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OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

MEMORANDUM

TO: PM NAAQS Review Docket (EPA-HQ-OAR-2007-0492)

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DATE: June 13, 2012

SUBJECT: Documentation of Measurement Uncertainty Estimates of Collocated Chemical Speciation Network and IMPROVE Data for Use in the Secondary PM_{2.5} Standard for Visibility

This memo summarizes the evaluation of measurement uncertainty of Chemical Speciation Network (CSN) and IMPROVE data that will be used to generate a visibility index for a proposed PM_{2.5} secondary standard.

Background

A secondary PM_{2.5} visibility standard is being proposed that will use data from the Chemical Speciation (CSN) and IMPROVE networks. Daily estimates of PM_{2.5}-related reconstructed light-extinction, in units of Mm⁻¹, are converted to visibility indices (VI) in units of deciviews. EPA has data quality objectives for the primary PM_{2.5} standard and the assessment was used to determine whether these objectives were adequate for the secondary standard.

Measurement Uncertainty Assessment Approach

Measurement uncertainty was evaluated using collocated data from:

1. CSN sites with collocated CSN instruments,
2. IMPROVE sites with collocated sampling modules, and
3. Sites with collocated CSN and IMPROVE samplers.

The collocated data provides EPA with a measure of precision while collocated samplers from the CSN and IMPROVE network can provide us some information of relative bias. OAQPS discussed a number of assessment approaches internally and with QA representatives from the IMPROVE network and agreed that comparing the VI value from collocated samplers each day both samplers produced valid results appeared to be a reasonable procedure for evaluating measurement variability.

Measurement variability was assessed using the 90th percentile upper bound coefficient of variation (CV) which is the same statistic used to estimate the PM_{2.5} variability of collocated sites for the primary standard. Precision estimates were made at each 10th percentile visibility index concentration at each collocated site as well as providing an overall estimate of precision for each site and for all collocated sites. The 90th percentile upper bound CV for all sites averaged about 5.5% with a per site range of 3.7% to 9.4%.

Although neither network has a program to measure bias, there are a number of sites where sampling instruments from both networks are collocated. Estimates of relative bias between the collocated sites demonstrated that VI estimates were within 0.5 to 6.1% of each other with an overall average percent difference of 1.5%. It was concluded that with the current quality systems being implemented in both the CSN and IMPROVE programs, EPA can expect that measurement uncertainty of the VI measurement can be controlled to the current PM_{2.5} precision data quality objective of 10%. As mentioned in the report, CVs around the proposed secondary NAAQS value are in the range of 5% and that both the CSN and IMPROVE networks were producing comparable results.

Measurement Uncertainty Estimates of Collocated CSN and IMPROVE Data for Use in the Secondary PM_{2.5} Standard for Visibility

Part of the NAAQS review process includes an assessment of the quality of the monitoring data in order to determine whether data quality objective (DQO) goals for precision and bias are acceptable. These DQO goals are then used to set measurement quality objectives that the monitoring organizations can use to assess and control the quality of its ambient air data. In 1997, data quality objectives goals were developed for precision and bias related to making PM_{2.5} NAAQS decisions and published in the ambient air quality assurance regulations (40 CFR Part 58, Appendix A). The DQO goals established for the primary PM_{2.5} standard will not change. However, a secondary PM_{2.5} visibility standard is being proposed that will use data from the Chemical Speciation (CSN) and Interagency Monitoring of Protected Visual Environments (IMPROVE) networks. Since these two networks are already collecting data for objectives other than NAAQS decisions, OAQPS needs to assess the measurement uncertainty relative to use in NAAQS decisions.

The secondary PM_{2.5} visibility standard will be measured in units of deciviews. Daily estimates of PM_{2.5}-related reconstructed light extinction, b_{ext} (expressed in units of inverse megameters (Mm⁻¹)), are derived from the following equation:

$$PM_{2.5} \ b_{ext,i} = (3 \times Sulfate_i \times f(RH)_{m,gp}) + (3 \times Nitrate_i \times f(RH)_{m,gp}) + (4 \times OM_i) + (10 \times EC_i)$$

Where:

- PM_{2.5} $b_{ext,i}$ = PM_{2.5}-related light extinction in Mm⁻¹ for day i;
- Sulfate_i = ammonium sulfate for day i;
- Nitrate_i = ammonium nitrate for day;
- OM_i = organic mass for day;
- EC_i = the reported concentration of elemental carbon for day i;
- FS_i = fine soil for day i; and
- $f(RH)_{m,gp}$ = the RH hygroscopic growth factor determined from the EPA "climatological $f(RH)$ database" corresponding to month m for day i for the grid point gp closest in distance to the monitoring site

Fine soil (FS_i) is PM_{2.5} crustal material. It is derived from the reported PM_{2.5} concentrations of aluminum (AL), silicon (Si), Calcium (Ca), Iron (Fe), and Titanium (Ti) using the formula: $FS = 2.20[AL] + 2.49[Si] + 1.63[Ca] + 2.42 [Fe] + 1.94 [Ti]$. $f(RH)$ is a hygroscopic factor used to relate a given relative humidity (RH) to its impact on PM_{2.5} light-scattering.

Daily estimates of β_{ext} , in units of Mm⁻¹, are converted into PM_{2.5} visibility index values, in units of deciviews,¹ according to the following equation:

$$PM_{2.5} \text{ visibility index}_i = 10 \times \ln \left(\frac{(PM_{2.5} - b_{ext,i} + 10)}{10} \right)$$

¹ Pitchford M (2010). Assessment of the Use of Speciated PM_{2.5} Mass-Calculated Light Extinction as a Secondary PM NAAQS Indicator of Visibility. Memorandum to PM NAAQS review docket. November 17, 2010. Docket ID number EPA-HQ-OAR-2007-0492-0337

The reader is referred to the NAAQS proposal ² for a more detailed explanation of the visibility index (VI) calculation.

Approaches to the Evaluation of Measurement Uncertainty for the Visibility Index

The best information to assess measurement uncertainty can be derived from the collocated data that are collected at a number of sites in the CSN and IMPROVE networks. One could evaluate measurement uncertainty by two possible approaches:

1. Estimate variability of each parameter used in the VI calculation separately and then perform some additive error (propagation of error) assessment.
2. Estimate the VI value of the primary sampler and the collocated sampler each day both samplers provide valid results. Estimate variability of the VI pairs and provide some statistically relevant estimate of the average variability or a distribution of variability.

OAQPS discussed both approaches internally and with QA representatives from the IMPROVE network and there was agreement to proceed with approach #2 and assess precision between VI values at sites with collocated CSN samplers and sites with collocated CSN/IMPROVE samplers³. The assessment should inform us of the measurement uncertainty associated with the VI estimate using the current data quality requirements documented in the IMPROVE and CSN QA Project Plans (QAPPs) and standard operating procedures (SOPs). Although we do not plan to use approach # 1, this paper will provide precision estimates, by parameter and site, for the six collocated CSN sites and for the nineteen IMPROVE sites that collocate PM_{2.5} sampler modules (further explained below). Since the VI values require input of the parameters listed in Table 1, data quality for these parameters must be evaluated and controlled to acceptable levels in order to achieve an acceptable level of data uncertainty of the VI estimate.

It is worth noting that $f(RH)$, a parameter that can influence measurement uncertainty, was not evaluated in this assessment. It was not estimated in the field and since the same $f(RH)$ value was used in the VI calculations for both collocated samplers, the parameter would not influence data uncertainty.

Data Sets and Data Manipulation

The evaluations that follow are derived from different sources of data. They can be characterized as follows:

- collocated CSN data for parameter level evaluations,
- collocated IMPROVE data for parameter level evaluations, and
- collocated CSN and IMPROVE data for VI evaluations.

² 40 CFR part 50 Appendix N

³ Comparing two different samplers can provide an estimate of relative bias which is evaluated later in the paper

Collocated CSN Data for Parameter Level Evaluations

Table 1. Parameters Used in Parameter Level and VI Measurement Uncertainty Evaluations

AQS Parameter Code	Parameter
88104	Aluminum
88111	Calcium
88126	Iron
88161	Titanium
88165	Silicon
88306	Nitrate
88403	Sulfate
88305	Organic Carbon*
88307	Elemental Carbon*
88370	Organic Carbon **
88380	Elemental Carbon **

* Parameter codes for carbon before the carbon conversion

** Parameter codes for carbon after the carbon conversion
(described below)

Details of the CSN program, including the QAPP and SOPs can be found on the AMTIC Webpage⁴. Table 1 provides a list of the parameters used for precision estimates. Collocated data from May 2007 through December 2010 were downloaded from AQS for the precision estimates. The list of collocated sites, along with the dates of carbon conversion (described below), is provided in Table 2.

Table 2 represents the collocated CSN sites that were used in the evaluation. Two CSN samplers are collocated at each of the sites and can consist of up to three sampler types:

1. URG 3000N for the new carbon parameters
2. Met-one SASS or super SASS for mass, ions, elements, and old carbon (prior to conversion)
3. URG MASS 400 for mass, elements and ions prior to replacement with a MetOne

The data from these sites were used to perform evaluations of variability for each parameter for the days both samplers operated and provided valid data. Data were removed for any pair of data points where one measurement was missing. The data were also removed for any pair of data points where one measurement was below the average parameter method detection limit (MDL). An MDL is associated with every sample value. For each parameter, the MDLs for each sample value were averaged. This average was then used to remove data for any measurement value below this MDL average. The MDLs used for this assessment can be found in Table 5 for each CSN parameter. No other data manipulation or reduction occurred.

Table 2. CSN Collocated Sites

CSN/CSN Collocation				
Site Name	Location	Site ID	Date of Carbon Conversion	Number of Paired Values
Bakersfield	Bakersfield, CA	060290014	May 1, 2007	127
Rubidoux	Rubidoux, CA	060658001	May 1, 2007	177
New Brunswick	New Brunswick, NJ	340230006	October 1, 2009	141
GT Craig	Cleveland, OH	390350060	October 1, 2009	133
Roxbury	Boston, MA	250250042	October 1, 2009	162
Deer Park	Houston, TX	482011039	April 1, 2009	123

⁴ <http://www.epa.gov/ttn/amtic/speciepg.html>

Carbon conversion- After review of the CSN and IMPROVE carbon data (around 2005) there was a realization that there were differences in the OC and EC estimates between the networks. This disparity led to a carbon conversion project⁵ which began conversion of the CSN sites to IMPROVE-like carbon sampling and analysis⁶ from May 2007 through October 2009. In general, it is expected that the CSN results for OC were higher than IMPROVE prior to the conversion due to differences in sampling filter face velocity (CSN had lower face velocity, resulting in higher OC). Differences in EC were generally smaller, not related to filter face velocity, and also site specific.

In addition, one CSN site (Deer Park) replaced their legacy sampler for mass, elements, and ions (URG MASS 400) with a MetOne sampler on February 3, 2009.

Collocated IMPROVE Data for Parameter Level Evaluations

Details of the IMPROVE program including the QAPP and SOPs can be found on the IMPROVE Webpage⁷. Table 3 lists the IMPROVE sites that had sampling modules collocated. The IMPROVE sampler is made up of four sampling modules⁸. Three of the modules are for PM_{2.5} sample collection (A, B, and C) and the fourth is for PM₁₀. Unlike CSN, the IMPROVE program does not collocate two complete samplers at

each site but collocates one of the three PM_{2.5} modules as a fifth sampling module at select sites. This results in about six sites with one of the collocated sampling modules (A, B, or C). The IMPROVE program provided the data for the collocated modules. Collocated data for the fine soil fraction were provided for the years 2006-2009 and data for OC, EC, sulfate and nitrate were provided for years 2007-2010.

Similar to the CSN data reduction, data were removed for any pair of data points where one measurement was missing or if the data points were below the average MDL for that parameter. MDLs were averaged in the same manner as described for the CSN data. MDLs are identified for the IMPROVE data in Table 6. No other data manipulation or reduction occurred.

Table 3. IMPROVE/IMPROVE Module Collocations

Common Site Name	Location	Site Code
Big Bend, NP	TX	BIBE1
Blue Mounds	MN	BLMO1
Everglades NP	FL	EVER1
Frostburg	MD	FRRE1
Gates of the Mountains	MT	GAMO1
Hercules-Glades	MO	HEGL1
Hoover	CA	HOOV1
Lassen Volcanic NP	CA	LAVO1
Medicine Lake	MT	MELA1
Mammoth Cave, NP	KY	MACA1
Mesa Verde	CO	MEVE1
Phoenix	AZ	PHOE1
Proctor Maple Research Facility	VT	PMRF1
Olympic	WA	OLYM1
Sac and Fox	KS	SAFO1
Saint Marks	FL	SAMA1
Sawtooth NF	ID	SAWE1
Seney	MI	SENE1
Trapper Creek	AK	TRCR1

⁵ AMTIC Carbon Implementation Website <http://www.epa.gov/ttn/amtic/specurg3000.html>

⁶ PM2.5 Speciation Newsletter Issue #5 <http://www.epa.gov/ttn/amtic/spenews.html>

⁷ <http://vista.cira.colostate.edu/IMPROVE/>

⁸ <http://vista.cira.colostate.edu/IMPROVE/Publications/OtherDocs/IMPROVEDataGuide/IMPROVEDataguide.htm>

Collocated CSN and IMPROVE Data for VI Evaluations

This section will describe the CSN and IMPROVE data used for the uncertainty evaluation using the visibility index.

Collocated CSN VI Data

Members of EPA's Air Quality Analysis Group (AQAG) extracted the CSN data from AQS for years 2007 to 2009 and performed the VI calculation for the collocated CSN sites listed in Table 2. Sampling frequency for the collocated CSN sampler was every 6 days.

As proposed in 40 CFR part 50 Appendix N, all 5 VI parameters need to be present for each day the index is calculated. The Appendix A quality assurance regulatory proposal for light extinction suggests a cutoff value of 5 deciviews be used before any collocated pair is included in the coefficient of variation (CV) calculation (both values would have to be greater than 5 deciviews). Therefore VI values less than 5 deciviews were removed from the database. There were no more than 4 values removed from the entire CSN and CSN/IMPROVE collocated sites based on this restriction. There was no data manipulation or reduction beyond the restrictions mentioned above. Unlike the CSN/IMPROVE collocation, there was no removal of data from sites that used other samplers to collect OC/EC before conversion to the URG 3000N, since the collocated pair of samplers at the site were the same make and model. Therefore, parameter codes 88305, 88307, 88370 and 88380 were used in the collocated CSN assessment

Collocated CSN/IMPROVE VI Data

The AQAG provided a VI data set of the collocated CSN/IMPROVE Sites (January, 2007 through December, 2009). Table 4 lists the sites with collocated CSN/IMPROVE samplers along with the dates of carbon conversion for the CSN samplers. Sampling frequency at the CSN/IMPROVE sites was every three days.

Table 4. Sites with Collocated CSN and IMPROVE

CSN/IMPROVE Collocation			
Site	AQS Site ID	Date of Carbon Conversion	Number of paired values
Birmingham, AL	010730023	May 1, 2007	288
Phoenix, AZ	040139997	October 1, 2009	30
Fresno, CA	060190008	April 1, 2009	80
New York, NY	360050110	May 1, 2007	263
Seattle, WA	530330080	May 1, 2007	254

Based on the issues described earlier in relation to the carbon conversion, data evaluations were performed only on data from CSN samplers after conversion to the URG 3000N. This had an effect on the number of collocated

VI values reported for the Phoenix and Fresno sites. Other than this data reduction, the same data manipulation techniques used in the collocated CSN data were used for this data set.

Data Evaluation

Data for each parameter were sorted by site and parameter and the 90th percentile upper bound coefficient of variation (CV) estimated. CV is estimated as follows:

Estimate relative percent difference for each collocated pair. The relative percent difference, d_i , is calculated by Equation 1.

Equation 1

$$d_i = \frac{X_i - Y_i}{(X_i + Y_i)/2} \cdot 100$$

where X_i is the concentration of the primary sampler and Y_i is the concentration value from the collocated sampler.

The precision upper bound statistic, CV_{ub} , is a standard deviation on d_i with a 90 percent upper confidence limit (Equation 2)⁹.

Equation 2

$$CV_{ub} = \sqrt{\frac{n \cdot \sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i\right)^2}{2n(n-1)}} \cdot \sqrt{\frac{n-1}{\chi_{0.1, n-1}^2}}$$

where, n is the number of valid data pairs being aggregated, and $\chi_{0.1, n-1}^2$ is the 10th percentile of a chi-squared distribution with $n-1$ degrees of freedom. The factor of 2 in the denominator adjusts for the fact that each d_i is calculated from two values with error. Since this estimate is currently being performed for the collocated sites in the PM_{2.5} network for the primary standard, and EPA is proposing to use the same statistics in the secondary standard, it made sense to use this statistic to evaluate the CSN and IMPROVE data. Tables 5 and 6 provide the variability estimates by site and parameter for CSN and IMPROVE collocated sites respectively.

Data evaluations were generated using the Data Assessment Statistical Calculator¹⁰ (DASC) software tool that was developed for monitoring agencies to evaluate data quality using the current CFR statistics. The tool can be used to generate the equation 1 and 2 statistics and graphically display the data. Appendix A and B provide the DASC tool results for individual parameters for both CSN and IMPROVE respectively.

In reviewing Tables 5 and 6, one can see there is more imprecision associated with the CSN fine soil fraction elements compared to fine soil fraction derived from the IMPROVE collocated sampling modules. The CSN precision values compare reasonably well to an assessment performed on 2002-2004 data¹¹. The measurement quality objectives (MQOs) listed in that assessment were 20% for trace

⁹ Equation 2 is equation 11 in 40 CFR Part 58 Appendix A and is so referenced in the Appendix A graphs

¹⁰ <http://www.epa.gov/ttn/amtic/gareport.html>

¹¹ PM2.5 Speciation Network Newsletter #4 <http://www.epa.gov/ttn/amtic/spenews.html>

elements, 15% for carbon and 10% for sulfate and nitrate. With the exception of the trace elements, the overall site averages are reasonably close to the original MQOs. A portion of the greater imprecision are a result of using the 90th percentile CV statistic that was used in this evaluation but not used in the earlier assessment. There is some disparity in the site level precision estimates that may be associated with sampler or lab errors (no outliers were removed from the evaluations).

Some of the differences between the CSN and IMPROVE data can also be attributed to smaller sample volumes and lighter particulate loadings in the CSN (where one or a few larger imprecision values can have an affect on the CV statistic) as well as lower concentration sites, where a relatively small difference can cause higher imprecision than sites with higher concentrations. IMPROVE samplers use higher flow rates along with smaller filters which results in higher particle loadings on the filter (~10 times higher) which can help improve the instrument's ability to detect the trace elements and resulting precision estimates. The sulfate, nitrate, organic carbon and elemental carbon precision results are more comparable between the networks with sulfate and nitrate having higher, but acceptable, imprecision at the CSN collocated sites and organic carbon and elemental carbon having a slightly higher, but acceptable, imprecision at the IMPROVE sites.

Table 5. 2007-2010 Collocated CSN Data Upper Bound 90th Percentile CV From Values > MDL

Site ID	Al	Ca	Fe	Ti	Si	NO3	SO4	OC	EC
MDL ug/m³	0.015	0.006	0.002	0.005	0.013	0.011	0.013	0.064	0.064
Bakersfield, CA	26.56	25.03	23.88	31.88	24.34	12.15	9.74	13.45	9.67
Rubidoux, CA	32.84	22.79	20.99	33.67	19.22	11.73	10.78	10.19	10.78
Boston, MA	43.49	30.12	20.53	39.09	27.36	12.68	8.51	8.67	13.18
New Brunswick, NJ	56.26	50.29	46.64	59.6	49.76	25.15	21.5	9.33	10.9
Cleveland, OH	50.42	43.86	25.81	37.34	33.61	8.24	8.24	26.57	24.62
Houston, TX	36.02	23.22	28.66	29.89	33.97	25.43	22.93	8.82	13.55
Site Average CV	37	32.55	28.83	32.32	30.41	16.61	13.09	12.84	13.13

Table 6. 2006-2010 IMPROVE Data Upper Bound 90th Percentile CV From Values > MDL

Site ID	Al	Ca	Fe	Ti	Si	NO3	SO4	OC	EC
MDL ug/m³	0.003	0.0001	0.00004	0.00005	0.0014	0.0124	0.0158	0.064	0.064
Big Bend, NP						9.32	1.79		
Blue Mounds						2.65	1.99		
Everglades NP								17.05	15.74
Frostburg						4.78	2.28		
Gates of the Mountains						8.46	5.11		
Hercules-Glades								9.85	12.25
Hoover								22.1	14.66
Lassen Volcanic NP						9.24	3.92		
Medicine Lake								19.86	16.84
Mammoth Cave, NP						5.54	1.79		
Mesa Verde	20.71	25.59	20.11	20.75	21.5				
Olympic	15.06	12.48	15.97	23.3	20.88				
Phoenix						12.07	11.41	9.43	10.27
Proctor Maple Research Facility	13.63	13.83	13.23	18.38	14.64				
Sac and Fox	12.29	12.02	9.02	12.1	10.99				
Saint Marks	13.72	8.02	7.23	11.9	13.62				
Sawtooth NF								17.63	15.3
Seney								17.8	13.19
Trapper Creek	16.78	19.42	16.72	24.69	22.41				
Site Average CV	15.37	15.23	13.71	18.52	17.34	7.44	4.04	16.25	14.04

Although this paper is not intended to provide a detailed discussion on the differences in precision estimates between the CSN and IMPROVE networks, some assessments related to this data have already been performed by IMPROVE^{12,13} and the EPA CSN contractor laboratory through technical papers¹⁴ and annual data summaries.

The parameters evaluated in Tables 5 and 6 are input parameters (along with RH) to the light extinction equation which produces a visibility index value in deciviews. The next step is to determine the variability in the visibility index value for collocated CSN/CSN sites (those listed in Table 2) and collocated CSN /IMPROVE sites.

¹² Hyslop NP and Warren White; Sources of Uncertainty from the Inter-species Covariance of Measurement Errors.. Environmental Science and Technology, 2011

¹³ Appendix E of Spatial and Seasonal Patterns and Temporal Variability of Haze and its Constituents in the United States: Report IV
November 2006 <http://vista.cira.colostate.edu/IMPROVE/Publications/Reports/2006/2006.htm>

¹⁴ James B. Flanagan, R.K.M. Jayanty, Edward E. Rickman. PM2.5 Speciation Trends Network: Evaluation of Whole-System Uncertainties Using Data from Sites with Collocated Samplers, 2006 *J. Air & Waste Manage. Assoc.* **56**:492–499

Table 7 provides site level summary results of the 90th percentile upper bound CV for the visibility index aggregated at 10th percentile visibility index levels. The overall CV results for the collocated CSN sites and the CSN/IMPROVE sites are very similar with an average CV of around 5.5%.

Site	Site ID	0-10%	10-20%	20-30%	30-40%	40-50%	50-60%	60-70%	70-80%	80-90%	90-100%	Overall
CSN/CSN Sites												
Bakersfield, CA	06-029-0014	5.08	1.45	14.37	2.53	4.34	1.62	1.83	1.11	1.18	0.54	3.97
Rubidoux, CA	06-065-8001	10.11	3.2	5.76	3.83	3.09	2.62	3.45	1.99	0.89	0.68	3.63
Boston, MA	25-025-0042	8.22	10.4	7.47	3.22	2.91	5.4	12.53	6.46	2.45	4.8	5.77
New Brunswick, NJ	34-023-0006	10.58	6.73	5.45	4.25	15.12	7.01	3.43	2.83	3.38	3.84	5.89
Cleveland, OH	39-035-0060	5.57	5.09	4.25	4.1	10.57	3.82	1.58	3.1	3.35	2.07	4.03
Houston, TX	48-201-1039	24.77	9.6	8.61	7.08	8.19	3.75	5.79	8.95	10.61	1.43	9.44
All CSN/CSN Average		10.90	1.31	6.45	6.87	6.21	3.42	4.20	2.92	2.20	1.11	5.46
CSN/IMPROVE Sites												
Birmingham, AL	01-073-0023	5.77	3.29	2.18	3.74	2.97	1.8	7.65	1.33	3	5.29	3.69
Phoenix, AZ *	04-013-9997	43.53	27.82	13.79	9.73	7.95	7.12	4.69	6.9	4.83	3.41	6.46
Fresno, CA*	06-019-0008	11.38	4.19	3.17	3.35	16.41	2.47	1.46	1.66	4.57	21.63	7.07
New York, NY	36-005-0010	6.02	3.57	3.34	3.54	2.4	2.05	2.75	6.41	2.45	2.51	3.38
Seattle, WA	53-033-0080	12.93	8.97	7.43	4.71	2.65	7.99	3.54	3.93	3.03	3.14	5.7
All CSN /IMPROVE Average		8.99	4.42	4.65	5.07	3.01	2.75	2.71	4.35	3.18	5.52	5.26
* Conversion to URG 300N sampler occurred in 2009 for Phoenix and Fresno site so CV estimates based on fewer values than other sites												

There was an expectation that the CV results between CSN/IMPROVE would be somewhat higher than the collocated CSN instruments due to difference in samplers, analytical methods and laboratories, and the fact that variability in the trace elements were greater in the CSN network. The CV results of the Phoenix and Fresno sites are somewhat higher than the other sites but those two sites have the least amount of data (30 and 80 collocated pairs respectively which result in 3 and 8 pairs respectively at each 10th percentile range) which will have an effect on the 90th percentile upper bound CV precision estimate. However, even with the complication of sample size for the Phoenix and Fresno sites, based on the assessment of precision, it would appear that both networks are within the current 10% precision goals for the primary standard. Appendix C provides the results of the data evaluations for each collocated CSN site and Appendix D provides the results of the data evaluations for each CSN/IMPROVE site.

Discussion

The secondary PM_{2.5} NAAQS is being proposed at a range of 28-30 deciviews¹⁵. This equates to the data from the collocated CSN and CSN/IMPROVE sites in the 60th percentile VI range and above (site dependent). Within the 60th through 100th percentiles, the 90th percentile upper bound CVs range from a high of 5.52% to a low of 1.11%. As the data in Appendix C and D illustrate, when collocated VI estimates are aggregated at 10th percentiles, the CVs are estimated on around 30 collocated pairs where a few values can influence the estimate. As mentioned in the data manipulation section, no outliers were removed from this data set so individual values may have an influence. Even with limited data manipulation (values < 5 deciviews removed) the average CV results from all the collocated sites in the range of the standard are below 5% CV (see Table 8). At the proposed NAAQS range a 5% CV would equate to about ± 1.5 deciview variability around the estimated value.

¹⁵ At the time this paper was written the NAAQS had not been proposed and therefore a range was used.

Table 8. 90 Percentile Upper Bound CV at Upper Percentile VI Values					
	60-70%	70-80%	80-90%	90-100%	Average
All CN/CSN Sites	4.20	2.92	2.20	1.11	2.61
All CSN /IMPROVE Sites	2.71	4.35	3.18	5.52	3.94

Bias Evaluation

In evaluating the collocated CSN/IMPROVE precision graphs in Appendix D, a pattern appeared to emerge. Most of the relative percent differences in the graphs were above zero indicating a bias between the two networks VI estimates. In order to assess this further, EPA ran the current PM_{2.5} bias statistics on the collocated VI values. The bias statistic assumes one value is an audit value (truth) of known concentration. In this case, we do not have a known value but as long as we identify a network as the “audit value” and we are consistent in applying the statistic, we can determine if there is a relative bias between the networks.

The current bias statistic simply estimates the percent difference between the two collocated values as follows:

$$di = \frac{\text{measured} - \text{audit}}{\text{audit}} * 100$$

where, *measured* is the concentration indicated by the CSN light extinction values and *audit* is the IMPROVE light extinction values. We then take the average of the percent differences to estimate average bias for a site. Appendix D also calculates confidence limits for these average bias estimates using equations 13 and 14 in 40 CFR Part 58 Appendix A:

Equation 13

$$\text{Upper 90\% Confidence Interval} = D + t_{0.95,df} \cdot \frac{s}{\sqrt{n_j}}$$

Equation 14

$$\text{Lower 90\% Confidence Interval} = D - t_{0.95,df} \cdot \frac{s}{\sqrt{n_j}}$$

Where, $t_{0.95,df}$ is the 95th quantile of a t-distribution with degrees of freedom $df = n_j - 1$ and s is an estimate of the variability of the average bias calculated using equation 15 in 40 CFR Part 58 Appendix A:

Equation 15

$$s = \sqrt{\frac{\sum_{i=1}^{n_j} (d_i - D)^2}{n_j - 1}}$$

Table 9. Visibility Index Bias Estimates for Collocated CSN/ IMPROVE Sites

Site	Average Bias (%)
Birmingham, AL	2.1
Phoenix, AZ	6.1
Fresno, CA	0.54
NY, NY	3.9
Seattle, WA	3.7
Average-All sites	1.5

Table 9 provides the bias estimates for the collocated CSN/IMPROVE sites. The CSN VI values are usually higher compared to the IMPROVE values but as Figure 1 indicates, the overall average of the 915 collocated CSN/IMPROVE pairs greater than 5 deciviews is 1.5%. Although we do not currently use the absolute value bias statistic that is in use for the gaseous pollutants,¹⁶ we ran the CSN/IMPROVE data through that statistic. This statistic assigns a positive or negative bias if both the 25

and 75 percentile values (when the bias values are rank ordered lowest to highest) have the same sign. With the exception of the Phoenix site (only 30 pairs), the other four CSN/IMPROVE sites had the 25th and 75th percentile bias value as positive, indicating the CSN VI estimate as biased high compared to IMPROVE.

There may be a few technical issues that can account for some of the bias. The IMPROVE program reports OC that are blank corrected. EC is not adjusted. CSN is recommending an approach to blank correction in the proposed secondary standard but it was not implemented for this evaluation. Therefore, CSN values for the OC fraction will be somewhat higher. The magnitude of this affect are unknown at this time but will be evaluated.

The PM_{2.5} DQO goals for bias for the primary standard is currently 10%. Although we do not have a performance evaluation program in the CSN or IMPROVE networks the evaluation seems to suggest that the networks are producing VI estimates within 2% of each other.

Conclusion

It appears that with the current quality systems being implemented in both the CSN and IMPROVE programs, we can expect that measurement uncertainty of the VI measurement can be controlled to the current PM_{2.5} precision data quality objective of 10%. As stated earlier, CVs around the NAAQS value are in the range of 5%. In addition, although we do not have a performance evaluation program in place, both networks are producing comparable VI results with the CSN network producing slightly higher VI values.

The CSN network is in the process of reviewing its QAPP and will look to determine if the current measurement quality objectives of the VI parameters need to be revised. Although the CSN and

Table 9 provides the bias estimates for the collocated CSN/IMPROVE sites. The CSN VI values are usually higher compared to the IMPROVE values but as Figure 1 indicates, the overall average of the 915 collocated CSN/IMPROVE pairs greater than 5 deciviews is 1.5%. Although we do not currently use the absolute value bias statistic that is in use for the gaseous pollutants,¹⁶ we ran the CSN/IMPROVE data through that statistic. This statistic assigns a positive or negative bias if both the 25

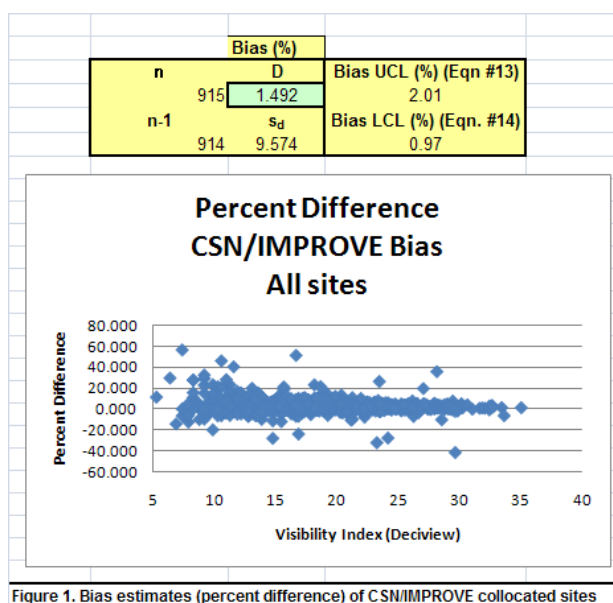


Figure 1. Bias estimates (percent difference) of CSN/IMPROVE collocated sites

¹⁶ Guideline on the Meaning and Use of Precision and Bias Data required by 40 CFR Part 58 Appendix A
<http://www.epa.gov/ttn/amtic/qareport.html>

IMPROVE participate in performance evaluation programs that can determine laboratory comparability, neither have a performance evaluation program that will allow for an estimate of overall bias from field sampling and laboratory measurement phases. Ensuring that collocated CSN/IMPROVE samplers continue to operate at a reasonable number of sites will help to evaluate data comparability.

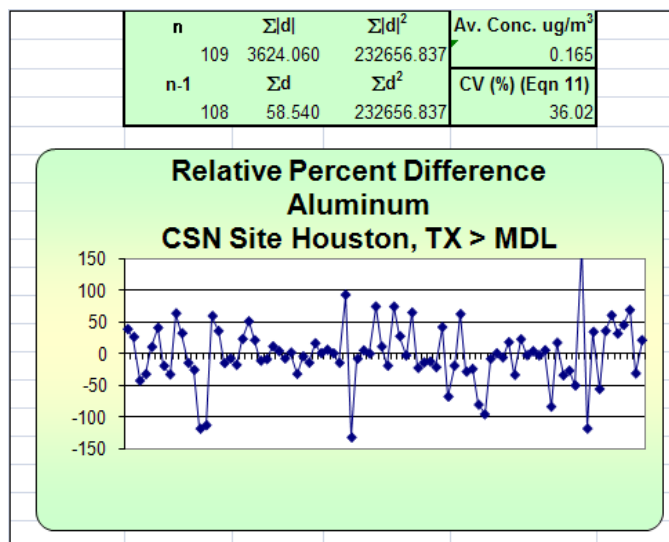
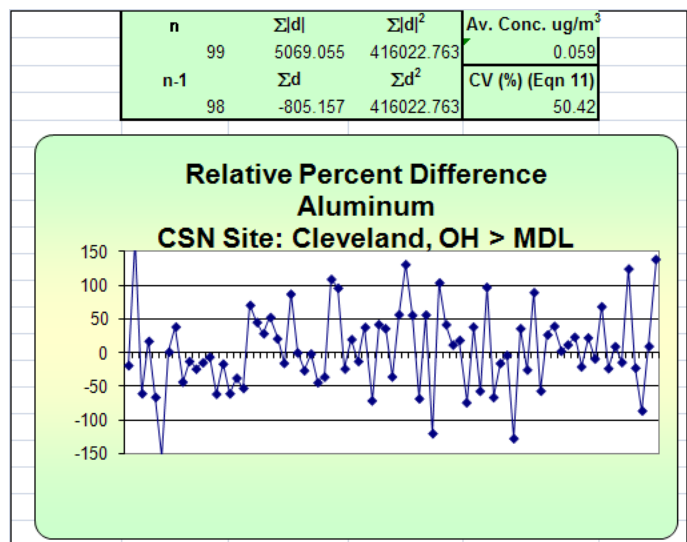
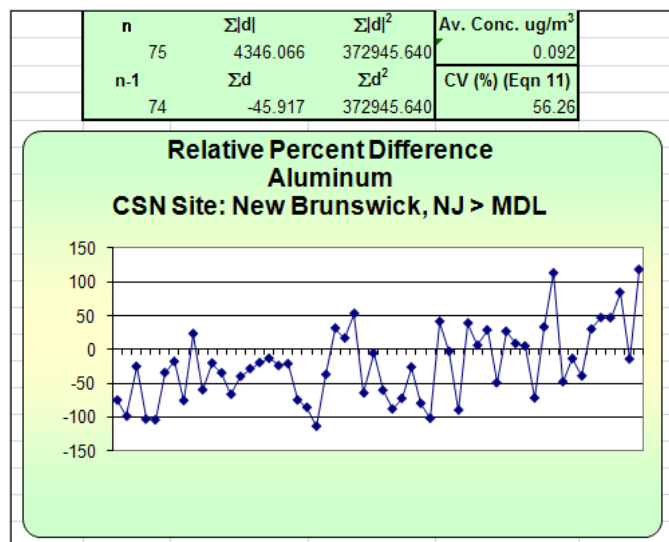
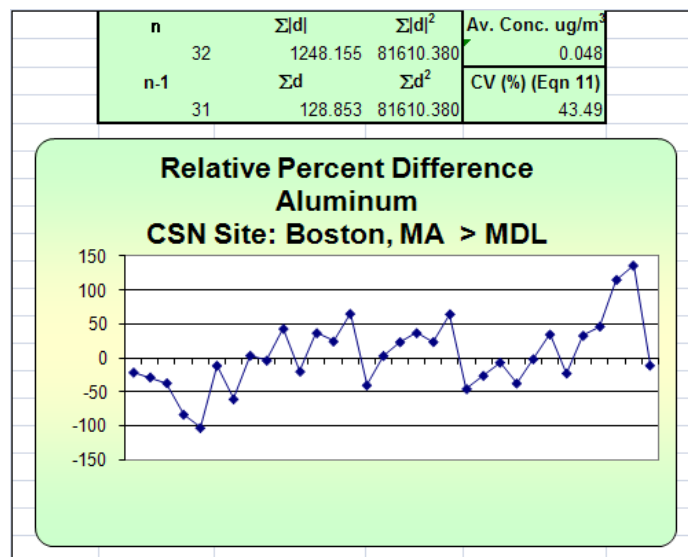
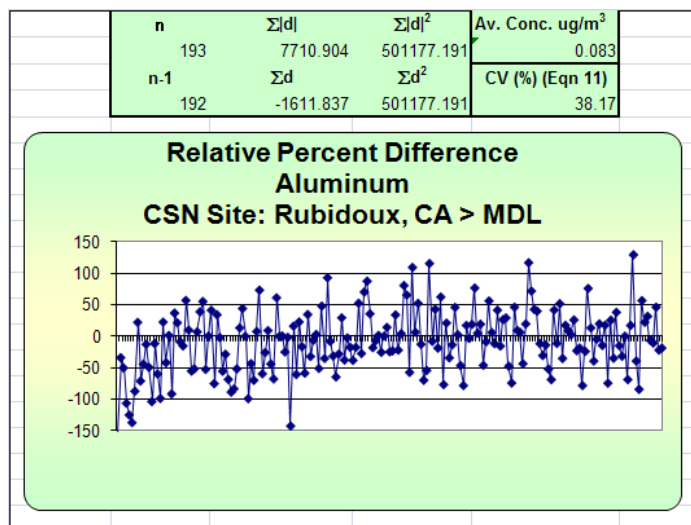
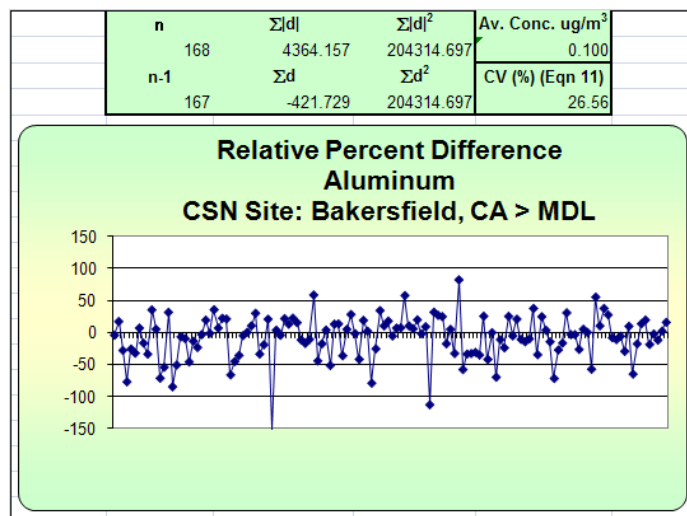
Decision makers need to determine whether this measurement uncertainty is acceptable or not. If not, further evaluation would need to occur to determine what error(s) play the largest roles in the VI estimate and attempt to look at ways of reducing and controlling these uncertainties. If the measurement uncertainty is acceptable, then the current IMPROVE and CSN quality systems are providing adequate data quality for the decisions makers estimates around the proposed NAAQS.

Appendix A

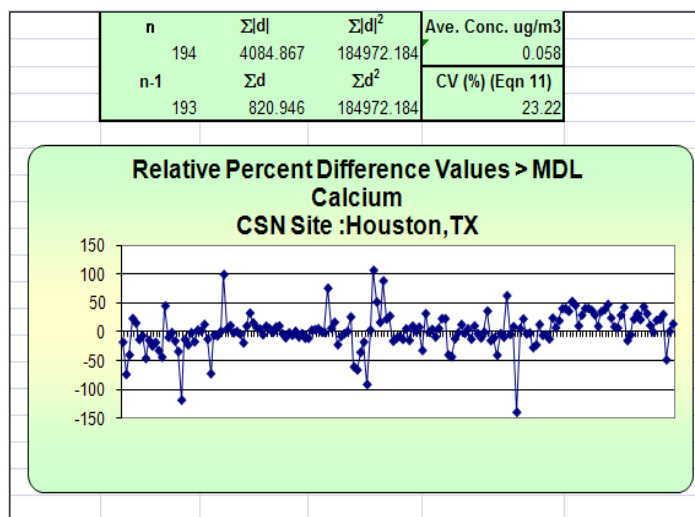
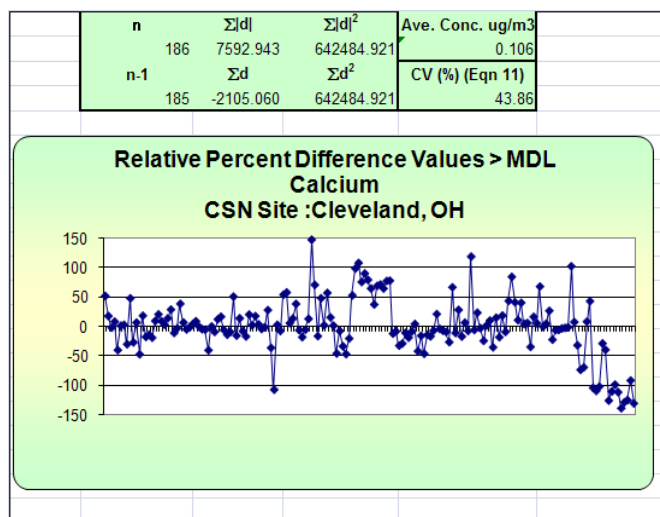
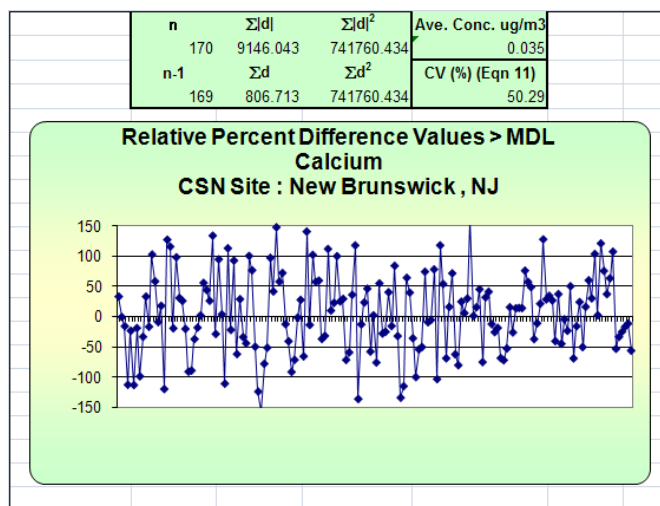
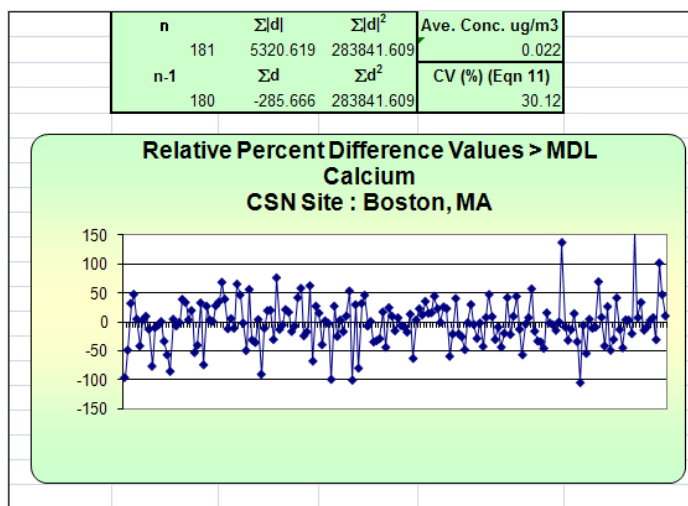
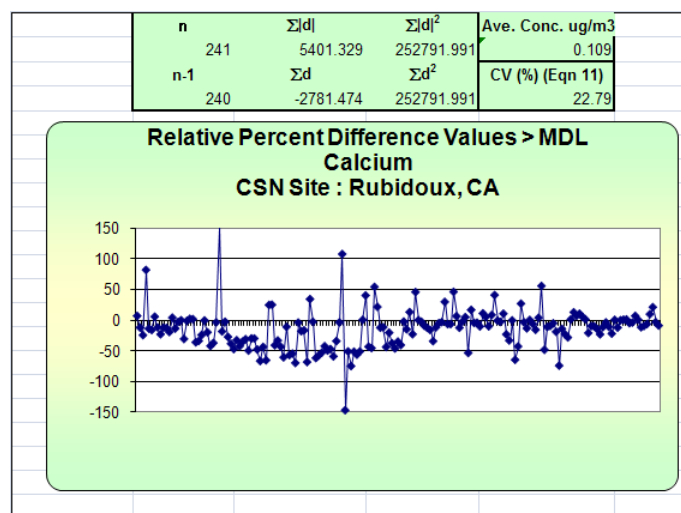
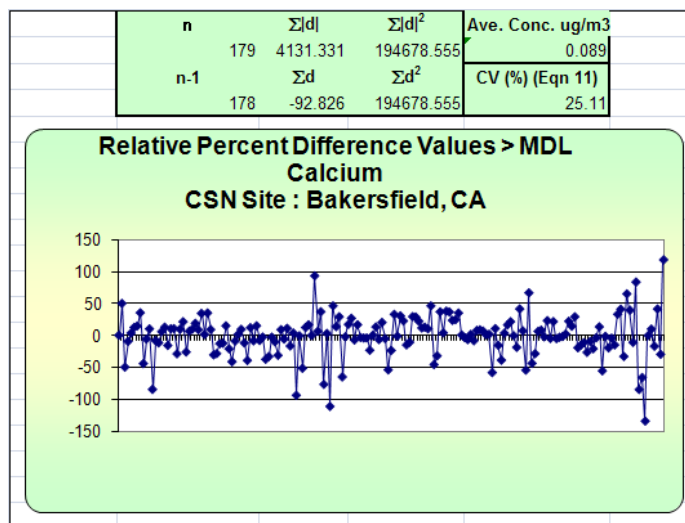
Graphs of Relative Percent Difference of Collocated CSN Data by Parameter and Site

Data set from 2007 – 2010 where values from the routine and collocated samplers were greater than the average MDL. Data was assessed using the Data Assessment Statistical Calculator (DASC). Some statistical summations are used in the derivation of the overall coefficient of variation and are an artifact of the output.

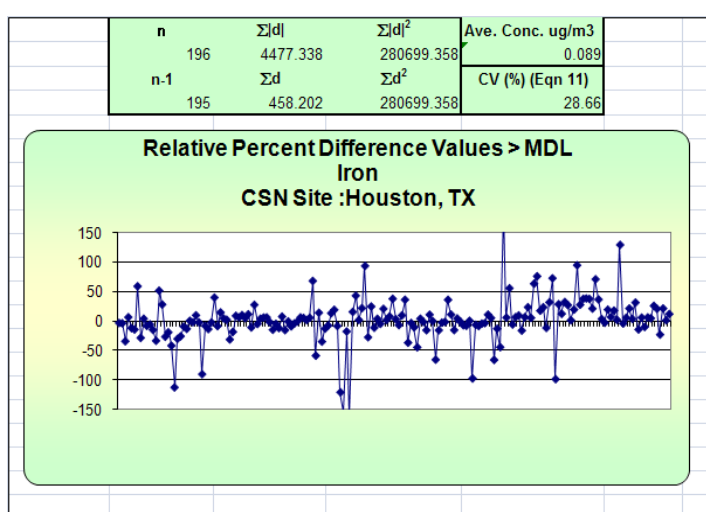
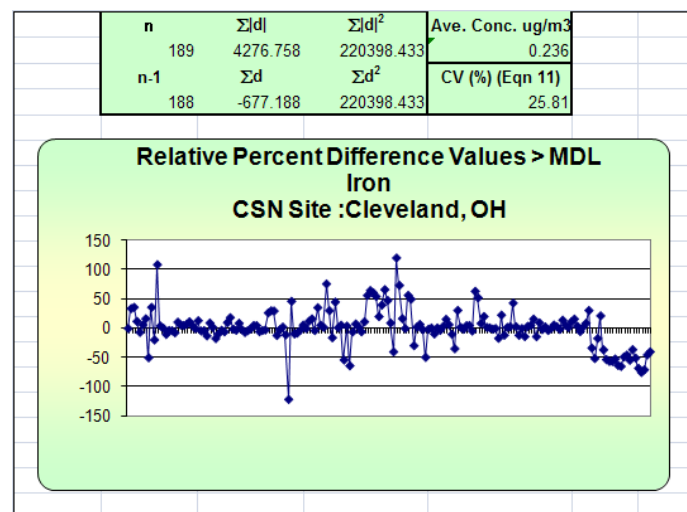
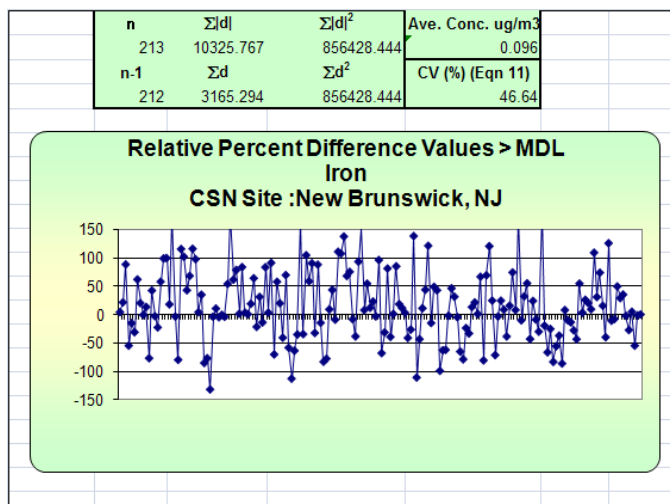
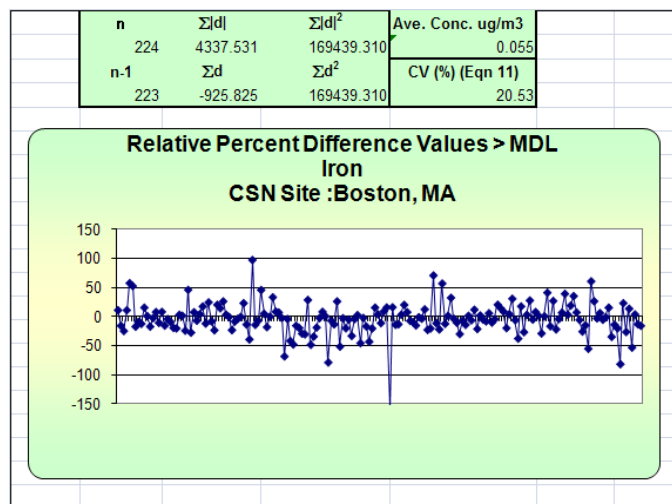
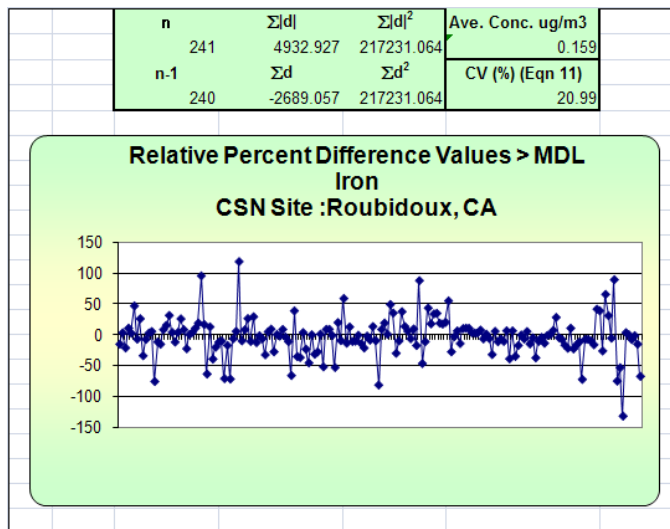
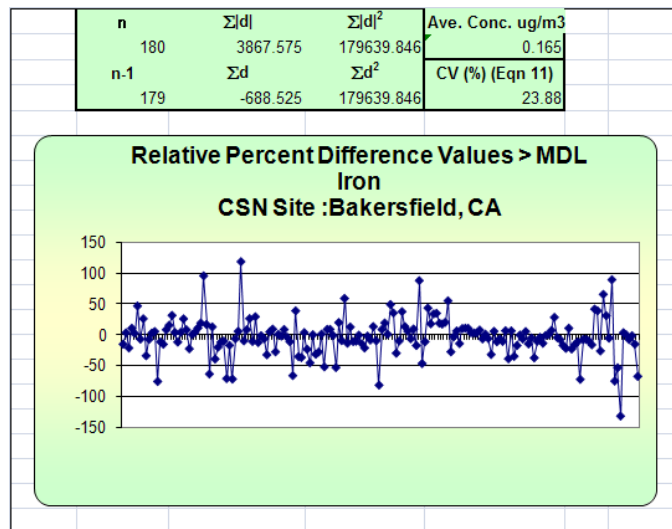
Collocated CSN Precision Estimates for Data Greater than the MDL- Parameter Aluminum



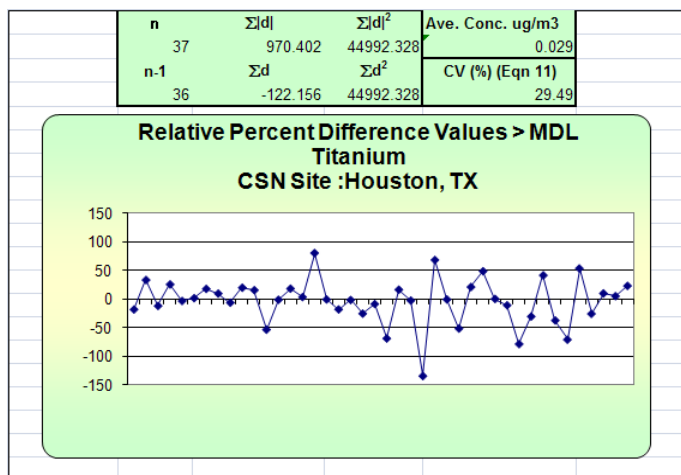
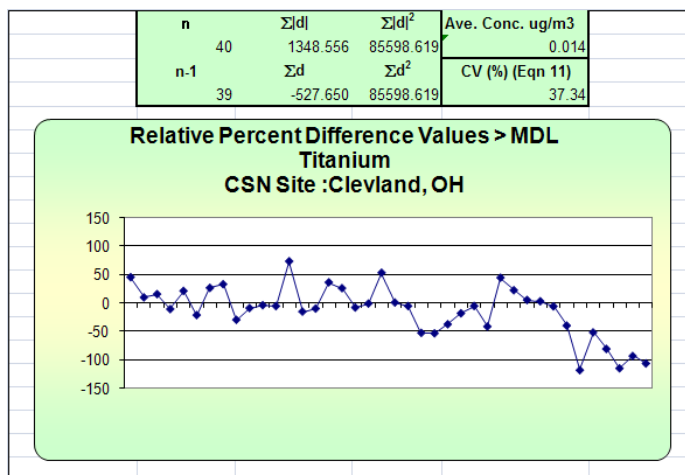
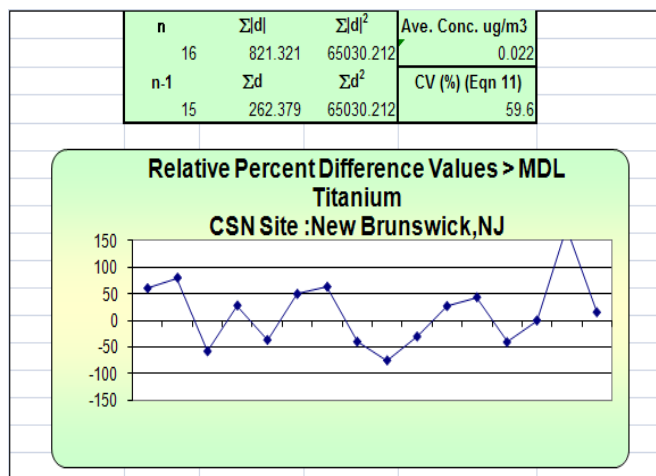
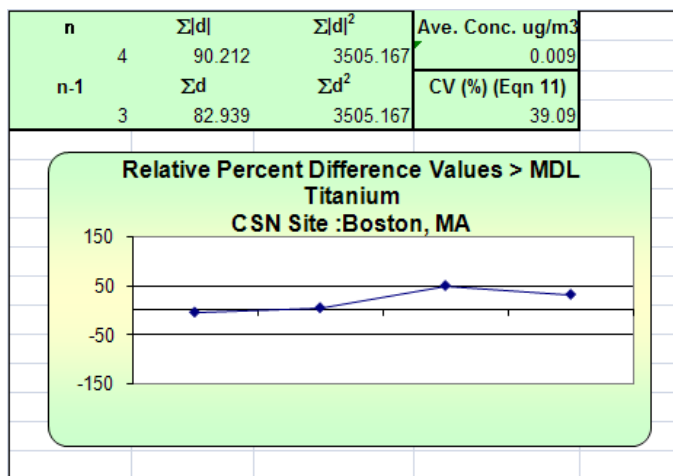
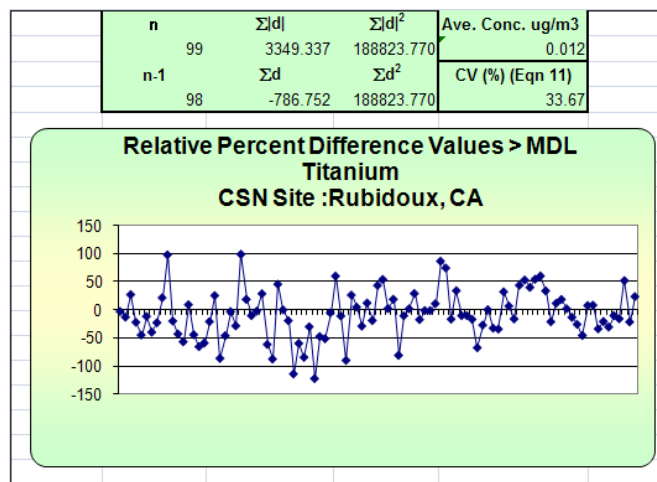
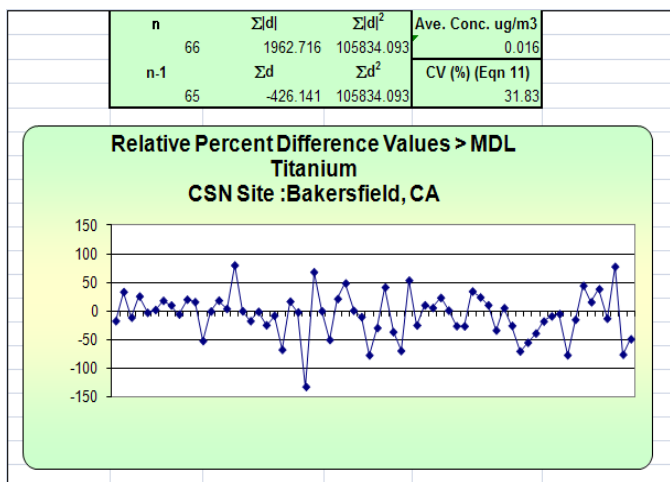
Collocated CSN Precision Estimates for Data Greater than the MDL – Calcium



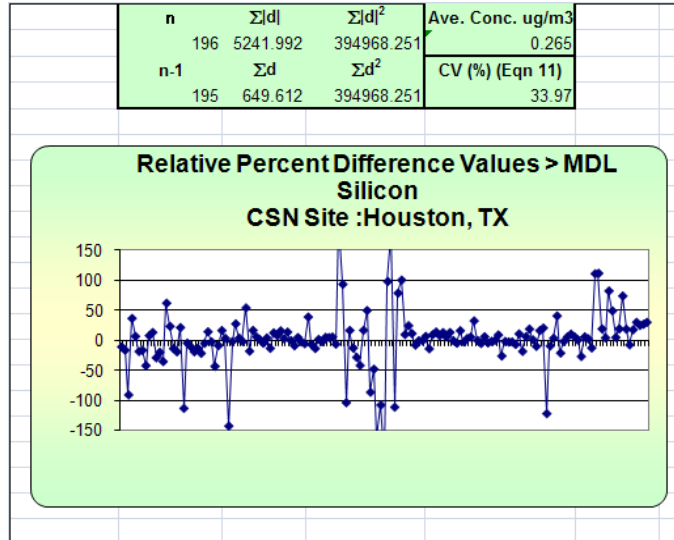
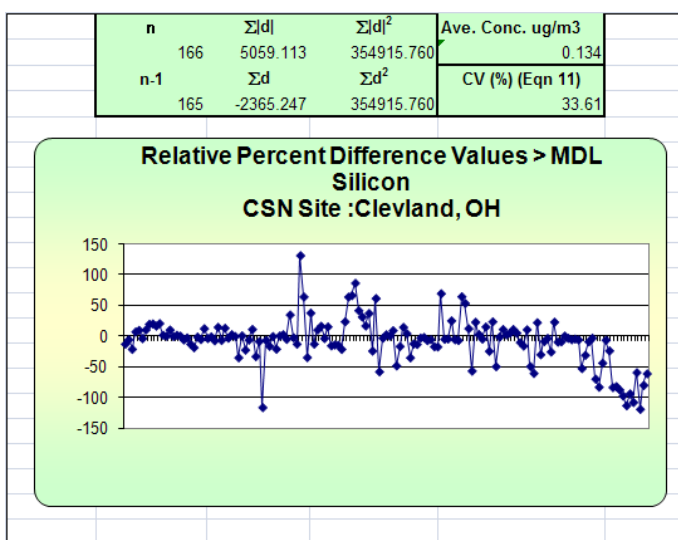
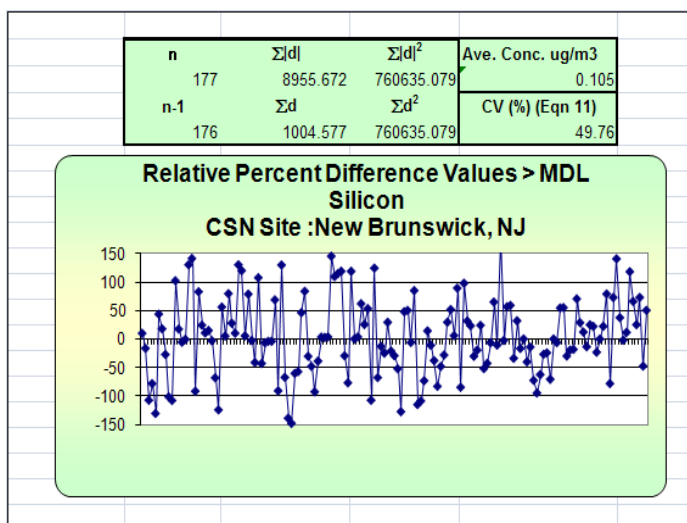
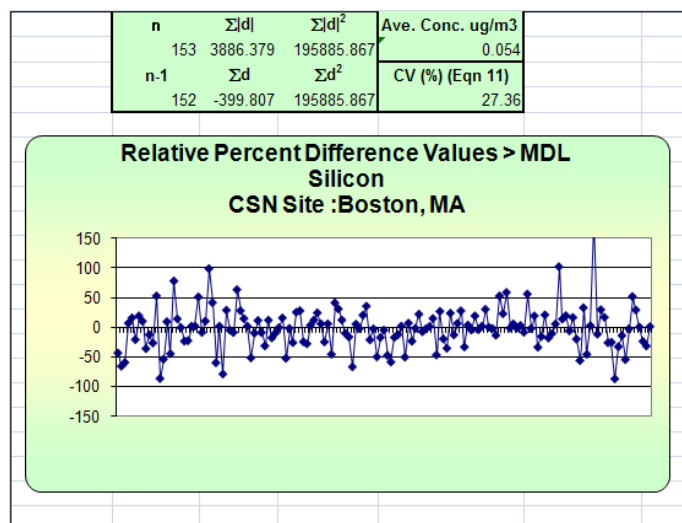
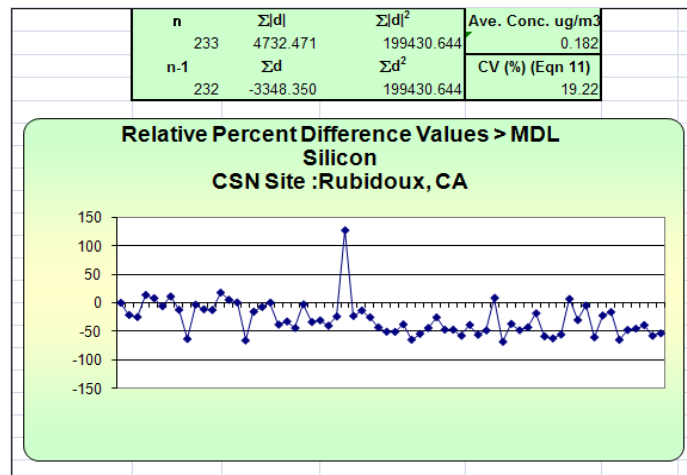
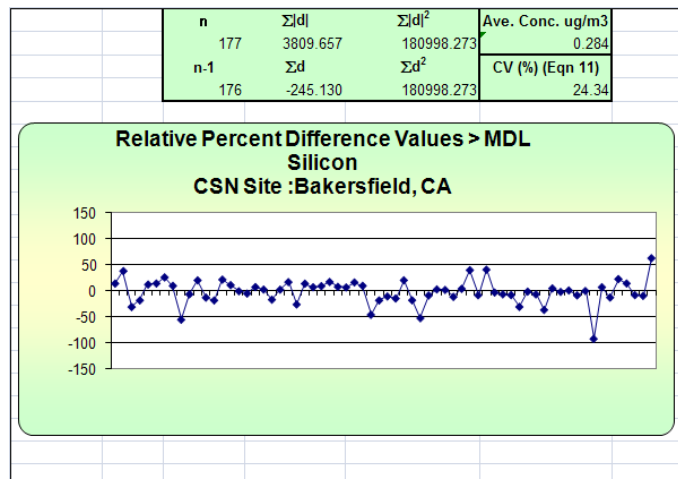
Collocated CSN Precision Estimates for Data Greater than the MDL – Iron



Collocated CSN Precision Estimates for Data Greater than the MDL - Titanium



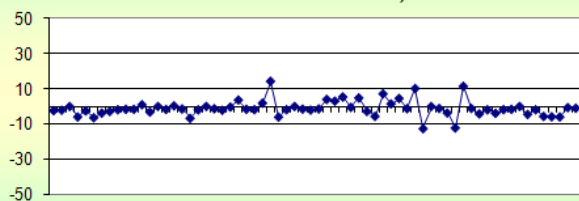
Collocated CSN Precision Estimates for Data Greater than the MDL -Silicon



Collocated CSN Precision Estimates for Data Greater than the MDL - Nitrate

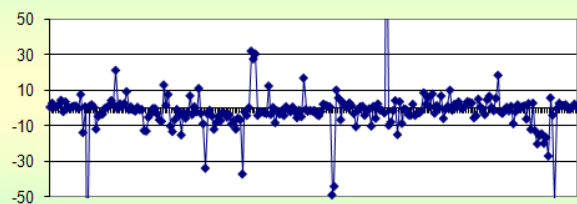
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181	1123.725	46101.282	6.692
n-1	Σd	Σd^2	CV (%) (Eqn 11)
180	-23.828	46101.282	12.15

**Relative Percent Difference Values > MDL
Nitrate
CSN Site :Bakersfield, CA**



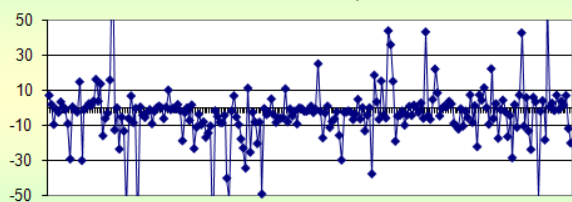
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242	1543.444	59120.625	6.585
n-1	Σd	Σd^2	CV (%) (Eqn 11)
241	-335.722	59120.625	11.73

**Relative Percent Difference Values > MDL
Nitrate
CSN Site :Rubidoux, CA**



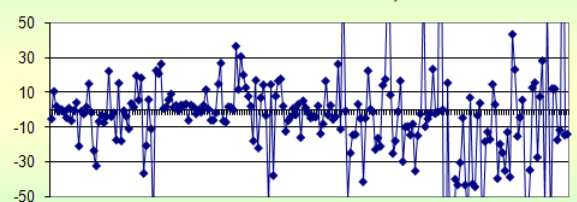
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224	2253.806	66234.984	0.940
n-1	Σd	Σd^2	CV (%) (Eqn 11)
223	-832.353	66234.984	12.68

**Relative Percent Difference Values > MDL
Nitrate
CSN Site :Boston, MA**



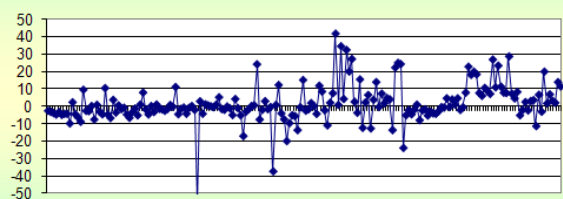
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208	3901.357	232214.184	1.294
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207	-750.434	232214.184	25.15

**Relative Percent Difference Values > MDL
Nitrate
CSN Site :New Brunswick, NJ**



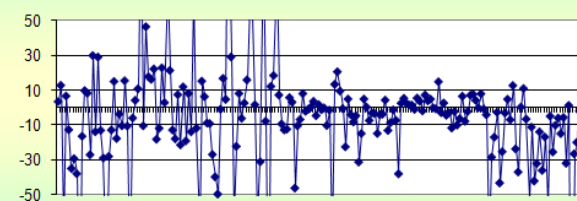
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190	1328.888	22632.715	2.354
n-1	Σd	Σd^2	CV (%) (Eqn 11)
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**Relative Percent Difference Values > MDL
Nitrate
CSN Site :Cleveland, OH**

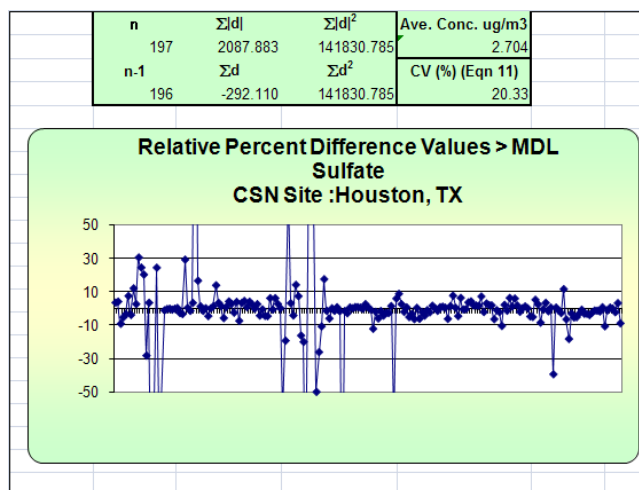
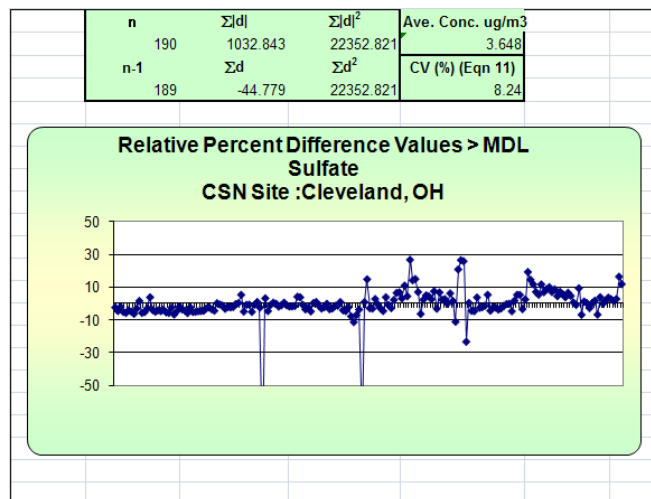
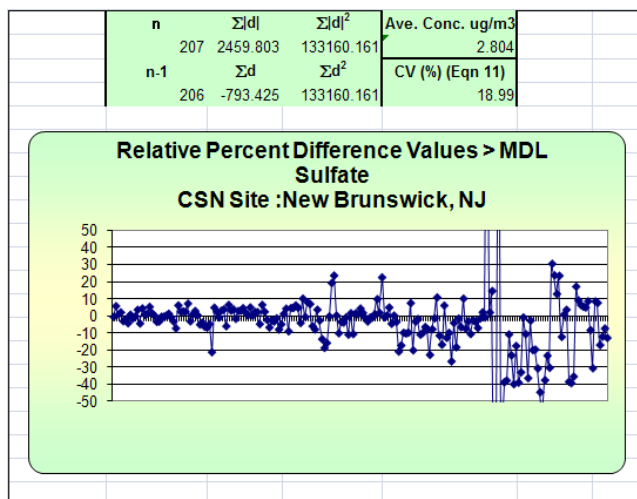
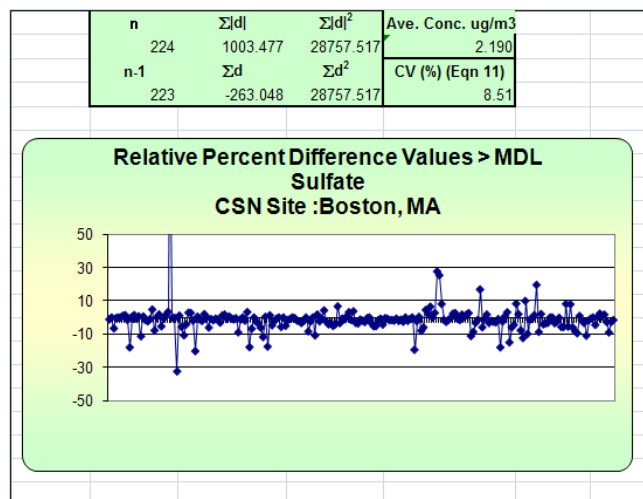
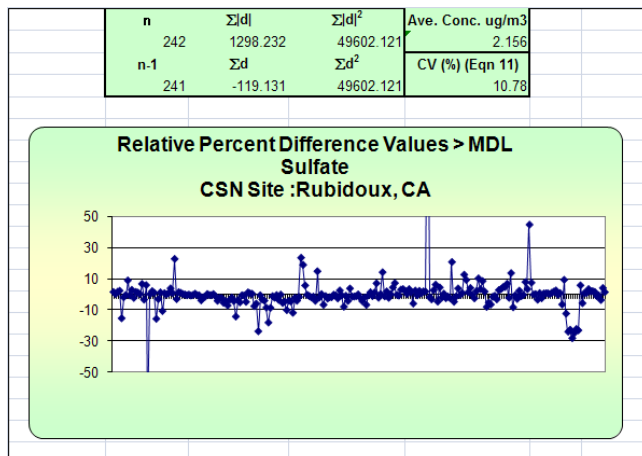
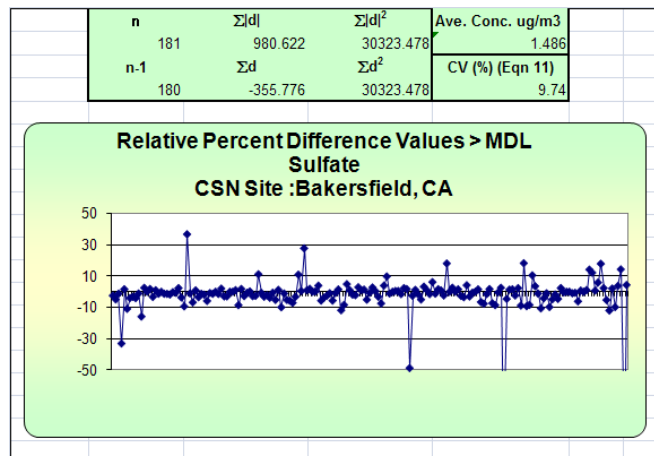


n	$\Sigma d $	$\Sigma d ^2$	Ave. Conc. ug/m3
198	4015.011	231360.108	0.755
n-1	Σd	Σd^2	CV (%) (Eqn 11)
197	-1329.600	231360.108	25.43

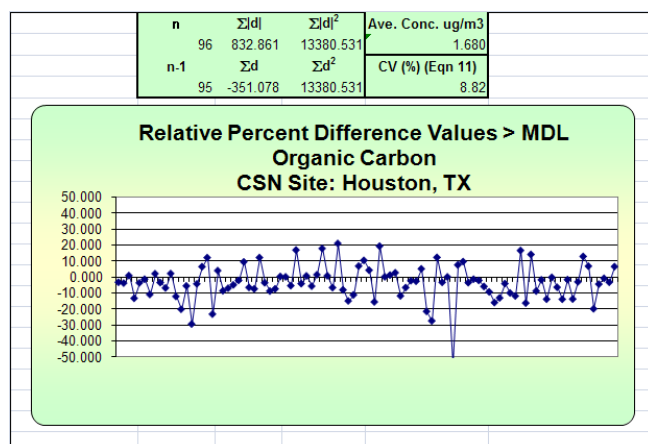
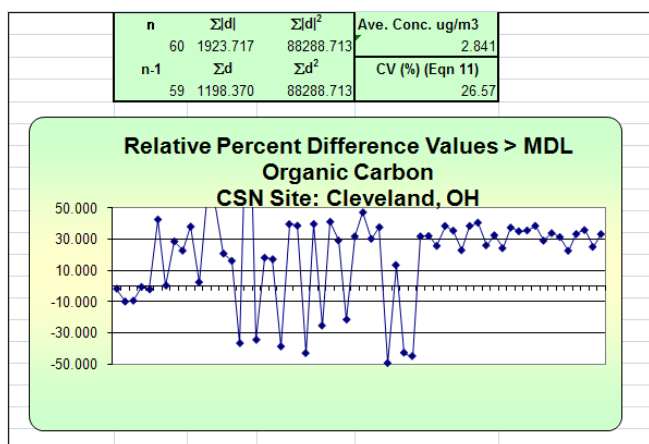
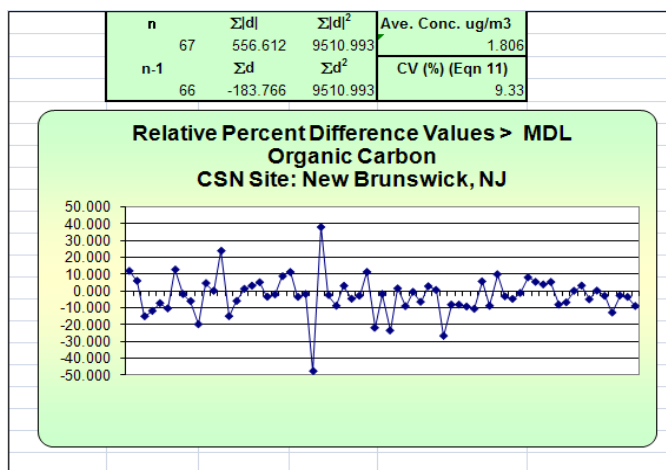
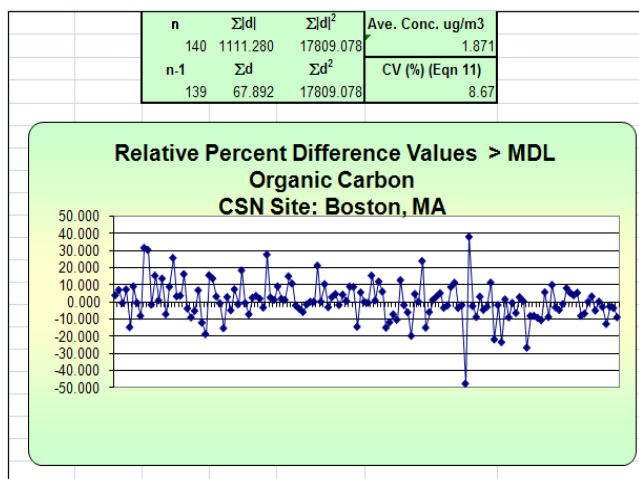
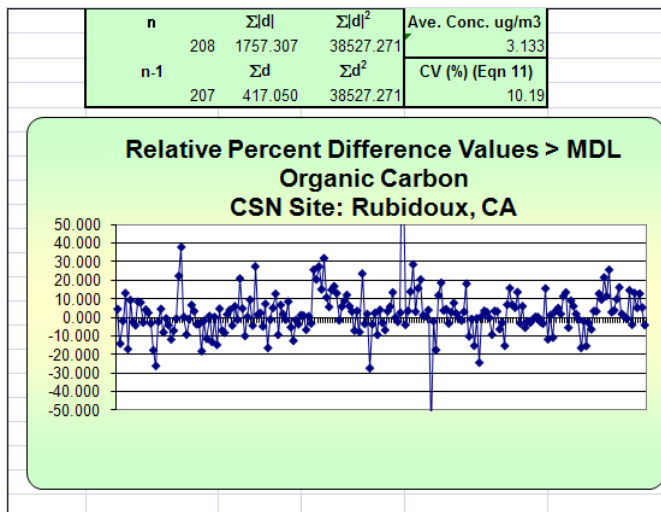
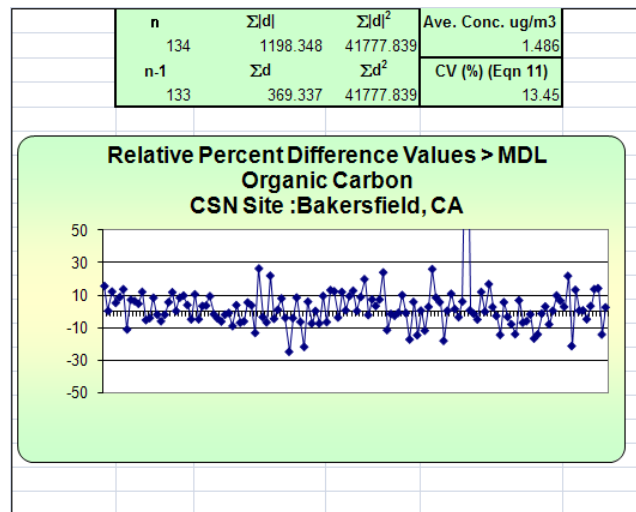
**Relative Percent Difference Values > MDL
Nitrate
CSN Site :Houston, TX**



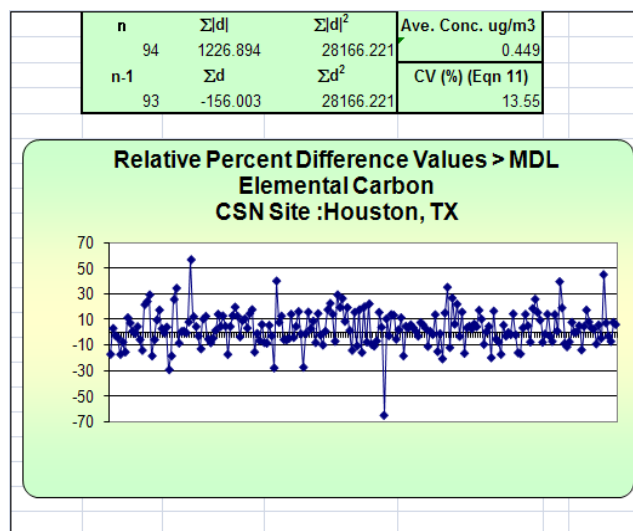
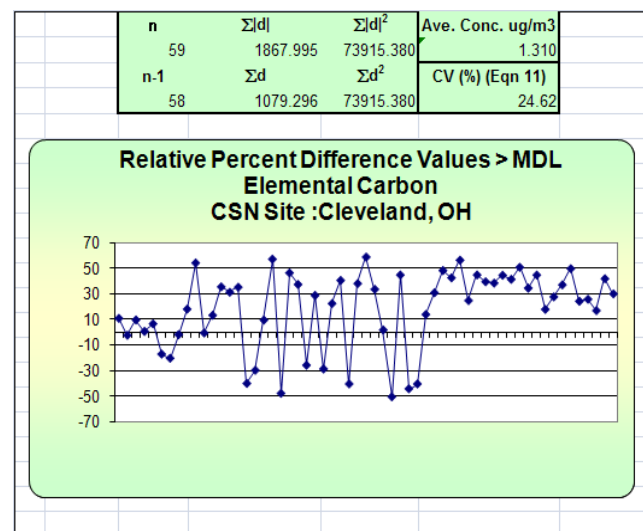
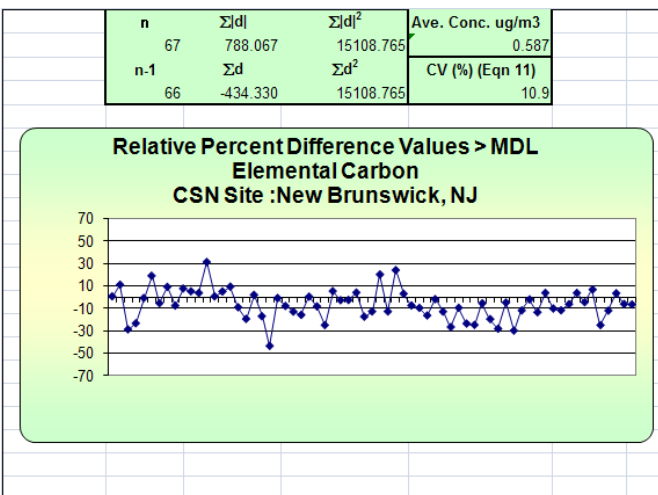
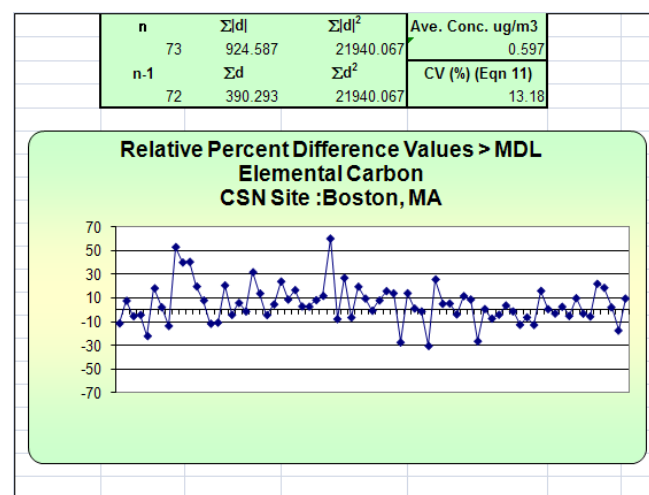
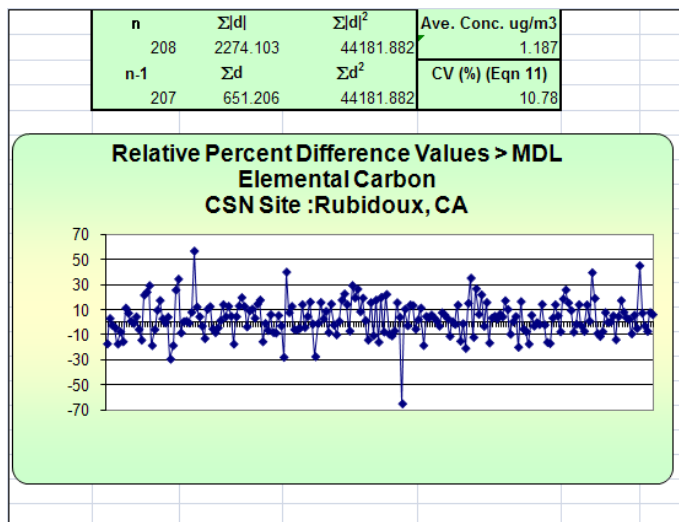
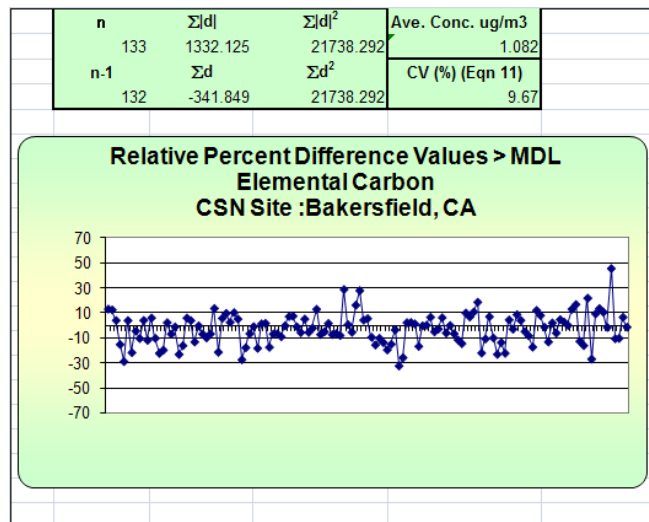
Collocated CSN Precision Estimates for Data Greater than the MDL - Sulfate



Collocated CSN Precision Estimates for Data Greater than the MDL - Organic Carbon



Collocated CSN Precision Estimates for Data Greater than the MDL - Elemental Carbon

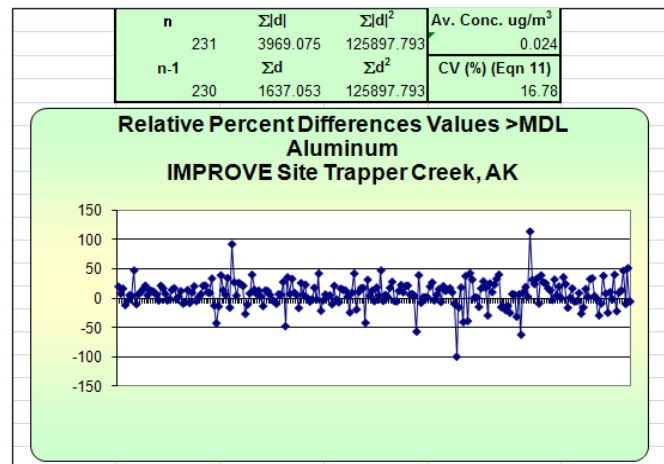
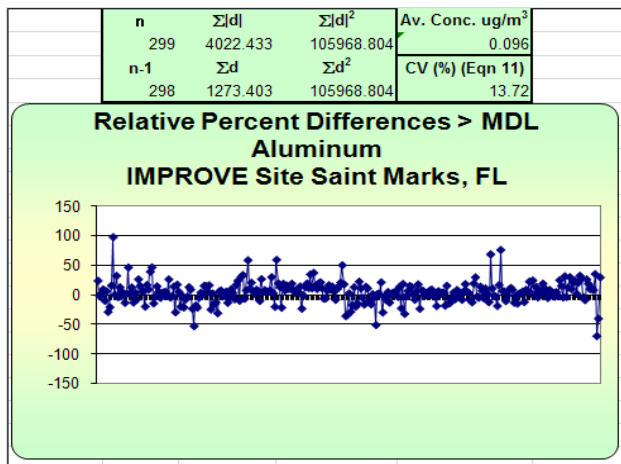
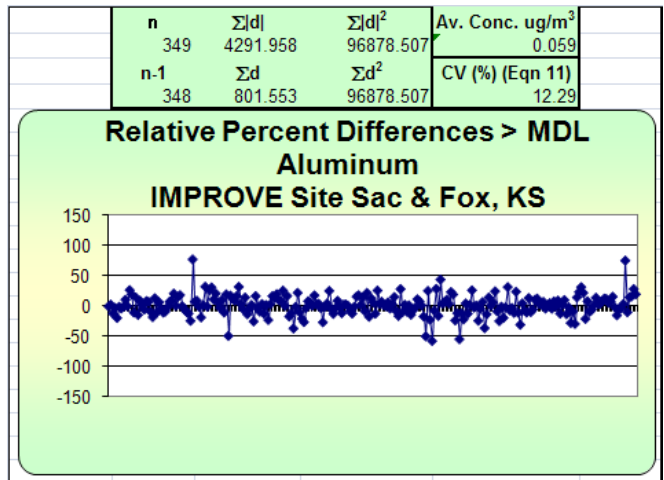
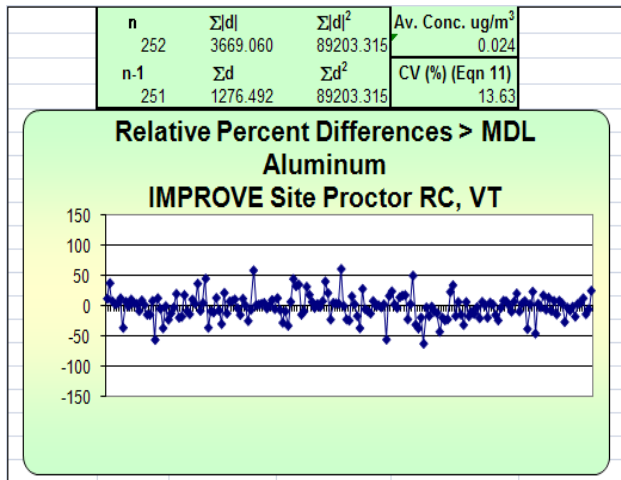
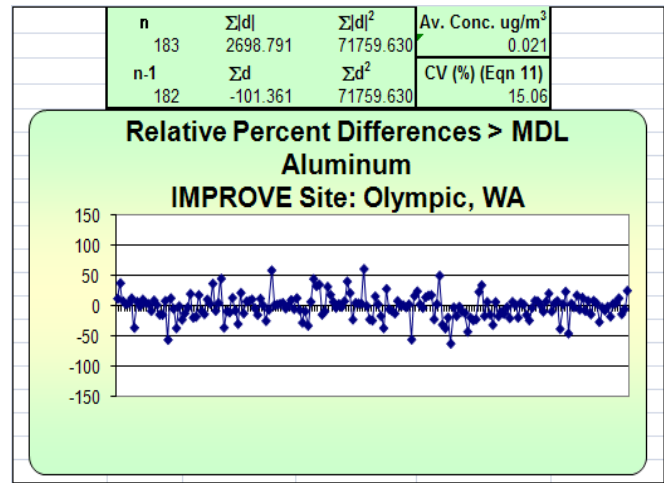
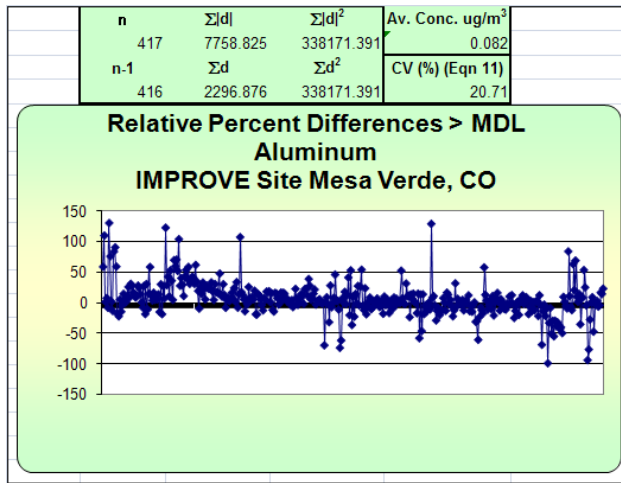


Appendix B

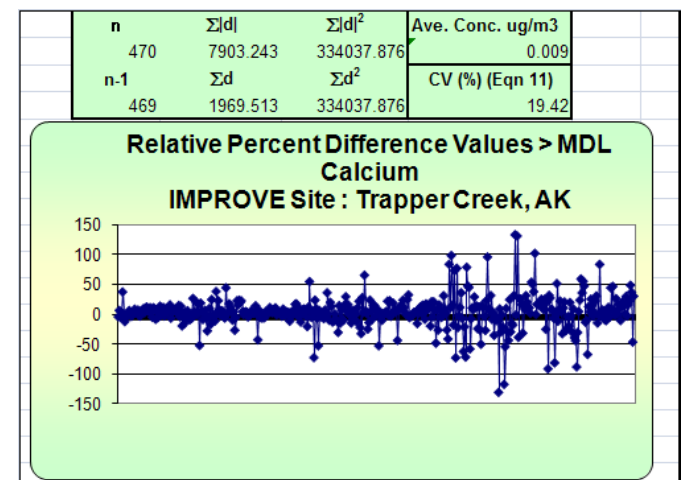
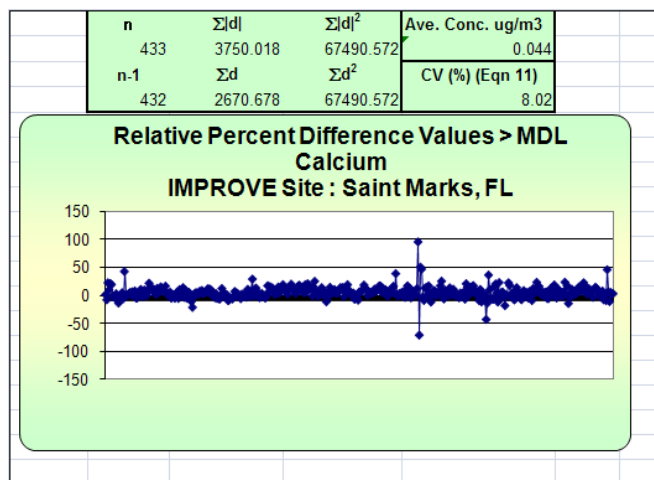
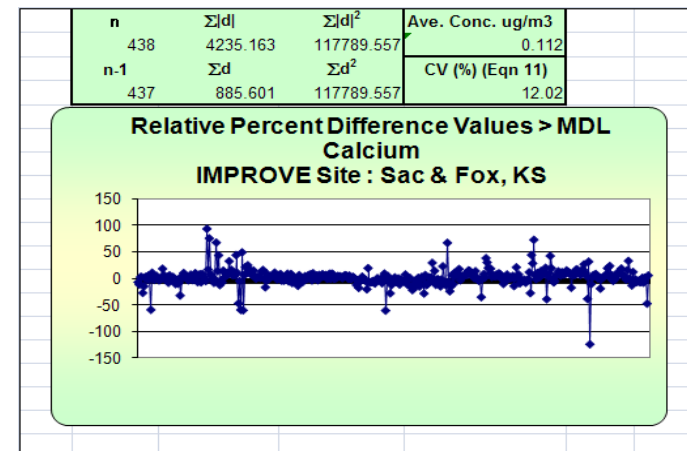
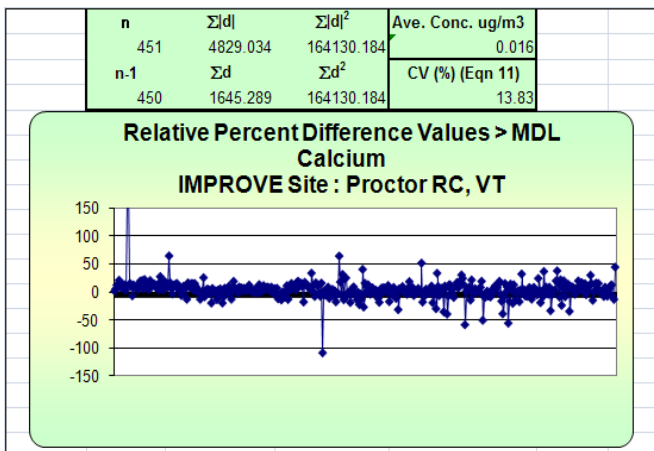
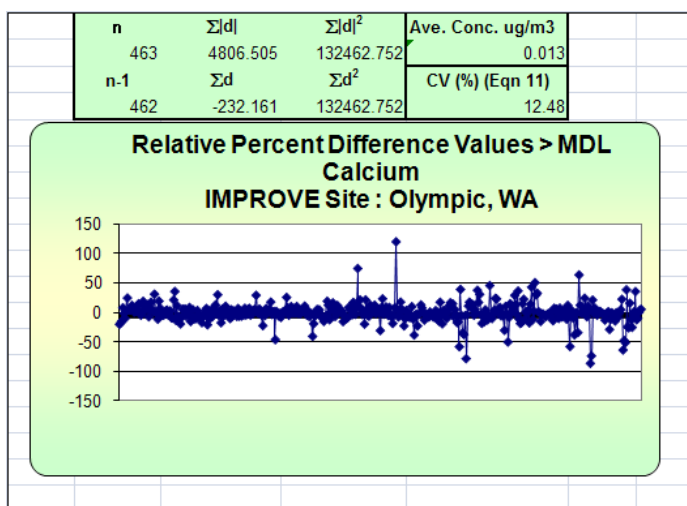
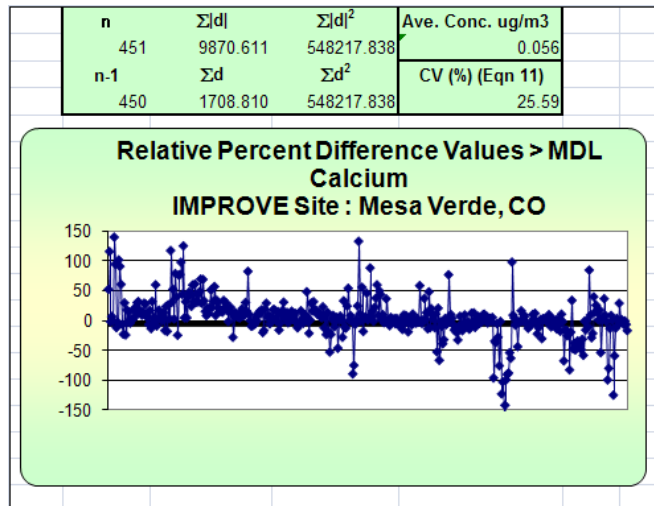
Graphs of Relative Percent Difference of Collocated IMPROVE Modules by Parameter and Site

Data set from 2006 – 2010 where values from the collocated sampler modules were greater than or equal to the average MDL. Data was assessed using the Data Assessment Statistical Calculator (DASC). Some statistical summations found above the graphs are used in the derivation of the overall coefficient of variation and are an artifact of the DASC output.

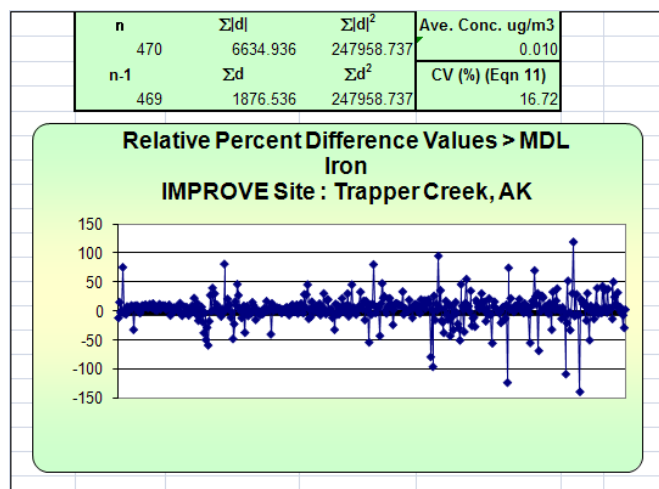
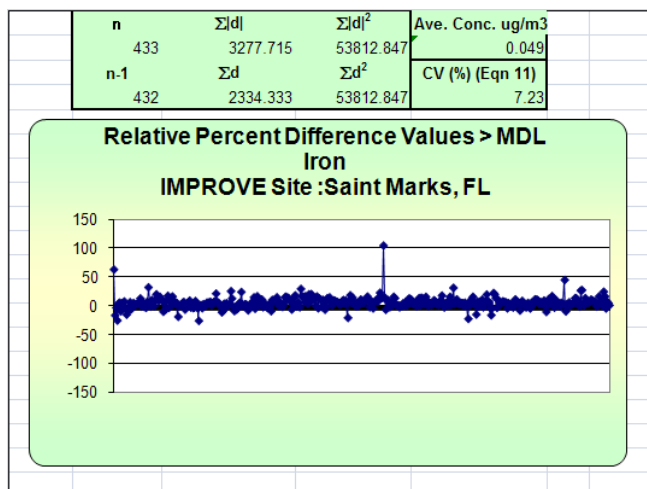
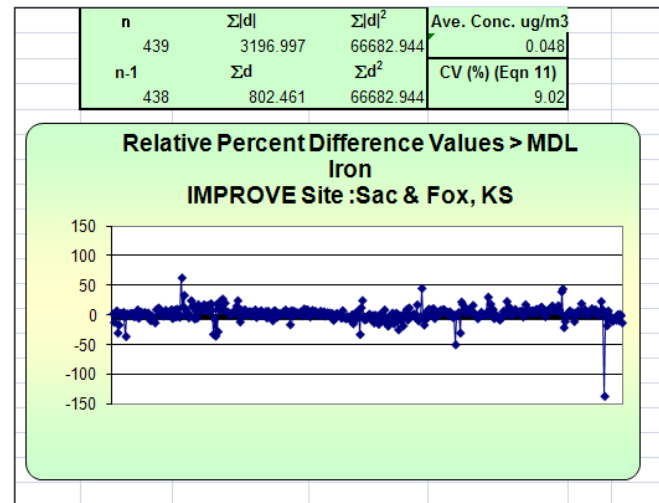
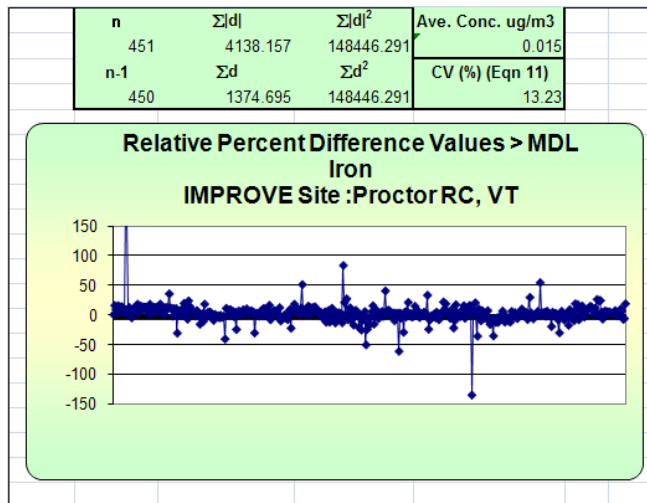
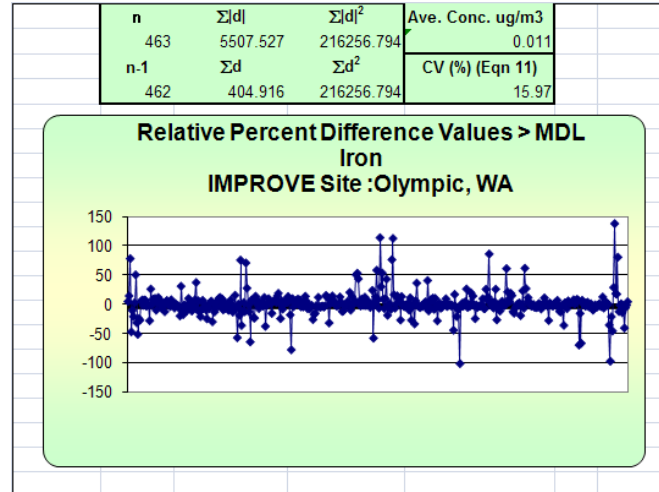
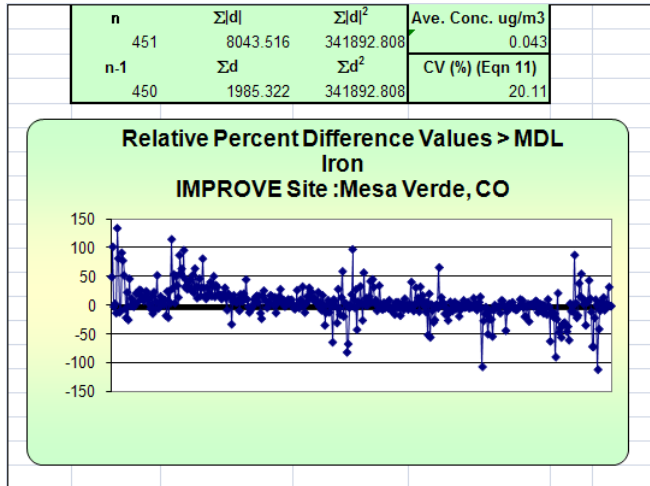
Collocated IMPROVE Precision Estimates for Data Greater than the MDL- Parameter Aluminum



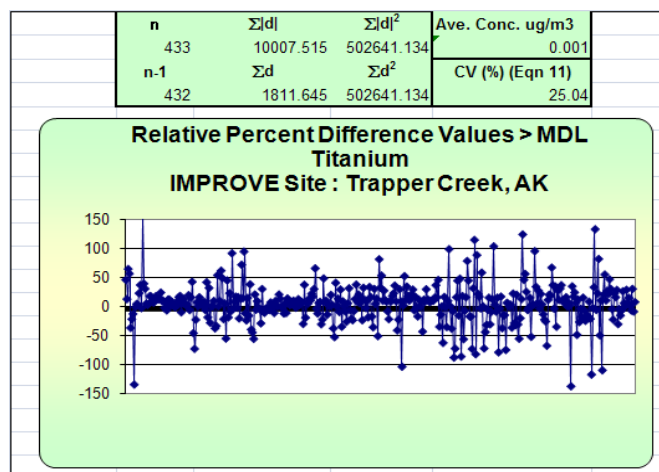
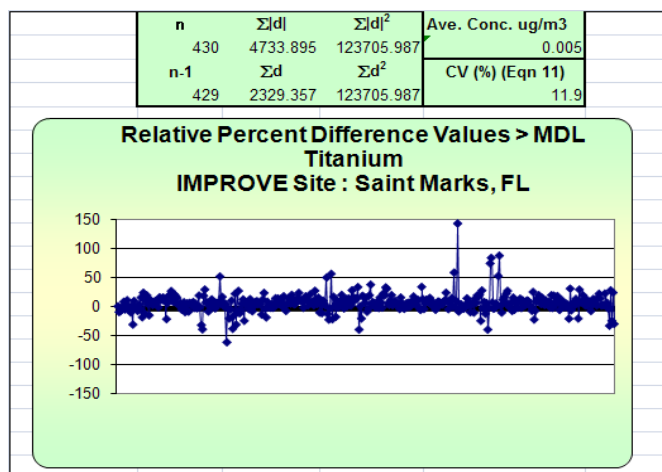
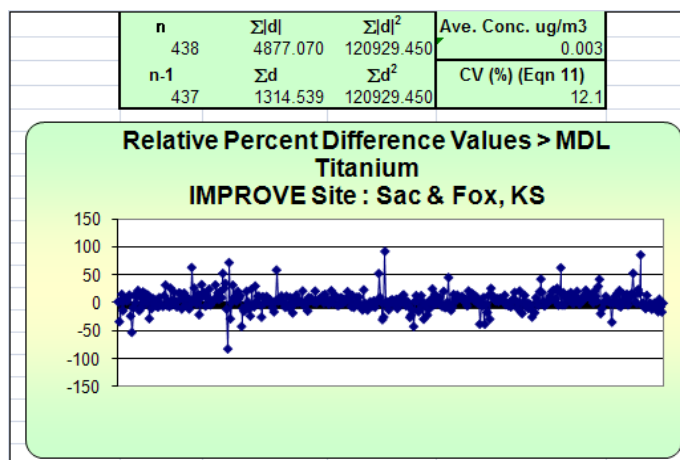
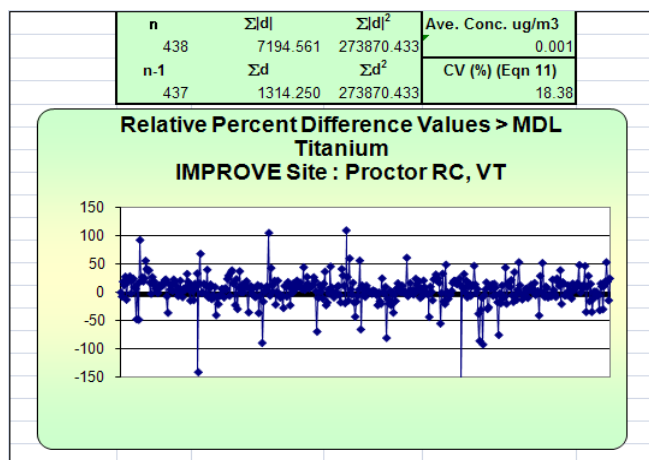
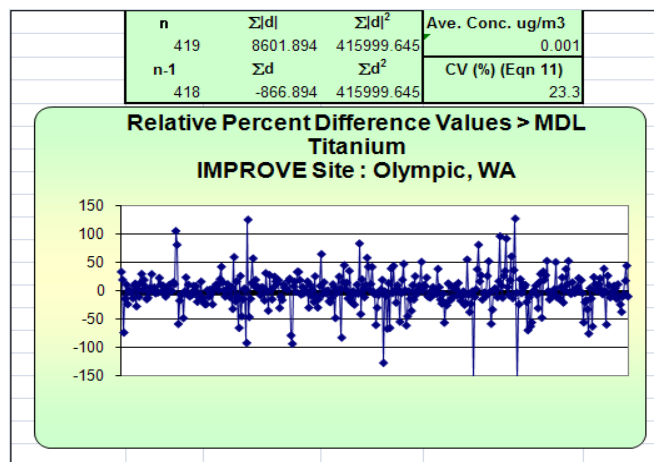
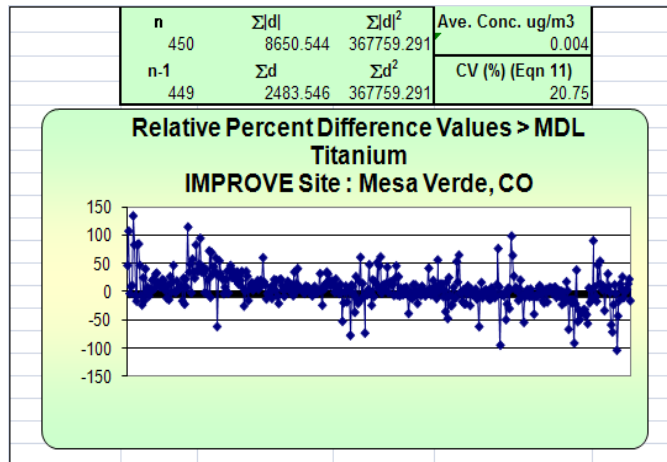
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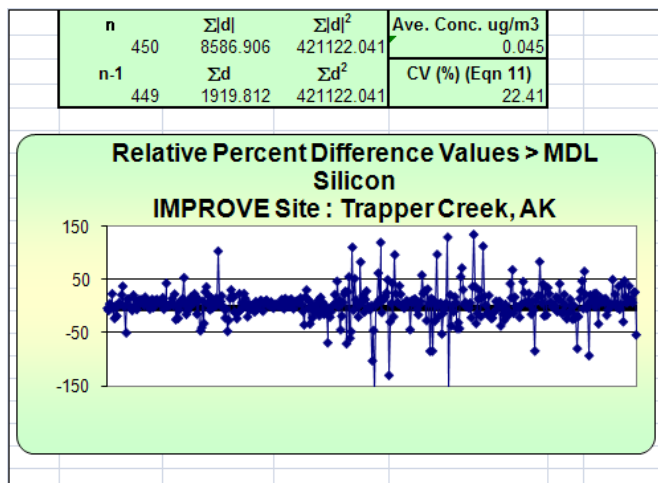
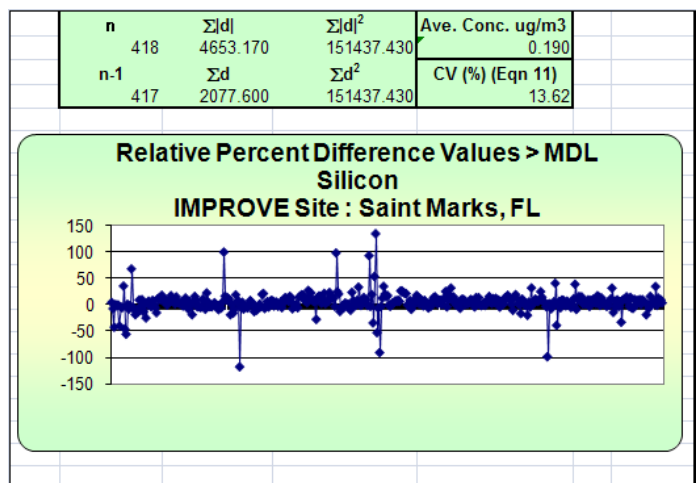
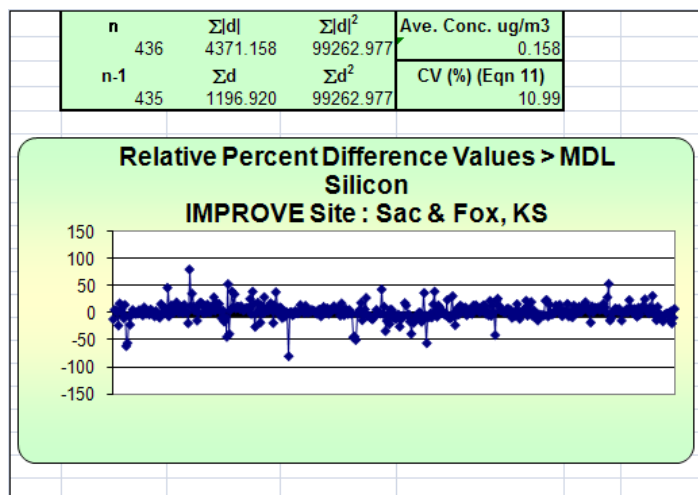
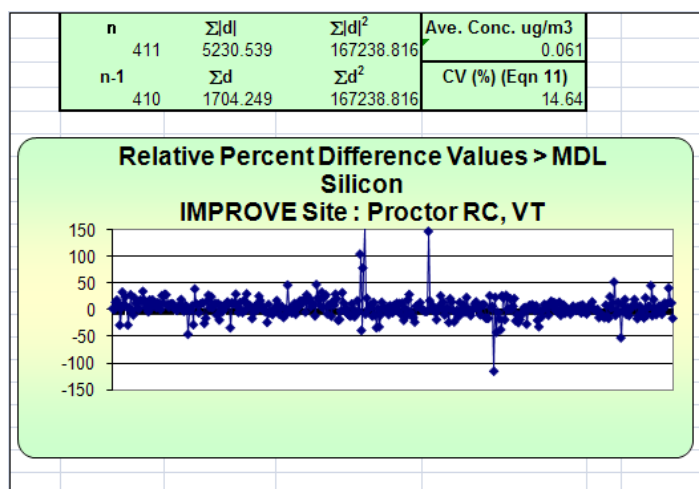
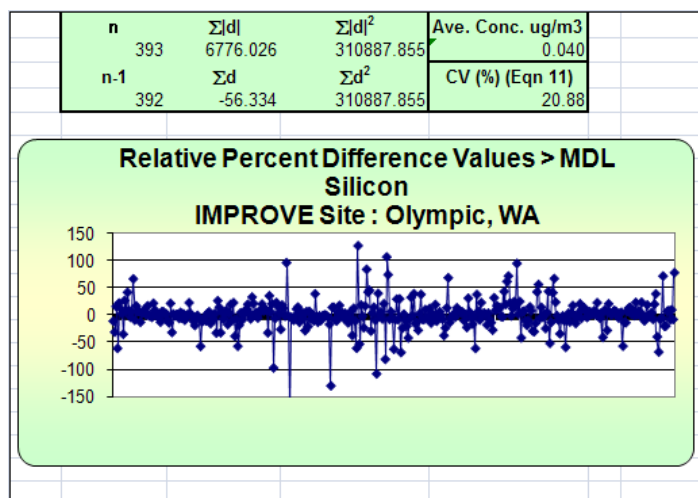
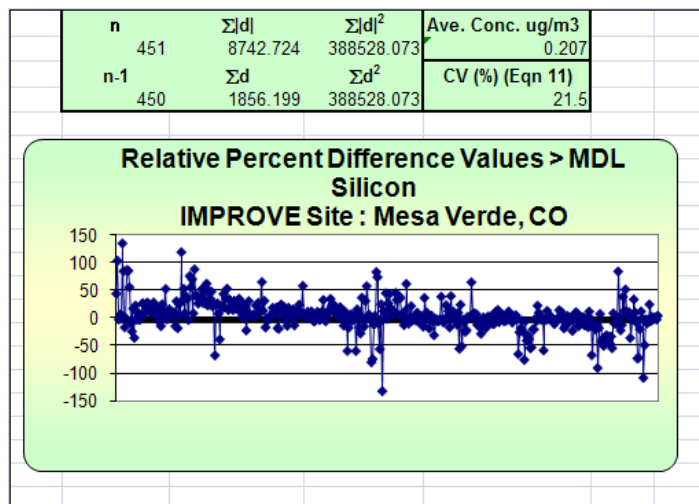
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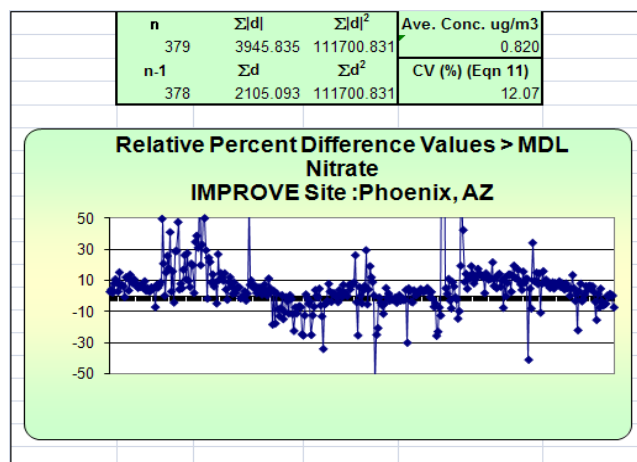
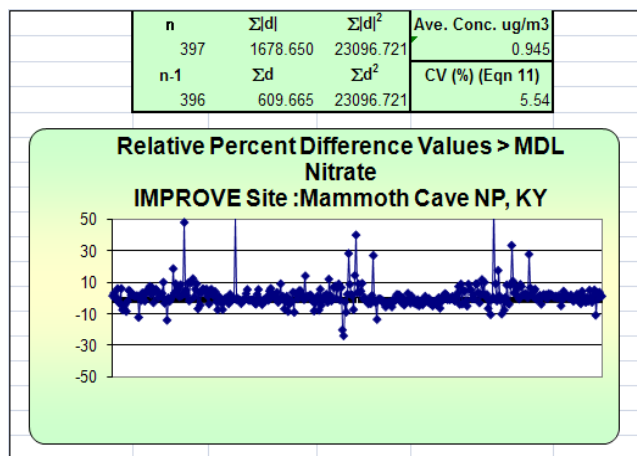
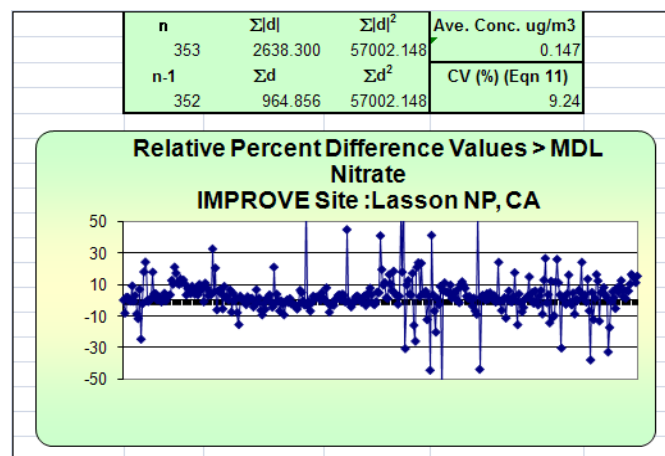
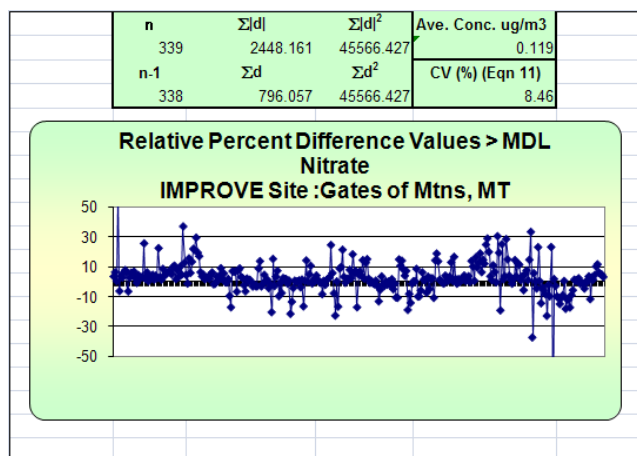
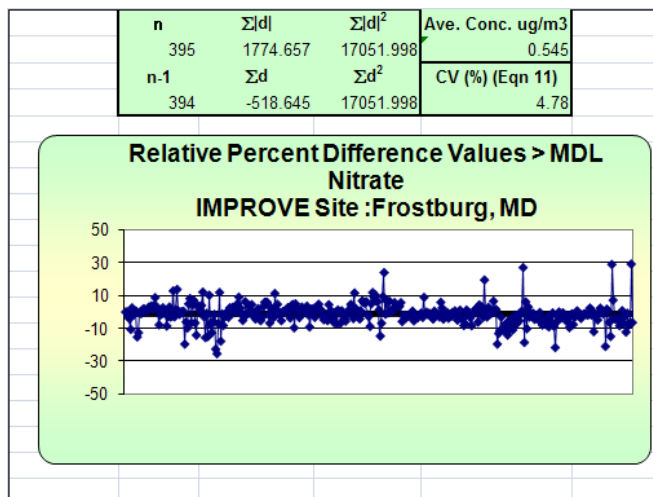
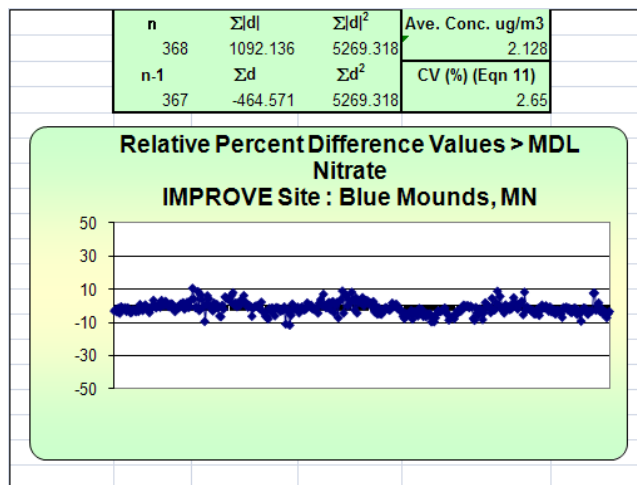
Collocated IMPROVE Precision Estimates for Data Greater than the MDL- Parameter Titanium



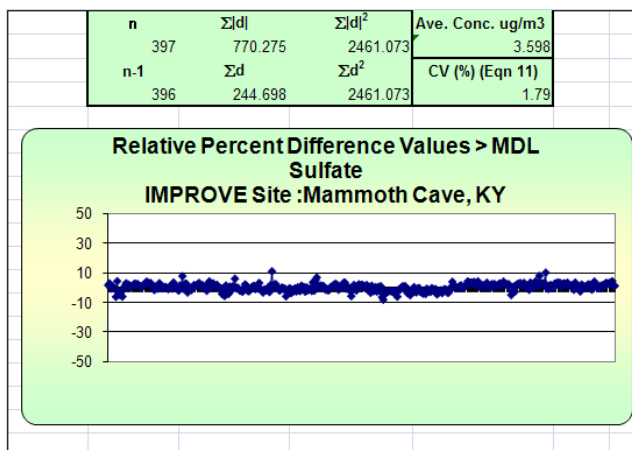
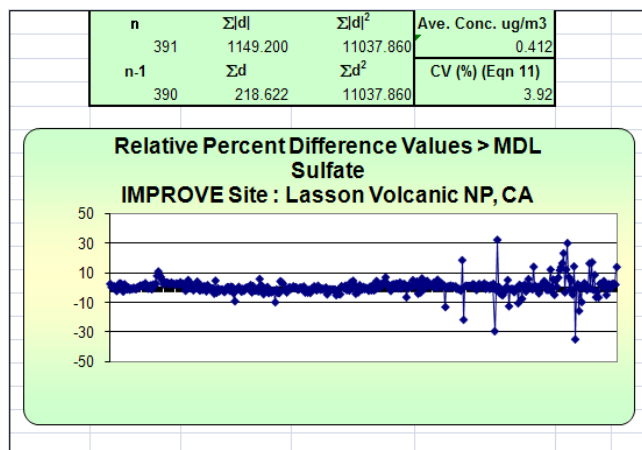
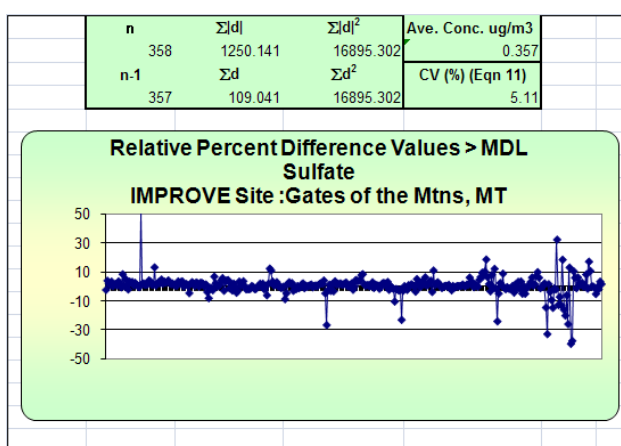
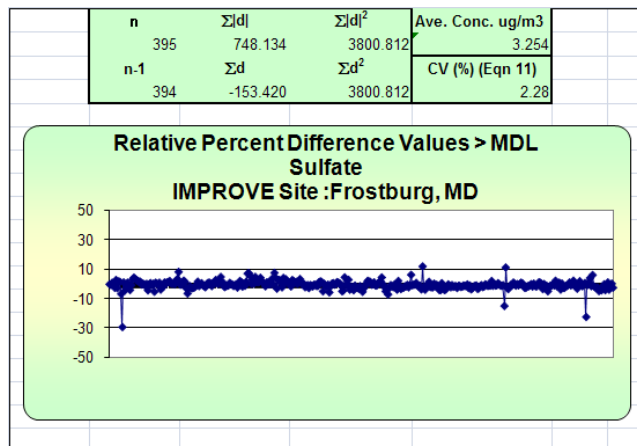
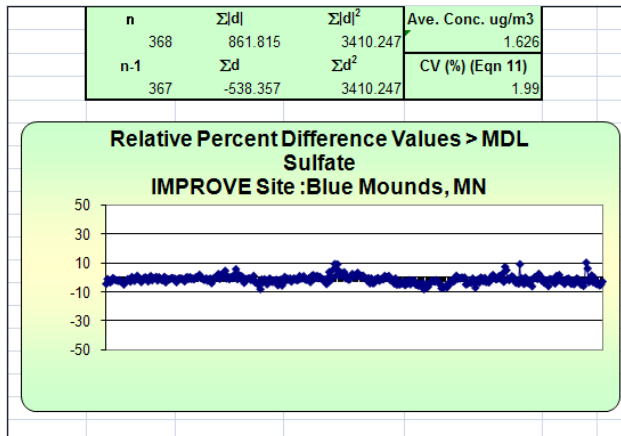
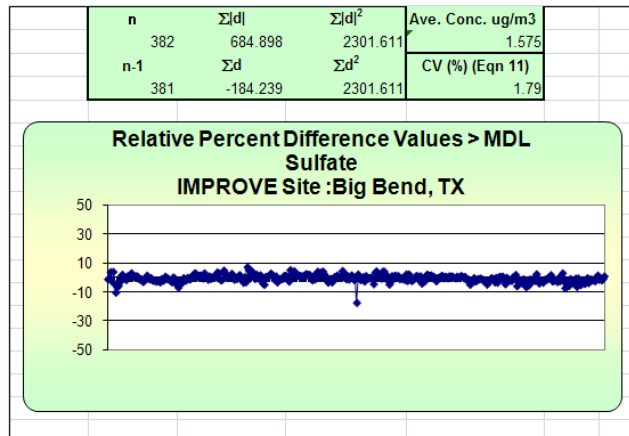
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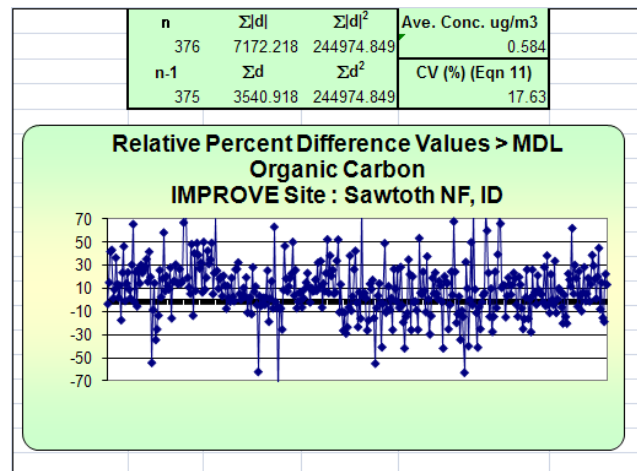
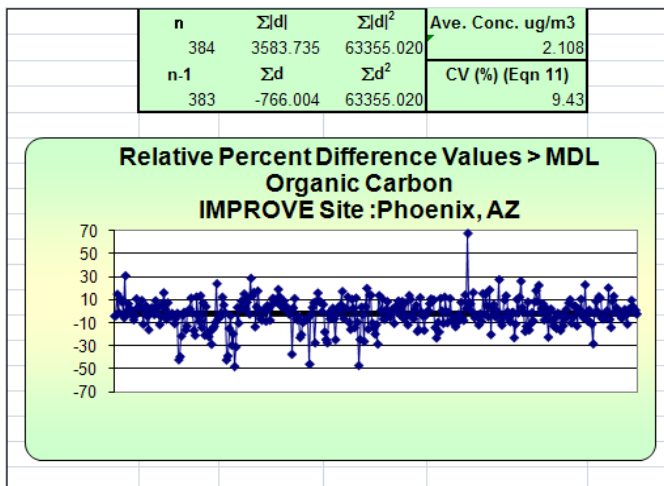
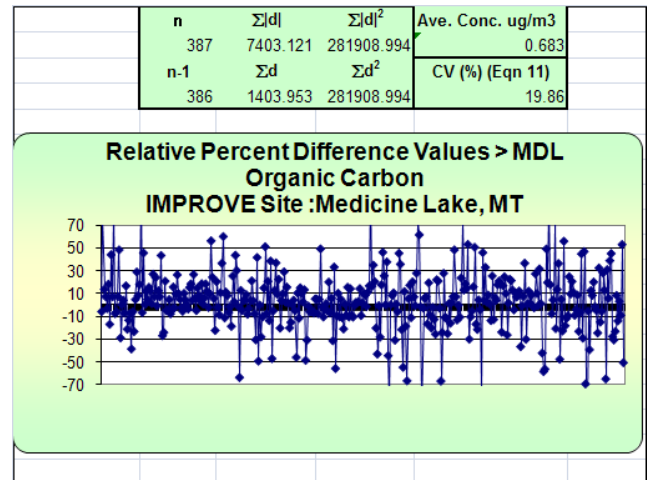
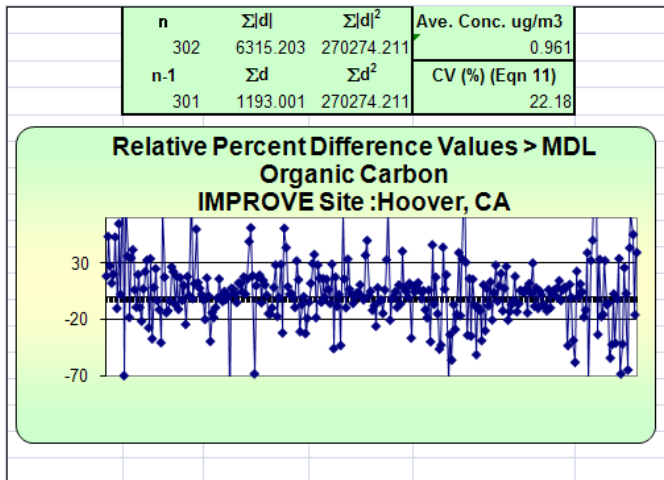
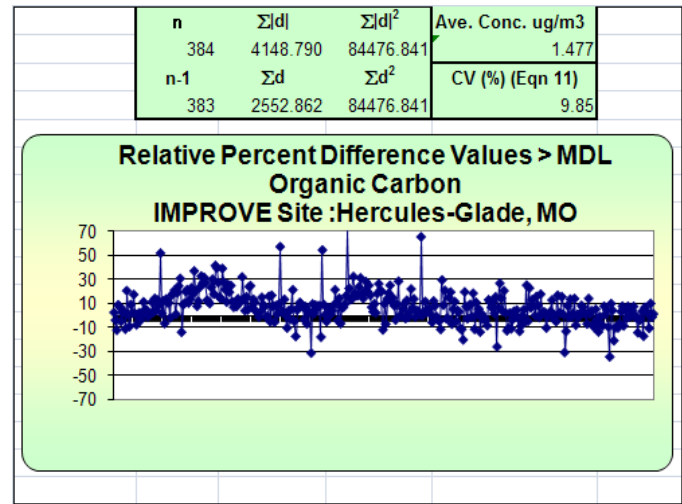
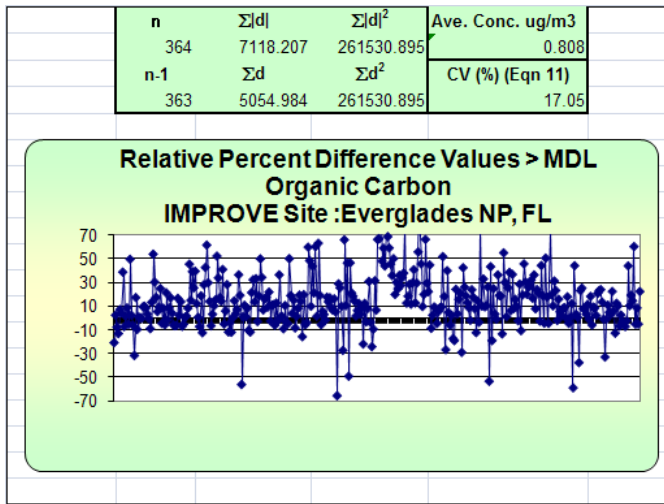
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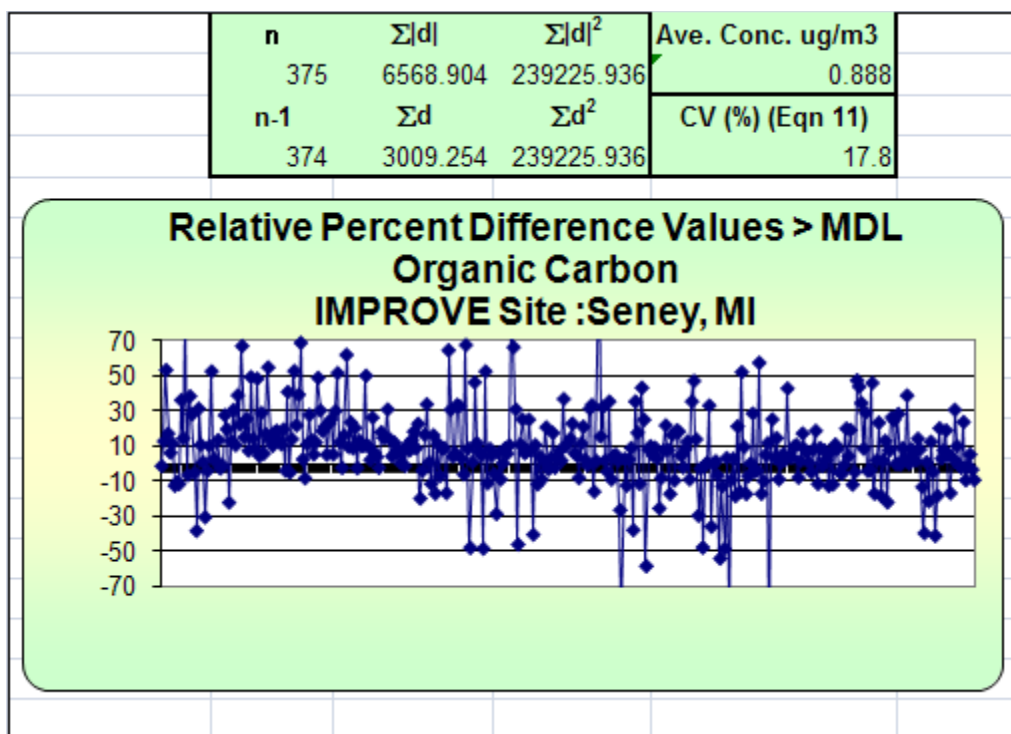
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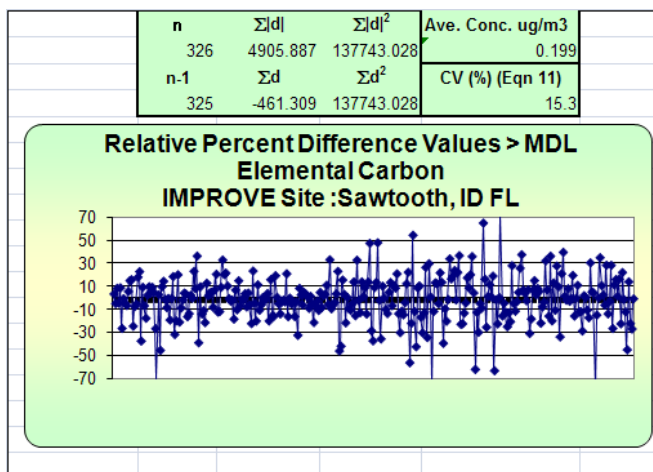
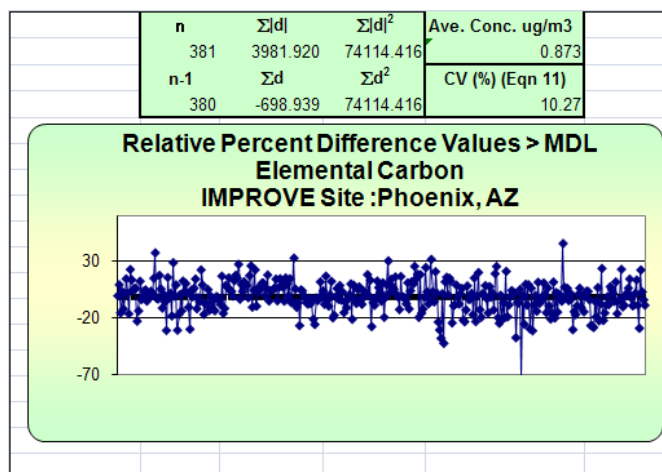
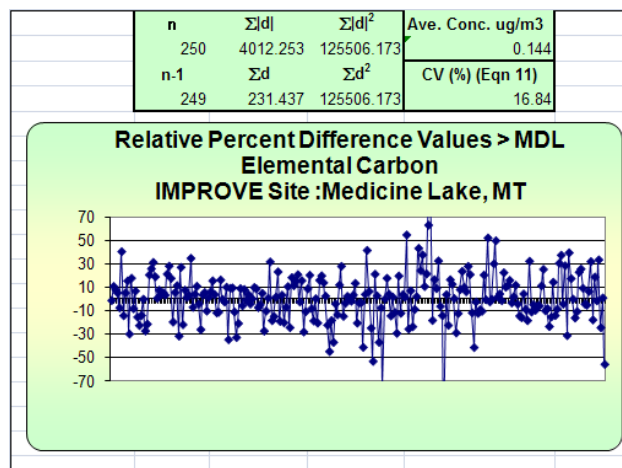
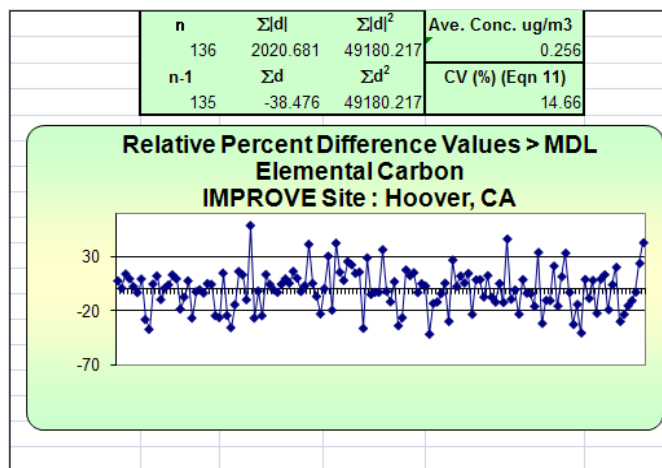
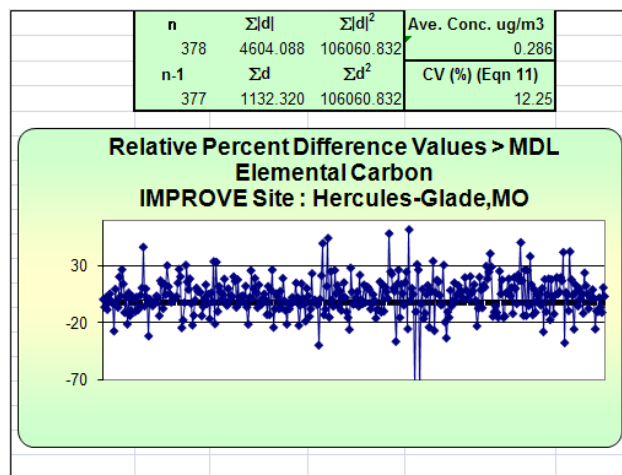
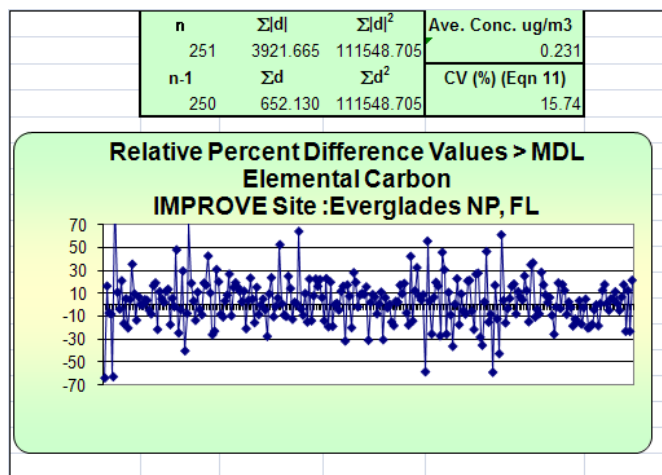
Collocated IMPROVE Precision Estimates for Data Greater than the MDL- Parameter Organic Carbon



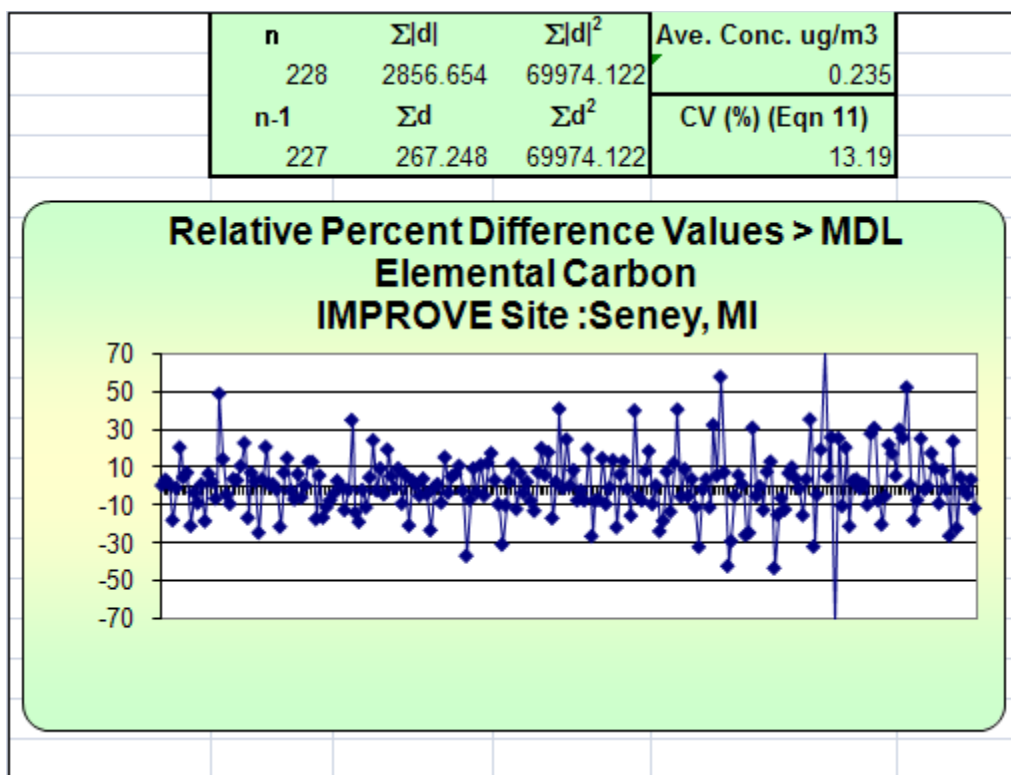
Collocated IMPROVE Precision Estimates for Data Greater than the MDL- Parameter Organic Carbon (Continued)



Collocated IMPROVE Precision Estimates for Data Greater than the MDL- Parameter Elemental Carbon

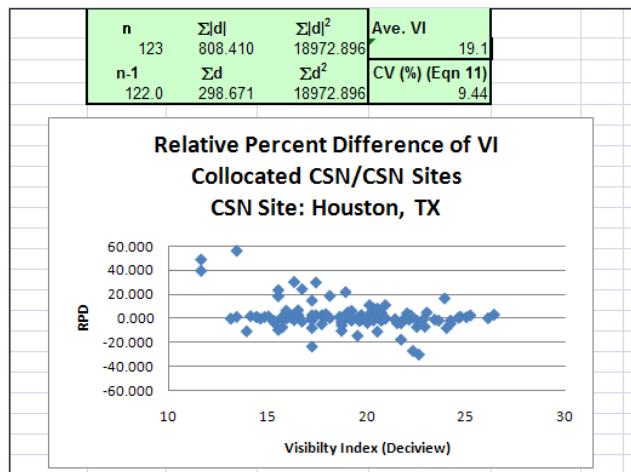
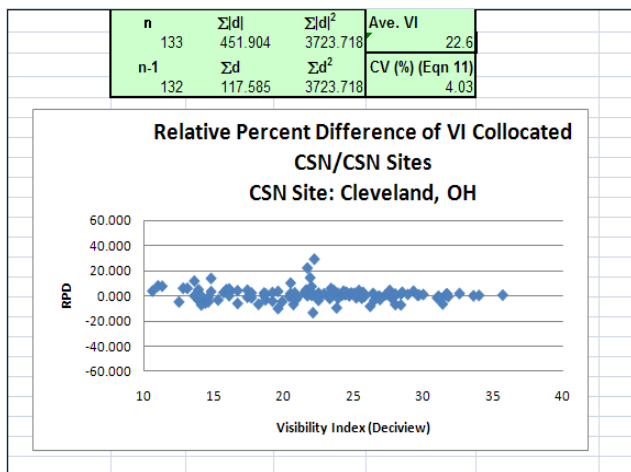
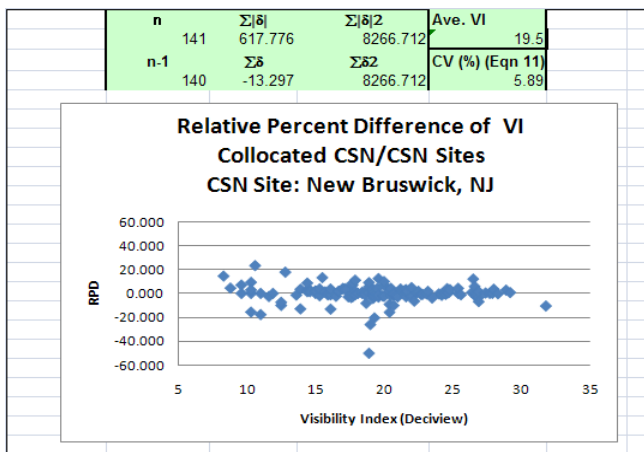
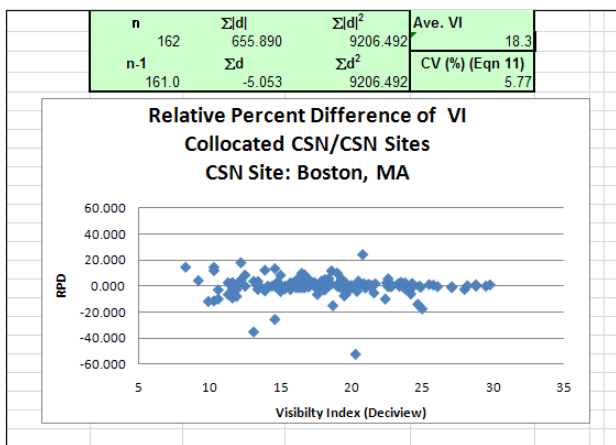
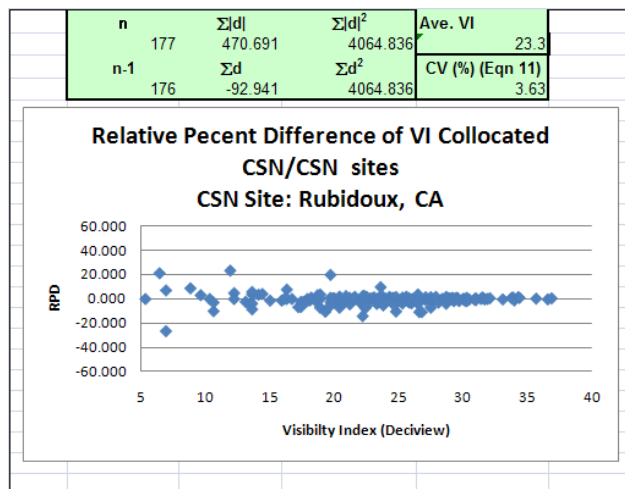
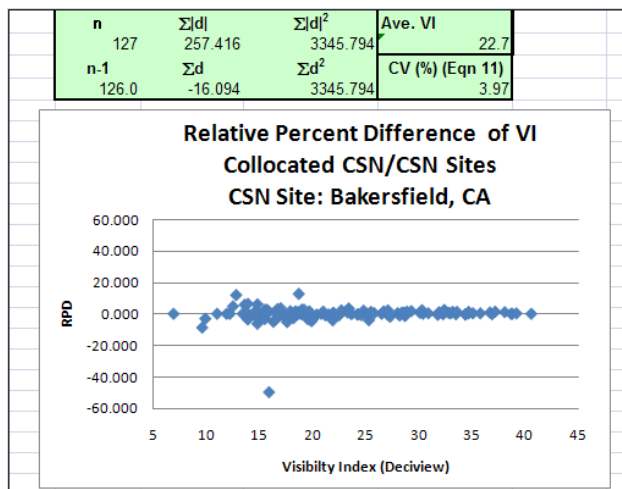


Collocated IMPROVE Precision Estimates for Data Greater than the MDL- Parameter Elemental Carbon (continued)



Appendix C

Relative Percent Difference and upper 90th Percentile Coefficient of Variation Estimates of Collocated Visibility Index (in Deciviews) from Sites with Two CSN Samplers



Measurement Uncertainty Evaluations at 10th Percentile Concentrations

Site: Bakerfield, CA		0-10 percentile		
n	Σ d	Σ d ²	Ave. VI	
12	37.602	291.533	13.4	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	6.731	291.533	5.08	
10-20 percentile				
n	Σ d	Σ d ²	Ave. VI	
12	25.207	126.403	16.9	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	4.425	25.207	1.45	
20-30 percentile				
n	Σ d	Σ d ²	Ave. VI	
12	72.758	2511.988	15.6	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	-50.094	2511.988	14.37	
30-40 percentile				
n	Σ d	Σ d ²	Ave. VI	
12	23.596	71.676	17.6	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	-0.682	71.676	2.53	
40-50 percentile				
n	Σ d	Σ d ²	Ave. VI	
12	34.229	221.569	19.3	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	11.490	221.569	4.34	
50-60 percentile				
n	Σ d	Σ d ²	Ave. VI	
12	15.199	38.567	21.4	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	-10.544	38.567	1.62	
60-70 percentile				
n	Σ d	Σ d ²	Ave. VI	
12	14.066	38.027	24.2	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	2.716	38.027	1.83	
70-80 percentile				
n	Σ d	Σ d ²	Ave. VI	
12	10.996	14.860	27.4	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	3.679	14.860	1.11	
80-90 percentile				
n	Σ d	Σ d ²	Ave. VI	
12	13.582	22.131	30.9	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
11	8.893	22.131	1.18	
90-100 percentile				
n	Σ d	Σ d ²	Ave. VI	
19	10.182	9.040	35.9	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
18	7.293	9.040	0.54	

Site: Rubidoux, CA		0-10 percentile		
n	Σ d	Σ d ²	Ave. VI	
18	134.990	2079.735	10.8	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	18.845	2079.735	10.11	
10-20 percentile				
n	Σ d	Σ d ²	Ave. VI	
18	44.829	207.969	16.8	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	-5.856	207.969	3.2	
20-30 percentile				
n	Σ d	Σ d ²	Ave. VI	
18	72.032	686.245	19.8	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	-17.496	686.245	5.76	
30-40 percentile				
n	Σ d	Σ d ²	Ave. VI	
18	49.055	326.923	21.6	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	-23.639	326.923	3.83	
40-50 percentile				
n	Σ d	Σ d ²	Ave. VI	
18	38.064	193.853	23.3	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	-5.110	193.853	3.09	
50-60 percentile				
n	Σ d	Σ d ²	Ave. VI	
18	34.833	156.099	24.7	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	-17.856	156.099	2.62	
60-70 percentile				
n	Σ d	Σ d ²	Ave. VI	
18	49.293	302.029	26.0	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	-33.543	302.029	3.45	
70-80 percentile				
n	Σ d	Σ d ²	Ave. VI	
18	23.156	85.057	28.1	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	-9.789	85.057	1.99	
80-90 percentile				
n	Σ d	Σ d ²	Ave. VI	
18	14.068	17.159	30.1	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
17.0	-4.718	17.159	0.89	
90-100 percentile				
n	Σ d	Σ d ²	Ave. VI	
15	10.372	9.766	33.8	
n-1	Σd	Σd ²	CV (%) (Eqn 11)	
14.0	6.221	9.766	0.68	

Site: Boston, MA			0-10 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	114.494	1160.355		10.7
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	-8.907	1160.355		8.22
			10-20 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	100.095	1850.813		13.9
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	4.288	1850.813		10.4
			20-30 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	68.964	957.619		15.0
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	-8.652	957.619		7.47
			30-40 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	42.636	244.184		16.5
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	32.818	244.184		3.22
			40-50 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	38.550	147.173		17.6
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	6.418	147.173		2.91
			50-60 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	66.547	572.606		18.7
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	34.568	572.606		5.4
			60-70 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	97.394	2921.978		19.4
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	-61.965	2921.978		12.53
			70-80 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	53.818	733.935		21.3
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	17.989	733.935		6.46
			80-90 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
16	29.756	105.908		23.4
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
15	7.654	105.908		2.45
			90-100 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI	
18	43.636	511.922		26.3
n-1	Σd	Σd^2	CV (%) (Eqn 11)	
17	-29.262	511.922		4.8

Site: New Brunswick, NJ				0-10 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	107.701	1591.519	10.5	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	15.235	1591.519	10.58	
				10-20 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	66.065	661.716	14.4	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	18.150	661.716	6.73	
				20-30 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	55.857	444.845	16.4	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	19.427	444.845	5.45	
				30-40 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	43.332	290.225	18.0	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	22.587	290.225	4.25	
				40-50 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	133.829	3866.320	18.5	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	-95.081	3866.320	15.12	
				50-60 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	73.883	694.295	20.0	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	5.249	694.295	7.01	
				60-70 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	35.757	172.097	21.0	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	-9.578	172.097	3.43	
				70-80 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	30.988	112.643	22.5	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	-0.609	112.643	2.83	
				80-90 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	14	30.320	196.018	25.2	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	13	22.162	196.018	3.38	
				90-100 percentile	
n		$\Sigma d $	$\Sigma d ^2$	Ave. VI	
	15	40.043	237.035	27.7	
n-1		Σd	Σd^2	CV (%) (Eqn 11)	
	14	-10.840	237.035	3.84	

Site: Cleveland, OH		0-10 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	65.250	462.268	13.1
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	30.525	462.268	5.57
10-20 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	56.757	378.584	15.7
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	26.100	378.584	5.09
20-30 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	46.579	260.241	18.1
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	-20.541	260.241	4.25
30-40 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	38.228	213.123	20.6
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	3.332	213.123	4.1
40-50 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	101.595	1834.688	22.7
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	74.542	1834.688	10.57
50-60 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	36.936	184.393	23.3
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	0.713	184.393	3.82
60-70 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	21.785	47.506	24.8
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	14.357	47.506	1.58
70-80 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	29.415	126.294	26.1
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	-7.977	126.294	3.1
80-90 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
13	32.444	143.144	27.9
n-1	Σd	Σd^2	CV (%) (Eqn 11)
12	-4.180	143.144	3.35
90-100 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
16	22.914	73.476	31.6
n-1	Σd	Σd^2	CV (%) (Eqn 11)
15	0.715	73.476	2.07

Site: Houston, TX		0-10 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	215.457	9987.394	14.5
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	194.245	9987.394	24.77
10-20 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	70.362	1085.513	15.8
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	26.316	1085.513	9.6
20-30 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	61.886	1074.407	16.8
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	54.568	1074.407	8.61
30-40 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	57.320	562.612	18.3
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	6.018	562.612	7.08
40-50 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	55.314	773.128	19.4
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	17.375	773.128	8.19
50-60 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	29.202	173.540	20.2
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	14.062	173.540	3.75
60-70 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	50.934	419.507	20.9
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	23.501	419.507	5.79
70-80 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	65.225	1103.507	21.4
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	-50.092	1103.507	8.95
80-90 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
12	84.558	1393.957	23.0
n-1	Σd	Σd^2	CV (%) (Eqn 11)
11	-40.672	1393.957	10.61
90-100 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
6	10.083	23.547	25.6
n-1	Σd	Σd^2	CV (%) (Eqn 11)
5	10.083	23.547	1.43

Appendix D

Relative Percent Difference and Upper 90th Percentile Coefficient of Variation Estimates of Visibility Index (in Deciviews) from Sites Collocated with an IMPROVE Sampler and a CSN Sampler

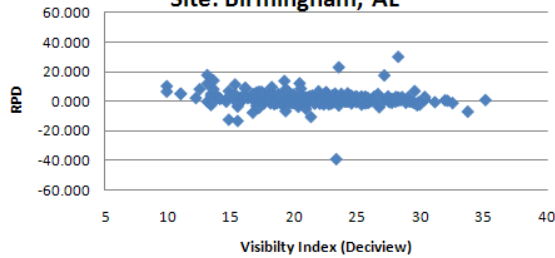
and

Bias Assessment of CSN/IMPROVE Sites Using Current PM_{2.5} Bias Statistic

CSN visibility index values used in the following assessments include data after conversion to URG samplers. With fewer data points, collocated pairs with large imprecision or bias estimates have more effect on the Phoenix and Fresno statistics especially when segregating data at the 10 percentile VI ranges.

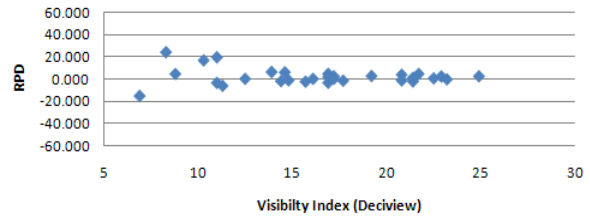
n	$\sum d $	$\sum d ^2$	Ave. VI
288	906.960	7713.394	22.0
n-1	$\sum d$	$\sum d^2$	CV (%) (Eqn 11)
287	574.638	7713.394	3.58

**Relative Percent Difference of VI
Collocated CSN/IMPROVE Sites
Site: Birmingham, AL**



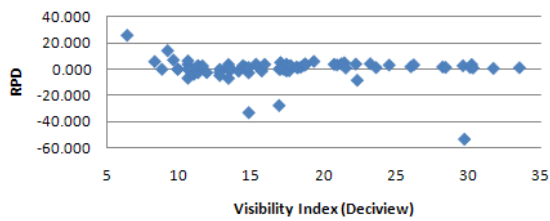
n	$\sum d $	$\sum d ^2$	Ave. VI
30	144.382	1777.285	16.5
n-1	$\sum d$	$\sum d^2$	CV (%) (Eqn 11)
29	61.701	1777.285	6.46

**Relative Percent Difference of VI
Collocated CSN/IMPROVE Sites
Site: Phoenix, AZ**



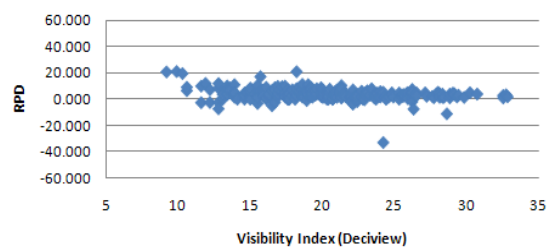
n	$\sum d $	$\sum d ^2$	Ave. VI
80	343.330	6332.611	17.3
n-1	$\sum d$	$\sum d^2$	CV (%) (Eqn 11)
79	15.835	6332.611	7.07

**Relative Percent Difference of VI
Collocated CSN/IMPROVE sites
Site: Fresno, CA**



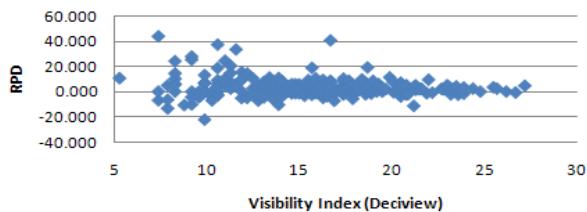
n	$\sum d $	$\sum d ^2$	Ave. VI
263	1163.491	8991.748	20.8
n-1	$\sum d$	$\sum d^2$	CV (%) (Eqn 11)
262.0	983.096	8991.748	3.38

**Relative Percent Difference of VI
Collocated CSN/IMPROVE Sites
Site: New York, NY**



n	$\sum d $	$\sum d ^2$	Ave. VI
254	1323.358	17518.195	16.0
n-1	$\sum d$	$\sum d^2$	CV (%) (Eqn 11)
253	864.709	17518.195	5.7

**Relative Percent Difference of VI
Collocated CSN/IMPROVE sites
Site: Seattle, WA**



Measurement Uncertainty Evaluations at 10th Percentile VI values

Site: Birmingham, AL		0-10 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	171.108	1673.931	13.86
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	109.533	1673.931	5.77
10-20 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	100.080	531.044	16.89
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	59.454	531.044	3.29
20-30 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	70.473	307.178	18.61
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	60.615	307.178	2.18
30-40 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	91.348	630.127	19.97
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	54.180	630.127	3.74
40-50 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	78.202	386.601	21.49
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	39.272	386.601	2.97
50-60 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	65.409	218.819	22.84
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	52.935	218.819	1.8
60-70 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	127.176	2285.742	24.02
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	44.055	2285.742	7.65
70-80 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	55.578	134.778	25.34
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	44.403	134.778	1.33
80-90 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	69.742	453.147	26.99
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	56.853	453.147	3
90-100 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
28	81.123	1102.779	30.05
n-1	Σd	Σd^2	CV (%) (Eqn 11)
27	50.060	1102.779	5.29

Site: Phoenix, AZ		0-10 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	44.408	856.262	8.28
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	13.158	856.262	43.53
10-20 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	40.265	685.945	11.42
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	32.857	685.945	27.82
20-30 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	12.664	80.202	12.60
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	-0.121	80.202	13.79
30-40 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	9.446	42.044	14.67
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	2.514	42.044	9.73
40-50 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	7.205	28.044	16.30
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	2.044	28.044	7.95
50-60 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	7.673	21.445	17.02
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	0.444	21.445	7.12
60-70 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	4.280	9.531	18.07
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	0.861	9.531	4.69
70-80 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	7.590	21.939	21.00
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	-2.364	21.939	6.9
80-90 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	5.878	21.353	22.08
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	5.878	21.353	4.83
90-100 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
3	4.973	10.520	23.83
n-1	Σd	Σd^2	CV (%) (Eqn 11)
2	4.109	10.520	3.41

Site: Fresno, CA		0-10 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	59.704	998.551	9.33
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	46.046	998.551	11.38
10-20 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	25.435	102.988	11.00
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	5.239	102.988	4.19
20-30 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	17.422	57.314	12.75
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	-2.027	57.314	3.17
30-40 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	15.339	63.795	14.06
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	-1.417	63.795	3.35
40-50 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	74.876	1897.068	15.01
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	-54.528	1897.068	16.41
50-60 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	11.427	44.858	17.26
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	9.115	44.858	2.47
60-70 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	15.382	33.506	18.14
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	13.096	33.506	1.46
70-80 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	30.556	132.357	20.69
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	30.556	132.357	1.66
80-90 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	28.119	134.380	24.72
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	11.297	134.380	4.57
90-100 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
8	65.069	2867.794	29.88
n-1	Σd	Σd^2	CV (%) (Eqn 11)
7	-41.541	2867.794	21.63

Site; New York, NY		0-10 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	199.122	2299.282	12.82
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	169.584	2299.282	6.02
10-20 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	126.520	962.801	15.42
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	119.963	962.801	3.52
20-30 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	119.601	790.372	17.29
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	104.814	790.372	3.34
30-40 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	138.169	1146.826	18.85
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	138.169	1146.826	3.54
40-50 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	124.252	762.982	19.97
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	122.124	762.982	2.4
50-60 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	91.074	457.327	21.07
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	91.074	457.327	2.05
60-70 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	78.633	380.971	22.17
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	58.490	380.971	2.75
70-80 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	113.187	1437.297	23.86
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	46.927	1437.297	6.41
80-90 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
26	79.867	340.874	25.98
n-1	Σd	Σd^2	CV (%) (Eqn 11)
25	61.024	340.874	2.45
90-100 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	93.066	413.017	29.37
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	70.926	413.017	2.51

Site: Seattle, WA		0-10 percentile	
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	264.701	5616.162	8.77
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	97.634	5616.162	12.93
10-20 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	207.199	3724.910	11.02
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	173.725	3724.910	8.97
20-30 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	169.440	2261.538	12.58
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	115.459	2261.538	7.43
30-40 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	127.032	936.122	13.90
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	77.482	936.122	4.71
40-50 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	66.882	328.266	15.09
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	52.074	328.266	2.65
50-60 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	144.092	2543.815	16.65
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	116.519	2543.815	7.99
60-70 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	83.408	467.464	17.73
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	43.286	467.464	3.54
70-80 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	84.164	719.634	18.98
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	76.616	719.634	3.93
80-90 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
25	89.635	488.573	20.37
n-1	Σd	Σd^2	CV (%) (Eqn 11)
24	70.873	488.573	3.03
90-100 percentile			
n	$\Sigma d $	$\Sigma d ^2$	Ave. VI
29	86.805	431.712	23.39
n-1	Σd	Σd^2	CV (%) (Eqn 11)
28	41.042	431.712	3.14

Bias Assessment of CSN/IMPROVE Sites Using Current PM2.5 Bias Statistic

Bias Estimate = D (green highlight)

