Chemical Speciation Network (CSN)
Annual Quality Report

November 20, 2015 through December 31, 2016

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1. Executive Summary

1.1 Introduction

The University of California Davis (UC Davis) Air Quality Group summarizes quality assurance (QA) annually in this report as a contract deliverable for the Chemical Speciation Network (CSN) program (contract #EP-D-15-020). The primary objectives of this report are:

1. Provide the U.S. Environmental Protection Agency (EPA) and other potential users with graphical and tabular illustrations of quality control (QC) for species measured within the network.
2. Identify and highlight observations of interest that may have short- or long-term impact on data quality across the network or at particular sites.
3. Serve as a record and tool for ongoing UC Davis QA efforts.

Each network site includes two samplers: (1) URG 3000N carbon sampler (URG Corporation; Chapel Hill, NC) for collection of particulate matter on quartz filters; and (2) Met One SASS or SuperSASS (Met One Instruments, Inc; Grants Pass, OR) for collection of particulate matter on polytetrafluoroethylene (PTFE) filters and nylon filters. The following analyses are performed:

- PTFE filters: Analyzed at UC Davis using energy dispersive x-ray fluorescence (EDXRF) for a suite of 33 elements.
- Nylon filters: Analyzed at the Desert Research Institute (DRI) using ion chromatography (IC) for a suite of six ions.
- Quartz filters: Analyzed at the Desert Research Institute (DRI) for organic and elemental carbon, including carbon fractions, using Thermal Optical Analysis (TOA).

Unless otherwise noted, data included in this report cover samples collected during the time period November 20, 2015 through December 31, 2016. CSN filters collected prior to November 20, 2015 were analyzed, and their data validated and delivered, by the previous contractor, Research Triangle Institute (RTI).

1.2 Data Quality Overview and Issues

Section 4 of this report provides laboratory performance details for each of the analytical measurement techniques. The laboratories met the QC criteria as detailed in Section 4.1 (DRI Ion Analysis Laboratory), Section 4.2 (UC Davis X-Ray Fluorescence Laboratory), and Section 4.3 (DRI Thermal/Optical Analysis Laboratory).

Across the network, completeness – determined by the total number of valid samples relative to the total number of scheduled samples – was 94.5% for PTFE filters, 94.4% for nylon filters, and 91.2% for quartz filters. As detailed in Section 3.1.1, there were nine sites with less than 75% completeness.

No Technical Systems Audit (TSA) of UC Davis was performed by the EPA in 2016.

2. Summary of Laboratory Operation Issues

2.1 DRI Ion Analysis Laboratory

2.1.1 Analysis Delays

Deliveries of analysis data from DRI to UC Davis were delayed, contributing to noncompliance with 120 days requirement for delivery of data to AQS following receipt of filters by analytical laboratories.

2.2 UC Davis X-Ray Fluorescence Laboratory

2.2.1 Vanadium

During this reporting period XRF analyses of vanadium were overestimated by about 30%. Results from an inter-laboratory comparison, confirmed by further comparison with ICP-MS analysis, revealed that vanadium calibrations based on commercial standards for samples collected from November 2015 through October 2017 resulted in erroneously high measurements.

For further detail and corrective actions see Section 3.2.1.1.

2.2.2 Lead

Corresponding with the November 2015 contract transition from RTI to UC Davis, measurements of lead on PTFE filters at the median and 90th percentile are higher than in previous years. Additionally, with the January 2016 transition to reporting negative values, 10th percentile lead concentrations are negative, whereas in previous years they were reported as 0.0.

For further detail see Section 6.4.1.1.

2.2.3 Copper and Zinc

For analyses performed March 2, 2016 to March 23, 2016 copper and zinc contamination was observed during QC checks of laboratory blanks run daily on the EDXRF instruments. It was determined that these contaminants were caused by faulty parts (spinner) on the instruments. The parts were replaced and new laboratory blanks showed copper and zinc backgrounds returned to normal levels. Samples analyzed during this period were checked for unusually high copper and zinc mass loadings compared to site specific and network wide historical values. Samples with unusual mass loadings were reanalyzed and if it was determined that the original result had contamination the reanalysis results were reported.

For further detail see Section 4.2.2.1.

2.2.4 Zinc

For analyses performed during June and July 2016, periodic zinc contamination was observed on the daily QC laboratory blank and daily QC multi-elemental reference sample on EDXRF instrument, XRF-4. The cause of this contamination was determined to be the sample changing arm on the instrument. Once the sample changing arm was replaced the Zn contamination from this component was no longer observed. Samples analyzed during this period were checked for unusually high zinc mass loadings compared to site specific and network wide historical values.

Samples with unusual Zn mass loadings were reanalyzed and if it was determined that the original result had contamination the reanalysis results were reported.

For further detail see Sections 3.2.1.3, 4.2.2.1 and 4.2.2.2.

2.2.5 Calcium

During the November 2015 through December 2016 time period, both XRF instruments showed gradual increase in calcium mass loadings of their daily analyzed laboratory blank QC. Calcium blank levels returned to normal when the blank was replaced with a new one. The calcium buildup was likely caused by atmospheric deposition or instrument wear on these filters which are analyzed daily and remain in the instruments' sample changers indefinitely. This gradual buildup of calcium is not expected on actual samples which are loaded and analyzed once. However, samples are monitored for unusually high calcium values and reanalyzed as necessary.

For further detail see Section 4.2.2.1.

2.3 DRI Thermal/Optical Analysis Laboratory

2.3.1 Analysis Delays

Deliveries of analysis data from DRI to UC Davis were delayed, contributing to noncompliance with 120 days requirement for delivery of data to AQS following receipt of filters by analytical laboratories.

2.3.2 Carbon Analyzer Calibrations

Multi-point calibrations were performed for the DRI Model 2001 analyzers per the schedule listed in Table 4.3-2a. For analyzer 9 more than six months passed between calibrations.

For further detail see Section 3.2.3.1 and Section 4.3.2.1.

2.3.3 Carbon Fractions

Corresponding with the transition from DRI Model 2001 to DRI Model 2015 analyzers (beginning with samples from January 2016), measurements of OC on quartz filters at the median and 10th percentile are lower than in previous years. The 2016 measurements of EC at the 10th percentile are also lower than in previous years.

For further detail see Section 3.2.3.2 and Section 6.4.1.1.

3. Quality Issues and Corrective Actions

3.1 Data Quality

3.1.1 Completeness

Completeness is evaluated network wide by filter type, and determined by the total number of valid samples relative to the total number of collected and scheduled samples (Table 3.1-1). The completeness is comparable for PTFE and nylon filters which are both collected by the Met One SASS / Super SASS sampler; however, the number of invalid samples is higher for quartz filters, which are collected by the URG sampler.

Table 3.1-1: Network sample completeness by filter type, November 2015 through December 2016. The total number of scheduled samples is calculated from the sampling schedule (does not include field blanks). The total number of collected samples is the actual number of samples collected in the field.

Filter Type	Total Number of Scheduled Samples	Total Number of Collected Samples	Number of Valid Samples	Number of Invalid Samples	% Valid (relative to # collected samples)	% Valid (relative to # of scheduled samples)
PTFE	14,478	14,291	13,680	611	95.7	94.5
Nylon	14,478	14,288	13,671	617	95.7	94.4
Quartz	14,478	14,242	13,211	1,031	92.8	91.2

Across the network there were nine sites with sample completeness less than 75% for at least one filter type (Table 3.1-2). Seven of the nine cases had low completeness resulting from invalid quartz filters.

Table 3.1-2: Network sites with less than 75% sample completeness (relative to the number of collected samples) for at least one filter type, November 2015 through December 2016. For each filter type, the percentage of different null codes is listed relative to the total number of null codes per site. For null code definitions, see Table 3.1-3.

AQS ID #	Location	Completeness (%)			Null Codes		
		PTFE	Nylon	Quartz	PTFE	Nylon	Quartz
06-029-0014-6	Bakersfield, CA	93	93	32	AF (50%) AN (25%) AU (25%)	AF (50%) AN (25%) AU (25%)	AF (56%) AN (24%) Other (20%)
48-113-0069-5	Hinton, TX	85	85	33	BA (65%) AH (18%) Other (17%)	BA (65%) AH (18%) Other (17%)	AN (86%) Other (14%)
28-049-0020-5	Jackson, MS	98	98	51	AB (50%) AN (50%)	AB (50%) AN (50%)	AN (63%) AH (31%) Other (6%)
20-209-0021-5	Kansas City, KS	91	91	58	AF (40%) AB (20%) Other (40%)	AF (40%) AN (20%) Other (40%)	AN (72%) Other (28%)
37-067-0022-5	Winston-Salem, NC	92	91	67	AL (40%) Other (60%	AL (33%) Other (67%)	AN (86%) Other (14%)
45-079-0007-5	Parklane, SC	87	87	67	AS (61%) Other (39%)	AS (61%) Other (39%)	AN (50%) AS (25%) Other (25%)
47-093-1020-5	Knoxville, TN	98	98	70	AV (100%)	AV (100%)	AN (60%) AS (25%) Other (15%)
50-007-0012-5	Zampieri State, VT	73	79	96	AN (80%) Other (20%)	AN (75%) Other (25%)	AB (50%) AN (25%) AV (25%)
06-073-1022-5	El Cajon, CA	74	76	90	AN (75%) Other (25%)	AN (80%) Other (20%)	AB (33%) AN (33%) Other (34%)

Samples can be invalidated for a variety of reasons, as detailed in the *UCD CSN TI 801C, CSN Data Validation*, and the *Data Validation for the Chemical Speciation Network* guide. Null codes indicate the reasons for invalidation (Table 3.1-3).

Table 3.1-3: Number and type of null codes applied to SASS and URG samples from November 2015 through December 2016. Codes are ordered by frequency of occurrence.

Null Code	SASS PTFE	SASS Nylon	URG Quartz	Null Code Description
SV	0	0	0	Sample Volume Out of Limits
AP	0	0	2	Vandalism
BK	0	0	10	Site computer/data logger down
AU	2	2	2	Monitoring Waived
AW	1	0	0	Wildlife Damage
AI	1	2	4	Insufficient Data (cannot calculate)
DA	2	2	3	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)
BI	5	4	3	Lost or damaged in transit
BB	6	5	8	Unable to Reach Site
AK	6	4	6	Filter Leak
AM	21	2	4	Miscellaneous Void
AL	7	7	21	Voided by Operator
AJ	7	4	6	Filter Damage
SA	3	3	5	Storm Approaching
AQ	13	13	7	Collection Error
BE	10	10	14	Building/Site Repair
AR	19	19	17	Lab Error
BA	20	20	23	Maintenance/Routine Repairs
AG	14	16	23	Sample Time out of Limits
AS	23	23	26	Poor Quality Assurance Results
AH	32	36	83	Sample Flow Rate or Flow CV out of Limits
AC	14	13	13	Construction/Repairs in Area
AB	43	41	50	Technician Unavailable
AO	20	17	15	Bad Weather
AV	53	51	54	Power Failure
AF*	54	53	64	Scheduled but not Collected
BJ	64	57	49	Operator Error
AN†	171	213	519	Machine Malfunction

* Filters that receive this flag were intended for sampling and shipped to the site, but were not sampled.

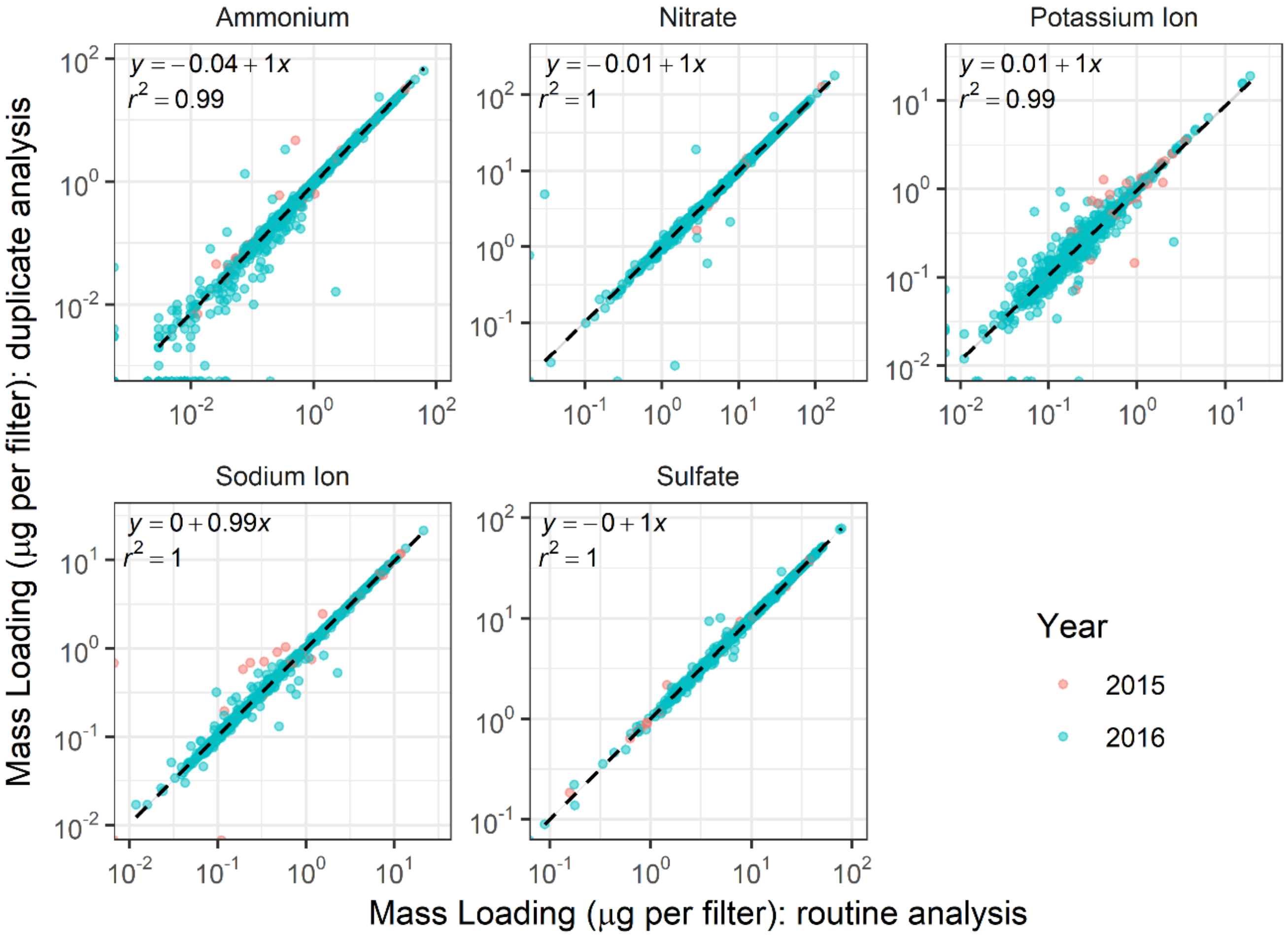
† Beginning with data from August 2016 the AH null code definition was updated to include flow CV out of limits, and use of the AN null code was discontinued for cases with flow CV out of limits. See Section 3.4.2.1.

3.1.2 Comparability and Analytical Precision

Analytical precision is evaluated by comparing data from duplicate analyses, where two analyses are performed on the same sample. Reliable laboratory measurements should be repeatable with good precision. Analytical precision includes only the uncertainties associated with the laboratory handling and analysis, whereas collocated precision (Section 6.5) also includes all the uncertainties associated with sample preparation, field handling, and sample collection. As such, collocated precision (Table 6.5-1, elements; Table 6.5-2, ions; Table 6.5-3, carbon) is reported, whereas analytical precision is used internally as a QC tool.

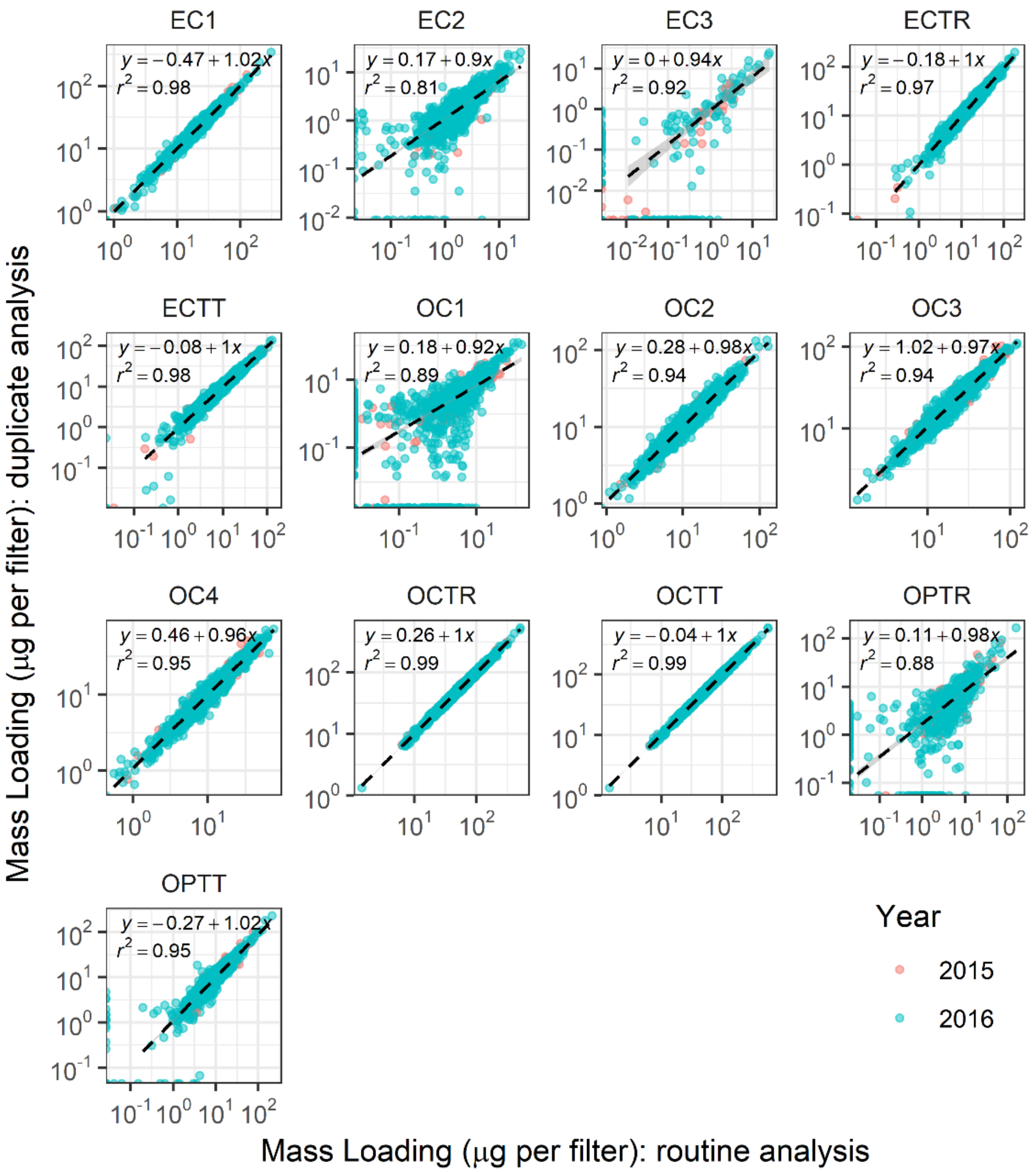
Comparisons of duplicate ion mass loadings on nylon filters analyzed by IC show generally good agreement (Figure 3.1-1). For ions, the first and second analyses are performed on the same instrument. Chloride is excluded from this analysis, as it was not reported to AQS during the time period covered by this report (see Section 3.2.2.1).

Figure 3.1-1: Duplicate ion analysis results. Red points designate 2015 data, blue points designate 2016 data.



Comparison of duplicate carbon mass loadings on quartz filters analyzed by TOA generally show agreement (Figure 3.1-2). For carbon, the second analysis is performed on a randomly selected instrument, which typically means a different instrument than the first analysis.

Figure 3.1-2: Duplicate carbon analysis results. Red points designate 2015 data, blue points designate 2016 data. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4), TR indicates measurement by reflectance, and TT indicates measurement by transmittance.



Duplicate XRF analyses are not performed on the routine CSN samples. Rather, reanalysis is performed on the same set of filters on a monthly basis to assess both the short- and long-term stability of the XRF measurements as described in *CSN SOP 302, XRF Analysis*. See Section 4.2.2.4.

3.1.3 Blanks

Field blanks are an integral part of the QC process, and field blank analysis results allow for artifact correction of the sampled filters as part of the concentration calculation. Artifacts can result from initial contamination in the filter material, contamination during handling and analysis, and adsorption of gases during sampling and handling.

There is some variability in field blank mass loadings by species and month, as shown in Figure 3.1-3 for ions measured from nylon filters and Figure 3.1-4 for organic carbon measured from quartz filters (elemental carbon and organic pyrolyzed carbon are rarely above zero and are not shown). Considering that field blanks capture artifacts from both field and laboratory processes, it is expected that field blank mass loadings are generally higher than lab blanks which have only been handled in a laboratory environment and have less opportunity for mishandling and contamination.

Figure 3.1-3: Nylon filter field blank mass loadings by month, 2016. The months of January and April are excluded because no nylon filter field blanks were collected. Numbers shown on plot indicate count of samples with mass loading > 0. The black horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers.

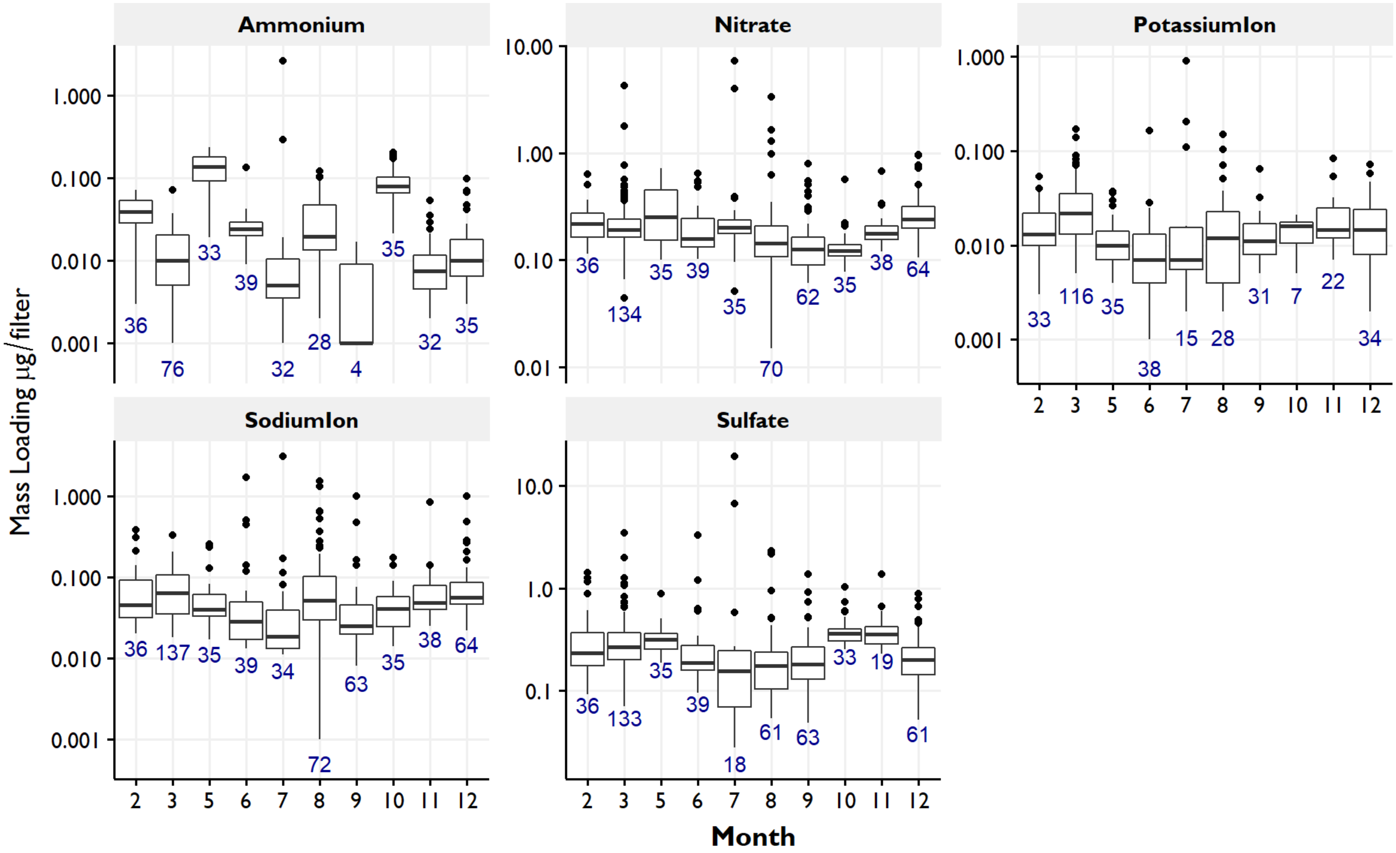
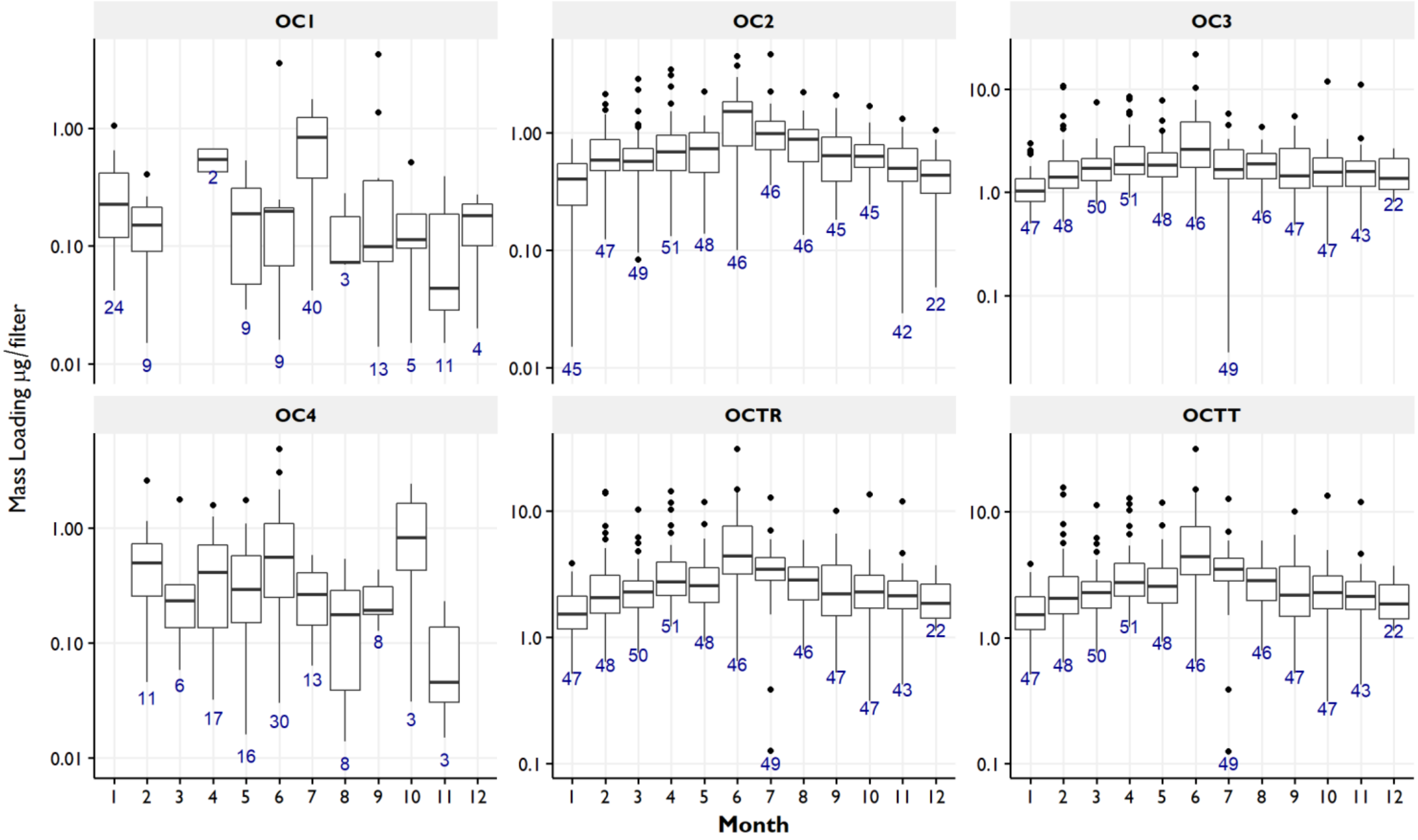


Figure 3.1-4: Quartz filter field blank mass loadings for organic carbon by month, 2016. Organic carbon (OC) fractions are indicated as (1) through (4), TR indicates measurement by reflectance, and TT indicates measurement by transmittance. Numbers shown on plot indicate count of samples with mass loading > 0. The black horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to the most extreme data point which is no more than 1.5× the length of the box away from the box. The dots are all of the points that lay outside the whiskers.



3.1.3.1 *Blank Correction*

Blank correction was implemented from sampling date November 20, 2015 onward for carbon measurements and from sampling date January 1, 2016 onward for ions measurements. Blank correction is performed using a rolling median value from at least 50 quartz and nylon field blanks collected in and closest to the sample month.

3.1.3.2 *Method Detection Limits*

Method detection limits (MDL) are calculated and delivered for each species every month. A sufficient number of field and/or laboratory blanks must be available in order to calculate MDLs representative of the network. Initially, the number of field blanks collected network wide per month was highly variable, and the MDLs were calculated as follows:

- Elements: Calculated for each species as 3× standard deviation of lab blanks. Recalculated for each new lot of PTFE filters.
- Ions and carbon: Calculated monthly for each species as 3× standard deviation of field blanks, using 50 nylon (for ions) or quartz (for carbon) field blanks collected in and closest to the sampling month.

MDLs for data from samples collected November 20, 2015 through December 31, 2016 are shown in Table 3.1-4. The percent of values reported above the MDL varies greatly among species.

Table 3.1-4: Average MDLs for all species, November 2015 through December 2016.

Species	Average MDL, µg/m^3	% Above MDL
Ag	0.019	1.4
Al	0.038	32.4
As	0.003	7.2
Ba	0.086	1.9
Br	0.005	17.7
Ca	0.027	65.1
Cd	0.024	0.7
Ce	0.116	0.9
Cl	0.005	42.9
Co	0.003	1.5
Cr	0.004	14.4
Cs	0.078	0.5
Cu	0.009	18.9
Fe	0.023	85.1
In	0.031	0.2
K	0.016	95.8
Mg	0.055	9.0
Mn	0.007	7.2
Na	0.070	27.3
Ni	0.002	11.1
P	0.002	9.9
Pb	0.015	4.7
Rb	0.008	1.1
S	0.009	99.4
Sb	0.047	1.1
Se	0.006	1.3
Si	0.015	90.3
Sn	0.046	0.9
Sr	0.007	2.7
Ti	0.003	45.8
V	0.002	5.5
Zn	0.004	78.0
Zr	0.037	0.9
Ammonium Ion	0.015	80.7
Nitrate Ion	0.095	89.7
Potassium Ion	0.008	90.5
Sodium Ion	0.043	53.2
Sulfate Ion	0.144	96.1
Elemental Carbon (1)	0.011	99.5

Species	Average MDL, µg/m^3	% Above MDL
Elemental Carbon (2)	0.010	95.7
Elemental Carbon (3)	0.002	3.6
Elemental Carbon (TR)	0.017	99.1
Elemental Carbon (TT)	0.014	98.6
Organic Carbon (1)	0.024	60.6
Organic Carbon (2)	0.050	98.9
Organic Carbon (3)	0.151	94.8
Organic Carbon (4)	0.031	99.3
Organic Carbon (TR)	0.213	98.9
Organic Carbon (TT)	0.216	99.0
Organic Pyrolyzed (TR)	0.010	79.2
Organic Pyrolyzed (TT)	0.013	95.8

The method used for calculating MDLs has evolved as availability of field blanks has increased. Beginning in March 2017, field blank collection increased to one field blank for each filter type per site per month, allowing for a more robust MDL calculation method. For data from samples collected February 2017 onward, the MDL calculation is harmonized for all analysis pathways, calculated as 95th percentile minus median of field blanks, using 50 field blanks collected in or closest to the sampling month for each respective filter type. New MDLs are lower for most elements, though higher in a few cases (Figure 3.1-5). Ion MDLs are lower (Figure 3.1-6), and carbon MDLs have modest change (Figure 3.1-7). Future reports will include MDLs calculated using the new method.

Figure 3.1-5: Element MDL comparison using data from filters collected January 2017. New MDLs calculated as 95th percentile minus mean of field blanks. Old MDLs calculated as 3× standard deviation of lab blanks. Horizontal bar indicates interquartile range (compressed because range is narrow), dots indicate outliers.

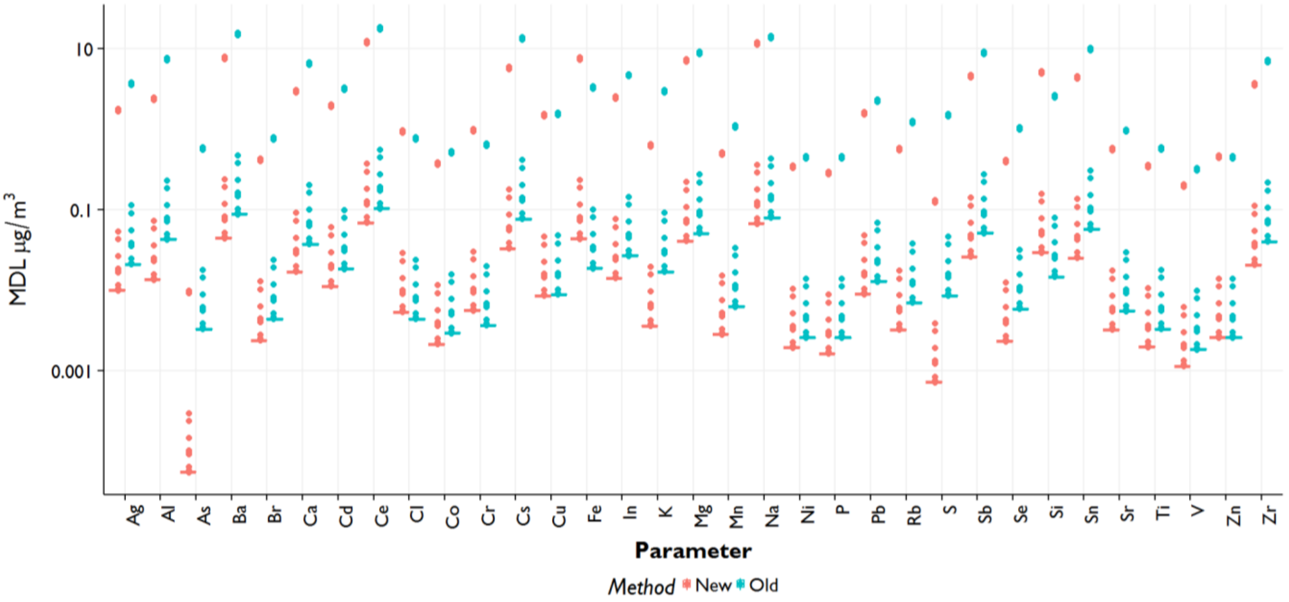


Figure 3.1-6: Ion MDL comparison using data from filters collected January 2017. New MDLs calculated as 95th percentile minus mean of field blanks. Old MDLs calculated as 3× standard deviation of field blanks. Horizontal bar indicates interquartile range (compressed because range is narrow), dots indicate outliers.

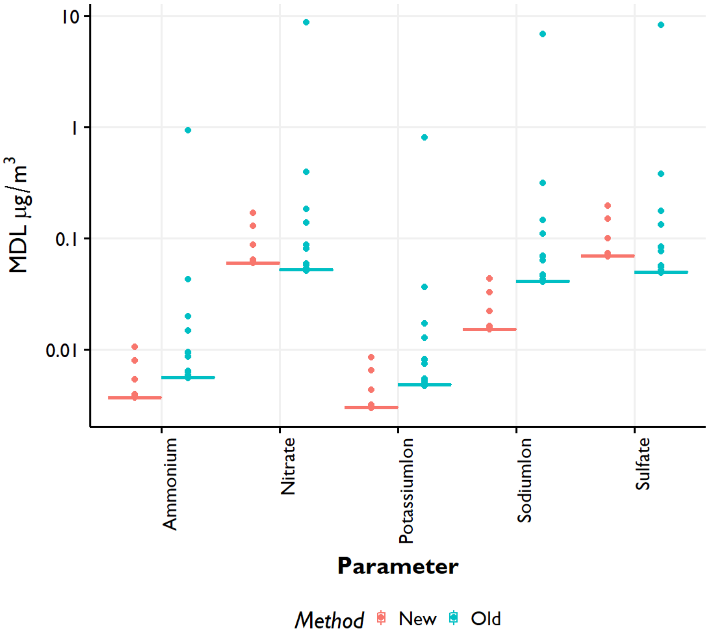
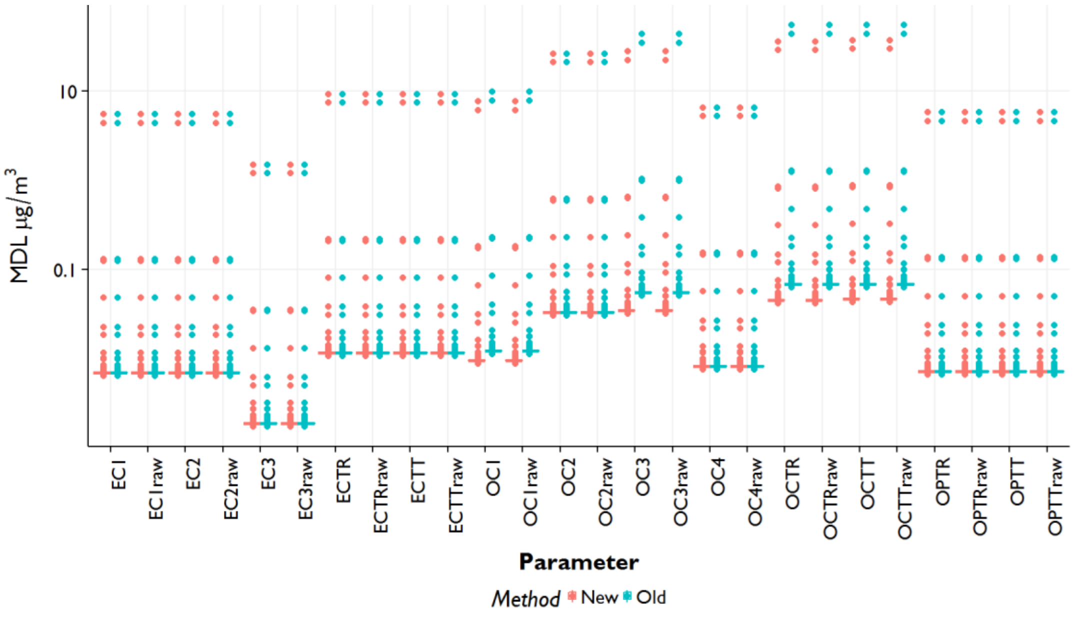


Figure 3.1-7: Carbon MDL comparison using data from filters collected January 2017. New MDLs calculated as 95th percentile minus mean of field blanks. Old MDLs calculated as 3× standard deviation of field blanks. Horizontal bar indicates interquartile range (compressed because range is narrow), dots indicate outliers.



3.2 Corrective Actions

To ensure ongoing quality work, UC Davis reacts as quickly and as decisively as possible to unacceptable changes in data quality. These reactions are usually in the form of investigations, and, if necessary, corrective actions. The following subsections describe significant corrective actions undertaken during 2016.

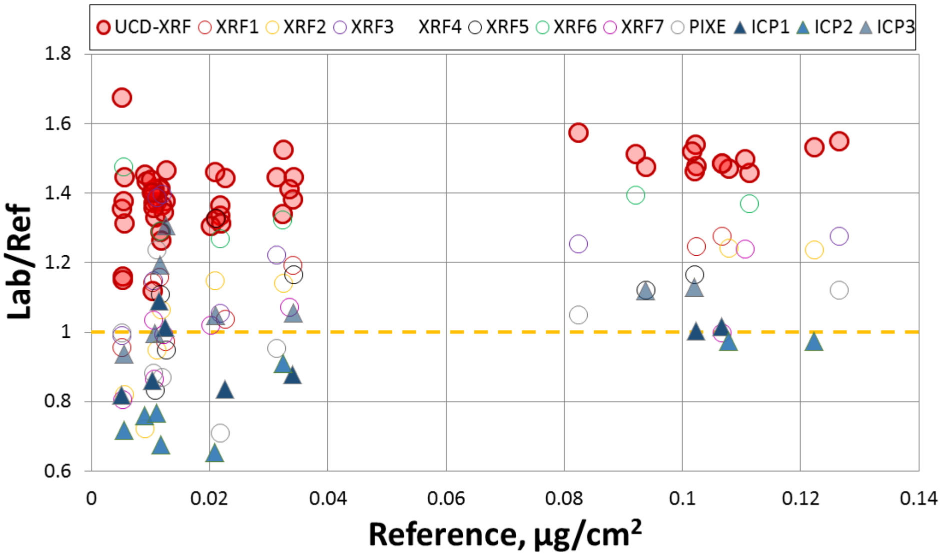
3.2.1 Elemental Analysis

3.2.1.1 Vanadium

Reported elemental concentrations rest on linear calibrations of the Panalytical Epsilon 5 instruments since their implementation for EDXRF analysis at UC Davis. The calibration factors are derived from observed instrumental responses to a variety of certified standards and reference materials of known composition. UC Davis certifies and calibrates with standards created in their own laboratory, aerosolizing known materials and collecting them on PTFE filters using IMPROVE (Interagency Monitoring of PROtected Visual Environments) samplers and/or Met One samplers utilized for CSN. The resulting deposits better mimic actual ambient samples than do the vacuum-deposited thin-film membranes traditionally obtained from commercial vendors. Such in-house standards have so far been certified for 16 of the elements reported for CSN. Calibrations for vanadium during this reporting period were based solely on two commercial standards in continuous use for samples collected November 2015 through December 2016.

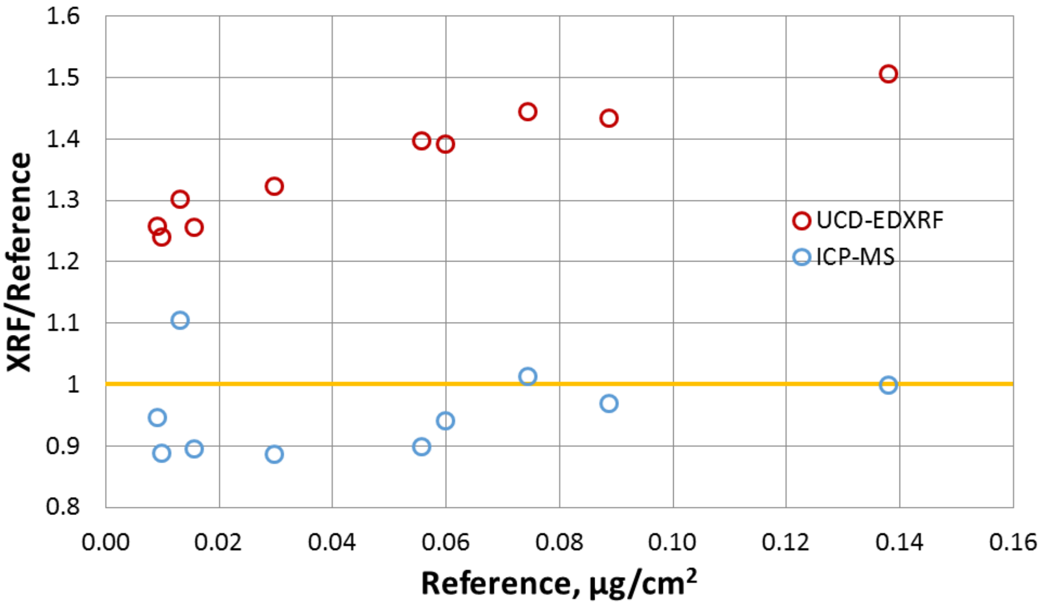
An important component of QA is the exchange of reference materials with other laboratories for comparative analyses. During inter-laboratory comparison studies of novel multi-element (ME) reference materials (RM) under development, it was discovered that UC Davis XRF results for vanadium (V) were higher than expected by about 30-50% while results from other laboratories (including XRF lab, PIXE and ICP-MS) were within 20% of expected values (Figure 3.2-1).

Figure 3.2-1: Inter-laboratory comparison of multi-element reference materials for vanadium, where the UC Davis results are shown as filled red circles and results from other laboratories are shown as circles and triangles.



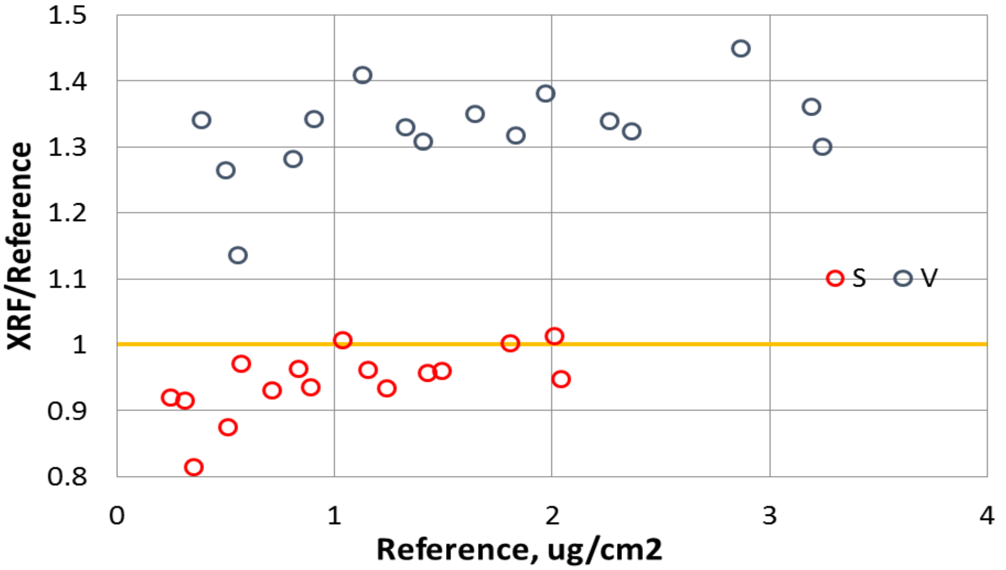
Overestimation by UC Davis XRF analysis was confirmed by further comparisons with ICP-MS analysis by a collaborating laboratory (Figure 3.2-2).

Figure 3.2-2: Comparison of multi-element reference materials for vanadium at UC Davis using EDXRF and a collaborating laboratory using ICP-MS.



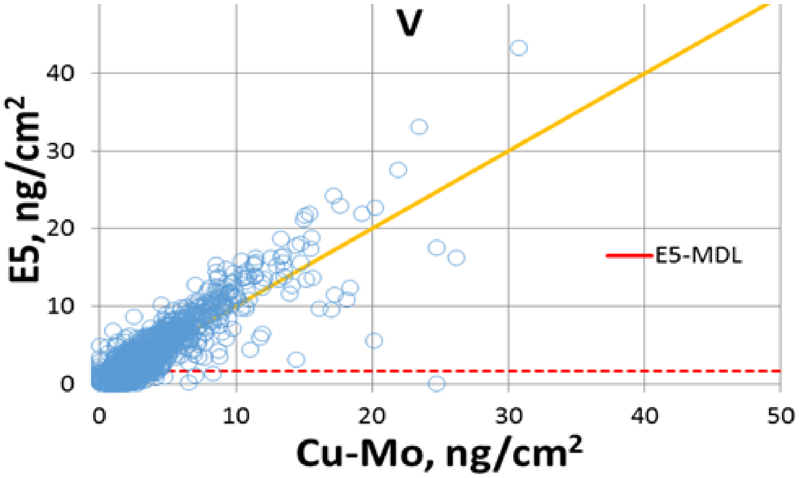
UC Davis' ability to design and generate custom reference materials provided further confirmation with single-compound (vanadyl sulfate) standards of known hydration, whose loadings could be gravimetrically certified (Figure 3.2-3).

Figure 3.2-3: UC Davis XRF results for single vanadyl sulfate standards that conform to expectations for sulfur (red circle) but are high for vanadium (blue circle).



Inter-laboratory comparison studies of UC Davis multi-element RMs, together with UC Davis' custom single-compound standards, converged to indicate that the existing calibration of the UC Davis Panalytical Epsilon-5 instruments for vanadium was about 30% high. Continuity of the historical vanadium record was already tested, when the newer Epsilon 5 (E5) instruments were used to reanalyze the 15-year archive of samples collected from 1995 to 2009 at Great Smoky Mountains NP (GRSM) as part of the IMPROVE program. These had previously been analyzed and reported from the UC Davis-built copper- and molybdenum-anode XRF systems, which had been calibrated using a different set of standards. The new measurements were about 30% higher than those previously reported (Figure 3.2-4).

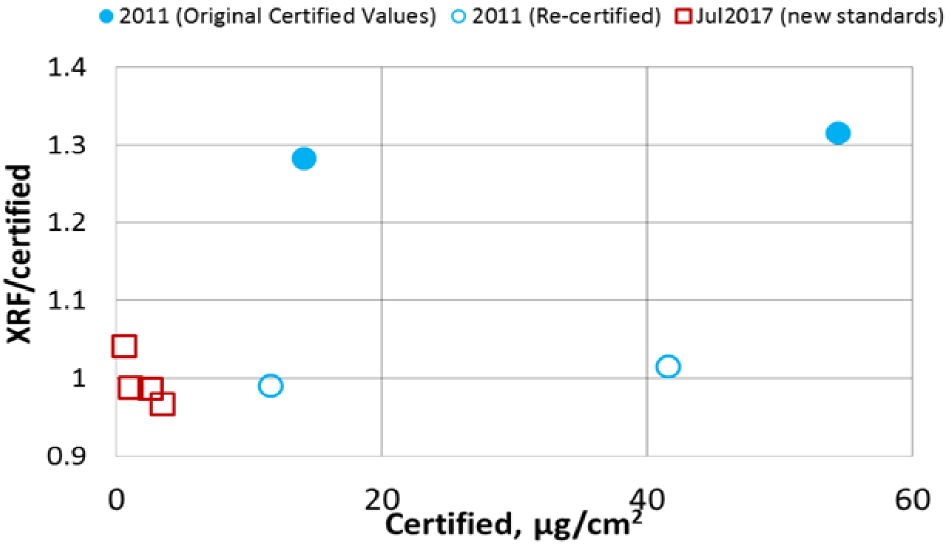
Figure 3.2-4: Reanalyses by Panalytical Epsilon 5 (E5) of 1995 – 2009 samples from Great Smoky Mountains National Park (GRSM, IMPROVE) previously analyzed versus earlier Cu-Mo XRF system.



As a final step, UC Davis returned the certified calibration standards from 2011 to the manufacturer for recalibration. UC Davis also purchased an additional set of standards. Recalibrated standards' values for vanadium mass loadings are about 30% lower compared to previously certified values and in agreement with newly purchased standards and standards generated at UC Davis (Figure 3.2-5).

Data were impacted for samples collected November 2015 through October 2017, and were not adjusted or flagged; further detail is available in the UC Davis data advisory: https://aqrc.ucdavis.edu/documentation.

Figure 3.2-5: Reported versus quoted vanadium mass loadings for commercial thin-film standards. The reported XRF values are based on a calibration to the loadings certified in 2017 for the two standards originally purchased in 2011.



Annual calibration records show the Panalytical analyzers' raw response to the two original standards was consistent throughout 2011 – 2017, indicating that the recertified values can be applied retroactively.

3.2.1.2 Zinc and Copper

As discussed in Section 2.2.3, a faulty component (brass brushes in sample spinners) on the EDXRF instruments resulted in cases of zinc and copper contamination. Filters identified as having potential contamination were reanalyzed and reanalysis results were reported accordingly (Section 4.2.2.1).

3.2.1.3 Zinc

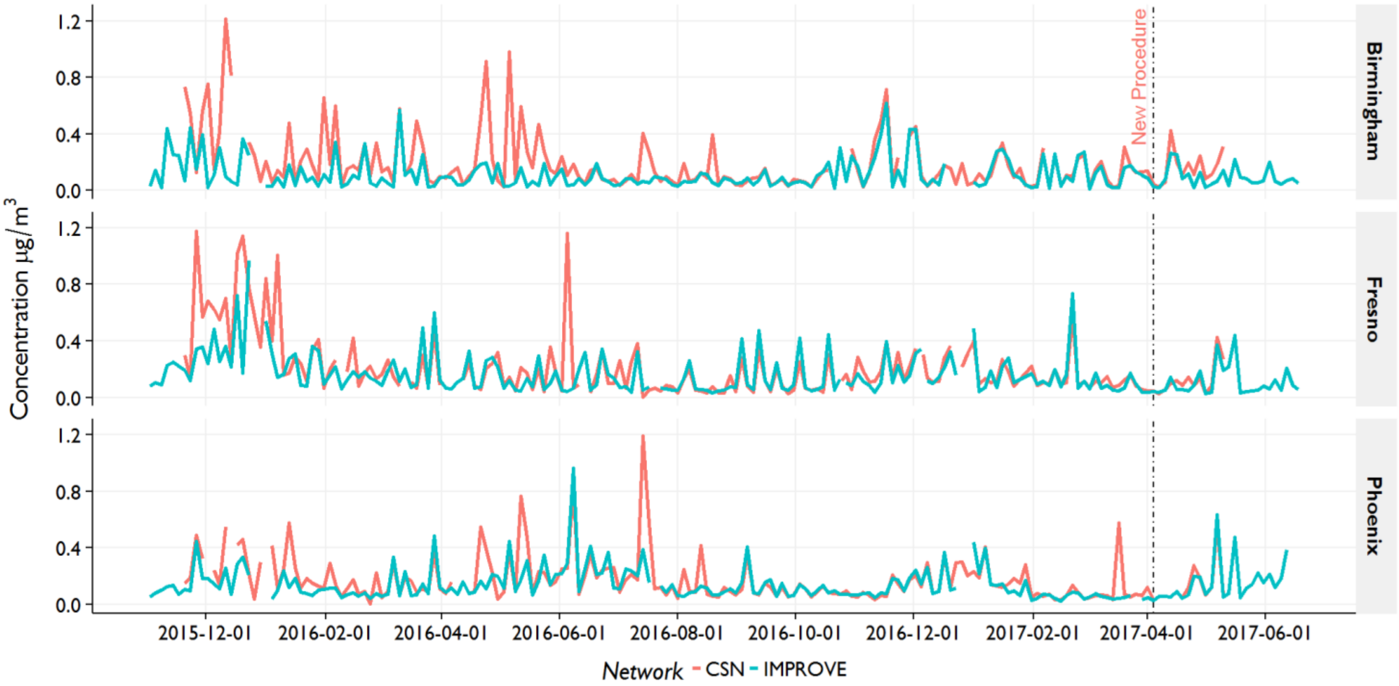
As discussed in Section 2.2.4, a faulty component (sample changer arm) on the EDXRF instruments resulted in cases of zinc contamination. Filters identified as having potential contamination were reanalyzed and reanalysis results were reported accordingly (Section 4.2.2.1).

3.2.2 Ion Analysis

3.2.2.1 Chloride

Data reported November 20, 2015 through December 31, 2016 does not include chloride, which is collected on nylon filters and analyzed using IC. A chloride contamination issue was discovered in the network beginning in November 2015; the contamination was traced to cleaning wipes used in the filter handling laboratory. Measurements at CSN sites collocated with IMPROVE (Interagency Monitoring of PROtected Visual Environments) network sites, seen in Figure 3.2-6, show high chloride that was attributed to contamination. The contamination issue appears to be resolved beginning August or September 2016, and a change in sample handling procedure effective April 2017 likely further reduced the chance of chloride contamination.

Figure 3.2-6: Chloride comparison as measured on filters collected from collocated CSN and IMPROVE network sites (Birmingham, AQS ID# 01-073-0023; Fresno, AQS ID# 06-019-0011; Phoenix, AQS ID# 04-013-9997). The dotted line for 'New Procedure' designates a change in the CSN sample handling lab procedure.



3.2.3 Carbon Analysis

3.2.3.1 Carbon Analyzer Calibration

As noted in Section 4.3.2.1, Table 4.3-2, the multi-point calibration for analyzer 9 was performed late. A calibration calendar has been established by DRI to avoid recurrence of this issue.

3.2.3.2 Carbon Data Reprocessing

All of the reportable CSN carbon analyses are performed by DRI, a subcontractor to UC Davis on the CSN contract. After examination of data from the IMPROVE and CSN programs, DRI determined that the Model 2015 (used for analyses from January 1, 2016 onward) carbon signal integrations threshold differed from that of the Model 2001 (used for analysis prior to January 1, 2016). DRI reprocessed CSN carbon data from January 1, 2016 through December 31, 2016, and analysis of the differences between the original and reprocessed data was prepared by UC Davis. After reviewing the differences, the EPA determined that the impact to the data was minor and that reprocessed carbon results would not be delivered to AQS. UC Davis prepared a data advisory: https://aqrc.ucdavis.edu/documentation.

3.2.4 Data Processing

3.2.4.1 Data Flagging Modifications

Data are flagged as part of the CSN data validation process as detailed in the *UCD CSN TI 801C, CSN Data Validation* and the *Data Validation for the Chemical Speciation Network* guide. Flags can be applied throughout the sampling, filter handling, analysis, and validation processes, using automated checks or on a case-by-case basis. The use and application of flags evolves as problems are identified and remedied. The following flagging updates and modifications were made during the process of validating network data during November 20, 2015 through December 31, 2016.

Sample Flow and Volume Flags

The flow rate coefficient of variation (CV; calculated as the standard deviation of flow rates divided by the mean 24-hour flow rate) is used to evaluate flow rate stability, where a high flow CV may be indicative of sampler malfunction.

Upon heavy use of the AN flag (machine malfunction) for flow CV out of limits (Table 3.1-3), UC Davis conducted an analysis to better understand the impact of expanding the acceptable range for the flow CV. Per direction from the EPA, the definition of the AH flag (sample flow rate or CV out of limits) was expanded to include flow CV out of limits, and the acceptable range for the SASS/Super Sass sampler was updated to include flow CV equal to or less than 5%; no changes were made to the range for the URG sampler (Table 3.2-1). Additionally, the SV flag (sample volume out of limits) was implemented for cases where the sample volume is outside of an acceptable range (Table 3.2-1). These changes became effective starting with August 2016 data, and also included discontinuation of the AN null code for flow CV out of limits.

Table 3.2-1: Summary of AH and SV null flags. Flags are applied when data is outside of the specified range.

Flag	Definition	URG Acceptable Range	SASS / Super SASS Acceptable Range
AH	Sample flow rate, or CV out of limits	19.8 to 24.2 LPM (±10% of 22 LPM expected flow)	6.0 to 7.4 LPM (±10% of 6.7 LPM expected flow)
		0 to 2% flow CV	0 to 5% flow CV
SV	Sample volume out of limits	28.5 to 34.9 m^3 (±10% of 31.7 m^3 expected SV)	8.6 to 10.6 m^3 (±10% of 9.6 m^3 expected SV)

Ambient Pressure and Temperature Flags

The QP (pressure sensor questionable) and QT (temperature sensor questionable) qualifier flags are informational indicators of potential issues with the sensors, but are not thought to be indicative of issues that affect species concentrations.

The QP qualifier flag is applied when ambient pressure is outside of a designated range, which was initially defined as 710 to 810 mmHg when the flag was implemented beginning August 2016. Ambient pressure below 710 mmHg is often observed, particularly at high elevation sites, which resulted in heavy application of the QP qualifier flag. The median pressure for valid filters collected within the network was determined to be 665 mm Hg. The EPA revised the lower limit for the QP flag range (Table 3.2-2), with the change effective starting with December 2016 data.

The EPA implemented the QT (temperature sensor questionable) flag based on the sampler manufacturer guidelines (Table 3.2-2). This change became effective starting with the August 2016 data.

Table 3.2-2: Summary of QT and QP informational flags, where flags are applied when data is outside of the specified range.

Flag	Definition	URG Acceptable Range	SASS / Super SASS Acceptable Range
QT	Temperature Sensor Questionable	-20 to 45 °C	-30 to 50 °C
QP	Pressure Sensor Questionable	600 to 810 mmHg	600 to 810 mmHg

4. Laboratory Quality Control Summaries

4.1 DRI Ion Analysis Laboratory

The DRI Ion Analysis Laboratory, as a subcontractor to UC Davis, received and analyzed nylon filters from batches 1 through 21 covering the sampling period November 20, 2015 through December 31, 2016. DRI performed analyses for both anions (i.e., chloride [Cl^-], nitrate [NO_3^-], and sulfate [SO_4^{2-}]) and cations (i.e., sodium [Na^+], ammonium [NH_4^+], and potassium[K^+]) on nylon filter samples using three DIONEX ICS-5000+ Systems (Chow and Watson, 2017) and reported the results of those analyses to UC Davis. Chloride was not reported to AQS during the time period covered by this report (see Section 3.2.2.1).

4.1.1 Summary of QC Checks and Statistics

Samples received at the DRI Ion Analysis Laboratory are logged in following the chain-of-custody procedure specified in *DRI CSN SOP #2-117*. Samples are analyzed using DIONEX ICS-5000+ Systems following *DRI CSN SOP #2-228* for anions and *DRI CSN SOP #2-229* for cations. QC measures for the DRI ion analysis are summarized in Table 4.1-1. The table indicates the frequency and standards required for the specified checks, along with the acceptance criteria and corrective actions.

During daily startup, a seven-point calibration is performed over the range from 0.02 to 3 µg/mL (i.e., 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, and 3.0 µg/mL) before analysis starts. Then two deionized-distilled water (DDW) samples and a method blank are analyzed, followed by two types of QC standards: (1) 1–2.5 µg/mL QC standards diluted from NIST certified Dionex standard solutions; and (2) DRI-made check standards (i.e., 1.01 µg/mL Cl^-, 1.00 µg/mLNO_3^-, 1.00 µg/mL SO_4^{2-} for anions and 0.39 µg/mL NH_4^+ and 1.03 µg/mL Na^+ for cations). During routine analysis, after every 10 samples, one duplicate, one DDW, and a selected number of QC standards (same as calibration solution concentrations; diluted from certified Environmental Research Associates (ERA) stock solutions) at various concentrations (0.005–10 µg/mL) are analyzed.

Table 4.1-1: QC measures for ion (anion and cation) analysis by ion chromatography.

Requirement	Frequency	Calibration Standard	Acceptance Criteria	Corrective Action
Multipoint Calibrations	Start of each analytical batch	ERA standards	$R^2 > 0.98$	Identify and correct problem before analyzing samples
Lower Quantifiable Limit (LQL)[a]	Quarterly	Field blanks	Change < 3 times historic standard deviation	Troubleshoot IC instrument and check filters
QC Samples: Reagent (DDW) Blank	10th samples	DDW	Within 3 σ of baseline	Check if method blank is clean and if duplicate sample and QC sample meet precision criteria. If not, reanalyze samples between this and previous QC standards.
QC Samples: Method Blank	Start of each analytical batch	DDW went through extraction process	Within 3 σ of baseline	Troubleshoot IC instrument and check extraction procedure
QC Samples: Check Standard	Daily, before analysis of samples, and 10th samples	Dionex, DRI, or ERA certified standard solutions	± 10% for at least two of the three anions or cations and ± 20% for all ions	Reanalyze samples between this and previous QC standards
QC Samples: Duplicates[b]	10th samples	Sample extract	<LQL for ion ≤10×LQL; ±10% for ion >10×LQL for at least 2 of the 3 anions or cations; and <two times of the above limits for all ions	Reanalysis of duplicate sample
Chromatogram Review	Every sample	N/A	No unusual peak shape, overlapping peaks, or background subtractions	Reanalysis of problem sample

[a] LQL is an internal QA indicator, distinct from the MDL reported to AQS.

[b] Duplicate indicates analysis results are obtained from two different aliquots of the same filter sample extract run on the same instrument.

4.1.2 Summary of QC Results

Table 4.1-1 outlines corrective actions for failed QC checks. For failed method blanks, instrument malfunction was ruled out first. Next, the blank was reanalyzed to rule out contamination during the extraction process and within the IC system. For the several cases of failed method blanks in Table 4.1-2, reanalysis of the blanks resulted in concentrations below QC threshold and sample data were not affected. When the Dionex and DRI-made QC control standards (Table 4.1-3 and 4.1-4) that were run after multipoint calibration and before sample analysis failed to pass acceptance criteria, the multipoint calibration, the QC control standard, and any samples that were analyzed were rerun to ensure that the QC standards passed acceptance criteria. Failed ERA QC standards that were analyzed every 10th sample (Table 4.1-5) resulted in reanalysis of all samples between the failed standard and the nearest previous passing QC standard. Reported sample data all passed acceptance criteria for the QC standards. Duplicate analyses (Table 4.1-6) that exceeded acceptance criteria were reanalyzed and compared to the original analysis. If the second duplicate met acceptable tolerance, the first duplicate data point was considered spurious and was replaced. If the second duplicate analysis did meet tolerance standards, all ten samples in the set were reanalyzed. Sample data were not affected by reanalyzing duplicates.

4.1.2.1 Method Blanks

Table 4.1-2 lists the number of method blanks analyzed during the report period and their concentration statistics.

Table 4.1-2: Method blank counts and concentrations for all reported ions.

Ions	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+
Count	337	337	337	324	324	324
Median (µg/mL)	0.001	0.005	0.000	0.000	0.000	0.000
Average (µg/mL)	0.002	0.007	0.001	0.002	0.001	0.001
St. Dev. (µg/mL)	0.005	0.009	0.002	0.007	0.004	0.002
Min (µg/mL)	0.000	0.000	0.000	0.000	0.000	0.000
Max (µg/mL)	0.037	0.070	0.017	0.065	0.028	0.021
# Fail	1	1	1	2	1	2

4.1.2.2 QC Control Standards

Tables 4.1-3 and 4.1-4 list the analysis statistics for Dionex and DRI-made ion QC control standards, respectively. The control charts of these analyses are shown in Figure 4.1-1. The average difference between the measured and nominal concentrations are <6%, within the ±10% limit (Table 4.1-1), although a few individual checks failed the 10% acceptance criteria. Corrective actions for failed analyses are shown in Table 4.1-1. Table 4.1-5 summarizes analysis statistics for the ERA QC standards at different concentration levels, showing that all average recoveries are within 90–110%.

Table 4.1-3: Statistics for Dionex ion QC control standards.

Ions	**Nominal (µg/mL)**	**Count**	**Median (µg/mL)**	**Average (µg/mL)**	**Min (µg/mL)**	**Max (µg/mL)**	**# fail**	**Ave % Recovery**	**% St. Dev.**
Cl^-	1.000	111	0.993	0.993	0.922	1.072	0	99.3%	2.5%
NO_3^-	1.000	111	0.953	0.957	0.884	1.040	3	95.7%	3.6%
SO_4^{2-}	1.000	111	0.997	0.998	0.916	1.093	0	99.8%	3.5%
Na^+	1.000	111	1.014	1.011	0.941	1.088	0	101.1%	3.3%
NH_4^+	1.250	111	1.318	1.319	1.224	1.505	8	105.5%	3.3%
K^+	2.500	111	2.591	2.618	2.345	3.482	8	104.7%	6.1%

Table 4.1-4: Statistics for DRI-made ion QC control standards.

Ions	**Nominal (µg/mL)**	**Count**	**Median (µg/mL)**	**Average (µg/mL)**	**Min (µg/mL)**	**Max (µg/mL)**	**# fail**	**Ave % Recovery**	**% St. Dev.**
Cl^-	1.010	90	0.971	0.973	92.1	1.035	0	96.4%	2.4%
NO_3^-	1.000	90	1.041	1.035	91.9	1.150	3	103.5%	4.7%
SO_4^{2-}	1.000	90	0.995	1.001	94.1	1.058	0	100.1%	2.8%
Na^+	1.030	84	1.024	1.031	96.3	1.200	8	100.1%	4.1%
NH_4^+	0.390	84	0.400	0.404	35.0	0.495	9	103.5%	5.6%
K^+	0.000	84	0.003	0.005	0.0	0.031	3	NA	NA

[a]NA=Not applicable

Table 4.1-5: Statistics for ERA QC control standards.

Ion	Nominal (µg/mL)	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	Ave% Recovery	% St. Dev.
Cl^-	0.005	12	0.005	0.005	0.004	0.006	94.5%	8.7%
	0.01	12	0.010	0.010	0.008	0.011	96.6%	9.8%
	0.02	39	0.018	0.018	0.016	0.025	90.6%	9.7%
	0.05	70	0.045	0.045	0.041	0.063	90.8%	8.0%
	0.1	198	0.091	0.092	0.080	0.118	92.4%	7.3%
	0.2	348	0.184	0.185	0.155	0.219	92.6%	5.2%
	0.5	468	0.478	0.479	0.402	0.536	95.7%	4.0%
	1	440	0.991	0.993	0.804	1.084	99.3%	3.5%
	2	383	2.018	2.029	1.855	2.312	101.5%	2.6%
	3	333	3.024	3.048	2.755	3.437	101.6%	3.0%
	5	45	5.027	5.069	4.950	5.276	101.4%	1.7%
	10	43	10.041	10.128	9.204	10.858	101.3%	2.8%
NO_3^-	0.005	12	0.005	0.005	0.004	0.006	99.8%	12.4%
	0.01	12	0.009	0.009	0.008	0.011	92.1%	8.8%
	0.02	39	0.017	0.018	0.016	0.026	91.1%	12.3%
	0.05	70	0.043	0.045	0.040	0.065	90.1%	11.4%
	0.1	198	0.089	0.091	0.073	0.127	90.8%	10.5%
	0.2	348	0.182	0.181	0.140	0.221	90.7%	7.7%
	0.5	468	0.464	0.467	0.362	0.568	93.4%	5.7%
	1	440	0.962	0.969	0.764	1.108	96.9%	4.4%
	2	383	2.010	2.022	1.800	2.555	101.1%	3.6%
	3	333	3.049	3.075	2.752	3.845	102.5%	3.8%
	5	45	5.037	5.070	4.586	5.454	101.4%	2.9%
	10	43	10.044	10.174	9.157	11.000	101.7%	3.4%
SO_4^{2-}	0.005	12	0.005	0.005	0.005	0.006	107.8%	11.2%
	0.01	12	0.011	0.011	0.010	0.011	110.1%	3.9%
	0.02	39	0.019	0.020	0.017	0.022	98.1%	6.6%
	0.05	70	0.049	0.049	0.046	0.054	98.6%	4.1%
	0.1	198	0.095	0.096	0.086	0.116	96.0%	6.5%
	0.2	348	0.187	0.187	0.157	0.226	93.6%	6.1%
	0.5	468	0.469	0.471	0.392	0.548	94.2%	4.7%
	1	440	0.965	0.970	0.773	1.115	97.0%	4.0%
	2	383	2.007	2.020	1.803	2.528	101.0%	3.6%
	3	333	3.047	3.069	2.763	3.836	102.3%	3.8%
	5	45	5.043	5.076	4.509	5.521	101.5%	3.3%
	10	43	10.043	10.240	9.819	12.125	102.4%	4.3%
Na^+	0.005	5	0.005	0.004	0.004	0.005	89.9%	12.5%
	0.01	6	0.009	0.009	0.006	0.013	93.6%	33.1%
	0.02	41	0.019	0.019	0.015	0.026	96.9%	15.0%
	0.05	68	0.044	0.046	0.038	0.065	92.9%	13.6%

Ion	Nominal (µg/mL)	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	Ave% Recovery	% St. Dev.
	0.1	157	0.088	0.091	0.078	0.118	91.2%	10.5%
	0.2	329	0.182	0.184	0.153	0.243	91.8%	7.2%
	0.5	440	0.477	0.480	0.439	0.567	96.0%	4.2%
	1	407	0.990	0.996	0.914	1.103	99.6%	3.3%
	2	358	2.015	2.025	1.902	2.168	101.2%	2.6%
	3	291	3.051	3.052	2.777	3.266	101.7%	3.1%
	5	29	5.041	5.077	4.889	5.235	101.5%	2.0%
	10	11	10.198	10.184	10.090	10.474	101.8%	1.1%
NH_4^+	0.005	5	0.005	0.005	0.005	0.006	98.1%	8.0%
	0.01	6	0.010	0.010	0.009	0.011	99.1%	8.8%
	0.02	41	0.019	0.020	0.017	0.024	97.7%	9.5%
	0.05	68	0.048	0.049	0.043	0.059	97.3%	8.6%
	0.1	157	0.097	0.098	0.088	0.119	98.2%	7.8%
	0.2	329	0.196	0.198	0.174	0.229	99.2%	5.7%
	0.5	440	0.504	0.507	0.444	0.565	101.3%	3.8%
	1	407	1.013	1.019	0.902	1.138	101.9%	3.4%
	2	358	1.994	1.998	1.912	2.147	99.9%	2.2%
	3	291	3.005	3.003	2.805	3.161	100.1%	2.2%
	5	29	5.000	4.971	4.560	5.419	99.4%	3.5%
	10	11	10.154	10.086	9.555	10.590	100.9%	3.5%
K^+	0.005	5	0.005	0.005	0.005	0.005	99.8%	0.7%
	0.01	6	0.010	0.010	0.009	0.011	96.9%	5.6%
	0.02	41	0.017	0.018	0.015	0.025	90.5%	13.2%
	0.05	68	0.045	0.046	0.039	0.059	91.4%	10.3%
	0.1	157	0.094	0.094	0.080	0.116	93.7%	8.6%
	0.2	329	0.188	0.190	0.140	0.250	94.9%	7.7%
	0.5	440	0.508	0.506	0.366	0.647	101.2%	6.0%
	1	407	1.025	1.029	0.833	1.291	102.9%	7.9%
	2	358	2.026	2.079	1.731	2.577	103.9%	8.2%
	3	291	3.094	3.162	2.722	3.909	105.4%	7.6%
	5	29	5.229	5.336	4.900	6.313	106.7%	8.0%
	10	11	10.260	10.262	9.182	10.891	102.6%	4.5%

Figure 4.1-1a: Control charts for Dionex ion QC control standards. The limits are ±10% of the nominal concentrations (red dashed lines).

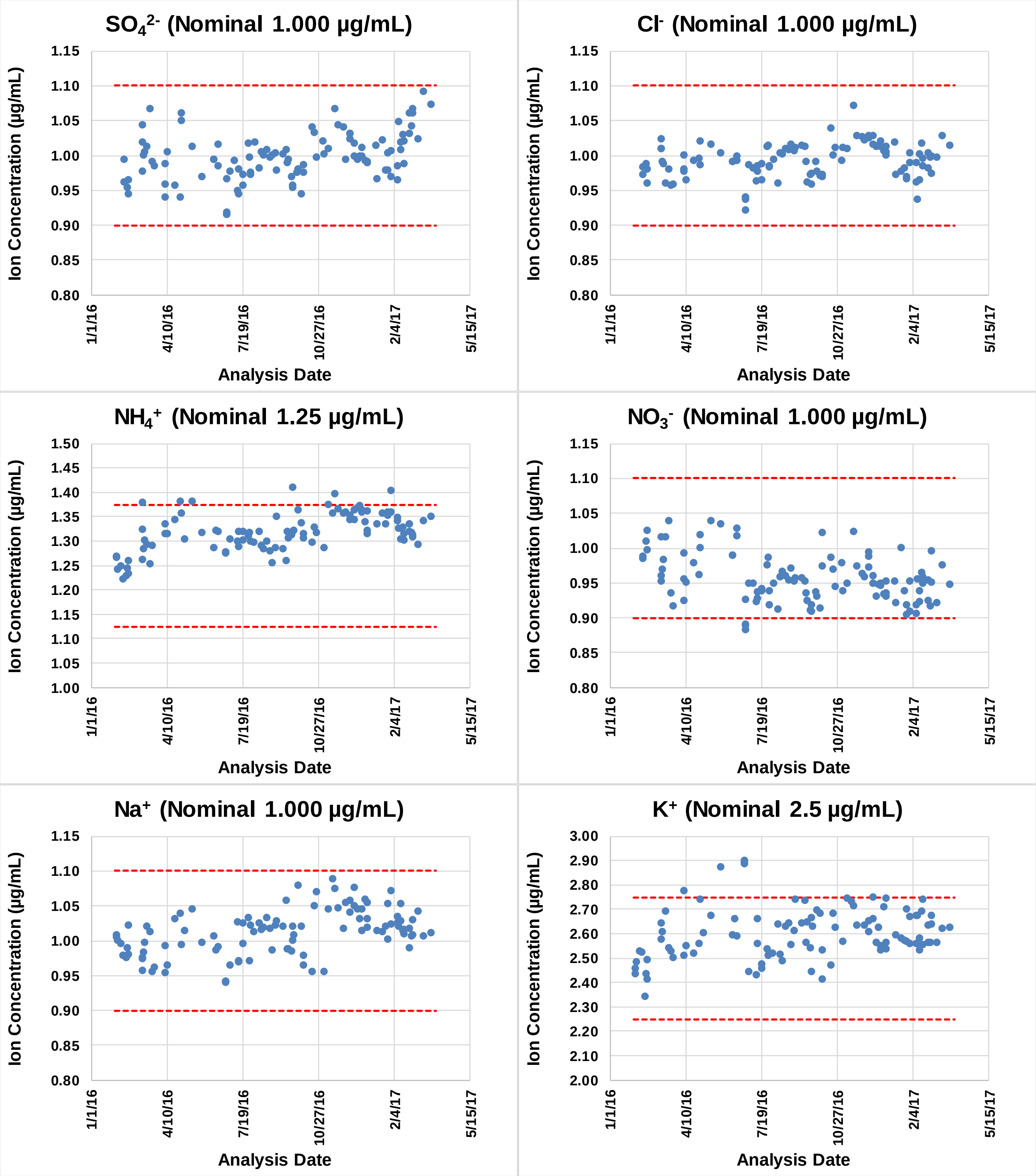
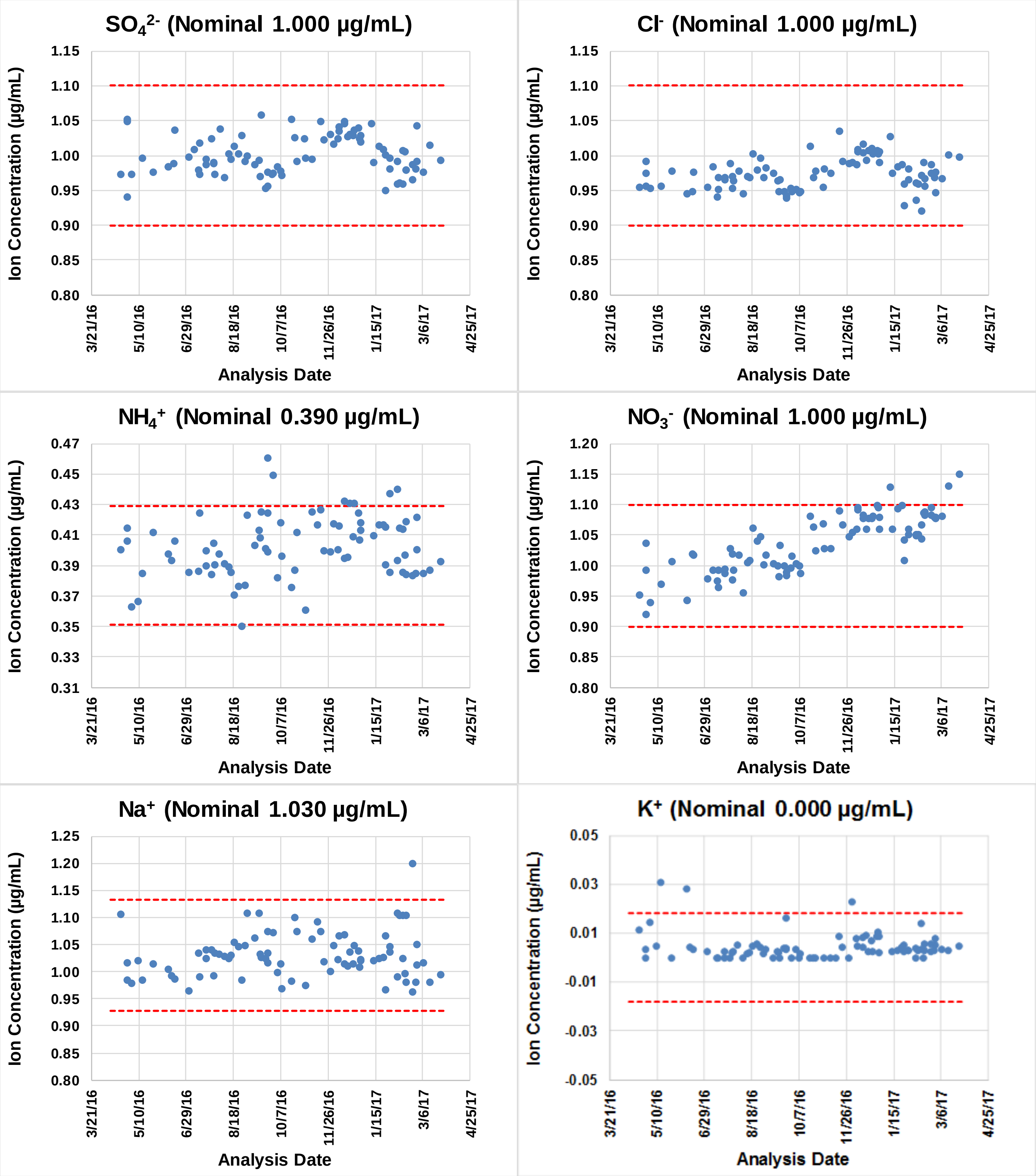


Figure 4.1-1b: Statistics for DRI-made ion QC control standards. The limits are ±10% of the nominal concentrations, except for K$^+$ which is 3×LOD (red dashed lines).



4.1.2.3 Duplicate Analyses

Table 4.1-6 gives the criteria and summary statistics for duplicate analysis results. Duplicate analysis results are obtained from two different aliquots of the same filter sample extract run on the same instrument. The criteria used for each ion were that 1) if the average concentration was less than or equal to 10 times the lower quantifiable limit (LQL), the absolute value of the average difference should be less than the LQL, and 2) if the average concentration was greater than the LQL, then the relative percent different difference (RPD) should be less than 10%. LQLs are given in Tables 4.1-7a and 4.1-7b. The LQLs are used as internal QA indicators, distinct from the MDLs reported to AQS.

Table 4.1-6: Ion duplicate analysis criteria and statistics.

Range	Criteria	Statistic	Na^+	NH_4^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	Units
All		Count	1482	1482	1482	1482	1482	1482	
Ion ≤ 10 x LQL	< LQL	Count	1389	780	1216	1398	797	560	
		No. Fail	0	0	0	0	0	0	
		% Fail	0%	0%	0%	0%	0%	0%	%
		Mean	0.008	0.018	0.010	0.012	0.034	0.043	µg/filter difference
		St. Dev.	0.026	0.052	0.017	0.038	0.101	0.075	µg/filter difference
		Max	0.447	1.152	0.244	1.184	2.440	1.270	µg/filter difference
		Min	0.000	0.000	0.000	0.000	0.000	0.000	µg/filter difference
		Median	0.002	0.006	0.005	0.005	0.014	0.021	µg/filter difference
Ion > 10 x LQL	RPD[a] <10%	Count	93	702	266	84	685	922	
		No. Fail	0	0	25	0	0	0	
		% Fail	0.0%	0.0%	9.4%	0.0%	0.0%	0.0%	%
		Mean	0.4%	2.1%	3.8%	0.3%	1.0%	1.0%	RPD
		St. Dev.	0.3%	2.0%	4.0%	0.2%	1.2%	1.1%	RPD
		Max	1.2%	9.9%	19.5%	0.8%	6.4%	6.0%	RPD
		Min	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	RPD
		Median	0.3%	1.3%	2.4%	0.3%	0.6%	0.6%	RPD

[a] RPD= 100 × absolute value [original sample – duplicate sample] / [(original sample + duplicate sample) / 2]

4.1.3 Determination of Uncertainties and Method Detection Limits

For discussion of Method Detection Limits (MDLs) see Section 3.1.3.2.

For discussion of analytical uncertainty and total uncertainty see Section 3.1.2 and Section 6.5, respectively.

4.1.4 Audits, Performance Evaluations, Training, and Accreditations

4.1.4.1 System Audits

The prime contractor (UC Davis) did not conduct any audits of the DRI Ion Analysis laboratory during 2016.

4.1.4.2 Performance Evaluations

The EPA did not conduct any performance evaluations of the DRI Ion Analysis laboratory during 2016.

4.1.4.3 Training

All new laboratory staff receive training in performing the tasks in the SOPs for their assigned work.

4.1.4.4 Accreditations

There are no accreditations for analysis of ions on aerosol filters by Ion Chromatography.

4.1.5 Summary of Filter Field Blanks

Over the analysis period, a were total of 636 nylon filters were received as field blanks. Table 4.1-7 summarizes the field blank statistics. The lower quantifiable limits (LQLs) are defined as three times the standard deviation of field blanks and are used an internal QA indicators, distinct from the MDLs reported to AQS.

Table 4.1-7a: Nylon filter field blank statistics in µg/mL.

Species	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)	LQL (µg/mL)
Cl^-	598	0.009	0.013	0.001	0.076	0.010	0.031
NO_3^-	598	0.012	0.014	0.000	0.065	0.009	0.026
SO_4^{2-}	598	0.015	0.017	0.000	0.083	0.012	0.037
Na^+	598	0.003	0.004	0.000	0.066	0.005	0.016
NH_4^+	598	0.000	0.002	0.000	0.015	0.003	0.008
K^+	598	0.001	0.001	0.000	0.009	0.001	0.003

Table 4.1-7b: Nylon filter field blank statistics in µg/filter (extraction volume 15 mL).

Species	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)	LQL (µg/filter)
Cl^-	598	0.132	0.188	0.010	1.133	0.155	0.465
NO_3^-	598	0.175	0.207	0.000	0.977	0.132	0.395
SO_4^{2-}	598	0.221	0.248	0.000	1.248	0.186	0.557
Na^+	598	0.044	0.065	0.002	0.991	0.081	0.243
NH_4^+	598	0.007	0.023	0.000	0.231	0.039	0.118
K^+	598	0.008	0.012	0.000	0.140	0.016	0.049

4.2 UC Davis X-Ray Fluorescence (XRF) Laboratory

The UC Davis XRF Laboratory received and analyzed PTFE filters from batches 1 through 21 covering the sampling period November 20, 2015 through December 31, 2016. UC Davis performed analysis for 33 elements using energy dispersive X-ray fluorescence (EDXRF) instruments. These analyses were performed over the analysis period from December 17, 2015 to July 6, 2017. Two EDXRF instruments, XRF-1 and XRF-4, performed all of the analyses during this period. The XRF-1 instrument was in service prior to 2016 and XRF-4 was acquired in early 2016 and started analysis of CSN samples on February 17, 2016. See Table 4.2-1 for details.

Table 4.2-1: Sampling dates and corresponding EDXRF analysis dates covered in this report.

Sampling Year	Sampling Month	XRF-1 Analysis Dates	XRF-4 Analysis Dates
2015	November (starting 11/20/2015)	12/17/2015 – 02/06/2016	2/29/2016 – 03/03/2016
2015	December	02/06/2016 – 03/18/2016	02/17/2016 – 03/21/2016
2016	January	04/22/2016 – 05/09/2016	03/30/2016 – 05/03/2016
2016	February	05/08/2016 – 05/24/2016	05/03/2016 – 08/31/2016
2016	March	06/04/2016 – 07/20/2016	05/31/2016 – 11/04/2016
2016	April	07/11/2016 – 07/29/2016	06/28/2016 – 12/07/2016
2016	May	07/29/2016 – 09/29/2016	08/18/2016 – 02/01/2017
2016	June	09/15/2016 – 12/14/2016	09/20/2016 – 10/25/2016
2016	July	10/24/2016 – 11/18/2016	10/25/2016 – 11/19/2016
2016	August	11/19/2016 – 12/19/2016	11/19/2016 – 12/19/2016
2016	September	12/16/2016 – 01/10/2017	12/16/2016 – 01/09/2017
2016	October	01/19/2017 – 02/12/2017	01/18/2017 – 07/06/2017
2016	November	02/14/2017 – 03/15/2017	02/13/2017 – 03/23/2017
2016	December	03/15/2017 – 04/06/2017	03/11/2017 – 04/06/2017

Analysis dates include reanalysis of any samples within the sampling year and month.

4.2.1 Summary of QC Checks and Statistics

Samples are received by the UC Davis XRF Laboratory following the chain-of-custody procedures detailed in the *UCD CSN TI 302B*. Samples are analyzed using Malvern-Panalytical Epsilon 5 EDXRF instruments following *UCD CSN SOP 302*. Calibration of the EDXRF instruments is performed annually and as needed to address maintenance or performance issues (e.g. an X-ray tube or detector is replaced). Quality control procedures are described in *UCD CSN TI 302D* and are summarized in Table 4.2-2.

Table 4.2-2: Frequency and types of checks performed and associated criteria and corrective actions for analysis by EDXRF.

Analysis	Frequency	Criterion	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	• XRF software automatically adjusts the energy channels
PTFE Blank	Daily	≤ acceptance limits with exceedance of a single element allowed for a maximum of two consecutive days	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UC Davis Multi-element sample	Daily	±10% of reference mass loadings	• Check sample for damage/contamination • Further cross-instrumental testing • Replace sample if necessary
Micromatter Al&Si sample	Weekly	±10% of reference mass loadings	
UC Davis Multi-element sample	Weekly	±10% of reference mass loadings	
Reanalysis samples	Monthly	z-score≤1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	
SRM 2783	Monthly	Absolute bias ≤ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	

Daily QC checks include a laboratory blank (PTFE blank) and a multi-elemental reference material (ME-RM) to monitor contamination and stability/performance of the instruments. A Micromatter Al&Si ME-RM and a UC Davis-made ME-RM are also analyzed weekly to check the instrumental performance. Inter-instrumental comparability is monitored by analyzing the bias and precision between instruments of the weekly UC Davis ME-RM. Long-term inter-instrumental comparability is monitored by a set of sample filters which are reanalyzed monthly on each instrument. Long-term reproducibility is monitored by analyzing a NIST SRM 2783 standard monthly and comparing the EDXRF error from the certified/reference mass loadings to acceptance limits.

The goal of the QC checks is to identify any measurement issues that may impact CSN results and allow corrective actions to be taken to ensure the reliability, accuracy, and precision of reported XRF results.

4.2.2 Summary of QC Results

QC tests conducted over the course of the analysis period showed good overall control of the instruments and process. There were sporadic failures of the QC criteria, but they were investigated promptly and corrected with minimal impact on sample analysis. The following summarizes the QC issues which occurred during the analysis period reported here.

Failures of the low atomic number elements, specifically Na, Mg, and P, did occur during the analysis period. These were investigated and determined to have no impact on the sample analysis. The reason for the failures was determined to be the difficulty of measuring the low atomic number elements with EDXRF. The acceptance criteria for these elements will be investigated and adjusted as necessary. See Section 4.2.2.1 and Section 4.2.2.2 for further detail.

Copper (Cu) and zinc (Zn) contamination was observed on the blank QC checks for both XRF-1 and XRF-4 in March 2016. It was determined that this was the result of small brass shavings contaminating the samples from faulty sample spinners on the instruments. The spinners were turned off to stop the contamination. Samples analyzed during this period were monitored closely for Cu and Zn contamination and reanalyzed as necessary. See Section 2.2.3, Section 3.2.1.2, and Section 4.2.2.1 for further detail.

Lead (Pb) contamination was observed on the daily blank QC of XRF-4 at the beginning of March 2016. There was no observed contamination of the QC ME-RM samples. This appeared to be a one-time contamination of the blank and the Pb concentrations returned to normal after the blank was replaced. No samples were affected, so no effect on the reported data. See Section 4.2.2.1 for further detail.

In June and July, 2016 there were multiple failures of the daily blank QC, daily ME-RM, and weekly ME-RM on XRF-4 for zinc (Zn). This was determined to be contamination from the sample changing arm of the instrument. The sample changing arm was replaced which reduced the Zn contamination. During this period the daily and weekly ME-RMs became contaminated with Zn which caused exceedances for XRF-1 as well. Samples analyzed during this period were monitored closely for any contamination and were reanalyzed if there was any question of contamination. No effect on the reported data. See Section 2.2.4, Section 3.2.1.3, and Section 4.2.2.1 for further detail.

During the analysis period XRF-4 had a small number of failures of the weekly ME-RM QC check for titanium (Ti). These were small exceedances of the acceptance limit attributed to higher variability of this element due to its small mass loading ~ 10 x MDL. This ME-RM was replaced with one which had a higher mass loading of Ti to eliminate these failures. This had no effect on reported data. See Section 4.2.2.2 for further detail.

Also, during the analysis period both XRF-1 and XRF-4 exhibit some failures of the QC acceptance for all QC checks of calcium (Ca). This is still being investigated but appears to be a gradual increase in Ca concentration on the QC samples due to environmental deposition. The reported data are not affected because they are only exposed to the environment for a very short time compared to the QC samples. See section 4.2.2.1 for further detail.

4.2.2.1 Results of Daily QC Checks

Possible contamination and instability issues are monitored by analyzing a PTFE blank daily. The EDXRF results are compared to acceptance limits, which are calculated as three times the standard deviation plus the mean of a set of laboratory PTFE blanks. Figure 4.2-1 shows the results of daily analyses of blanks on both instruments. If the mass loading exceeds the limit for more than two consecutive days, the blank is replaced to distinguish between blank contamination and instrument contamination. Some occasional exceedance of the acceptance limits is expected but not continuous or repeated exceedances. In all cases of exceedance, the other QC samples are checked to see if this is an instrumental problem or strictly contamination of a blank. All samples are monitored for elemental contamination during QA Level 1 validation (*UCD CSN TI 801C*). When contamination is suspected in samples they are reanalyzed and the reanalysis result is reported if contamination was present in the original analysis. A total of 14 samples from 2016 were reanalyzed for suspected Zn contamination (2 from XRF-1, 12 from XRF-4). Of those, 8 were found to have Zn contamination and their reanalysis results were reported (all originally analyzed on XRF-4).

Both instruments show gradual increases in Ca, which drops immediately after the blank is changed. This indicates contamination of the blank filter likely to arise from atmospheric deposition and/or instrument wear. XRF-4 showed Zn contamination in June and July 2016, which was determined to be caused by a faulty sample changer arm (see Section 2.2.4). The sample changer arm on this instrument was replaced, and the Zn contamination was drastically reduced although it still sporadically appears. In March 2016, faulty brass brushes in both instruments’ sample spinners were the cause of observed Cu and Zn (Section 2.2.3) contamination. Replacing the faulty parts resolved the issue. Also, in March 2016, XRF-4 showed multiple exceedances of the Pb acceptance limit for laboratory blanks. These were sporadic events, and because they did not occur on consecutive days they did not fail the acceptance criteria for the QC checks. The replacement of contaminated blank resolved the issue.

Figure 4.2-1: Results of daily analyzed PTFE blanks.

Daily operational performance of the instruments is monitored by a multi-element reference material (ME-RM). Each instrument had its own daily ME-RM purchased from Micromatter containing Si, Cl, K, Fe, Zn, Cs and Br, and these were replaced in August of 2016 by UC Davis produced ME-RMs, which provide better representation of CSN samples in terms of elemental composition and mass loadings. Along with the change in ME-RM, the acceptance limits were increased from +/- 5% to +/- 10% RSD of the reference loadings to match the higher uncertainty in the UC Davis ME-RM due to the lower mass loadings of the elements. When more than two consecutive measurements exceed these limits the results are marked unacceptable (*UCD CSN TI 302D*).

Tables 4.2-3 and 4.2-4 show the results for the Micromatter ME-RMs which were analyzed from January through August, 2016 (see Table 4.2-1 for corresponding sampling dates). Chlorine and bromine results are omitted from the tables as these elements are volatile and their concentrations are not stable in repeated analyses. These tables show, (1) the average measured mass loadings, (2) acceptance limits, (3) percent of results that exceeded the acceptance limits, (4) percent of results that were unacceptable because they failed QC acceptance criteria (e.g., more than two consecutive exceedances), and (5) the relative standard deviation (RSD) over the analysis period for the daily ME-RMs. The Zn contamination on XRF-4 from the sample changer arm, discussed above, is apparent in the 5.9% of unacceptable Zn results on XRF-4 for the Micromatter ME-RM. Zn levels on the Micromatter ME-RM for XRF-4 remained high after the sample changer arm was replaced from contamination of the ME-RM itself. This can be verified by observing the daily PTFE blanks, which are replaced after contamination, show a reduction in Zn blank levels after the part replacement. No attempt was made to clean the Zn contamination from the Micromatter ME-RM to prevent further contamination or possible damage to the filter.

Table 4.2-3: Descriptive statistics of XRF-1 results (µg/cm^2) of the QC Micromatter ME-RM sample analyzed daily from 01/07/2016 to 08/08/2016, N = 196 (see Table 4.2-1 for corresponding sampling dates). Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Si	6.098	5.713	6.315	0	0	1.5
K	5.130	4.826	5.334	0	0	1.3
Fe	13.552	12.753	14.095	0	0	1.3
Zn	4.009	3.774	4.171	0	0	1.2
Cs	7.582	7.195	7.952	0	0	1.2

Limits are +/- 5% of the reference loadings (TI 302D).

Table 4.2-4: Descriptive statistics of XRF-4 results (µg/cm^2) of the QC Micromatter ME-RM sample analyzed daily from 02/17/2016 to 08/17/2016, N = 187 (see Table 4.2-1 for corresponding sampling dates). Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Si	6.656	6.441	7.119	0.5	0	1.1
K	4.729	4.539	5.017	0	0	1.1
Fe	11.098	10.578	11.691	0	0	0.7
Zn	3.208	2.956	3.267	15.5	5.9	6.3
Cs	5.830	5.492	6.070	0	0	1.3

Limits are +/- 5% of the reference loading (TI 302D).

Tables 4.2-5 and 4.2-6 show the results of the UC Davis ME-RMs which replaced the Micromatter ME-RMs in August 2016. Only elements with mass loadings greater than ten times their MDLs are displayed. XRF-1 does not include results for the UC Davis ME-RM for the entire analysis period because the instrument did not perform CSN analysis over the entire analysis period. Chlorine and bromine results are omitted from the tables as these elements are volatile, and their concentrations on the ME-RM are not stable. The relative standard deviations of the UC Davis ME-RMs are noticeably higher than those of the Micromatter ME-RMs, but this is expected due to the much smaller mass loadings of the UC Davis ME-RMs. A small number of exceedances of the limit is expected statistically, but this should be no more than 3% of the total number of measures. Exceedances of Na, Mg, and P reflect the difficulty of measuring these elements with the EDXRF method. Investigations following the exceedances for these elements did not identify issues, so no corrective actions were taken. Because of the difficulty measuring these elements with EDXRF, new acceptance limits will be investigated for the future.

Table 4.2-5: Descriptive statistics of XRF-1 results (µg/cm^2) of the QC UC Davis ME-RM sample analyzed daily from 09/15/2016 to 06/26/2017, N = 285 (see Table 4.2-1 for corresponding sampling dates). Only elements with mass loadings > 10*MDL are reported. Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Na	5.596	5.104	6.239	1.8	0	3.8
Mg	0.770	0.656	0.802	36.8	12.3	8.4
Al	1.596	1.424	1.740	0	0	3.0
Si	2.757	2.466	3.014	0	0	1.1
P	0.114	0.109	0.133	32.3	10.5	19.0
S	11.006	9.837	12.023	0	0	0.6
K	1.627	1.454	1.777	0	0	2.3
Ca	1.839	1.610	1.967	0	0	3.2
Ti	0.127	0.114	0.139	0.4	0	3.4
V	0.165	0.148	0.181	0	0	2.0
Cr	0.697	0.625	0.763	0	0	0.8
Mn	0.337	0.303	0.370	0	0	1.9
Fe	1.996	1.778	2.173	0	0	0.8
Co	0.130	0.117	0.143	0	0	2.4
Ni	0.116	0.104	0.127	0	0	2.3
Cu	0.540	0.479	0.586	0	0	1.5
Zn	0.399	0.354	0.433	0	0	1.8
As	0.492	0.444	0.542	0	0	1.7
Se	0.305	0.274	0.335	0	0	1.6
Rb	0.129	0.116	0.142	0	0	3.4
Sr	0.137	0.122	0.149	0	0	2.9
Cd	0.132	0.115	0.141	21.8	0	7.0
Pb	0.647	0.581	0.710	0	0	2.2

Limits are +/- 10% of the reference loading (TI 302D).

Table 4.2-6: Descriptive statistics of XRF-4 results (µg/cm^2) of the QC UC Davis ME-RM sample analyzed daily from 08/18/2016 to 07/05/2017, N = 340 (see Table 4.2-1 for corresponding sampling dates). Only elements with mass loadings > 10*MDL are reported. Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Na	5.559	5.011	6.125	7.4	1.2	5.3
Mg	0.476	0.409	0.500	47.1	26.2	10.7
Al	1.407	1.250	1.527	0	0	3.8
Si	2.849	2.552	3.119	0	0	2.5
P	0.251	0.221	0.270	13.5	2.1	7.1
S	10.432	9.351	11.429	0	0	2.2
K	1.607	1.448	1.769	0	0	3.3
Ca	1.851	1.626	1.987	0	0	5.1
Ti	0.128	0.114	0.140	0.3	0	4.1
V	0.162	0.147	0.179	0	0	3.2
Cr	0.689	0.618	0.755	0	0	2.8
Mn	0.327	0.293	0.359	0	0	2.9
Fe	1.950	1.750	2.138	0	0	3.1
Co	0.128	0.115	0.140	0.3	0	3.5
Ni	0.113	0.102	0.124	0.3	0	3.2
Cu	0.531	0.479	0.586	0	0	2.3
Zn	0.374	0.339	0.414	0.3	0	4.0
As	0.495	0.446	0.545	0	0	2.5
Se	0.296	0.266	0.325	0	0	2.7
Rb	0.127	0.115	0.141	0.6	0	3.9
Sr	0.135	0.122	0.149	0.3	0	3.3
Cd	0.133	0.119	0.146	20.0	0	8.3
Pb	0.628	0.568	0.694	0	0	2.7

Limits are +/- 10% of the reference loading (TI 302D).

4.2.2.2 Results of Weekly QC Checks

Weekly QC checks include analysis of a UC Davis produced ME-RM (different than the daily ME-RM) and a ME-RM purchased from Micromatter containing only Al and Si. The UC Davis ME-RM was damaged and replaced with a new one in November of 2016. Weekly results are compared to acceptance limits of +/- 10% of the reference values. When more than two consecutive measurements exceed these limits the results are marked unacceptable (*UCD CSN TI 302D*). A weekly QC report is generated internally, which includes checks of the PTFE blanks and the daily and weekly ME-RMs.

Table 4.2-7 and Table 4.2-8 show the EDXRF statistics of the weekly UC Davis ME-RM run until November 2016 for elements with mass loadings greater than ten times the MDL. As with the daily ME-RM discussion above, some elements such as Na and P are difficult to quantify with the EDXRF method and show some exceedances. Ti shows a few exceedances, but its mass loading is near ten times the MDL, so this is expected and acceptable (as discussed in *UCD CSN*

TI 302D). Zn shows some exceedances because of the sample changer arm contamination (see Section 2.2.4 and Section 4.2.2.1). This contaminated the weekly ME-RM and as a result Zn exceedance and RSD are high for both instruments. Also, note the number of measures for XRF-1 is lower than would be expected for weekly measures between January and November 2016. This is due to maintenance issues and time spent analyzing samples outside of the CSN project where a different set of QC samples are used.

Table 4.2-7: Descriptive statistics of XRF-1 results (µg/cm^2) of the QC UC Davis ME-RM sample analyzed weekly from 01/07/2016 to 11/03/2016, N = 33 (see Table 4.2-1 for corresponding sampling dates). Only elements with mass loadings > 10*MDL are reported. Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Na	1.658	1.459	1.783	27.3	3.0	8.4
Al	0.536	0.476	0.582	0	0	3.2
Si	0.866	0.783	0.957	0	0	1.8
P	0.035	0.031	0.038	45.5	6.1	12.9
S	3.153	2.819	3.446	0	0	1.2
K	0.461	0.412	0.504	0	0	0.9
Ca	0.519	0.462	0.564	0	0	1.8
Ti	0.035	0.031	0.038	9.1	0	5.5
V	0.045	0.040	0.049	0	0	4.4
Cr	0.193	0.174	0.213	0	0	1.6
Mn	0.095	0.084	0.103	0	0	4.3
Fe	0.557	0.502	0.614	0	0	1.3
Co	0.035	0.031	0.038	6.1	0	5.1
Ni	0.033	0.029	0.035	0	0	4.4
Zn	0.051	0.041	0.050	48.5	6.1	11.0
As	0.136	0.126	0.154	3.0	0	4.4
Se	0.088	0.080	0.097	3.0	0	4.4
Pb	0.174	0.159	0.194	3.0	0	4.8

Limits are +/- 10% of the reference loading (TI 302D).

Table 4.2-8: Descriptive statistics of XRF-4 results (µg/cm^2) of the QC UC Davis ME-RM sample analyzed Weekly from 03/12/2016 to 11/03/2016, N = 42 (see Table 4.2-1 for corresponding sampling dates). Only elements with mass loadings > 10*MDL are reported. Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Na	1.876	1.734	2.119	11.9	2.4	6.3
Al	0.473	0.433	0.529	2.4	0	4.2
Si	0.873	0.798	0.975	0	0	2.8
P	0.069	0.061	0.075	16.7	0	7.0
S	3.060	2.803	3.426	0	0	2.2
K	0.463	0.423	0.517	0	0	1.8
Ca	0.511	0.461	0.563	0	0	1.6
Ti	0.034	0.031	0.038	16.7	2.4	6.5
V	0.044	0.040	0.049	0	0	4.5
Cr	0.188	0.172	0.210	0	0	2.3
Mn	0.092	0.084	0.103	0	0	3.8
Fe	0.546	0.497	0.608	0	0	1.8
Co	0.035	0.032	0.039	4.8	0	5.3
Ni	0.033	0.030	0.037	7.1	0	5.2
Zn	0.051	0.041	0.050	57.1	9.5	13.4
As	0.135	0.124	0.152	2.4	0	4.0
Se	0.087	0.079	0.097	0	0	3.6
Pb	0.173	0.159	0.195	4.8	0	5.2

Limits are +/- 10% of the reference loading (TI 302D).

Table 4.2-9 and Table 4.2-10 show results of the weekly UC Davis ME-RM which started service in November 2016. Again, only elements with mass loadings greater than ten times their MDLs are shown and Cl and Br are removed due to their volatility. Exceedances of Mg and P result from difficulties in quantifying these elements by EDXRF. Following these exceedances, the instruments were inspected but no issues were found and no remedial actions were taken. The Zn exceedance in XRF-4 is higher than would be expected and that instrument is monitored closely for ongoing random Zn contamination.

Table 4.2-9: Descriptive statistics of XRF-1 results (µg/cm^2) of the QC UC Davis ME-RM sample analyzed weekly from 11/10/2016 to 07/06/2017, N = 31 (see Table 4.2-1 for corresponding sampling dates). Only elements with mass loadings > 10*MDL are reported. Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Na	2.975	2.740	3.349	9.7	0	4.9
Mg	0.451	0.386	0.472	61.3	9.7	14.0
Al	0.891	0.796	0.973	0	0	2.9
Si	1.435	1.289	1.576	0	0	1.3
P	0.062	0.054	0.066	38.7	3.2	11.2
S	5.371	4.826	5.898	0	0	1.0
K	0.783	0.699	0.854	0	0	1.5
Ca	0.836	0.742	0.906	0	0	2.6
Ti	0.060	0.054	0.066	0	0	4.4
V	0.075	0.068	0.083	0	0	3.7
Cr	0.318	0.287	0.350	0	0	1.0
Mn	0.155	0.139	0.170	0	0	2.4
Fe	0.893	0.803	0.981	0	0	0.9
Co	0.059	0.054	0.065	6.5	0	4.6
Ni	0.053	0.047	0.057	0	0	3.6
Cu	0.116	0.105	0.128	0	0	2.2
Zn	0.103	0.090	0.110	3.2	0	3.9
As	0.218	0.196	0.239	0	0	2.1
Se	0.142	0.127	0.156	0	0	2.0
Sr	0.061	0.055	0.067	0	0	3.2
Pb	0.280	0.251	0.307	0	0	3.9

Limits are +/- 10% of the reference loading (TI 302D).

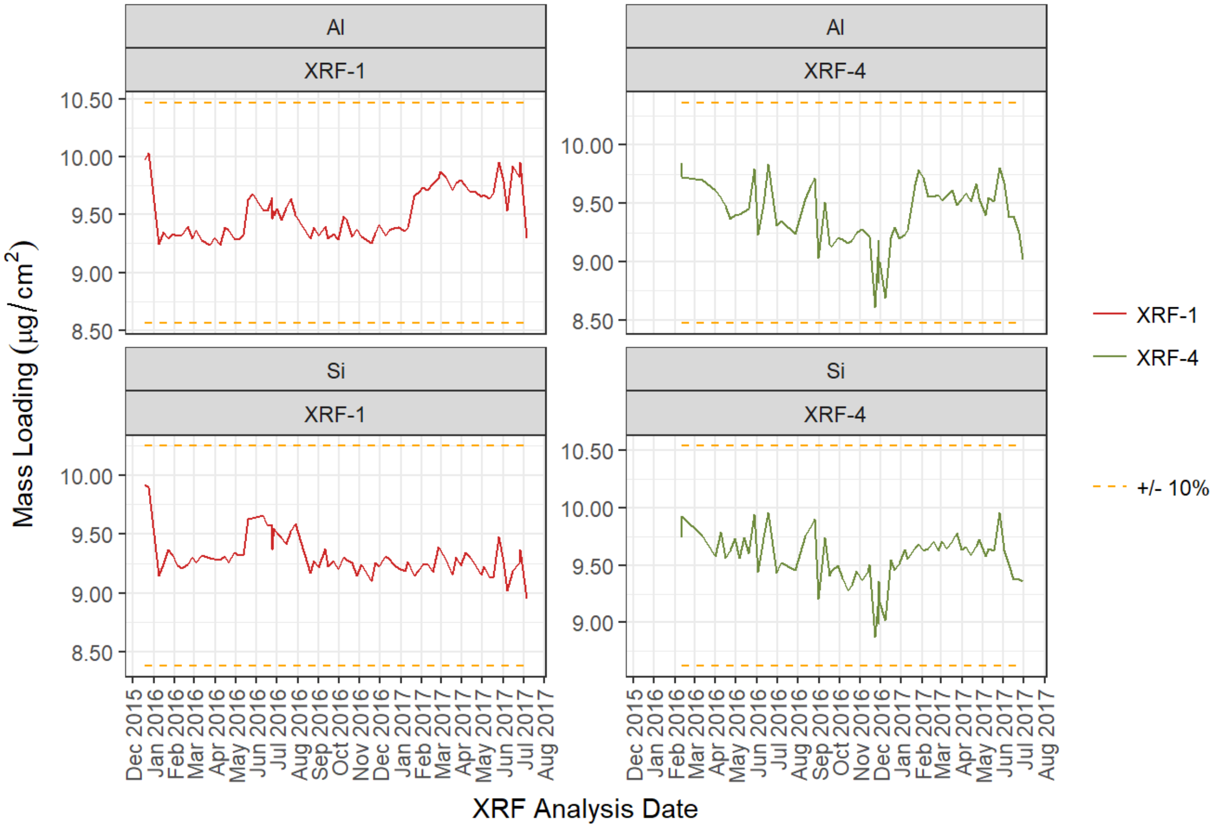
Table 4.2-10: Descriptive statistics of XRF-4 results (μg/cm^2) of the QC UC Davis ME-RM sample analyzed weekly from 11/11/2016 to 07/06/2017, N = 35 (see Table 4.2-1 for corresponding sampling dates). Only elements with mass loadings > 10*MDL are reported. Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Average	Lower Limit	Upper Limit	%Exceedance	% Unacceptable	RSD %
Na	3.197	2.838	3.469	0	0	4.5
Al	0.766	0.668	0.817	5.7	0	4.2
Si	1.454	1.297	1.585	0	0	2.5
P	0.121	0.104	0.127	45.7	5.7	7.8
S	5.180	4.580	5.598	0	0	2.6
K	0.777	0.682	0.834	0	0	3.3
Ca	0.832	0.727	0.888	2.9	0	3.8
Ti	0.061	0.053	0.065	5.7	0	5.1
V	0.075	0.066	0.080	2.9	0	4.1
Cr	0.315	0.279	0.341	0	0	2.5
Mn	0.152	0.134	0.164	5.7	0	4.0
Fe	0.887	0.784	0.958	0	0	2.7
Co	0.058	0.052	0.063	2.9	0	4.1
Ni	0.052	0.046	0.056	0	0	3.9
Cu	0.115	0.102	0.124	0	0	3.3
Zn	0.101	0.088	0.107	20.0	2.9	5.6
As	0.225	0.200	0.245	0	0	2.9
Se	0.142	0.127	0.155	0	0	3.0
Sr	0.061	0.053	0.065	8.6	0	5.7
Pb	0.279	0.250	0.305	0	0	3.8

Limits are +/- 10% of the reference loading (TI 302D).

A Micromatter ME-RM containing Al and Si is also run weekly. The results from this sample are plotted in Figure 4.2-2. The acceptance limits are set as +/- 10% of the average of the first five measurement results from each XRF. No issues are observed.

Figure 4.2-2: EDXRF results of the weekly Micromatter ME-RM containing Al and Si. Limits are +/- 10% of the reference loading.



4.2.2.3 *Reproducibility and Inter-instrument Performance Tests*

The weekly ME-RM is also used as an inter-instrument comparison as the same sample is run on both EDXRF instruments. Figures 4.2-3 and 4.2-4 plot the elemental concentrations for both of the weekly UC Davis ME-RM samples used during this analysis period (the first one was damaged in November 2016 and was replaced). The following approach is used to quantify the differences observed in the plots. The scaled relative difference (SRD) between the two instruments is calculated for each element each week as:

$$SRD_i = \frac{(\mathrm{XRF1}_i\mathrm{XRF1} - \mathrm{XRF4}_i\mathrm{XRF4})\ /\ \sqrt{2}}{(\mathrm{XRF1}_i\mathrm{XRF1} +\ \mathrm{XRF4}_i\mathrm{XRF4})\ /\ 2},$$

where, $XRF1_i$ and $XRF4_i$ are the mass loadings of the i^{th} element measured by each instrument.

For each element, $i$the random error (precision) of each instrument is estimated as the standard deviation of the weekly results $SRD_w,\ w = 1, \ldots, N$:

$$Precision_i = \sqrt{\frac{1}{N}\sum_w\left(SRD_{i,w} - \overline{SRD_i SRD}\right)^2} \qquad ,$$

where $\overline{SRD_i}$ is the mean scaled relative difference for element i over the analysis period.

The bias between instruments is the mean value of the unscaled relative differences,

$$Bias_i = \frac{1}{N}\sum_w \left(\frac{\mathrm{XRF1}_i - \mathrm{XRF4}_i\mathrm{XRF1} - \mathrm{XRF4}}{(\mathrm{XRF1}_i + \mathrm{XRF4}_i\mathrm{XRF1} + \mathrm{XRF4})\ /\ 2}\right)_w$$

The precision acceptance limit for the i^{th} element is calculated from the variation in the response of each instrument,

$$Precision\ Acceptance\ Limit_i = \sqrt{\sigma^2_{i,XRF1} + \sigma^2_{i,XRF4}}\,,$$

where σ is the standard deviation in the mass loading measured by the instrument. The bias acceptance limit is calculated as the sum of the error of both instruments to a mean reference mass loading for the i^{th} element of the ME-RM,

$$Bias\ Acceptance\ Limit_i = k * \frac{1}{N}\left(\sum_w \frac{\left|XRF1_{i,w} - C_{i,ref}\right|}{C_{i,ref}} + \sum_w \frac{\left|XRF4_{i,w} - C_{i,ref}\right|}{C_{i,ref}}\right),$$

where $C_{i,ref}$ is the reference elemental mass loading and k is a coverage factor which is set to a value of two to account for distribution of uncertainties possible in a given measurement. The acceptance limits are based on the mean mass loading for both instruments and provide a historical bias from which to compare the weekly bias of each instrument.

The results of this analysis for elements greater than ten times the detection limit and averaged over both UC Davis ME-RM samples are presented in Table 4.2-11. The results of the inter-instrument comparison show a larger bias for Na, Al, and P. Na and P are difficult to quantify using the EDXRF method and some differences are expected. The observed bias between instruments for Al is 14.5%. This discrepancy in Al measurements between instruments is caused by differences in detector efficiencies and is monitored for changes.

Table 4.2-11: Precision and bias between XRF-1 and XRF-4 from the weekly UC Davis ME-RM calculated over the entire analysis period. Only elements with mass loadings > 10*MDL are reported. Cl and Br are not reported because they are volatile and mass loadings degrade over time.

Element	Bias %	Bias Acceptance Limit %	Precision %	Precision Acceptance Limit %
Na	-8.6	±23.7	6.1	8.2
Al	14.5	±28.2	3.3	5.3
Si	-1.2	±7.1	1.8	3.0
P	-64.8	±129.1	8.4	13.2
S	3.7	±8.0	1.7	2.5
K	0.6	±5.8	1.2	2.6
Ca	1.1	±8.2	1.6	3.4
Ti	-1.2	±18.9	4.4	8.1
V	1.8	±14.7	4.2	6.0
Cr	1.8	±6.1	1.9	2.6
Mn	2.3	±12.3	3.5	5.0
Fe	1.0	±5.4	1.6	2.5
Co	-0.5	±14.2	4.4	6.5
Ni	0.3	±13.7	4.0	5.9
Cu	0.1	±7.6	2.4	3.2
Zn	0.0	±23.2	6.4	11.8
As	-2.8	±11.9	2.5	4.6
Se	-1.1	±9.4	2.7	4.4
Sr	-2.2	±11.9	3.8	4.8
Pb	0.2	±14.9	3.6	6.6

Figure 4.2-3: Instrumental comparison using the weekly UC Davis ME-RM sample which was in use between January 2016 and November 2016. XRF-1: 3/18/2016 to 11/3/2016, N = 25. XRF-4: 3/12/2016 through 11/3/2016, N = 42. (See Table 4.2-1 for corresponding sampling dates.)

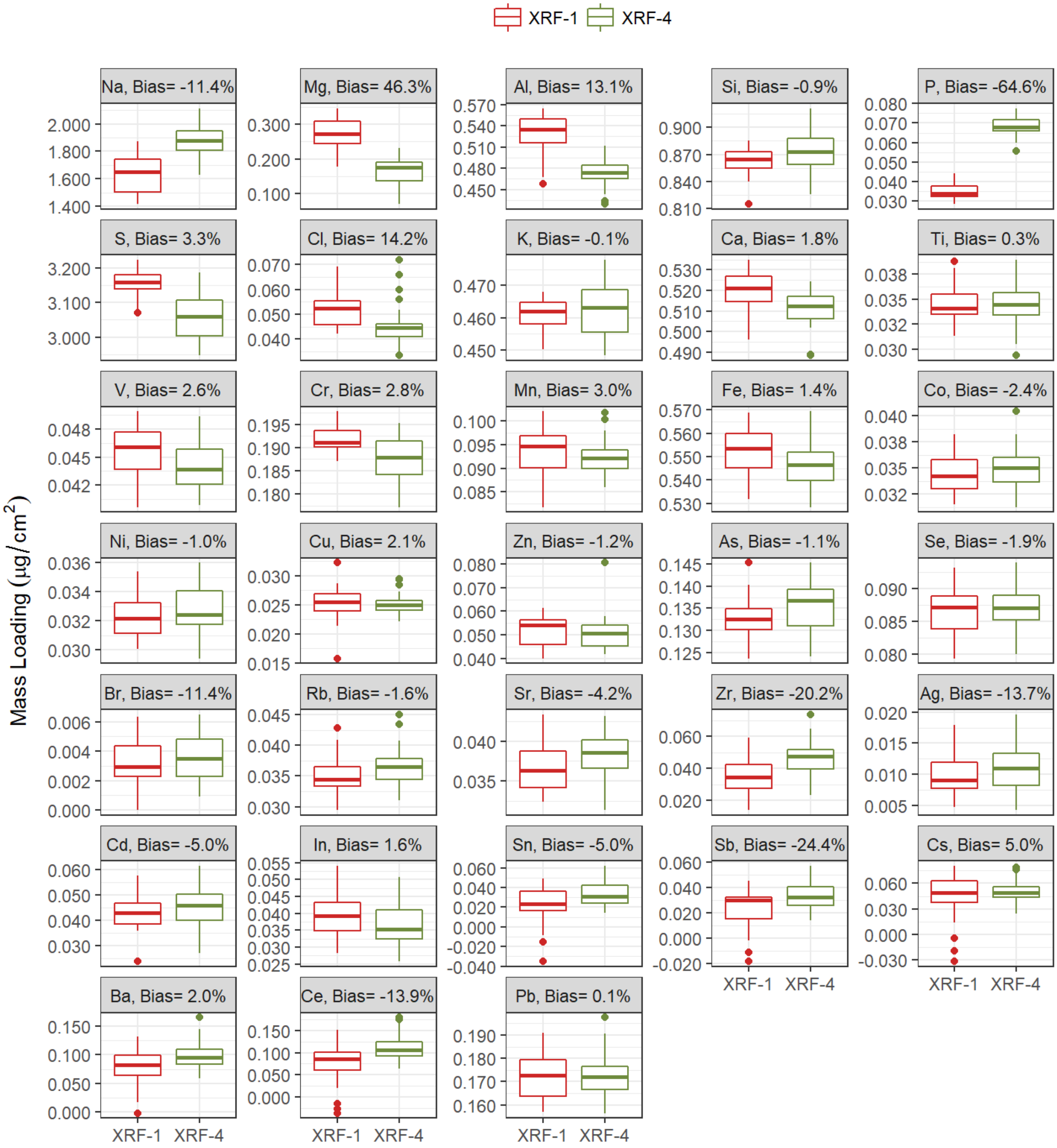
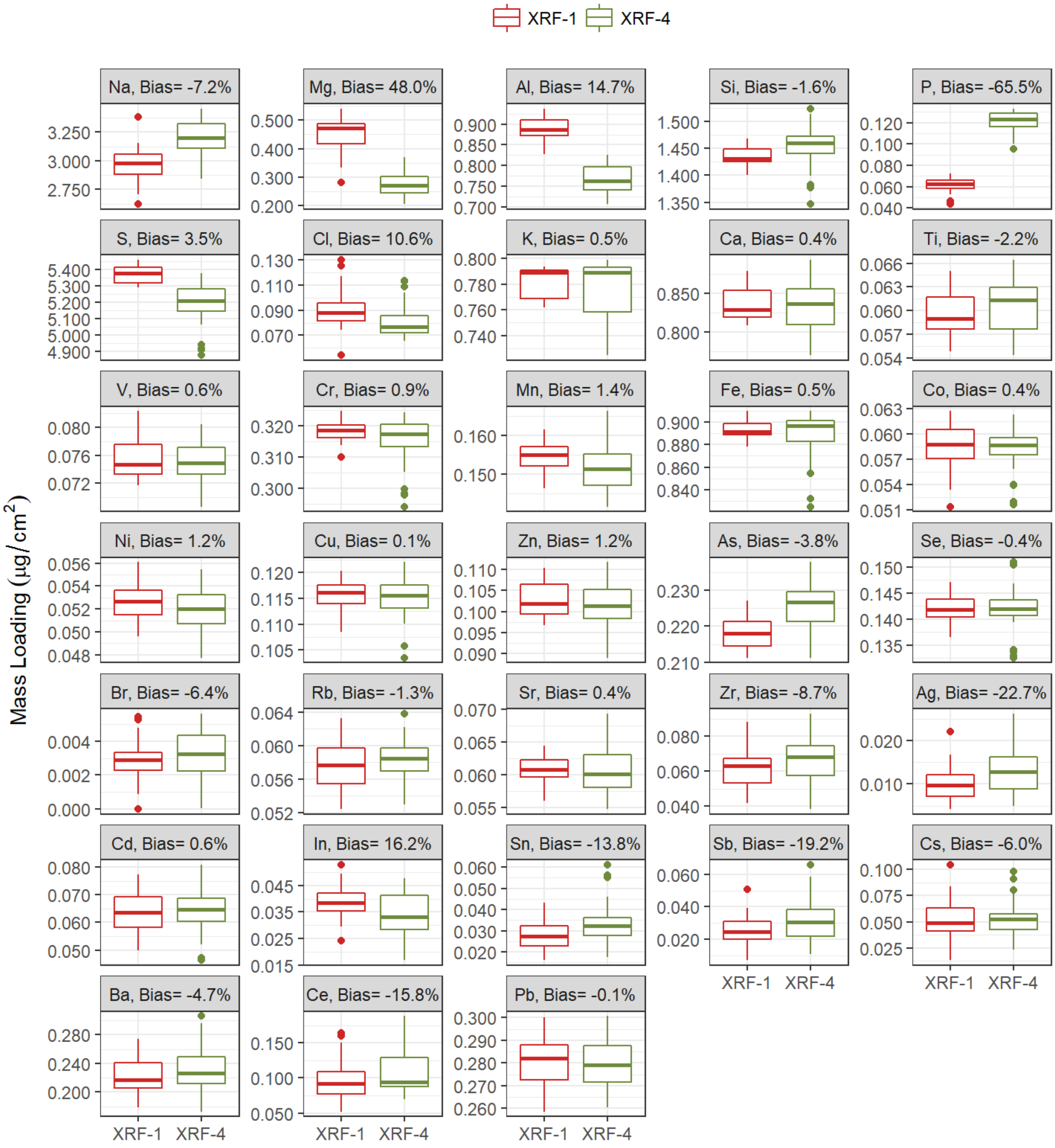


Figure 4.2-4: Instrumental comparison using the weekly UC Davis ME-RM sample which was put into use beginning in November 2016. XRF-1: 11/10/2016 to 6/13/2017, N = 31. XRF-4: 11/11/2016 to 7/7/2017, N = 36. (See Table 4.2-1 for corresponding sampling dates.)



4.2.2.4 *Long-term Stability, Reproducibility, and Inter-instrument Performance*

A set of samples is chosen for monthly reanalysis to monitor the long-term performance of the instruments. This set of samples was changed once during 2016. A set of 16 ambient air samples collected from rural IMPROVE network sites on 25 mm Pall PTFE filters were used from the beginning of 2016 through September 2016. In October 2016, a new set of 16 CSN samples and one UC Davis produced ME-RM were selected for reanalysis. These samples are on MTL 47 mm PTFE filters and were selected to better represent the range of mass loadings present in the CSN. In addition to these samples, a NIST SRM 2783 standard is included in the set. In order to compare multiple filters with different mass loadings, the results of reanalysis are first converted to z-scores. For a given month, the z-score for the i^{th} element and j^{th} filter is

$$z_{ij} = \frac{x_{ij} - \widehat{x_{ij}}}{\sqrt{U(x_{ij})^2 + U(\widehat{x_{ij}})^2}}$$

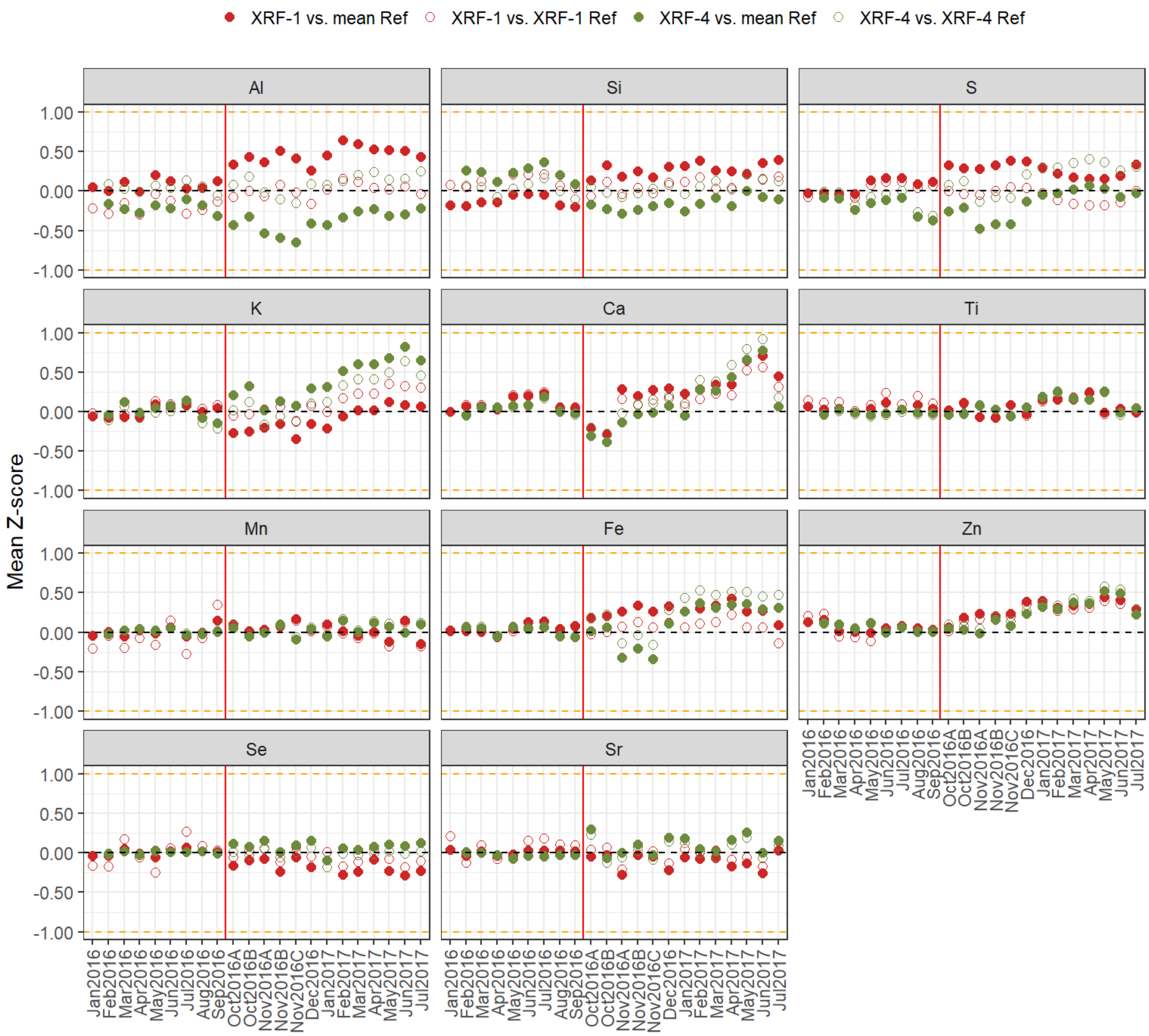
where x_{ij} is that month's result, $\widehat{x_{ij}}$ is the reference value for element *i* in filter j, and $U(x_{ij})$ and $U(\widehat{x_{ij}})$ are the uncertainty of that month's result and the reference uncertainty respectively. The instrument-specific reference values for the samples of the reanalysis set are determined as the mean and standard deviation of five initial measurements, while the values for SRM 2783 are the certified or reference loadings. Monthly z-scores for each element are then summarized across the N filters in terms of

$$Bias_i = \frac{1}{N}\sum_j z_{ij} \text{ and } RMS_i = \sqrt{\frac{1}{N}\sum_j {z_{ij}}^2}$$

Every month, two different reference values are used to calculate z-scores: (1) one reference value is only based on the average response from the one instrument for which the z-score is being calculated, (2) while the other reference value is based on the average response from both instruments. The first z-score serves as long-term reproducibility of each instrument while the second z-score is an inter-instrumental comparison. These two z-scores are plotted and checked to be within -1 to 1 for elements which have mass loadings well above the MDL: Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se, and Sr. For further detail see *UCD CSN TI 302D*.

Figure 4.2-5 shows the mean z-score plots over the analysis period. All elemental z-scores remained within ±1 throughout 2016.

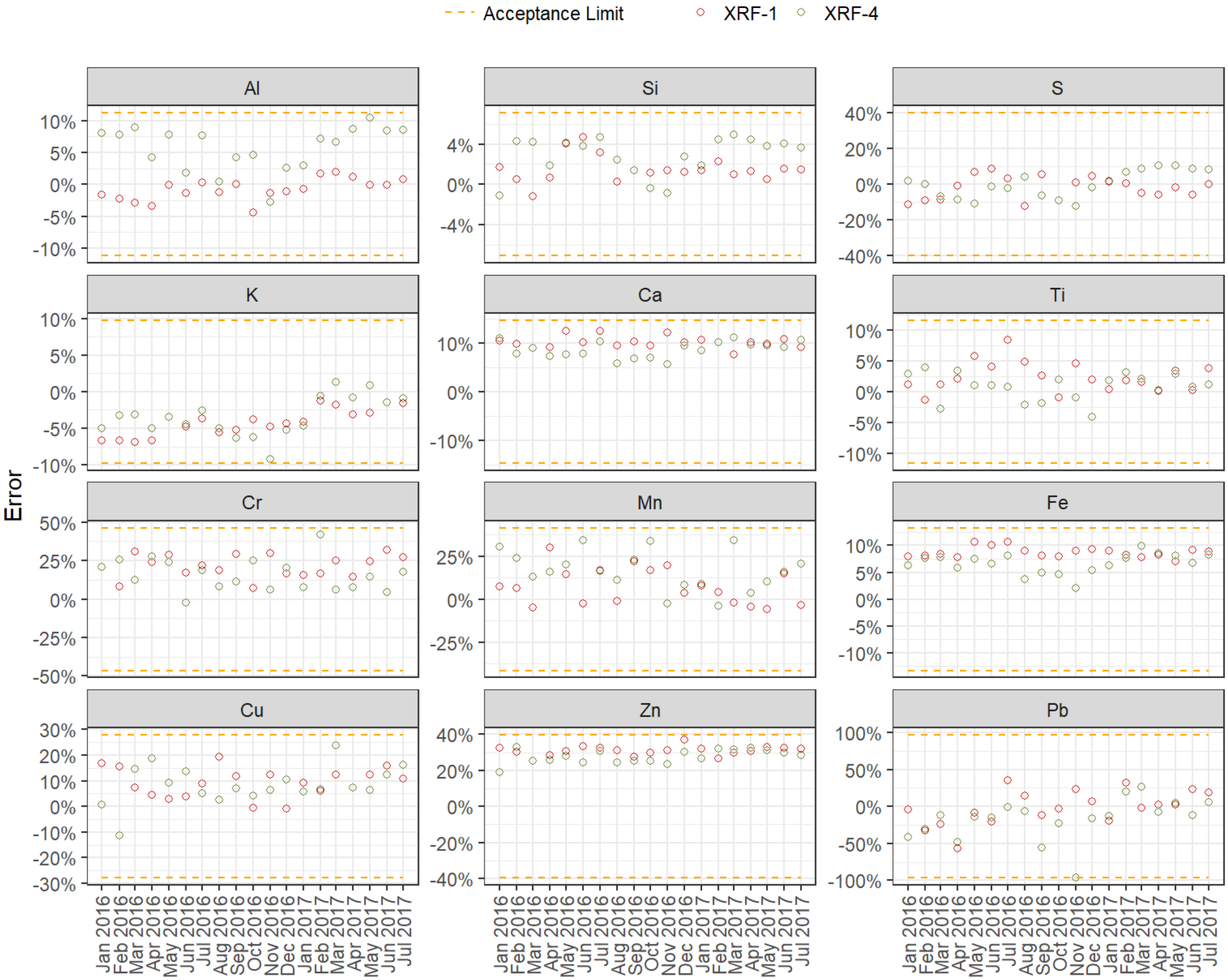
Figure 4.2-5: Inter-instrument comparison by z-score of reanalysis sample set. Vertical red line between September and October 2016 denotes change in re-analysis sample set.



4.2.2.5 Calibration Verification with NIST SRM 2783

The errors of EDXRF instruments from the NIST SRM 2783 certified/reference mass loadings are monitored monthly for selected elements whose loadings are at least three times higher than the EDXRF detection limits. The error, calculated as the difference between the measured and certified/reference mass loading relative to the certified/reference mass loading, is plotted for each instrument, and provides a measure of the stability and accuracy of the instruments. The error is compared to element specific acceptance limits calculated as +/- the root-mean-squared-relative-error plus three times the standard deviation for a set of monthly measurements (n=44). More details of these calculations can be found in the *UCD CSN TI 302D*. The results for the analysis period are shown in Figure 4.2-6. XRF-1 was calibrated in August 2016 due to the X-ray tube being replaced. Both instruments underwent routine calibrations in January 2016 and January 2017. The results of the monthly NIST SRM 2783 analyses on the instruments show that the calibration is stable over the typical calibration period, a year. The overall error for most elements is less than 20%. The only exception to this is Zn; the error in Zn is around 30%. Micromatter and UC Davis produced XRF standards follow the same calibration line whereas the Zn response of SRM 2783 falls ~30% over the line. In the literature, XRF labs reported Zn error of SRM 2783 varying between -15 to 30% (Yatkin et al., 2016b). All elements stay within the acceptance limits and there is no apparent trend in any of the data.

Figure 4.2-6: Error of each XRF instrument from the NIST SRM standard run monthly.



4.2.3 Determination of Uncertainties and Method Detection Limits

For discussion of Method Detection Limits (MDLs) see Section 3.1.3.2.

For discussion of analytical uncertainty and total uncertainty see Section 3.1.2 and Section 6.5, respectively.

4.2.4 Audits, Performance Evaluations, Training, and Accreditations

4.2.4.1 System Audits

The EPA did not conduct any audits or performance evaluations of the UC Davis XRF laboratory during 2016.

4.2.4.2 Performance Evaluations

The XRF laboratory actively participates in inter-laboratory comparisons. In 2016, UC Davis participated in an inter-laboratory comparison of aerosol filter elemental analysis which included XRF, PIXE, and ICP-MS analyses. Details of this study can be found in Yatkin et al. 2016b.

4.1.4.3 Training

Training of all personnel who assist with or operate the XRF instruments is mandatory through UC Davis. Personnel in the XRF laboratory are required to take the following UC Davis safety trainings: UC Laboratory Safety Fundamentals, Radiation Safety for Users of Radiation Producing Machines, Analytical X-ray Quiz, and Cryogen Safety.

Only personnel listed in *UC Davis CSN Quality Assurance Project Plan (QAPP)*, trained on the appropriate SOPs and Technical Instructions (*CSN SOP 302* and *CSN TI 302A-D*), and authorized by the Laboratory Manager can perform XRF analysis on CSN samples.

4.1.4.4 Accreditations

There are no accreditations for elemental analysis on aerosol filters by XRF.

4.2.5 Summary of Filter Field Blanks

Over the analysis period, there were a total of 573 PTFE filter field blanks. Table 4.2-12 summarizes the field blank statistics.

Table 4.2-12: PTFE filter field blank statistics.

Species	Count	Median ($\mu g/cm^2$)	Average ($\mu g/cm^2$)	Min ($\mu g/cm^2$)	Max ($\mu g/cm^2$)	St. Dev. ($\mu g/cm^2$)
Ag	550	0.013	0.014	0.004	0.035	0.005
Al	550	0.080	0.081	0.049	0.185	0.015
As	550	0.000	0.000	0.000	0.005	0.001
Ba	550	0.099	0.102	0.046	0.193	0.025
Br	550	0.002	0.002	0.000	0.007	0.001
Ca	550	0.004	0.008	0.000	0.125	0.013
Cd	550	0.013	0.013	0.003	0.031	0.005
Ce	550	0.123	0.124	0.054	0.249	0.031
Cl	550	0.002	0.003	0.001	0.129	0.006
Co	550	0.002	0.002	0.000	0.005	0.001
Cr	550	0.004	0.005	0.002	0.185	0.008
Cs	550	0.064	0.066	0.027	0.133	0.020
Cu	550	0.006	0.007	0.002	0.028	0.003
Fe	550	0.024	0.026	0.009	0.668	0.031
In	550	0.036	0.036	0.016	0.061	0.008
K	550	0.007	0.007	0.000	0.069	0.006
Mg	550	0.014	0.017	0.000	0.112	0.016
Mn	550	0.007	0.007	0.002	0.014	0.002
Na	550	0.000	0.012	-0.001	0.272	0.022
Ni	550	0.001	0.002	0.000	0.055	0.002
P	550	0.000	0.000	0.000	0.003	0.001
Pb	550	0.014	0.014	0.003	0.033	0.004
Rb	550	0.004	0.004	0.000	0.012	0.002
S	550	0.000	0.002	0.000	0.786	0.035
Sb	550	0.042	0.043	0.010	0.090	0.012
Se	550	0.003	0.003	0.000	0.009	0.001
Si	550	0.010	0.015	0.000	0.298	0.022
Sn	550	0.043	0.044	0.016	0.092	0.012
Sr	550	0.005	0.005	0.001	0.011	0.002
Ti	550	0.001	0.001	0.000	0.018	0.001
V	550	0.000	0.000	0.000	0.003	0.001
Zn	550	0.003	0.003	0.000	0.085	0.004
Zr	550	0.024	0.025	0.000	0.057	0.010

4.3 DRI Carbon Laboratory

The DRI Carbon Analysis Laboratory, as a subcontractor to UC Davis, received and analyzed quartz filters from batches 01 through 21 covering the sampling period from November 20, 2015 through December 31, 2016. For batches 01 through 04 sampled during 2015, analysis was performed using the DRI Model 2001 carbon analyzer with the IMPROVE_A method and analysis results were reported to UC Davis. Nine DRI Model 2001 Thermal/Optical Carbon Analyzers (designated as units # 0, 6-10, 12, and 20) were used for these CSN IMPROVE_A analyses. Starting with samples taken on or after January 1, 2016 from batches 05 – 21, analysis was performed using the DRI Model 2015 multi-wavelength carbon analyzer with the IMPROVE_A method and analysis results were reported to UC Davis. Twelve DRI Model 2015 Thermal/Optical Carbon Analyzers (designated as units # 21, 31, 34-38, 40-43, and 47) were used for these CSN IMPROVE_A analyses.

4.3.1 Summary of QC Checks and Statistics

Samples received at the DRI Carbon Laboratory follow the chain-of-custody procedure specified in *DRI CSN SOP #2-111*. Samples analyzed using the Model 2001 carbon analyzer followed *DRI SOP # 2-216*, while samples analyzed using the Model 2015 carbon analyzer followed *DRI CSN SOP # 2-231*. These SOPs are specific for the Chemical Speciation Network. Quality control (QC) measures for the DRI carbon analysis are included in the SOP and summarized in Table 4.3-1a and 4.3-1b for the Model 2001 and Model 2015 carbon analyzers, respectively. The tables specify the frequency and standards required for the checks, along with the acceptance criteria, failure rate and corrective actions for the carbon analyzers. The QC measures for each carbon analyzer model have been developed and refined from experience with each model; thus measures and acceptance criteria are not always the same for both models.

Table 4.3-1a: DRI carbon analysis QC measures for Model 2001 analyzer.

Requirement	Calibration Standard and Range	Calibration Frequency	Acceptance Criteria	Corrective Action
System Blank Check	NA[a]	Once per week	<0.2 µg C/cm^2. See Table 4.3-2a and Figure 4.3-1a	Check instrument for leaks and repair if needed.
Laboratory Blank Check	NA	Beginning of analysis day	<0.2 µg C/cm^2. See Table 4.3-3a and Figure 4.3-2a	Check instrument and filter punch and rebake.
Calibration Peak Area Check	NIST 5% CH$_4$/He gas standard; 20 µg C (Carle valve injection loop, 1000 µl)	Every analysis	Typical counts 20,000 and 32,000 and 95-105% of average calibration peak area of the day. See Figure 4.3-4a.	Void analysis result; check flowrates, leak, and 6-port valve temperature; conduct an auto-calibration; and repeat analysis with second filter punch.
Auto-Calibration Check	NIST 5% CH$_4$/He gas standard; 20 µg C (Carle valve injection loop, 1000 µl).	Beginning of analysis day	Relative standard deviation of the three injection peaks <5% and calibration peak area 90-110% of weekly average. See Table 4.3-4 and Figure 4.3-3a.	Troubleshoot and correct system before analyzing samples.
Manual Injection Calibration	NIST 5% CH$_4$/He or NIST 5% CO$_2$/He gas standards; 20 µg C (Certified gas-tight syringe, 1000 µl)	End of analysis day	95-105% recovery and calibration peak area 90-110% of weekly average. Data archived.	Troubleshoot and correct system before analyzing samples.
Sucrose Calibration Check	10µL of 1800 ppm C sucrose standard; 18 µg C.	Thrice per week (began March, 2009)	17.1-18.9 ug C/filter. See Figure 4.3-5a.	Troubleshoot and correct system before analyzing samples.
Potassium Hydrogen Phthalate (KHP) Calibration Check	10µL of 1800 ppm C KHP standard; 18 µg C	Twice per week (Tue. and Thu.)	17.1-18.9 ug C/filter. See Figure 4.3-6a.	Troubleshoot and correct system before analyzing samples.
Multiple Point Calibrations	1800 ppm C Potassium hydrogen phthalate (KHP) and sucrose; NIST 5% CH$_4$/He, and NIST 5% CO$_2$/He gas standards; 9-36 µg C for KHP and sucrose; 2-30 µg C for CH$_4$ and CO$_2$	Every six months or after major instrument repair	All slopes ±5% of average. See Table 4.3-5a.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Sample Replicates (on the same or a different analyzer)	NA	Every 10 analyses	±10% when OC and TC $\geq$10 µg C/cm^2 ±20% when EC $\geq$ 10µg C/cm^2 or <±1 µg/cm^2 when OC and TC <10 µg C/cm^2 <±2 µg/cm^2 when EC <10µg C/cm^2. See Table 4.3-8a and Figure 4.3-8.	Investigate instrument and sample anomalies and rerun replicate when difference is > ±10%.
Temperature Calibrations	Tempilaq® G (Tempil, Inc., South Plainfield, NJ, USA); Three replicates each of 121, 184, 253, 510, 704, and 816 °C	Every six months, or whenever the thermocouple is replaced	Linear relationship between thermocouple and Tempilaq® G values with R^2 >0.99. See Table 4.3-6a.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Oxygen Level in Helium Atmosphere (using GC/MS)[b]	Certified gas-tight syringe; 0-100 ppmv	Every six months, or whenever leak is detected	Less than the certified amount of He cylinder. See Table 4.3-7a.	Replace the He cylinder and/or O$_2$ scrubber.

[a] NA: Not Applicable.

[b] Gas chromatography/mass spectrometer (Model 5975, Agilent Technology, Palo Alto, CA, USA).

Table 4.3-1b. DRI carbon analysis QC measures for Model 2015 analyzer.

QA/QC Activity	Calibration Standard and Range	Calibration Frequency	Acceptance Criteria	Corrective Action
System Blank Check	NA[a]	Once per week	<0.2 µg C/cm^2. See Table 4.3-2b and Figure 4.3-1b.	Check instrument.
Laboratory Blank Check	NA	Beginning of analysis day	<0.2 µg C/cm^2. See Table 4.3-3b and Figure 4.3-2b.	Check instrument and filter punch and rebake
Calibration Peak Area Check	NIST 5% CH_4/He gas standard; 20 µg C (6-port valve injection loop, 1000 µl)	Every analysis	Typical counts 15,000-25,000 and 95-105% of average calibration peak area of the day. See Figure 4.3-4b.	Void analysis result; check flowrates, leak, and 6-port valve temperature; conduct an auto-calibration; and repeat analysis with second filter punch.
Auto-Calibration Check	NIST 5% CH_4/He gas standard; 20 µg C (Carle valve injection loop, 1000 µl)	Alternating beginning or end of each analysis day	Relative standard deviation of the three injection peaks <5% and calibration peak area 90-110% of weekly average. See Table 4.3-4 and Figure 4.3-3b.	Verify if major maintenance has occurred. Troubleshoot and correct system before analyzing samples.
Manual Injection Calibration	NIST 5% CH_4/He or NIST 5% CO_2/He gas standards; 20 µg C (Certified gas-tight syringe, 1000 µl)	Four times a week (Sun., Tue., Thu., and Sat.)	95-105% recovery and calibration peak area 90-110% of weekly average. See Figure 4.3-7.	Troubleshoot and correct system before analyzing samples.
Sucrose Calibration Check	10µL of 1800 ppm C sucrose standard; 18 µg C	Thrice per week (began March, 2009)	17.1-18.9 µg C/filter. See Figure 4.3-5b.	Troubleshoot and correct system before analyzing samples.
Potassium Hydrogen Phthalate (KHP) Calibration Check	10µL of 1800 ppm C KHP standard; 18 µg C	Twice per week (Tue. and Thu.)	17.1-18.9 µg C/filter. See Figure 4.3-6b.	Troubleshoot and correct system before analyzing samples.
Multiple Point Calibrations	1800 ppm C Potassium hydrogen phthalate (KHP) and sucrose; NIST 5% CH_4/He, and NIST 5% CO_2/He gas standards; 9-36 µg C for KHP and sucrose; 2-30 µg C for CH_4 and CO_2	Every six months or after major instrument repair	All slopes ±5% of average. See Table 4.3-5b.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Sample Replicates (on the same or a different analyzer)	NA	Every 10 analyses	±10% when OC and TC $\geq$10 µg C/cm^2 ±20% when EC > 10µg C/cm^2 or <±1 µg/cm^2 when OC and TC <10 µg C/cm^2 <±2 µg/cm^2 when EC <10µg C/cm See Table 4.3-8b and Figure 4.3-9.	Investigate instrument and sample anomalies and rerun replicate when difference is > ±10%.
Temperature Calibrations	NIST-certified thermocouple	Every six months, or whenever the thermocouple is replaced	Linear relationship between analyzer and NIST thermocouple values with R^2>0.99. See Table 4.3-6b.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Oxygen Level in Helium Atmosphere (using GC/MS)[b]	Certified gas-tight syringe; 0-100 ppmv	Every six months, or whenever leak is detected	Less than the certified amount of He cylinder. See Table 4.3-7b.	Replace the He cylinder and/or O_2 scrubber.

[a] NA: Not Applicable.

[b] Gas chromatography/mass spectrometer (Model 5975, Agilent Technology, Palo Alto, CA, USA).

4.3.2 Summary of QC Results

Detailed results of the carbon QC are presented in the subsections below. All system blanks (Table 4.3-2) or laboratory blanks (Table 4.3-3) that did not meet the acceptance criteria were reanalyzed and if they did not pass the second analysis, instrument maintenance was performed and additional blanks were run before the analyzer was placed on-line. Exceedance in multipoint calibrations (Tables 4.3-5) result in verification of individual calibration points, troubleshooting the instrument, and repeating calibrations. Exceedances in auto-calibrations (Table 4.3-4), internal calibrations (Figure 4.3-4), as well as sucrose (Figure 4.3-5), KHP (Figure 4.3-6) and CO_2 (Figure 4.3-7) calibrations result in reanalysis and/or instrument maintenance. For cases where CSN samples were analyzed after an exceedance, data were flagged in data files delivered to UC Davis.

4.3.2.1 System and Laboratory Blanks

Table 4.3-2a and b list the number of system blanks analyzed during the report period and their concentration statistics. The system blank control charts are shown in Figure 4.3-1. System blanks are used to ensure that the system is not introducing bias in the carbon analysis. Most system blanks were below the limit of 0.2 µgC/cm^2. When an exceedance is observed, possible contamination is checked, suspicious parts are cleaned, the sample oven is baked, and a second system blank is rerun to ensure that it passes the criterion.

Table 4.3-2a: Statics of system blanks ran weekly on the Model 2001 analyzer between 1/3/2016 and 4/24/2016.

Parameter	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)	# Exceedance
O1TC	99	0.000	0.002	0.000	0.046	0.007	0
O2TC	99	0.000	0.010	0.000	0.086	0.019	0
O3TC	99	0.008	0.015	0.000	0.131	0.022	0
O4TC	99	0.000	0.001	0.000	0.114	0.012	0
OPTRC	99	0.000	0.001	0.000	0.050	0.005	0
OPTTC	99	0.000	0.002	0.000	0.214	0.022	1
OCTRC	99	0.016	0.029	0.000	0.366	0.051	2
OCTTC	99	0.016	0.031	0.000	0.580	0.066	2
E1TC	99	0.000	0.001	0.000	0.032	0.004	0
E2TC	99	0.000	0.001	0.000	0.063	0.007	0
E3TC	99	0.000	0.002	0.000	0.136	0.014	0
ECTRC	99	0.000	0.003	0.000	0.230	0.023	1
ECTTC	99	0.000	0.001	0.000	0.050	0.006	0
TCTC	99	0.016	0.032	0.000	0.596	0.069	2

Table 4.3-2b: Statics of system blanks ran on the Model 2015 analyzer between 5/22/2016 and 4/30/2017.

Parameter	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)	# Exceedance
O1TC	267	0.000	0.000	0.000	0.000	0.000	0
O2TC	267	0.000	0.000	0.000	0.061	0.004	0
O3TC	267	0.000	0.005	0.000	0.211	0.021	1
O4TC	267	0.000	0.000	0.000	0.000	0.000	0
OPTRC	267	0.000	0.000	0.000	0.000	0.000	0
OPTTC	267	0.000	0.000	0.000	0.000	0.000	0
OCTRC	267	0.000	0.005	0.000	0.272	0.024	1
OCTTC	267	0.000	0.005	0.000	0.272	0.024	1
E1TC	267	0.000	0.000	0.000	0.000	0.000	0
E2TC	267	0.000	0.000	0.000	0.000	0.000	0
E3TC	267	0.000	0.000	0.000	0.000	0.000	0
ECTRC	267	0.000	0.000	0.000	0.000	0.000	0
ECTTC	267	0.000	0.000	0.000	0.000	0.000	0
TCTC	267	0.000	0.005	0.000	0.272	0.024	1

Figure 4.3-1: Control chart of weekly system blank concentrations on (a) DRI Model 2001 and (b) DRI Model 2015 carbon analyzers. The red dash lines indicate the limit of 0.2 µgC/cm^2.

(a) (b)

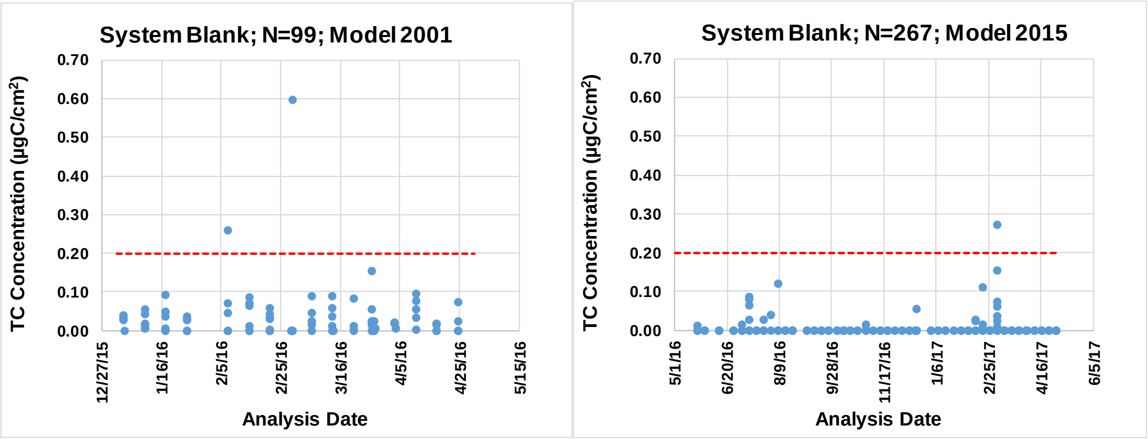


Table 4.3-3a and b list the number of laboratory blanks analyzed during the report period and their concentration statistics. The laboratory blank control charts are shown in Figure 4.3-2. Laboratory blank analyses are performed daily to check for system contamination and evaluate laser response. Most laboratory blanks were below the limit of 0.2 µgC/cm^2. When an exceedance is observed, the sample oven is baked and a second laboratory blank is run. If the second blank still exceeds the limit, the analyzer is taken offline for cleaning and maintenance.

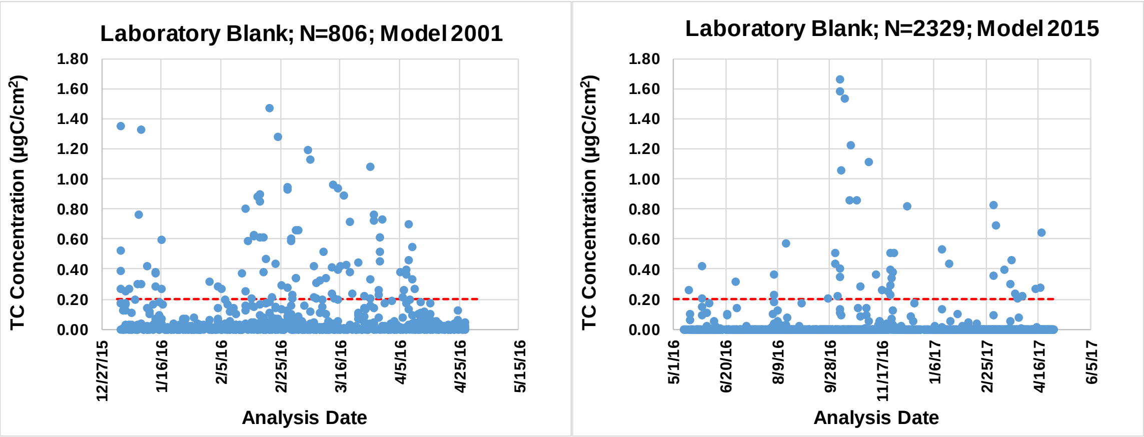
Table 4.3-3a: Statics of laboratory blanks ran weekly on the Model 2001 analyzer between 1/2/2016 and 4/27/2016.

Parameter	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)	# Exceedance
O1TC	806	0.000	0.008	0.000	0.355	0.039	10
O2TC	806	0.000	0.021	0.000	0.392	0.054	18
O3TC	806	0.002	0.036	0.000	0.730	0.077	30
O4TC	806	0.000	0.009	0.000	0.265	0.029	2
OPTRC	806	0.000	0.000	0.000	0.082	0.004	0
OPTTC	806	0.000	0.003	0.000	0.275	0.019	1
OCTRC	806	0.007	0.074	0.000	1.339	0.178	88
OCTTC	806	0.007	0.077	0.000	1.472	0.185	91
E1TC	806	0.000	0.001	0.000	0.126	0.007	0
E2TC	806	0.000	0.003	0.000	0.134	0.015	0
E3TC	806	0.000	0.002	0.000	0.405	0.021	2
ECTRC	806	0.000	0.006	-0.004	0.500	0.033	5
ECTTC	806	0.000	0.004	0.000	0.424	0.025	4
TCTC	806	0.008	0.080	0.000	1.472	0.191	93

Table 4.3-3b: Statics of laboratory blanks ran on the Model 2015 analyzer between 5/11/2016 and 5/2/2017.

Parameter	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)	# Exceedance
O1TC	2329	0.000	0.001	0.000	0.197	0.008	0
O2TC	2329	0.000	0.004	0.000	0.456	0.031	20
O3TC	2329	0.000	0.006	0.000	0.804	0.046	22
O4TC	2329	0.000	0.001	0.000	0.285	0.011	2
OPTRC	2329	0.000	0.001	0.000	0.597	0.017	3
OPTTC	2329	0.000	0.002	0.000	0.597	0.024	6
OCTRC	2329	0.000	0.013	0.000	1.455	0.088	50
OCTTC	2329	0.000	0.014	0.000	1.662	0.095	51
E1TC	2329	0.000	0.001	0.000	0.418	0.014	3
E2TC	2329	0.000	0.001	0.000	0.597	0.014	1
E3TC	2329	0.000	0.000	0.000	0.434	0.009	1
ECTRC	2329	0.000	0.001	0.000	0.434	0.015	3
ECTTC	2329	0.000	0.000	0.000	0.041	0.001	0
TCTC	2329	0.000	0.014	0.000	1.662	0.095	51

Figure 4.3-2: Control chart of daily laboratory blank concentrations ran on (a) DRI Model 2001 and (b) DRI Model 2015 carbon analyzers. The red dash lines indicate the limit of 0.2 µgC/cm^2.



(a)

(b)

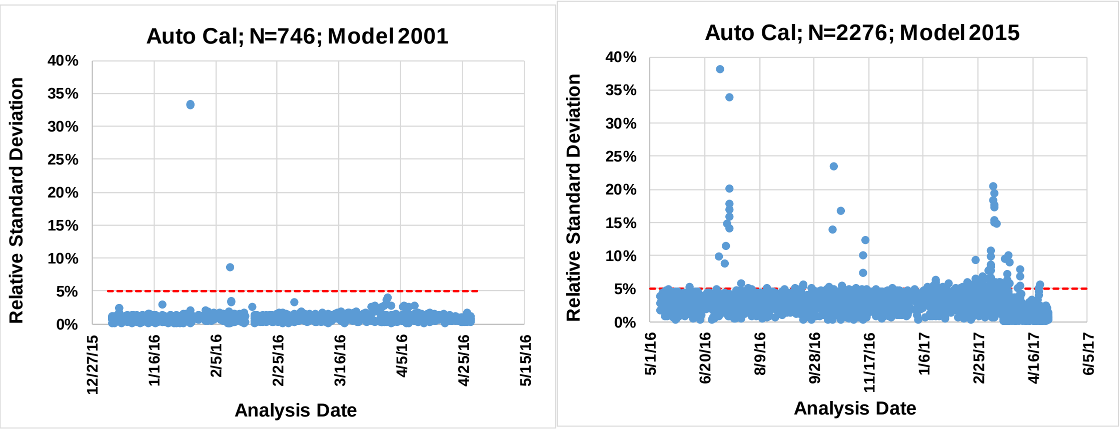
4.3.2.2 *Auto-Calibration and Internal Calibration Peak Area Check*

Once per day each analyzer runs an auto-calibration protocol. Using the Carle valve, an aliquot of methane standard is injected once in a He-only atmosphere (OC stage), once in a He/O_2 atmosphere (EC stage), and finally as the normal internal calibration peak. The three peaks should have similar peak areas if the catalysts are in good condition. The similarity of the three peaks are measured by the relative standard deviation (RSD), which is the standard deviation divided by the average of the three peak areas. The acceptance limit is RSD <5% and ±10% from weekly average. Table 4.3-4 summarizes the RSD of the three methane injection peaks during the analysis period and the control charts are shown in Figure 4.3-3. There were 4 and 107 exceedances for the Model 2001 and 2015, respectively. Most of these exceedances occurred when the analyzer was under maintenance and no samples were run. When an exceedance is observed, the analyzer is checked and the auto-calibration is rerun. The calibration peak areas of previous runs are examined and/or manual injections are done to ensure the analyzer is working properly. A total of 255 CSN samples were analyzed during auto-calibration peak area exceedances; these cases were flagged in data files delivered to UC Davis. As a corrective action, software tools are being developed to generate QC control charts and summaries to ensure QC exceedances are captured and corrected immediately.

Table 4.3-4: Statistics of the relative standard deviation (RSD) of the three methane injection peaks from auto-calibration checks.

Statistic	Model 2001	Model 2015
Count	746	2276
Median	0.9%	2.8%
Average	1.1%	2.8%
Min	0.0%	0.0%
Max	86.8%	38.2%
Standard deviation	3.6%	2.2%
Exceedance	4	107

Figure 4.3-3: Control chart of the relative standard deviation of the three methane injection peaks from daily auto-calibration ran on: (a) DRI Model 2001 and (b) DRI Model 2015 carbon analyzers. The red dash lines indicate the limit of 5% RSD.

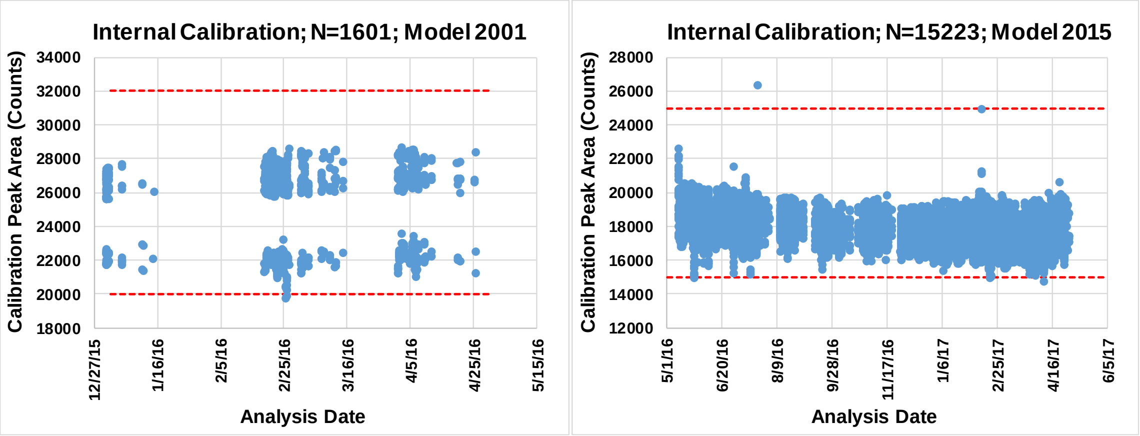


(a)

(b)

At the end of each run, a fixed amount of methane is injected via a Carle valve as an internal calibration standard. The internal calibration peak area is examined for each sample. Significant changes in calibration peak area counts are monitored and instruments are checked for performance against daily calibrations. Typical ranges for the internal calibration peaks fall between 20,000 and 32,000 counts for Model 2001 and between 15,000 and 25,000 counts for Model 2015. The different count ranges of the Model 2001 and Model 2015 are due to their different carbon detection method. In addition to peak area ranges, the peak areas are also compared to the daily averages. Sudden changes or atypical counts result in instrument maintenance. Metadata concerning QC measures and instrument maintenance are reported to UC Davis quarterly. Figures 4.3-4a and 4.3-4b show the daily internal calibration peak area during the reporting period for all analyzers. For the Model 2001, 1,599/1,601 analyses met both criteria of peak area range of 20,000-32,000 counts and within ±5% of daily average. For the Model 2015, 14,669/15,223 (96.4%) passed both peak area and daily average criteria. A total of 556 CSN samples and 59 replicates were flagged in data files delivered to UC Davis due to exceeded internal calibration QC limits. However, other QC analyses (i.e., replicates and duplicates, auto-calibration, and internal calibration peak area check) within the time period indicate acceptable values. As a corrective action, software tools are being developed to generate QC control charts and summaries to ensure QC exceedances are captured and corrected immediately.

Figure 4.3-4: Control chart of the internal calibration peak area for: (a) DRI Model 2001 and (b) DRI Model 2015 carbon analyzers. The red dash lines indicate the typical internal calibration peak area between 20,000 and 32,000 for Model 2001 and between 15,000 and 25,000 for Model 2015.



(a) (b)

4.3.2.3 Multipoint Calibration and Manual Injection Check

Multipoint carbon calibrations are performed semi-annually or whenever major repairs or changes are made to the instruments. The calibration uses four different sources of carbon: methane (CH_4), carbon dioxide (CO_2), sucrose ($C_{12}H_{22}O_{11}$), and potassium hydrogen phthalate (KHP), each with four injections with different carbon content (except that 15 µL sucrose and KHP are injected twice), resulting in a total of 18 calibration points in the set. The calibration result is plotted as µg carbon in the calibration standard versus total carbon peak area normalized by the internal calibration peak area. A regression slope is obtained by fitting the calibration points with a linear line forced through the origin. The slope relates the measured normalized peak area to carbon content. It represents the response of the entire analyzer to generic carbon compounds, including the efficiencies of the oxidation and methanator zones, sensitivity of the FID on the Model 2001, and sensitivity of the NDIR on the Model 2015. If the ratio of carbon over normalized peak area for individual calibration point differs from the regression slope by more than 10%, the calibration point is treated as an outlier and redone. Daily calibration injections and replicate analysis also verify acceptable slopes. Average calibration slopes differ between the Model 2001 and Model 2015 analyzers because they use different detection methods (i.e., FID vs. NDIR). Tables 4.3-5a and 4.3-5b provide summary statistics for full multi-point calibrations by analyzer for the period during which the project samples were analyzed. The QC criterion requires the slope to be within ±5% of average by each analyzer (Table 4.3-1), where the slope is obtained after individual calibration outlier points are removed and redone. When there is no major change in the analyzer, the calibration slope usually differs from the previous slope of the same analyzer by less than 10%. As shown in Table 4.3-5b, the slope of Analyzer #31 was 17% lower on 2/9/2016 than that on 2/11/2016. This was the first time that the analyzer was calibrated after it was delivered to DRI by the manufacturer. No samples were run on this unit until it was recalibrated on 2/11/2016 with a reasonable slope. Other cases where calibrations had changes >5% from analyzer averages were usually related to major instrument maintenance (e.g., change of the detector). There were 337 cases where samples were run with carbon calibration slopes outside of the QC criteria (Table 4.3.5b), these data were flagged in data files delivered to UC Davis. To ensure QC exceedances are captured and corrected immediately, software tools are being developed to generate QC control charts and summaries.

Table 4.3-5a: DRI Model 2001 multi-point calibration statistics (CSN sample dates 11/20/2015-12/29/2015). Units for the slope are µg carbon per ratio of standard injection peak count/internal calibration gas peak count. For analyzers 6, 9, and 12 more than 6 months passed between calibrations. As noted in Sections 2.3.2 and 3.2.3.1, a calibration calendar has been established by DRI to avoid recurrence of this issue.

Analyzer No.	Calibration Date	Slope	R^2	Difference from Analyzer Average	No. Sample Flagged	Comment
0	1/29/2016	21.940	0.995	0%	0	
6	10/23/2015	22.414	0.998	4%	0	
6	6/13/2016	22.522	0.996	4%	0	
7	10/15/2015	20.862	0.996	-2%	0	
7	2/24/2016	21.702	0.998	2%	0	
7	3/18/2016	21.126	0.999	0%	0	
8	10/7/2015	22.484	0.996	0%	0	
8	4/5/2016	22.282	0.998	0%	0	
9	8/14/2015	21.063	0.998	0%	0	
9	4/6/2016	20.936	0.995	0%	0	
10	10/30/2015	22.071	0.998	1%	0	
10	4/28/2016	21.644	0.996	-1%	0	
11	11/18/2015	21.139	0.994	-2%	0	
11	2/8/2016	21.784	0.990	1%	0	
11	2/24/2016	22.002	0.996	2%	0	
11	5/3/2016	21.352	0.998	-1%	0	
12	8/14/2015	22.294	0.996	0%	0	
12	2/25/2016	22.321	0.995	0%	0	
12	3/3/2016	22.862	0.995	2%	0	
12	4/7/2016	21.888	0.996	-2%	0	
12	8/22/2016	22.277	0.996	0%	0	
20	11/11/2015	20.765	0.997	0%	0	

Table 4.3-5b: DRI Model 2015 multi-point calibration statistics (CSN sample dates 1/1/2016-12/31/16). Units for the slope are µg carbon per ratio of standard injection peak count/internal calibration peak count. For analyzers 21 and 47, more than 6 months passed between calibrations. As noted in Sections 2.3.2 and 3.2.3.1, a calibration calendar has been established by DRI to avoid recurrence of this issue.

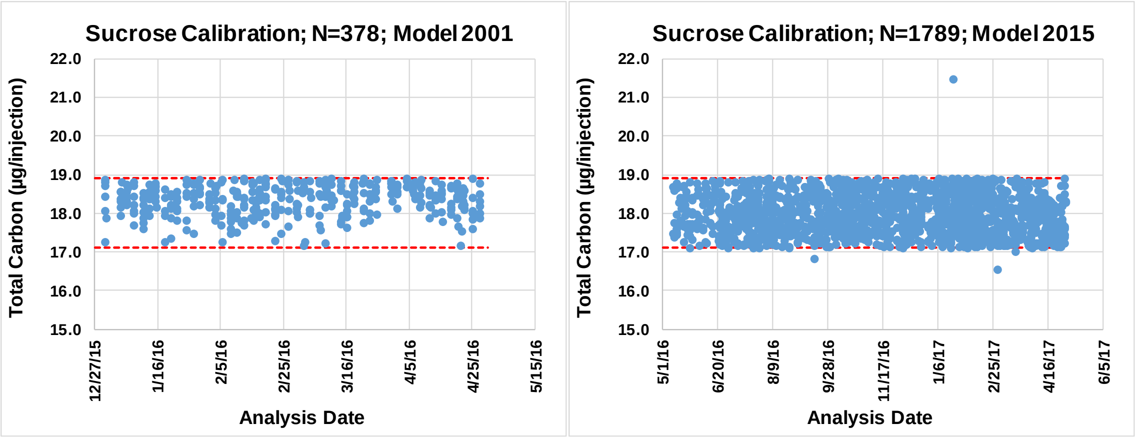
Analyzer No.	Calibration Date	Slope	R^2	Difference from Analyzer Average	No. Sample Flagged	Comment
21	10/16/2015	19.164	0.998	-1%	0	
	1/22/2016	18.987	0.993	-2%	0	
	5/20/2016	19.503	0.994	0%	0	
	12/29/2016	18.964	0.993	-2%	0	
	4/19/2017	20.313	0.996	5%	0	
	6/2/2017	19.963	0.998	3%	0	
	9/22/2017	18.841	0.994	-3%	0	
	11/30/2017	19.658	0.995	1%	0	
31	**2/9/2016**	**15.950**	**0.992**	**-17%**	**0**	**Instrument testing; did not run sample**
	2/11/2016	19.309	0.989	0%	0	
	3/14/2016	18.461	0.988	-4%	0	
	8/19/2016	**20.413**	**0.990**	**6%**	**46**	**Semiannual with major maintenance**
	9/14/2016	18.833	0.994	-2%	0	
	9/30/2016	19.565	0.996	2%	0	
	2/23/2017	18.743	0.994	-3%	0	
	2/25/2017	18.691	0.995	-3%	0	
	3/28/2017	19.399	0.994	1%	0	
	4/4/2017	19.234	0.996	0%	0	
	6/12/2017	19.703	0.997	2%	0	
34	**5/13/2016**	**16.279**	**0.996**	**-11%**	**13**	
	5/18/2016	17.860	0.999	-2%	0	
	9/16/2016	18.733	0.994	2%	0	
	2/25/2017	18.902	0.995	3%	0	
	3/20/2017	18.792	0.996	3%	0	
	5/5/2017	19.238	0.999	5%	0	
35	3/25/2016	19.892	0.941	4%	0	
	8/26/2016	**20.775**	**0.991**	**8%**	**0**	**Instrument testing; did not run sample**
	8/31/2016	19.681	0.989	3%	0	
	10/3/2016	**17.286**	**0.989**	**-10%**	**0**	**Instrument testing; did not run sample**
	1/10/2017	18.492	0.985	-4%	0	
	2/16/2017	18.649	0.993	-3%	0	
	4/11/2017	18.889	0.996	-1%	0	
	6/8/2017	19.343	0.996	1%	0	
	10/9/2017	18.620	0.995	-3%	0	
	12/5/2017	19.421	0.999	1%	0	
	1/26/2018	19.808	0.995	3%	0	
36	4/5/2016	19.033	0.990	-1%	0	
	7/29/2016	19.393	0.997	1%	0	
	8/24/2016	19.400	0.990	1%	0	
	1/31/2017	19.229	0.995	0%	0	
	2/22/2017	18.277	0.992	-4%	0	
	4/3/2017	19.370	0.992	1%	0	
	4/28/2017	19.307	0.997	1%	0	
	6/23/2017	19.065	0.997	0%	0	
37	7/20/2016	18.495	0.995	-1%	0	
	8/23/2016	**19.657**	**0.994**	**6%**	**238**	
	12/14/2016	18.748	0.991	1%	0	
	1/10/2017	**17.473**	**0.992**	**-6%**	**35**	**Soda lime change**
	1/25/2017	18.357	0.997	-1%	0	
	3/13/2017	18.612	0.993	0%	0	
	5/3/2017	18.814	0.994	1%	0	

Table 4.3-5b continued.

Analyzer No.	Calibration Date	Slope	R^2	Difference from Analyzer Average	No. Samples Flagged	Comment
38	6/17/2016	20.042	0.993	4%	0	
	7/29/2016	19.221	0.992	0%	0	
	1/24/2017	19.058	0.995	-1%	0	
	5/10/2017	18.478	0.995	-4%	0	
40	8/4/2016	18.934	0.995	-3%	0	
	1/6/2017	20.564	0.961	5%	0	
	4/7/2017	19.277	0.997	-1%	0	
	6/21/2017	19.350	0.993	-1%	0	
41	8/22/2016	18.555	0.994	-3%	0	
	11/3/2016	18.528	0.991	-3%	0	
	1/5/2017	19.423	0.996	1%	0	
	3/2/2017	20.153	0.992	5%	0	
	4/18/2017	19.142	0.989	0%	0	
	7/5/2017	19.254	0.995	0%	0	
42	10/3/2016	19.095	0.996	0%	0	
	12/29/2016	18.660	0.994	-3%	0	
	3/28/2017	19.390	0.997	1%	0	
	9/28/2017	19.443	0.997	2%	0	
43	2/16/2017	18.185	0.991	-2%	0	
	3/2/2017	18.468	0.994	0%	0	
	3/8/2017	18.331	0.994	-1%	0	
	4/25/2017	19.214	0.993	4%	0	
	5/19/2017	18.580	0.995	0%	0	
47	1/10/2017	19.284	0.993	4%	0	
	7/15/2017	**17.520**	**0.991**	**-6%**	**5**	**Semiannual with major maintenance**
	8/1/2017	19.013	0.998	2%	0	

Sucrose calibration checks are done on each analyzer three times per week. Control charts for the Model 2001 and Model 2015 analyzers are shown in Figures 4.3-5. For the Model 2001, one of the 378 sucrose calibrations exceeded the 17.1-18.9 µgC criterion but no CSN samples were run during this time period. For the Model 2015, 5 of the 1789 sucrose calibrations exceeded the criterion and 53 CSN samples were run after the sucrose exceedance; these cases were flagged in data files delivered to UC Davis. However, other QC analyses (i.e., replicates and duplicates, auto-calibration, and internal calibration peak area check) within the time period indicate acceptable values.

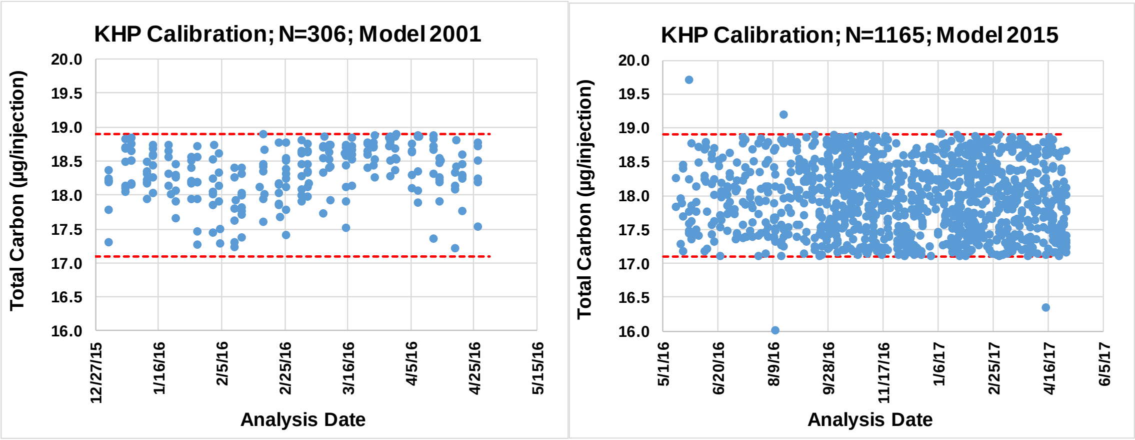
Figure 4.3-5: Control chart of sucrose manual injection calibration check for: (a) DRI Model 2001 and (b) DRI Model 2015 carbon analyzers. The red dash lines indicate the total carbon limits of 17.1 and 18.9 µgC per injection.


(a)

(b)

KHP calibrations are done twice weekly for the Model 2001 and Model 2015 analyzers. The control charts for KHP calibrations are shown in Figure 4.3-6. For the Model 2001, all KHP calibration passed the 17.1-18.9 µgC criterion. For the Model 2015, 6 of the 1165 calibrations exceeded the criterion and 16 CSN samples were run after the KHP exceedance; these cases were flagged in data files delivered to UC Davis. However, other QC analyses (i.e., replicates and duplicates, auto-calibration, and internal calibration peak area check) within the time period indicate acceptable values.

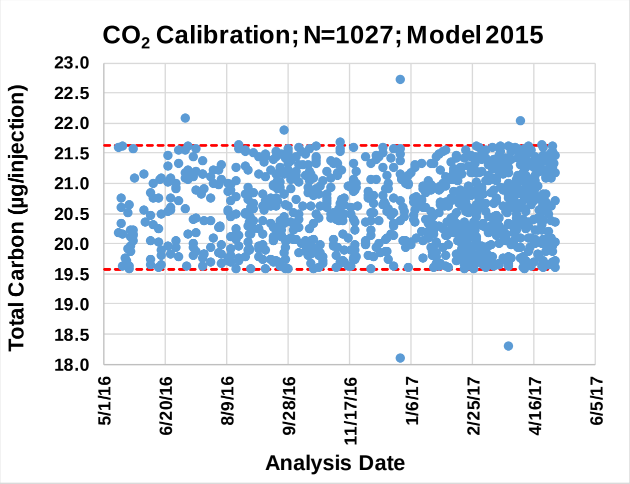
Figure 4.3-6: Control chart of KHP manual injection calibration check for: (a) DRI Model 2001 and (b) DRI Model 2015 carbon analyzers. The red dash lines indicate the total carbon limits of 17.1 and 18.9 µgC per injection.


(a)

(b)

CO_2 calibrations are done four times weekly for the Model 2015 analyzers. The control chart for CO_2 calibrations is shown in Figure 4.3-7. Seven of the 1027 calibrations exceeded the TC limits and 61 CSN samples were run after the exceedance; these cases were flagged in data files delivered to UC Davis. However, other QC analyses (i.e., replicates and duplicates, auto-calibration, and internal calibration peak area check) within the time period indicate acceptable values. CO_2 calibrations were done daily for the Model 2001 analyzers; however this data has been archived and is not immediately available; therefore, this data is not included.

Figure 4.3-7. CO_2 calibration control chart for Model 2015 Analyzers. The red dash lines indicate the total carbon limits of 19.57 and 21.63 µgC per injection.



4.3.2.4 *Temperature Calibrations*

Tables 4.3-6 provide summary statistics for the multi-point temperature calibrations of each carbon analyzer. The temperature calibrations are performed every six months or after a major instrument repair. Criteria for an acceptable calibration is linear regression coefficient of determination (R^2) >0.99. Many of the Model 2001 instruments were taken offline before the next temperature calibration was completed. DRI stopped running CSN samples on the Model 2001 after April 27, 2016 (corresponding with sample dates through 12/29/2015). For more precise temperature control, the Model 2015 uses a separate linear regression for the lower temperatures and higher temperature ranges. These two ranges are separated with a toggle point typically around 200-300 °C, which is set to the temperature at which the two regression lines intercept (see Figure 3-6 in Model 2015 SOP).

Table 4.3-6a: DRI Model 2001 multi-point temperature calibration statistics (CSN sample dates 11/20/2015-12/29/2015).

Carbon Analyzer	Calib Date	Slope	Intercept	r^2	Offline
0	8/31/2015	1.021	-1.2	0.9996	
0	1/27/2016	1.069	3.714	0.9975	4/28/2016
6	10/20/2015	1.027	-2.395	0.999	
6	6/9/2016	1.019	4.689	0.9997	
7	7/17/2015	1.021	-1.2	0.9996	
7	10/7/2015	1.0211	-1.2008	0.9996	
7	3/16/2016	1.012	8.8179	0.9989	
7	4/11/2016	1.0306	-5.4402	0.9992	
7	5/18/2017	1.0107	-0.8733	0.9989	
8	9/22/2015	1.011	-3.6038	0.999	
8	4/1/2016	0.9917	12.906	0.9997	
9	8/11/2015	1.0046	-1.3248	0.9989	
9	4/4/2016	0.9982	8.4512	0.9995	5/30/2016
10	10/28/2015	1.0444	4.5738	0.9994	
10	4/29/2016	1.0122	8.8035	0.9992	5/6/2016
11	11/17/2015	1.0211	-1.2008	0.9996	
11	2/3/2016	1.0544	-7.6363	0.9978	
11	8/24/2016	1.0205	-0.5932	0.9991	
12	8/12/2015	0.9885	9.3238	0.9998	
12	2/23/2016	1.0298	2.3308	0.9995	
12	4/5/2016	1.0306	0.033	0.9995	
12	8/16/2016	1.0376	-13.843	0.9998	
20	11/5/2015	1.0334	2.9435	0.9996	3/16/2016

Table 4.3-6b: DRI Model 2015 multi-point temperature calibration statistics (CSN sample dates 1/1/2016-12/31/2016).

Carbon Analyzer	Calib Date*	Low T Slope	Low T Intercept	Low T r^2	High T Slope	High T Intercept	High T r^2
21	10/31/2016	1.059	6.603	0.999	1.011	18.847	0.999
	3/5/2017	1.026	10.389	0.997	0.987	18.757	0.999
	4/7/2017	1.085	9.570	0.998	1.006	26.710	0.999
	5/25/2017	1.082	2.647	0.996	1.007	21.494	0.999
31	12/14/2015	1.049	11.964	0.995	0.998	29.343	0.997
	8/5/2016	1.064	6.556	0.998	1.018	18.955	0.999
	2/21/2017	1.078	-3.030	0.999	0.995	14.839	0.999
	8/31/2017	1.003	27.743	1.000	1.024	24.987	0.995
32	6/9/2017	1.076	5.717	1.000	1.032	19.474	1.000
	8/28/2017	1.086	10.185	1.000	1.013	29.379	0.996
33	12/14/2015	1.160	-0.391	1.000	1.016	37.943	1.000
	2/8/2016	1.132	0.594	0.999	1.018	29.132	1.000
	3/7/2016	1.085	0.162	0.999	1.022	13.976	1.000
	3/21/2016	1.035	15.367	0.993	1.021	20.536	1.000
34	3/4/2016	1.096	12.279	0.991	1.019	37.183	0.999
	5/27/2016	1.066	5.008	0.999	1.021	17.060	0.999
	10/24/2016	1.055	12.930	0.992	1.019	25.831	1.000
	11/4/2016	1.122	-4.610	0.999	1.011	23.310	1.000
	12/19/2016	1.134	-1.986	1.000	1.016	29.182	1.000
	2/15/2017	1.132	-5.494	0.999	1.005	21.250	1.000
	3/14/2017	1.134	-3.224	0.999	1.004	28.575	1.000
	8/1/2017	1.110	4.964	1.000	1.015	31.440	0.995
	8/24/2017	1.079	3.448	1.000	1.019	19.294	0.997
35	12/20/2016	1.103	0.379	0.999	1.018	21.140	1.000
	2/17/2017	1.070	4.230	1.000	1.008	20.119	1.000
	4/3/2017	1.081	-0.055	0.999	0.993	20.585	1.000
	8/28/2017	1.053	2.086	1.000	0.996	15.357	0.999
36	8/23/2016	1.067	4.612	0.999	1.020	16.499	1.000
	11/14/2016	1.087	1.620	0.999	1.012	19.784	1.000
	4/25/2017	1.077	10.096	0.995	1.019	23.091	1.000
	5/23/2017	1.046	8.541	0.998	1.010	15.871	1.000
37	6/15/2016	1.061	7.655	0.996	1.023	18.435	1.000
	10/17/2016	1.063	4.419	0.998	1.014	17.679	1.000
	11/30/2016	1.071	10.600	0.996	1.008	28.316	1.000
	4/25/2017	1.041	8.825	0.996	0.994	20.678	1.000
	12/7/2017	1.034	21.554	1.000	0.979	35.483	0.997
38	6/14/2016	1.116	1.655	0.999	1.019	28.927	1.000
	1/17/2017	1.116	1.655	0.999	1.019	28.927	1.000
	6/20/2017	1.034	2.173	1.000	1.024	5.939	0.999
40	7/1/2016	1.113	1.981	1.000	1.007	30.059	1.000
	3/7/2017	1.018	12.013	0.993	0.994	17.622	1.000
	8/1/2017	1.053	2.086	1.000	0.996	15.357	0.999
41	8/16/2016	1.062	13.386	0.993	1.009	30.120	1.000
	11/1/2016	1.057	9.716	0.993	1.022	20.691	1.000
	12/23/2016	1.085	6.885	0.997	1.024	25.251	1.000
	3/1/2017	1.055	2.977	0.997	0.994	17.329	1.000
	8/22/2017	1.033	4.682	1.000	1.027	7.430	1.000
42	10/26/2016	1.067	12.421	0.995	1.016	27.676	1.000
	3/24/2017	1.022	11.876	0.994	1.017	13.961	1.000
	9/26/2017	1.086	3.827	1.000	1.020	21.993	0.997

*Includes both regular maintenance and semi-annual calibration data

4.3.2.5 Oxygen Level Check

Tables 4.3-7a and 4.3-7b provide a summary of the oxygen leak tests results that are performed every six months or after major instrument repairs. The results are considered acceptable if the O_2 concentration is < 100 ppm. The O_2 contents were well below 100 ppm, in the range of 9-53 ppm.

Table 4.3-7a: DRI Model 2001 oxygen test statistics (CSN sample dates 11/20/2015-12/29/2015).

Analyzer No.	O_2 Statistics		Aug 2015		Feb 2016		Aug 2016	
			140 (°C)	580 (°C)	140 (°C)	580 (°C)	140 (°C)	580 (°C)
0	Mean O_2	(ppm)			14.5	13.4		
	Std Dev	(ppm)			4.6	4.1		
6	Mean O_2	(ppm)	53.9	45.9	19.2	38.9	13.6	14.1
	Std Dev	(ppm)	12.3	8.0	5.0	4.6	3.7	3.9
7	Mean O_2	(ppm)	14.8	13.6	36.7	38.1	16.0	12.7
	Std Dev	(ppm)	5.7	5.7	4.8	4.8	4.5	3.8
8	Mean O_2	(ppm)	17.2	17.7	39.9	40.1	16.2	14.6
	Std Dev	(ppm)	7.9	8.0	4.8	4.3	3.7	3.9
9	Mean O_2	(ppm)	19.5	16.0	37.5	37.1		
	Std Dev	(ppm)	6.4	8.1	5.0	4.6		
10	Mean O_2	(ppm)	19.9	15.3	28.7	30.1		
	Std Dev	(ppm)	5.8	8.0	4.4	4.2		
11	Mean O_2	(ppm)	18.3	14.1	20.0	20.1	10.5	9.6
	Std Dev	(ppm)	5.7	7.4	4.9	4.2	3.8	3.6
12	Mean O_2	(ppm)	19.0	16.5	36.4	36.9	21.9	21.2
	Std Dev	(ppm)	6.0	6.8	4.5	4.1	2.9	1.3
20	Mean O_2	(ppm)	19.6	10.6	40.6	27.0		
	Std Dev	(ppm)	9.8	7.1	4.0	3.8		

Note that the acceptance criteria is < 100 ppm O_2

Table 4.3-7b: DRI Model 2015 oxygen test statistics (CSN sample dates 1/1/2016-12/31/2016).

Analyzer No.	O_2 Statistics		Feb 2016		Jul 2016		Aug 2016		Feb 2017		Aug 2017	
			140 (°C)	580 (°C)	140 (°C)	580 (°C)	140 (°C)	580 (°C)	140 (°C)	580 (°C)	140 (°C)	580 (°C)
17	Mean O_2	(ppm)	25.4	27.0								
	Std Dev	(ppm)	4.4	3.8								
21	Mean O_2	(ppm)					11.6	11.4	28.1	21.3	14.1	10.9
	Std Dev	(ppm)					4.6	3.6	8.9	5.0	0.3	0.1
31	Mean O_2	(ppm)	16.8	16.6			26.1	22.0	19.5	18.1	20.0	19.3
	Std Dev	(ppm)	4.8	4.7			3.9	3.8	5.4	5.1	0.0	0.1
32	Mean O_2	(ppm)									18.7	13.9
	Std Dev	(ppm)									0.7	0.5
34	Mean O_2	(ppm)					20.2	18.2	55.3	74.4	12.3	8.7
	Std Dev	(ppm)					4.1	4.5	8.1	10.2	0.1	0.0
35	Mean O_2	(ppm)	16.5	4.5			22.8	19.9	28.5	21.4	19.8	19.9
	Std Dev	(ppm)	14.1	4.5			4.0	4.0	5.3	5.2	0.0	0.4
36	Mean O_2	(ppm)	12.6	15.3			20.7	19.9	20.0	21.0	24.3	24.3
	Std Dev	(ppm)	4.6	4.4			4.2	3.6	5.1	5.5	0.0	0.0
37	Mean O_2	(ppm)			13.1	11.0	19.1	18.4	34.8	25.5	21.0	15.7
	Std Dev	(ppm)			4.0	3.5	3.8	3.6	8.6	5.2	0.7	0.1
38	Mean O_2	(ppm)			14.1	11.0	21.0	19.1	22.4	23.5	20.3	18.5
	Std Dev	(ppm)			5.0	3.8	3.4	3.6	5.1	5.3	1.2	1.3
40	Mean O_2	(ppm)			11.1	10.8	22.6	19.4	33.1	24.8	16.7	19.9
	Std Dev	(ppm)			3.9	3.5	4.0	3.7	7.6	5.3	0.2	0.1
41	Mean O_2	(ppm)							29.0	24.4	14.2	14.5
	Std Dev	(ppm)							6.7	5.3	3.0	1.4
42	Mean O_2	(ppm)							21.8	21.0	14.5	14.9
	Std Dev	(ppm)							6.9	5.2	0.4	0.0
43	Mean O_2	(ppm)							24.3	19.3	21.7	14.5
	Std Dev	(ppm)							5.8	5.1	1.3	0.3
47	Mean O_2	(ppm)							26.1	22.9	19.1	17.0
	Std Dev	(ppm)							7.6	5.2	0.5	0.6

Note that the acceptance criteria is < 100 ppm O_2

4.3.2.6 Replicate and Duplicate Analyses

Replicate analysis results are from two or more punches from the same sample filter analyzed on different instruments. Duplicate analysis results are from two punches from the same sample filter analyzed on the same instruments. A replicate or duplicate analysis was performed randomly on one sample from every group of 10 samples. Table 4.3-8a gives the criteria and summary statistics for replicate and duplicate IMPROVE_A carbon analyses run on the Model 2001 analyzers for the CSN filter samples during the reporting period November 20, 2015 through December 31, 2015. Table 4.3-8b gives the criteria and summary statistics for replicate and duplicate IMPROVE_A carbon analyses run on the Model 2015 analyzers for the CSN filter samples during the reporting period January 1, 2016 through December 31, 2016. Control charts for replicate and duplicate analyses for Model 2001 and Model 2015 are plotted in Figures 4.3-8 and 4.3-9, respectively.

Duplicate and replicate analysis results for TC, OC, and EC agree well, with higher relative percent differences (RPD) at loading levels below 10.0 µg C/cm^2. All 137 replicate pairs and 11 duplicate pairs analyzed by Model 2001 analyzers and all 24 duplicate pairs analyzed by Model 2015 analyzers met the precision criteria. Only one out of 1577 replicate sample pairs analyzed by Model 2015 exceeded TC and OC precision limits. Replicate analyses results are more variable than duplicate analyses, but remain within acceptable limits. The small size (25 mm) of the filter used in the IMPROVE_A carbon analysis method does not permit more than three punches (each ~0.5 cm^2) to be taken from the filter. Samples not meeting replicate criteria (i.e., for TC, OC, or EC < 10 µg C/cm^2, TC, OC < ± 1.0 µg C/cm^2 and EC < ± 2.0 µg C/cm^2; and for TC, OC or EC ≥ 10 µg C/cm^2, TC or OC < 10% RPD and EC < 20% RPD) are re-analyzed, typically on a third analyzer. Filter inhomogeneities, which are flagged prior to first analysis, are also examined.

Table 4.3-8a: DRI Model 2001 carbon replicate analysis criteria and statistics (CSN sample dates 11/20/2015-12/29/2015).

		Replicates					Duplicates				
Range	Criteria	Statistic	No.	TC	OC	EC	No.	TC	OC	EC	Units
All		Count	137				11				
TC, OC, & EC < 10 µg C/cm^2	TC, OC < ±1.0 µg C/cm^2 EC < ±2.0 µg C/cm^2	Count		21	28	110		3	3	11	
		No. Fail		0	0	0		0	0	0	
		%Fail		0.0	0.0	0.0		0.0	0.0	0.0	%
		Mean		0.145	0.165	0.294		0.076	0.118	0.148	µg C/cm^2
		StdDev		0.093	0.129	0.309		0.105	0.095	0.151	µg C/cm^2
		Max		0.314	0.441	1.923		0.197	0.192	0.537	µg C/cm^2
		Min		0.006	0.006	0.000		0.011	0.011	0.000	µg C/cm^2
		Median		0.164	0.124	0.201		0.020	0.151	0.133	µg C/cm^2
TC, OC, & EC ≥ 10 µg C/cm^2	TC, OC %RPD < 10% EC %RPD < 20%	Count		116	109	27		8	8	0	
		No. Fail		0	0	0		0	0	-	
		%Fail		0.00	0.00	0.00		0.00	0.00	-	%
		Mean		1.64	2.20	2.63		1.63	2.38	-	RPD
		StdDev		1.16	1.54	2.20		1.12	0.84	-	RPD
		Max		4.60	3.33	5.07		4.10	3.33	-	RPD
		Min		0.00	0.01	0.81		0.32	1.07	-	RPD
		Median		1.32	1.99	2.01		1.45	2.50	-	RPD

Note: RPD= 100 x absolute value [original sample-duplicate sample]/[(original sample+ duplicate sample)/2]

Table 4.3-8b: DRI Model 2015 carbon replicate analysis criteria and statistics (CSN sample dates 1/1/2016-12/31/2016).

		Replicates					Duplicates				
Range	Criteria	Statistic	No.	TC	OC	EC	No.	TC	OC	EC	Units
All		Count	1577				24				
TC, OC, & EC	TC, OC < ±1.0 μg C/cm^2	Count		186	331	1349		5	7	20	
	EC < ±2.0 μg C/cm^2	No. Fail		0	1	0		0	0	0	
< 10 μg C/cm^2		%Fail		0.0	0.3	0.0		0.0	0.0	0.0	%
		Mean		0.208	0.209	0.241		0.208	0.206	0.126	μg C/cm^2
		StdDev		0.184	0.175	0.215		0.152	0.111	0.138	μg C/cm^2
		Max		0.851	1.030	1.286		0.460	0.315	0.610	μg C/cm^2
		Min		0.000	0.001	0.000		0.018	0.055	0.000	μg C/cm^2
		Median		0.145	0.163	0.179		0.164	0.256	0.080	μg C/cm^2
TC, OC, & EC	TC, OC %RPD < 10%	Count		1391	1246	228		19	17	4	
	EC %RPD < 20%	No. Fail		1	0	0		0	0	0	
≥ 10 μg C/cm^2		%Fail		0.1	0.0	0.0		0.0	0.0	0.0	%
		Mean		2.25	2.48	4.33		2.06	2.86	3	RPD
		StdDev		1.64	1.79	2.86		2.24	2.40	6.00	RPD
		Max		14.08	9.81	16.26		8.68	8.45	0.25	RPD
		Min		0.00	0.00	0.00		0.01	0.20	2.39	RPD
		Median		1.96	2.09	3.89		1.45	1.99	0.00	RPD

Figure 4.3-8a: DRI Model 2001 replicate (two punches from the same sample filter analyzed on different instruments) analysis results. The limits are ±1.0 µg/cm^2 for TC and OC <10 µg/cm^2, ±2.0 µg/cm^2 for EC <10 µg/cm^2, ±10% relative percent difference for TC and OC ≥10 µg/cm^2, and ±20% relative percent difference for EC ≥10 µg/cm^2.

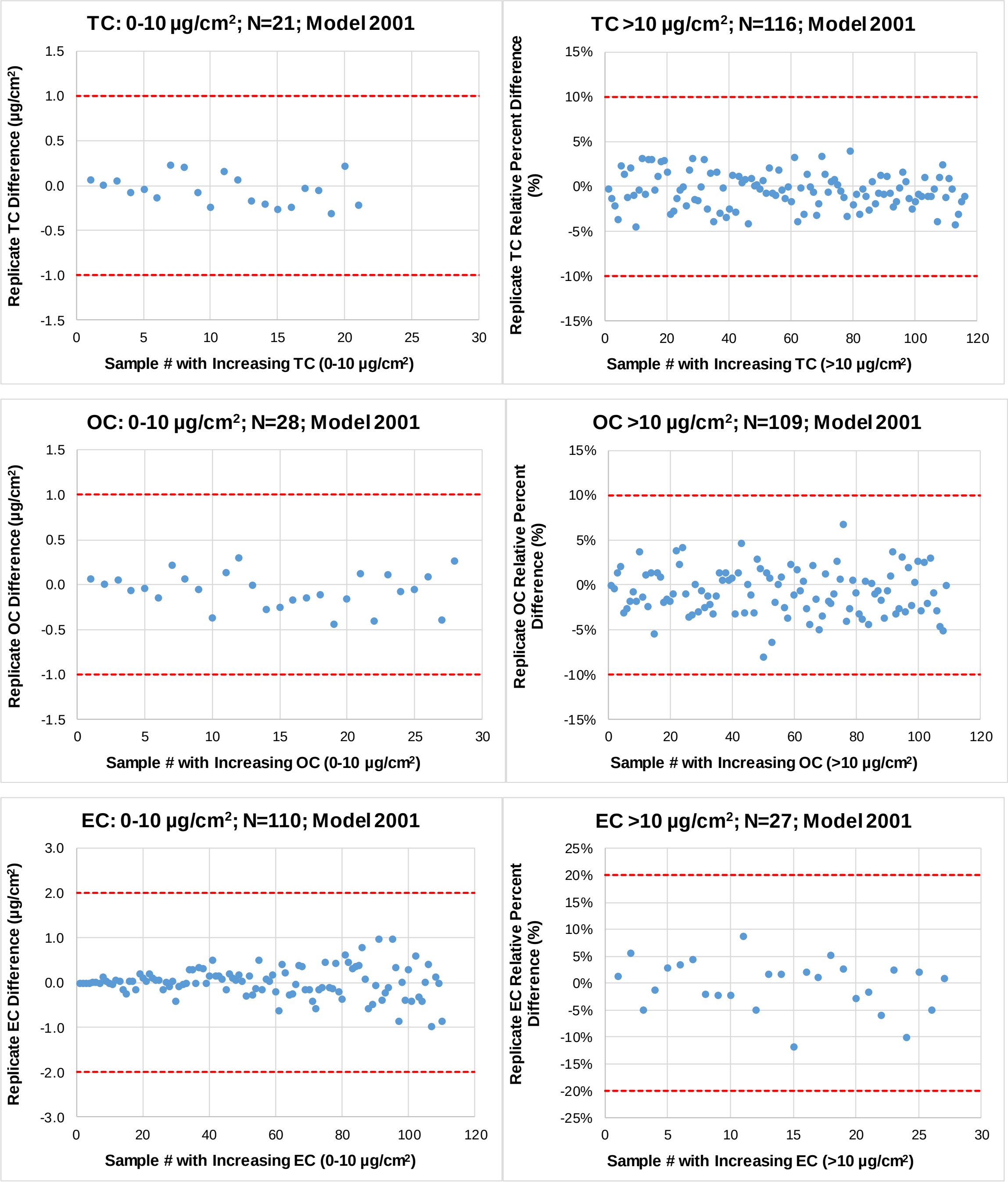


Figure 4.3-8b: DRI Model 2001 duplicate (two punches from the same sample filter analyzed on same instruments) analysis results. The limits are ±1.0 µg/cm^2 for TC and OC <10 µg/cm^2, ±2.0 µg/cm^2 for EC <10 µg/cm^2, ±10% relative percent difference for TC and OC ≥10 µg/cm^2, and ±20% relative percent difference for EC ≥10 µg/cm^2.

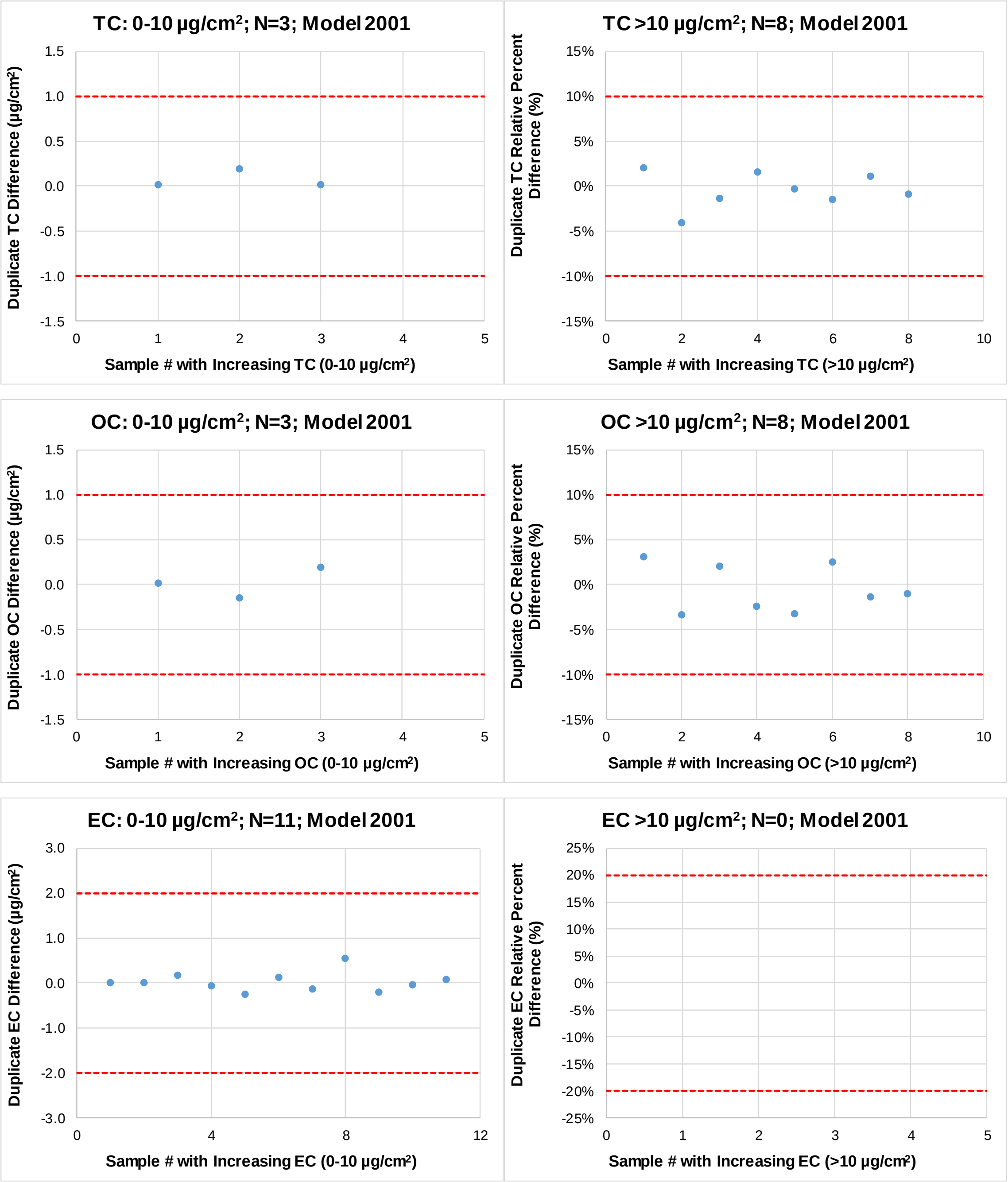


Figure 4.3-9a: DRI Model 2015 replicate (two punches from the same sample filter analyzed on different instruments) analysis results. The limits are ±1.0 µg/cm^2 for TC and OC <10 µg/cm^2, ±2.0 µg/cm^2 for EC <10 µg/cm^2, ±10% relative percent difference for TC and OC ≥10 µg/cm^2, and ±20% relative percent difference for EC ≥10 µg/cm^2.

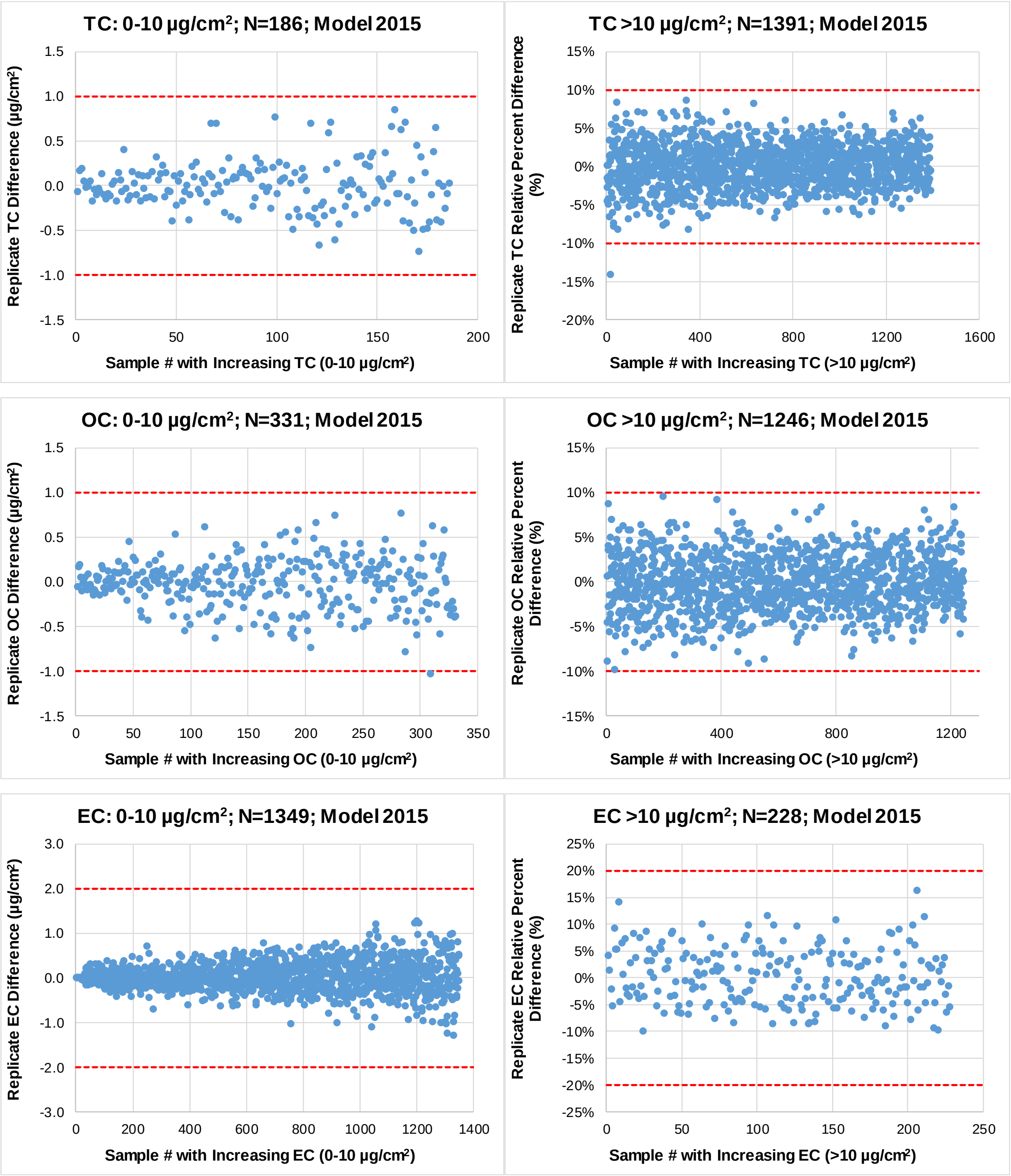
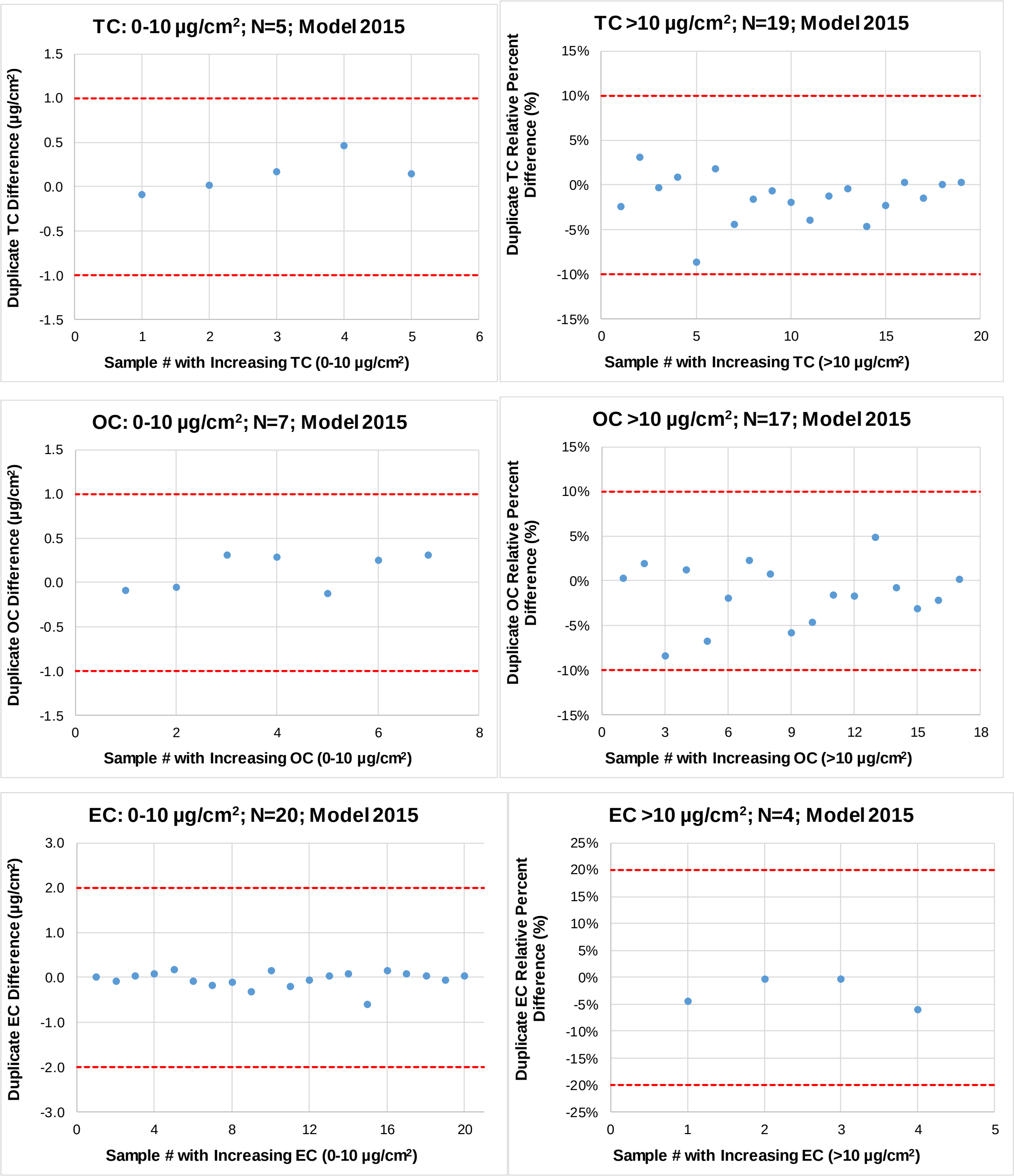


Figure 4.3-9b: DRI Model 2015 duplicate (two punches from the same sample filter analyzed on same instruments) analysis results. The limits are ±1.0 µg/cm^2 for TC and OC <10 µg/cm^2, ±2.0 µg/cm^2 for EC <10 µg/cm^2, ±10% relative percent difference for TC and OC ≥10 µg/cm^2, and ±20% relative percent difference for EC ≥10 µg/cm^2.



4.3.3 Determination of Uncertainties and Method Detection Limits

For discussion of Method Detection Limits (MDLs) see Section 3.1.3.2.

For discussion of analytical uncertainty and total uncertainty see Section 3.1.2 and Section 6.5, respectively.

4.3.4 Audits, Performance Evaluations, Training, and Accreditations

4.3.4.1 System Audits

The prime contractor (UC Davis) did not conduct any audits of the DRI Thermal/Optical Analysis Laboratory during 2016.

4.3.4.2 Performance Evaluations

The EPA did not conduct any performance evaluations of the DRI Thermal/Optical Analysis Laboratory during 2016.

4.3.4.3 Training

All new laboratory staff receive training in performing the tasks in the SOPs for their assigned work.

4.3.4.4 Accreditations

There are no accreditation programs for analysis of carbon on aerosol filters by TOA.

4.3.5 Summary of Filter Blanks

Over the analysis period, a total of 628 quartz filters were received as field blanks; 37 of these filters were invalidated. Table 4.3-9 summarizes the field blank statistics. The lower quantifiable limits (LQLs) are defined as three times the standard deviation of field blanks and are used an internal QA indicators, distinct from the MDLs reported to AQS.

Table 4.3-9: Quartz filter field blank statistics. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4), TR indicates measurement by reflectance, and TT indicates measurement by transmittance.

Species	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)	LQL (µg/cm^2)
EC1	591	0.000	0.004	0.000	0.333	0.028	0.084
EC2	591	0.000	0.003	0.000	0.380	0.027	0.081
EC3	591	0.000	0.000	0.000	0.007	0.000	0.001
ECTR	591	0.000	0.005	0.000	0.527	0.039	0.117
ECTT	591	0.000	0.002	0.000	0.388	0.024	0.071
OC1	591	0.000	0.034	0.000	1.195	0.099	0.297
OC2	591	0.190	0.221	0.000	1.306	0.153	0.459
OC3	591	0.480	0.582	0.000	6.137	0.462	1.385
OC4	591	0.000	0.034	0.000	1.386	0.110	0.329
OCTR	591	0.724	0.873	0.000	8.777	0.681	2.042
OCTT	591	0.724	0.876	0.000	8.982	0.692	2.077
OPTR	591	0.000	0.002	0.000	0.388	0.022	0.067
OPTT	591	0.000	0.005	0.000	0.527	0.037	0.111

5. Data Management and Reporting

5.1 Number of Events Posted to AQS

Summarized in Table 5.1-1 are dates that data were delivered to AQS for samples collected November 20, 2015 through December 31, 2016. Data are expected to be delivered to AQS within 120 days of receipt of filters by the analytical laboratories. Delays in filter delivery and laboratory analysis resulted in later deliveries to AQS. In a small number of cases, AQS monitors were not established, and data delivery resulted in failed transactions. For these cases, data will be redelivered at a later date per discussion with the EPA.

Table 5.1-1: Summary of data deliveries to AQS, November 2015 through December 2016.

Data (Month Samples Collected)	AQS Delivery Date
November 2015	July 15, 2016
December 2015	July 15, 2016
January 2016	October 27, 2016
February 2016	December 16, 2016
March 2016	January 20, 2017
April 2016	April 6, 2017
May 2016	April 3, 2017
June 2016	May 17, 2017
July 2016	May 17, 2017
August 2016	August 15, 2017
September 2016	August 15, 2017
October 2016	September 15, 2017
November 2016	September 15, 2017
December 2016	October 27, 2017

6. Quality Assurance and Data Validation

6.1 QAPP Revisions

The UC Davis Quality Assurance Project Plan (QAPP) for Laboratory Analysis and Data Processing/Validation for Chemical Speciation of $PM_{2.5}$ Filter Samples was accepted by the EPA on November 29, 2017. Revisions to the QAPP will be made annually, with the first revision to be released November 2018.

6.2 SOP Revisions

The UC Davis Standard Operating Procedures (SOPs) for Laboratory Analysis and Data Processing/Validation for Chemical Speciation of $PM_{2.5}$ Filter Samples were accepted by the EPA on November 29, 2017. Revisions to the SOPs will be made annually, with the first revision to be released November 2018.

6.3 Summary of Internal QA Activities

Following laboratory analysis all analytical results are assembled by UC Davis for processing and initial validation. Data processing involves calculating ambient concentration, uncertainty, and MDL for each analyte using the laboratory result plus the sample volume and sampling duration determined from the field data. The calculated concentrations undergo two levels of validation at UC Davis: (1) Level 0 validation to examine the fundamental information associated with each measured variable, such as chain of custody, shipping integrity, sample identification, and damaged samples, and (2) Level 1 review for technical acceptability and reasonableness based on information such as routine QC sample results, data quality indicator calculations, performance evaluation samples, internal and external audits, statistical screening, internal consistency checks, and range checks. Further detail regarding the UC Davis data processing and validation can be found in *UCD CSN SOP 801, Processing and Validating Raw Data*, and in the associated Technical Information (TI) documents as follows:

1) *UCD CSN TI 801A, Data Ingest*: Sample event information (including filter IDs, flow rates, flags, and comments) are received from the Sample Handling Lab via email and uploaded to the UC Davis CSN database. XRF results are transferred into the database through an automated service. IC and TOR analysis result files are received via email from DRI. Results are ingested to the UC Davis CSN database.
2) *UCD CSN TI 801C, Level 0 Validation*: Data and metadata are reviewed through several visualizations to identify oddities such as inconsistent dates that appear to be data transcription and/or data entry errors. These are resolved through communication with the Sample Handling Lab.
3) *UCD CSN TI 801B, Data Processing*: Sample volume and analysis results are combined to calculate concentrations. Blank values are used to derive MDLs. MDLs and concentrations are used to estimate uncertainty.
4) *UCD CSN TI 801C , Level 1 Data Validation*: Several statistical and visual checks are applied and examined. Reanalyses are requested as needed. Data are flagged with qualifier or null codes.
5) *UCD CSN TI 801D, Data Posting*: Initially validated concentration data and metadata are posted to DART for SLT (State, Local, and Tribal) review. After the specified 30-day review period, changed or unchanged data are re-ingested to the UC Davis CSN database.
6) *UCD CSN TI 801D, AQS Delivery*: SLT initiated changes and comments are reviewed and resolved. Data are formatted for delivery to AQS and posted.

6.4 Data Validation and Review

The validation graphics shown in this section are a small subset of the many QC evaluations that UC Davis performs on a routine basis. They are selected to illustrate the nature and use of the QC tools, and provide an overview of the review process.

Additional information and detail regarding analytical and validation procedures can be found in the standard operation procedure (SOP) documents, *UC Davis CSN Quality Assurance Project*

Plan (QAPP), and the *Data Validation for the Chemical Speciation Network* guide, all available at the UC Davis CSN site: https://aqrc.ucdavis.edu/documentation.

6.4.1 Summary of Monthly Data Validation Review Results

6.4.1.1 Comparisons Across Years

Multi-year time series plots are used to examine large-scale trends and/or analytical problems. UC Davis is currently constructing a database backfilled to year 2000 with CSN historical data. Comprehensive access to historical network data will provide context for validation and review of more recent data. The backfill is not yet complete and limited multi-year time series are available at this time.

Figures 6.4-1 and 6.4-2 show time series for the network-wide 90th percentile, median (50th percentile), and 10th percentile concentrations of organic carbon (OC) and elemental carbon (EC). The carbon fractions OC and EC are determined by DRI using thermal analysis with a correction for pyrolysis based on optical monitoring as it is heated. Measurements from 2005 through 2015 were made with DRI Model 2001 analyzers monitoring at the single wavelength 633 nm; starting with January 2016 samples, DRI switched to Model 2015 analyzers monitoring seven wavelengths centered at 635 nm. The 2016 data shown in Figures 6.4-1 and 6.4-2 are for the 635 nm measurements and should be comparable to the earlier data with some allowance for seasonal and annual variability. With the exception of November and December, the 2016 median OC values are lower than previous years. The 2016 10th percentile OC values are lower across all months. The 2016 EC median values align better with past years; however, the 10th percentile EC values are lower for 9 of 12 months.

Figure 6.4-1: Multi-year time series, organic carbon (OC).

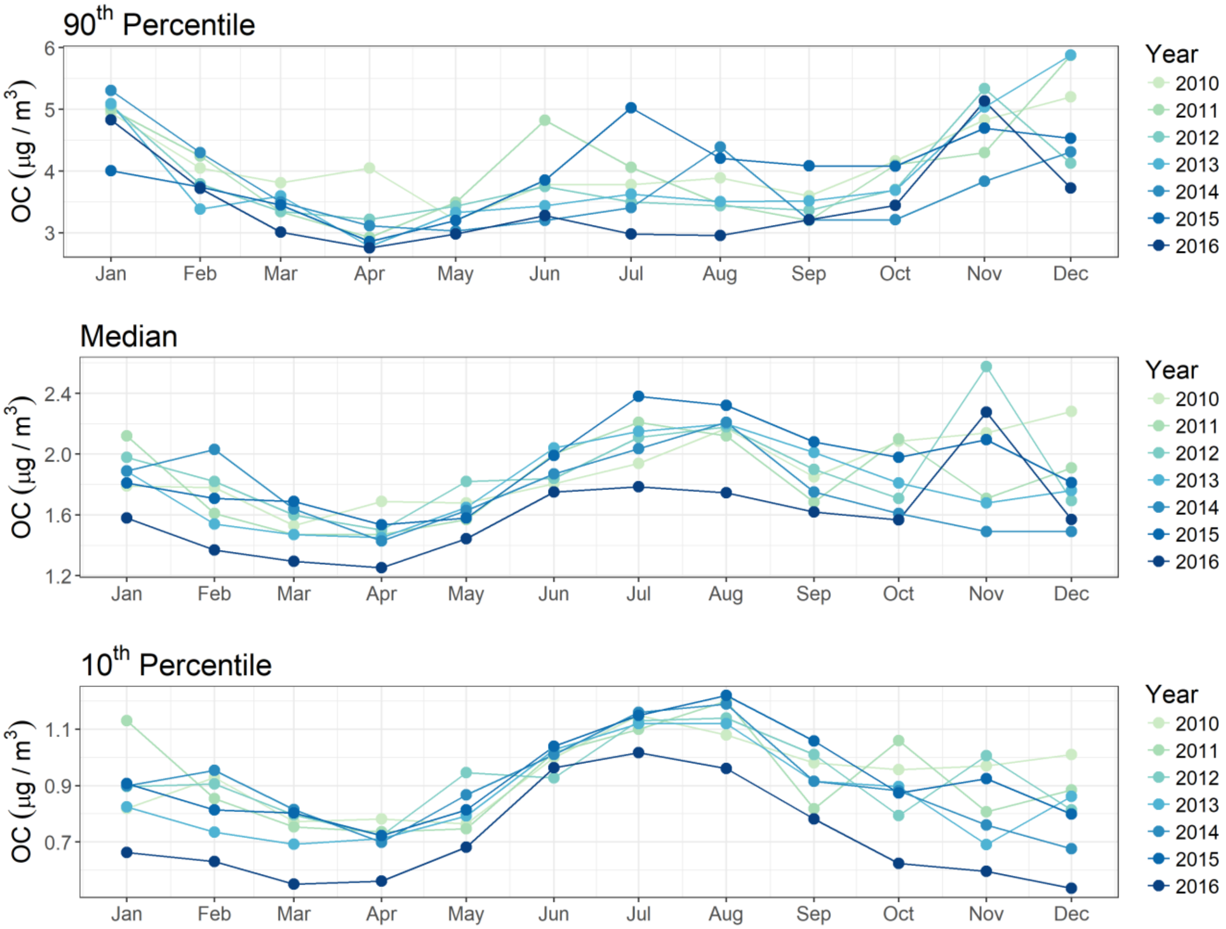
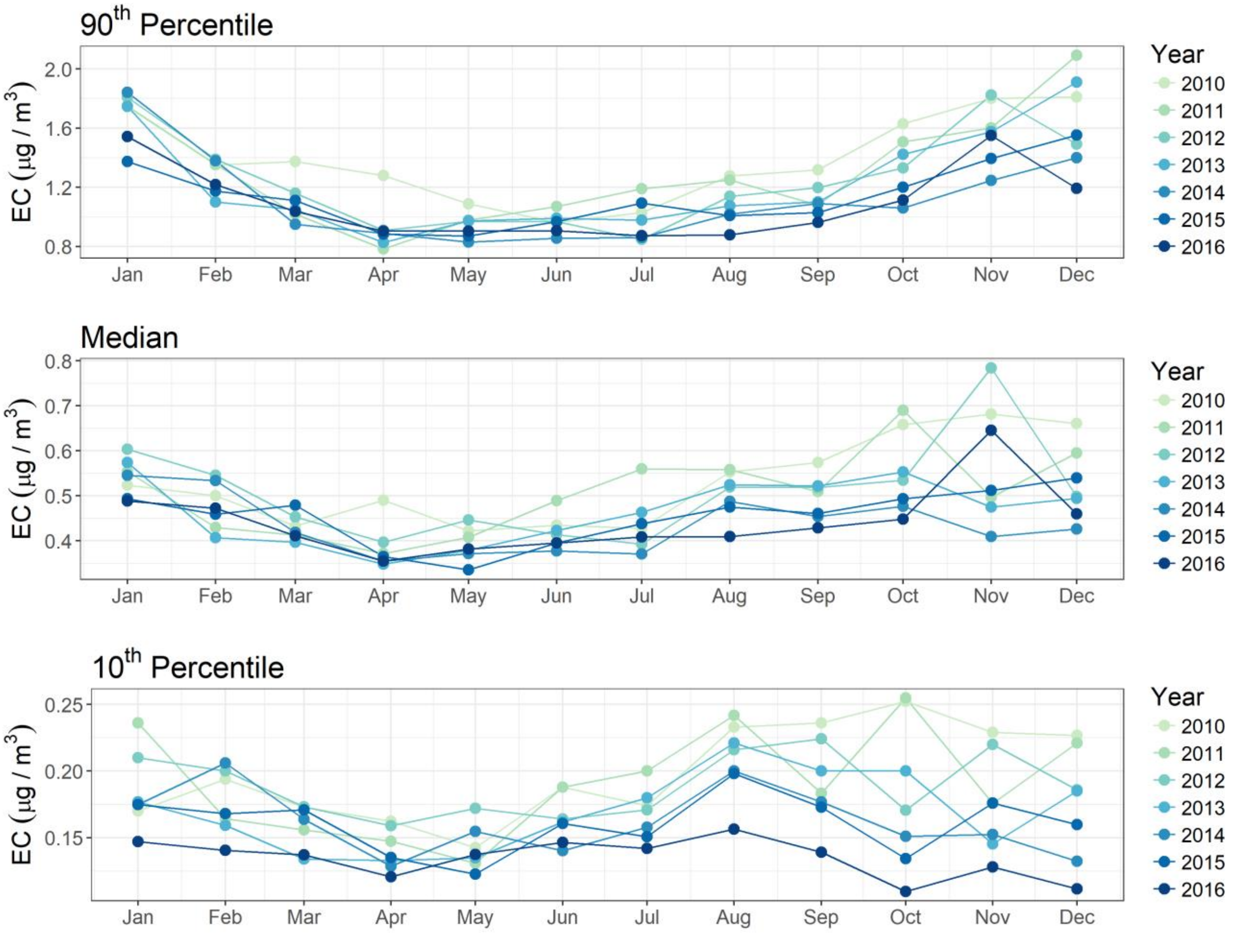


Figure 6.4-2: Multi-year time series, elemental carbon (EC).


90th Percentile

Median

10th Percentile

Not shown here are multi-year time series plots of lead, which show discontinuity across the contract transition from RTI to UC Davis that occurred in November 2015. See Section 2.2.2 and Section 3.2.1.1 for further detail. UC Davis is currently investigating the differences.

6.4.1.2 Comparisons Between Modules

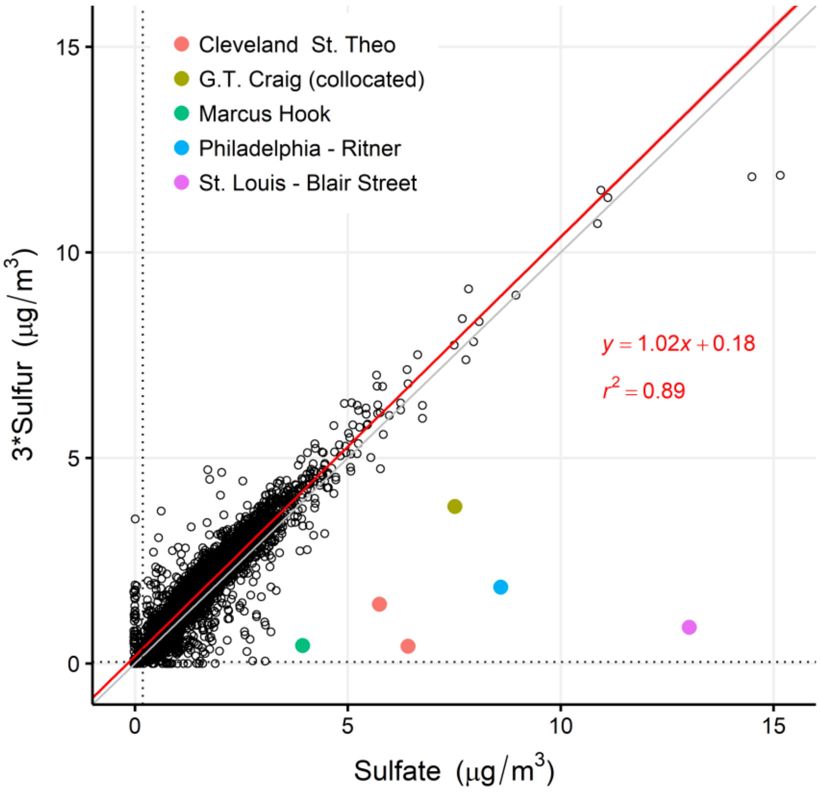
The following graphs compare two independent measures of aerosol properties that are expected to correlate. These graphs highlight cases where the two measurements do not correlate well, which can result from real atmospheric and anthropogenic events or analytical and sampling issues. As part of the data validation process, the highlighted cases are investigated.

Sulfur versus Sulfate

PTFE filters are analyzed for elemental sulfur using EDXRF, and nylon filters are analyzed for sulfate (SO_4) using IC. The molecular weight of SO_4 (96 g/mol) is three times the atomic weight of S (32 g/mol), so the concentration ratio $(3\times S)/SO_4$ should be one if all particulate sulfur is present as water-soluble sulfate. In practice, real measurements routinely yield a ratio greater than one (Figure 6.4-3), suggesting the presence of some sulfur in a non-water soluble form of sulfate or in a chemical compound other than sulfate. However, instances are observed where $(3\times S)/SO_4$ ratios are lower than typically observed (Figure 6.4-3; colored points). Three of the six instances of low (3×S)/SO_4 in Figure 6.4-3 are from the Cleveland St. Theo (AQS ID#39-035-0038-6) and G.T. Craig collocated (AQS ID#39-035-0060-6) sites, which are in close proximity and located in Cleveland, OH. This behavior may result from sampling artifacts on the nylon filter (resulting in higher SO_4 concentrations) associated with industrial processes, though is only seen on a few occasions during this time period.

The highest sulfur and corresponding sulfate measurements (3.96 µg/m^3 S and 15.16 µg/m^3 SO_4) in the network were on July 5, 2016 at the Riverside-Rubidoux site (AQS ID#06-065-8001-5), and were likely related to Independence Day firework activity. The collocated Riverside-Rubidoux sampler (AQS ID#06-065-8001-6) measured similarly high concentrations on the same day. Both samplers also measured elevated concentrations of potassium, aluminum, barium, copper, magnesium, titanium, and strontium on July 5, further evidence that the high S and SO_4 concentrations were related to fireworks.

Figure 6.4-3: Scatter plot of (3xS) versus SO4, November 2015 through December 2016. Number of observations (complete pairs) is 13,537. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression.



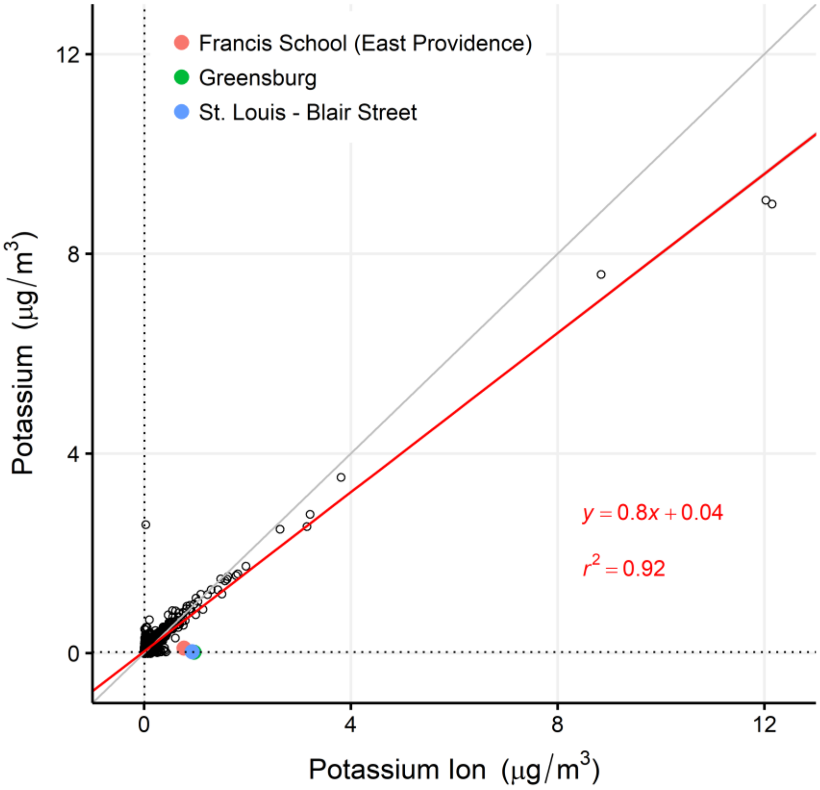
Potassium versus Potassium Ion

PTFE filters are analyzed for elemental potassium using XRF, and nylon filters are analyzed for potassium ion using IC. Similar to the S/SO_4 relationship, the potassium/potassium ion ratio can be used to identify outliers as well as atmospherically unusual events. In a scenario where all the particulate potassium is present as water-soluble potassium ion, the potassium/potassium ion ratio is expected to be near one. This expectation is generally met, with greater variability at low concentrations (Figure 6.4-4). A known exception to this expectation is for soil-borne potassium, which is not water soluble; high soil contributions are thus expected to result in ratios greater than one.

Notable outliers are observed (Figure 6.4-4; colored points), where the potassium/potassium ion ratio is lower than expected. Unlike the (3×S)/SO_4 outliers, these outliers correspond with different sites.

The highest potassium and corresponding potassium ion measurements (9.00 µg/m^3 potassium and 12.15 µg/m^3 potassium ion) in the network were on July 5, 2016 at the Riverside-Rubidoux site (AQS ID#06-065-8001-5) and the collocated Riverside-Rubidoux sampler (AQS ID#06-065-8001-6). As noted above in the discussion of S and SO_4, these high concentrations are likely from firework activity.

Figure 6.4-4: Scatter plot of potassium versus potassium ion, November 2015 through December 2016. Number of observations (complete pairs) is 13,537. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression.



PM2.5 versus Reconstructed Mass (RCM)

Gravimetric data are compared to RCM, where the RCM composite variable is estimated from chemical speciation measurements, to test many different aspects of overall data quality. The formulas used to estimate the mass contributions from various chemical species are detailed in *UCD CSN TI 801B, CSN Data Processing*. In the simple case where valid measurements are available for all needed variables, reconstructed mass is the following sum:

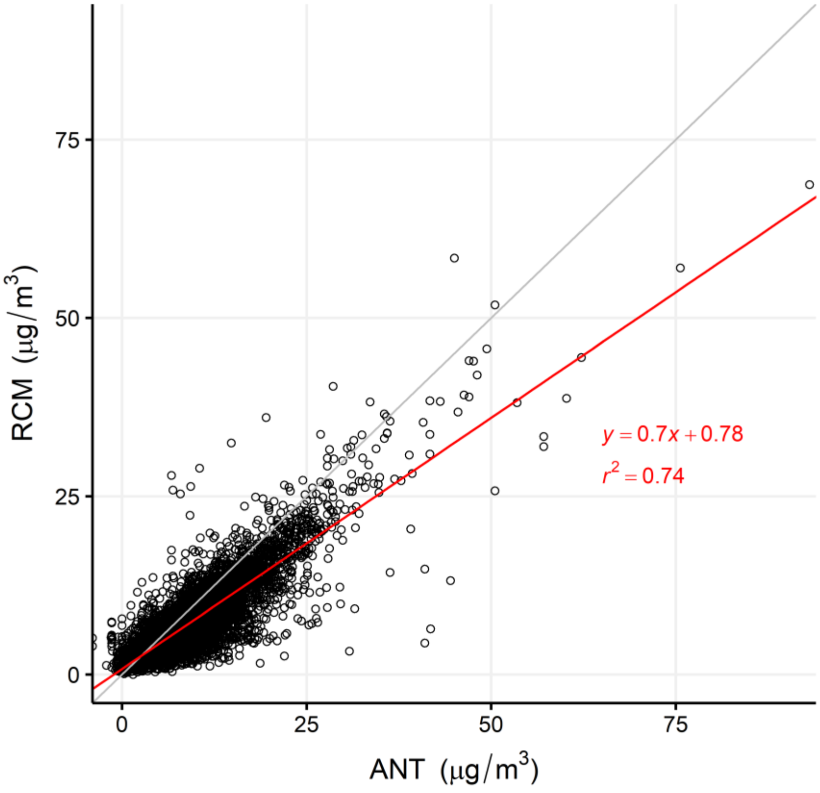
$$\text{RCM} = (4.125 \times \text{S}) + (1.29 \times \text{NO}_3^-) + (1.4 \times \text{OC}) + (\text{EC}) + (2.2 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti}) + (1.8 \times \text{chloride})$$

The parenthesized components represent the mass contributions from, in order, ammonium sulfate, ammonium nitrate, organic compounds, elemental carbon, soil, and sea salt.

As of April 2016, gravimetric analysis (i.e., weight before and after sample collection) was only performed for one site in the network (Douglas, GA, AQS ID#13-069-0002). Thus, for comparison purposes 24-hour average gravimetric PM2.5 mass data from AirNow Tech (ANT) is used as part of the validation process. The data provided by AirNow Tech is not final, so the data used here is a snapshot, downloaded at the time the plots were generated.

If the RCM completely captures and accurately estimates the different mass components, the RCM/ANT ratio is expected to be near one. The gravimetric mass is likely to include some water associated with hygroscopic species, which is not accounted for by any of the chemical measurements. Conversely, some ammonium nitrate measured on the retentive nylon filter may volatilize from the inert PTFE filter during and after sampling. The RCM and ANT masses generally correlate (Figure 6.4-5), but RCM tends to underestimate ANT mass.

Figure 6.4-5: Scatter plot of RCM versus AirNow Tech (ANT) PM2.5 mass data, November 2015 through December 2016. Number of observations (complete pairs) is 9,697. Solid gray line indicates 1:1. Solid red line indicates regression.



When considered for the entire network, the depressed RCM/ANT ratio shows no seasonal pattern (Figure 6.4-6). Considered individually, sites across the network exhibit a range of RCM/ANT ratio behavior including seasonality with high wintertime ratios relative to summer (Figure 6.4-7; San Jose, CA; AQS ID#06-085-0005), and low wintertime ratios relative to summer (Figure 6.4-8; Omaha, NE; AQS ID#31-055-0019). These patterns reflect the varying chemical composition at the sites by season. However, many sites exhibit no seasonal pattern and variable RCM/ANT ratios.

Low RCM/ANT ratios can result from an underestimate of variable(s) for derived RCM. The organic mass estimate (1.4 × OC) is generally considered representative of a regime where organic matter is dominated by fresh motor vehicle emissions (urban locations). However, there are many scenarios where a higher multiplier may be more appropriate. The IMPROVE (Interagency Monitoring of Protected Visual Environments) network uses a 1.8 multiplier for the organic mass estimate, which is thought to be more appropriate for a more aged air mass (rural locations).

Figure 6.4-6: Network wide time series of RCM/ANT ratios, November 2015 through December 2016. The white horizontal line indicates median and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively.

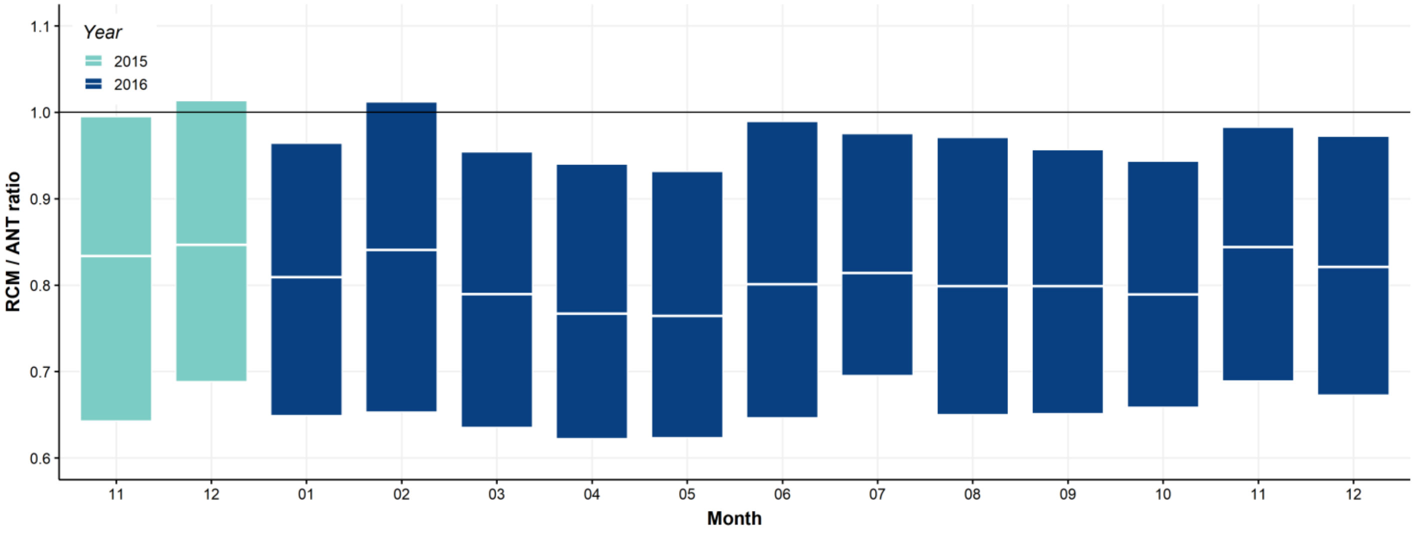


Figure 6.4-7: RCM/ANT ratios at San Jose, CA site (AQS ID#06-085-0005), November 2015 through December 2016. The white horizontal line indicates median and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively.

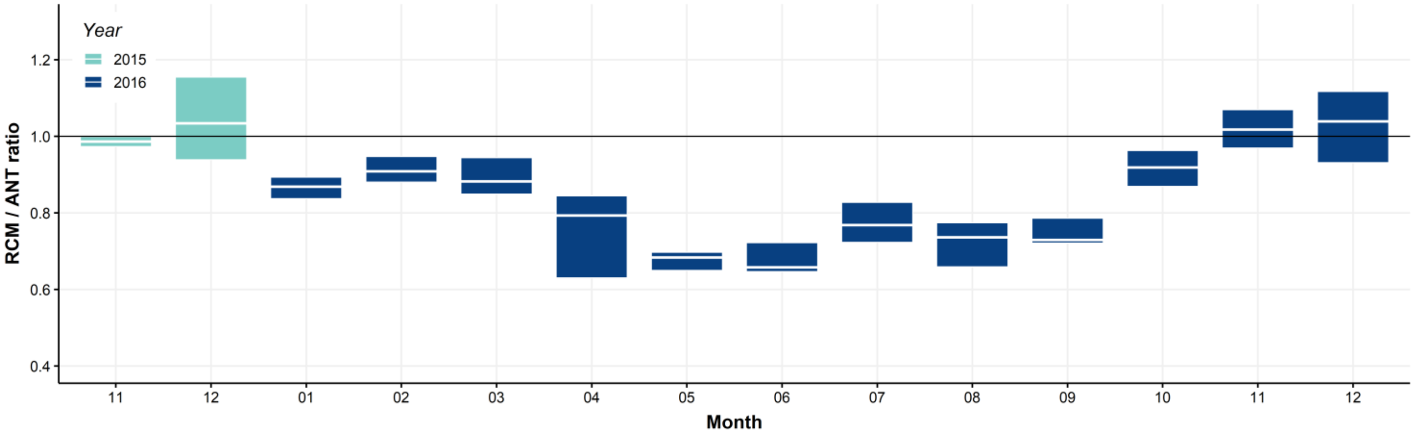
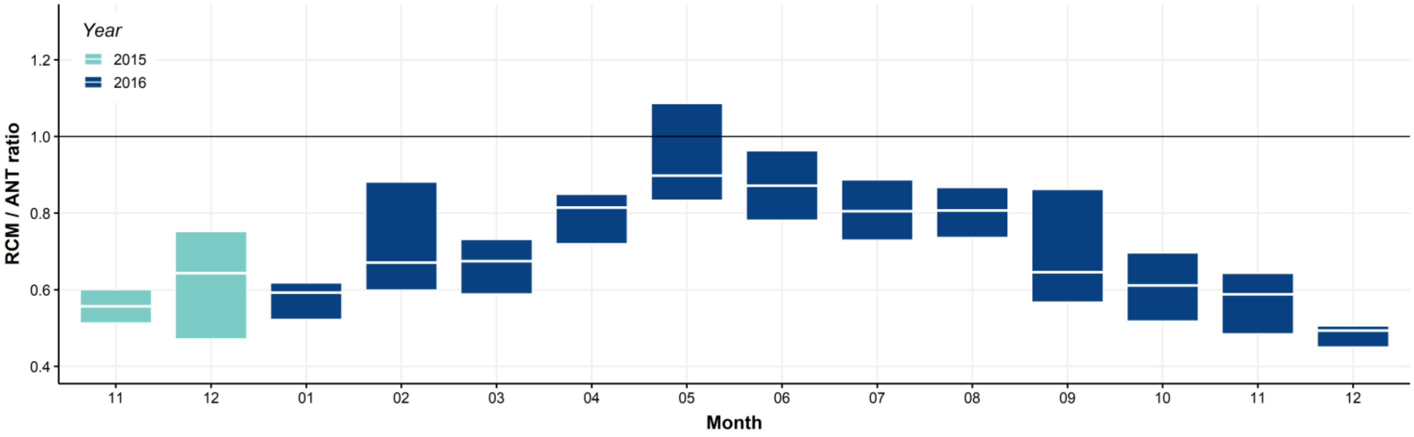


Figure 6.4-8: RCM/ANT ratios at Omaha, NE site (AQS ID#31-055-0019), November 2015 through December 2016. The white horizontal line indicates median and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively.



6.4.1.3 Comparisons Across Sites

Evaluating species data across the network by site allows for identification of site-specific and regional trends. Additionally, plots shown in this section can be used to identify outliers, which can be real atmospheric or anthropogenic events, or analytical outliers indicative of contamination.

Sulfur shows a distinct east/west gradient with lower concentrations primarily in the far western United States (Figure 6.4-9). However, there are several California sites, indicated by AQS ID#s beginning with 06-, where sulfur concentrations are higher than the other western sites (Figure 6.4-9).

Concentrations of nitrate (Figure 6.4-10) exhibit regional trends with elevated concentrations in the west, particularly California.

Figure 6.4-9: Sulfur concentrations (µg/m3) for the entire CSN network. Sites are ordered west to east on the x-axis, designated by XX-XXX-XXXX-Y, where XX-XXX-XXXX indicates AQS ID# and Y indicates site POC. Red points designate 2015 data, blue points designate 2016 data. Gray box and whisker indicate historical 90th percentile and 99th percentile, respectively.

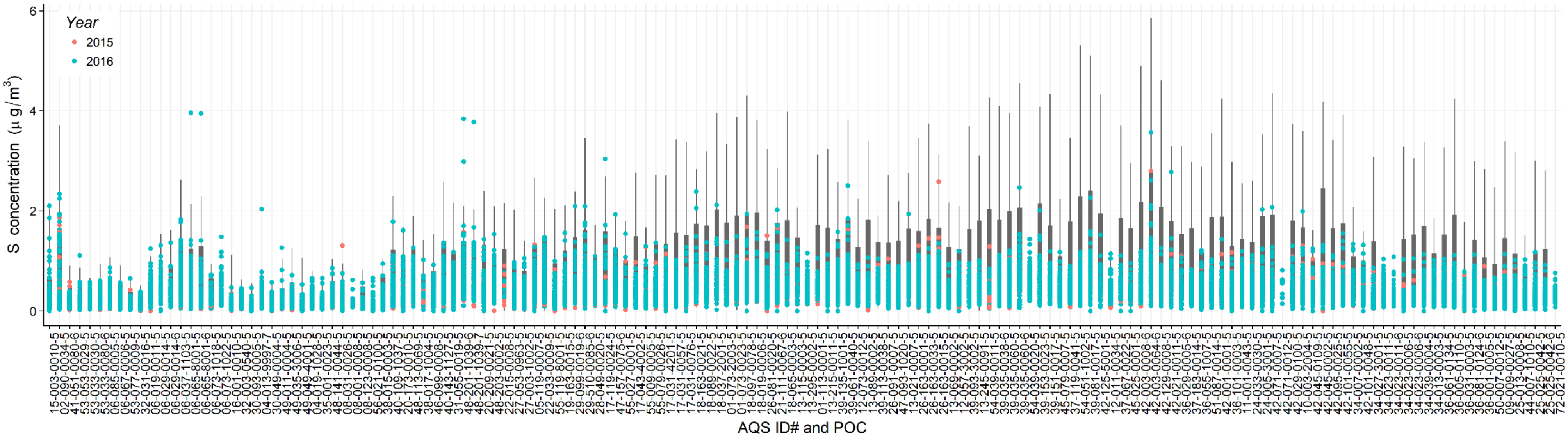
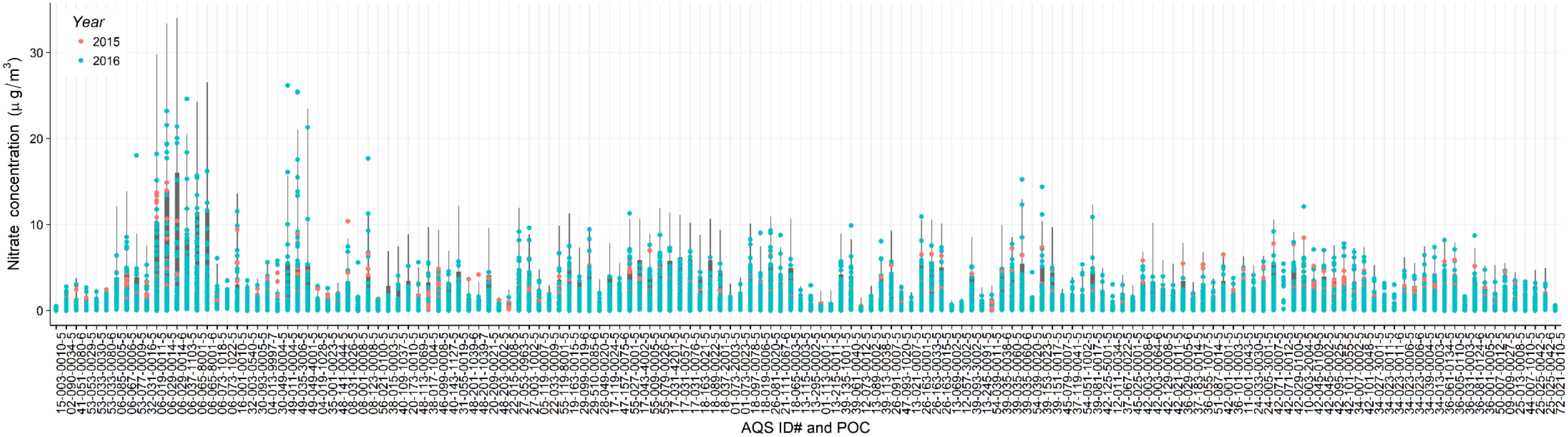


Figure 6.4-10: Nitrate concentrations (μg/m3) for the entire CSN network. Sites are ordered west to east on the x-axis, designated by XX-XXX-XXXX-Y, where XX-XXX-XXXX indicates AQS ID# and Y indicates site POC. Red points designate 2015 data, blue points designate 2016 data. Gray box and whisker indicate historical 90th percentile and 99th percentile, respectively.



6.5 Uncertainty Estimates and Collocated Precision Summary Statistics

Several network sites are equipped with collocated samplers, where simultaneous samples are collected on independent samplers and then analyzed using the same analytical protocols. Differences between the resulting data provide a measure of the total uncertainty associated with filter substrates, sampling and handling in the field, and laboratory analysis. Collocated precision is reported as fractional uncertainty, allowing determination of uncertainty without the influence of field blank outliers.

Collocated precision is calculated from the scaled relative differences (SRD) between the collocated sample pairs, from the subset of observations with concentrations at least three times the MDL. The collocated precision formula is a robust estimate of the standard deviation of the differences. To limit uncertainty in the determination of the necessary percentiles, a minimum of 50 collocated pairs is required for this estimate. To obtain an estimate of the mean standard deviation over multiple years, the mean of the variances is calculated, and the fractional uncertainty is square root of the mean variance.

$$Scaled\ Relative\ Difference = \frac{(\text{collocated} - \text{routine})\ /\ \sqrt{2}}{(\text{collocated} + \text{routine})\ /\ 2}$$

$$Collocated\ Precision\ (cp) = \frac{(84th\ percentile\ of\ SRD) - (16the\ percentile\ of\ SRD)}{2}$$

$$Fractional\ Uncertainty = 100 \times \sqrt{\frac{1}{n}\sum_{i=1}^{n}(cp)_i^2}$$

The scaled relative differences are ±√2 when one of the two measurements is zero, and vary between these limits at concentrations close to the detection limit. They generally decrease with increasing concentration, and are expected to converge to a distribution representative of multiplicative measurement error when the concentration is well above the detection limit (Figure 6.5.1, elements; Figure 6.5-2, ions; Figure 6.5-3, carbon). Fe, K, Si, and Zn are examples of elements that are measured at a wide range of concentrations and display this behavior. S is always measured well above the MDL and has good collocated measurement agreement throughout the range. This convergence is not observed for many elements and carbon fractions that are rarely measured above the MDL.

For several species, outliers are observed at the G.T. Craig site (AQS ID# 39-035-0060; Figures 6.5-1, 6.5-2, and 6.5-3). The instances of poor agreement between the collocated samplers at G.T. Craig do not fall within a clear time period, rather are dispersed throughout the year.

For some species, notably As (Figure 6.5-1) and EC3 (Figure 6.5-3), most measurements are zero and the scaled relative differences are ±√2.

Figure 6.5-1: Scaled relative difference for element measurements at sites with collocated samplers across the network (November 2015 through December 2016). Dotted vertical lines indicates MDL.

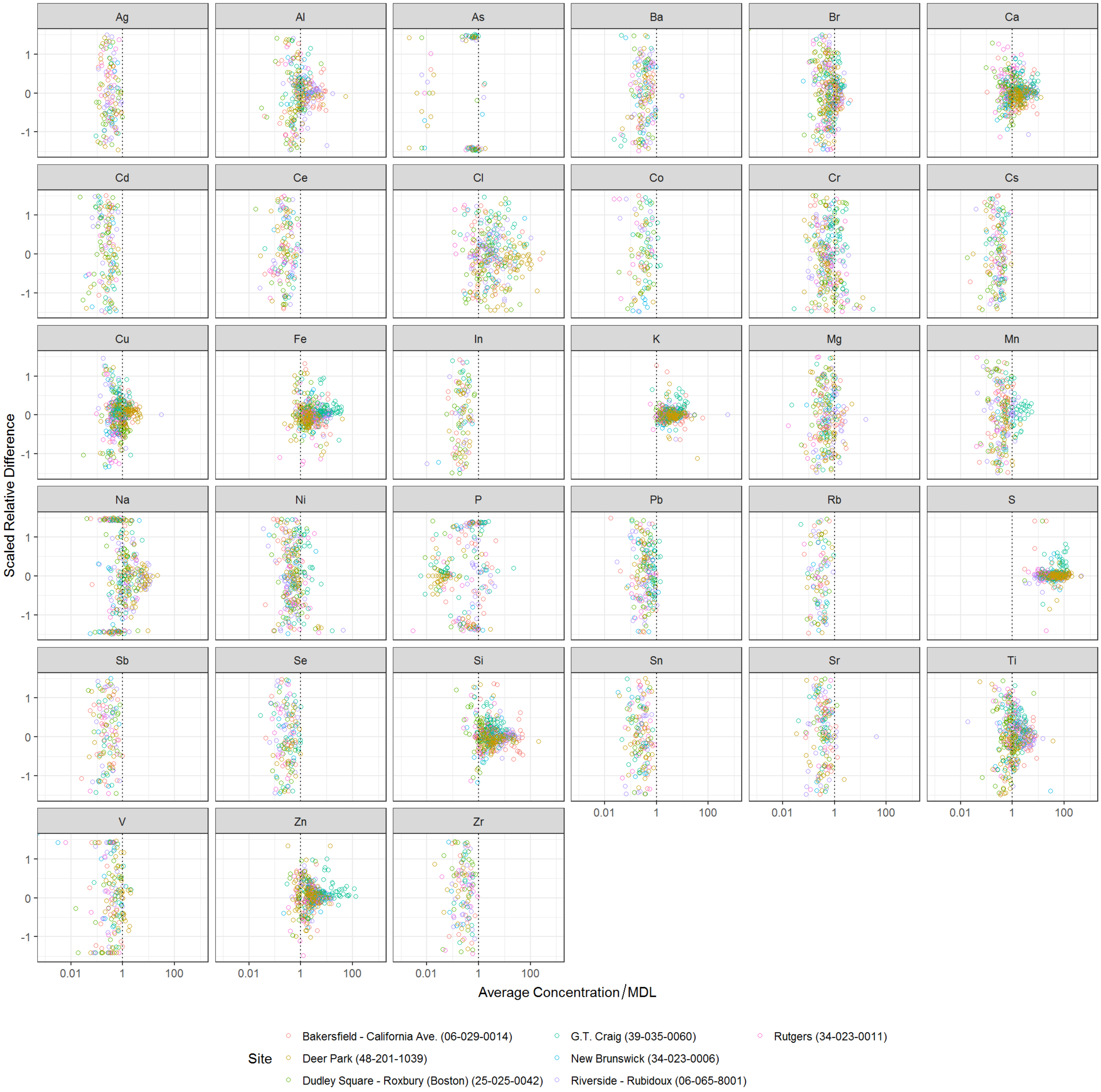


Figure 6.5-2: Scaled relative difference for ion measurements at sites with collocated samplers across the network (November 2015 through December 2016). Dotted vertical lines indicates MDL.

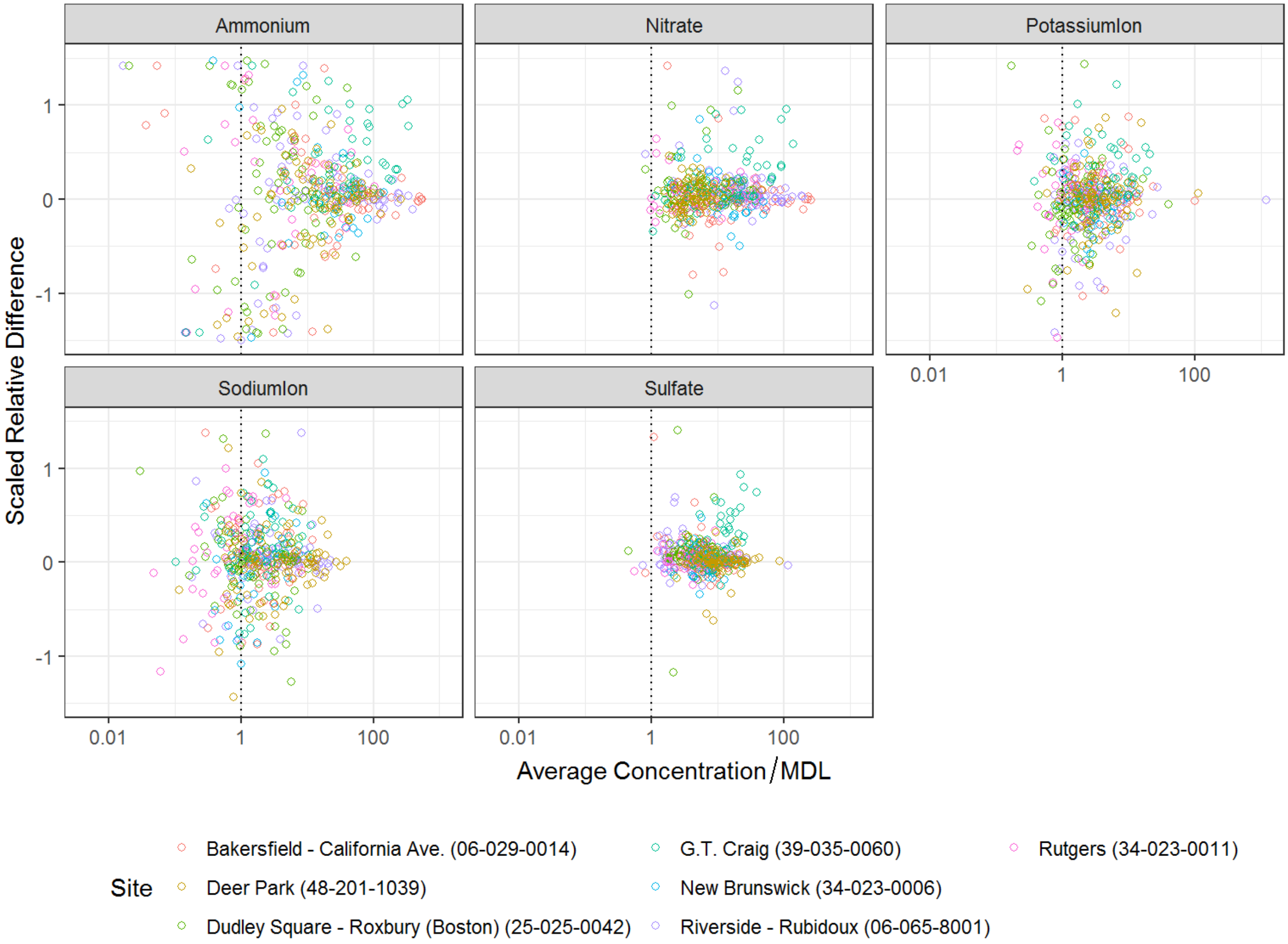
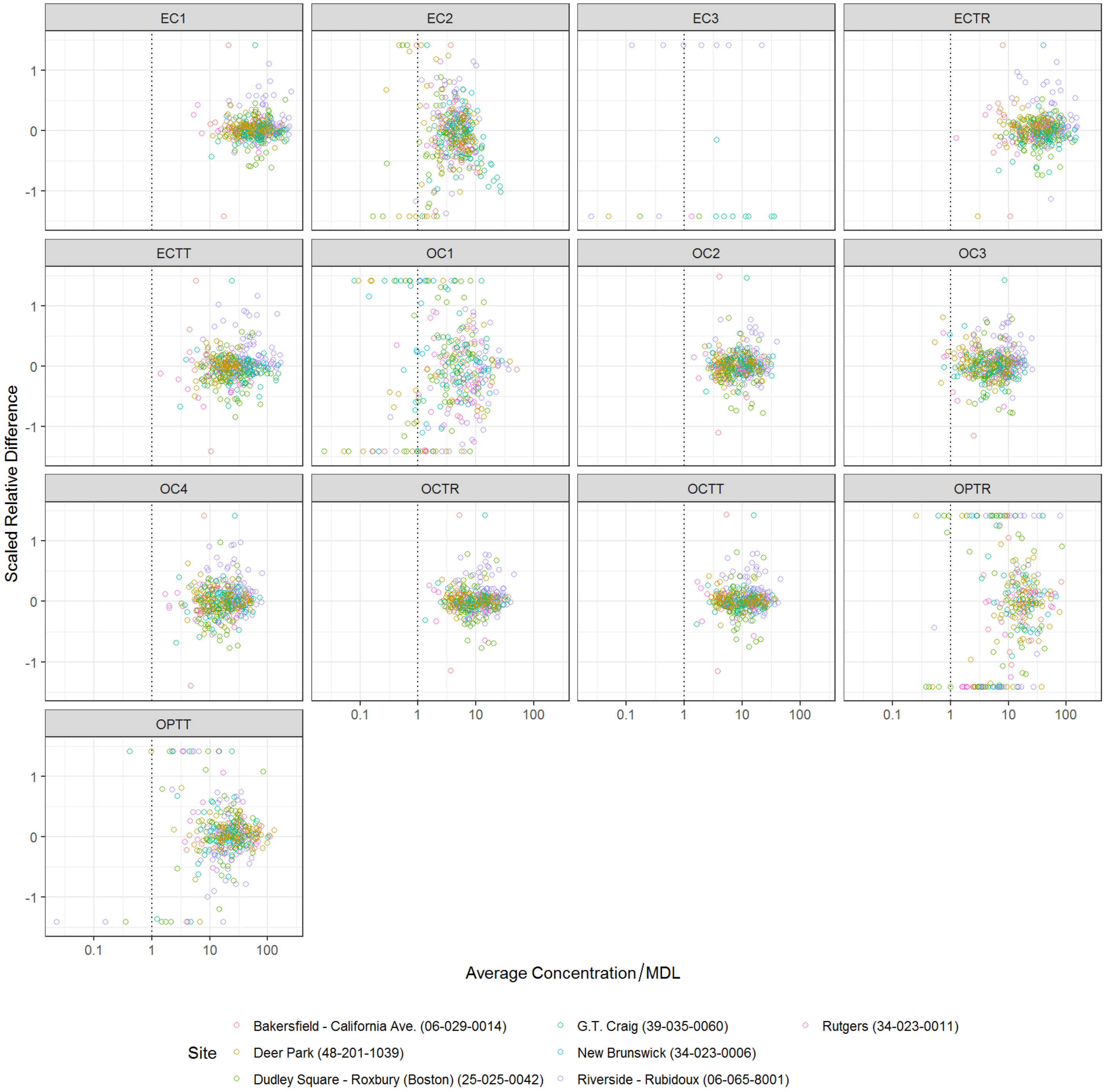


Figure 6.5-3: Scaled relative difference for carbon measurements at sites with collocated samplers across the network (November 2015 through December 2016). Dotted vertical lines indicates MDL. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4), TR indicates measurement by reflectance, and TT indicates measurement by transmittance.



UCD CSN TI 801B, CSN Data Processing documents the calculation of fractional uncertainty. Tables 6.5-1 (elements), 6.5-2 (ions), and 6.5-3 (carbon) compare the updated fractional uncertainties, calculated using data from November 2015 through December 2016, to the historical fractional uncertainties calculated using 2009-2014 collocated data from the previous contract. Since many species are routinely measured at or below the MDL, there are numerous instances where there are no or few pairs of available data to calculate the collocated precision. These fractional uncertainty estimates are used to calculate the uncertainties reported to AQS with each concentration and are updated annually.

Table 6.5-1: Fractional uncertainty estimates for the elements.

Species	Fractional Uncertainty (%) Nov 2015 – Dec 2016	Pairs	Fractional Uncertainty (%) 2009 – 2014	Pairs
Na	---	38	16.4	1,270
Mg	---	2	24.5	365
Al	---	35	25.2	1,209
Si	15.3	178	15.2	3,897
P	---	6	17.3	93
S	6.6	331	6.2	5,530
Cl	31.4	104	34.2	1,740
K	7.4	199	10.6	4,825
Ca	16.1	91	16.8	4,067
Ti	---	46	17.4	697
V	---	0	12.8	499
Cr	---	1	38.9	83
Mn	---	4	15.4	623
Fe	12.2	167	17	5,520
Co	---	0	---	10
Ni	---	1	17.8	400
Cu	---	11	26.9	2,313
Zn	11.5	125	12.3	3,144
As	---	0	18.8	155
Se	---	0	---	43
Br	---	1	15	1,610
Rb	---	0	---	0
Sr	---	1	---	58
Zr	---	0	---	3
Ag	---	0	---	1
Cd	---	0	---	0
In	---	0	---	0
Sn	---	0	---	0
Sb	---	0	---	0
Cs	---	0	---	7
Ba	---	1	16.5	123
Ce	---	0	---	21
Pb	---	0	18.5	381

Table 6.5-2: Fractional uncertainty estimates for the ions.

Species	Fractional Uncertainty (%) Nov 2015 – Dec 2016	Pairs	Fractional Uncertainty (%) 2009 – 2014	Pairs
Ammonium	29	222	7.1	5,466
Nitrate	12.6	257	7.6	5,767
Potassium Ion	17.7	213	12.6	2,072
Sodium Ion	19	130	24.7	3,562
Sulfate	9.8	279	4.9	5,680

Table 6.5-3: Fractional uncertainty estimates for carbon fractions. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4), TR indicates measurement by reflectance, and TT indicates measurement by transmittance.

Species	Fractional Uncertainty (%) Nov 2015 – Dec 2016	Pairs	Fractional Uncertainty (%) 2009 – 2014	Pairs
Elemental Carbon (1)	12.5	274	12.9	1,948
Elemental Carbon (2)	28.6	189	36.8	992
Elemental Carbon (3)	---	1	---	4
Elemental Carbon (TR)	17.3	271	15.5	1955
Elemental Carbon (TT)	18.7	272	12.8	1,606
Organic Carbon (1)	35.9	110	32.9	1,039
Organic Carbon (2)	15.4	254	13.6	1,877
Organic Carbon (3)	17.8	194	17.8	1,860
Organic Carbon (4)	19.2	263	15.7	1,487
Organic Carbon (TR)	12.8	256	11.6	2,033
Organic Carbon (TT)	11.6	256	7.3	1,774
Organic Pyrolyzed (TR)	37.9	143	25.1	919
Organic Pyrolyzed (TT)	12.2	253	17.3	1,557

7. References

Chen, L.-W.A.; Chow, J.C.; Wang, X.L.; Robles, J.A.; Sumlin, B.J.; Lowenthal, D.H.; Watson, J.G. (2015). Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol. Atmos. Meas. Tech. ., 8:451-461. http://www.atmos-meas-tech.net/8/451/2015/amt-8-451-2015.html.

Chen, L.-W.A.; Chow, J.C.; Watson, J.G.; Schichtel, B.A. (2012). Consistency of long-term elemental carbon trends from thermal and optical measurements in the IMPROVE network. Atmos. Meas. Tech., 5:2329-2338. http://www.atmos-meas-tech.net/5/2329/2012/amt-5-2329-2012.pdf.

Chow, J.C., Watson, J.G. (2017). "Enhanced ion chromatographic speciation of water-soluble $PM_{2.5}$ to improve aerosol source apportionment." Aerosol Science and Engineering 1:7-24.

Chow, J.C.; Wang, X.L.; Sumlin, B.J.; Gronstal, S.B.; Chen, L.-W.A.; Trimble, D.L.; Kohl, S.D.; Mayorga, S.R.; Riggio, G.M.; Hurbain, P.R.; Johnson, M.; Zimmermann, R.; Watson, J.G. (2015). Optical calibration and equivalence of a multiwavelength thermal/optical carbon analyzer. AAQR, 15(4):1145-1159. doi:10.4209/aaqr.2015.02.0106. http://aaqr.org/ArticlesInPress/AAQR-15-02-OA-0106_proof.pdf.

Chow, J.C.; Watson, J.G.; Robles, J.; Wang, X.L.; Chen, L.-W.A.; Trimble, D.L.; Kohl, S.D.; Tropp, R.J.; Fung, K.K. (2011). Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon. Anal. Bioanal. Chem., 401(10):3141-3152. DOI 10.1007/s00216-011-5103-3.

Chow, J.C.; Watson, J.G.; Chen, L.W.; Chang, M.C..; Robinson, N.F..; Dana Trimble; Steven Kohl. (2007). The IMPROVE_A Temperature Protocol for Thermal/Optical Carbon Analysis: Maintaining Consistency with a Long-Term Database. J. Air Waste Manage. Assoc., 57:1014-1023.

EPA 40 CFR Part 58. Available at http://origin.www.gpo.gov/fdsys/pkg/FR-2010-12-27/pdf/2010-32153.pdf#page=1

Yatkin, S., Amin, H. S., Trzepla, K., Dillner, A.M. (2016a). Preparation of Lead (Pb) X-ray Fluorescence Reference Materials for the EPA Pb Monitoring Program and the IMPROVE Network Using an Aerosol Deposition Method. Aerosol Sci. Technol. 50:309-320.

Yatkin, S., Belis, C.A., Gerboles, M., Calzolai, G., Lucarelli, F., Fabrizia, C., Trzepla, K. (2016b). An Interlaboratory Comparison Study on the Measurement of Elements in PM_{10}. Atmos. Environ. 125: 61-68.