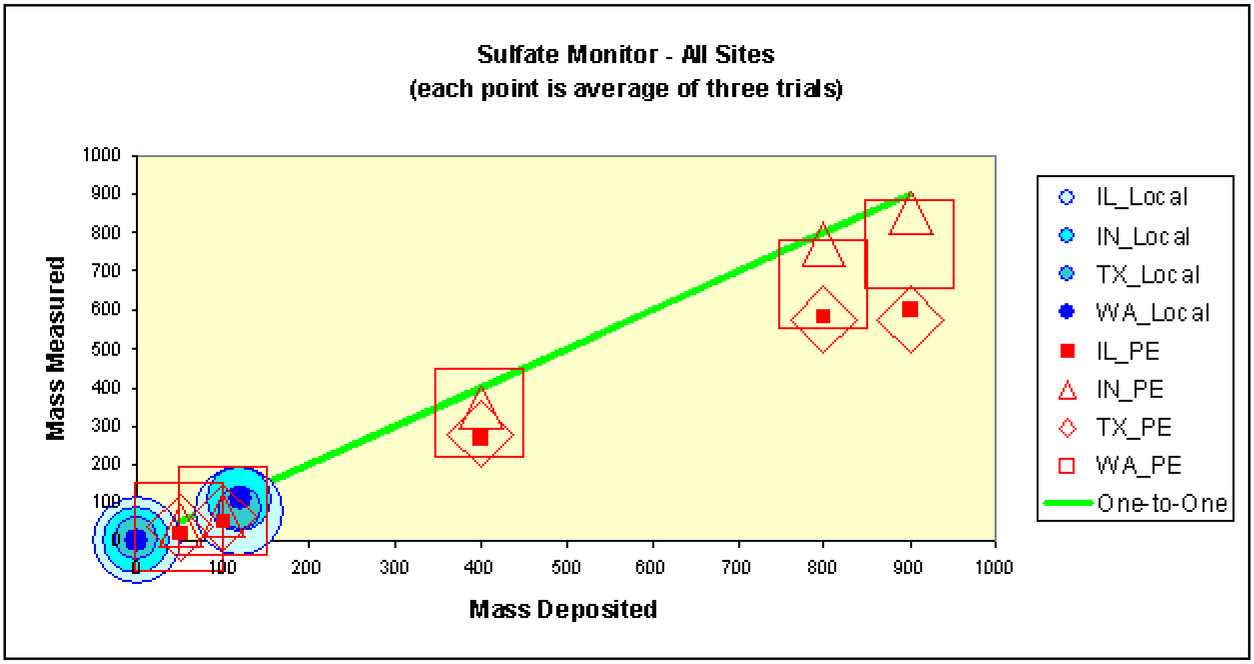


Figure 13

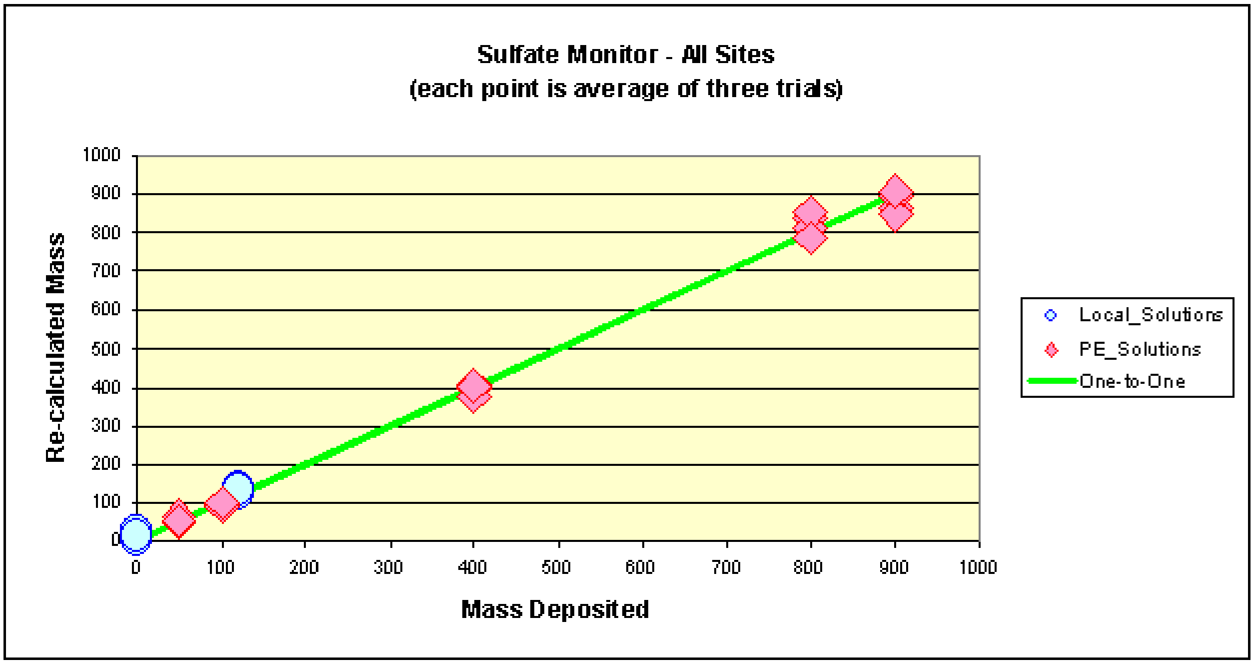


Figure 13 shows re-calculated mass from all of the sites. Results were re-calculated from a calibration curve established at each instrument by the analysis of PE samples. Again, notice how well the re-calculated results in Figure 13 fit the green One-to-One line, but the uncorrected results in Figure 12 consistently fall below the One-to-One line.

Analysis of the Nitrate Spike Solutions Made from Various Salts

All five of the sites reported spike results from four additional solutions that were prepared at NAREL using different nitrate salts. Site operators were instructed to perform duplicate analysis of the four salt solutions using only one spike volume, 0.8 µL. The spikes were performed immediately following the blind PE spikes. The four salt solutions were identified to the operator by listing the name and concentration [100 ng/µL] of the salt on the label of the shipping vial. The results reported from the sites are included in Table 5 at the end of this report. 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.

The results of spiking the various salts are presented in Figure 14 along with results from triplicate spikes of the 100 ng/µL local calibration solution which were run earlier in the day. It should be stated that the values of measured mass shown in Figure 14 are the original values reported from each site, and are not values re-calculated from a calibration curve to correct for inefficient pulse generation.

Figure 14

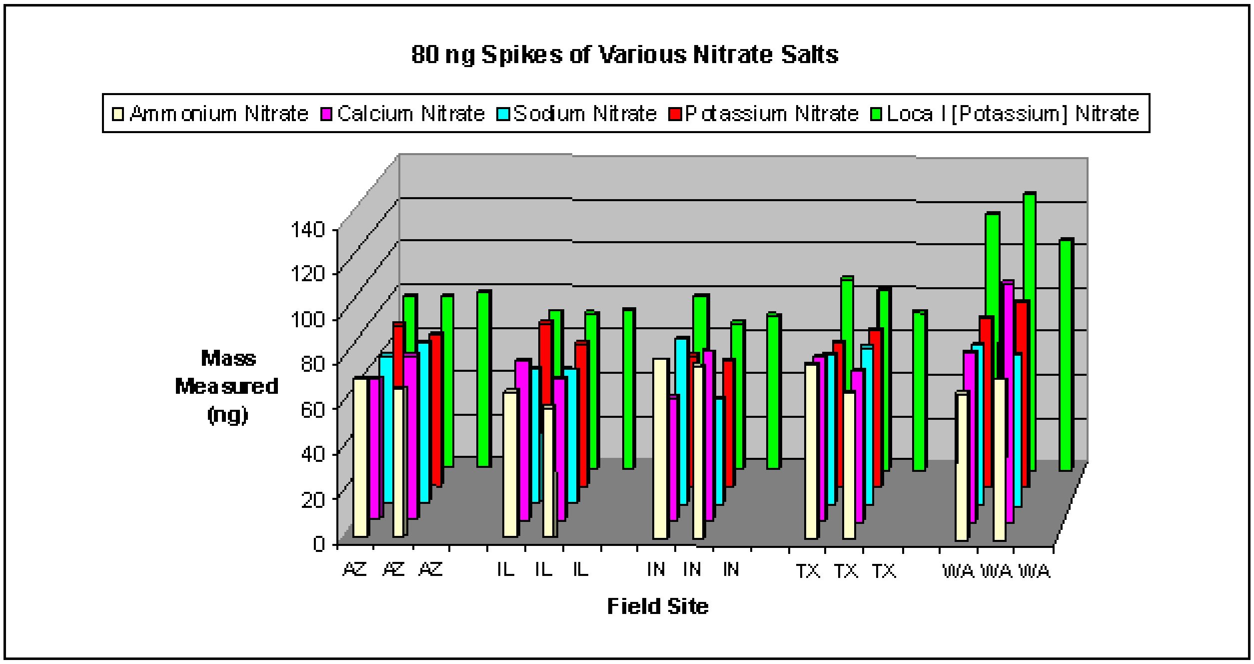
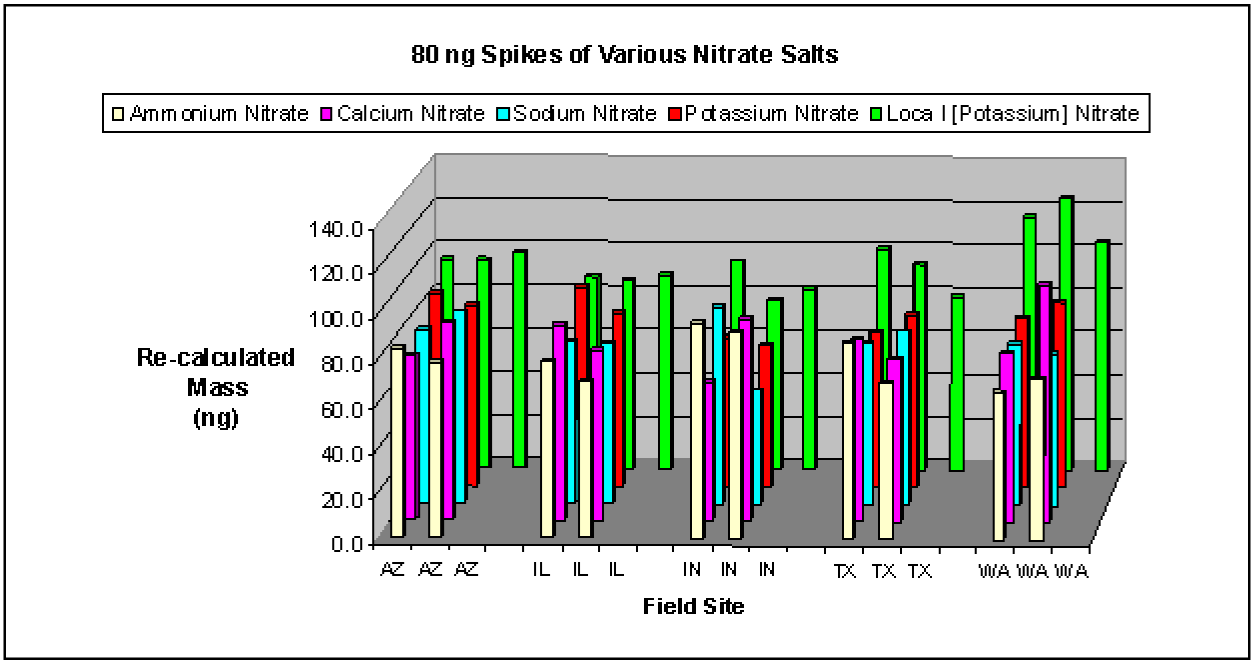


Figure 15 shows re-calculated mass from all of the sites. Results were re-calculated from a calibration curve established at each instrument by the analysis of the PE samples. The re-calculated mass values are shown in Figure 15 to normalize the results from all of the instruments which may have different pulse generating efficiencies.

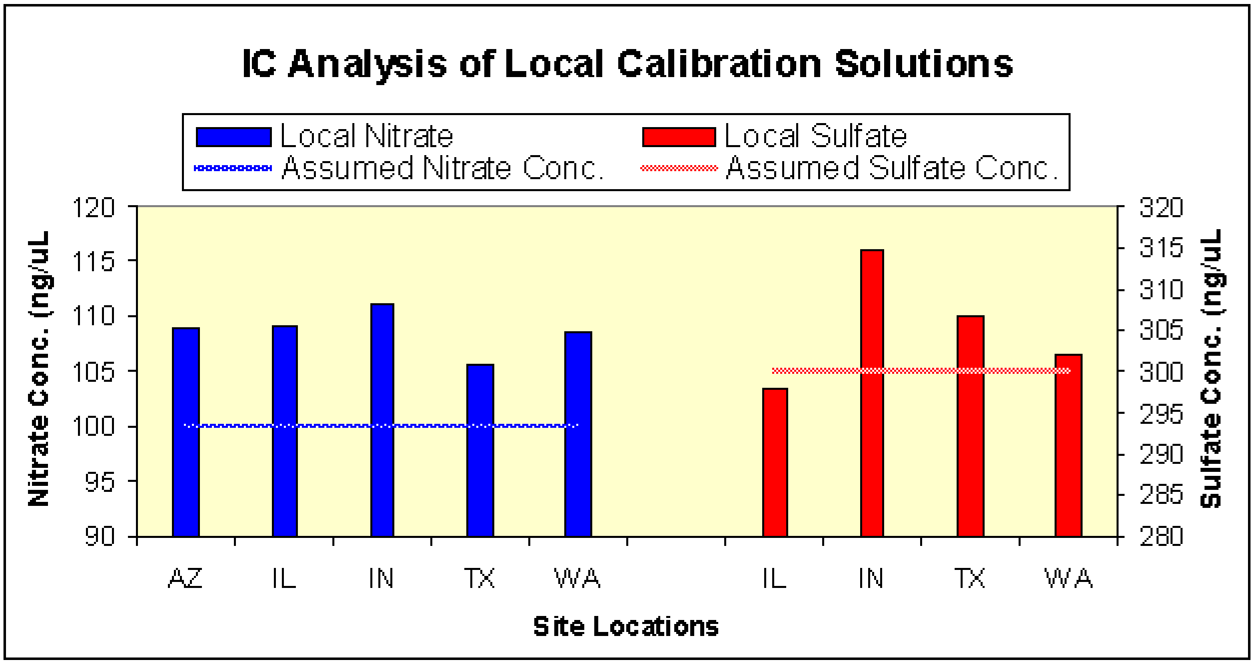
Figure 15



IC Analysis of the Local Nitrate and Sulfate Calibration Solutions

Each of the sites submitted a small portion of their local calibration solutions to NAREL for subsequent analysis using IC. Results of the IC analyses are presented in Table 6 at the end of this report along with the historical information that was provided by the site operators regarding the local solutions. Results of the IC analyses are also presented in Figure 16 as a bar graph with lines that represent the assumed [nominal] concentration of nitrate and sulfate respectively.

Figure 16



Conclusions

This study was similar to the previous study except that two extra activities were added to learn more about performance of the nitrate monitors. Single blind aqueous spikes were analyzed at each site to establish the instrument response curve and evaluate the instrument precision. The nitrate spikes covered a range of 20 to 400 ng deposited onto the flash strip. This corresponds to an ambient nitrate concentration of approximately 2.5 to 50 µg/m^3. A linear response was observed over this range for the monitors located in Arizona and Illinois. Some evidence for a non-linear response curve can be seen in the nitrate data from Texas. This can be seen most clearly in Figure 4 and again in Figure 6. Poor precision was observed from Indiana's high-level nitrate spikes (see Figure 3), and this adds uncertainty to the shape of a response curve. One of Washington's nitrate spikes appears to be an outlier (see Figure 5). A comment was made by Washington's site operator regarding a shift in the analyzer flow rate during the nitrate spiking, and he also had been observing abnormal fluctuations in the RCELL pressure and sample flow rates.

Single blind aqueous sulfate spikes were analyzed at each site which covered a range of 50 to 900 ng deposited onto the flash strip. This corresponds to an ambient sulfate concentration of approximately 6 to 112 µg/m^3. Reasonable precision was observed from the five solutions spiked in triplicate, and a linear response curve was indicated for all of the monitors tested.

Extra solutions of ammonium nitrate, calcium nitrate, potassium nitrate, and sodium nitrate were prepared at NAREL and were analyzed at all of the sites. This study was unable to show a significant difference in spike results among the four different nitrate salts tested. The duplicate spiking performed for each salt solution generally shows just as much variability in the results as changing to a different salt solution.

Earlier evidence that the local nitrate solutions were more concentrated than the assumed value of 100 ng/µL was confirmed by direct IC analysis of the local solutions at NAREL. The IC instrument at NAREL is routinely subjected to a seven-level initial calibration verified by continuing calibration checks after every ten injections. The accuracy of the IC working standards are routinely checked by analysis of a primary standard from a second source. The evidence is very strong now that all of the local nitrate standards are too concentrated, but how long has this been true? The historical information listed in Table 6 shows that these standards have been used at the sites for several months. If we assume that the nitrate standards have always been too concentrated, then the past cycle data will contain a low bias.

Table 1. 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	15-Aug-03	10:37 AM	4910	4830.7	4181.5	3.4	3081.7	220
Illinois	16-Jul-03	8:00 AM	5120	5129	4465	0.6	3330	13
Indiana	04-Jun-03	9:19 AM	5100	5028.9	4499.8	0.6	3027.4	2
Texas	28-Jun-03	10:15 AM	5593	5535.5	4850.6	-2.7	2774	27
Washington	14-Jun-03	1:00 PM	5140	5137.8	4528	0.3	2943	22
*** Span gas concentration as labeled on the bottle (should be 5000 ppb).								

Table 2. 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	0.8	0	9.9	51.9	1.9	0.85	-10.4
Arizona	Local blank water	0.8	0	14.2	101.6	3.6	0.85	-8.0
Arizona	Local blank water	0.8	0	-2	51.4	1.8	0.85	-10.5

Table 2. 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 100 ng/µL std	0.8	80	-30.2	2211.3	79	0.85	96.1
Arizona	Local 100 ng/µL std	0.8	80	-15.7	2209.4	78.9	0.85	96.0
Arizona	Local 100 ng/µL std	0.8	80	-30	2270.5	81.1	0.85	99.0
Arizona	N1-05-03	0.8	20	-26.8	588.6	21	0.85	16.0
Arizona	N1-05-03	0.8	20	-27.1	571.2	20.4	0.85	15.2
Arizona	N1-05-03	0.8	20	-12.3	566.4	20.2	0.85	14.9
Arizona	N2-05-03	0.8	60	-24.6	1436.3	51.3	0.85	57.9
Arizona	N2-05-03	0.8	60	-3.3	1559.8	55.7	0.85	63.9
Arizona	N2-05-03	0.8	60	-16	1473.4	52.6	0.85	59.7
Arizona	N3-05-03	0.8	150	-6.3	3531.3	126.1	0.85	161.2
Arizona	N3-05-03	0.8	150	-15.9	3013	107.6	0.85	135.6
Arizona	N3-05-03	0.8	150	-18.9	3700.7	132.2	0.85	169.6
Arizona	N4-05-03	0.8	350	-4.8	7261.2	259.3	0.85	345.2
Arizona	N4-05-03	0.8	350	-18.2	7569.4	270.3	0.85	360.4
Arizona	N4-05-03	0.8	350	-9.8	7516.9	268.4	0.85	357.8
Arizona	N5-05-03	0.8	400	-21	7944.8	283.7	0.85	378.9
Arizona	N5-05-03	0.8	400	-25.4	8674	309.7	0.85	414.8
Arizona	N5-05-03	0.8	400	-10.8	8144.9	290.9	0.85	388.9
Illinois	Local blank water	0.8	0	-0.4	26.4	0.9	0.83	-4.5
Illinois	Local blank water	0.8	0	3.1	32.8	1.1	0.83	-4.2
Illinois	Local blank water	0.8	0	12.6	32.2	1.1	0.83	-4.2
Illinois	Local 100 ng/µL std	0.8	80	10	2065.9	72.2	0.83	88.2
Illinois	Local 100 ng/µL std	0.8	80	-10.6	2028.1	71	0.83	86.6
Illinois	Local 100 ng/µL std	0.8	80	-0.8	2077.2	72.7	0.83	88.8

Table 2. 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	N1-05-03	0.8	20	4.2	508.8	17.8	0.83	17.5
Illinois	N1-05-03	0.8	20	-1	536.4	18.8	0.83	18.8
Illinois	N1-05-03	0.8	20	13.6	499.2	17.5	0.83	17.1
Illinois	N2-05-03	0.8	60	-4.4	1421.1	49.7	0.83	59.0
Illinois	N2-05-03	0.8	60	-7.8	1472.8	51.5	0.83	61.3
Illinois	N2-05-03	0.8	60	5.2	1409.7	49.3	0.83	58.4
Illinois	N3-05-03	0.8	150	6.7	3409.8	119.3	0.83	149.4
Illinois	N3-05-03	0.8	150	-3.2	3536.7	123.8	0.83	155.2
Illinois	N3-05-03	0.8	150	-1.4	3573.3	125	0.83	156.8
Illinois	N4-05-03	0.8	350	13.4	8074.5	282.5	0.83	361.4
Illinois	N4-05-03	0.8	350	3.3	8010	280.3	0.83	358.6
Illinois	N4-05-03	0.8	350	-4	7420.9	259.7	0.83	331.8
Illinois	N5-05-03	0.8	400	2.8	9193.3	321.7	0.83	412.4
Illinois	N5-05-03	0.8	400	7	8837	309.2	0.83	396.1
Illinois	N5-05-03	0.8	400	2	8616.1	301.5	0.83	386.1
Indiana	Local blank water	0.8	0	1.6	32.4	1.2	0.89	-12.8
Indiana	Local blank water	0.8	0	-5	38.4	1.4	0.89	-12.5
Indiana	Local blank water	0.8	0	-8.6	35.6	1.3	0.89	-12.6
Indiana	Local 100 ng/µL std	0.8	80	-1.4	2116.7	79.6	0.89	95.5
Indiana	Local 100 ng/µL std	0.8	80	1.8	1777.6	66.8	0.89	77.8
Indiana	Local 100 ng/µL std	0.8	80	-1	1878.3	70.6	0.89	83.0
Indiana	N1-05-03	0.8	20	-4.1	426.6	16	0.89	7.6
Indiana	N1-05-03	0.8	20	0.2	485.9	18.3	0.89	10.8
Indiana	N1-05-03	0.8	20	-5.2	552.3	20.8	0.89	14.3

Table 2. 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)
Indiana	N2-05-03	0.8	60	0.6	1141.8	42.9	0.89	44.8
Indiana	N2-05-03	0.8	60	-7.6	1488.5	56	0.89	62.9
Indiana	N2-05-03	0.8	60	-5.8	1335.1	50.2	0.89	54.9
Indiana	N3-05-03	0.8	150	1.9	3555.6	133.7	0.89	170.1
Indiana	N3-05-03	0.8	150	1.2	3198.2	120.2	0.89	151.5
Indiana	N3-05-03	0.8	150	0.3	3669	137.9	0.89	175.9
Indiana	N4-05-03	0.8	350	3.8	7658.7	287.9	0.89	383.0
Indiana	N4-05-03	0.8	350	-9	8356	314.1	0.89	419.2
Indiana	N4-05-03	0.8	350	5.2	6747.1	253.6	0.89	335.7
Indiana	N5-05-03	0.8	400	2.8	9658.9	363.1	0.89	486.9
Indiana	N5-05-03	0.8	400	-10.2	7163.4	269.3	0.89	357.4
Indiana	N5-05-03	0.8	400	-2.4	5384.3	202.4	0.89	265.0
Texas	Local blank water	0.8	0	-60.9	214.9	8.2	0.91	-10.9
Texas	Local blank water	0.8	0	-75.9	50.7	1.9	0.91	-19.8
Texas	Local blank water	0.8	0	-81.7	47.3	1.8	0.91	-20.0
Texas	Local 100 ng/µL std	0.8	80	-62	2289.5	87.9	0.91	101.7
Texas	Local 100 ng/µL std	0.8	80	-93.1	2152.9	82.6	0.91	94.2
Texas	Local 100 ng/µL std	0.8	80	-76.6	1878.1	72.1	0.91	79.4
Texas	N1-05-03	0.8	20	-67.8	540.8	20.8	0.91	6.9
Texas	N1-05-03	0.8	20	-82.6	555.1	21.3	0.91	7.6
Texas	N1-05-03	0.8	20	-75.1	542.1	20.8	0.91	6.9
Texas	N2-05-03	0.8	60	-68	1553	59.6	0.91	61.7
Texas	N2-05-03	0.8	60	-95.2	1465.3	56.2	0.91	56.9
Texas	N2-05-03	0.8	60	-87.2	1558.8	59.8	0.91	62.0

Table 2. 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	N3-05-03	0.8	150	-89.6	3565.6	136.8	0.91	170.8
Texas	N3-05-03	0.8	150	-78.6	3311	127.1	0.91	157.1
Texas	N3-05-03	0.8	150	-75.3	3550.8	136.3	0.91	170.1
Texas	N4-05-03	0.8	350	-75	7303.7	280.3	0.91	373.6
Texas	N4-05-03	0.8	350	-97.2	7342	281.7	0.91	375.6
Texas	N4-05-03	0.8	350	-87.6	6884.1	264.2	0.91	350.9
Texas	N5-05-03	0.8	400	-77.5	7335.1	281.5	0.91	375.3
Texas	N5-05-03	0.8	400	-81.9	7272.9	279.1	0.91	371.9
Texas	N5-05-03	0.8	400	-97.2	7660	293.9	0.91	392.8
Washington	Local blank water	0.8	0	14.6	17.5	0.7	0.9	3.4
Washington	Local blank water	0.8	0	26	35.8	1.5	1.02	4.2
Washington	Local blank water	0.8	0	1.9	15	0.6	1.02	3.3
Washington	Local 100 ng/µL std	0.8	80	-1.5	2724.5	117.4	1.02	116.3
Washington	Local 100 ng/µL std	0.8	80	11	2940.8	126.7	1.02	125.3
Washington	Local 100 ng/µL std	0.8	80	9.9	2462.4	106.1	1.02	105.3
Washington	N1-05-03	0.8	20	13.7	388.8	16.8	1.02	19.0
Washington	N1-05-03	0.8	20	15.2	351.8	15.2	1.02	17.4
Washington	N1-05-03	0.8	20	17.7	328	14.1	1.02	16.3
Washington	N2-05-03	0.8	60	26.6	1894.6	81.6	1.02	81.6
Washington	N2-05-03	0.8	60	26.5	1188.3	51.2	1.02	52.2
Washington	N2-05-03	0.8	60	22.8	1548.2	66.7	1.02	67.2
Washington	N3-05-03	0.8	150	23.9	3930.5	169.3	1.02	166.5
Washington	N3-05-03	0.8	150	30.7	3251.6	140.1	1.02	138.2
Washington	N3-05-03	0.8	150	37	3569.6	153.8	1.02	151.5

Table 2. 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)
Washington	N4-05-03	0.8	350	31.5	7278.5	313.6	1.02	306.0
Washington	N4-05-03	0.8	350	23.2	7417.2	319.6	1.02	311.8
Washington	N4-05-03	0.8	350	27.8	7457.6	321.3	1.02	313.5
Washington	N5-05-03	0.8	400	18.8	12202.7	525.8	1.02	511.3
Washington	N5-05-03	0.8	400	27.4	9687.8	417.4	1.02	406.4
Washington	N5-05-03	0.8	400	29.7	9076.4	391.1	1.02	381.0

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

Table 3. 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)
Arizona	-----	-----	-----	-----	-----	-----	-----
Illinois	16-Jul-03	8:00 AM	1010	1020	890.3	0.9	1
Indiana	04-Sep-03	9:15 AM	1200	1212.8	1048.5	0.0	6
Texas	28-Jun-03	10:15 AM	912	896.7	780.4	0.7	13
Washington	04-Jun-03	12:10 PM	1089	1071.8	925.7	0.7	6

*** Span gas concentration as labeled on the bottle (should be 1000 ppb).

Table 4. Aqueous Sulfate 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	Local blank water	0.2	0	-18.5	1.6	0.1	1.17	2.8
Illinois	Local blank water	0.2	0	-14.8	4	0.3	1.17	3.1
Illinois	Local blank water	0.2	0	-28.4	22.3	1.7	1.17	5.3
Illinois	Local 300 ng/µL std	0.2	60	-33	612.7	47.1	1.17	76.4

Table 4. Aqueous Sulfate 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	Local 300 ng/µL std	0.2	60	-32.6	526.1	40.4	1.17	65.9
Illinois	Local 300 ng/µL std	0.2	60	-36.7	785.2	60.4	1.17	97.3
Illinois	S1-01-03	0.2	80	-45.4	794.1	61	1.17	98.2
Illinois	S1-01-03	0.2	80	-38.3	760.8	58.5	1.17	94.3
Illinois	S1-01-03	0.2	80	-50.6	924	71	1.17	113.9
Illinois	S2-01-03	0.2	200	-55.4	1441.3	110.8	1.17	176.2
Illinois	S2-01-03	0.2	200	-34.3	1527.9	117.4	1.17	186.5
Illinois	S2-01-03	0.2	200	-50.8	1653.2	127.1	1.17	201.7
Illinois	S3-01-03	0.2	600	-50.4	4209.8	323.6	1.17	509.5
Illinois	S3-01-03	0.2	600	-51.6	4774.9	367	1.17	577.4
Illinois	S3-01-03	0.2	600	-66	5081.9	390.6	1.17	614.4
Illinois	S4-01-03	0.2	1000	-58.4	8879.4	682.5	1.17	1071.6
Illinois	S4-01-03	0.2	1000	-51.3	9027.7	693.9	1.17	1089.4
Illinois	S4-01-03	0.2	1000	-42.4	7797.8	599.4	1.17	941.4
Illinois	S5-01-03	0.2	1200	-50.8	10284.1	790.5	1.17	1240.7
Illinois	S5-01-03	0.2	1200	-35.8	10081.2	774.9	1.17	1216.3
Illinois	S5-01-03	0.2	1200	-31.4	9186.2	706.1	1.17	1108.5

Table 4. Aqueous Sulfate 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)
Indiana	Local blank water	0.4	0	-12.3	32.3	3	1.41	28.5
Indiana	Local blank water	0.4	0	48.2	-4.7	-0.4	1.41	25.0
Indiana	Local blank water	0.4	0	-4.2	35	3.2	1.41	28.7
Indiana	Local 300 ng/µL std	0.4	120	2.3	1248.3	114.9	1.41	142.8
Indiana	Local 300 ng/µL std	0.4	120	-0.4	1130.6	104	1.41	131.7
Indiana	Local 300 ng/µL std	0.4	120	1.4	1162.5	107	1.41	134.7
Indiana	S1-05-03	0.4	50	-27	470.9	43.3	1.41	69.7
Indiana	S1-05-03	0.4	50	11.4	374.5	34.5	1.41	60.7
Indiana	S1-05-03	0.4	50	-10.8	442.7	40.7	1.41	67.0
Indiana	S2-05-03	0.4	100	-12.1	734	67.5	1.41	94.4
Indiana	S2-05-03	0.4	100	6.6	788	72.5	1.41	99.5
Indiana	S2-05-03	0.4	100	-6.6	705.9	65	1.41	91.8
Indiana	S3-05-03	0.4	400	-15	3609.9	332.1	1.41	364.6
Indiana	S3-05-03	0.4	400	-21	3968.9	365.2	1.41	398.4
Indiana	S3-05-03	0.4	400	-24.8	3677.8	338.4	1.41	371.1
Indiana	S4-05-03	0.4	800	46.6	8884.3	817.5	1.41	860.4
Indiana	S4-05-03	0.4	800	-26.4	8288.8	762.7	1.41	804.4
Indiana	S4-05-03	0.4	800	-22.7	7985.6	734.8	1.41	775.9
Indiana	S5-05-03	0.4	900	-47.2	9368.7	862.1	1.41	906.0
Indiana	S5-05-03	0.4	900	-25	10095.3	928.9	1.41	974.2
Indiana	S5-05-03	0.4	900	10.2	8367.3	769.9	1.41	811.8
Texas	Local blank water	0.4	0	13.7	120.1	10.7	1.36	15.7
Texas	Local blank water	0.4	0	24.2	4.3	0.4	1.36	0.4
Texas	Local blank water	0.4	0	21.8	3.4	0.3	1.36	0.3

Table 4. Aqueous Sulfate 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 300 ng/µL std	0.4	120	19.8	860.1	76.7	1.36	113.4
Texas	Local 300 ng/µL std	0.4	120	24	851.1	75.9	1.36	112.2
Texas	Local 300 ng/µL std	0.4	120	17.6	1014.2	90.4	1.36	133.7
Texas	S1-05-03	0.4	50	4.8	389.1	34.7	1.36	51.2
Texas	S1-05-03	0.4	50	27.6	364.8	32.5	1.36	47.9
Texas	S1-05-03	0.4	50	-0.4	342.4	30.5	1.36	45.0
Texas	S2-05-03	0.4	100	20	677.2	60.4	1.36	89.2
Texas	S2-05-03	0.4	100	25.9	752.4	67.1	1.36	99.2
Texas	S2-05-03	0.4	100	14.1	630.7	56.2	1.36	83.0
Texas	S3-05-03	0.4	400	1	3113.9	277.6	1.36	410.9
Texas	S3-05-03	0.4	400	15.8	2926.1	260.8	1.36	386.0
Texas	S3-05-03	0.4	400	12.8	3236.1	288.5	1.36	427.0
Texas	S4-05-03	0.4	800	7.7	6044.4	538.8	1.36	797.6
Texas	S4-05-03	0.4	800	-6.4	6486.4	578.2	1.36	855.9
Texas	S4-05-03	0.4	800	1.4	6864	611.9	1.36	905.8
Texas	S5-05-03	0.4	900	10.5	6529.5	582.1	1.36	861.7
Texas	S5-05-03	0.4	900	13	6536.6	582.7	1.36	862.6
Texas	S5-05-03	0.4	900	1.6	6266.5	558.6	1.36	826.9
Washington	Local blank water	0.4	0	29.8	9	0.8	1.31	10.5
Washington	Local blank water	0.4	0	16.1	28.3	2.4	1.31	12.3
Washington	Local blank water	0.4	0	14.1	5.1	0.4	1.31	10.0
Washington	Local 300 ng/µL std	0.4	120	17	1344.6	115	1.31	144.2
Washington	Local 300 ng/µL std	0.4	120	18.8	1130.8	96.7	1.31	122.7
Washington	Local 300 ng/µL std	0.4	120	3.2	1250.4	107	1.31	134.8

Table 4. Aqueous Sulfate 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)
Washington	S1-05-03	0.4	50	43.7	480.3	41.1	1.31	57.6
Washington	S1-05-03	0.4	50	12	431	36.9	1.31	52.7
Washington	S1-05-03	0.4	50	28.5	366.3	31.3	1.31	46.2
Washington	S2-05-03	0.4	100	-13.6	958	82	1.31	105.5
Washington	S2-05-03	0.4	100	31.6	812.1	69.5	1.31	90.9
Washington	S2-05-03	0.4	100	14.1	882.2	75.5	1.31	97.9
Washington	S3-05-03	0.4	400	22.6	3611.5	309	1.31	371.3
Washington	S3-05-03	0.4	400	4.2	4584.8	392.3	1.31	468.8
Washington	S3-05-03	0.4	400	12.4	3543.4	303.2	1.31	364.5
Washington	S4-05-03	0.4	800	33.6	8108.7	693.7	1.31	821.7
Washington	S4-05-03	0.4	800	35.7	7445.1	637	1.31	755.3
Washington	S4-05-03	0.4	800	22.7	7789.8	666.5	1.31	789.8
Washington	S5-05-03	0.4	900	29.2	10538.9	901.7	1.31	1065.2
Washington	S5-05-03	0.4	900	26.6	8281.9	708.6	1.31	839.1
Washington	S5-05-03	0.4	900	10.8	8127.2	695.3	1.31	823.5

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

Table 5. Nitrate Spike Solutions Made from Various Salts

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	Local blank water	0.2	0	-18.5	1.6	0.1	1.17	2.8
Arizona	NH_4NO_3 (100 ng/µL)	0.8	80	-14.3	1980.3	70.7	0.85	84.7
Arizona	NH_4NO_3 (100 ng/µL)	0.8	80	-42.5	1849.2	66	0.85	78.2
Arizona	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	-30.9	1764.9	63	0.85	74.0
Arizona	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	-29.3	2059.8	73.6	0.85	88.7
Arizona	$NaNO_3$ (100 ng/µL)	0.8	80	-30.6	1854.9	66.2	0.85	78.4
Arizona	$NaNO_3$ (100 ng/µL)	0.8	80	-16.6	2013.3	71.9	0.85	86.3
Arizona	KNO_3 (100 ng/µL)	0.8	80	-24.8	2030.8	72.5	0.85	87.2
Arizona	KNO_3 (100 ng/µL)	0.8	80	-28.9	1924.1	68.7	0.85	81.9
Illinois	NH_4NO_3 (100 ng/µL)	0.8	80	1.6	1855.5	64.9	0.83	78.7
Illinois	NH_4NO_3 (100 ng/µL)	0.8	80	-5.4	1664.8	58.3	0.83	70.1
Illinois	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	11.8	2045.5	71.6	0.83	87.4
Illinois	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	11.2	1813.5	63.5	0.83	76.9
Illinois	$NaNO_3$ (100 ng/µL)	0.8	80	-5.2	1733.7	60.7	0.83	73.2
Illinois	$NaNO_3$ (100 ng/µL)	0.8	80	11.7	1725.3	60.4	0.83	72.9
Illinois	KNO_3 (100 ng/µL)	0.8	80	-1.4	2108	73.8	0.83	90.3
Illinois	KNO_3 (100 ng/µL)	0.8	80	-1.8	1852.8	64.8	0.83	78.6
Indiana	NH_4NO_3 (100 ng/µL)	0.8	80	3.2	2119.1	79.7	0.89	95.6
Indiana	NH_4NO_3 (100 ng/µL)	0.8	80	5.3	2044.8	76.9	0.89	91.7
Indiana	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	-10.9	1472.5	55.4	0.89	62.0
Indiana	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	-1.8	2030.9	76.3	0.89	90.9
Indiana	$NaNO_3$ (100 ng/µL)	0.8	80	0.4	1990.5	74.8	0.89	88.8

Table 5. Nitrate Spike Solutions Made from Various Salts

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)
Indiana	$NaNO_3$ (100 ng/µL)	0.8	80	-4.4	1269.5	47.7	0.89	51.4
Indiana	KNO_3 (100 ng/µL)	0.8	80	0.4	1588.7	59.7	0.89	68.0
Indiana	KNO_3 (100 ng/µL)	0.8	80	-8.2	1522.5	57.2	0.89	64.5
Texas	NH_4NO_3 (100 ng/µL)	0.8	80	-81.3	2026.1	77.8	0.91	87.4
Texas	NH_4NO_3 (100 ng/µL)	0.8	80	-73.2	1698.8	65.2	0.91	69.6
Texas	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	-107.1	1934.4	74.2	0.91	82.3
Texas	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	-101.9	1767.7	67.8	0.91	73.3
Texas	$NaNO_3$ (100 ng/µL)	0.8	80	-85.6	1763.6	67.7	0.91	73.1
Texas	$NaNO_3$ (100 ng/µL)	0.8	80	-76.2	1855.6	71.2	0.91	78.1
Texas	KNO_3 (100 ng/µL)	0.8	80	-81.6	1712.1	65.7	0.91	70.3
Texas	KNO_3 (100 ng/µL)	0.8	80	-103.9	1858.4	71.3	0.91	78.2
Washington	NH_4NO_3 (100 ng/µL)	0.8	80	30.1	1509.1	65	1.02	65.6
Washington	NH_4NO_3 (100 ng/µL)	0.8	80	27.8	1660.5	71.5	1.02	71.9
Washington	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	28	1762.9	76	1.02	76.2
Washington	$Ca(NO_3)_2$ (100 ng/µL)	0.8	80	27	2483.7	107	1.02	106.2
Washington	$NaNO_3$ (100 ng/µL)	0.8	80	33.2	1679.7	72.4	1.02	72.7
Washington	$NaNO_3$ (100 ng/µL)	0.8	80	33.5	1579.4	68	1.02	68.5
Washington	KNO_3 (100 ng/µL)	0.8	80	34.8	1792.9	77.2	1.02	77.4
Washington	KNO_3 (100 ng/µL)	0.8	80	28.9	1951.8	84.1	1.02	84.1

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

Table 6. IC Analysis of the Local Calibration Solutions

Site	Solution ID	Assumed [Nominal] Conc. (ng/µL)	Conc. Determined by IC (ng/µL)	Accuracy of the Solution	Source of the Solution	Date Solution Opened	Storage Temp. (°F)
Arizona	Local [Potassium] Nitrate	100	109	109%	R&P/Aldrich	17-Apr-01	70
Illinois	Local [Potassium] Nitrate- new	100	107	107%	R&P/Aldrich	01-Jun-03	50
Illinois	Local [Potassium] Nitrate- old	100	109	109%	R&P/Aldrich	01-May-02	50
Indiana	Local [Potassium] Nitrate	100	111	111%	Aldrich	16-May-02	45
Texas	Local [Potassium] Nitrate	100	106	106%	TCEQ	01-Aug-02	78
Washington	Local [Potassium] Nitrate	100	108	108%	R&P	25-Apr-02	4
Arizona	Local [Ammonium] Sulfate	-----	-----	-----	-----	-----	-----
Illinois	Local [Ammonium] Sulfate	300	298	99%	R&P/Supelco	01-May-02	50
Indiana	Local [Ammonium] Sulfate	300	315	105%	R&P/Supelco	18-Jun-02	45
Texas	Local [Ammonium] Sulfate	300	307	102%	TCEQ	01-Aug-02	78
Washington	Local [Ammonium] Sulfate	300	302	101%	R&P	15-Apr-02	4