Chemical Speciation Network (CSN)
Annual Quality Report

Samples Collected January 1, 2018 through December 31, 2018

Prepared for:
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
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AIR QUALITY RESEARCH CENTER

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1. Executive Summary

1.1 Introduction

The University of California—Davis (UC Davis) Air Quality Research Center 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: filters are analyzed at UC Davis using energy dispersive X-ray fluorescence (EDXRF) for a suite of 33 elements.
- Nylon filters: for samples collected through September 30, 2018, filters were analyzed at the Desert Research Institute (DRI) using ion chromatography (IC) for a suite of six ions. For samples collected beginning October 1, 2018, filters are analyzed at Research Triangle Institute International (RTI) using IC for a suite of six ions.
- Quartz filters: for samples collected through September 30, 2018, filters were analyzed at the Desert Research Institute (DRI) for organic and elemental carbon — including carbon fractions — using Thermal Optical Analysis (TOA). For samples collected beginning October 1, 2018, filters are analyzed at UC Davis for organic and elemental carbon — including carbon fractions — using TOA.

Unless otherwise noted, data and discussions included in this report cover samples collected during the time period January 1, 2018 through December 30, 2018.

1.2 Data Quality Overview and Issues

Section 4 of this report provides laboratory performance details for each of the analytical measurement techniques. The laboratory performance is detailed in Section 4.1.A (DRI Ion Chromatography Laboratory, covering analysis of samples collected January 1, 2018 through September 30, 2018), Section 4.1.B (RTI Ion Chromatography Laboratory, covering analysis of samples collected October 1, 2018 through December 31, 2018), Section 4.2 (UC Davis X-Ray Fluorescence Laboratory), Section 4.3.A (DRI Thermal Optical Analysis Laboratory, covering analysis of samples collected January 1, 2018 through September 30, 2018), and Section 4.3.B (UC Davis Thermal Optical Analysis Laboratory, covering analysis of samples collected October 1, 2018 through December 31, 2018).

Across the network, completeness — determined by the total number of valid samples relative to the total number of scheduled samples — was 96.3% for PTFE filters, 96.2% for nylon filters, and 93.7% for quartz filters. As detailed in Section 3.1.1, there were seven sites with less than 75% completeness for at least one filter type.

No Technical Systems Audit (TSA) of UC Davis was performed by the EPA in 2018.

2. Summary of Laboratory Operation Issues

2.1 DRI Ion Analysis Laboratory

2.1.1 Analysis Delays

Some deliveries of analysis data from DRI to UC Davis were delayed, contributing to noncompliance with the 120-day requirement for delivery of data to AQS following receipt of filters by analytical laboratories. See Section 5.1.

2.2 RTI Ion Analysis Laboratory

2.2.1 Analysis Delays

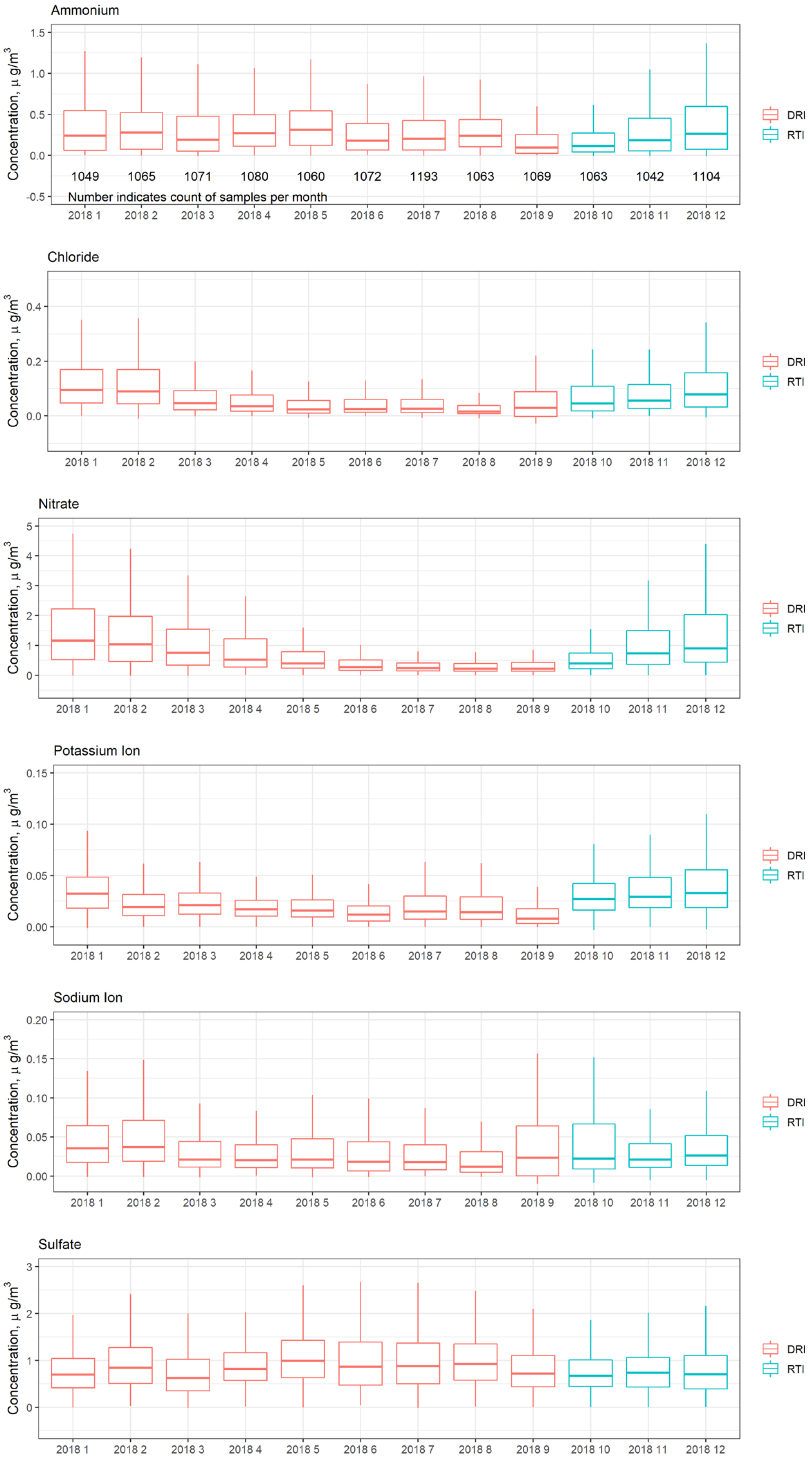
UC Davis issued a subcontract to RTI for ions analysis of filters beginning with samples collected October 1, 2018. The subcontract analysis laboratory transition from DRI to RTI resulted in some initial analysis delays. Deliveries for samples collected in October (132 days) and December 2018 (125 days) were noncompliant with the 120-day requirement for delivery of data to AQS following receipt of filters by analytical laboratories. See Section 5.1.

2.2.2 Laboratory Transition

Beginning with samples collected October 1, 2018, nylon filters are analyzed for ions using Ion Chromatography (IC) at RTI. They were previously analyzed for ions using IC at DRI. At the network level there is no evidence of a step change in the ion concentrations associated with the laboratory transition (see Figure 2.2-1).

Different filter extraction methods were used by RTI and DRI. RTI performed filter extraction with one hour of sonication followed by eight hours on a shaker table in a cold room (*RTI SOP Ions1)*; DRI performed filter extraction with one hour of sonication followed by one hour on a shaker table (*DRI SOP #2-109r7*). UC Davis will continue to closely monitor and evaluate data to identify changes that may be associated with the laboratory transition.

Figure 2.2-1: Monthly network wide results for ions; data from samples collected January 1, 2018 through December 31, 2018. Samples collected January 1, 2018 through September 30, 2018 were analyzed by DRI (red boxes) and samples collected October 1, 2018 through December 30, 2018 were analyzed by RTI (blue boxes). The thick horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles).



2.3 UC Davis X-Ray Fluorescence Laboratory

2.3.1 Application Change

The XRF analysis conditions, including the secondary targets and integration times (collectively referred to as the *application),* were changed in December 2018 during the XRF instrument calibrations. The changes were made to lower the detection limits and the variability in some elements as well as to reduce the overall bias between instruments.

For further details, see Section 4.2.2.5.

2.3.2 Zinc

For analyses performed during this reporting period, periodic zinc contamination was observed on the daily QC laboratory blank and daily QC multi-elemental reference sample on the EDXRF instruments, XRF-1 and XRF-4. The cause of these random contamination events was determined to be related to the instrument design, specifically operation of the sample changer. Samples analyzed during this period were checked for unusually high zinc mass loadings compared to site specific and network wide historical values. Nine samples in 2018 with unusual Zn mass loadings were investigated, with seven of those resulting in reanalysis. Reanalysis results for one of the cases indicated contamination during the original analysis; the reanalysis results for this case were reported.

For further detail see Sections 3.2.1.1 and Section 4.2.2.1.

2.3.3 Calcium

During this reporting period, XRF-1, XRF-4, and XRF-5 showed gradual increase in calcium mass loadings of their QC samples. 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. During this reporting period there was one case of reanalysis request because of suspected calcium contamination. The reanalysis confirmed that contamination was not present and the original results were reported.

For further detail see Section 3.2.1.2 and Section 4.2.2.1.

2.4 DRI Thermal Optical Analysis Laboratory

2.4.1 Analysis Delays

Some deliveries of analysis data from DRI to UC Davis were delayed, contributing to noncompliance with the 120-day requirement for delivery of data to AQS following receipt of filters by analytical laboratories. See Section 5.1.

2.4.2 QC Criteria Failures

In some cases, DRI analyzed samples while instruments were operating outside of the defined QC criteria. There are instances of impacted data for samples collected during 2018.

Per direction from the EPA, these data were redelivered to AQS with the QX (Does Not Meet QC Criteria) qualifier flag applied.

For further detail see Section 3.2.3.1 and Section 4.3.A.2.

2.5 UC Davis Thermal Optical Analysis Laboratory

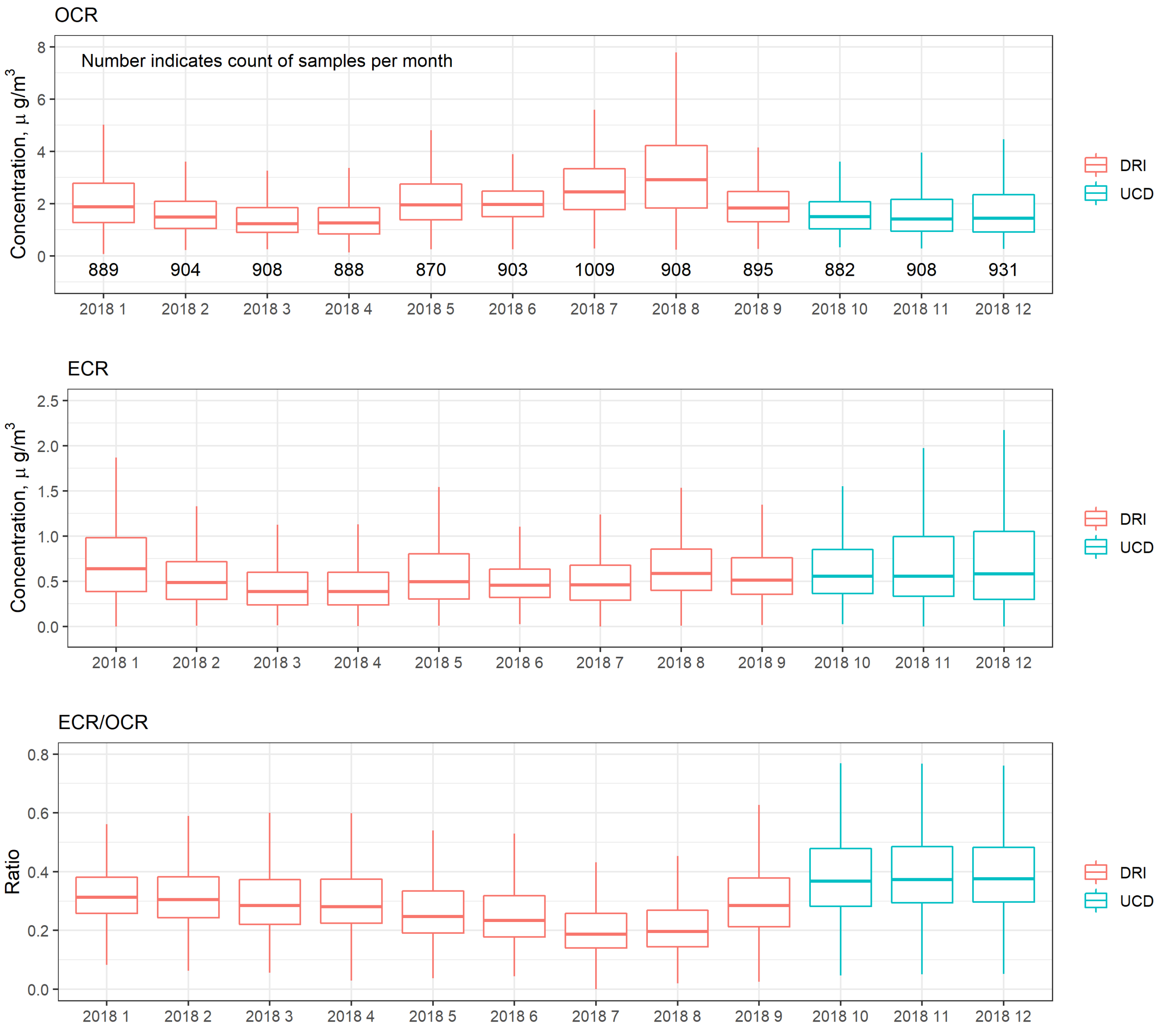
2.5.1 Analysis Delays

UC Davis began TOA analysis of filters beginning with samples collected October 1, 2018. The analysis laboratory transition from subcontractor DRI to UC Davis resulted in some initial analysis delays. Deliveries for samples collected in October (132 days) and December 2018 (125 days) were noncompliant with the 120-day requirement for delivery of data to AQS following receipt of filters by analytical laboratories. See Section 5.1.

2.5.2 Laboratory Transition

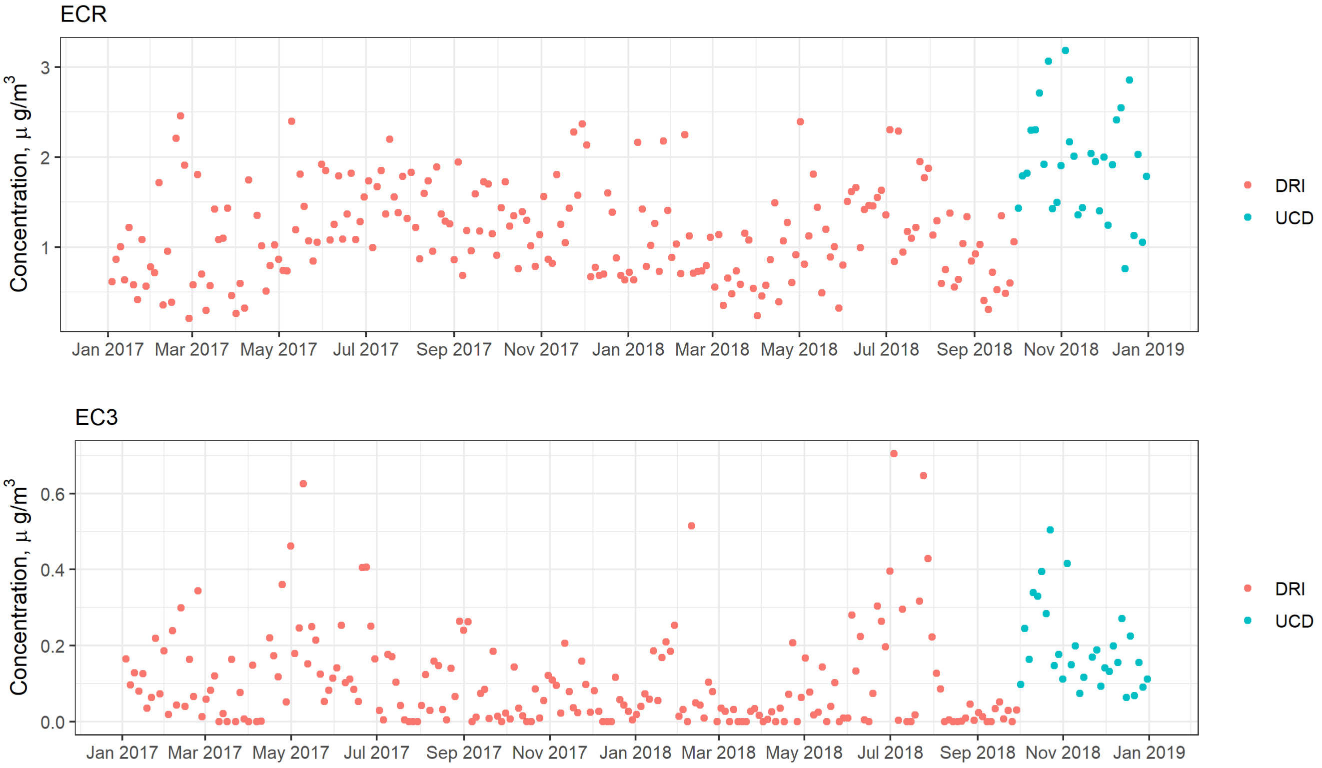
Beginning with samples collected October 1, 2018, quartz filters are analyzed for carbon using Thermal Optical Analysis (TOA) at UC Davis. They were previously analyzed for carbon using TOA at DRI. At the network level, there is no evidence of a step change in the organic carbon (OC) or elemental carbon (EC) concentrations associated with the laboratory transition, but the EC to OC ratios are slightly elevated after the transition, especially at higher percentiles (Figure 2.5-1).

Figure 2.5-1: Monthly network wide results for organic carbon by reflectance (OCR), elemental carbon by reflectance (ECR) and ratio of ECR to OCR (ECR/OCR); data from samples collected January 1, 2018 through December 31, 2018. Samples collected January 1, 2018 through September 30, 2018 were analyzed by DRI (red boxes) and samples collected October 1, 2018 through December 30, 2018 were analyzed by UC Davis (blue boxes). The thick horizontal lines indicate median, and the upper and lower limits of the boxes represent 75th and 25th percentile, respectively. The whiskers extend to 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles).



Individual sites within the network are also evaluated in an effort to identify changes in data trends that may be related to the laboratory transition. A distinct change in the ECR concentration corresponding to the laboratory transition is observed at the Charleston NCore site (AQS ID #54-039-0020; Figure 2.5-2). The change is also pronounced in the highest temperature elemental carbon fraction (e.g. EC3) and is likely related to small differences in the operating temperatures of the instruments.

Figure 2.5-2: Time series of elemental carbon by reflectance (ECR) and EC3 concentrations at the Charleston NCore site (AQS ID #54-039-0020); data from samples collected January 1, 2017 through December 31, 2018.



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. Quartz filters flagged with the QX qualifier, as detailed in Section 2.4.2, were not invalidated and are included in the count of valid samples.

Table 3.1-1: Network sample completeness by filter type, January 1, 2018 through December 31, 2018. 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	13,410	13,400	12,918	482	96.4	96.3
Nylon	13,410	13,400	12,894	506	96.2	96.2
Quartz	13,410	13,397	12,567	830	93.8	93.7

Across the network there were seven sites with sample completeness less than 75% for at least one filter type (Table 3.1-2). Five of the seven 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, and determined for null codes applied at the filter level) for at least one filter type, January 1, 2018 through December 30, 2018. 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
12-011-0034-5 (Region 4)	Broward County, FL (NCore/STN)	74.6%	74.6%	86.1%	AN (29%) BA (29%) Other (42%)	AN (29%) BA (29%) Other (42%)	BA (53%) Other (47%)
15-003-0010-5 (Region 9)	Kapolei, HI	78.5%	73.6%	82.0%	AO (27%) AB (19%) Other (54%)	AO (22%) AH (19%) Other (59%)	AH (36%) AN (23%) Other (41%)
17-031-4201-5 (Region 5)	Northbrook, IL	93.4%	94.3%	71.3%	AO (38%) AV (38%) Other (25%)	AO (43%) AV (43%) SV (14%)	AH (94%) AO (6%)
32-003-0540-5 (Region 9)	Jerome Mack Middle School, NV	99.2%	99.2%	68.9%	AH (100%)	AH (100%)	AH (90%) AK (5%) AN (5%)
42-045-0109-5 (Region 3)	Marcus Hook, PA	98.4%	98.4%	62.3%	AG (100%)	AG (100%)	AH (96%) AN (4%)
49-049-4001-5 (Region 8)	Lindon, UT	100.0%	100.0%	42.6%	---	---	AH (100%)
72-021-0010-5 (Region 2)	Bayamon, Puerto Rico (NCore/STN)	95.0%	95.0%	24.8%	AV (50%) AF (33%) BJ (17%)	AV (50%) AF (33%) BJ (17%)	AH (90%) AV (6%) Other (4%)

Samples can be invalidated for a variety of reasons, as detailed in the *UCD CSN TI 801C* 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 at the filter level to SASS and URG samples from January 1, 2018 through December 30, 2018. Codes are ordered by frequency of occurrence.

Null Code	SASS PTFE	SASS Nylon	URG Quartz	Null Code Description
AU	0	0	1	Monitoring Waived
AS	0	0	2	Poor Quality Assurance Results
AW	1	1	0	Wildlife Damage
BI	0	0	2	Lost or damaged in transit
AK	1	0	3	Filter Leak
AZ	2	2	0	Q C Audit
AM	0	3	2	Miscellaneous Void
AC	2	2	2	Construction/Repairs in Area
BE	2	2	2	Building/Site Repair
BB	3	3	2	Unable to Reach Site
SA	4	4	4	Storm Approaching
AL	4	4	6	Voided by Operator
AI	6	6	3	Insufficient Data (cannot calculate)
SV	2	2	12	Sample Volume Out of Limits
AQ	3	7	7	Collection Error
AR	4	6	14	Lab Error
AB	19	19	14	Technician Unavailable
AG	21	21	18	Sample Time out of Limits
AJ	26	31	4	Filter Damage
AO	24	24	15	Bad Weather
BA	15	15	42	Maintenance/Routine Repairs
BJ	52	59	28	Operator Error
AF*	49	49	71	Scheduled but not Collected
AV	78	78	66	Power Failure
AN	104	105	166	Machine Malfunction
AH	67	70	355	Sample Flow Rate or CV out of Limits

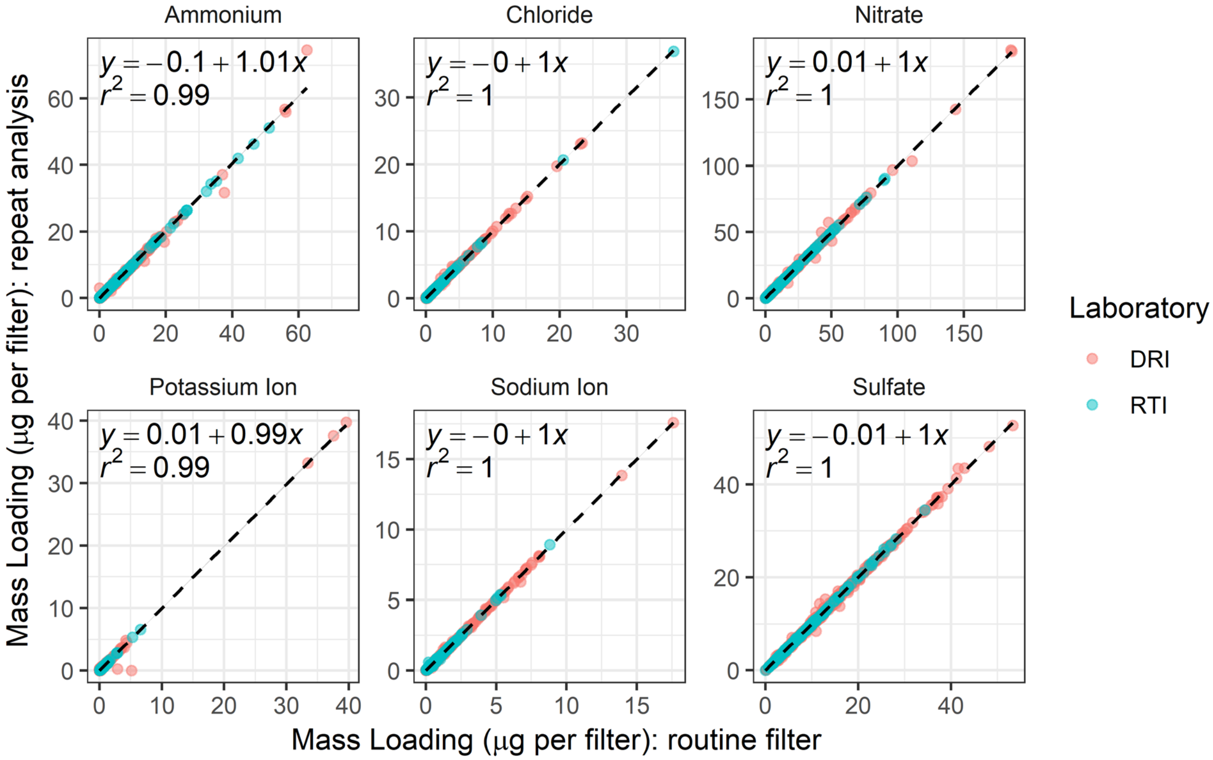
* Records that receive this flag can be associated with events that were not sampled.

3.1.2 Comparability and Analytical Precision

Analytical precision is evaluated by comparing data from repeat analyses, where two analyses are performed on the same sample using either the same instrument (duplicate) or different instruments (replicate). 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 the uncertainties associated with sample preparation, field handling, and sample collection. Analytical precision is used internally as a QC tool.

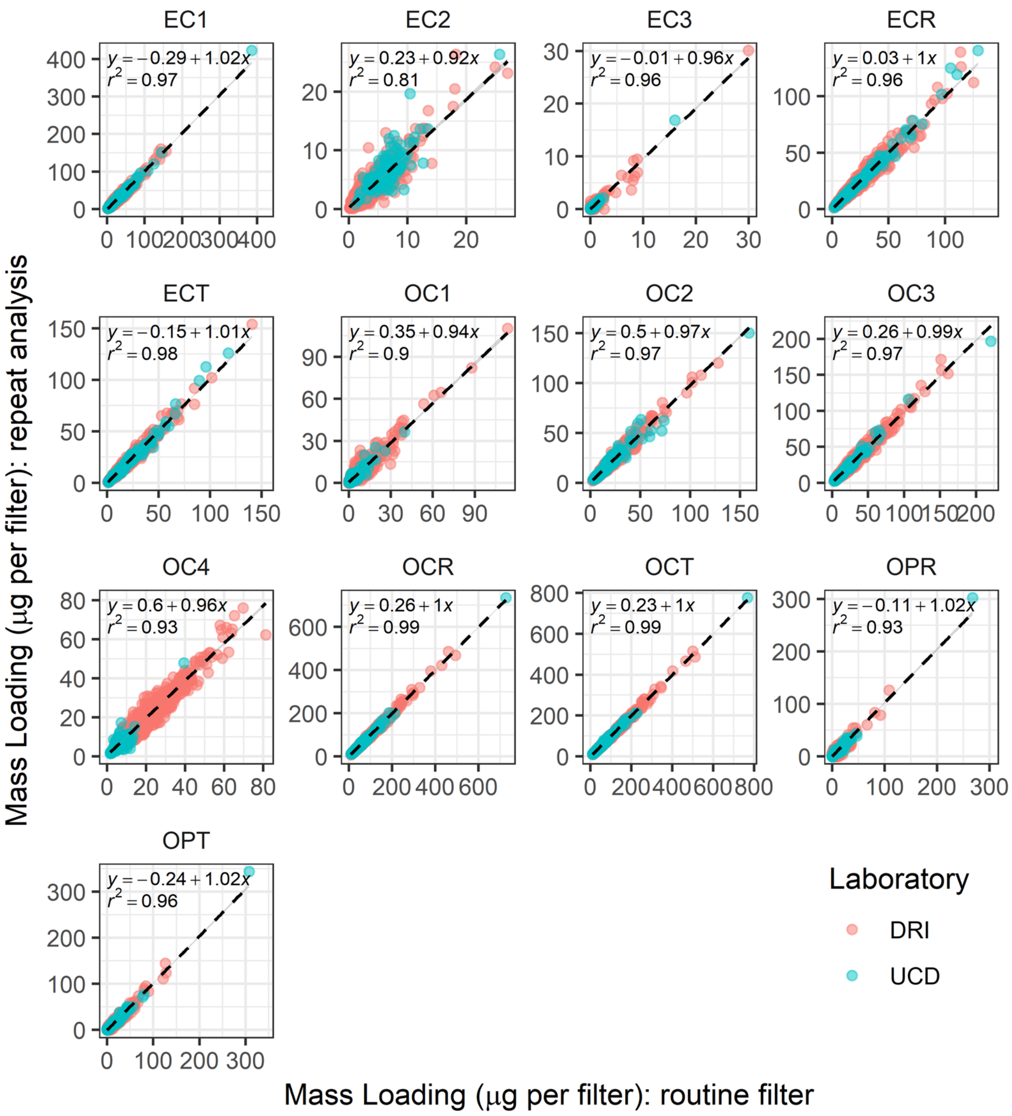
Comparisons of ion mass loadings from repeat analyses (replicates and/or duplicates) on nylon filters analyzed by IC show agreement (Figure 3.1-1).

Figure 3.1-1: Ion repeat analysis (replicates and/or duplicates) results; data from samples collected January 1, 2018 through December 31, 2018. Samples collected January 1, 2018 through September 30, 2018 were analyzed by DRI (red points) and samples collected October 1, 2018 through December 31, 2018 were analyzed by RTI (blue points).



Comparison of carbon mass loadings from repeat analyses (replicates and/or duplicates) on quartz filters analyzed by TOA generally show agreement (Figure 3.1-2).

Figure 3.1-2: Carbon repeat analysis (replicates and/or duplicates) results; data from samples collected during January 1, 2018 through December 31, 2018. Samples collected January 1, 2018 through September 30, 2018 were analyzed by DRI (red points) and samples collected October 1, 2018 through December 31, 2018 were analyzed by UC Davis (blue points). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).



Repeat analyses (replicates and/or duplicates) are not performed by EDXRF for 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 EDXRF measurements as described in *UCD CSN SOP 302*. 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 are used to artifact correct the sampled filters as part of the concentration calculation (see Section 3.1.3.1). Artifacts can result from initial contamination in the filter material, contamination during handling and analysis, and adsorption of gases during sampling and handling. Additionally, field blanks are used to calculate method detection limits (MDLs; see Section 3.1.3.2).

There is some variability in field blank mass loadings by species and month, as shown in Figure 3.1-3 through 3.1-8 for ions measured from nylon filters, and Figure 3.1-9 and 3.1-10 for organic carbon and elemental carbon, respectively, measured from quartz filters. The 10th percentile of network sample concentrations is indicated in Figure 3.1-3 through Figure 3.1-10 to facilitate understanding of field blank concentrations in context of network sample concentrations; 90% of network sample concentrations fall above the indicated 10th percentile. As part of the validation process (see Section 6), field blank outliers are investigated but are only invalidated if there is cause to do so. Artifact correction (Section 3.1.3.1) and MDL (Section 3.1.3.2) calculation methods are robust to accommodate occasional outliers.

For most species there does not appear to be a step change in the field blank time series corresponding with the October 2018 laboratory transitions (see Section 2.2.2 and Section 2.5.2), though ammonium (Figure 3.1-3) and potassium ion (Figure 3.1-6) median field blank mass loadings appear slightly elevated, which may be related to the laboratory transition. Nitrate field blank mass loadings were elevated in February 2018 (Figure 3.1-5) corresponding with temporary use of Pall Ultipore N66 nylon filters, which were used when the supply of MTL nylon filters was depleted.

Figure 3.1-3: Time series of ammonium measured on nylon filter field blanks (FB), for field blanks collected January 1, 2016 through December 31, 2018. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018) 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 that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). The dots are all of the points that lay outside the whiskers. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

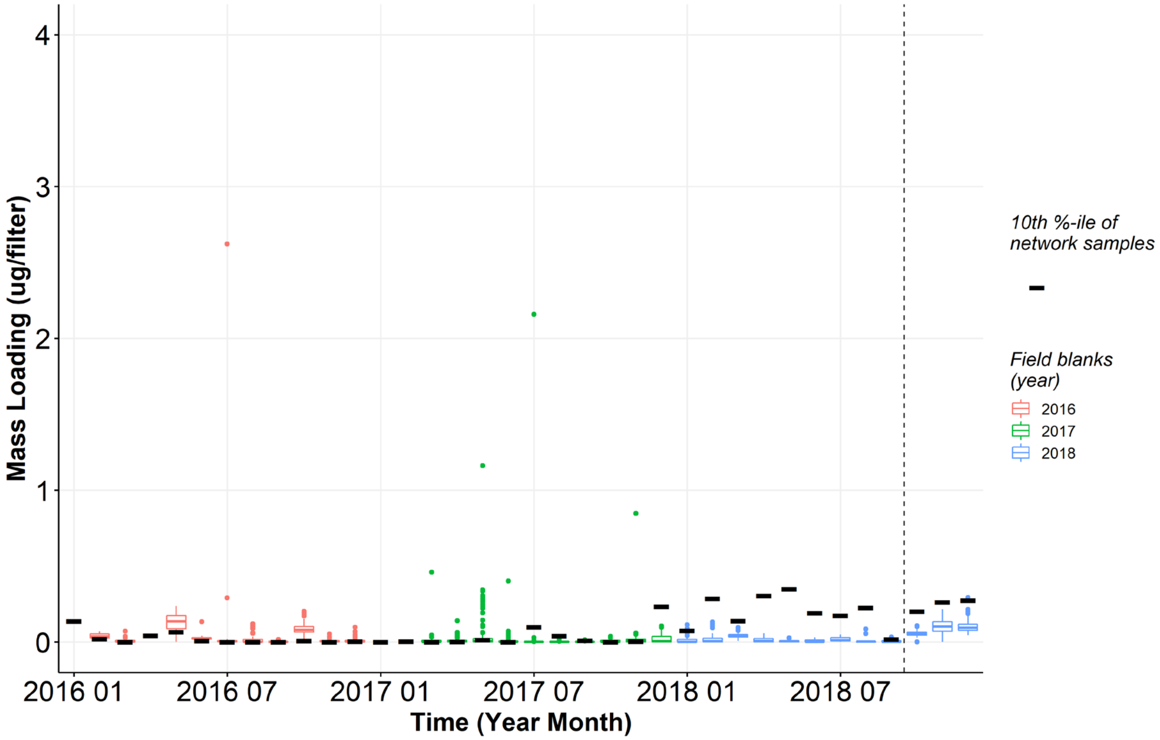


Figure 3.1-4: Time series of chloride measured on nylon filter field blanks (FB), for field blanks collected January 1, 2016 through December 31, 2018. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018) horizontal lines indicate 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 that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). The dots are all of the points that lay outside the whiskers. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

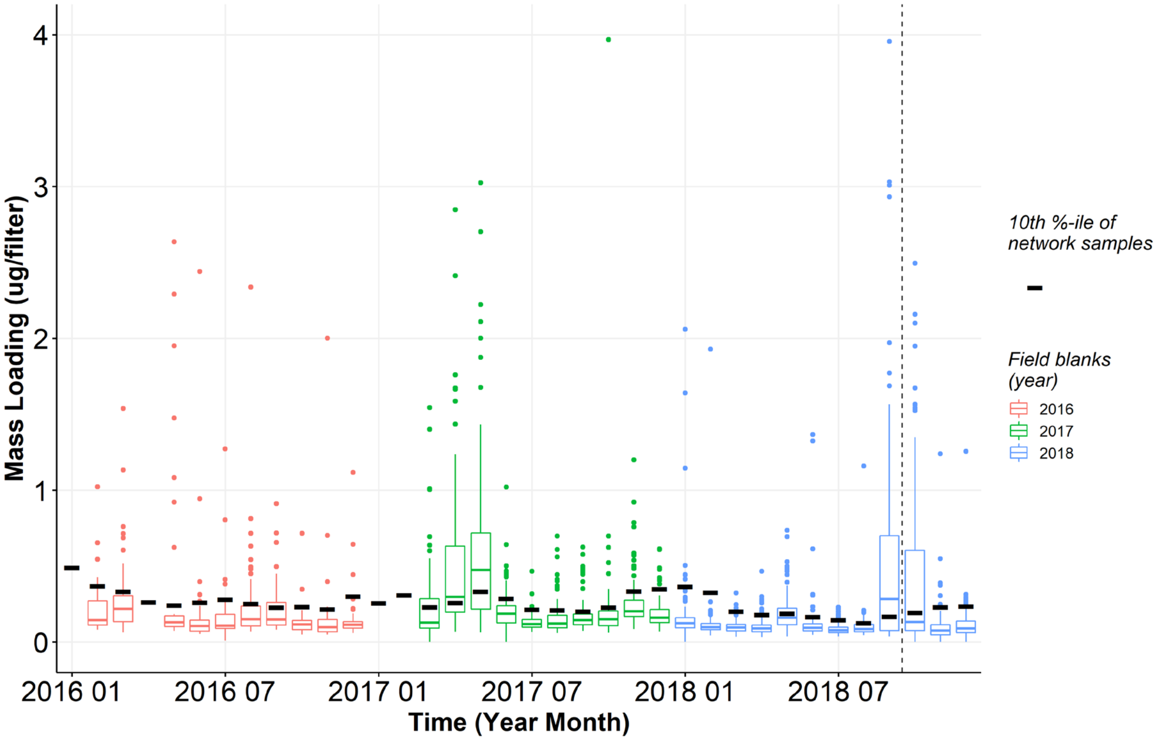


Figure 3.1-5: Time series of nitrate measured on nylon filter field blanks (FB), for field blanks collected January 1, 2016 through December 31, 2018. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018) horizontal lines indicate 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 that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). The dots are all of the points that lay outside the whiskers. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

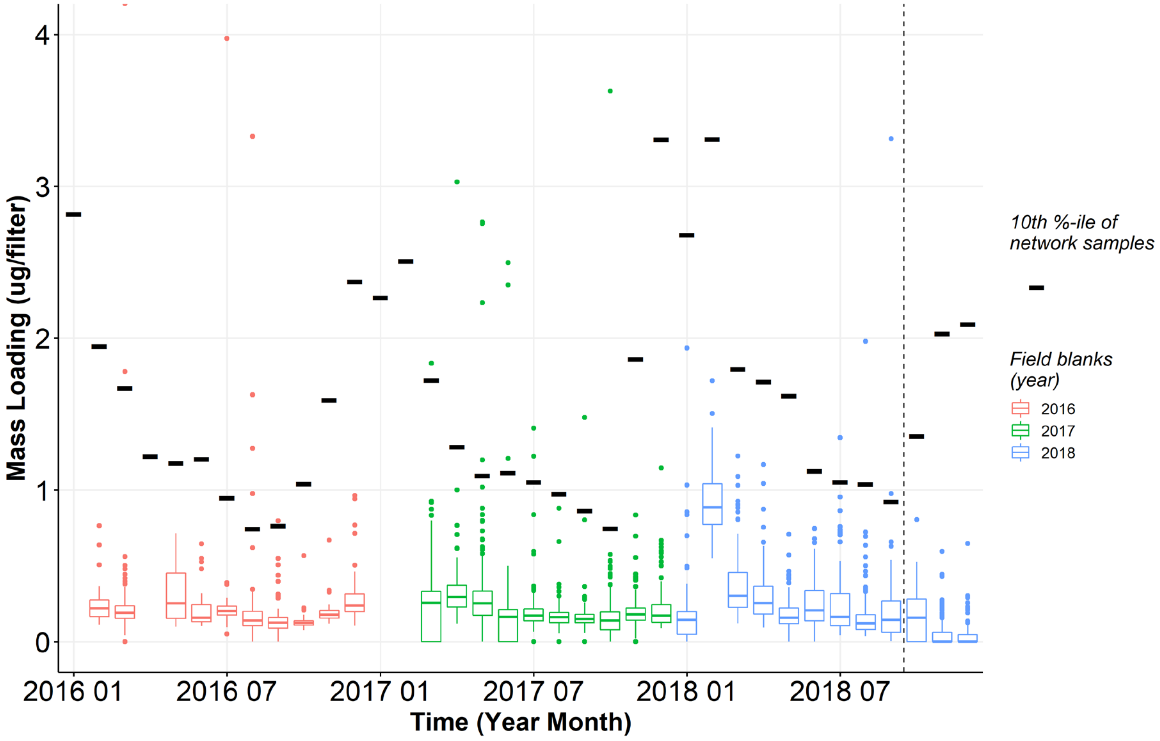


Figure 3.1-6: Time series of potassium ion measured on nylon filter field blanks (FB), for field blanks collected January 1, 2016 through December 31, 2018. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018) horizontal lines 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 that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). The dots are all of the points that lay outside the whiskers. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

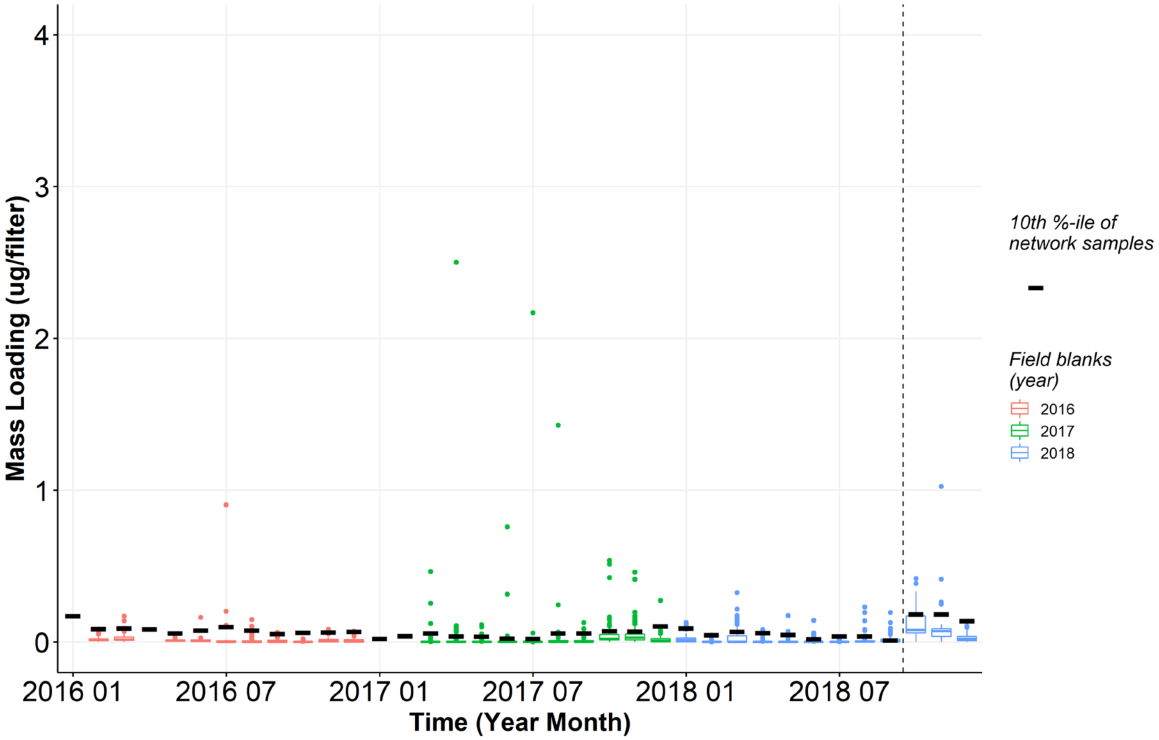


Figure 3.1-7: Time series of sodium ion measured on nylon filter field blanks (FB), for field blanks collected January 1, 2016 through December 31, 2018. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018) horizontal lines 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 that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). The dots are all of the points that lay outside the whiskers. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

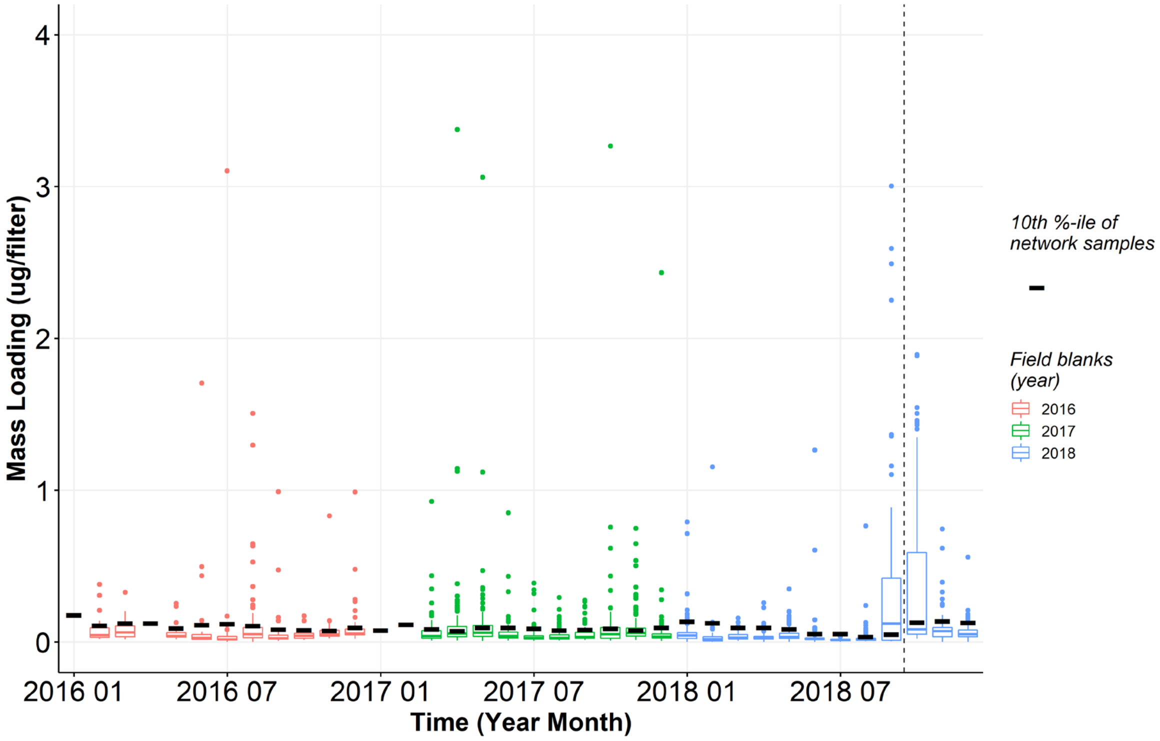


Figure 3.1-8: Time series of sulfate measured on nylon filter field blanks (FB), for field blanks collected January 1, 2016 through December 31, 2018. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018) horizontal lines indicate 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 that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). The dots are all of the points that lay outside the whiskers. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

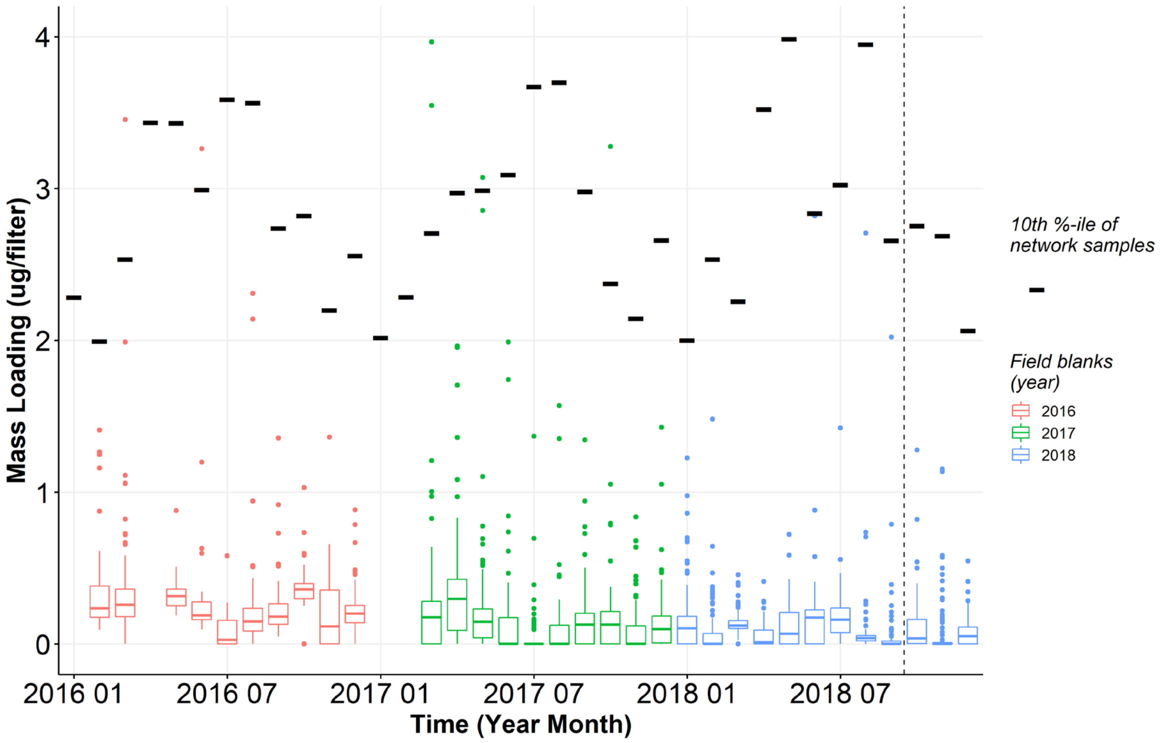


Figure 3.1-9: Time series of organic carbon by reflectance (OCR) measured on quartz filter field blanks (FB), for field blanks collected January 1, 2016 through December 31, 2018. Gaps in time series are present when no quartz filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018) 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 that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). The dots are all of the points that lay outside the whiskers. Black vertical dotted line indicates laboratory transition from DRI to UC Davis. The black horizontal dashes indicate the 10th percentile of network samples.

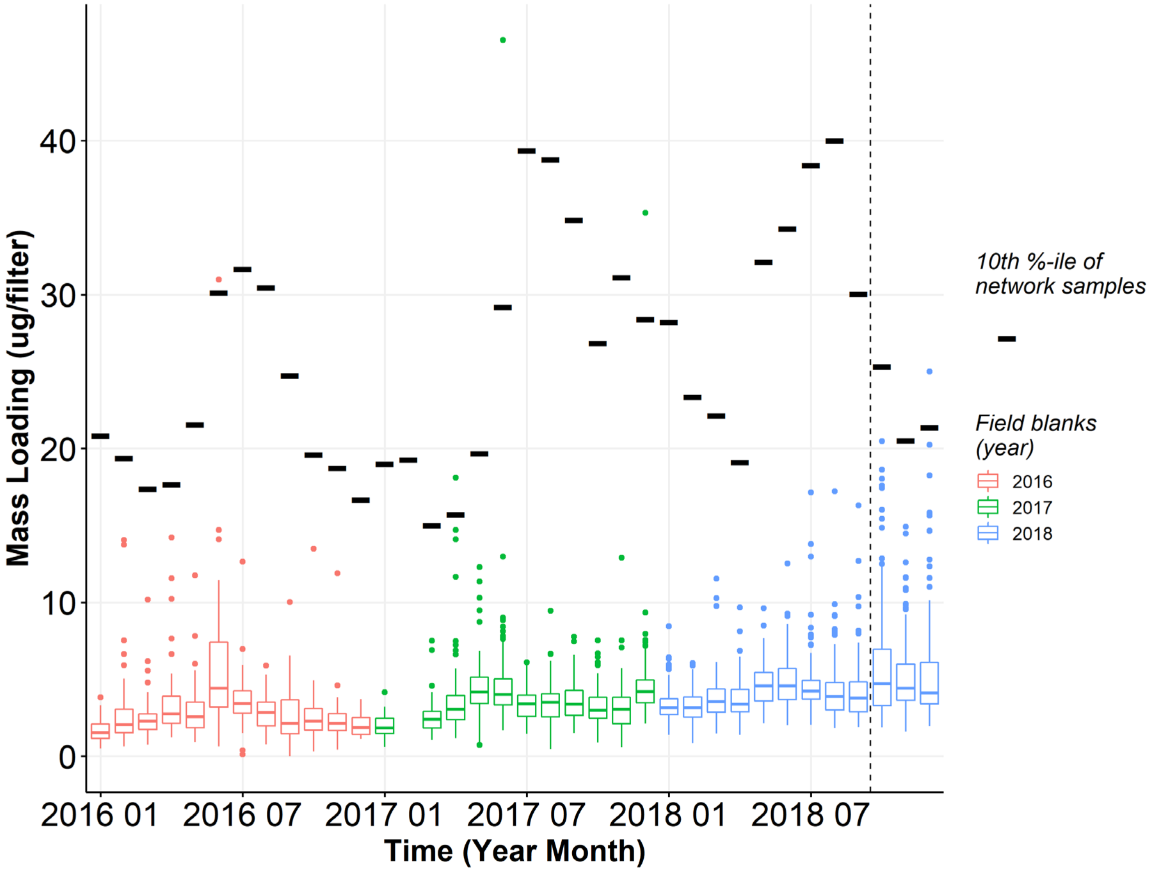
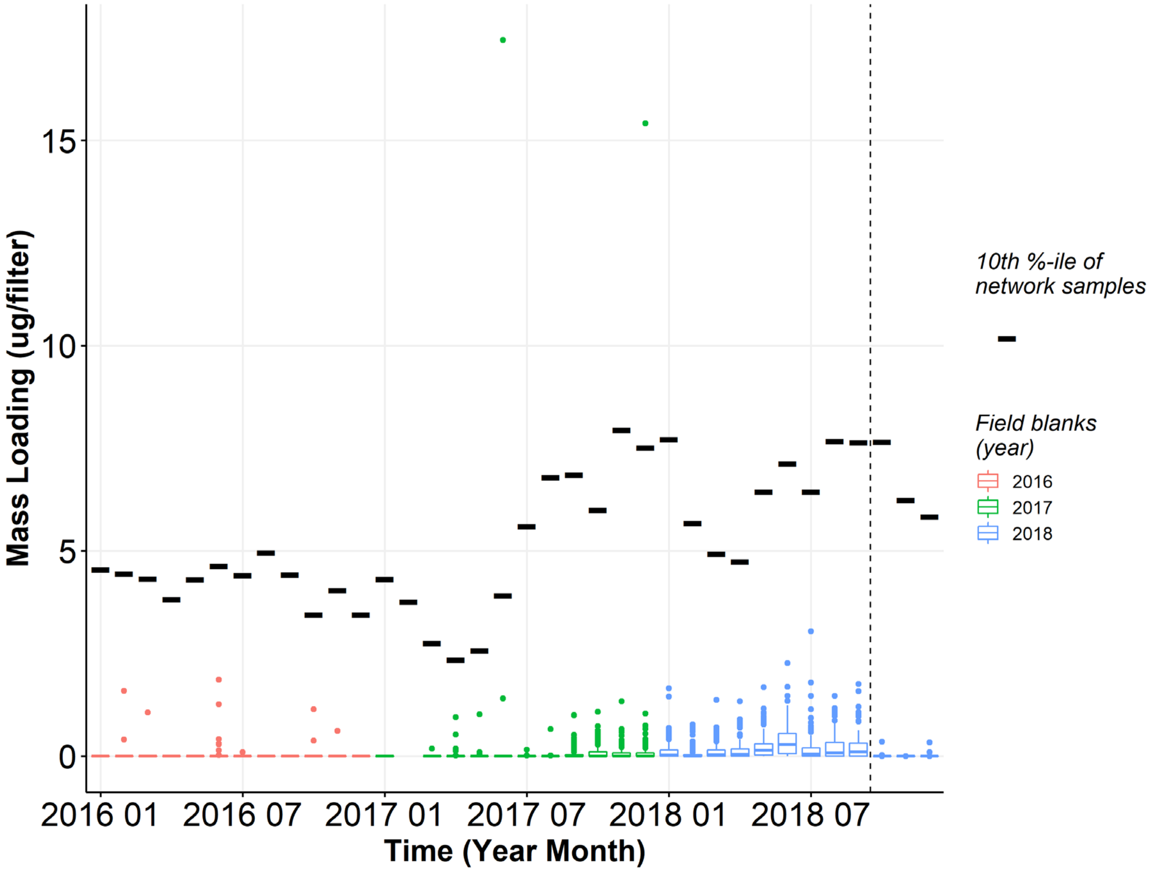


Figure 3.1-10: Time series of elemental carbon by reflectance (ECR) measured on quartz filter field blanks (FB), for field blanks collected November 20, 2015 through December 31, 2018. Gaps in time series are present when no quartz filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018) 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 that is no more than 1.5×IQR (where IQR is the interquartile range, or the distance between the 25th and the 75th percentiles). The dots are all of the points that lay outside the whiskers. Black vertical dotted line indicates laboratory transition from DRI to UC Davis. The black horizontal dashes indicate the 10th percentile of network samples.



3.1.3.1 *Blank Correction*

Blank correction is performed on data from all filter types (quartz, nylon, and PTFE) by subtracting a rolling median value from at least 50 field blanks collected in and closest to the sample month.

3.1.3.2 *Method Detection Limits*

Network wide method detection limits (MDLs) are updated monthly and are delivered to AQS for each species. Beginning with samples collected February 2017, and including this reporting period, the MDL calculation was 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. Field blanks are collected one per month for each filter type per site, allowing for a robust MDL calculation. Field blanks capture artifacts from both field and laboratory processes, thus 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. When the MDL determined from field blanks is lower than the analytical MDL (calculated by the laboratories using laboratory blanks), the analytical MDL is assigned as a floor value.

The average MDLs calculated for this reporting period (samples collected January 1, 2018 through December 31, 2018) are compared to those calculated using the same method from the previous reporting period (samples collected February 1, 2017 through December 31, 2017) (Table 3.1-4). MDLs calculated during this reporting period compare well with those from the previous reporting period for many species. However, there are some cases where 2018 MDLs are lower (improved) or higher (degraded): (1) elemental species Ca and K 2018 MDLs are both lower relative to 2017 MDLs; (2) ion species sodium ion and sulfate 2018 MDLs are higher and lower, respectively, relative to 2017 MDLs; (3) most carbon species and fractions have higher 2018 MDLs relative to 2017 MDLs. MDL differences may be related to changes in filter media cleanliness, EDXRF application changes (see Section 2.3.1 and Section 4.2.2.5), and laboratory transitions (see Section 2.2.2 and Section 2.5.2).

Table 3.1-4: Average method detection limits (MDLs) and percentage of reported data above the MDLs for all species, calculated for data from samples collected February 1, 2017 through December 31, 2017 (previous reporting period) and January 1, 2018 through December 31, 2018 (current reporting period). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T). Species shown in bold have differences >50% between those reported for the previous reporting period (2017) and the current reporting period (2018).

Species	2017 (previous reporting period)		2018 (current reporting period)	
	Average MDL, µg/m^3	% Above MDL	Average MDL, µg/m^3	% Above MDL
Ag	0.017	2.7	0.016	2.6
Al	0.038	30.1	0.032	37.0
As	0.003	6.2	0.002	4.3
Ba	0.081	1.5	0.080	1.3
Br	0.005	15.8	0.005	12.0
Ca	**0.034**	**56.8**	**0.018**	**74.1**
Cd	0.016	2.9	0.016	3.2
Ce	0.096	1.3	0.095	1.3
Cl	0.007	31.9	0.005	38.2
Co	0.003	0.9	0.003	0.9
Cr	0.004	20.1	0.003	25.4
Cs	0.056	2.5	0.054	2.2
Cu	0.011	10.9	0.011	9.8
Fe	0.027	79.8	0.018	88.7
In	0.037	0.0	0.038	0.0
K	**0.012**	**98.4**	**0.005**	**99.2**
Mg	0.042	12.5	0.043	14.4
Mn	0.006	8.3	0.006	8.2
Na	0.088	20.9	0.089	23.5
Ni	0.002	14.7	0.002	16.2

Species	2017 (previous reporting period)		2018 (current reporting period)	
	Average MDL, µg/m³	% Above MDL	Average MDL, µg/m³	% Above MDL
P	0.002	8.0	0.002	7.3
Pb	0.012	7.4	0.012	6.9
Rb	0.009	0.3	0.009	0.2
S	0.005	99.5	0.004	99.5
Sb	0.040	2.3	0.039	1.8
Se	0.005	1.6	0.005	1.4
Si	0.020	83.7	0.016	82.3
Sn	0.050	0.5	0.049	0.4
Sr	0.007	2.2	0.007	1.7
Ti	0.003	41.4	0.003	44.1
V	**0.002**	**7.9**	**0.001**	**6.7**
Zn	0.003	78.9	0.003	79.6
Zr	0.036	1.0	0.036	0.7
Ammonium	0.006	81.6	0.005	95.2
Chloride	0.047	60.1	0.036	71.1
Nitrate	0.036	98.5	0.035	99.0
Potassium Ion	0.047	29.5	0.061	10.4
Sodium Ion	0.016	66.6	0.026	73.5
Sulfate	**0.047**	**99.4**	**0.025**	**99.6**
Elemental Carbon (EC1)	**0.007**	**99.5**	**0.015**	**99.9**
Elemental Carbon (EC2)	0.009	95.5	0.017	97.7
Elemental Carbon (EC3)	0.002	3.6	0.003	22.2
Elemental Carbon (ECR)	0.013	99.4	0.018	99.8
Elemental Carbon (ECT)	0.012	98.9	0.016	99.7
Organic Carbon (OC1)	0.019	76.8	0.015	84.9
Organic Carbon (OC2)	0.036	99.5	0.035	99.8
Organic Carbon (OC3)	0.053	98.7	0.077	96.1
Organic Carbon (OC4)	**0.012**	**99.7**	**0.034**	**96.1**
Organic Carbon (OCR)	0.081	99.6	0.134	99.5
Organic Carbon (OCT)	0.083	99.6	0.138	99.6
Organic Pyrolyzed (OPR)	**0.008**	**72.4**	**0.022**	**78.8**
Organic Pyrolyzed (OPT)	**0.010**	**93.9**	**0.028**	**94.2**

3.2 Corrective Actions

To ensure ongoing quality work, UC Davis reacts as quickly and 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 for data from samples collected during 2018.

3.2.1 Elemental Analysis

3.2.1.1 Zinc

As discussed in Section 2.3.2 and Section 4.2.2.1, the design of the sample changer arm on the EDXRF instruments results in sporadic cases of zinc contamination. During this reporting period, seven filters identified as having potential contamination were reanalyzed.

3.2.1.2 Calcium

As discussed in Section 2.3.3 and Section 4.2.2.1 laboratory QC filters that are exposed to the environment for prolonged periods for repeat analysis show a general increase in calcium mass loadings. These increases are not observed if the QC filter is cleaned with air or replaced with a new filter. The contamination appears to occur mostly on filters that are analyzed multiple times and therefore should not impact routine samples or field blanks. Even so, CSN sample and field blank filters were monitored during QA checks for calcium contamination. During this reporting period, one filter identified as having potential contamination was reanalyzed.

3.2.1.3 Cr and Ni Contamination

UC Davis identified a potential Cr and Ni contamination issue that impacts data from prior to the contract transition (November 20, 2015) through this reporting period. The sampler modules may be the source of contamination and are being investigated. Wipes from inside the sampling modules were collected and analyzed by ICP-MS at RTI. Additionally, screens and screws from the sampling modules were analyzed by EDXRF at UC Davis. Results are forthcoming and the investigation is ongoing.

3.2.2 Ion Analysis

No corrective actions during this reporting period.

3.2.3 Carbon Analysis

3.2.3.1 QC Criteria Failures

As discussed in Section 2.4.2, in some instances, DRI analyzed samples while instruments were operating outside of the defined QC criteria.

Per direction from the EPA, these data will be redelivered to AQS with QX (Does Not Meet QC Criteria) qualifier flag applied.

For further detail see Section 2.4.2 and Section 4.3.A.2.

3.2.3.2 Data Flagging (LJ Flag)

UC Davis identified a potential source of uncertainty in the OC and EC split upon thermogram review. Specifically, for heavily loaded quartz samples or samples that contain light-absorbing materials that volatilize at a lower temperature, pyrolysis of OC does not lead to any more light absorbed by the sample deposit (i.e. no further decrease in the laser signals). As a result, the laser signal does not return to its initial value, thus no OC/EC split can be automatically determined. In these cases, the split is forced to correspond with the system switch to the oxidizing environment, and any pyrolyzed OC (i.e. OP) is quantified as EC. The reported OC is the lower limit and EC is the upper limit. Beginning with samples collected November 2018, UC Davis has started applying the 'LJ' AQS flag (LJ: Identification of analyte is acceptable; Reported value is an estimate) for these cases. 5.1% (64 out of 1249) and 5.7% (77 out of 1353) of the samples collected in November and December 2018 have the LJ flag applied, respectively.

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* and the *Data Validation for the Chemical Speciation Network* guide. Flags are applied throughout the sampling, filter handling, analysis, and validation processes, using automated checks and on a case-by-case basis. The use and application of flags evolves as problems are identified and remedied, and also in response to process improvements that are implemented to improve the quality and consistency of data for the end user.

4. Laboratory Quality Control Summaries

4.1.A DRI Ion Chromatography Laboratory

The DRI Ion Chromatography Laboratory, as a subcontractor to UC Davis, received and analyzed nylon filters from batches 39 through 47 covering the sampling period January 1, 2018 through September 30, 2018. Analysis of these samples was performed June 14, 2018 through December 14, 2018. Using ion chromatography, DRI analyzed 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^+]) using three DIONEX ICS-5000+ systems (Chow and Watson, 2017) and two DIONEX ICS-6000 systems and reported the results of those analyses to UC Davis.

4.1.A.1 Summary of QC Checks and Statistics

Samples were received by the DRI Ion Chromatography Laboratory following the chain-of-custody procedures specified in *DRI SOP #2-117*. Samples were analyzed using DIONEX ICS-5000+ or ICS-6000 Systems following *DRI SOP #2-228* for anions and *DRI SOP #2-229* for cations. QC measures for the DRI ion analysis are summarized in Table 4.1.A -1. The table indicates the frequency and standards required for the specified checks, along with the acceptance criteria and corrective actions.

During daily startup, an eight-point calibration was performed over the range from 0.02 to 3.0 µg/mL (i.e., 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, and 3.0 µg/mL) before beginning analysis. Then two deionized-distilled water (DDW) samples and a method blank were analyzed, followed by two types of QC control standards: (1) 1.0–2.5 µg/mL QC standards diluted from NIST certified Dionex standard solutions; and (2) DRI-made control standards (i.e., 1.00 µg/mL Cl^-, 1.00 µg/mL NO_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 QC standard (same as calibration solution concentrations; diluted from certified Environmental Research Associates (ERA) stock solutions) at various concentrations (0.1–3.0 µg/mL) were analyzed.

Table 4.1.A-1: DRI quality control measures for ion (anion and cation) analysis by ion chromatography.

Requirement	Frequency	Calibration Standard	Acceptance Criteria	Corrective Action
Multipoint Calibration	Daily or every batch of ~100, whichever comes first	NIST certified ERA	± 10% of certified value	Identify and correct problem before analyzing samples; and recalibrate
Minimum Detection Limit (MDL)[a]	Initially, then annually or after major instrument maintenance	Nylon filter lab blanks (7 or more)	Within ± 10% of previous instrument limit	Troubleshoot instrument and check filter lots
DDW	Four initially to establish background, followed by one every 10 samples	DDW with resistance ≥ 18 MΩ	Within 3 standard deviations of MDLs[a]	Verify instrument response to DDW without extraction
Method blank [b]	One for every 40 samples	DDW with resistance ≥ 18 MΩ	Within 3 standard deviations of MDLs[a]	Check instrument response for DDW with extraction
QC Control Standards	Daily or every run	DRI-made or Dionex NIST-certified multi-component standard solution	± 10% of listed value	Rerun the QC standard and reanalyze samples between this standard and previous QC standard
QC Check Standards	Every 10 samples	NIST-certified multi-component standard solution from ERA	± 10% of listed value	Reanalyze samples between this standard and previous check standard
Duplicates[c]	10% of samples	N/A	± 10% when value > 10× MDL[a]	Reanalysis of duplicate sample

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

[b] 15 mL DDW solution that follows the same extraction procedure as the sample extraction.

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

4.1.A.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 cases of failed method blanks in Table 4.1.A-2, reanalysis of the blanks resulted in concentrations below QC threshold and sample data are not affected. In the cases where the Dionex and DRI-made QC control standards (Tables 4.1.A-3 and 4.1.A-4; run after the multipoint calibration and before sample analysis) failed to pass the 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. For cases where the ERA QC check standards failed (Table 4.1.A-5; analyzed every 10th sample), all samples between the failed standard and the nearest previous passing QC standard were reanalyzed. Reported sample data all passed acceptance criteria for the QC standards. Duplicate analyses (Table 4.1.A-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 are not affected by reanalyzing duplicates.

4.1.A.2.1 Method Blanks

Table 4.1.A-2 lists the number of method blanks analyzed during this reporting period and their concentration statistics. Both median and average concentrations are near or below the MDLs

(MDL indicated here is an internal laboratory QA indicator, distinct from the MDL reported to AQS).

Table 4.1.A-2: Method blank counts and concentrations for all reported ions for the analysis period 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018).

Ions	**Cl^-**	**NO_3^-**	**SO_4^{2-}**	**Na^+**	**NH_4^+**	**K^+**
Count	286	286	286	286	286	286
Median (µg/mL)	0.001	0.003	0.000	0.000	0.000	0.000
Average (µg/mL)	0.001	0.004	0.001	0.001	0.000	0.000
St. Dev. (µg/mL)	0.002	0.005	0.006	0.001	0.000	0.001
Min (µg/mL)	0.000	0.000	0.000	0.000	0.000	0.000
Max (µg/mL)	0.021	0.039	0.088	0.010	0.002	0.011
# Exceed 3×MDL[a]	0	4	1	0	0	0

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

4.1.A.2.2 QC Control Standards and Check Standards

Table 4.1.A-3 and Table 4.1.A-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.A-1. The average difference between the measured and nominal concentrations are within the ±10% limit (Table 4.1.A-1), although a few individual checks failed the 10% acceptance criteria. Corrective actions for failed analyses are shown in Table 4.1.A-1. Table 4.1.A-5 summarizes analysis statistics for the ERA QC check standards at different concentration levels. Some individual standards failed QC criteria, but were reanalyzed following the procedure outlined in Table 4.1.A-1. All reported CSN sample ion concentrations passed the QC control and check standard verification.

Table 4.1.A-3: Statistics for Dionex ion QC control standards for the analysis period 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018).

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	121	0.971	0.972	0.900	1.027	0	97.2%	2.1%
NO_3^-	1.000	121	0.931	0.933	0.901	1.085	0	93.3%	2.6%
SO_4^{2-}	1.000	121	0.966	0.972	0.927	1.092	0	97.2%	2.6%
Na^+	1.000	122	0.975	0.975	0.931	1.031	0	97.5%	1.5%
NH_4^+	1.250	122	1.308	1.302	1.157	1.348	0	104.2%	2.8%
K^+	2.500	122	2.523	2.525	2.294	2.737	0	101.0%	6.0%

Table 4.1.A-4: Statistics for DRI-made ion QC control standards for the analysis 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018).

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	110	0.997	1.000	0.928	1.122	1	100.0%	2.5%
NO_3^-	1.000	110	0.967	0.970	0.903	1.090	0	97.0%	3.5%
SO_4^{2-}	1.000	110	0.954	0.957	0.901	1.088	0	95.7%	2.6%
Na^+	1.030	105	1.006	1.009	0.960	1.076	0	100.9%	1.9%
NH_4^+	0.390	105	0.380	0.379	0.338	0.405	1	97.1%	1.0%
K^+	0.000	105	0.000	0.001	0.000	0.006	0	NA	0.1%

[a]NA=Not applicable

Table 4.1.A-5: Statistics for ERA QC control standards for the analysis period 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018).

Ion	Nominal (µg/mL)	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	Ave% Recovery	% St. Dev.
Cl^-	0.1	18	0.086	0.089	0.082	0.099	88.6%	0.6%
	0.2	84	0.180	0.183	0.161	0.318	91.3%	1.7%
	0.5	293	0.467	0.469	0.278	0.548	93.7%	2.1%
	1	277	0.967	0.969	0.869	1.107	96.9%	3.5%
	2	218	1.992	2.002	1.849	2.329	100.1%	6.5%
	3	231	3.031	3.046	2.806	3.488	101.5%	9.2%
NO_3^-	0.1	18	0.083	0.086	0.076	0.099	85.6%	0.7%
	0.2	84	0.175	0.176	0.138	0.216	87.8%	1.4%
	0.5	293	0.454	0.453	0.255	0.544	90.5%	2.5%
	1	277	0.937	0.941	0.822	1.098	94.1%	3.4%
	2	218	1.982	1.990	1.744	2.345	99.5%	7.5%
	3	231	3.039	3.056	2.740	3.438	101.9%	10.9%
SO_4^{2-}	0.1	18	0.088	0.092	0.082	0.106	91.7%	0.8%
	0.2	84	0.185	0.184	0.152	0.213	91.9%	1.4%
	0.5	293	0.470	0.471	0.324	0.584	94.2%	2.4%
	1	277	0.957	0.962	0.841	1.149	96.2%	3.8%
	2	218	1.987	1.991	1.768	2.455	99.6%	6.8%
	3	231	3.033	3.043	2.757	3.690	101.4%	10.4%
Na^+	0.1	18	0.073	0.074	0.058	0.092	73.9%	1.0%
	0.2	79	0.175	0.175	0.143	0.202	87.6%	1.2%
	0.5	291	0.462	0.463	0.404	0.512	92.5%	1.1%
	1	278	0.973	0.975	0.861	1.088	97.5%	2.4%
	2	222	1.999	2.005	1.812	2.219	100.3%	3.8%
	3	234	3.025	3.036	2.703	3.352	101.2%	6.1%
NH_4^+	0.1	18	0.083	0.082	0.073	0.094	82.1%	0.6%

Ion	Nominal (µg/mL)	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	Ave% Recovery	% St. Dev.
	0.2	79	0.186	0.186	0.167	0.211	93.1%	0.8%
	0.5	291	0.500	0.498	0.449	0.537	99.6%	1.2%
	1	278	1.008	1.005	0.824	1.065	100.5%	2.3%
	2	222	1.992	1.992	1.772	2.159	99.6%	4.1%
	3	234	3.004	3.018	2.812	3.528	100.6%	7.7%
K$^+$	0.1	18	0.076	0.080	0.069	0.099	79.7%	1.1%
	0.2	79	0.186	0.186	0.142	0.252	92.8%	1.9%
	0.5	291	0.486	0.483	0.390	0.571	96.6%	2.8%
	1	278	1.011	1.002	0.811	1.114	100.2%	3.8%
	2	222	1.996	1.994	1.459	2.169	99.7%	7.3%
	3	234	3.001	3.026	2.791	3.606	100.9%	11.1%

Figure 4.1.A-1a: Control charts for Dionex ion QC control standards for the analysis period 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018). The limits are ±10% of the nominal concentrations (red dashed lines).

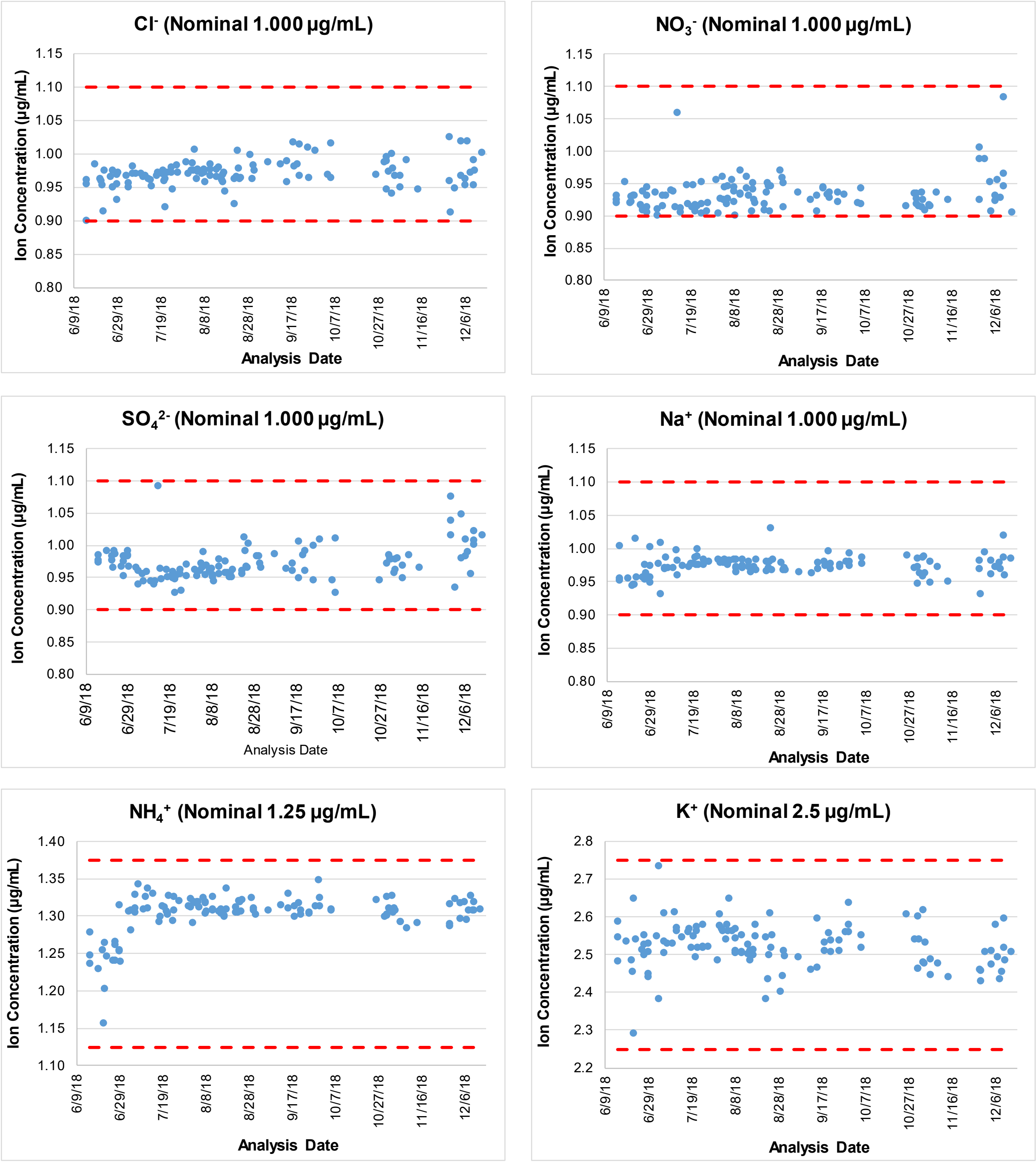
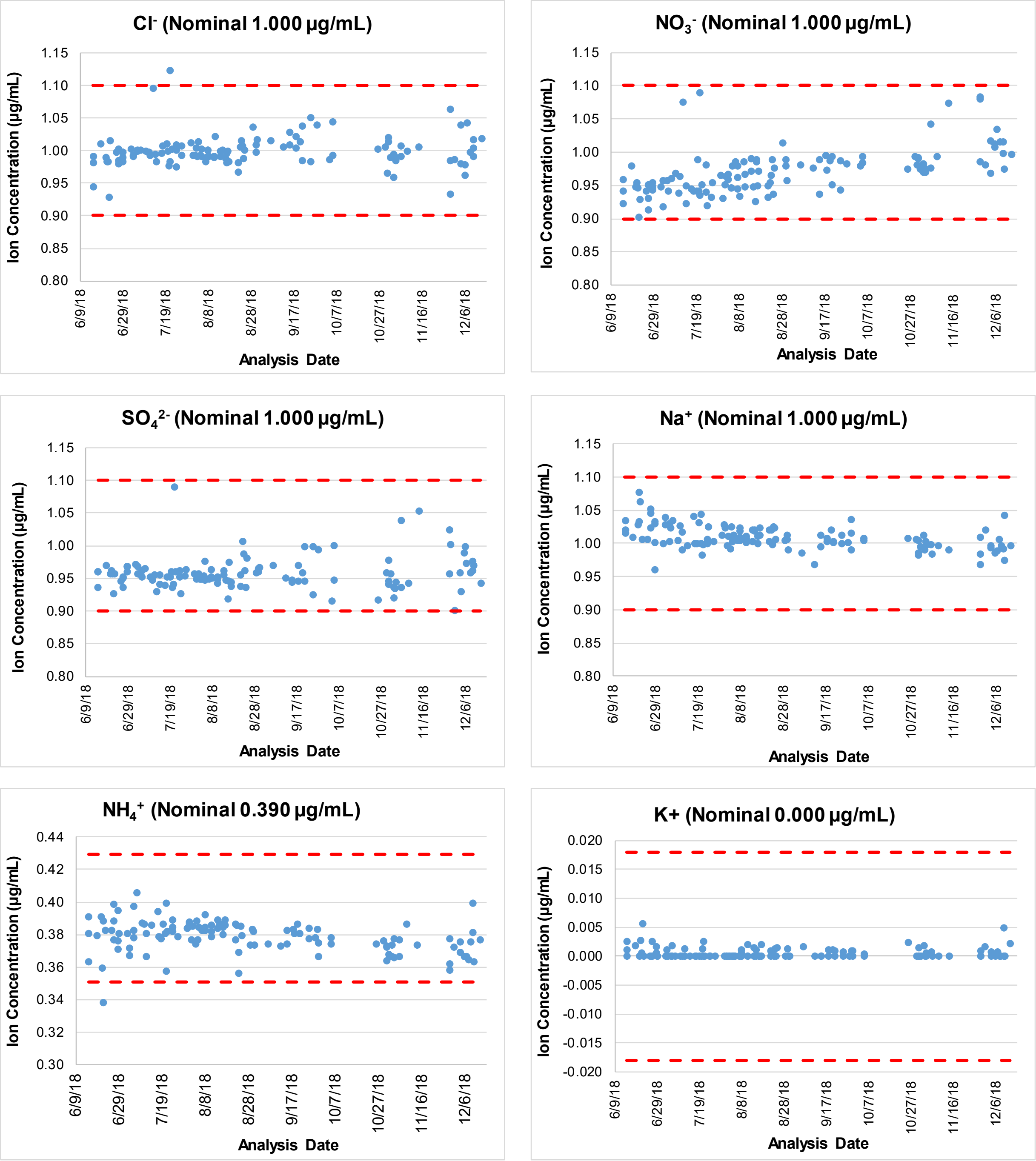


Figure 4.1.A-1b: Control charts for DRI-made ion QC control standards for the analysis period 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018). The limits are ±10% of the nominal concentrations (red dashed lines), except for K^+ which is 3×MDL[a] (red dashed lines).



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

4.1.A.2.3 Duplicate Analyses

Table 4.1.A-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 10 times the lower quantifiable limit (LQL), the absolute value of the average difference should be less than ten times the LQL, and 2) if the average concentration was greater than or equal to ten times the LQL, then the relative percent different difference (RPD) should be less than 10%. LQLs are given in Tables 4.1.A-7a and 4.1.A-7b. The LQLs are used as internal QA indicators, distinct from the MDLs reported to AQS. A total of 1,010 duplicate analyses were run for samples taken during the reporting period, excluding samples with field or analysis flags.

Table 4.1.A-6: Ion duplicate analysis criteria and statistics for the analysis period 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018).

Range	Criteria	Statistic	Na^+	NH_4^+	K^+	Cl^-	NO_3^-	SO_4^{2-}	Units
All		Count	1010	1010	1010	1010	1010	1010	
Ion ≤ 10× LQL	< LQL	Count	995	305	961	994	777	364	
		No. Fail	0	0	0	0	0	0	
		% Fail	0	0	0	0	0	0	%
		Mean	0.006	0.013	0.012	0.010	0.030	0.034	µg/filter difference
		St. Dev.	0.014	0.021	0.020	0.021	0.052	0.053	µg/filter difference
		Max	0.205	0.128	0.223	0.430	0.698	0.357	µg/filter difference
		Min	0.000	0.000	0.000	0.000	0.000	0.000	µg/filter difference
		Median	0.002	0.004	0.005	0.004	0.015	0.015	µg/filter difference
Ion > 10× LQL	RPD[a] <10%	Count	15	705	49	16	233	646	
		No. Fail	0	15	3	0	0	0	
		% Fail	0	2.1	6.1	0.0	0.0	0.0	%
		Mean	1.0%	2.5%	2.8%	0.7%	0.8%	1.2%	RPD
		St. Dev.	1.7%	2.7%	3.5%	0.7%	1.0%	1.5%	RPD
		Max	7.0%	12.0%	13.5%	2.9%	6.8%	9.3%	RPD
		Min	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%	RPD
		Median	0.6%	1.4%	1.5%	0.6%	0.4%	0.7%	RPD

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

4.1.A.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.A.4 Audits, Performance Evaluations, Training, and Accreditations

4.1.A.4.1 System Audits

UC Davis contracted a third-party auditor (Technical & Business Systems; Placerville, CA) to perform a Laboratory Systems Audit of the DRI Ion Chromatography Laboratory. The audit was conducted on September 19, 2018. No issues were identified that affected data quality; auditors provided minor recommendations for improved documentation and tracking, and assured QA/QC documentation was in agreement with existing procedures.

4.1.A.4.2 Performance Evaluations

No performance evaluations were reported during the time period.

4.1.A.4.3 Training

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

4.1.A.4.4 Accreditations

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

4.1.A.5 Summary of Filter Field Blanks

Over the sampling period (January 1, 2018 through September 30, 2018) there were 1,250 valid nylon filter field blanks. Table 4.1-7a and Table 4.1-7b summarize the field blank statistics.

Table 4.1.A-7a: Nylon filter field blank statistics in µg/mL for the analysis period 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl^-	1250	0.007	0.011	0.000	0.264	0.018
NO_3^-	1250	0.014	0.021	0.000	0.221	0.020
SO_4^{2-}	1250	0.004	0.007	0.000	0.188	0.012
Na^+	1250	0.002	0.004	0.000	0.200	0.013
NH_4^+	1250	0.000	0.001	0.000	0.009	0.001
K^+	1250	0.000	0.001	0.000	0.022	0.002

Table 4.1.A-7b: Nylon filter field blank statistics in µg/filter (extraction volume 15 mL) for the analysis period 6/14/2018 through 12/14/2018 (samples collected 1/1/2018 through 9/30/2018).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl^-	1250	0.098	0.165	0.000	3.956	0.274
NO_3^-	1250	0.204	0.315	0.000	3.313	0.307
SO_4^{2-}	1250	0.056	0.108	0.000	2.819	0.183
Na^+	1250	0.025	0.066	0.000	3.003	0.196
NH_4^+	1250	0.006	0.014	0.000	0.132	0.021
K^+	1250	0.000	0.010	0.000	0.326	0.026

4.1.B RTI Ion Chromatography Laboratory

The RTI Ion Chromatography Laboratory, as a subcontractor to UC Davis, received and analyzed extracts from nylon filters for batches 48 through 50, covering the sampling period October 1, 2018 through December 30, 2018. Analysis of these samples was performed January

25, 2019 through March 26, 2019. Using ion chromatography, RTI analyzed for both anions (e.g. chloride [Cl^-], nitrate [NO_3^-], and sulfate [SO_4^{2-}]) and cations (e.g. sodium [Na^+], ammonium [NH_4^+], and potassium[K^+]) using five Thermo Dionex ICS systems (three anion systems, two cation systems) and reported the results of those analyses to UC Davis.

4.1.B.1 Summary of QC Checks and Statistics

Samples are received by the RTI Ion Chromatography Laboratory following the chain-of-custody procedures specified in *RTI SOP #Ions1*. Samples are analyzed using Thermo Dionex ICS-2000 and ICS-3000 systems following *RTI SOP #Ions1*. Extraction procedures are documented on worksheets which are maintained with the batch files. The QC measures for the RTI ion analysis are summarized in Table 4.1.B-1. The table details the frequency and standards required for the specified checks, along with the acceptance criteria and corrective actions. Stated QC criteria are verified and documented on review worksheets, and reviewers document QC criteria not met, corrective actions, samples flagged for reanalysis, and subsequent reanalysis dates.

Table 4.1.B-1: RTI quality control measures for ion (anion and cation) analysis by ion chromatography.

Requirement	Frequency	Acceptance Criteria	Corrective Action
Calibration regression	Daily	$R^2 \geq 0.999$	Investigate; Repeat calibration
Continuing calibration verification (CCV) check standard; RTI dilution of a commercially prepared, NIST-traceable QC sample	Daily, immediately after calibration and at every 10 samples	Measured concentrations < 0.050 ppm: within 35% of known values. Measured concentrations >0.050 ppm: within 10% of known values.	Investigate; reanalyze samples
Duplicate sample	3 per batch of 50 samples	RPD = 10% at 10x MDL RPD = 200% at MDL	Investigate; reanalyze
Spiked sample extract	2 per batch of 50 samples	Recoveries within 90 to 110% of target values	Investigate; reanalyze
Reagent blanks	One reagent blank per reagent used (DI H_2O and/or eluent) At least one per day	No limit set. The data is compiled for comparability studies. < 10 times MDL	Investigate; reanalyze
Round Robin (External QA by USGS)	4/month	Not applicable; data reported and compared annually	Investigate
Reanalysis	5% per batch reanalyzed on different day and as requested	MDL to10 times MDL: RPD up to 200%, 10 to 100 times MDL: RPD < 20%, >100 times MDL: differences within 10%	Investigate from batch reanalyze samples if needed

4.1.B.2 Summary of QC Results

RTI followed the quality control criteria stated in Table 4.1.B-1. Instruments were recalibrated when calibration failed to meet the criteria. For cases where CCV failures occurred during analyses, samples bracketed by the CCV failure were reanalyzed. When duplicate precision or spiked sample recoveries failed to meet the criteria, the duplicated samples or matrix spike sample plus additional samples (5% of analytical batch) were reanalyzed. The original data were only replaced with reanalysis data in cases where precision between the reanalysis and original result failed to meet the criteria. For cases where check samples failed to meet the reanalysis criteria, the remaining samples not already reanalyzed from the batch were reanalyzed.

4.1.B.2.1 Calibration regression

Ion chromatographs are calibrated daily with calibration standards prepared as serial dilutions of a NIST traceable stock standard. Anion instruments are calibrated from 10 – 2000 parts per billion (ppb) for chloride and from 50 – 10000 ppb for nitrate and sulfate. A high calibration standard at 5000 ppb for chloride and 25000 ppb for sulfate and nitrate are used in the calibration curve only for samples exceeding 10000 ppb. Cation instruments are calibrated from 10 – 1000 ppb for sodium, ammonium and potassium. A high calibration standard at 3000 ppb is used only for samples whose concentrations exceed 1000 ppb. The correlation coefficients for the daily calibration must be at least 0.999. If this criterion is not met, the curve is investigated. A calibration standard or standards that are suspect are removed from the curve and not used for calculations. If the calibration still fails to meet the stated QC criteria, the situation is further investigated until it has been confirmed that the instrument is performing correctly.

After calibration, an analytical sequence is assigned to an instrument and includes 50 batch samples, extraction QC checks, three sets of replicate samples, two matrix spikes, and continuing calibration verification (CCV) standards.

4.1.B.2.2 Continuing calibration verification (CCV) check standard

Instrument QC samples are used to verify the initial and continuing calibration of the ion chromatographs. These solutions are prepared at the low, medium, medium-high and high end of the calibration curve. Table 4.1.B-2 and 4.1.B-3 lists the concentrations.

Table 4.1.B-2: Target concentrations for anion CCV check standards for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018).

QC Sample	Cl^- (ppb)	NO_3^- (ppb)	SO_4^{2-} (ppb)
Instrument Low QC	200	600	1200
Instrument Medium QC	500	1500	3000
Instrument Medium High QC	1000	3000	6000
Instrument High QC	2000	6000	12000

Table 4.1.B-3: Target concentrations for cation CCV check standards for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018).

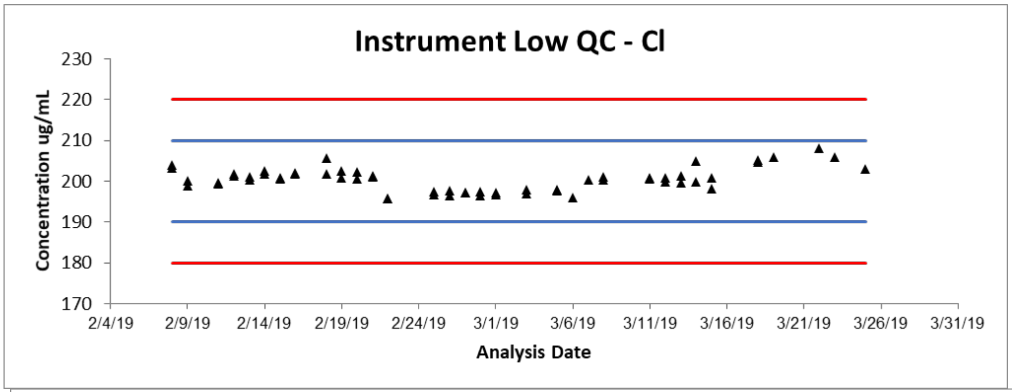
QC Sample	Na^+ (ppb)	NH_4^+ (ppb)	K^+ (ppb)
Instrument Low QC	20	20	20
Instrument Medium QC	250	250	250
Instrument Medium High QC	750	750	750
Instrument High QC	2000	2000	2000

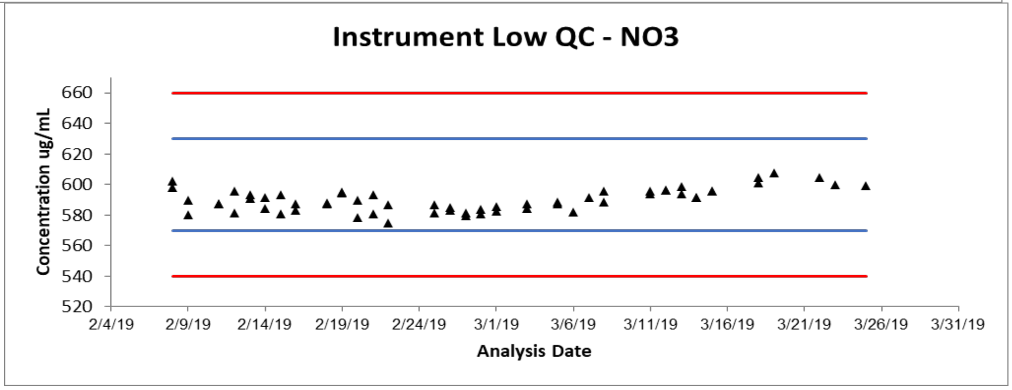
At least two CCV check standards are analyzed immediately after the calibration standards and a single CCV check standard is analyzed after every ten samples throughout the batch. When an instrument CCV check standard falls outside of the control limits, impacted samples are reanalyzed. If a CCV check standard fails, and there is a second CCV check standard measured immediately following the failure, samples are not reanalyzed. The failed CCV check standard, samples flagged for reanalysis, and date of reanalysis are documented on the review worksheet and maintained with the complete set of batch records for each batch analyzed.

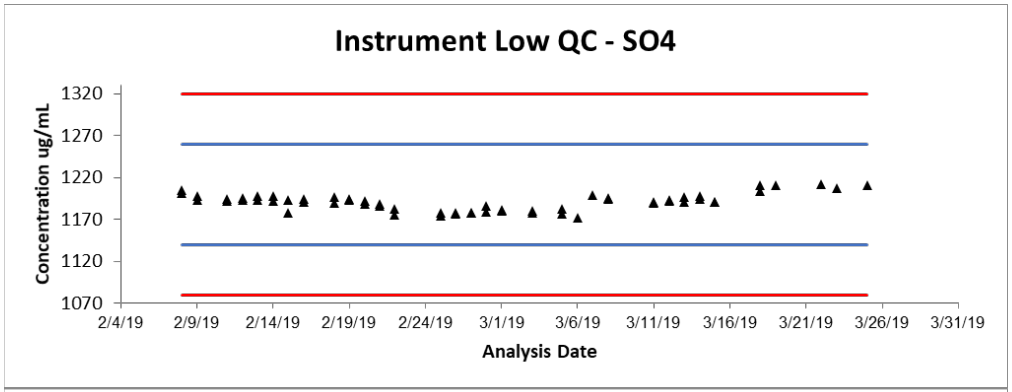
Control charts were prepared for anion (Figure 4.1.B-1) and cation (Figure 4.1.B-2) CCV check standards. Most CCV check standards were within the stated control limits. There were two cases where CCV check standards failed the QC criteria: (1) one of these was a medium-high CCV check standard for sodium, and the impacted samples were reanalyzed; (2) the other was a low CCV check standard for potassium, the impacted samples were not reanalyzed because there was a second CCV check standard that was successful.

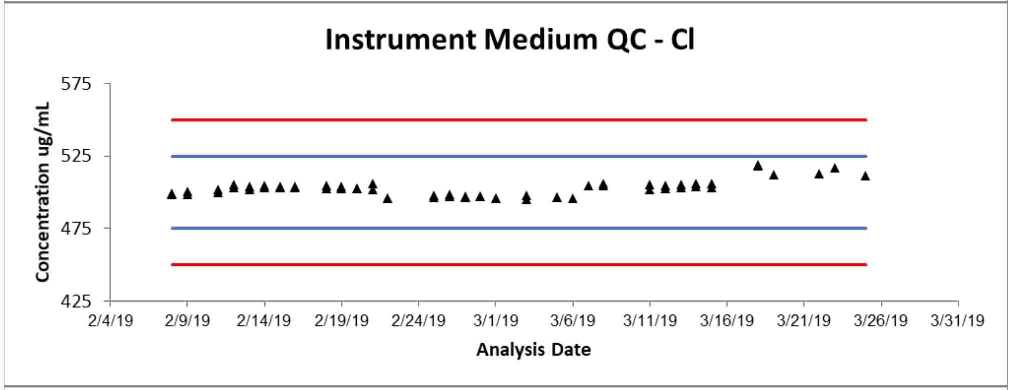
For the purpose of demonstrating instrument to instrument performance, control charts for the lowest CCV check standards were generated, where instruments A9 and A10 were compared for anions (Figure 4.1.B-3) and instruments C3 and C6 were compared for cations (Figure 4.1.B-4). The control charts illustrate consistent performance between instruments.

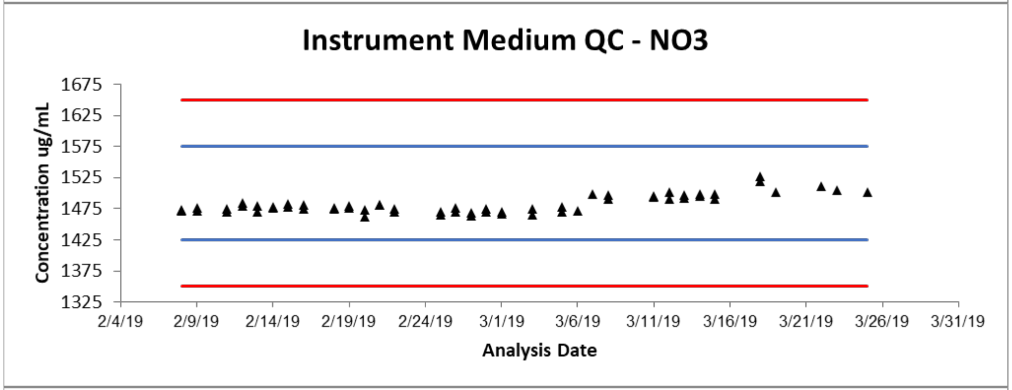
Figure 4.1.B-1: Control charts for anion CCV check standards at low, medium, medium-high, and high concentrations measured in µg/mL (see Table 4.1.B-2) for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018). Red lines show upper and lower control limits set at ±10% of the nominal concentrations for the low, medium, medium-high, and high standards. Blue lines show upper and lower warning limits.

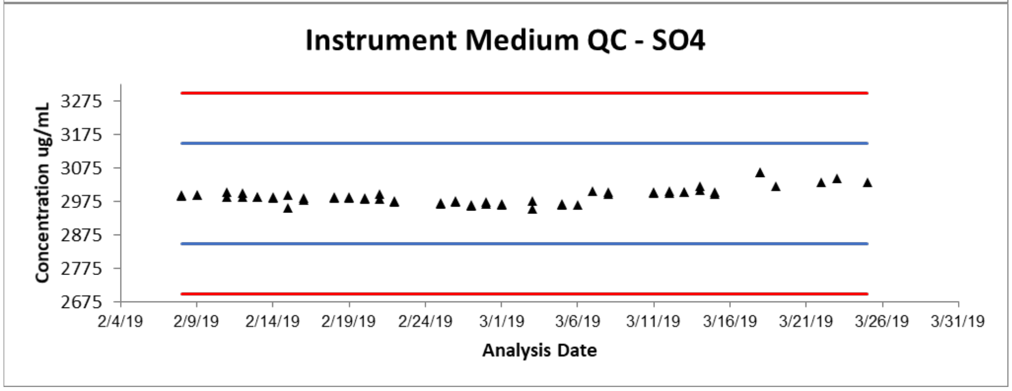


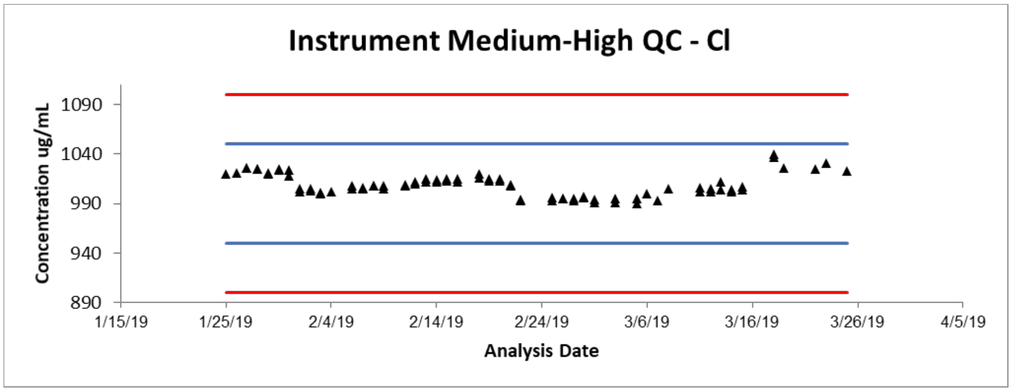


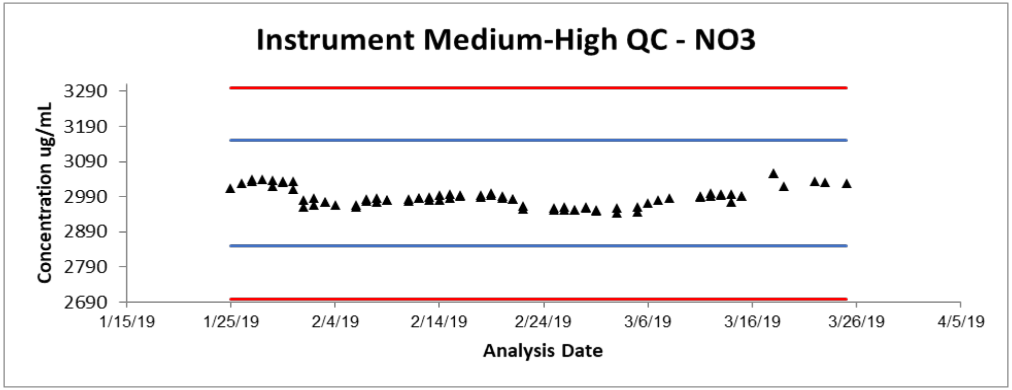

Instrument Low QC - SO4
Concentration ug/mL
1320
1270
1220
1170
1120
1070
2/4/19
2/9/19
2/14/19
2/19/19
2/24/19
3/1/19
3/6/19
3/11/19
3/16/19
3/21/19
3/26/19
3/31/19
Analysis Date

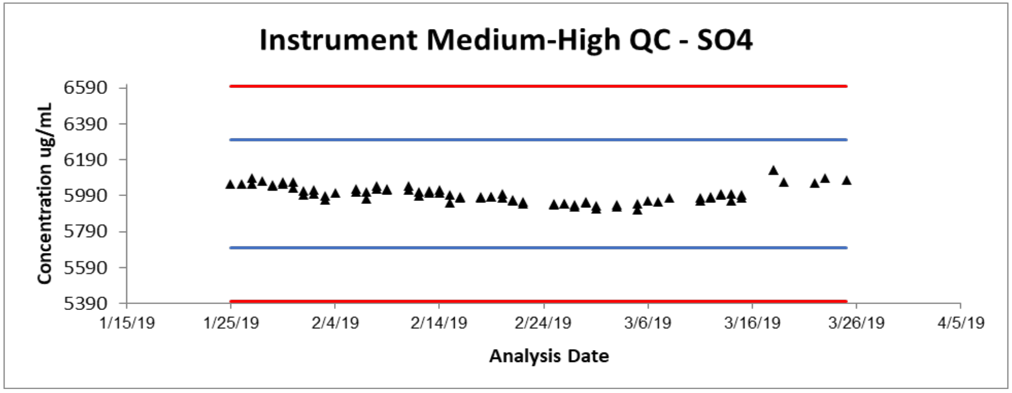

Instrument Medium QC - Cl
Concentration ug/mL
575
525
475
425
2/4/19
2/9/19
2/14/19
2/19/19
2/24/19
3/1/19
3/6/19
3/11/19
3/16/19
3/21/19
3/26/19
3/31/19
Analysis Date

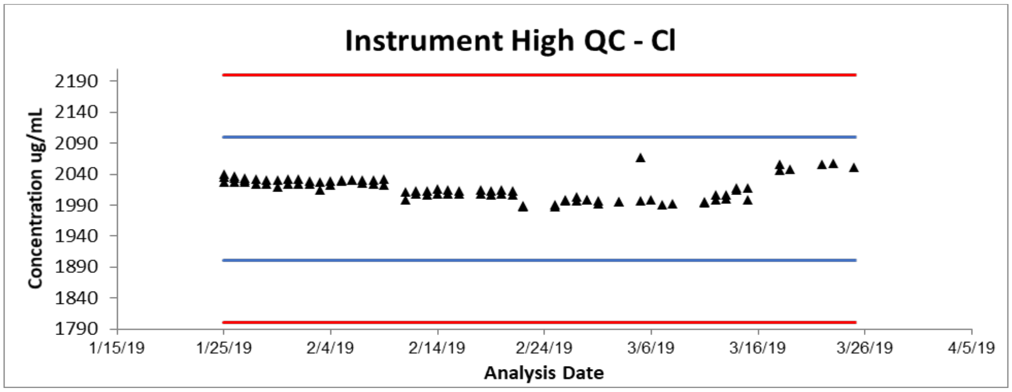

Instrument Medium QC - NO3
Concentration ug/mL
1675
1625
1575
1525
1475
1425
1375
1325
2/4/19
2/9/19
2/14/19
2/19/19
2/24/19
3/1/19
3/6/19
3/11/19
3/16/19
3/21/19
3/26/19
3/31/19
Analysis Date

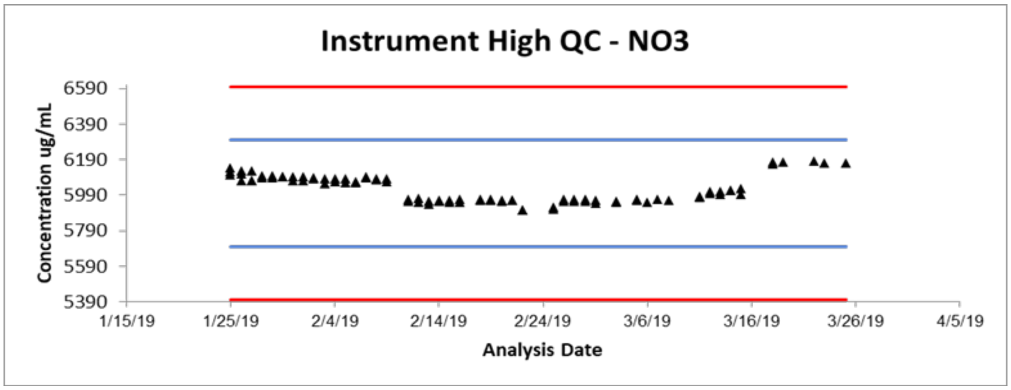

Instrument Medium QC - SO4
Concentration ug/mL
3275
3175
3075
2975
2875
2775
2675
2/4/19
2/9/19
2/14/19
2/19/19
2/24/19
3/1/19
3/6/19
3/11/19
3/16/19
3/21/19
3/26/19
3/31/19
Analysis Date


Instrument Medium-High QC - Cl
Concentration ug/mL
1090
1040
990
940
890
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Medium-High QC - NO3
Concentration ug/mL
3290
3190
3090
2990
2890
2790
2690
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Medium-High QC - SO4
Concentration ug/mL
6590
6390
6190
5990
5790
5590
5390
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument High QC - Cl
Concentration ug/mL
2190
2140
2090
2040
1990
1940
1890
1840
1790
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date



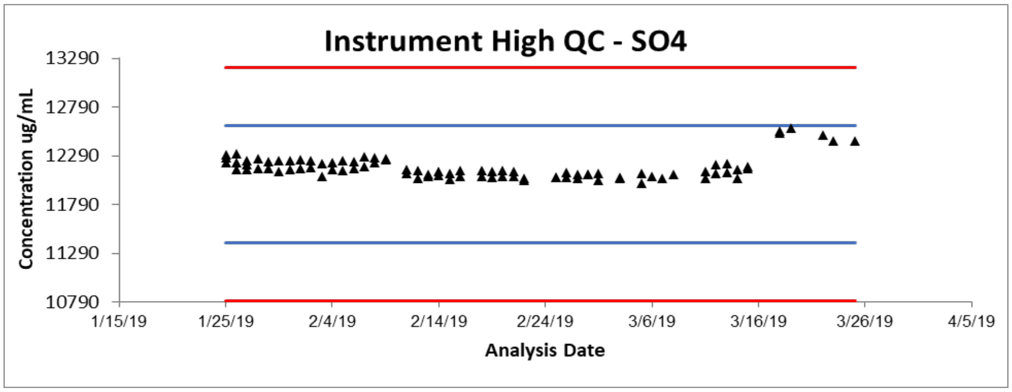
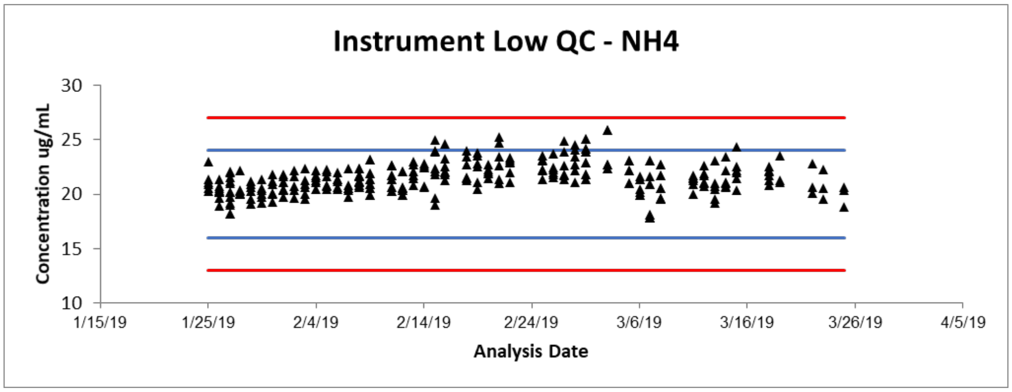
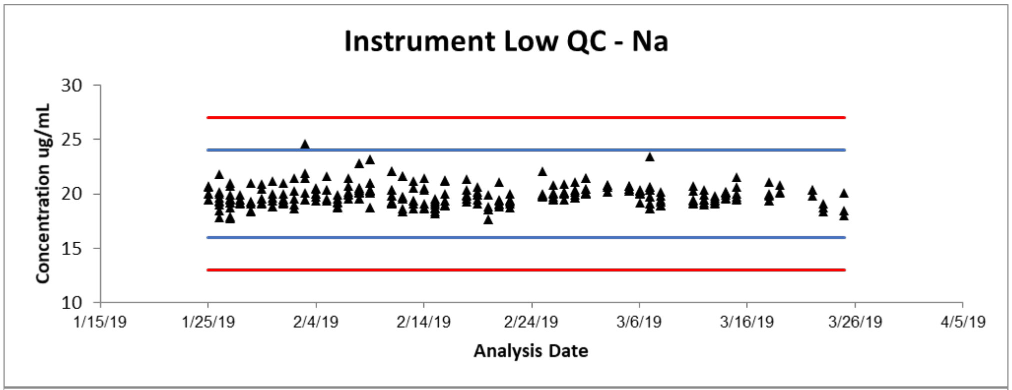
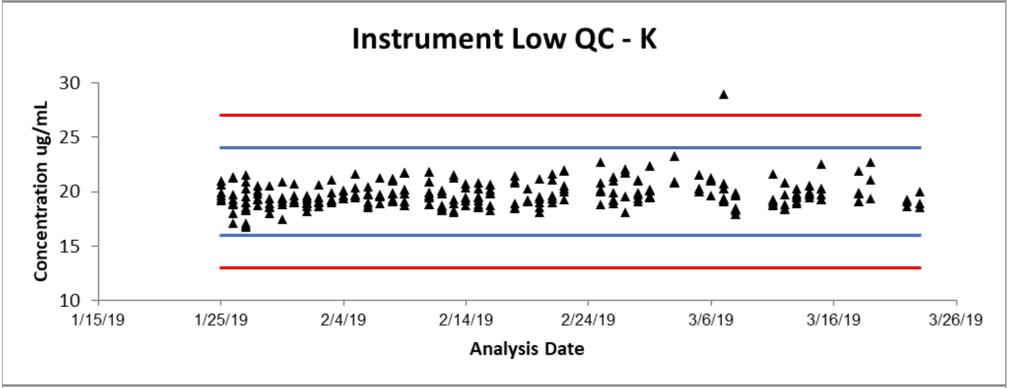
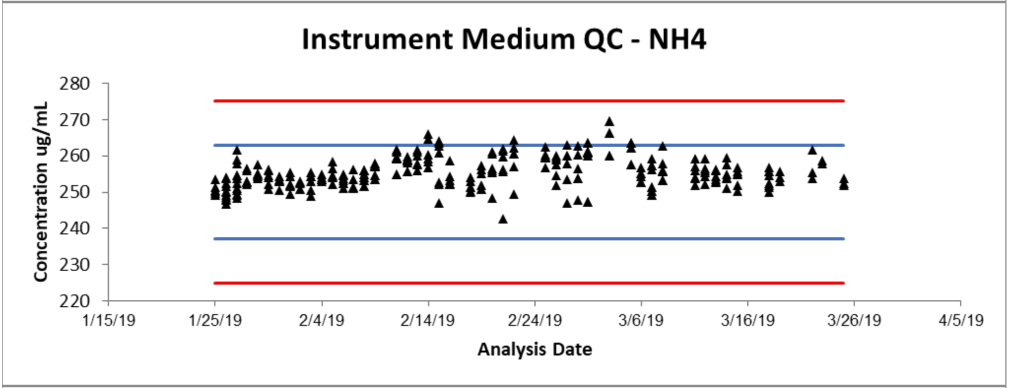


Figure 4.1.B-2: Control charts for cation CCV check standards at low, medium, medium-high, and high concentrations measured in µg/mL (see Table 4.1.B-3) for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018). Red lines show upper and lower control limits set at ±35% of the nominal concentrations for the low standards and ±10% of the nominal concentrations for the medium, medium-high, and high standards. Blue lines show upper and lower warning limits.




Instrument Low QC - Na
Concentration ug/mL
30
25
20
15
10
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Low QC - K
Concentration ug/mL
30
25
20
15
10
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date


Instrument Medium QC - NH4
Concentration ug/mL
280
270
260
250
240
230
220
1/15/19
1/25/19
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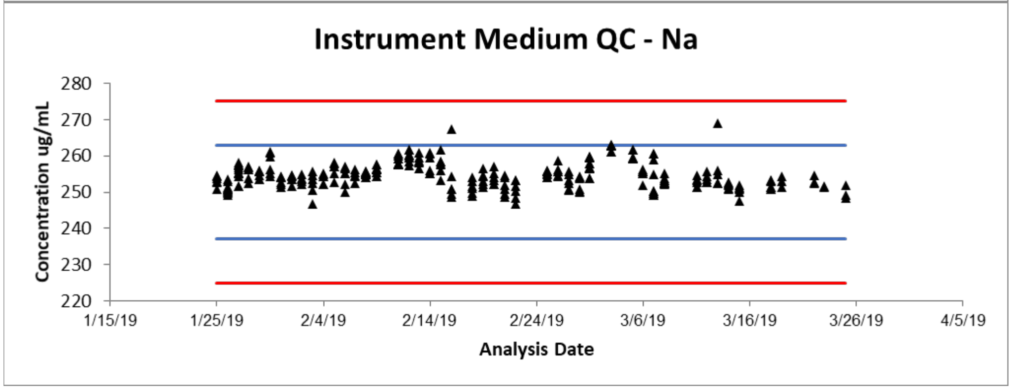
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Medium QC - Na
Concentration ug/mL
280
270
260
250
240
230
220
1/15/19
1/25/19
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2/24/19
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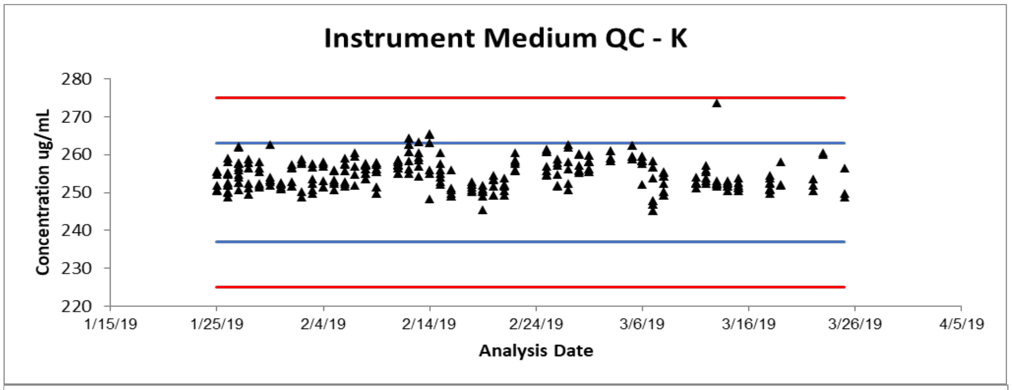
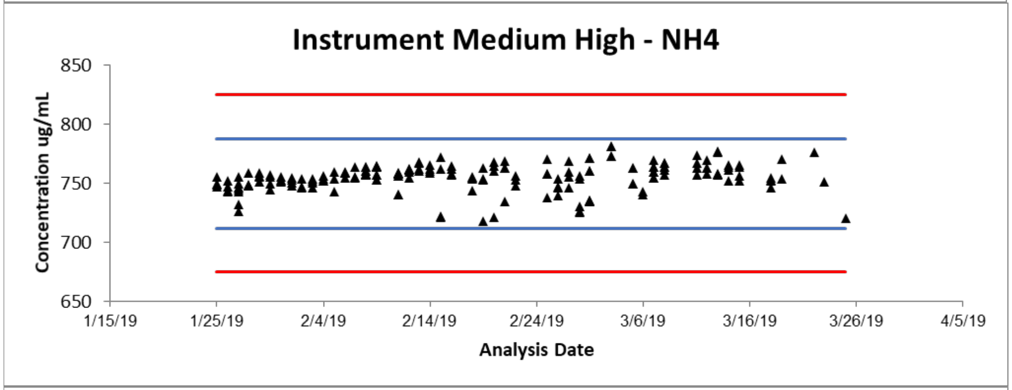
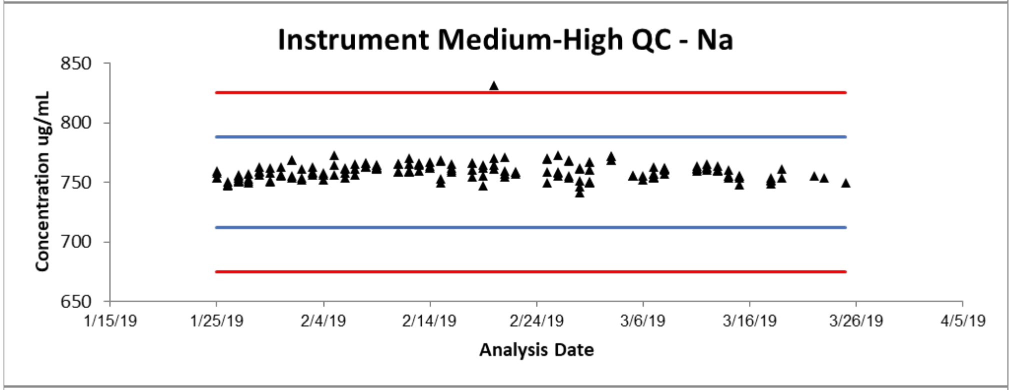
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Medium QC - K
Concentration ug/mL
280
270
260
250
240
230
220
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Medium High - NH4
Concentration ug/mL
850
800
750
700
650
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Medium-High QC - Na
Concentration ug/mL
850
800
750
700
650
1/15/19
1/25/19
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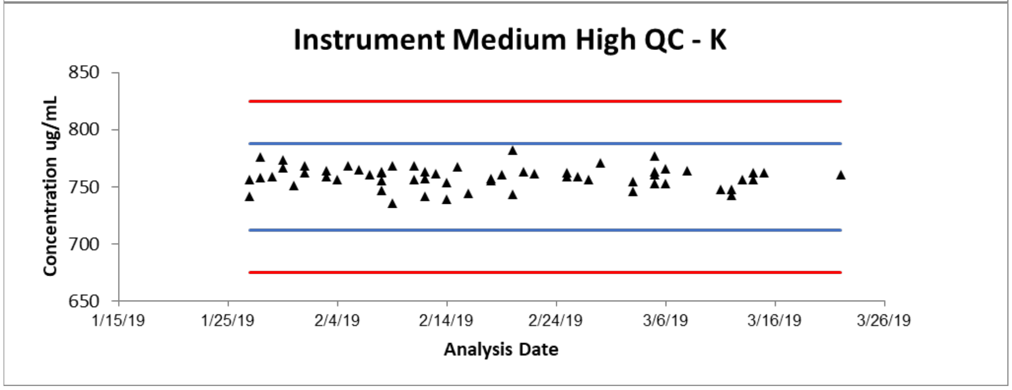
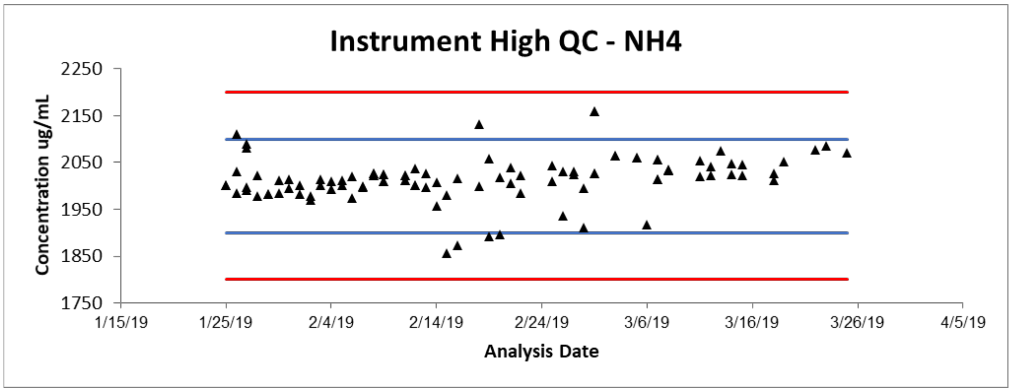
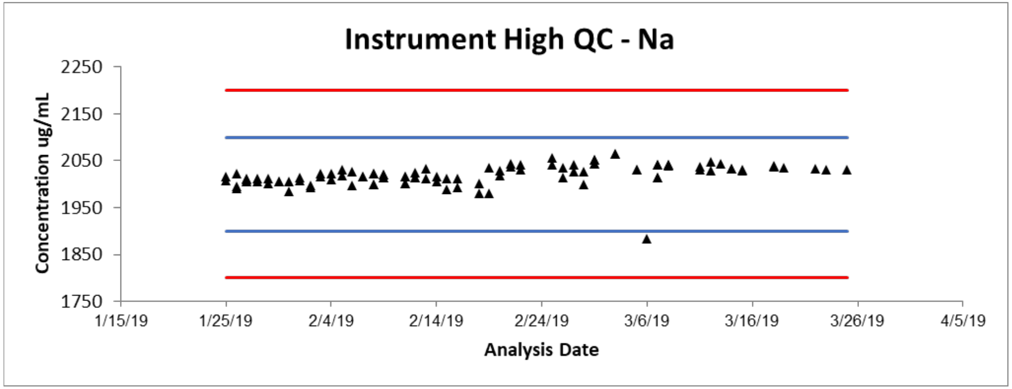
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Medium High QC - K
Concentration ug/mL
850
800
750
700
650
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date


Instrument High QC - NH4
Concentration ug/mL
2250
2150
2050
1950
1850
1750
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument High QC - Na
Concentration ug/mL
2250
2150
2050
1950
1850
1750
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date

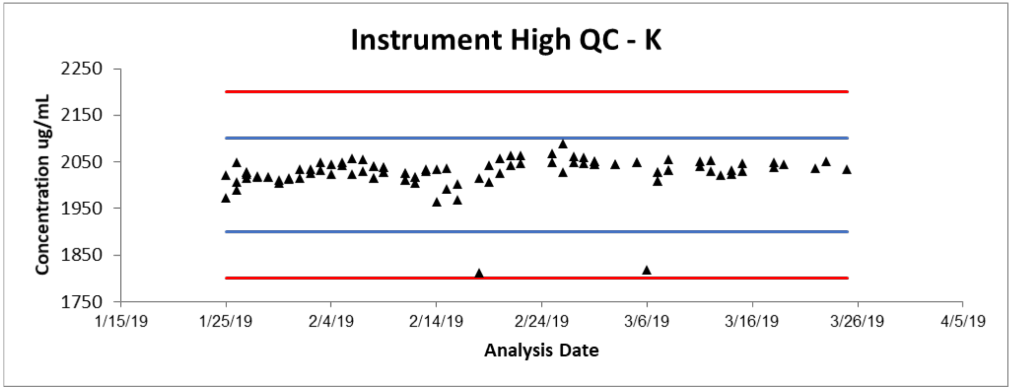
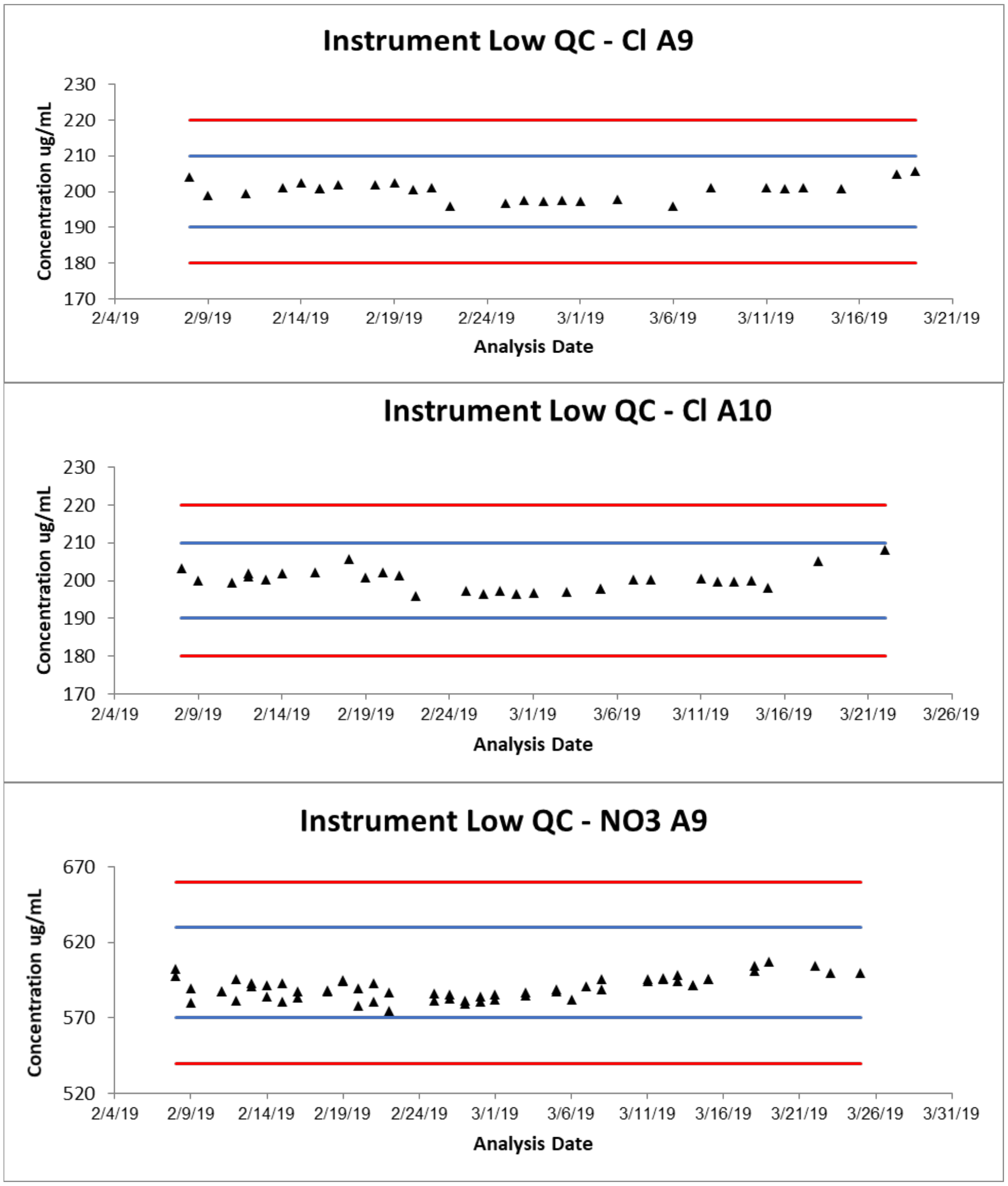
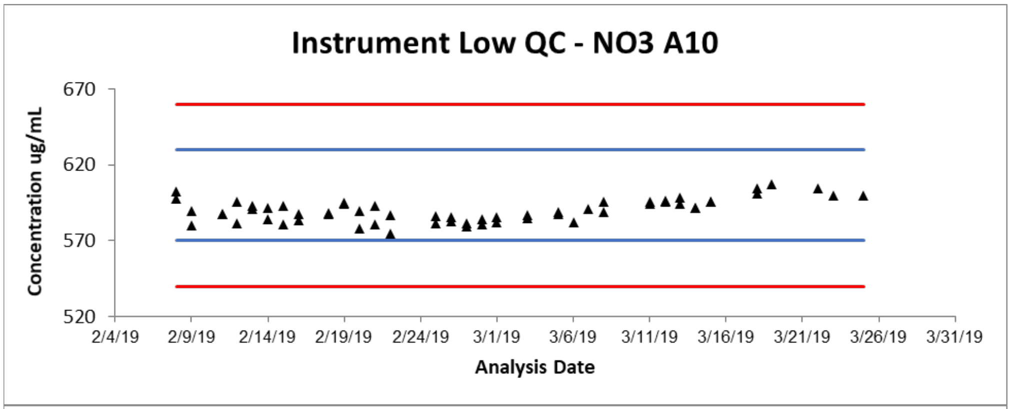
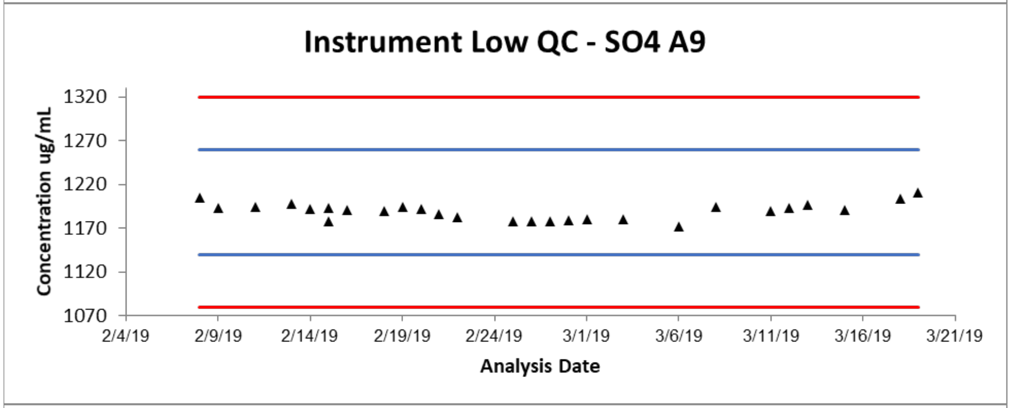
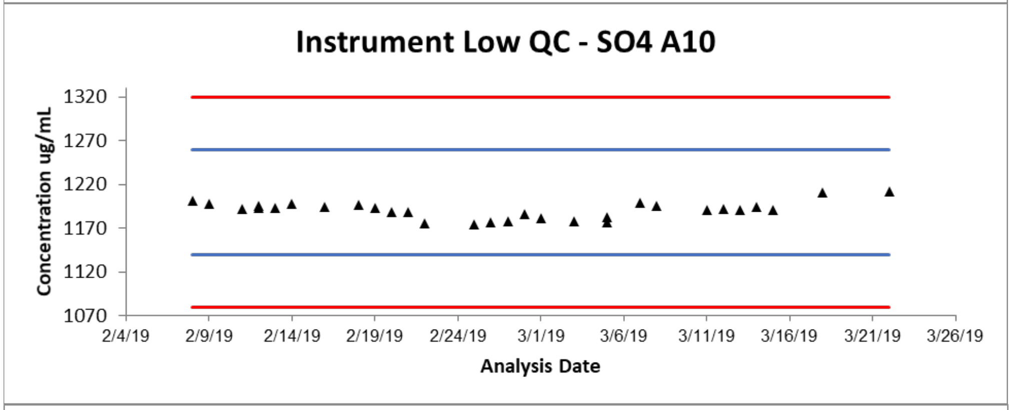

Instrument High QC - K
Concentration ug/mL
2250
2150
2050
1950
1850
1750
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date

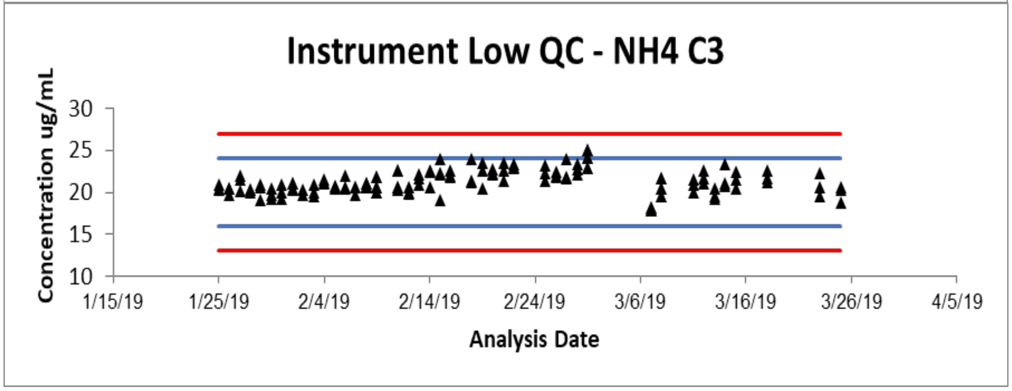
Figure 4.1.B-3: Control charts for anion and cation CCV check standards showing comparability between instruments (A9 and A10 for anions; C3 and C6 for cations) at low concentrations (see Table 4.1.B-2 and Table 4.1.B-3) for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018). Red lines show upper and lower control limits set at ±10% of the nominal concentrations for anions and ±35% of the nominal concentrations for cations. Blue lines show upper and lower warning limits.

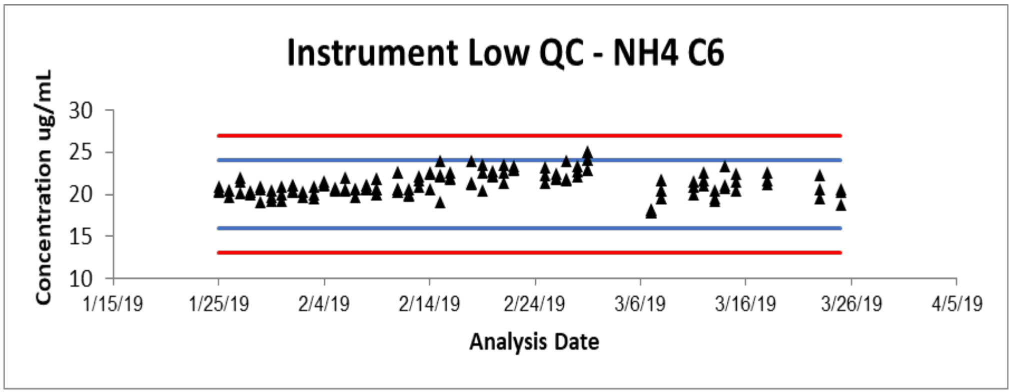


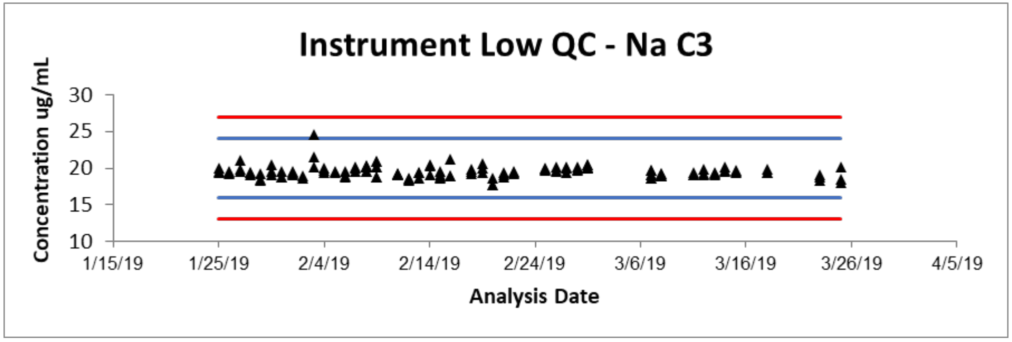

Instrument Low QC - NO3 A10

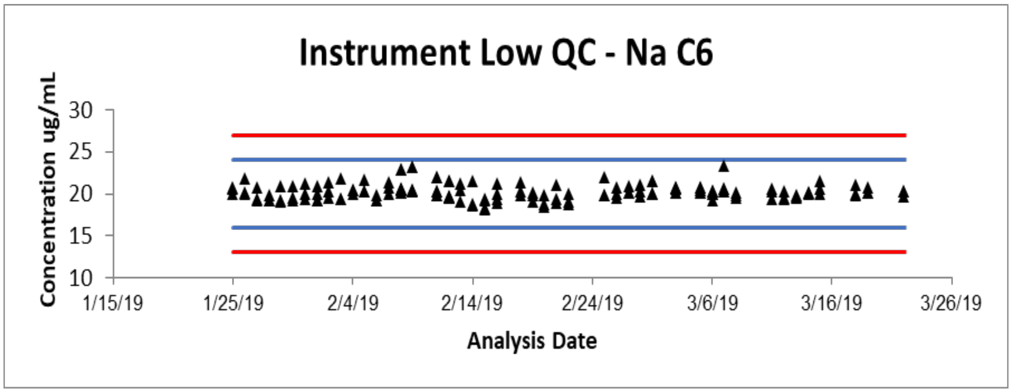

Instrument Low QC - SO4 A9

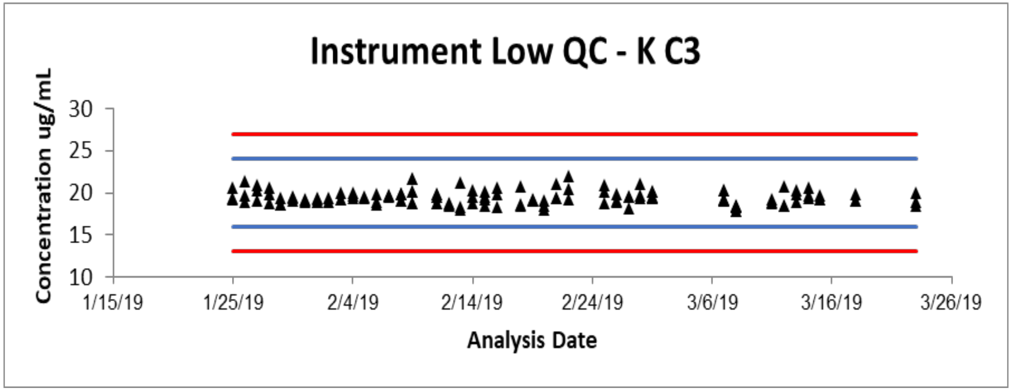

Instrument Low QC - SO4 A10

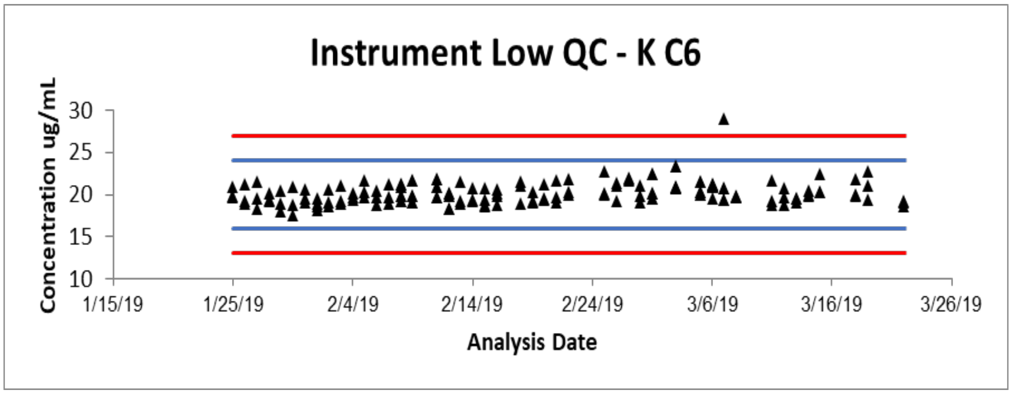

Instrument Low QC - NH4 C3


Instrument Low QC - NH4 C6
Concentration ug/mL
30
25
20
15
10
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Low QC - Na C3
Concentration ug/mL
30
25
20
15
10
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
4/5/19
Analysis Date


Instrument Low QC - Na C6
Concentration ug/mL
30
25
20
15
10
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

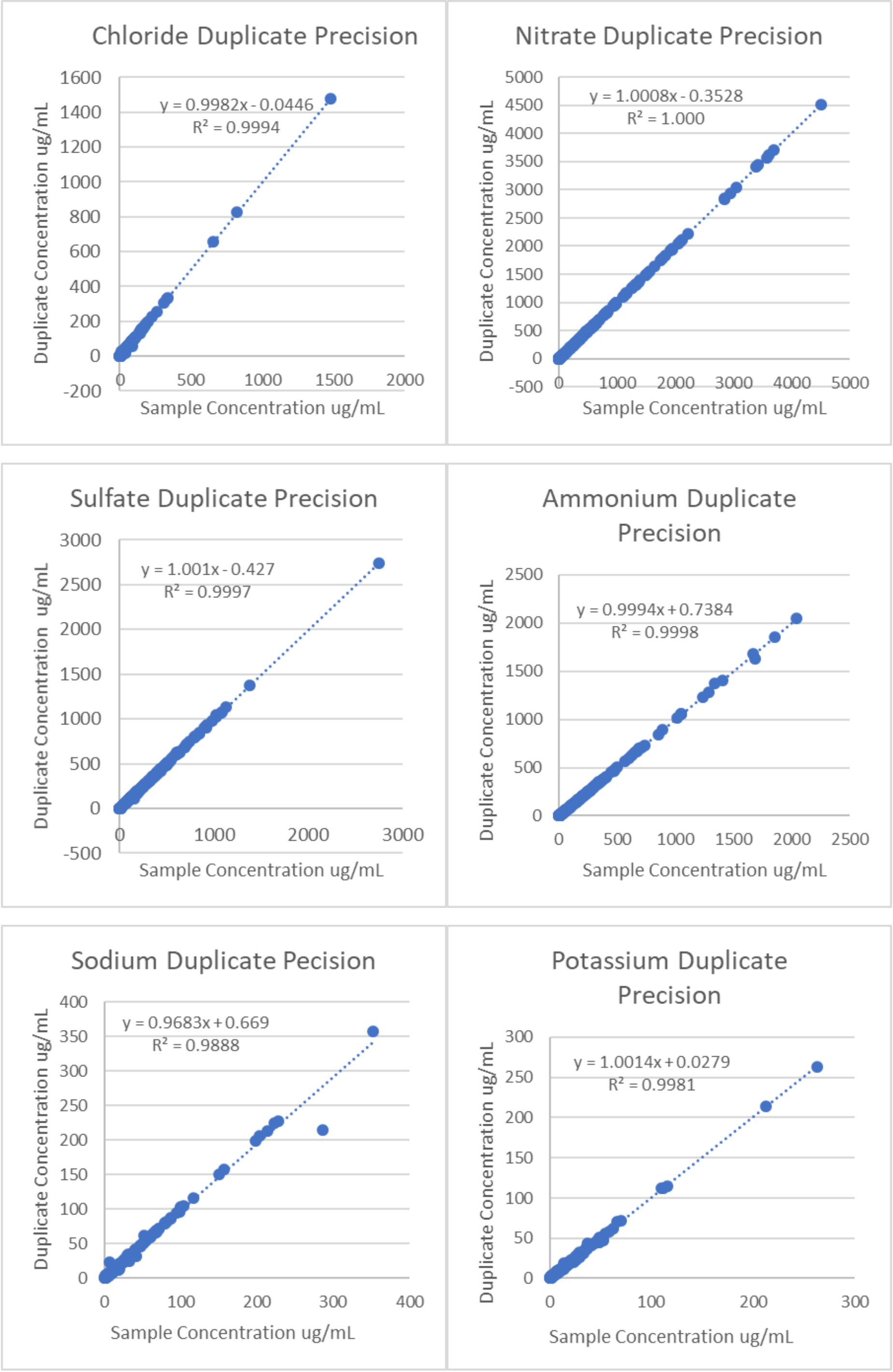

Instrument Low QC - K C3
Concentration ug/mL
30
25
20
15
10
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date



4.1.B.2.3 Duplicate Samples

Duplicate analysis results are obtained from two different aliquots of the same filter sample extract run on the same instrument sequentially in the analytical batch. Each analytical batch includes three sets of duplicate samples. The relative percent difference (RPD) for duplicate samples must be within ± 10% when sample concentrations are greater than ten times the analytical MDL and within ± 100% when sample concentrations are at or up to ten times the analytical MDL. There was a total of 256 duplicate samples analyzed for anions (Figure 4.1.B-4), with two cases where the RPD did not meet the QC criteria for chloride and one case for sulfate; all RPD results met the QC criteria for nitrate. There was a total of 251 duplicate samples analyzed for cations (Figure 4.1.B-4), with two cases where the RPD did not meet the QC criteria for potassium and three cases for sodium; all RPD results met the QC criteria for ammonium. In all cases where duplicate precision fails to meet the QC criteria, five samples (duplicate plus four randomly selected samples) from the analysis set are reanalyzed. If any of the reanalyzed samples fail to meet the QC criteria, the entire batch is reanalyzed.

Figure 4.1.B-4: Ion duplicate analysis results for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018).



4.1.B.2.4 Spiked Sample Extracts

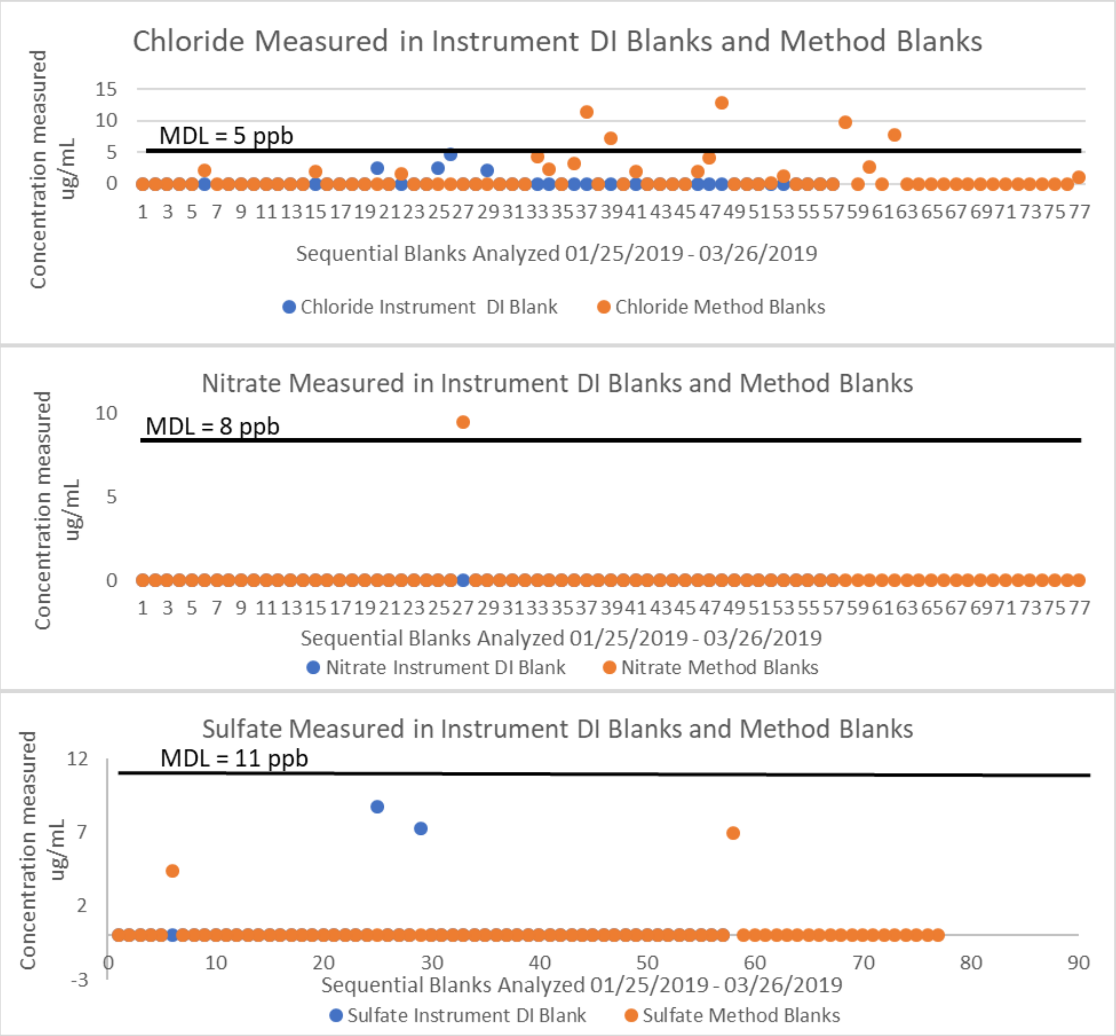
Matrix spikes are performed on 4% (two per batch of 50) of the samples analyzed. The matrix is deionized (DI) water, and spike samples typically meet the QC criteria with failures most likely from introduced contamination. All spike recoveries met the QC criteria except for one chloride case (Figure 4.1.B-5); the sample and four other samples from the same analysis set were reanalyzed.

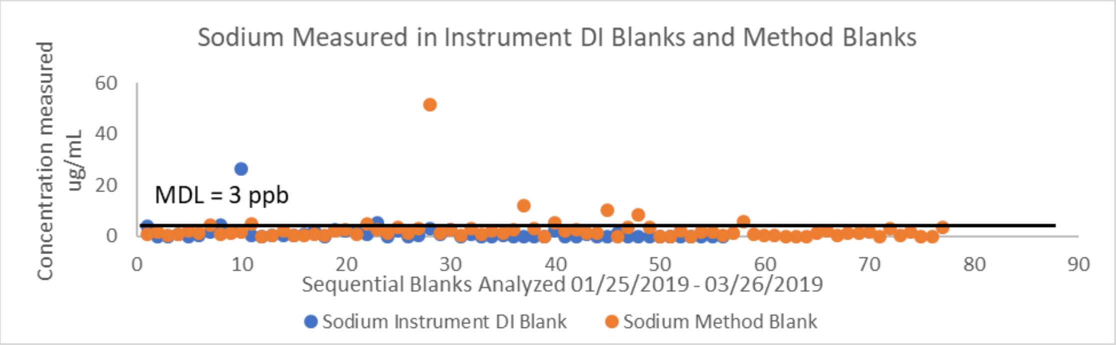
Figure 4.1.B-5: Time series of recovery percentage for anion and cation of matrix spikes for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018).

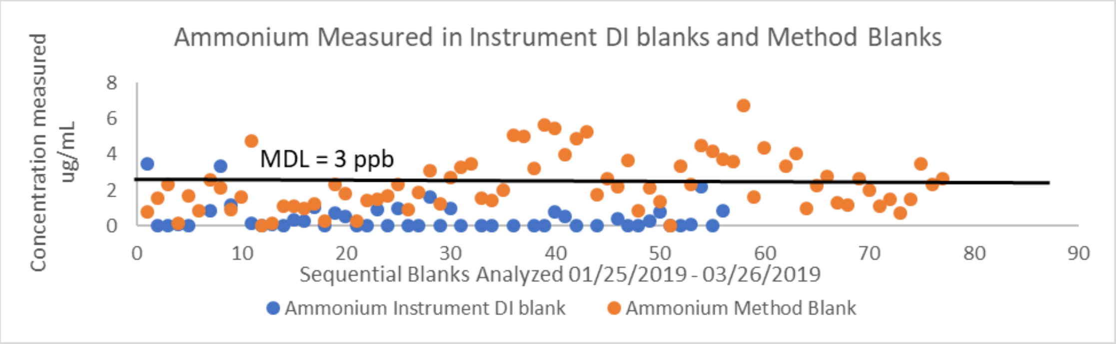
4.1.B.2.5 Reagent Blanks and Spikes

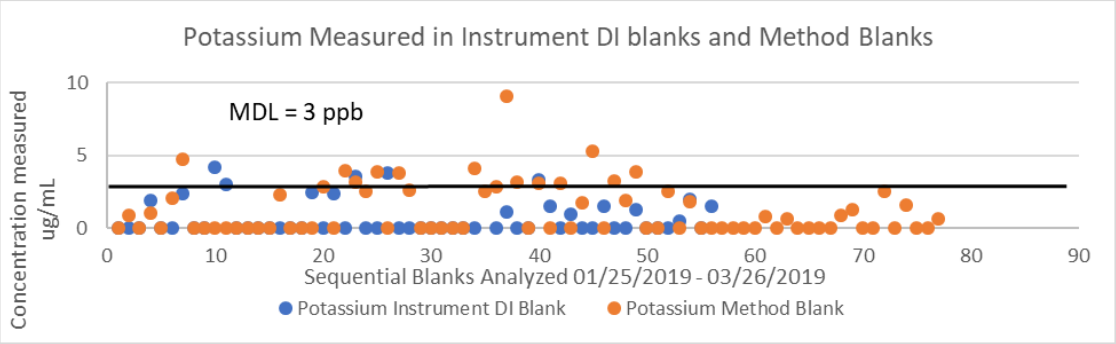
Analyses began with the analysis of two DI water instrument blanks which clean the sample loop prior to injection of calibration standards. Method blanks and laboratory control spikes (LCS) are used to measure the background contamination that could be introduced during the extraction, sample handling, or analysis processes. At the time of filter extraction, an empty extraction vial is included as a method blank at a rate of 1 for every 50 samples. Empty extraction vials are also spiked with exact volumes of concentrated solutions for both anions and cations a rate of 1 for every 25 samples for LCS analysis. The same volume of water (20.0 mL) is added to the method blank and LCS vials as is added to the vials with the filter samples to be extracted.

Figure 4.1.B-6: Concentrations of anions and cations in DI water blanks and method blanks for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018). Black line indicates the analytical method detection limit.









The laboratory does not use the reagent blanks (instrument DI blanks and method blanks) or the LCS analyses for control purposes. Because the concentrations in the LCS (Table 4.1.B-4 and Table 4.1.B-5) are very close to the CCV check standards, it is useful to compare the LCS results with the CCV check standard criteria for evidence of outlier frequency. The LCS analyses (Figure 4.1.B-7) have more frequent outliers relative to the CCV check standards (Figure 4.1.B-1 and Figure 4.1.B-2), suggesting that background contamination is introduced during the sample handling and processing of samples and not typically due to instrumental issues. The method blanks and LCS analysis results are useful for internal laboratory quality control, as they can alert the analyst to background issues early during the analysis process. Review of the LCS and method blank results relative to the CCV check standards is performed for each analysis set.

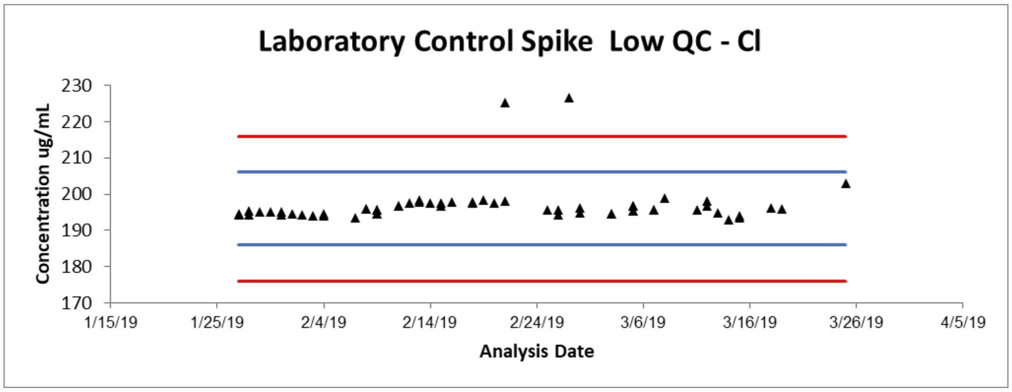
Table 4.1.B-4: Target concentrations for anion LCS for the analysis period 01/25/2019 through 03/26/2019 (samples collected 10/1/2018 through 12/31/2018).

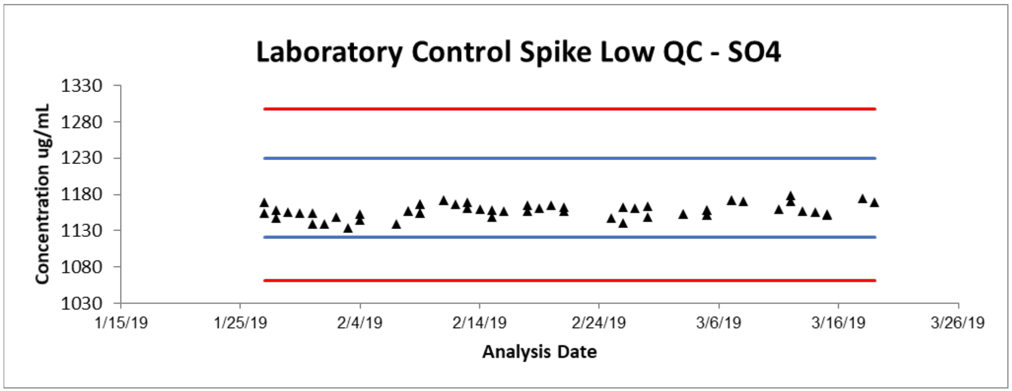
QC Sample	Cl^- (ppb)	NO_3^- (ppb)	SO_4^{2-} (ppb)
LCS Low	196	392	1180
LCS Med	476	1430	2860
LCS High	2000	6000	12000

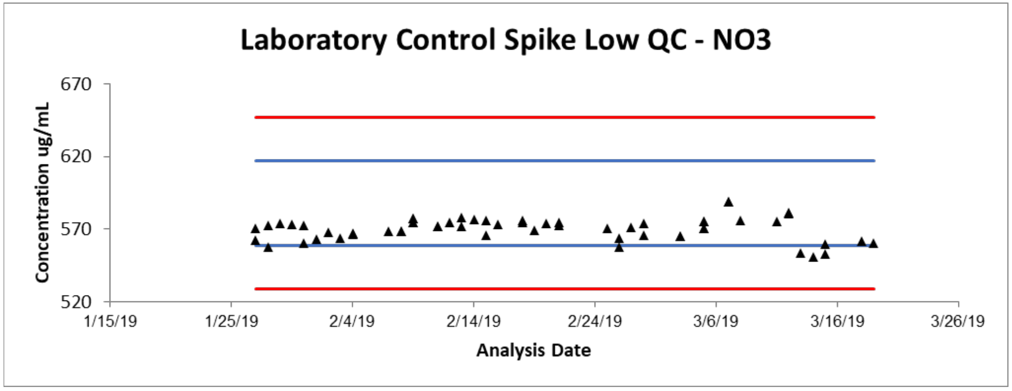
Table 4.1.B-5 Target concentrations for cation LCS for the analysis period 01/25/2019 through 03/26/2019 (samples collected 10/1/2018 through 12/31/2018).

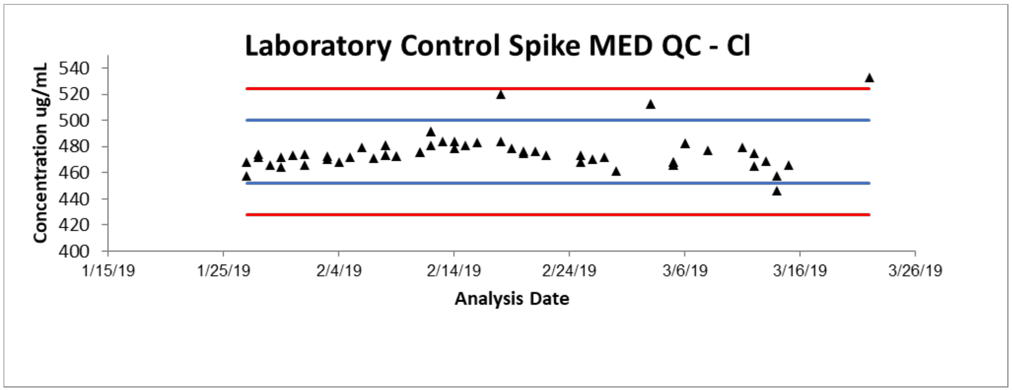
QC Sample	Na^+ (ppb)	NH_4^+ (ppb)	K^+ (ppb)
LCS Low	20	20	20
LCS Med	276	276	276
LCS High	769	769	769

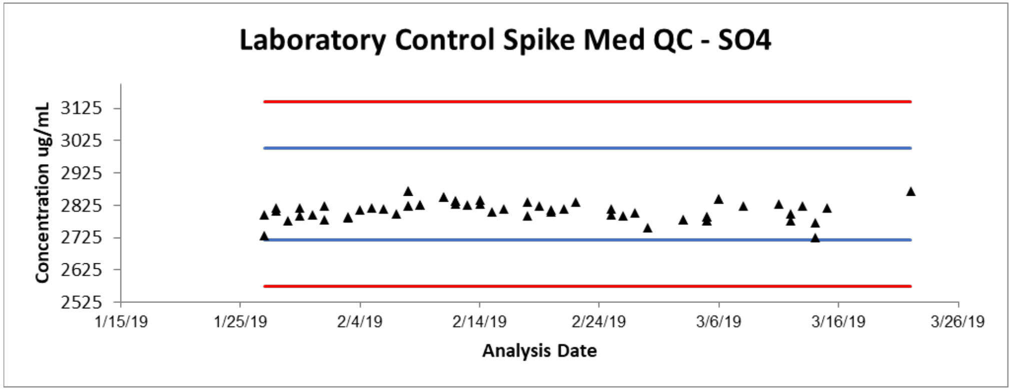
Figure 4.1.B-7: Control charts for anion and cation LCS analyses relative to the CCV check standard QC criteria for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018). Red lines show upper and lower control limits per the CCV check standard QC criteria Blue lines show upper and lower warning limits.

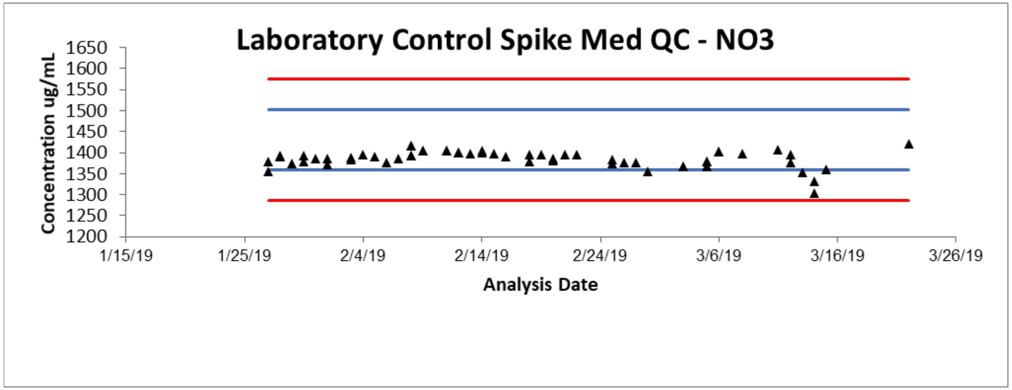


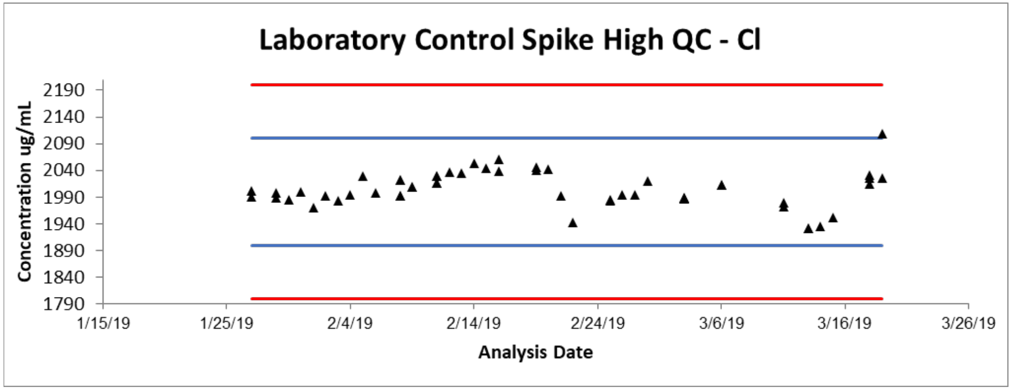


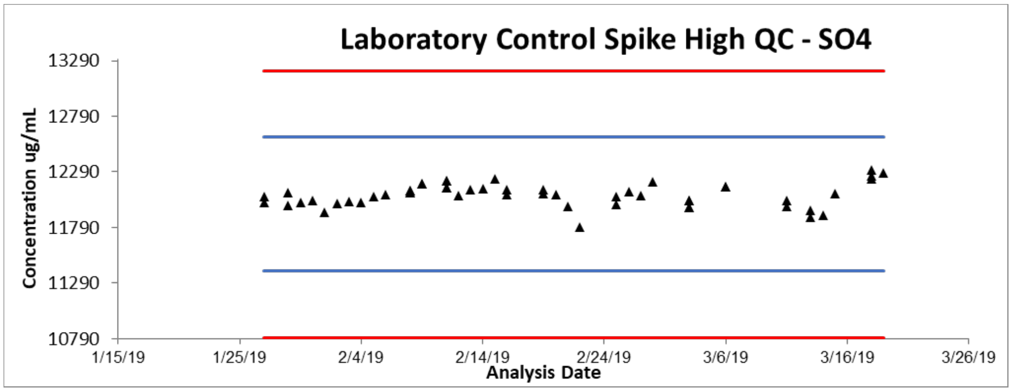


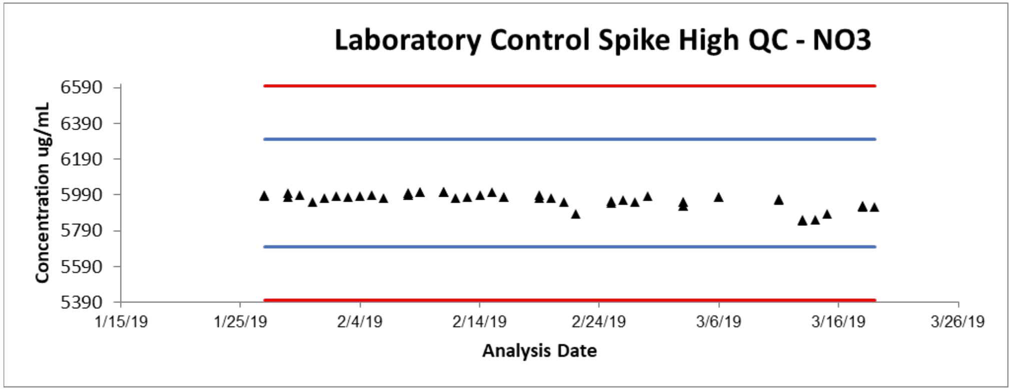

Laboratory Control Spike MED QC - Cl
Concentration ug/mL
540
520
500
480
460
440
420
400
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

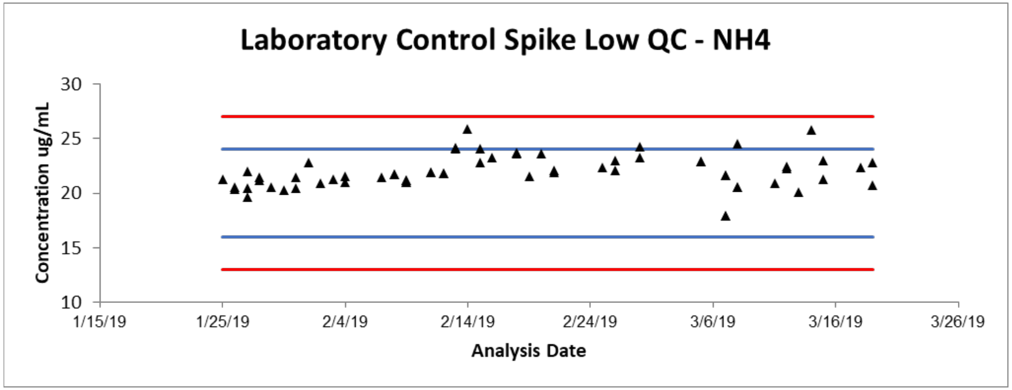

Laboratory Control Spike Med QC - SO4
Concentration ug/mL
3125
3025
2925
2825
2725
2625
2525
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

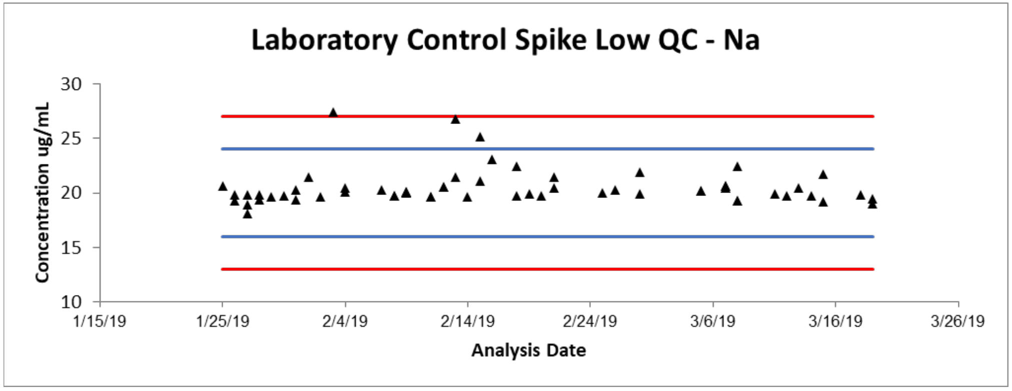

Laboratory Control Spike Med QC - NO3
Concentration ug/mL
1650
1600
1550
1500
1450
1400
1350
1300
1250
1200
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

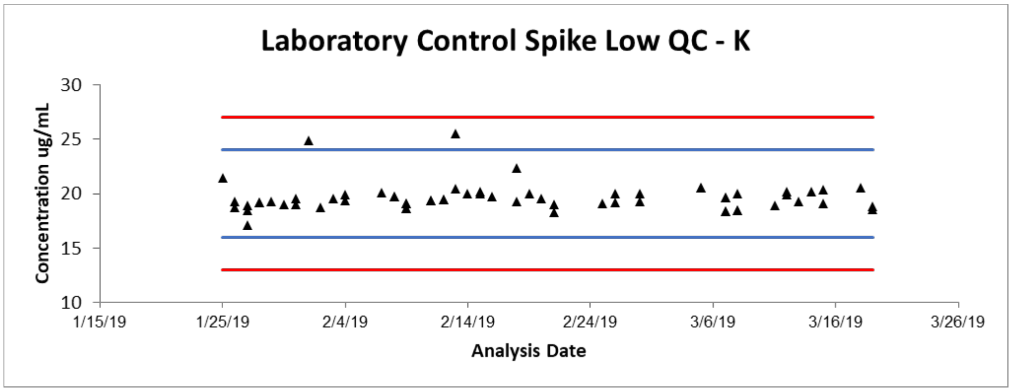

Laboratory Control Spike High QC - Cl
Concentration ug/mL
2190
2140
2090
2040
1990
1940
1890
1840
1790
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

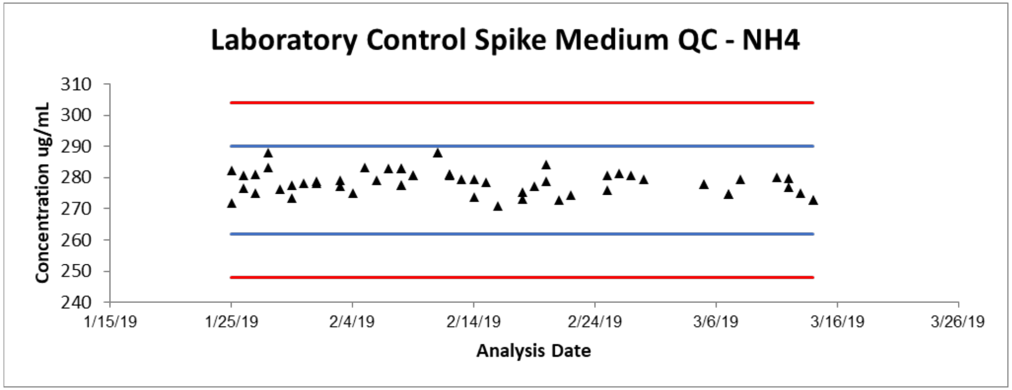

Laboratory Control Spike High QC - SO4
13290
12790
12290
11790
11290
10790
Concentration ug/mL
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

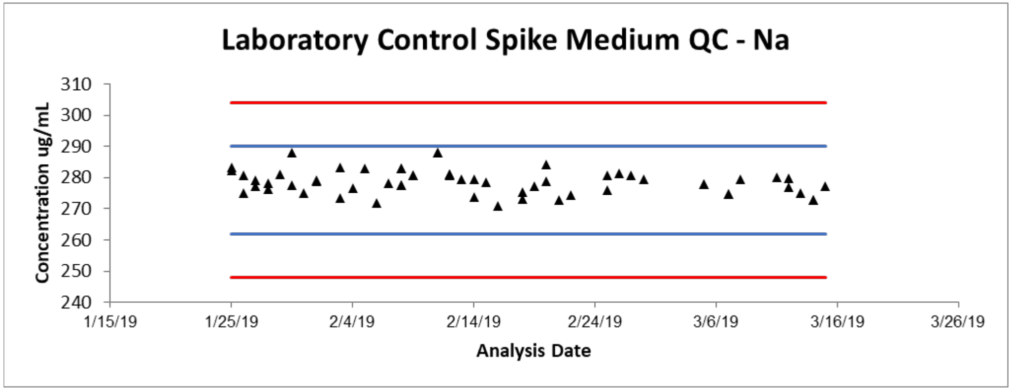

Laboratory Control Spike High QC - NO3
6590
6390
6190
5990
5790
5590
5390
Concentration ug/mL
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

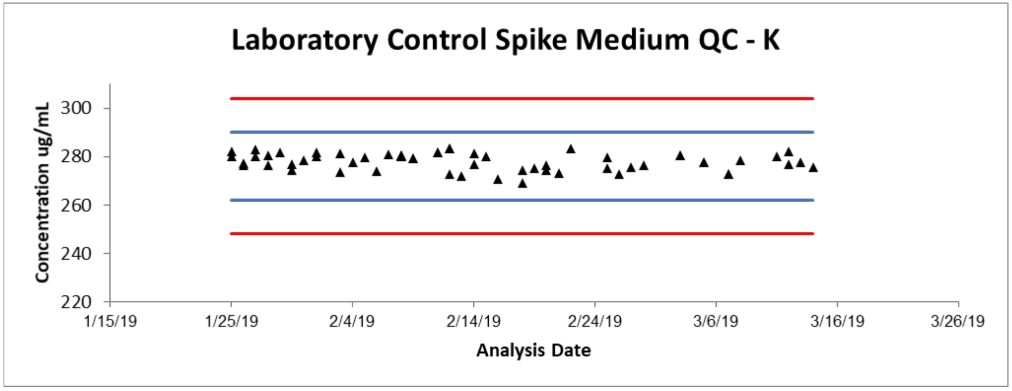

Laboratory Control Spike Low QC - NH4
30
25
20
15
10
Concentration ug/mL
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

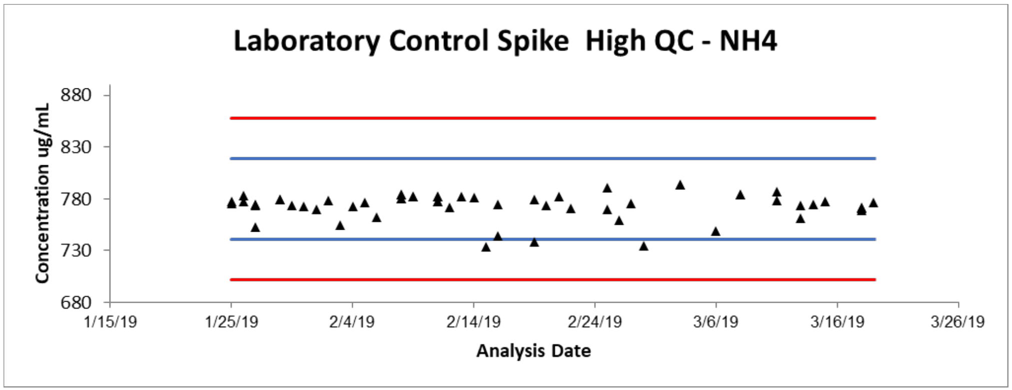

Laboratory Control Spike Low QC - Na
30
25
20
15
10
Concentration ug/mL
1/15/19
1/25/19
2/4/19
2/14/19
2/24/19
3/6/19
3/16/19
3/26/19
Analysis Date

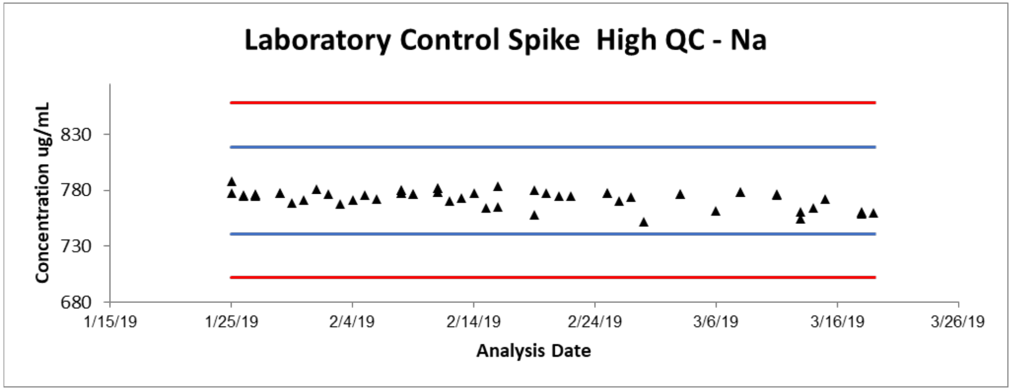

Laboratory Control Spike Low QC - K

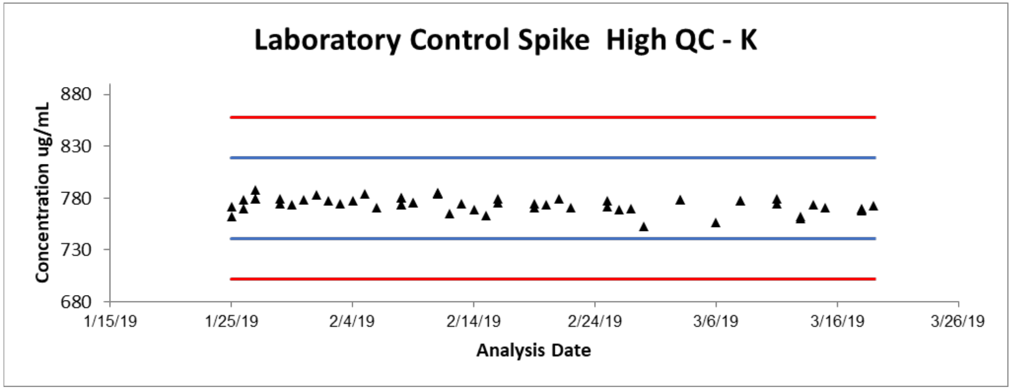

Laboratory Control Spike Medium QC - NH4


Laboratory Control Spike Medium QC - Na


Laboratory Control Spike Medium QC - K


Laboratory Control Spike High QC - NH4


Laboratory Control Spike High QC - Na


Laboratory Control Spike High QC - K

4.1.B.2.6 Round robin (USGS)

The RTI Ions Chromatography Laboratory participated in the National Atmospheric Deposition Program/Mercury Deposition Network Interlaboratory Comparison Program. The program is administered by the United States Geological Survey (USGS) Branch of Quality Systems. Four samples per month were sent to participating laboratories for analysis. A website reporting participant results is currently in development; a report for the 2018 results is available upon request.

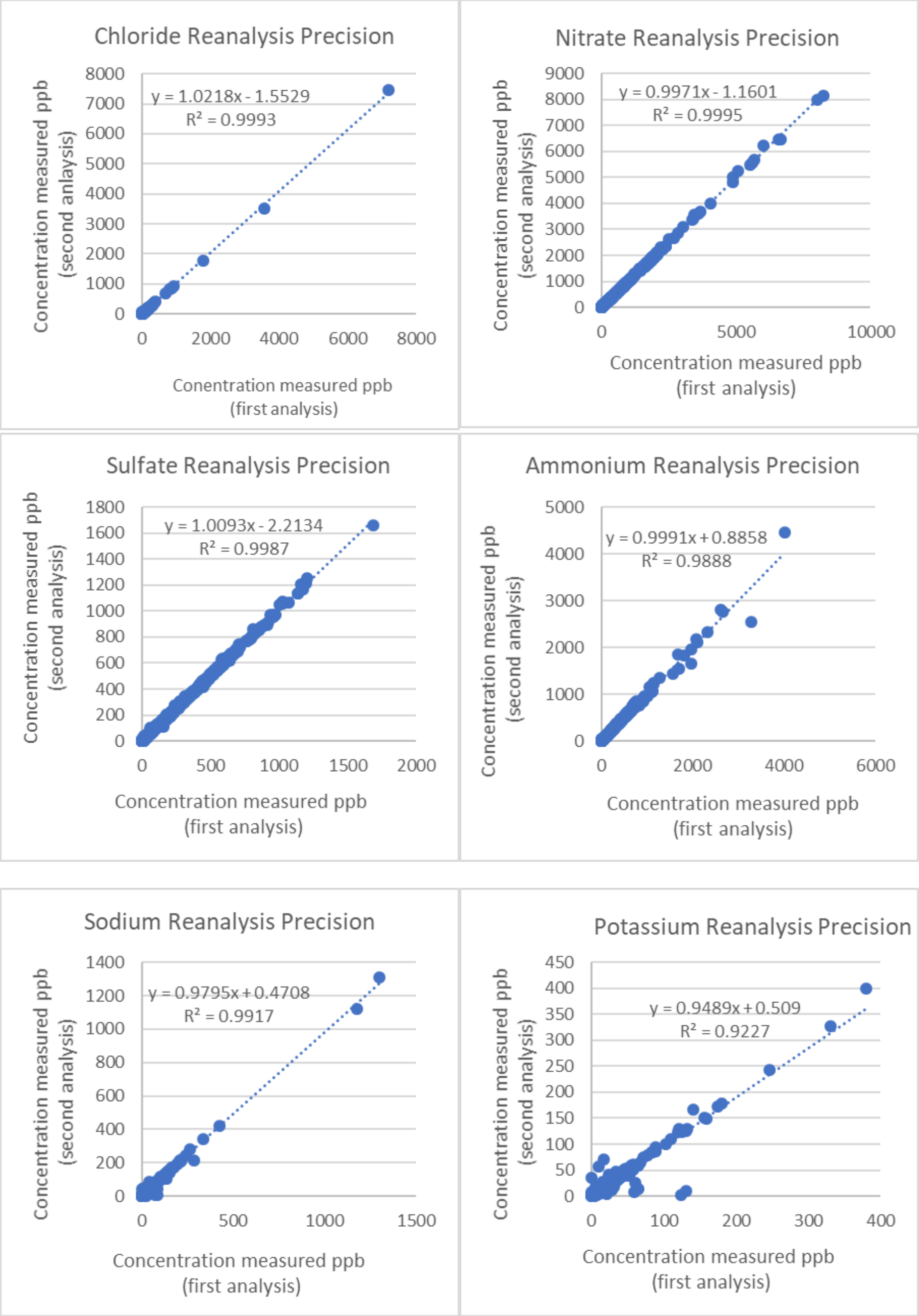
4.1.B.2.7 Reanalysis

Five percent of all samples are reanalyzed using different instruments and different calibration curves. Samples are flagged for reanalysis during analyst review of analytical results, and reasons include poorly integrated peaks and cases where one peak is significantly higher than the other peaks in the chromatograph (particularly for cations peaks, which elute very close together). In these cases, the sample may be diluted for reanalysis. Samples are also flagged if the QC criteria for reanalysis samples are not met. When more than one analysis within an analysis set fails to meet the QC criteria as outlined in Table 4.1.B-1, the whole set of samples is reanalyzed. The majority of reanalyzed samples are from QC criteria failure for background contamination from sodium, chloride, and/or potassium detected in either the original or reanalysis result. In cases where the entire set of samples were reanalyzed, background contamination did not propagate through the whole set.

During this reporting period there were cases of sodium, potassium, chloride, and sulfate contamination from the pre-cleaned filter caps used in the analysis vials. The problem was identified quickly and analysis data for impacted samples were not reported; these samples were reanalyzed using caps that were verified as clean. The faulty caps were from a new manufacturer batch, and the laboratory had a supply of clean filter caps from a previous batch that were used until a suitable replacement was found. The laboratory began purchasing and cleaning caps without a filter and found no background issues with these caps.

During this reporting period, there were 731 samples reanalyzed for anions and 752 samples reanalyzed for cations (Figure 4.1.B-8). At most, about 1.5% (10-11 samples) of the samples required edits (failed criteria for precision between the original and reanalysis result) for both sodium and chloride. In these cases, the reanalysis result was reported only for the ion with the poor precision. The failures were likely caused by contamination introduced during the analyses. The percentage was slightly higher for potassium, however most of the edits required were for samples flagged for reanalysis to check baseline level samples.

Figure 4.1.B-8: Ion reanalysis results for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018).



4.1.B.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.B.4 Audits, Performance Evaluations, Training, and Accreditations

4.1.B.4.1 System Audits

The prime contractor (UC Davis) did not conduct any audit of the RTI Ion Chromatography Laboratory during this reporting period.

4.1.B.4.2 Performance Evaluations

RTI performance was satisfactory in the Interlaboratory OAQPS 2018 Mega PE Speciation Event.

4.1.4.3 Training

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

4.1.4.4 Accreditations

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

4.1.B.5 Summary of Filter Field Blanks

Over the sampling period (October 1, 2018 through December 31, 2018) there were 420 valid nylon filter field blanks. Table 4.1-6a and Table 4.1-6b summarize the field blank statistics.

Table 4.1-6a: Nylon filter field blank statistics in µg/mL for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018).

Ions	Count	Median (µg/mL)	Average (µg/mL)	Min (µg/mL)	Max (µg/mL)	St. Dev. (µg/mL)
Cl^-	420	0.003	0.004	0.000	0.332	0.016
NO_3^-	420	0.004	0.017	0.000	3.661	0.179
SO_4^{2-}	420	0.001	0.006	0.000	0.953	0.047
Na^+	420	0.002	0.003	0.000	0.041	0.003
NH_4^+	420	0.003	0.013	0.000	2.335	0.114
K^+	420	0.001	0.004	0.000	0.369	0.019

Table 4.1-6b: Nylon filter field blank statistics in µg/filter (extraction volume 15 mL) for the analysis period 1/25/2019 through 3/26/2019 (samples collected 10/1/2018 through 12/31/2018).

Ions	Count	Median (µg/filter)	Average (µg/filter)	Min (µg/filter)	Max (µg/filter)	St. Dev. (µg/filter)
Cl^-	420	0.080	0.107	0.000	8.308	0.403
NO_3^-	420	0.092	0.428	0.000	91.517	4.469
SO_4^{2-}	420	0.022	0.157	0.000	23.837	1.184
Na^+	420	0.058	0.075	0.000	1.024	0.084
NH_4^+	420	0.067	0.315	0.000	58.385	2.857
K^+	420	0.017	0.103	0.000	9.217	0.470

4.2 UC Davis X-Ray Fluorescence Laboratory

The UC Davis X-Ray Fluorescence Laboratory received and analyzed PTFE filters from batches 39 through 50, which includes samples collected January 1, 2018 through December 31, 2018. UC Davis performed analysis for 33 elements using energy dispersive X-ray fluorescence (EDXRF) instruments. These analyses were performed during an analysis period from March 23, 2018 through April, 26, 2019. Three EDXRF instruments, XRF-1, XRF-4, and XRF-5 performed all of the analyses during this period; see Table 4.2-1 for details.

Table 4.2-1: Sampling dates and corresponding EDXRF analysis dates during this reporting period. Analysis dates include reanalysis – as requested during QA Level 1 validation – of any samples within the sampling year and month.

Sampling Year	Sampling Month	XRF-1 Analysis Dates	XRF-4 Analysis Dates	XRF-5 Analysis Dates
2018	January	3/23/2018 – 4/17/2018	3/23/2018 – 4/16/2018	N/A
2018	February	4/16/2018 – 5/12/2018	4/16/2018 – 5/12/2018	N/A
2018	March	5/12/2018 – 6/14/2018	5/13/2018 – 6/12/2018	N/A
2018	April	6/13/2018 – 7/27/2018	6/19/2018 – 7/23/2018	N/A
2018	May	7/19/2018 – 9/12/2018	7/23/2018 – 8/30/2018	N/A
2018	June	8/20/2018 – 10/4/2018	8/17/2018 – 9/14/2018	N/A
2018	July	9/15/2018 – 10/18/2018	9/14/2018 – 10/19/2018	N/A
2018	August	10/18/2018 – 11/15/2018	10/19/2018 – 11/15/2018	N/A
2018	September	11/15/2018 – 12/18/2018	11/15/2018 – 12/17/2018	N/A
2018	October	12/29/2018 – 1/20/2019	12/29/2018 – 1/20/2019	12/26/2018 – 1/24/2019
2018	November	1/20/2019 – 2/6/2019	1/20/2019 – 2/19/2019	1/24/2019 – 2/19/2019
2018	December	3/27/2019 – 4/2/2019	2/19/2019 – 3/31/2019	2/19/2019 – 4/26/2019
2018	All Months	3/23/2018 – 4/2/2019	3/23/2018 – 3/31/2019	12/26/2018 – 4/26/2019

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: UC Davis quality control measures for element 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 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	- 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 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	
Reanalysis samples	Monthly	z-score between ±1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	
SRM 2783	Monthly	Bias between ±1 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 instrument 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 using a set of reanalysis filters which are reanalyzed monthly on each instrument. Long-term reproducibility is monitored using the reanalysis filters and by analyzing a NIST SRM 2783 standard monthly and comparing the EDXRF error from the certified/reference mass loadings to acceptance limits.

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, which 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.

Random occasional zinc contamination was observed on QC filters for XRF-1, XRF-4, and XRF-5. This sporadic zinc contamination appears to be related to the design of the instrument and is unavoidable. Samples analyzed during this period were monitored closely for any contamination and were reanalyzed if there was any question of contamination. The reported data are not impacted. See Section 2.3.2, Section 3.2.1.1, and Section 4.2.2.1 for further detail.

XRF-1, XRF-4, and XRF-5 also exhibited some failures of the acceptance criteria for all QC checks of Ca. Investigation is ongoing, but initial findings suggest that gradual increase in Ca concentrations on QC filters might be caused by environmental deposition during extended residence in the instruments. Samples are only exposed to the environment for a day or two during routine analysis, thus are not susceptible to gradual Ca contamination. However, samples are carefully monitored for atypical and abrupt calcium contamination events and reanalyzed as necessary. The reported data are not impacted. See Section 2.3.3, Section 3.2.1.2, and Section 4.2.2.1 for further detail.

In addition to the QC results above, the conditions under which the elements are analyzed by EDXRF (e.g. secondary targets and integration times) were changed during the annual calibration of all EDXRF systems in December 2018. These changes were made to help reduce variability, detection limits, and bias in some elements. See Section 2.3.1 and Section 4.2.2.5 for further details.

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 4.2-1a and Figure 4.2-1b show the results of daily analyses of laboratory blanks for each instrument. The acceptance limits shift in late December 2018 because of changes made to the XRF applications, (see Section 4.2.2.5 for details). The application changes included modification of the deconvolution parameters effecting the background in the spectra that necessitated the changes in the blank acceptance limits. 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 filters are checked to determine if the problem is instrumental or strictly contamination of a blank. Sample analysis results are reviewed during QA Level 1 validation (*UCD CSN TI 801C*), and elements associated with occasional contamination (Zn and Ca; see Section 2.3.2, Section 2.3.3, Section 3.2.1.1, and Section 3.2.1.2) are monitored closely. When contamination is suspected, filters are reanalyzed and the reanalysis result is reported if contamination was present in the original analysis. A total of nine samples from 2018 were reanalyzed for suspected Zn contamination (three from XRF-1, six from XRF-4, and none from XRF-5). Of those, one was found to have Zn contamination and the reanalysis result was reported. For the rest the original valid result was reported. One sample was reanalyzed for suspected Ca contamination (from XRF-5). The sample was found to have no Ca contamination and the original valid result was reported.

Both XRF-1 and XRF-4 had sporadic elevated measurements of Zn on laboratory blanks throughout the analysis period (as discussed in Section 2.3.2 and Section 3.2.1.1). These elevated levels were not measured over consecutive days thus did not fail the acceptance criteria; however, these occurrences are monitored closely. Zn contamination likely comes from wear on the sample changer; Zn is a common contaminant in elemental analysis systems.

XRF-1, XRF-4, and XRF-5 all show gradual increases in Ca (as discussed in Section 2.2.3 and Section 3.2.1.2), which is reduced immediately after the blank filter is changed. This indicates contamination of the blank filter likely from atmospheric deposition and/or instrument wear. The cause of Ca increases on QC filters with long, multi-day residences in the instrument is being investigated.

Lastly, Cl had few exceedances on XRF-1 and XRF-4 instruments during the analysis period. For the larger exceedances, laboratory blanks were replaced which corrected the exceedance; for others the signal decreased without correction. The cause of the Cl exceedances is unknown; as a volatile element, Cl has a highly variable signal from QC filters. These exceedances are caused by variability in the Cl measurement, not contamination in the EDXRF instruments.

Figure 4.2-1a: Results of daily analyzed PTFE laboratory blanks for the analysis period 3/23/2018 through 4/26/2019 (samples collected 1/1/2018 through 12/31/2018). Elements Na through Zn shown. Acceptance limits were recalculated for the December 2018 calibrations resulting in the shifts seen in the plots, see text for details.

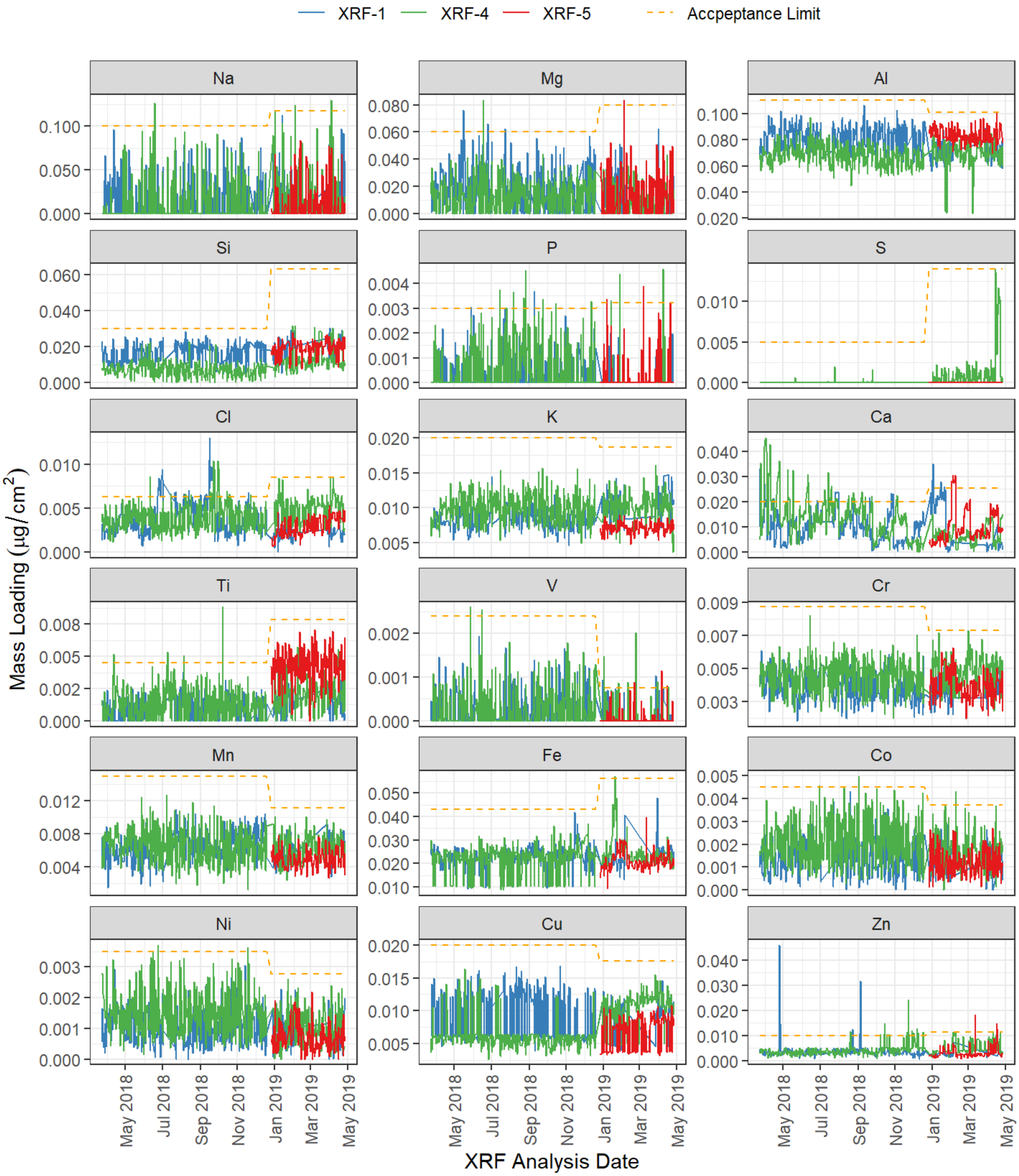
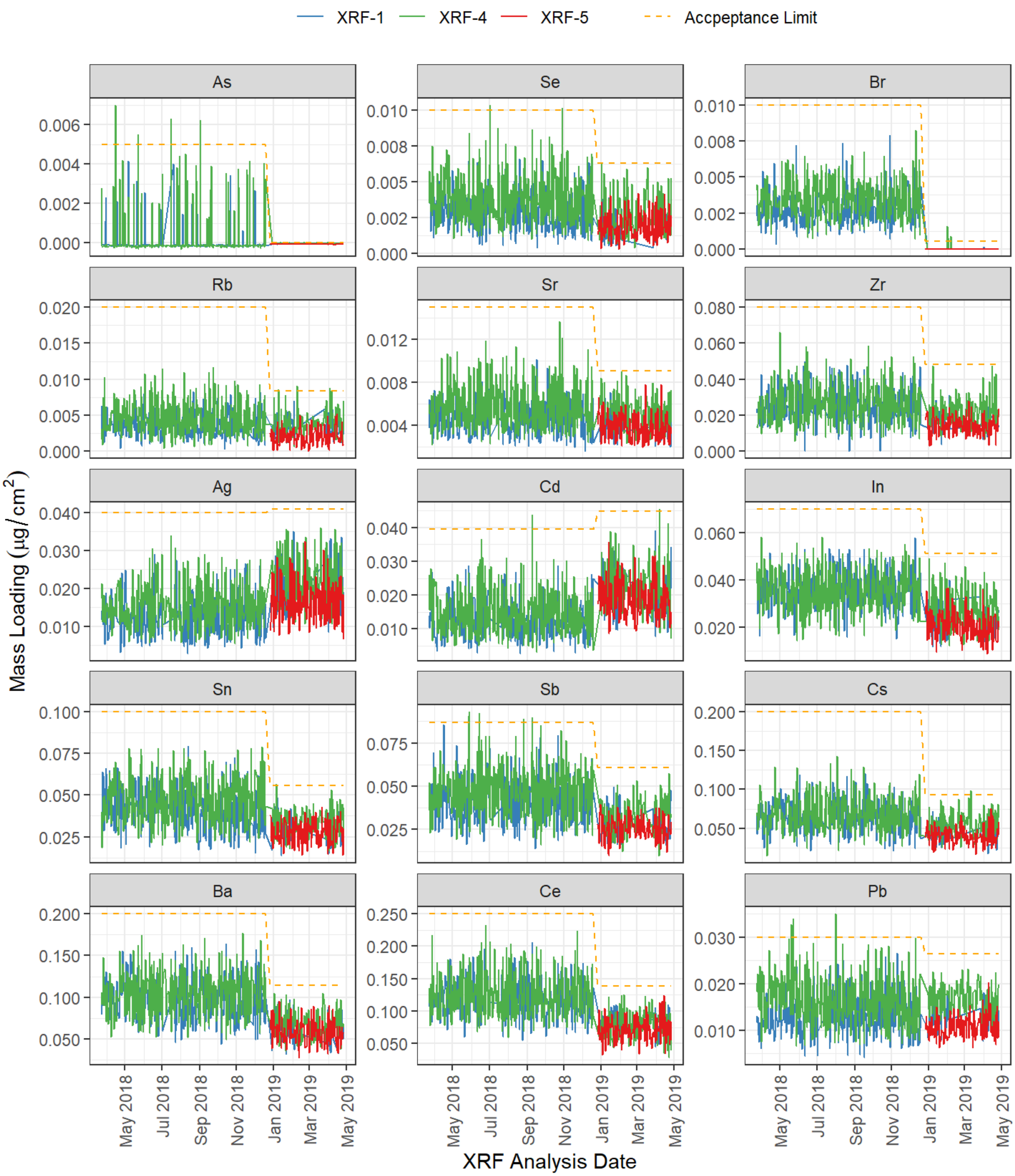


Figure 4.2-1b: Results of daily analyzed PTFE laboratory blanks for the analysis period 3/23/2018 through 4/26/2019 (samples collected 1/1/2018 through 12/31/2018). Elements As through Pb shown. Acceptance limits were recalculated for the December 2018 calibrations resulting in the shifts seen in the plots, see text for details.



Daily operational performance of the instruments is monitored by a multi-element reference material (ME-RM). Each instrument had its own daily ME-RM produced by UC Davis. The acceptance limits are set to +/- 10% RSD of the reference values for the relevant elements, as listed in Table 4.2-2. When more than two consecutive measurements exceed these limits, the results are marked unacceptable. Corrective actions for unacceptable QC results include checking the sample for damage or contamination, checking the results for the affected element on other QC samples, cross-instrumental testing if necessary to determine if the unacceptable result is due to the instrument or the QC sample, and further investigations as necessary. Sample analysis is halted or samples analyzed after the unacceptable QC result are noted for possible reanalysis depending on the outcome of the investigation. When a problem with the instrument is found the affected samples are reanalyzed on a different instrument or the same instrument after the issue is corrected and once it has been demonstrated to be within control again. QC samples which have been found to be damaged or contaminated will be replaced (*UCD CSN TI 302D*).

Tables 4.2-3, 4.2-4, and 4.2-5 show the results of the UC Davis ME-RMs. The UC Davis ME-RM QC samples were replaced in December 2018 (at time of calibrations). The new QC samples have different mass loadings relative to those previously used. Si, Ti, Cu, and Pb have lower loadings which may result in a higher number of exceedances relative to previously reported QC results. A small number of criteria exceedances are expected statistically, but not more than a few percent of the total number of measurements. Investigations of other QC filters and laboratory blanks following these exceedances did not show any contamination or instrumental issues, so no corrective actions were taken. Unacceptable QC results for Ca and Zn are expected to be from the same source as discussed for laboratory blank contamination (see Section 2.3.2, Section 2.3.3, Section 3.2.1.1, and Section 3.2.1.2). The laboratory blanks were replaced when contamination occurred; however, the ME-RM samples were not replaced in response to contamination.

Table 4.2-3: Descriptive statistics of XRF-1 results (µg/cm^2) of the daily UC Davis ME-RM for the analysis period 3/23/2018 through 4/26/2019 (see Table 4.2-1 for corresponding sampling dates), N = 540.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.918	1.724	2.107	0.0	0	1.7
Si	1.786	1.605	1.961	0.0	0	1.5
S	13.726	12.426	15.188	0.0	0	0.7
K	2.008	1.813	2.216	0.0	0	0.7
Ca	2.129	1.884	2.303	0.0	0	2.0
Ti	0.094	0.082	0.100	4.3	0	4.5
Cr	0.816	0.735	0.899	0.0	0	0.8
Mn	0.403	0.362	0.442	0.0	0	1.7
Fe	2.283	2.039	2.492	0.0	0	0.8
Ni	0.141	0.128	0.156	0.0	0	2.1
Cu	0.428	0.383	0.469	0.0	0	1.3
Zn	0.361	0.319	0.390	0.2	0	1.6
Pb	0.364	0.327	0.400	3.5	0	4.8

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

Table 4.2-4: Descriptive statistics of XRF-4 results (µg/cm^2) of the daily UC Davis ME-RM for the analysis period 3/23/2018 through 4/26/2019 (see Table 4.2-1 for corresponding sampling dates), N = 667.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.656	1.488	1.818	0	0	2.3
Si	1.923	1.741	2.128	0.3	0	2.3
S	13.536	12.239	14.959	0	0	0.6
K	1.987	1.797	2.196	0	0	0.5
Ca	2.171	1.955	2.390	10.0	5.8	2.9
Ti	0.098	0.089	0.108	1.6	0	4.4
Cr	0.822	0.744	0.910	0	0	0.7
Mn	0.401	0.363	0.443	0	0	1.8
Fe	2.263	2.034	2.486	0	0	0.9
Ni	0.143	0.129	0.157	0	0	2.0
Cu	0.426	0.386	0.472	0	0	1.3
Zn	0.356	0.313	0.383	2.4	0.4	3.4
Pb	0.358	0.327	0.400	5.5	0	5.6

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

Table 4.2-5: Descriptive statistics of XRF-5 results (µg/cm^2) of the daily UC Davis ME-RM for the analysis period 12/25/2018 through 4/26/2019 (see Table 4.2-1 for corresponding sampling dates), N = 143.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	2.233	1.988	2.430	0	0	1.4
Si	0.750	0.644	0.787	0	0	2.2
S	16.603	14.852	18.153	0	0	0.5
K	2.370	2.132	2.606	0	0	0.3
Ca	2.267	2.022	2.471	0	0	0.8
Ti	0.053	0.0463	0.566	9.8	2.1	4.9
Cr	0.954	0.855	1.045	0	0	0.6
Mn	0.469	0.418	0.511	0	0	1.5
Fe	2.602	2.330	2.848	0	0	0.6
Ni	0.166	0.150	0.183	0	0	1.5
Cu	0.337	0.302	0.370	0	0	1.2
Zn	0.357	0.319	0.390	0	0	1.3
Pb	0.076	0.068	0.083	17.5	2.1	7.8

Limits are +/- 10% of the reference loading (see *UCD CSN 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 weekly ME-RM was replaced in December 2018. Weekly results are compared to acceptance limits of +/- 10% of the reference values for the relevant elements, as listed in Table 4.2-2. When more than two consecutive measurements exceed these limits, the results are marked unacceptable. Corrective actions for unacceptable results are described in section 4.2.2.1 and can be found in the UCD XRF SOP and Technical Instructions (*UCD CSN TI 302D*). A weekly QC report is generated internally, which includes checks of the laboratory blanks and the daily and weekly ME-RMs.

Table 4.2-6, Table 4.2.7, and Table 4.2-8 show the EDXRF statistics of the weekly UC Davis ME-RM run until March 2019.

Table 4.2-6: Descriptive statistics of XRF-1 results (µg/cm^2) of the weekly UC Davis ME-RM for the analysis period 3/28/2018 through 1/25/2019 (see Table 4.2-1 for corresponding sampling dates), N = 41.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.574	1.403	1.715	0	0	3.4
Si	2.597	2.313	2.828	0	0	1.8
S	9.692	8.632	10.551	0	0	0.8
K	1.483	1.316	1.608	0	0	0.7
Ca	1.618	1.426	1.743	0	0	1.8
Ti	0.121	0.106	0.130	0	0	2.8
Cr	0.604	0.537	0.658	0	0	0.8
Mn	0.291	0.258	0.315	0	0	2.1
Fe	1.667	1.479	1.807	0	0	1.1
Ni	0.100	0.089	0.109	0	0	2.7
Cu	0.287	0.257	0.314	0	0	1.3
Zn	0.233	0.203	0.249	4.9	0	3.7
Pb	0.537	0.486	0.594	0	0	2.2

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

Table 4.2-7: Descriptive statistics of XRF-4 results (µg/cm^2) of the weekly UC Davis ME-RM for the analysis period 3/23/2018 through 3/5/2019 (see Table 4.2-1 for corresponding sampling dates), N = 47.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.388	1.242	1.518	0	0	3.7
Si	2.629	2.358	2.881	0	0	2.4
S	9.640	8.664	10.589	0	0	1.2
K	1.460	1.312	1.603	0	0	0.7
Ca	1.600	1.436	1.755	0	0	2.2
Ti	0.123	0.108	0.132	0	0	3.5
Cr	0.603	0.541	0.661	0	0	0.8
Mn	0.287	0.259	0.317	0	0	2.4
Fe	1.626	1.459	1.783	0	0	1.0
Ni	0.100	0.089	0.109	0	0	2.6
Cu	0.286	0.258	0.315	0	0	1.7
Zn	0.231	0.203	0.249	2.1	0	3.9
Pb	0.542	0.484	0.592	0	0	3.0

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

Table 4.2-8: Descriptive statistics of XRF-5 results (µg/cm^2) of the weekly UC Davis ME-RM for the analysis period 1/3/2019 through 2/28/2019 (see Table 4.2-1 for corresponding sampling dates), N = 9.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.465	1.319	1.612	0	0	1.3
Si	2.675	2.410	2.946	0	0	1.1
S	9.598	8.648	10.570	0	0	0.6
K	1.475	1.329	1.625	0	0	0.3
Ca	1.616	1.455	1.779	0	0	0.9
Ti	0.123	0.112	0.136	0	0	2.8
Cr	0.605	0.544	0.665	0	0	0.6
Mn	0.291	0.263	0.321	0	0	1.4
Fe	1.645	1.481	1.810	0	0	0.5
Ni	0.100	0.090	0.110	0	0	2.4
Cu	0.290	0.261	0.319	0	0	1.1
Zn	0.241	0.217	0.265	0	0	1.2
Pb	0.549	0.496	0.606	0	0	1.7

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

Table 4.2-9, Table 4.2-10, and Table 4.2-11 show results of the new weekly UC Davis ME-RM, used beginning March 2019.

Table 4.2-9: Descriptive statistics of XRF-1 results (µg/cm^2) of the new weekly UC Davis ME-RM for the analysis period 4/4/2019 through 4/23/2019 (see Table 4.2-1 for corresponding sampling dates), N = 2).

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.196	1.075	1.313	0	0	0.4
Si	1.153	1.037	1.268	0	0	0.6
S	9.635	8.672	10.599	0	0	0.1
K	1.289	1.160	1.418	0	0	0.4
Ca	1.161	1.045	1.277	0	0	0.6
Ti	0.049	0.044	0.054	0	0	13.9
Cr	0.461	0.415	0.508	0	0	0.4
Mn	0.236	0.212	0.260	0	0	0.8
Fe	1.290	1.161	1.419	0	0	1.2
Ni	0.085	0.077	0.094	0	0	1.2
Cu	0.353	0.318	0.388	0	0	0.5
Zn	0.352	0.317	0.388	0	0	0.5
Pb	0.227	0.205	0.250	0	0	1.3

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

Table 4.2-10: Descriptive statistics of XRF-4 results (μg/cm^2) of the new weekly UC Davis ME-RM for the analysis period 3/7/2019 through 4/24/2019 (see Table 4.2-1 for corresponding sampling dates), N = 8.

Element	Average	Lower Limit	Upper Limit	%Exceedance	% Unacceptable	RSD %
Al	1.027	0.917	1.120	0	0	3.8
Si	1.189	1.067	1.304	0	0	2.7
S	9.600	8.599	10.510	0	0	1.0
K	1.300	1.166	1.425	0	0	0.9
Ca	1.167	1.044	1.277	0	0	1.3
Ti	0.048	0.040	0.049	25	0	13.0
Cr	0.464	0.416	0.509	0	0	1.0
Mn	0.240	0.216	0.264	0	0	1.1
Fe	1.282	1.149	1.405	0	0	0.9
Ni	0.083	0.076	0.092	0	0	2.4
Cu	0.352	0.315	0.385	0	0	1.3
Zn	0.344	0.309	0.378	0	0	0.9
Pb	0.249	0.223	0.273	0	0	3.5

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

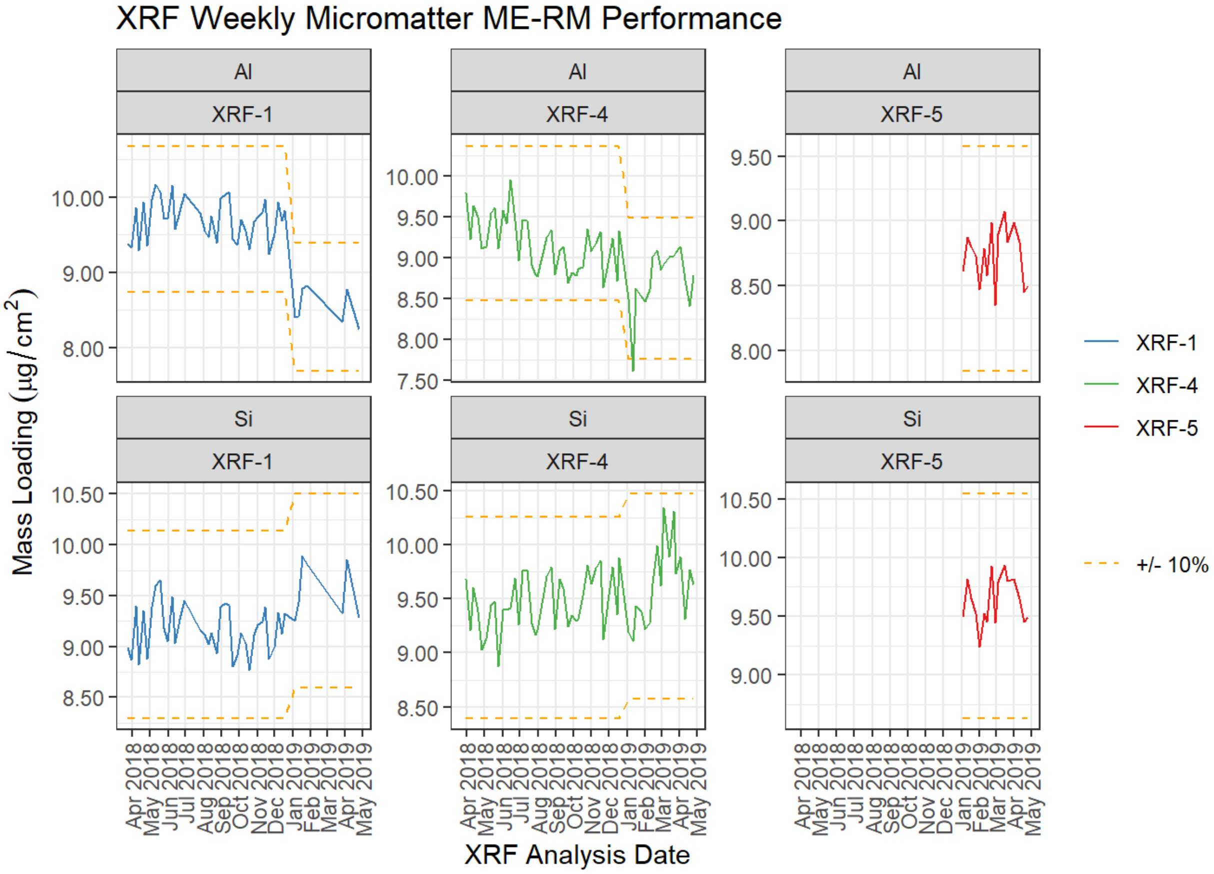
Table 4.2-11: Descriptive statistics of XRF-5 results (μg/cm^2) of the new weekly UC Davis ME-RM for the analysis period 3/6/2019 through 4/24/2019 (see Table 4.2-1 for corresponding sampling dates), N = 8.

Element	Average	Lower Limit	Upper Limit	%Exceedance	% Unacceptable	RSD %
Al	1.209	1.094	1.337	0	0	1.5
Si	1.117	0.997	1.219	0	0	1.7
S	9.514	8.581	10.487	0	0	0.8
K	1.266	1.141	1.384	0	0	0.4
Ca	1.119	1.005	1.228	0	0	0.8
Ti	0.056	0.052	0.063	0	0	6.1
Cr	0.459	0.413	0.505	0	0	0.6
Mn	0.233	0.210	0.256	0	0	2.2
Fe	1.271	1.146	1.400	0	0	0.9
Ni	0.080	0.071	0.087	0	0	3.2
Cu	0.350	0.34	0.384	0	0	0.9
Zn	0.344	0.309	0.378	0	0	0.7
Pb	0.226	0.203	0.249	0	0	3.6

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

A Micromatter ME-RM containing Al and Si is also analyzed weekly. The results from these analyses 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 EDXRF, thus a shift in the reference value is usually observed when the instrument is recalibrated. The large shift in the XRF-4 reference value corresponds with changes made to the EDXRF measurement conditions in an effort to reduce the inter-instrument bias (see Section 2.3.1 and Section 4.2.2.5 for further details). No issues were observed other than one drop in Al on XRF-4. However, no other QC checks for Al showed any issue with the instrument during this time and the next measurement returned to acceptable levels, thus no corrective actions were taken.

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, with the same sample analyzed by all 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. As mentioned in Section 4.2.2.2, the UC Davis weekly ME-RM was replaced in March 2019. The following approach is used to quantify the differences observed in the plots. A reference value for the weekly ME-RM is calculated by the mean of all three instrument results:

$$Ref_i = \frac{1}{N}\left(\sum XRF1_i + \sum XRF4_i + \sum XRF5_i\right),$$

where $XRF1_i$, $XRF4_i$, and $XRF5_i$ are the mass loadings of the i^{th} element measured by each instrument and N is the total number of results of all instruments.

For each element, i, the bias of each instrument is estimated as the mean relative error from the reference,

$$error = d_{i,j} = \frac{XRF_{i,j} - Ref_i}{Ref_i},$$

$$Bias_i = \frac{1}{n}\sum_{j=1}^{n} d_{i,j}$$
,

where n is the number of measurements, j, made of the weekly ME-RM by the EDXRF instrument over the analysis period.

The precision is estimated by,

$$Precision_i = \sqrt{\frac{n\sum_{j=1}^{n} d_{i,j}^2 - \left(\sum_{j=1}^{n} d_{i,j}\right)^2}{n(n-1)}}$$

The results from this analysis, for the elements listed for the weekly ME-RM in Table 4.2-2, averaged over both UC Davis ME-RM samples used during the analysis period, are presented in Table 4.2-12. Boxplots of the mass loading results from the instruments are presented in figures 4.2-3 and 4.2-4 for each weekly ME-RM sample.

Table 4.2-12: Precision and bias of all EDXRF instruments from the weekly UC Davis ME-RM calculated for the analysis period 3/23/2018 through 4/24/2019 (see Table 4.2-1 for corresponding sampling dates). Only elements listed in Table 4.2-2 for the weekly UC ME-RM are evaluated.

Element	XRF-1 Bias %	XRF-4 Bias %	XRF-5 Bias %	XRF-1 Precision %	XRF-4 Precision %	XRF-5 Precision %
Al	6.4	-7.3	3.4	2.0	3.5	1.5
Si	-0.4	1.7	-0.5	1.2	2.6	1.4
S	0.5	0.1	-0.6	0.5	1.1	0.7
K	0.6	0.3	-0.6	0.6	0.8	0.4
Ca	1.0	0.7	-0.9	1.2	1.8	0.8
Ti	-3.1	-3.6	4.8	7.9	7.8	4.7
V	-0.1	0.6	-2.0	1.8	1.8	1.9
Cr	0.0	0.2	-0.2	0.6	0.9	0.6
Mn	0.2	0.5	-0.5	1.5	1.8	1.8
Fe	1.1	-0.4	-0.3	1.1	1.0	0.7
Ni	2.2	0.8	-1.4	2.0	2.5	2.7
Cu	0.3	0.0	0.4	0.9	1.5	1.0
Zn	1.1	-0.5	1.5	2.4	2.4	1.0
Pb	-2.2	3.3	-1.3	1.7	3.3	2.6

Figure 4.2-3: Instrumental comparison using the weekly UC Davis ME-RM. Bias shown in plot labels is the maximum of the three instruments. XRF-1: 3/28/2018 to 1/25/2019, N = 41. XRF-4: 3/23/2018 through 3/5/2019, N = 47. XRF-5: 1/3/2019 through 2/28/2019, N = 9. (See Table 4.2-1 for corresponding sampling dates.)

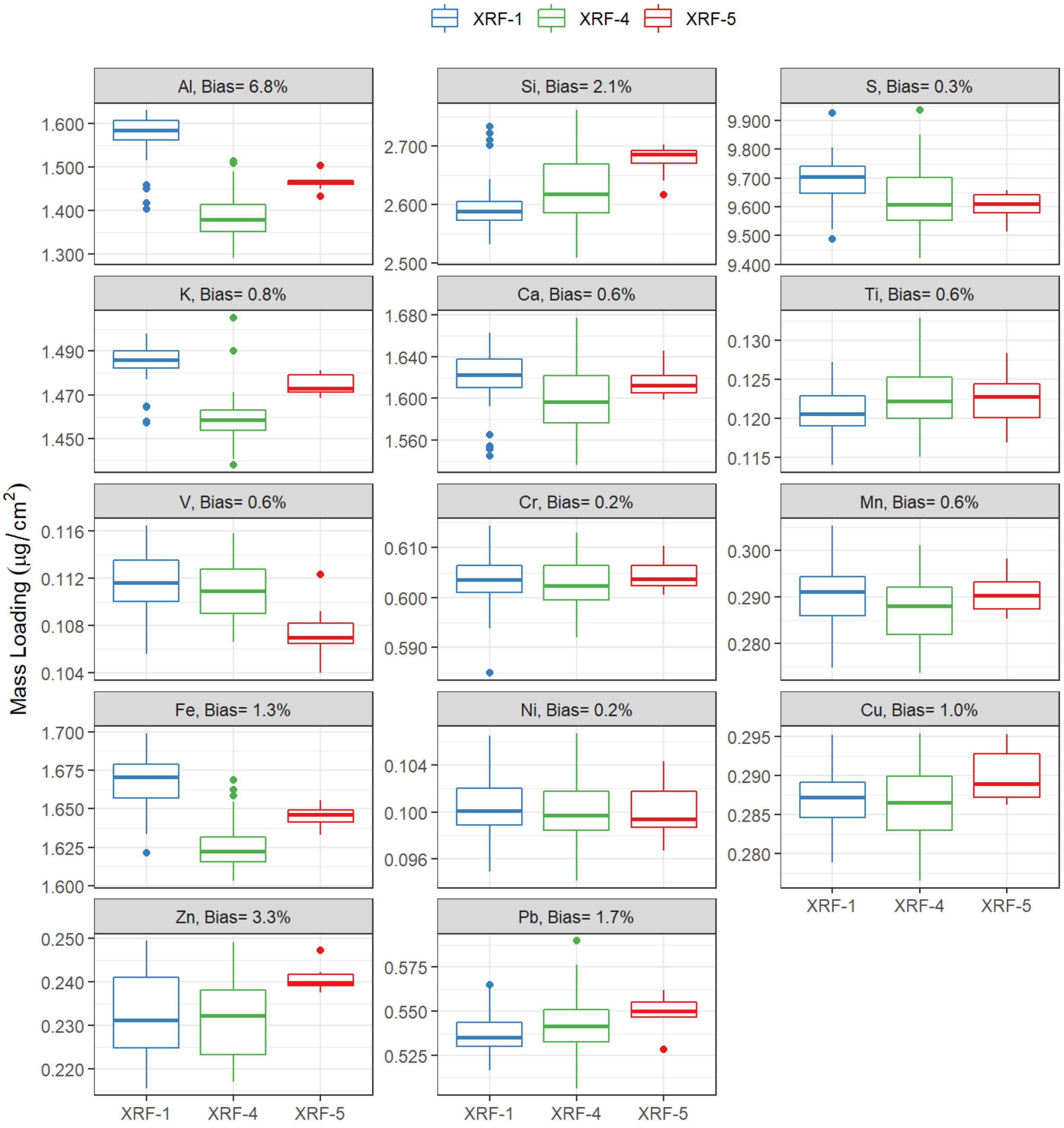
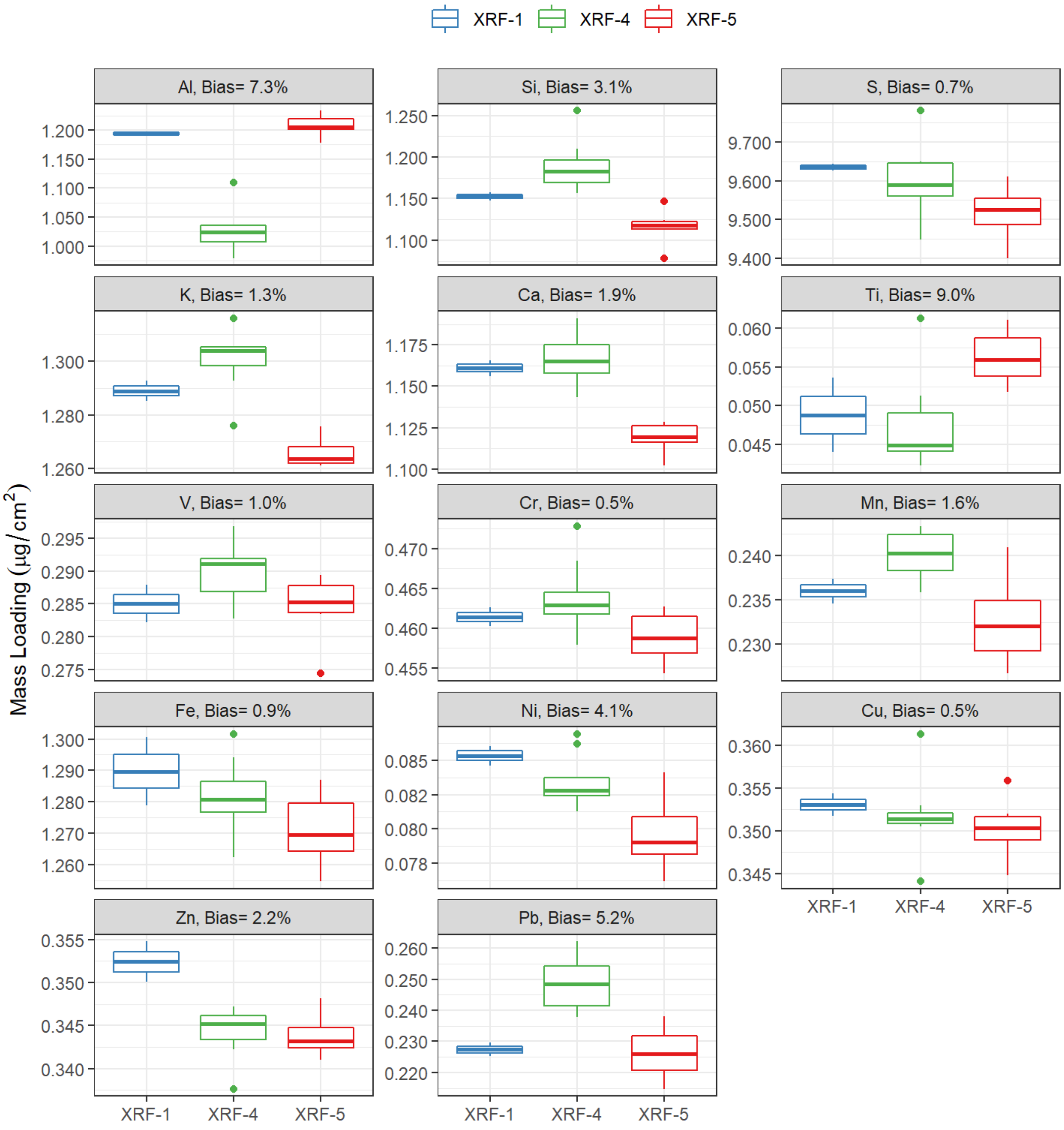


Figure 4.2-4: Instrumental comparison using the new weekly UC Davis ME-RM. Bias shown in plot labels is the maximum of the three instruments. XRF-1: 4/4/2019 to 4/23/2019, N = 2. XRF-4: 3/7/2019 through 4/24/2019, N = 8. XRF-5: 3/6/2019 through 4/24/2019, N = 8. (See Table 4.2-1 for corresponding sampling dates.)



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

A set of filters are reanalyzed monthly to monitor the long-term instrument performance; the set was changed once during 2018. For analyses performed through May 2018, the set consisted of 16 CSN samples and one UC Davis produced ME-RM. The samples were on MTL 47 mm PTFE filters and covered a range of mass loadings representative of the CSN. The second set of 16 filters, used beginning June 2018, were UC Davis ME-RMs and covered a range of mass loadings simulating the CSN and higher for trace elements. 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

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

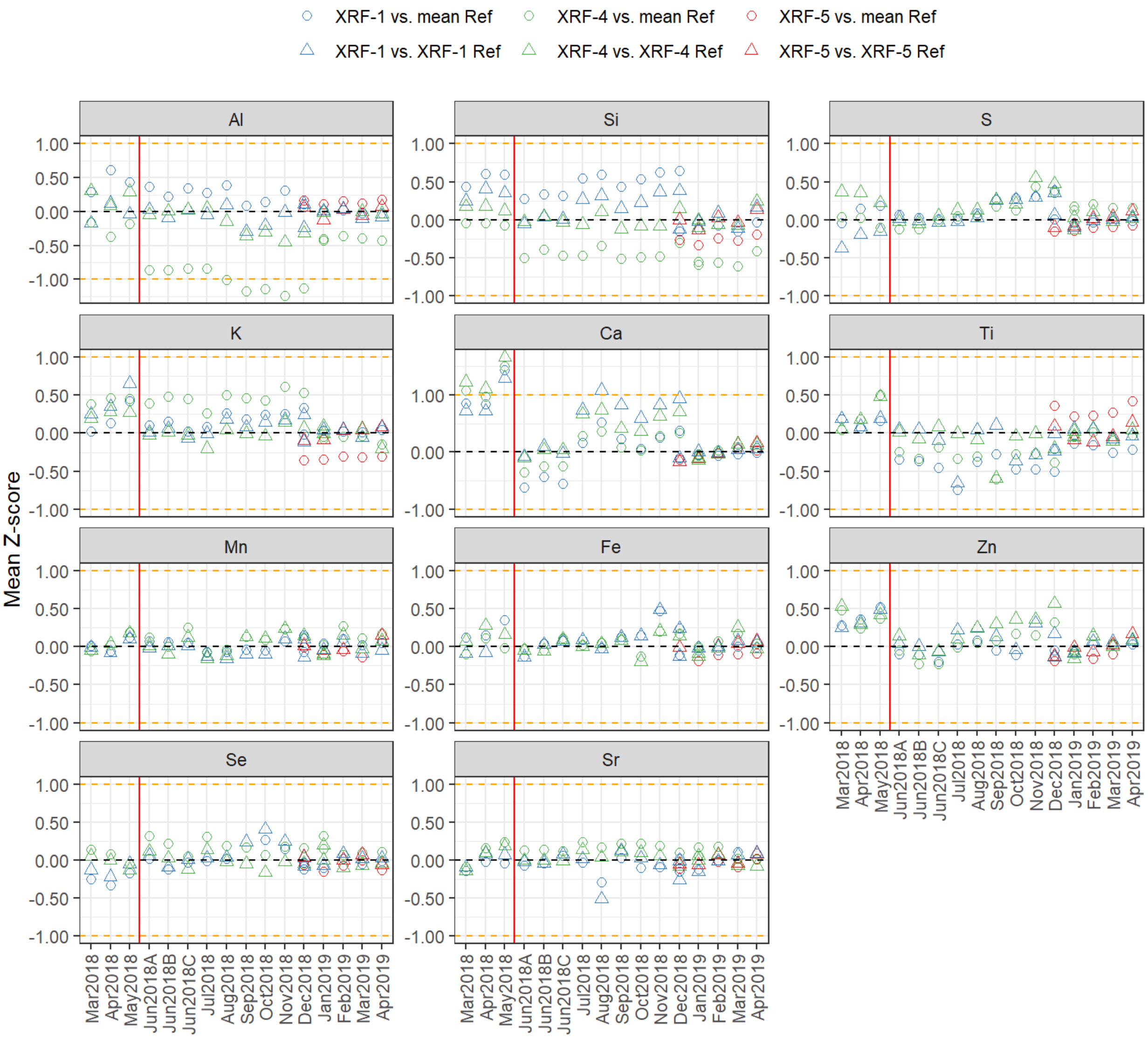
where X_{ij} is that month's result, $\widehat{x_{ij}}$ is the reference value for element *i* in filter *j*, and U_{xij} and $U(\widehat{x_{ij}})$ are the uncertainty of that month's result and the reference uncertainty respectively. The instrument-specific reference values for the samples of the reanalysis 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

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

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, and (2) the other reference value is based on the average response from all 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. Issues observed include increasing mean z-scores for Ca on XRF-1 and XRF-4 instruments and low XRF-4 mean z-scores for Al. The increasing Ca z-scores relate to the previously mentioned Ca contamination on QC filters (see Section 2.3.3, Section 3.2.1.2, Section 4.2.2.1), and are observed on both sets of reanalysis filters, occasionally resulting in acceptance criteria exceedances. The XRF-4 low mean z-score for Al is from bias between the XRF-4 and XRF-1 Al values (Table 4.2-9), which drives the XRF-4 mean z-score down with respect to the mean reference. However, the XRF-4 mean z-score with respect to its own reference remains constant with only a slight decrease in September 2018. This indicates the low z-score values are from an inherent bias in the XRF-4 Al measurement, and are not indicative of instrument change during the analysis period. Changes were made in the December 2018 calibration to the EDXRF analysis protocols to reduce the inter-instrument bias and this can be seen in the improved z-score values beginning in January 2019. The reference values for the reanalysis samples were also recalculated in January 2019 to reflect the changes to that calibration.

Figure 4.2-5: Inter-instrument comparison by z-score of reanalysis sample set. Vertical red line denotes change in reanalysis set. Multiple measures of the new reanalysis set during the month of June 2018 (denoted by A, B, and C) were made for determination of reference values.



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 with loadings 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 instrument stability and accuracy. 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); see *UCD CSN TI 302D* for further detail.

The NIST SRM 2783 standard results from this analysis period (3/23/2018 through 4/26/2019) are shown in Figure 4.2-6, and Table 4.2-13 outlines the calibrations performed during this analysis period. XRF-1 and XRF-4 underwent routine calibrations in January 2018 and all three instruments were calibrated at the end of December 2018. XRF-4 also underwent calibration in June 2018 due to a replacement of the CaF2 target in the secondary target wheel. The results from the monthly NIST SRM 2783 analyses indicate that calibrations for all instruments are stable over the calibration periods. The overall error for most elements is less than 20%. However, the error in Zn is around 30%. Per Yatkin et al. (2016b), an XRF interlaboratory comparison reported SRM 2783 Zn error varying from -15% to 30%; the results shown here fit within that range. There were no exceedances of the acceptance criteria during this analysis period.

Figure 4.2-6: Error of each EDXRF instrument from the NIST SRM standard run monthly for the analysis period 3/23/2018 through 4/26/2019.

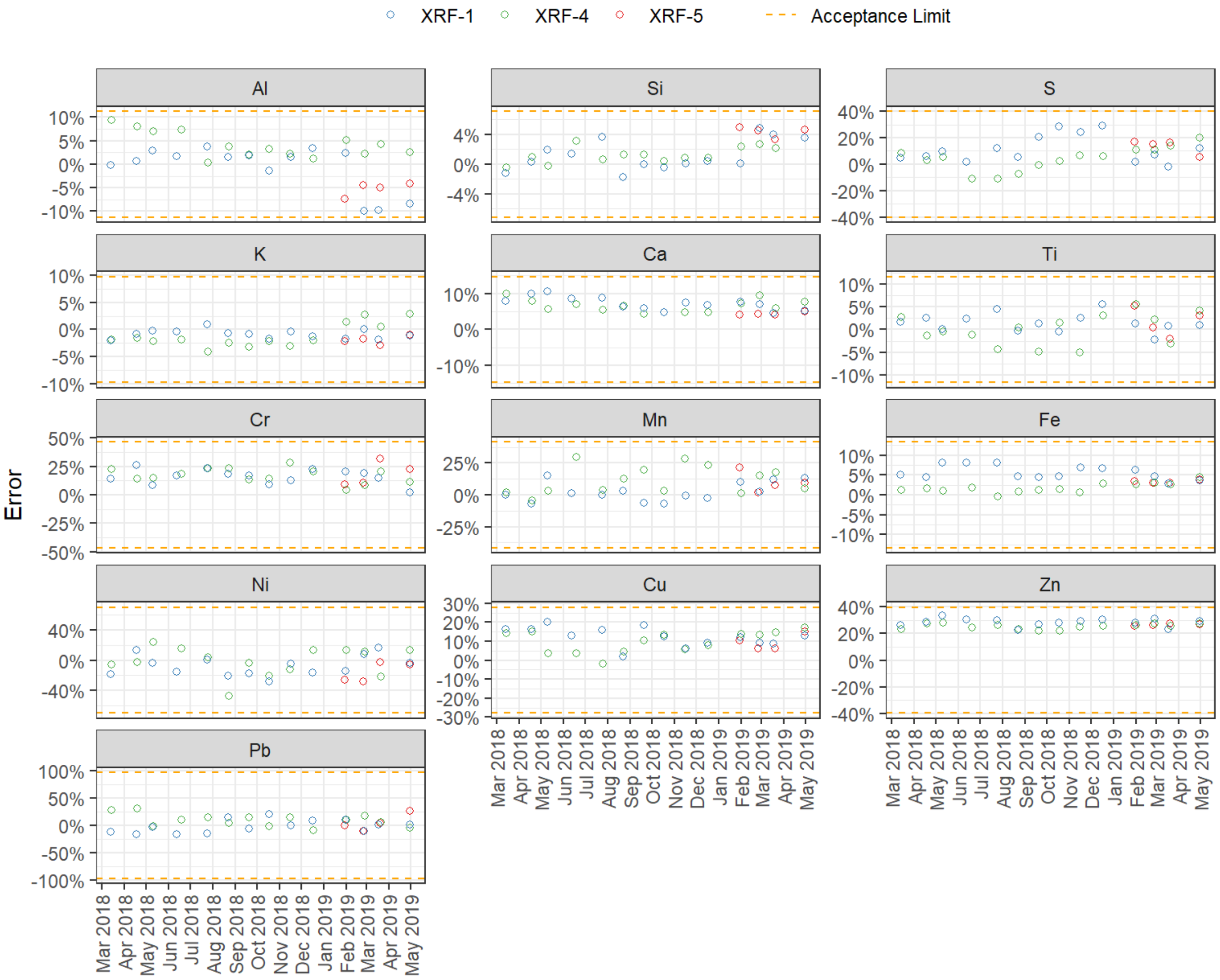


Table 4.2-13: Dates for calibrations performed on each EDXRF instrument during this analysis period.

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-1	1/19/2018	Annual calibration	1/14/2018 – 9/29/2018
XRF-4	1/19/2018	Annual calibraiton	1/2/2018 – 3/30/2018
XRF-4	6/15/2018	CaF2 secondary target was replaced	4/2/2018 – 9/29/2018
XRF-5	12/17/2018	Annual calibration	10/2/2018 – 12/31/2018
XRF-4	12/19/2018	Annual calibration	10/5/2018 – 12/23/2018
XRF-1	12/21/2018	Annual calibration	10/11/2018 – 12/28/2018

In addition to the calibration verification QC results shown in Figure 4.2-6, the conditions under which the EDXRF instruments measure the elemental results were changed in December 2018 (see Section 2.3.1). The EDXRF measurement applications, which include the secondary targets and integration times, were adjusted in an effort to reduce the variability and detection limits for some elements. Also, efforts were made to improve the bias between instruments, especially for low atomic weight elements such as Al and Si. The measurement applications for calibrations prior to the December 2018 calibration and after that calibration are compared in Table 4.2-14. The results of the application change are still being analyzed to determine the effect on variability and detection limits, although inter-instrument bias has improved for the low atomic weight elements.

Table 4.2-14: EDXRF measurement condition changes.

Calibration January 2018			Calibration December 2018		
Secondary Target	Time (seconds)	Elements	Secondary Target	Time (seconds)	Elements
CaF2	600	Na, Mg, Al, Si, P, S, Cl, K	CaF2	600	Na, Mg, Al, Si, P, S, Cl, K
Fe	400	Ca, Ti, V, Cr	Fe	400	Ca, Ti, V, Cr
Ge	300	Mn, Fe, Co, Ni, Cu, Zn	Ge	400	Mn, Fe, Co, Ni, Cu, Zn
KBr	300	As	SrF2	500	As, Se, Br
SrF2	300	Se, Br	Mo	500	Rb, Sr
Mo	300	Rb, Sr, Pb	Al2O3	500	Zr, Ag, Cd, In, Sn, Sb, Cs, Ba, Ce
Al2O3	200	Zr, Sn, Sb, Cs, Ba, Ce	Zr	500	Pb
CsI	200	Ag, Cd, In			

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 this reporting period.

4.2.4.2 Performance Evaluations

The UC Davis XRF Laboratory actively participates in interlaboratory comparisons.

In 2018 (during the analysis period for samples collected during 2018), UC Davis participated in an interlaboratory comparison with Environment and Climate Change Canada. $CuSO_4$ and CuO reference materials, generated at UC Davis, were analyzed by XRF, IC, and ICP-MS. Results indicate agreement between the laboratories with less than 5% absolute difference.

4.2.4.3 Training

Training of all personnel who assist with or operate the EDXRF 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 EDXRF analysis on CSN samples.

4.2.4.4 Accreditations

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

4.2.5 Summary of Filter Field Blanks

Over the sampling period (January 1, 2018 through December 31, 2018) there were 1,665 valid PTFE filter field blanks. Table 4.2-15 summarizes the field blank statistics.

Table 4.2-15: PTFE filter field blank statistics for the analysis period 3/23/2018 through 4/26/2019 (samples collected 1/1/2018 through 12/31/2018).

Species	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)
Ag	1665	0.014	0.015	0.002	0.049	0.006
Al	1665	0.078	0.079	0.023	0.258	0.015
As	1665	0.000	0.000	0.000	0.006	0.001
Ba	1665	0.089	0.090	0.000	0.183	0.026
Br	1665	0.002	0.002	0.000	0.008	0.002
Ca	1665	0.003	0.006	0.000	0.162	0.009
Cd	1665	0.014	0.015	0.003	0.040	0.006
Ce	1665	0.107	0.111	0.032	0.219	0.034
Cl	1665	0.002	0.004	0.000	0.608	0.019
Co	1665	0.002	0.002	0.000	0.021	0.001
Cr	1665	0.004	0.005	0.002	0.072	0.003
Cs	1665	0.060	0.061	0.000	0.141	0.020
Cu	1665	0.006	0.007	0.000	0.029	0.003
Fe	1665	0.022	0.023	0.000	0.262	0.012
In	1665	0.033	0.033	0.010	0.063	0.009
K	1665	0.008	0.009	0.002	0.257	0.007
Mg	1665	0.012	0.014	0.000	0.091	0.015
Mn	1665	0.006	0.007	0.000	0.017	0.002
Na	1665	0.000	0.014	-0.002	0.270	0.024
Ni	1665	0.001	0.001	0.000	0.022	0.001
P	1665	0.000	0.000	0.000	0.028	0.001
Pb	1665	0.014	0.014	0.003	0.032	0.004
Rb	1665	0.004	0.004	0.000	0.014	0.002
S	1665	0.000	0.001	0.000	0.286	0.013
Sb	1665	0.038	0.040	0.009	0.093	0.014
Se	1665	0.003	0.003	0.000	0.009	0.001
Si	1665	0.012	0.015	0.000	0.438	0.017
Sn	1665	0.039	0.040	0.010	0.086	0.013
Sr	1665	0.005	0.005	0.002	0.012	0.002
Ti	1665	0.001	0.001	0.000	0.065	0.002
V	1665	0.000	0.000	0.000	0.002	0.000
Zn	1665	0.003	0.003	0.000	0.049	0.002
Zr	1665	0.022	0.023	0.000	0.074	0.010

4.3.A DRI Thermal Optical Analysis Laboratory

The DRI Thermal Optical Analysis Laboratory, as a subcontractor to UC Davis, received and analyzed quartz filters from batches 39 through 47 covering the sampling period January 1, 2018 through September 30, 2018. Analysis of these samples was performed May 23, 2018 through December 17, 2018. All analyses were performed using the DRI Model 2015 multi-wavelength carbon analyzer with the IMPROVE_A protocol and analysis results were reported to UC Davis. Thirteen DRI Model 2015 Thermal Optical Carbon Analyzers (designated as units # 21, 31, 32, 34-38, 40-43, and 47) were used for these CSN analyses.

4.3.A.1 Summary of QC Checks and Statistics

Samples were received by the DRI Thermal Optical Analysis Laboratory following the chain-of-custody procedure specified in *DRI CSN SOP # 2-231* (specific to CSN). Samples are analyzed using DRI Model 2015 analyzers following *DRI CSN SOP 2-226r3*. Quality control (QC) measures for the DRI carbon analysis are included in the SOP and summarized in Table 4.3.A-1. The table specifies the frequency and standards required for the checks, along with the acceptance criteria, and corrective actions for the carbon analyzers. More detail on individual control measures is provided in specific subsections.

Table 4.3.A-1 DRI quality control measures for carbon analysis by TOA (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.A-2 and Figure 4.3.A-1.	Check instrument.
Laboratory Blank Check	NA	Beginning of analysis day	<0.2 µg C/cm^2. See Table 4.3.A-3 and Figure 4.3.A-2.	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.A-4.	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.A-4 and Figure 4.3.A-3.	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.A-5a.	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.A-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.A-5c.	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.A-5.	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 ECR <10µg C/cm See Table 4.3.A-8 and Figure 4.3.A-6, and Table 4.3.A-9 and Figure 4.3.A-7.	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.A-6.	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.A-7.	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.A.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 (Table 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 CO_2 (Figure 4.3-5a), sucrose (Figure 4.3-5b), and KHP (Figure 4.3-5c) calibrations result in reanalysis and/or instrument maintenance. For cases where CSN samples were analyzed after an exceedance, data were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.4.2 and Section 3.2.3.1).

4.3.A.2.1 System and Laboratory Blanks

Table 4.3.A-2 lists the number of system blanks analyzed during the report period and their concentration statistics. The system blank control chart is shown in Figure 4.3.A-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. Two system blanks did not pass and nine CSN samples were analyzed after this system blank failure. These cases were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.4.2 and Section 3.2.3.1). 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.A-2: Statistics of system blanks ran on the Model 2015 analyzer for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).

Parameter	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)	# Exceedance
OC1	308	0.000	0.000	0.000	0.050	0.003	0
OC2	308	0.000	0.001	0.000	0.048	0.004	0
OC3	308	0.000	0.008	0.000	0.229	0.023	1
OC4	308	0.000	0.001	0.000	0.089	0.006	0
OCR	308	0.000	0.011	0.000	0.286	0.028	1
OCT	308	0.000	0.012	0.000	0.318	0.032	2
OPR	308	0.000	0.000	0.000	0.012	0.001	0
OPT	308	0.000	0.002	0.000	0.126	0.009	0
EC1	308	0.000	0.000	0.000	0.028	0.003	0
EC2	308	0.000	0.002	0.000	0.122	0.008	0
EC3	308	0.000	0.000	0.000	0.033	0.002	0
ECR	308	0.000	0.002	0.000	0.126	0.010	0
ECT	308	0.000	0.000	0.000	0.038	0.003	0
TC	308	0.001	0.013	0.000	0.318	0.033	2

Figure 4.3.A-1: Control chart of system blank total carbon concentrations on the DRI Model 2015 carbon analyzers. The red dash lines indicate the limit of 0.2 µg C/cm^2.

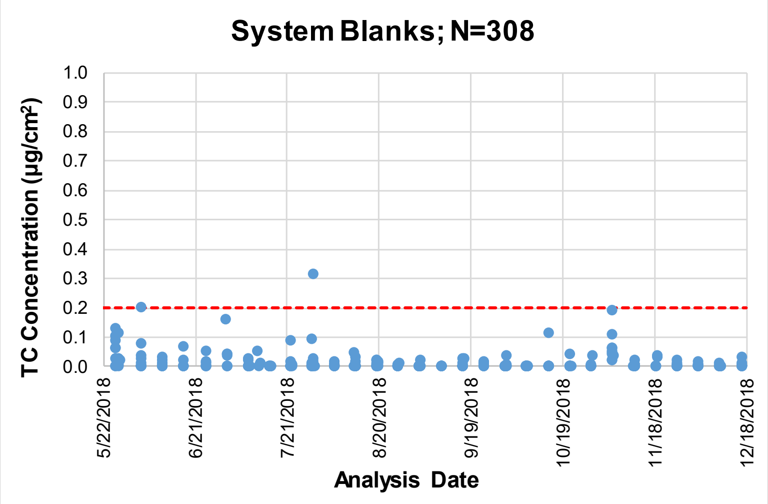
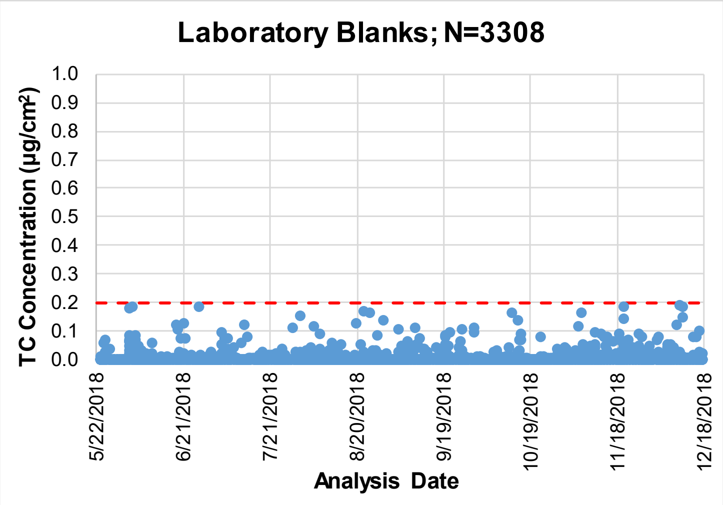


Table 4.3.A-3 lists the number of laboratory blanks analyzed during the report period and their concentration statistics. The laboratory blank control charts are shown in Figure 4.3.A-2. Laboratory blank analyses are performed daily to check for system contamination and evaluate laser response. All 3,308 laboratory blanks were below the limit of 0.20 µgC/cm^2 during this reporting period. 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.A-3: Statistics of laboratory blanks run on the Model 2015 analyzer for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).

Parameter	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St. Dev. (µg/cm^2)	# Exceedance
OC1	3308	0.000	0.000	0.000	0.079	0.002	0
OC2	3308	0.000	0.000	0.000	0.068	0.003	0
OC3	3308	0.000	0.001	0.000	0.130	0.005	0
OC4	3308	0.000	0.001	0.000	0.078	0.004	0
OCR	3308	0.000	0.003	0.000	0.187	0.012	0
OCT	3308	0.000	0.004	0.000	0.190	0.015	0
OPR	3308	0.000	0.001	0.000	0.184	0.006	0
OPT	3308	0.000	0.002	0.000	0.184	0.009	0
EC1	3308	0.000	0.000	0.000	0.078	0.003	0
EC2	3308	0.000	0.002	0.000	0.150	0.009	0
EC3	3308	0.000	0.000	0.000	0.095	0.002	0
ECR	3308	0.000	0.002	0.000	0.150	0.010	0
ECT	3308	0.000	0.001	0.000	0.138	0.007	0
TC	3308	0.000	0.005	0.000	0.190	0.017	0

Figure 4.3.A-2: Control chart of daily laboratory blank total carbon concentrations run on the DRI Model 2015 carbon analyzers for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). The red dash lines indicate the limit of 0.2 µgC/cm^2.



4.3.A.2.2 Auto-Calibration and Internal Calibration Peak Area Check

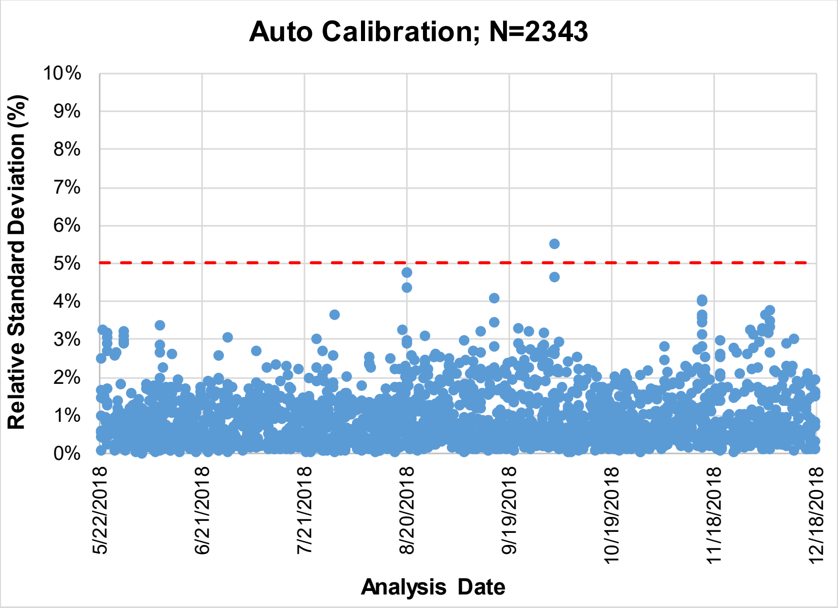
Once per day each analyzer runs an auto-calibration protocol. Using the Carle valve, an aliquot of methane standard is injected once in a He-only atmosphere (organic carbon stage), once in a He/O_2 atmosphere (elemental carbon stage), and finally as the normal internal calibration peak. The three peaks 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.A-4 summarizes the RSD of the three methane injection peaks during the analysis period and the control chart is shown in Figure 4.3.A-3. There were three exceedances during this reporting period. 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 106 CSN samples were analyzed during auto-calibration peak area exceedances; these cases were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.4.2 and Section 3.2.3.1). 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.A-4: Statistics of the relative standard deviation (RSD) of the three methane injection peaks from auto-calibration checks for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018).

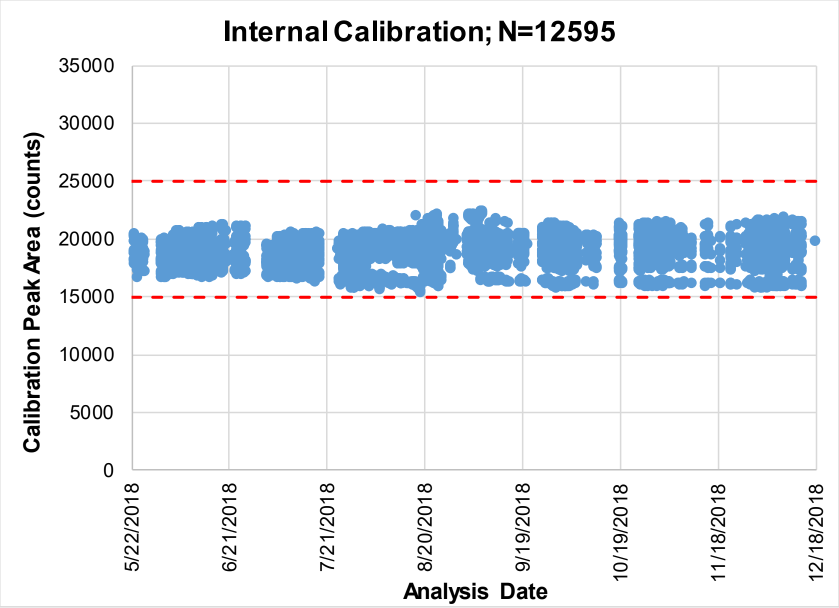
Statistic	Auto-Calibration
Count	2343
Median	0.71%
Average	0.93%
Min	0.01%
Max	5.5%
Standard deviation	0.71%
Exceedance	3

Figure 4.3.A-3: Control chart of the relative standard deviation of the three methane injection peaks from daily auto-calibration ran on the DRI Model 2015 carbon analyzers for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). The red dash lines indicate the limit of 5% RSD.



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 15,000 and 25,000 counts for Model 2015. 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. Figure 4.3.A-4 shows the daily internal calibration peak area during the reporting period for all analyzers. During this reporting period, 12,583/12,595 (99.9%) passed both peak area and daily average criteria. There were 12 CSN samples analyzed during exceedance of internal calibration QC limits; these cases were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.4.2 and Section 3.2.3.1). However, other QC analyses (e.g. replicates, auto-calibration, and internal calibration peak area check) within the time period indicated 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.A-4: Control chart of the internal calibration peak area for the DRI Model 2015 carbon analyzers. The red dash lines indicate the typical internal calibration peak area between 15,000 and 25,000 for Model 2015. Twelve samples were run after there was an exceedance outside of the daily average (but within the typical peak area).



4.3.A.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 efficiency of the oxidation oven and sensitivity of the NDIR. 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. Table 4.3.A-5 provides summary statistics for full multipoint calibrations by analyzer for the period during which the project samples were analyzed. All multipoint calibrations met the QC criterion during this reporting period.

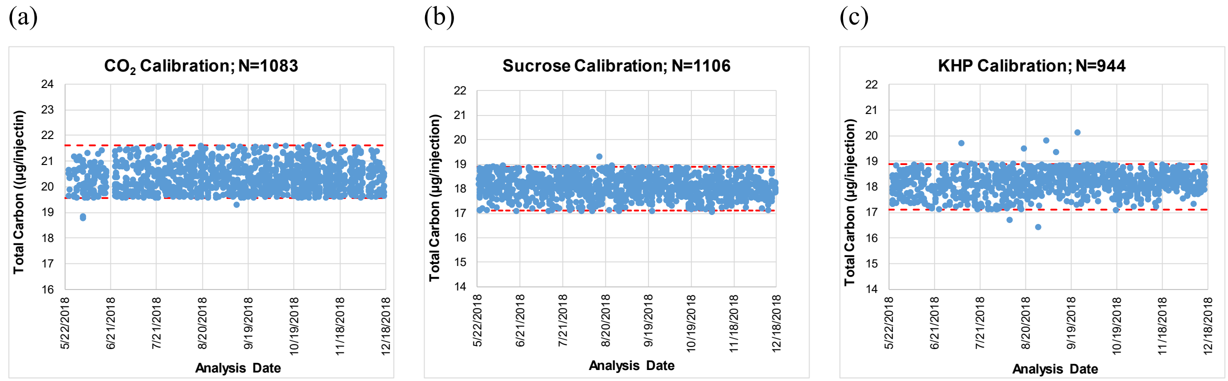
Table 4.3.A-5: Multipoint calibration statistics for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). Units for the slope are µg carbon per ratio of standard injection peak count/calibration gas peak count.

Carbon Analyzer	Calibration Date	Slope	r^2	Difference from Analyzer Average	# of Samples Flagged
21	5/30/2018	19.348	0.998	2%	0
	7/25/2018	19.155	0.996	1%	0
	11/20/2018	18.548	0.992	-3%	0
	12/20/2018	19.069	0.998	0%	0
31	8/22/2018	19.627	0.996	5%	0
	11/16/2018	17.851	0.996	-5%	0
32	6/29/2018	17.870	0.998	3%	0
	8/16/2018	16.611	0.995	-4%	0
	9/3/2018	17.489	0.995	1%	0
	10/11/2018	17.419	0.996	1%	0
	12/2/2018	17.021	0.988	-2%	0
34	8/10/2018	18.919	0.995	-2%	0
	10/12/2018	19.560	0.995	2%	0
35	9/6/2018	19.134	0.997	0%	0
	10/11/2018	19.304	0.992	0%	0
36	5/30/2018	18.853	0.995	-2%	0
	6/26/2018	19.547	0.996	2%	0
	7/11/2018	19.658	0.9966	2%	0
	7/27/2018	19.027	0.9955	-1%	0
	9/4/2018	19.302	0.987	0%	0
	9/28/2018	18.885	0.998	-2%	0
37	6/1/2018	19.180	0.998	0%	0
	6/26/2018	19.242	0.998	0%	0
	12/17/2018	19.208	0.999	0%	0
38	6/26/2018	18.964	0.996	-1%	0
	12/20/2018	19.167	0.998	1%	0
40	7/25/2018	19.636	0.998	0%	0
	8/10/2018	19.596	0.995	0%	0
41	7/27/2018	19.538	0.997	2%	0
	8/27/2018	19.332	0.995	0%	0
	11/8/2018	18.518	0.994	-4%	0
	12/11/2018	19.584	0.999	2%	0
42	5/17/2018	19.090	0.997	0%	0

Carbon Analyzer	Calibration Date	Slope	r^2	Difference from Analyzer Average	# of Samples Flagged
	9/5/2018	18.911	0.998	0%	0
43	6/5/2018	18.022	0.971	-3%	0
	7/26/2018	18.984	0.998	3%	0
47	7/24/2018	18.435	0.996	1%	0
	9/25/2018	18.234	0.998	-1%	0

CO_2 calibrations are performed on each analyzer four times per week, sucrose calibration checks are done on each analyzer three times per week, and KHP calibrations are done twice per week. Calibration control charts for the Model 2015 analyzers are shown in Figures 4.3.A-5a through 4.3.A-5c. For this reporting period, 4 out of 1,083 CO_2 calibrations, 6 out of 1,106 sucrose calibration, and 10 out of 944 KHP calibrations exceeded the criteria. When an exceedance is observed, the analyzer is checked and the calibration is rerun. In some cases, a full carbon calibration was conducted. There were 9, 29, and 49 CSN samples analyzed after CO_2, sucrose, and KHP exceedances, respectively; these cases were flagged with the QX (Does Not Meet QC Criteria) qualifier in files delivered to AQS by UC Davis (see Section 2.4.2 and Section 3.2.3.1). However, for all samples that were run after an exceedance calibration, other QC analyses (i.e., replicates, auto-calibration, and internal calibration peak area checks) 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.A-5: Control chart of manual calibration checks for: (a) CO_2, (b) sucrose, and (c) KHP injections for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). The red dash lines indicate the total carbon limits of 17.1 and 18.9 µgC per injection for sucrose and KHP and 19.57 and 21.63 µC per injection for CO_2.



4.3.A.2.4 Temperature Calibrations

Table 4.3.A-6 provides summary statistics for the multi-point temperature calibrations of each Model 2015 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. Separate linear regressions are used 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. All calibrations met the acceptable r^2 criteria ($r^2 > 0.99$) during this report period.

Table 4.3.A-6: Multi-point temperature calibration statistics on the Model 2015 carbon analyzer for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018).

Carbon Analyzer	Calibration Date*	Low T Slope	Low T Intercept	Low T r^2	High T Slope	High T Intercept	High T r^2
21	5/25/2018	1.038	11.702	0.999	0.989	25.596	0.999
	11/16/2018	1.066	3.619	**	1.008	19.441	**
31	8/17/2018	1.048	7.391	0.999	0.984	24.259	0.999
32	9/26/2018	1.033	4.141	0.999	1.018	11.423	0.999
34	7/16/2018	1.069	2.360	1.000	1.001	20.822	1.000
	9/10/2018	1.035	4.474	0.999	0.977	20.427	0.999
35	10/4/2018	1.047	1.344	0.999	1.014	11.078	0.999
36	6/5/2018	0.998	14.056	1.000	0.986	19.062	1.000
	7/6/2018	1.039	12.666	0.999	0.984	27.854	0.999
	7/23/2018	1.091	12.163	0.998	0.989	39.248	0.999
	9/25/2018	1.048	9.961	0.999	0.993	26.625	0.999
	11/7/2018	1.068	4.743	0.999	1.008	21.873	0.999
37	5/29/2018	1.060	4.289	1.000	0.978	27.330	1.000
	6/13/2018	1.049	8.293	0.999	0.975	27.800	0.999
	12/9/2018	1.039	0.227	0.999	1.004	9.502	0.999
38	6/18/2018	1.096	2.330	1.000	1.006	27.547	1.000
	12/14/2018	1.142	-1.087	0.999	1.010	36.195	0.999
40	8/1/2018	0.999	8.688	0.999	0.989	11.705	0.999
	10/16/2018	1.068	2.923	0.999	1.025	15.200	0.999
	12/14/2018	1.094	1.094	0.999	1.021	20.659	0.999
41	7/23/2018	1.025	9.735	1.000	1.005	16.973	1.000
42	8/28/2018	0.981	11.410	0.999	0.999	7.769	0.999
	11/26/2018	1.053	9.056	0.999	1.037	15.267	0.999
43	5/18/2018	1.050	5.926	1.000	1.005	19.394	1.000
	5/29/2018	1.060	4.289	1.000	0.978	27.330	1.000
	8/1/2018	1.122	-9.090	0.998	0.989	27.277	0.999
	9/2/2018	1.112	2.344	1.000	0.998	33.237	1.000
	10/23/2018	1.144	-0.606	1.000	1.014	35.429	1.000
47	7/18/2018	1.037	9.090	1.000	0.988	23.588	1.000

* Includes both regular maintenance and semi-annual calibration data

** Calibration point data were deleted from file, therefore r^2 data not available

4.3.A.2.5 Oxygen Level Check

Table 4.3.A-7 provides a summary of the Model 2015 oxygen leak test 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 17-73 ppm.

Table 4.3.A-7: Model 2015 oxygen test statistics for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018).

Analyzer No.	**O_2 Statistics (ppm)**	**Feb 2018**		**Aug 2018**	
		140 (°C)	**580 (°C)**	**140 (°C)**	**580 (°C)**
21	Mean O_2 Std Dev	17.9 4.7	16.7 4.6	32.6 9.9	30.1 9.8
31	Mean O_2 Std Dev	19.8 4.6	18.3 4.6	28.7 10.2	23.9 9.9
32	Mean O_2 Std Dev	24.8 4.7	26.5 4.8	47.2 10.5	48.0 10.1
34	Mean O_2 Std Dev	39.1 5.6	50.5 5.6	Offline Aug 2018	Offline Aug 2018
35	Mean O_2 Std Dev	22.6 4.7	26.6 4.8	35.1 10.0	32.5 9.7
36	Mean O_2 Std Dev	20.0 4.7	22.7 4.7	21.9 9.7	24.3 9.7
37	Mean O_2 Std Dev	18.8 4.9	16.6 4.6	37.4 10.0	33.7 9.7
38	Mean O_2 Std Dev	31.2 4.9	28.1 4.7	35.9 9.8	29.2 9.8
40	Mean O_2 Std Dev	24.3 4.7	25.3 4.8	42.2 9.9	47.3 10.5
41	Mean O_2 Std Dev	23.8 4.8	20.9 4.7	25.3 9.8	22.7 9.7
42	Mean O_2 Std Dev	17.5 4.8	16.7 4.7	66.4 12.4	72.6 10.7
43	Mean O_2 Std Dev	26.7 5.0	24.8 4.8	33.6 9.8	32.3 9.9
47	Mean O_2 Std Dev	17.8 4.7	16.8 4.8	46.6 9.9	45.0 9.8

4.3.A.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.A-8 and 4.3.A-9 give the criteria and summary statistics for replicate and duplicate carbon analyses, respectively, for this reporting period. Control charts for replicate and duplicate analyses are shown in Figure 4.3.A-6 and Figure 4.3.A-7, respectively.

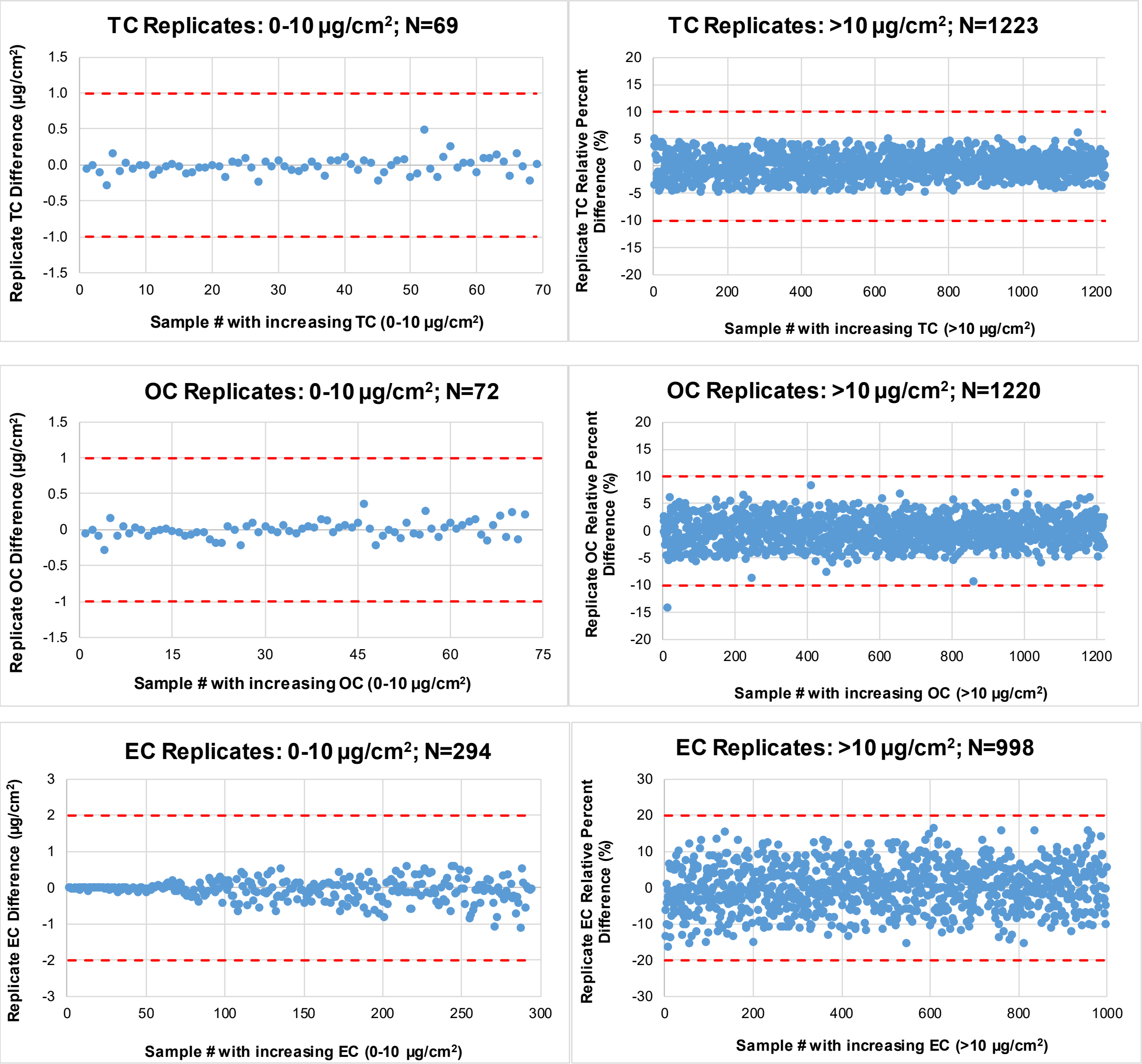
Replicate analysis results for total carbon (TC), organic carbon (OCR), and elemental carbon (ECR) by reflectance agree well, with only 24/3876 data points (0.6%) for OCR, ECR, and TC exceeding the criteria. Duplicate analysis results for total carbon (TC), organic carbon (OCR), and elemental carbon (ECR) by reflectance agree well, with zero data points exceeding the criteria. Samples not meeting replicate/duplicate criteria (i.e., for TC, OCR, or ECR < 10 µg C/cm^2, TC, OCR < ± 1.0 µg C/cm^2 and ECR < ± 2.0 µg C/cm^2; and for TC, OCR or ECR ≥ 10 μg C/cm^2, TC or OCR < 10% RPD and ECR < 20% RPD) are reanalyzed, typically on a third analyzer. However, the small size (25 mm) of the filter does not permit more than three punches (each ~0.5 cm^2) to be taken from the filter. Filter inhomogeneity, which is flagged prior to first analysis, is also examined.

Table 4.3.A-8: Replicate analysis criteria and statistics for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). Total carbon (TC), organic carbon (OCR), and elemental carbon (ECR) are shown by reflectance.

		Replicates			
Range	**Criteria**	**Statistic**	**TC**	**OC**	**EC**
TC, OCR, & ECR < 10 μg C/cm^2	TC, OCR < ±1.0 μg C/cm^2 ECR < ±2.0 μg C/cm^2 Units: μg C/cm^2	Count	69	72	294
		No. Fail	1	1	21
		%Fail	1.4	1.3	6.8
		Mean	0.30	0.30	0.72
		StdDev	0.29	0.26	0.73
		Max	1.73	1.25	3.90
		Min	0.00	0.00	0.00
		Median	0.22	0.23	0.44
TC, OCR, & ECR ≥ 10 μg C/cm^2	TC, OCR %RPD < 10% ECR %RPD < 20% Units: %	Count	1223	1220	998
		No. Fail	0	1	0
		%Fail	0	0.10	0
		Mean	1.77	2.12	5.03
		StdDev	1.22	1.52	3.63
		Max	5.94	15.22	17.86
		Min	0.00	0.00	0.00
		Median	1.53	1.86	4.41

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

Figure 4.3.A-6: Replicate (two punches from the same sample filter analyzed on different instruments) analysis results for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). The limits are ±1.0 µg/cm^2 for TC and OCR <10 µg/cm^2, ±2.0 µg/cm^2 for ECR <10 µg/cm^2, ±10% relative percent difference for TC and OCR ≥10 µg/cm^2, and ±20% relative percent difference for ECR ≥10 µg/cm^2.


TC Replicates: 0-10 µg/cm^2; N=69

TC Replicates: >10 µg/cm^2; N=1223

OC Replicates: 0-10 µg/cm^2; N=72

OC Replicates: >10 µg/cm^2; N=1220

EC Replicates: 0-10 µg/cm^2; N=294

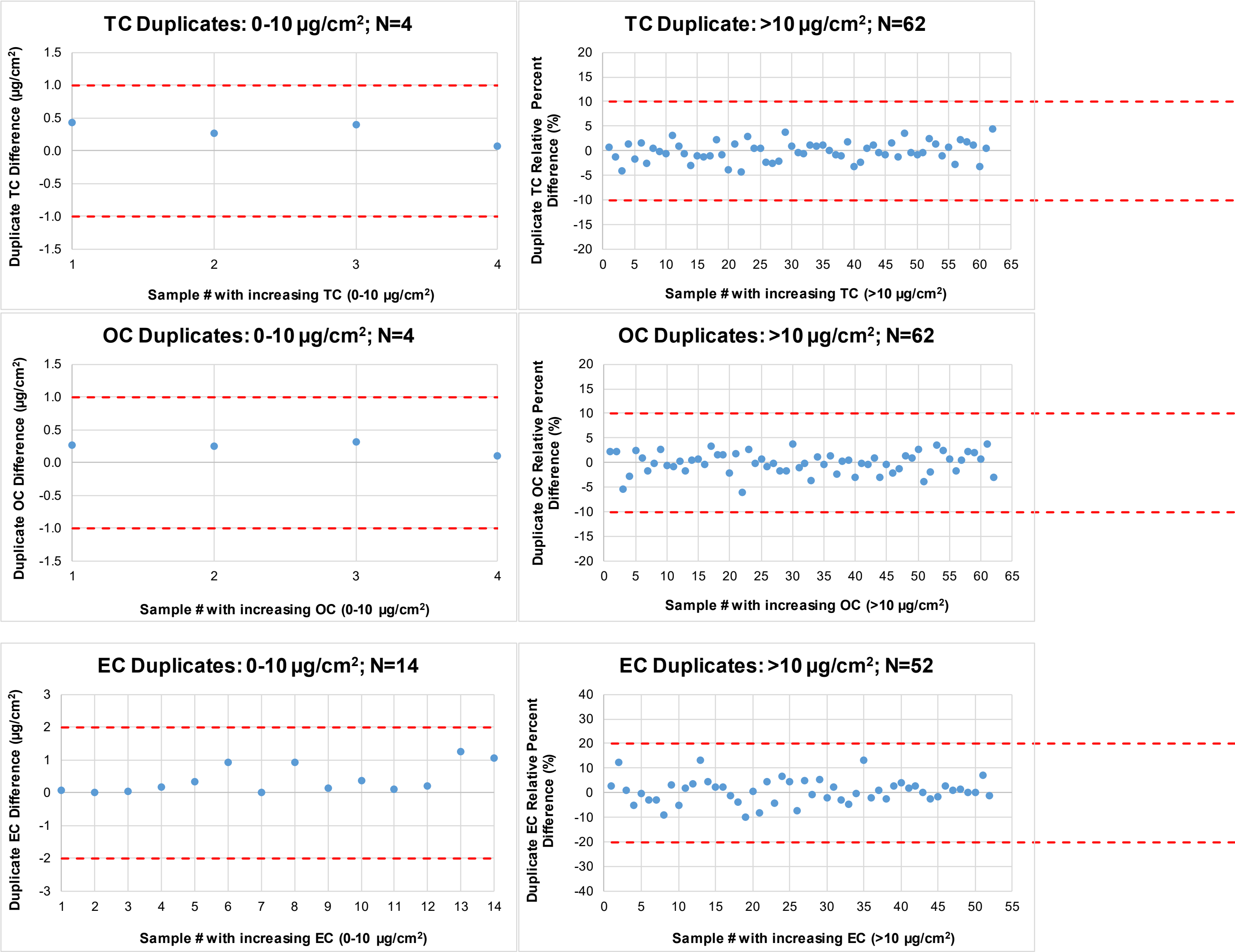
EC Replicates: >10 µg/cm^2; N=998

Table 4.3.A-9: Duplicate analysis criteria and statistics for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). Total carbon (TC), organic carbon (OCR), and elemental carbon (ECR) are shown by reflectance.

Range	Criteria	Duplicates			
		Statistic	**TC**	**OC**	**EC**
TC, OCR, & ECR < 10 µg C/cm^2	TC, OCR < ±1.0 µg C/cm^2 ECR < ±2.0 µg C/cm^2 Units: µg C/cm^2	Count	4	4	14
		No. Fail	0	0	0
		%Fail	0	0	0
		Mean	0.29	0.23	0.40
		StdDev	0.14	0.08	0.42
		Max	0.43	0.31	1.25
		Min	0.07	0.10	0.01
		Median	0.33	0.25	0.18
TC, OCR, & ECR ≥ 10 µg C/cm^2	TC, OCR %RPD < 10% ECR %RPD < 20% Units: %	Count	62	62	52
		No. Fail	0	0	0
		%Fail	0	0	0
		Mean	1.61	1.72	3.70
		StdDev	1.15	1.32	3.13
		Max	4.36	6.36	12.52
		Min	0.01	0.07	0.08
		Median	1.24	1.64	2.63

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

Figure 4.3.A-7: Duplicate (two punches from the same sample filter analyzed on the same instrument) analysis results for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). The limits are ±1.0 µg/cm^2 for TC and OCR <10 µg/cm^2, ±2.0 µg/cm^2 for ECR <10 µg/cm^2, ±10% relative percent difference for TC and OCR ≥10 µg/cm^2, and ±20% relative percent difference for ECR ≥10 µg/cm^2.



4.3.A.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.A.4 Audits, Performance Evaluations, Training, and Accreditations

4.3.A.4.1 System Audits

UC Davis contracted a third-party auditor (Technical & Business Systems; Placerville, CA) to perform a Laboratory Systems Audit of the DRI Thermal Optical Analysis Laboratory. The audit was conducted on September 19, 2018. No issues were identified that affected data quality;

auditors provided minor recommendations for improved documentation and tracking, and assured QA/QC documentation agreed with existing procedures.

4.3.A.4.2 Performance Evaluations

No performance evaluations were conducted during this reporting period.

4.3.A.4.3 Training

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

4.3.A.4.4 Accreditations

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

4.3.A.5 Summary of Filter Blanks

Over the sampling period (January 1, 2018 through September 30, 2018) there were 1,253 valid quartz filter field blanks. Table 4.3.A-10 summarizes the field blank statistics.

Table 4.3.A-10: Quartz filter field blank statistics for the analysis period 5/23/2018 through 12/17/2018 (samples collected 1/1/2018 through 9/30/2018). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon are shown by reflectance (R) and transmittance (T).

Species	Count	Median (μg/cm^2)	Average (μg/cm^2)	Min (μg/cm^2)	Max (μg/cm^2)	St. Dev. (μg/cm^2)
EC1	1253	0.000	0.016	0.000	0.728	0.050
EC2	1253	0.028	0.054	0.000	0.396	0.065
EC3	1253	0.000	0.000	0.000	0.000	0.000
ECR	1253	0.016	0.053	0.000	0.860	0.086
ECT	1253	0.000	0.024	0.000	0.478	0.060
OC1	1253	0.147	0.148	0.000	1.697	0.101
OC2	1253	0.293	0.323	0.028	1.445	0.147
OC3	1253	0.513	0.566	0.151	3.555	0.262
OC4	1253	0.080	0.100	0.000	0.784	0.089
OCR	1253	1.075	1.154	0.244	4.879	0.469
OCT	1253	1.099	1.184	0.244	5.715	0.500
OPR	1253	0.000	0.017	0.000	0.591	0.058
OPT	1253	0.005	0.046	0.000	0.860	0.086

4.3.B UC Davis Thermal Optical Analysis Laboratory

The UC Davis Thermal Optical Analysis Laboratory received and analyzed quartz filters from batches 48 through 50, covering the sampling period October 1, 2018 through December 31, 2018. Analyses of these samples were performed January 2, 2019 through April 3, 2019. Five Thermal Optical Carbon Analyzers (Sunset Laboratory Model 5L; designated as Alpha, Beta, Delta, Gamma and Zeta) were used for analysis during this period using the IMPROVE_A protocol.

Table 4.3.B-1: Sampling dates and corresponding TOA analysis dates covered in this reporting period. Analysis dates include reanalysis – as requested during QA level 0 and level 1 validation – of any samples within the sampling year and month.

Sampling Year	Sampling Month	Analysis Batch #	TOA Analysis Date
2018	October	48	1/2/2019 – 2/15/2019
2018	November	49	2/7/2019 – 3/5/2019
2018	December	50	3/4/2019 – 4/3/2019
2018	All Months	48-50	1/2/2019 – 4/3/2019

4.3.B.1 Summary of QC Checks and Statistics

Samples are received by the UC Davis Thermal Optical Analysis Laboratory following the chain-of-custody procedures specified in the *UCD CSN TI 402A*. Samples are analyzed using Sunset Laboratory Model 5L OCEC analyzers following *UCD CSN SOP #402*. Daily and weekly quality control (QC) checks are implemented to ensure data quality. Calibrations of the analyzers are performed semi-annually or as needed (e.g. when the CH_4/He mixture gas cylinder is replaced). Maintenance is performed as needed by trained laboratory staff. Quality control procedures are described in *UCD CSN SOP #402* and are summarized in Table 4.3.B-2.

Table 4.3.B-2: UC Davis quality control measures for carbon analysis by TOA (Sunset Laboratory OCEC analyzer).

QA/QC Activity	Frequency	Acceptance Criteria	Corrective Action
Laboratory Blank Check	Beginning of analysis day	<1.0 µg C/cm^2	Repeat analysis. If same result, check filter lots for possible contamination and perform pre-firing
Instrument Blank Check	Beginning of analysis day	<0.3 µg C/cm^2	Repeat analysis. If same result, check instrument and gas lines for possible contamination
Single-point Sucrose Standard Check	Beginning of analysis day	Within ±7% of the calculated value	Repeat analysis. If same result, run a different sucrose solution to determine if the problem is with the solution or instrument. If former, make new sucrose solution. If latter, perform full 5-point calibration to determine new calibration constant.
Calibration Peak Area Check	Every analysis	Within ±10% of the average value for a specific instrument	Void analysis result; Repeat analysis with second filter punch
Laser Performance Check	Beginning of analysis day	Laser Transmittance signal for Instrument blank >5000	Check laser alignment and/or examine oven for frosting
Network Sample Replicates	Every 20th network sample analyses	±10% when TC ≥10 µg /cm^2 ±20% when ECR ≥ 2.5 µg /cm^2 or <±1 µg/cm^2 when TC <10 µg /cm^2 <±0.5 µg/cm^2 when ECR <2.5 µg/cm^2.	Investigate instrument and sample anomalies. Analyze the third punch on a difference analyzer
Inter-instrument Comparison Check	Weekly	Measurement bias for a given analyzer should be ≤ 10% for TC and OC and ≤ 20% for ECR.	Investigate instrument and sample anomalies and rerun replicate when criterion is not met
Multi-point Sucrose Standard Check	Every six months or after major instrument repair or change of calibration gas cylinder	NA[a]	Calculate new calibration constant based on calibration slope and update in the parameter file
Temperature Calibrations	Every six months or after major instrument repair	NA	Change the temperature offset values in IMPROVE_A.par files accordingly

[a] NA: Not Applicable.

4.3.B.2 Summary of QC Results

Detailed results from the carbon quality control checks are presented in the subsections below. In addition to performing routine daily and weekly QC activities, readings of oven pressure, back oven and methanator oven temperatures, FID baseline and initial laser are verified to be within the acceptable range specified for each analyzer before starting sample analysis. After analysis, each thermogram is reviewed for the following: 1) correct peak identification and integration, 2) correct laser response, 3) system pressure stability, and 4) to ensure data quality objectives are met. Individual samples with unusual laser response, baseline shift, low system pressure, erroneous split point, or samples impacted by failure to meet QC criteria outlined in Table 4.3.B-2 are reanalyzed.

4.3.B.2.1 Laboratory and Instrument Blanks

At the beginning of the analysis day, following the clean oven procedure, a quartz filter laboratory blank and an instrument blank are analyzed to check for system contamination and evaluate laser response. Results are reviewed immediately upon analysis completion and are compared against the acceptance limits. Table 4.3.B-3 lists the number of blanks analyzed during the report period and their areal density statistics.

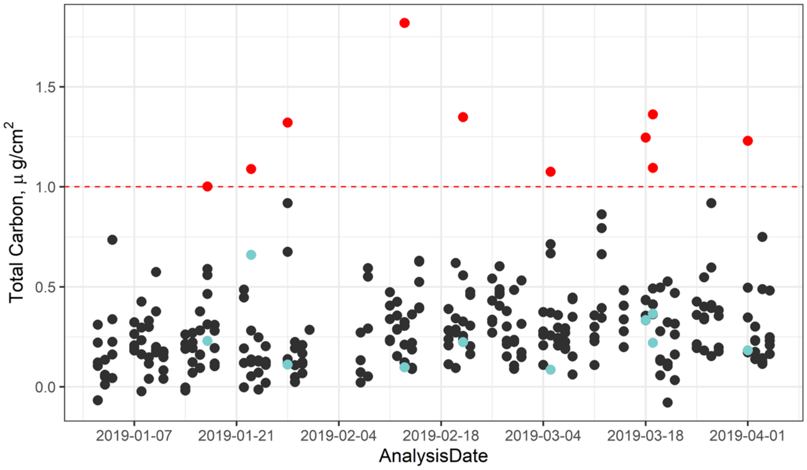
Table 4.3.B-3: Statistics of daily quartz filter laboratory blank and instrument blank analyses on all carbon analyzers for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018).

Blank Type	Count	Median (μg/cm^2)	Average (μg/cm^2)	Min (μg/cm^2)	Max (μg/cm^2)	St.Dev. (μg/cm^2)	# Exceedance
Laboratory Blank	283	0.249	0.309	-0.078	1.819	0.255	10
Laboratory Blank – R*	10	0.222	0.251	0.086	0.660	0.171	0
Instrument Blank	283	-0.052	-0.050	-0.239	0.146	0.075	0

*Laboratory Blank - R: repeated laboratory blank when original fails the QC criterion

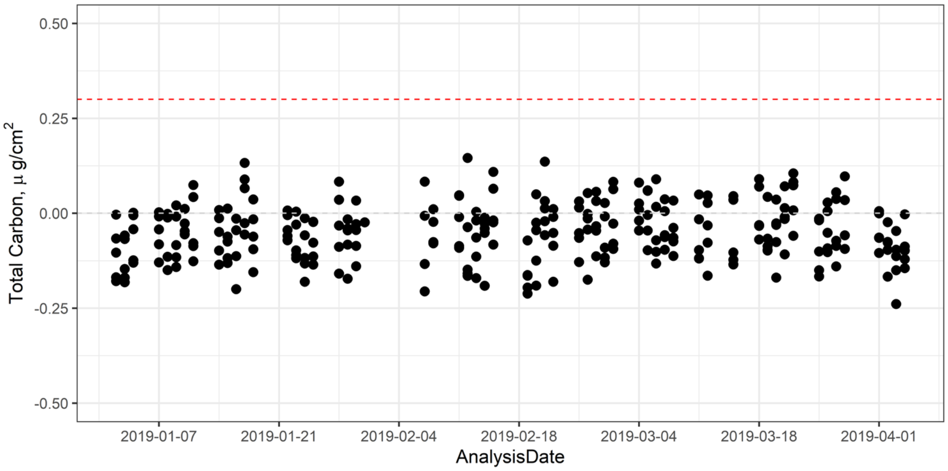
For laboratory blanks, if the TC areal density exceeds 1.0 μg C/cm^2, a second punch taken from the same blank filter lot is analyzed (Laboratory Blank – R). If the original and repeated blank analyses on more than one instruments exceeds the limit, a new lot of quartz blank filters is used to distinguish filter lot contamination from system contamination. Figure 4.3.B-1 shows the results of daily laboratory and instrument blank analyzed on all five analyzers during this reporting period.

Figure 4.3.B-1: Results of daily quartz filter laboratory blanks for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018). Red dashed line indicates the acceptance limit of 1.0 μg C/cm^2 for total carbon areal density. For cases when the acceptance limit was exceeded (red points), a repeated analysis (blue points) was performed.



Instrument blank analysis is performed following the laboratory blank analysis by reusing the sample punch. The instrument blank acceptance limit is 0.3 μg C/cm^2 of total carbon. Figure 4.3.B-2 shows the results of daily analyses of instrument blanks on all five analyzers. The TC values center around 0 µg C/cm^2, with small fluctuations due mostly to the slight baseline shift during the analysis. There were no instrument blank exceedances during this report period.

Figure 4.3.B-2: Results of daily instrument blanks for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018). Red dash line indicates the acceptance limit of 0.3 µg C/cm^2 for total carbon areal density.



4.3.B.2.2 Single-Point Sucrose Standard Check

Following the daily blank analyses, a single-point sucrose calibration check is performed to evaluate FID response by injecting 10 µL of sucrose standard solution onto a clean filter punch and analyzing for total carbon content. Table 4.3.B-4 summarizes the concentrations of the sucrose standard solutions generated for calibrating the analyzers. They cover a full range of the TC levels typically seen on the CSN network samples. Sucrose #5 and #15 are chosen for daily single-point calibration check because their concentrations are most comparable to the CSN network median TC value.

Table 4.3.B-4: Lookup table of sucrose solution standard concentration in µgC/cm^2.

Sucrose ID	Concentration (µg C/cm^2)
Sucrose|1	41.97
Sucrose|2	25.27
Sucrose|3	36.01
Sucrose|4	5.05
*Sucrose|5	10.10
Sucrose|6	55.00
Sucrose|7	2.00
Sucrose|11	210.50
Sucrose|12	105.25
Sucrose|13	42.10
Sucrose|14	21.05
*Sucrose|15	10.53
Sucrose|16	2.11

*Sucrose #5 and #15 are chosen for the daily single-point sucrose calibration check.

Upon completion of the sucrose analysis, the measured TC is processed and compared against the true value (i.e. calculated TC). The % error between the measured and calculated TC is derived using Equation 4.3.B-1. If the error exceeds the ± 7% acceptance limits, a second analysis is performed before any network samples are analyzed on that instrument. If the second analysis still exceeds the limit, or if a consistent one-sided bias (with error within ± 7%) is observed on multiple instruments, a different sucrose solution is analyzed to determine if the problem is with the solution or with the instrument. If the former, a new sucrose solution is made and verified; if the latter, a full five-point calibration is performed to determine the new calibration constant for that instrument. Table 4.3.B-5 summarizes the statistics of the daily sucrose check. There were 25 exceedances out of the 298 sucrose runs during the report period. All second analyses of the sucrose solution showed acceptable results (Figure 4.3.B-3).

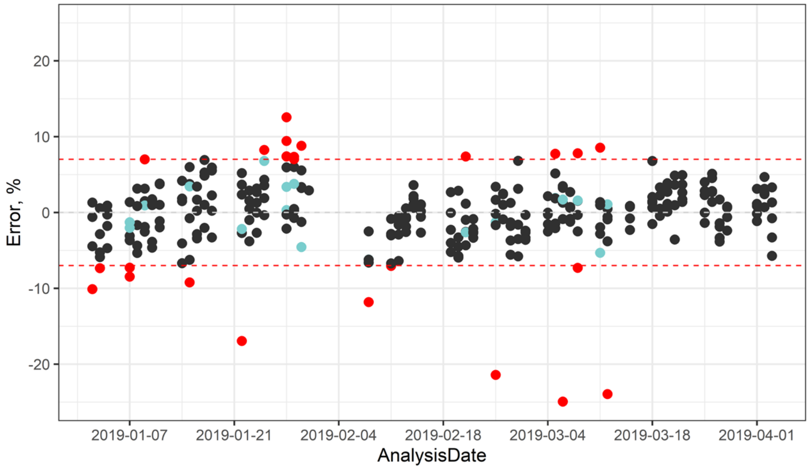
$$Error\ (\%) = \left(\frac{Measured\ TC - Calculated\ TC}{Calculated\ TC}\right) \times 100\%$$

(Eq. 4.3.B-1)

Table 4.3.B-5: Statistics of daily single-point sucrose standard analyses on all carbon analyzers for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018).

Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
298	0.387	-0.108	-24.938	12.560	4.467	25

Figure 4.3.B-3: Results of daily single-point sucrose calibration standard check for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018). Red dashed lines indicate the acceptance limit of ±7% error. For cases when original measured sucrose value (red points) exceeded the acceptance limit, a repeated analysis was performed (blue points).



4.3.B.2.3 Calibration Peak Area Check

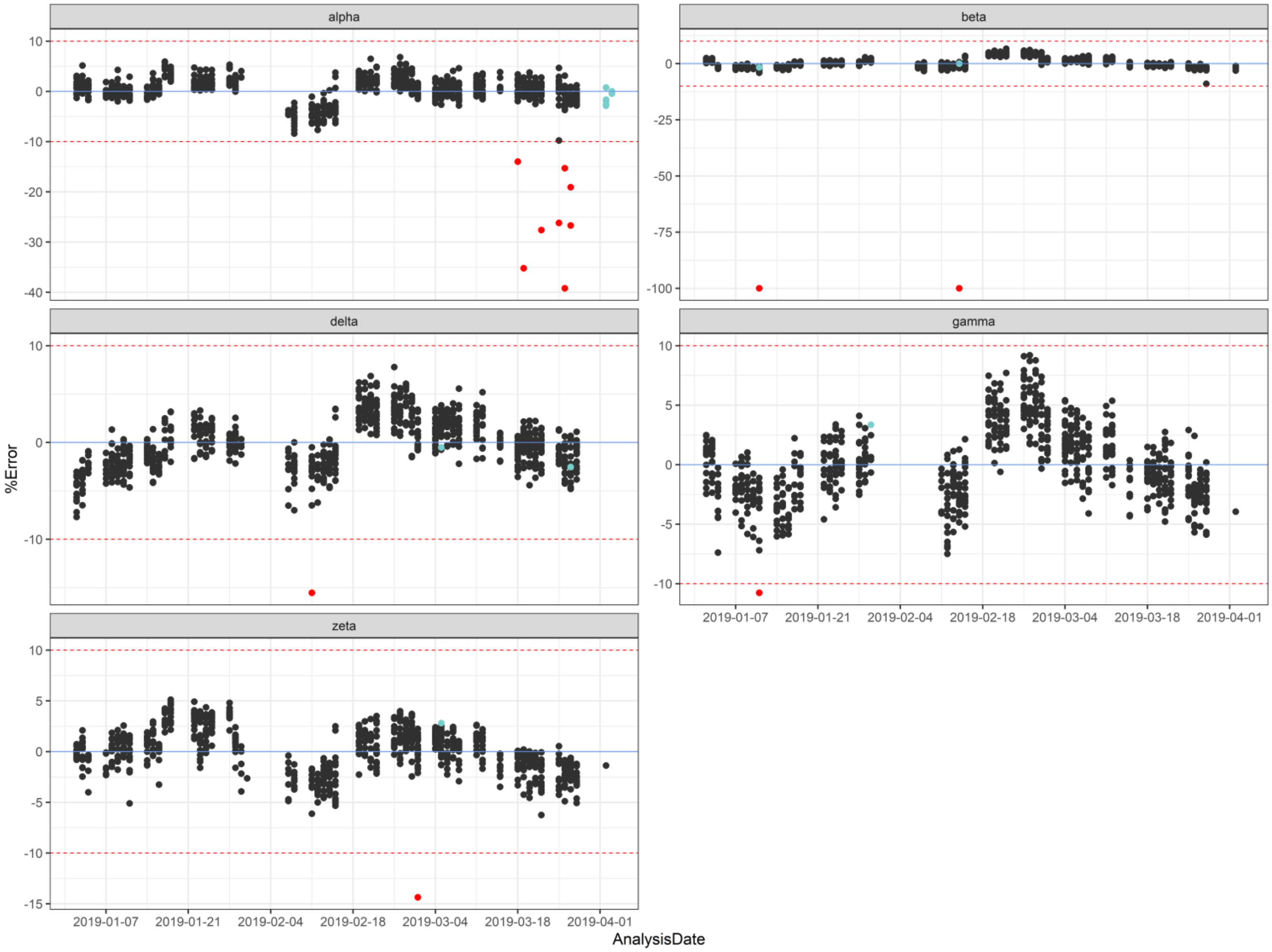
At the end of each analysis, a fixed amount of methane (CH_4) from a cylinder containing 5% CH_4 in Helium is injected into the system as an internal gaseous standard. The CH_4 peak area is quantified and compared to the average peak area of all analyses performed on that instrument. If the error (calculated using Equation 4.3.B-2) exceeds ± 10% acceptance limits, the analysis result is voided; the flowrate of the calibration gas and sample oven pressure are verified; corrective actions (if applicable) are taken immediately after the problem is identified; and the analysis is repeated using a second filter punch — usually after the completion of analysis for that batch (not on the same day). Table 4.3.B-6 summarizes the statistics of the calibration peak area check. There were 13 exceedances during this reporting period, most of which occurred when the clamp that connects the oven ball joint was not sufficiently tightened, resulting in a leak in the system. Eight exceedances occurred on Alpha over a short period of time due to a worn-out O-ring (Figure 4.3.B-4). The problem was eliminated after the O-ring was replaced. All reanalyses of the affected samples had acceptable results.

$$Error\ (\%) = \left(\frac{Cal.Peak - Average\ Cal.Peak}{Average\ Cal.Peak}\right) \times 100\% \qquad \text{(Eq. 4.3.B-2)}$$

Table 4.3.B-6: Statistics of internal calibration peak area check on all carbon analyzers for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018).

Analyzer	Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
Alpha	758	0.499	0.000	-39.197	6.827	3.711	8
Beta	759	-0.034	0.000	-99.998	6.680	6.667	2
Delta	802	-0.153	0.000	-15.532	7.795	2.738	1
Gamma	785	-0.360	0.000	-10.766	9.195	3.142	1
Zeta	786	0.087	0.000	-14.361	5.133	2.232	1

Figure 4.3.B-4: Results of internal calibration area check for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018). Blue solid line indicates the mean calibration area for the specific instrument. Red dashed lines indicate the acceptance limit of ±10% error from the mean value. For cases when calibration area exceeded the acceptance limit, a repeated analysis (blue points) was performed and the original analysis was voided (red points).



4.3.B.2.3 Laser Performance Check

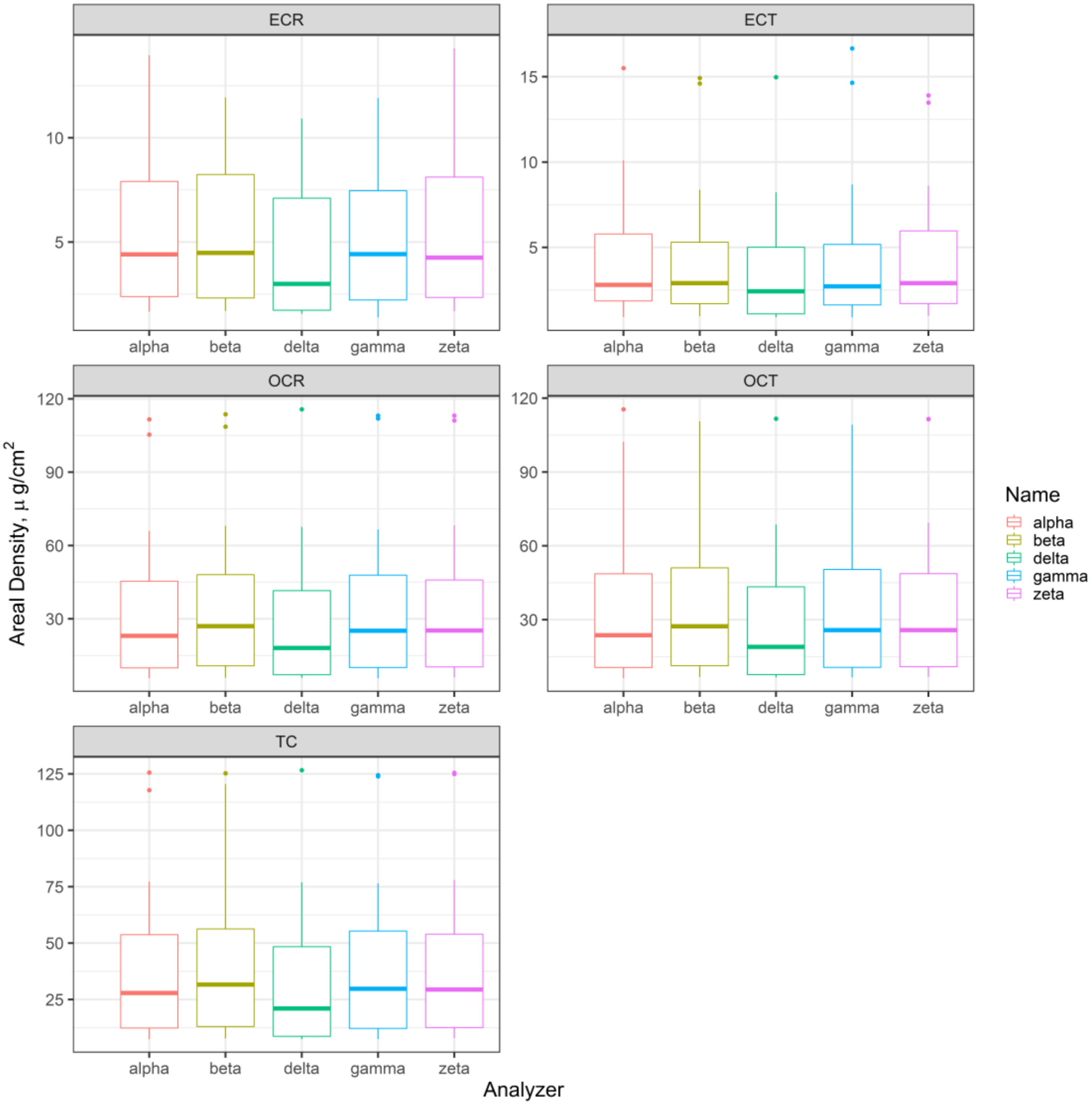
Laser signals (both reflectance and transmittance) are monitored throughout the TOA analysis and are examined for stability during post-analysis thermogram review. Any unusual laser response results in reanalysis of the sample. In addition, before starting the instrument blank analysis each day, the reading of laser reflectance and transmittance signals is checked to make sure it is above the initial laser acceptance criterion (i.e. 5000 a.u.). Figure 4.3.B-5 shows the initial readings of the reflectance and transmittance signals for instrument blank analysis. The laser signals show good overall stability during this analysis period. There was a step increase in the laser signal for most of the five analyzers on 3/14/2019 resulting from laser fine-tuning and signal optimization during a major instrument maintenance. There were no exceedances within during this analysis period.

Figure 4.3.B-5: Initial laser readings (top: Reflectance; bottom: Transmittance) of the instrumental blank analysis for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018). Red dashed line indicates the acceptance limit of 5000 a.u. of the laser signal. Black vertical line indicates date of instrument maintenance (3/14/2019). Points are colored by analyzer.

4.3.B.2.4 Inter-instrument Comparison Check

Instrument inter-comparison is evaluated weekly by analyzing performance check samples collected at UC Davis. Pre-fired 37-mm quartz filters are used to allow enough deposit area for at least five 0.58 cm^2 punches. A total of 19 weekly performance check samples were analyzed during this reporting period. Figure 4.3.B-6 shows the statistical distribution of the EC, OC and TC areal densities measured by each analyzer.

Figure 4.3-6: Statistical distribution of the elemental, organic and total carbon areal densities measured from the weekly performance check samples by each analyzer for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018). Elemental carbon (EC) and organic carbon (OC) are shown by reflectance (R) and transmittance (T); total carbon is indicated as TC. The thick horizontal line in each box represents the median value.



The measured carbon areal density from each analyzer (A_X) is compared against the average value derived from all analyzers available. The bias for each carbon parameter ($Bias_i$) is calculated for each analyzer each week as:

$$Bias_i = \left(\frac{Ax - average}{average}\right) * 100\% \quad \text{(Eq. 4.3.B-3)}$$

The acceptance criteria for inter-instrumental bias is 10% for TC and 20% for ECR. Exceeding the acceptance limits results in further investigation of the instrument and sample anomalies. A second performance check sample is run on all analyzers once the issue is resolved. Table 4.3.B-7 summarizes the statistics of the instrument bias for ECR and TC. There was no exceedance during the report period.

Table 4.3.B-7: Statistics of the instrument bias from the weekly performance check for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018).

		Elemental Carbon by Reflectance (ECR)					**Total Carbon (TC)**				
Analyzer	**Count**	**Median**	**Average**	**Min**	**Max**	**St.Dev.**	**Median**	**Average**	**Min**	**Max**	**St.Dev.**
Alpha	19	4.097	4.325	-5.870	16.074	6.233	-1.697	-1.899	-6.571	2.068	2.751
Beta	19	0.899	1.105	-7.375	16.229	5.893	1.047	1.796	-1.702	7.249	2.741
Delta	19	-6.275	-5.861	-10.723	1.070	3.028	0.353	0.834	-5.294	8.046	3.454
Gamma	19	-1.344	-1.587	-15.927	9.478	6.307	0.007	-0.489	-7.356	3.803	2.566
Zeta	19	2.484	2.019	-7.137	14.511	5.028	-0.296	-0.242	-6.202	2.788	1.982

4.3.B.2.5 Network Sample Replicates

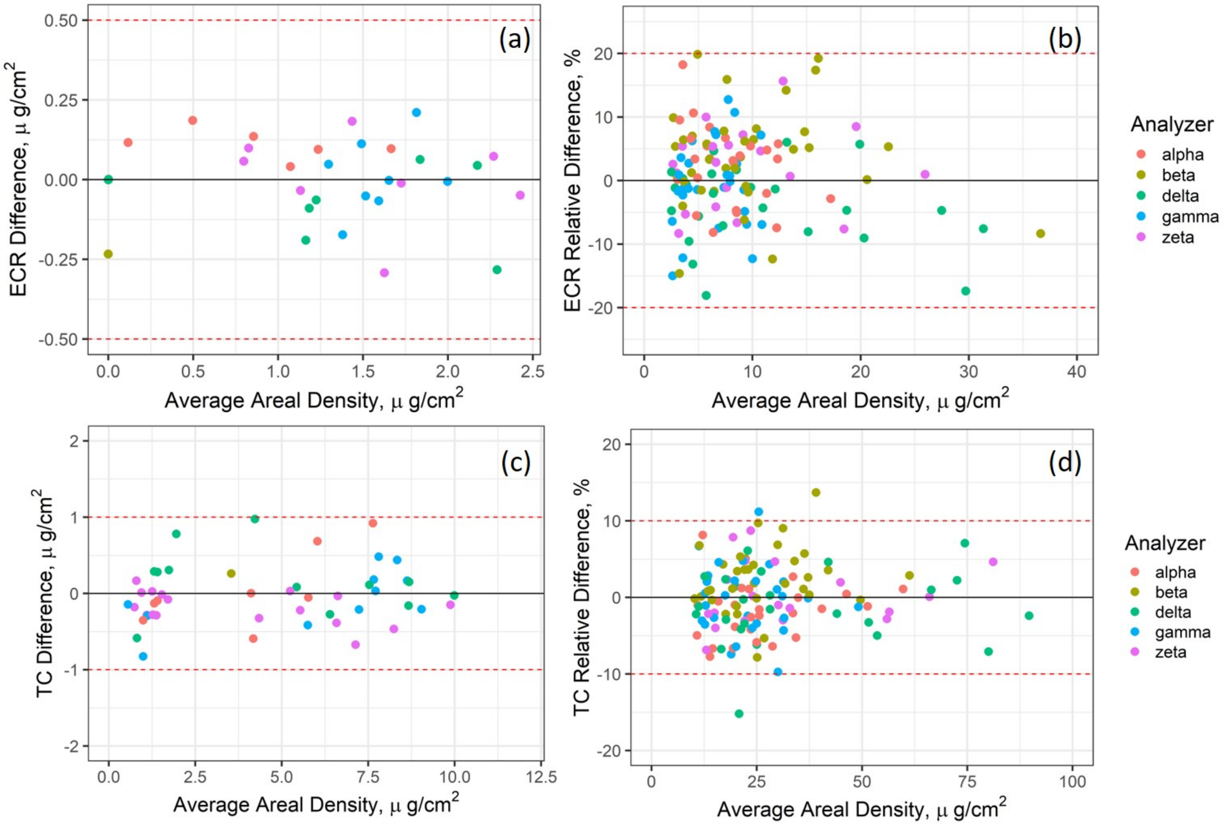
Replicate analyses are performed on approximately 5% of samples, where replicate analysis results are obtained from a second punch from the same filter analyzed on a randomly selected analyzer. Table 4.3.B-8 lists the acceptance criteria for replicate analysis and the summary statistics from this reporting period. A total of 194 replicate analyses were performed out of the 3,851 samples. For cases that exceeded the acceptance limits, a third punch (if available) was analyzed on a different analyzer. All three sets of results (routine, replicate, and reanalysis) from the same sample are compared to determine analysis validity. Instrument anomaly and/or sample inhomogeneity are also examined. Figure 4.3.B-7 shows the results of the replicate analysis. There were 12 TC exceedances and seven ECR exceedances during this reporting period. Affected samples were reanalyzed on a third analyzer. Three samples (F128113, F132000, and F129430) failed the replicate analysis criteria for TC and were not reanalyzed because there was insufficient deposit area remaining (see Figure 4.3.B-7, panel d). All other reanalyses had satisfactory results.

Table 4.3.B-8: Acceptance criteria and the summary statistics of the replicate analyses for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018).

Parameter	**Acceptance Criteria**	**# Replicate**	**# Exceedance**	**# Reanalysis passed**
TC	*RPD < ±10% when TC ≥10 µg /cm^2 or Absolute difference <±1 µg/cm^2 when TC <10 µg /cm^2	194	12	9
ECR	*RPD < ±20% when ECR ≥ 2.5 µg /cm^2 or Absolute difference <±0.5 µg/cm^2 when ECR <2.5 µg/cm^2	194	7	7

*RPD: Relative Percentage Difference = (Replicate-Routine)/Average *100%

Figure 4.3.B-7: Results of CSN replicate analysis for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018). The red dashed lines in each panel represents the acceptance limits.



4.3.B.2.6 Multi-point Sucrose Standard Check

A multi-point calibration is performed every six months, when the calibration gas cylinder is replaced, or if a consistent one-sided bias is observed with the daily single-point sucrose standard check, whichever comes first. The calibration uses sucrose standards at five different concentration levels (see Table 4.3.B-4 for details). The least-square correlation coefficient (r^2) of measured versus calculated mass of carbon, force-fit through the origin (0,0), should be higher than 0.995. The calibration constant for each analyzer is updated if the measured and calculated sucrose concentrations deviate from the 1:1 line by more than 1% (i.e. calibration slope > 1.01 or < 0.99). Table 4.3.B-9 summarizes the multi-point sucrose calibrations performed during this reporting period.

Table 4.3.B-9: Summary of multi-point sucrose standard checks performed for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018).

Analyzer	Calibration Date	Slope	r^2	Calibration Constant
Beta	2/5/2019	1.0009	0.9999	20.8463
Alpha	2/5/2019	0.9634	0.9999	20.6972
Gamma	2/5/2019	0.9993	0.9999	20.3398
Delta	2/5/2019	1.0125	0.9988	20.0899
Zeta	2/5/2019	0.9694	0.9993	20.7421

4.3.B.2.7 Temperature Calibration

A temperature calibration is performed every six months (usually along with a multi-point sucrose calibration) or after a major instrument repair (e.g., replacement of main oven or heating coils). The sample temperature probe is calibrated using a manufacturer-provided temperature calibration device, inserted into the sample oven so that the external temperature probe sits at where a filter punch would be during a routine analysis. The oven temperature cycles through the IMPROVE_A protocol temperature set points (from 140°C to 840°C). The differences in temperature readings by the calibration probe and the sample temperature probe (i.e. temperature offsets) are calculated and updated in the instrument parameter file. The system then goes through the IMPROVE_A temperature cycle again to verify that the temperature readings from the two probes are within 10°C at all temperature steps. Table 4.3.B-10 summarizes the temperature calibrations performed on each analyzer during this reporting period. Differences in the temperature offsets between the two calibrations are expected if the heating coils are replaced or re-wrapped around the main oven.

Table 4.3.B-10: Summary of the temperature calibrations performed on each analyzer for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018).

Analyzer	Calibration Date	Oven Re-Wrapped?	Temperature Offsets (°C)					
			140°C	280°C	480°C	580°C	740°C	840°C
Beta	2/1/2019	N	-12	-27	-33	-32	4	-3
	3/14/2019	Y	8	7	-21	-55	-4	-16
Alpha	2/1/2019	N	16	31	30	28	-5	-18
	3/14/2019	Y	12	31	30	28	-5	-18
Gamma	1/31/2019	N	8	22	32	30	30	18
	3/14/2019	Y	-24	-53	-50	-65	-37	-40
Delta	1/31/2019	N	30	36	36	29	32	19
	3/14/2019	Y	0	-15	-21	-21	-5	-11
Zeta	1/31/2019	N	11	23	31	30	39	18
	3/14/2019	Y	-34	-63	-71	-60	-8	-20

4.3.B.3 Determination of Uncertainties and Method Detection Limits

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

For uncertainty estimates see Section 6.5.

4.3.B.4 Audits, Performance Evaluations, Training, and Accreditations

4.3.B.4.1 System Audits

The EPA did not conduct any audits or performance evaluations of the UC Davis Carbon Laboratory during this reporting period.

4.3.B.4.2 Performance Evaluations

The UC Davis Thermal Optical Analysis Laboratory participated in an interlaboratory comparison study organized by the European Centre for Aerosol Calibration (ECAC) in March 2019. Eight quartz filter samples and one solution sample were received and analyzed for OC, EC and TC. UC Davis passed the evaluation with good data repeatability and no systematic bias. The full report is available at https://www.actris-ecac.eu/files/OCEC-2019-1-REPORT_final.pdf.

4.3.B.4.3 Training

All new laboratory staff and student assistants working in the UC Davis Thermal Optical Analysis Laboratory receive mandatory UC Laboratory Safety Fundamentals training. Personnel who operate the TOA analyzers receive additional training on the *CSN SOP 402* and relevant Technical Instructions.

4.3.B.4.4 Accreditations

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

4.3.B.5 Summary of Filter Blanks

Over the sampling period (October 1, 2018 through December 31, 2018) there were 423 valid quartz filter field blanks. Table 4.3.B-11 summarizes the field blank statistics.

Table 4.3.B-11: Quartz filter field blank statistics for the analysis period 1/2/2019 through 4/3/2019 (samples collected 10/1/2018 through 12/31/2018). Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).

Species	Count	Median (µg/cm^2)	Average (µg/cm^2)	Min (µg/cm^2)	Max (µg/cm^2)	St.Dev. (µg/cm^2)
EC1	423	0.025	0.065	-0.050	0.989	0.121
EC2	423	0.065	0.095	-0.010	0.675	0.089
EC3	423	0.013	0.017	-0.025	0.287	0.028
ECR	423	0.000	0.000	-0.002	0.098	0.007
ECT	423	0.000	0.000	-0.002	0.001	0.000
OC1	423	0.225	0.230	0.017	0.689	0.096
OC2	423	0.310	0.343	0.122	1.949	0.176
OC3	423	0.367	0.562	0.121	4.672	0.529
OC4	423	0.140	0.261	0.022	1.580	0.273
OCR	423	1.250	1.572	0.455	7.078	0.963
OCT	423	1.250	1.573	0.455	7.078	0.963
OPR	423	0.107	0.176	-0.080	1.593	0.206
OPT	423	0.107	0.177	-0.080	1.593	0.206

5. Data Management and Reporting

5.1 Number of Events Posted to AQS

Table 5.1-1 summarizes dates that data were delivered to AQS for samples collected January 1, 2018 through December 31, 2018. Data are expected to be delivered to AQS within 120 days of receipt of filters by the analytical laboratories. Laboratory analysis delays resulted in later deliveries to AQS (see Section 2.1.1, Section 2.2.1, Section 2.4.1, and Section 2.5.1).

Table 5.1-1: Summary of data deliveries to AQS, January 1, 2018 through December 31, 2018.

Data (Month Samples Collected)	Filter Receipt Date	AQS Delivery Date	Days
January 2018	March 7, 2018	August 31, 2018	177
February 2018	April 4, 2018	September 14, 2018	163
March 2018	May 2, 2018	September 28, 2018	149
April 2018	June 7, 2018	October 16, 2018	131
May 2018	July 10. 2018	November 3, 2018	115
June 2018	August 8, 2018	December 4, 2018	118
July 2018	September 6, 2018	January 3, 2019	119
August 2018	October 9, 2018	January 30, 2019	113
September 2018	November 7, 2018	February 28, 2019	113
October 2018	December 11, 2018	April 22, 2019	132
November 2018	January 9, 2019	May 9, 2019	120
December 2018	February 6, 2019	June 11, 2019	125

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. Updated versions were delivered to the EPA on November 30, 2018 and July 31, 2019.

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. Updated versions were delivered to the EPA on November 30, 2018 and July 31, 2019.

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 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 (Wood PLC) via email and uploaded to the UC Davis CSN database. UC Davis EDXRF results are transferred into the UC Davis CSN database through an automated service. For samples collected through September 30, 2018, IC and TOA analysis result files were received via email from DRI. Beginning October 1, 2018, IC analysis result files are received via email from RTI; and, UC Davis TOA results are transferred into the UC Davis CSN database through an automated service. Result files received via email (DRI and RTI) 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/csn-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. Comparisons to historical network data provide context for validation and review of more recent data.

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 by reflectance (OCR) and elemental carbon by reflectance (ECR). These figures show raw data without blank correction to enable comparison across a wider timeframe. The carbon fractions OCR and ECR are determined by thermal optical analysis (TOA) with a correction for pyrolysis based on optical monitoring as the sample is heated. Measurements for samples collected from 2005 through 2015 were made at DRI with DRI Model 2001 analyzers monitoring at the single wavelength 633 nm; samples collected from January 2016 through September 2018 were analyzed at DRI using their DRI Model 2015 analyzers monitoring seven wavelengths centered at 635 nm; and, beginning with samples collected from October 2018 analysis was performed at UC Davis using the Sunset Laboratory Model 5L analyzer monitoring at the single wavelength 658 nm. The OCR 2018 concentrations at the median and 90th percentile were elevated during July and August, but otherwise trended lower than previous years for most months, particularly at the 90th percentile. The ECR concentrations for 2018 trend similarly to previous years with modestly elevated concentrations during the summer months.

Figure 6.4-1: Multi-year time series of network-wide organic carbon by reflectance concentrations (OCR; raw data without blank correction). Symbols denote laboratory and type of analyzer: DRI Model 2001 (circle), DRI Model 2015 (triangle), and UCD Sunset Laboratory Model 5L (square).

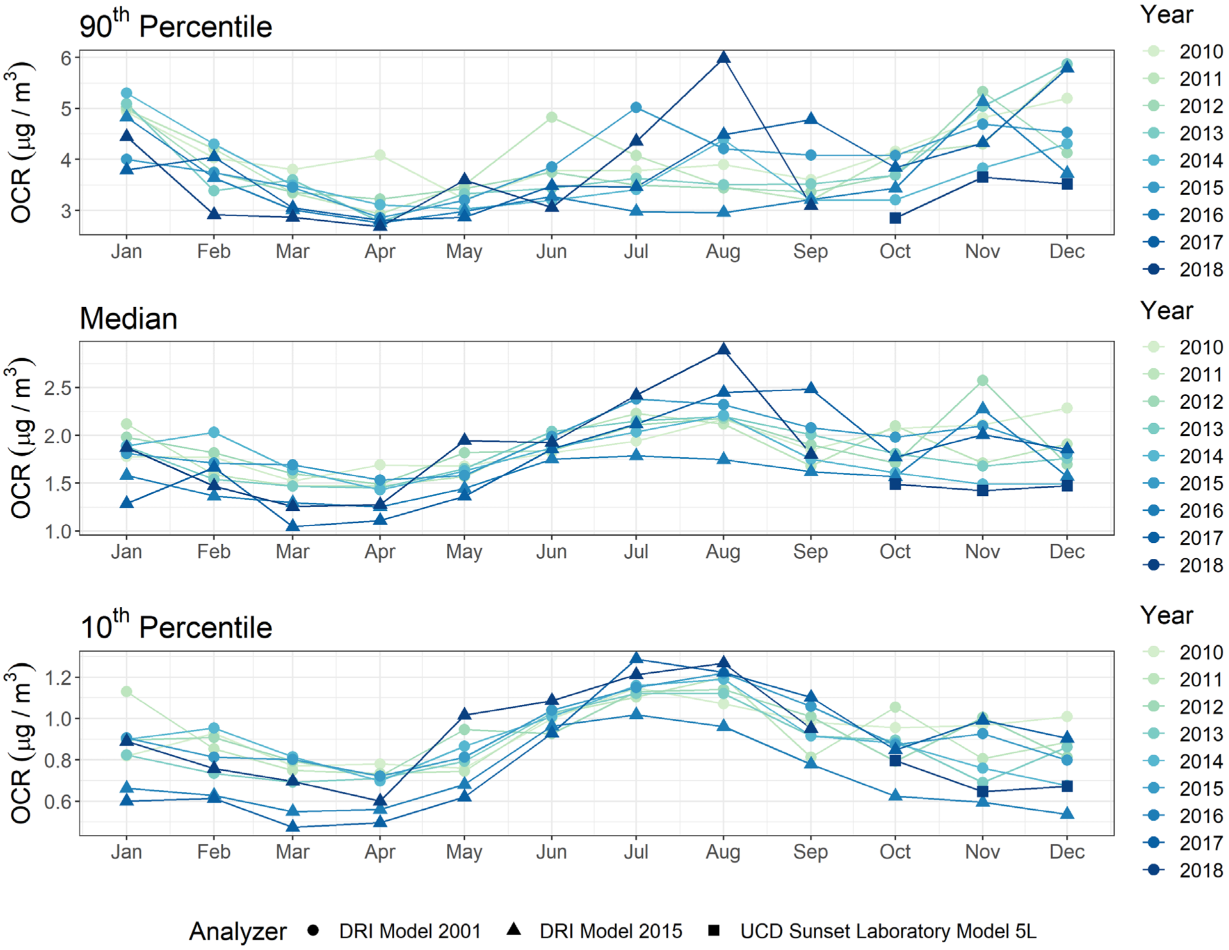
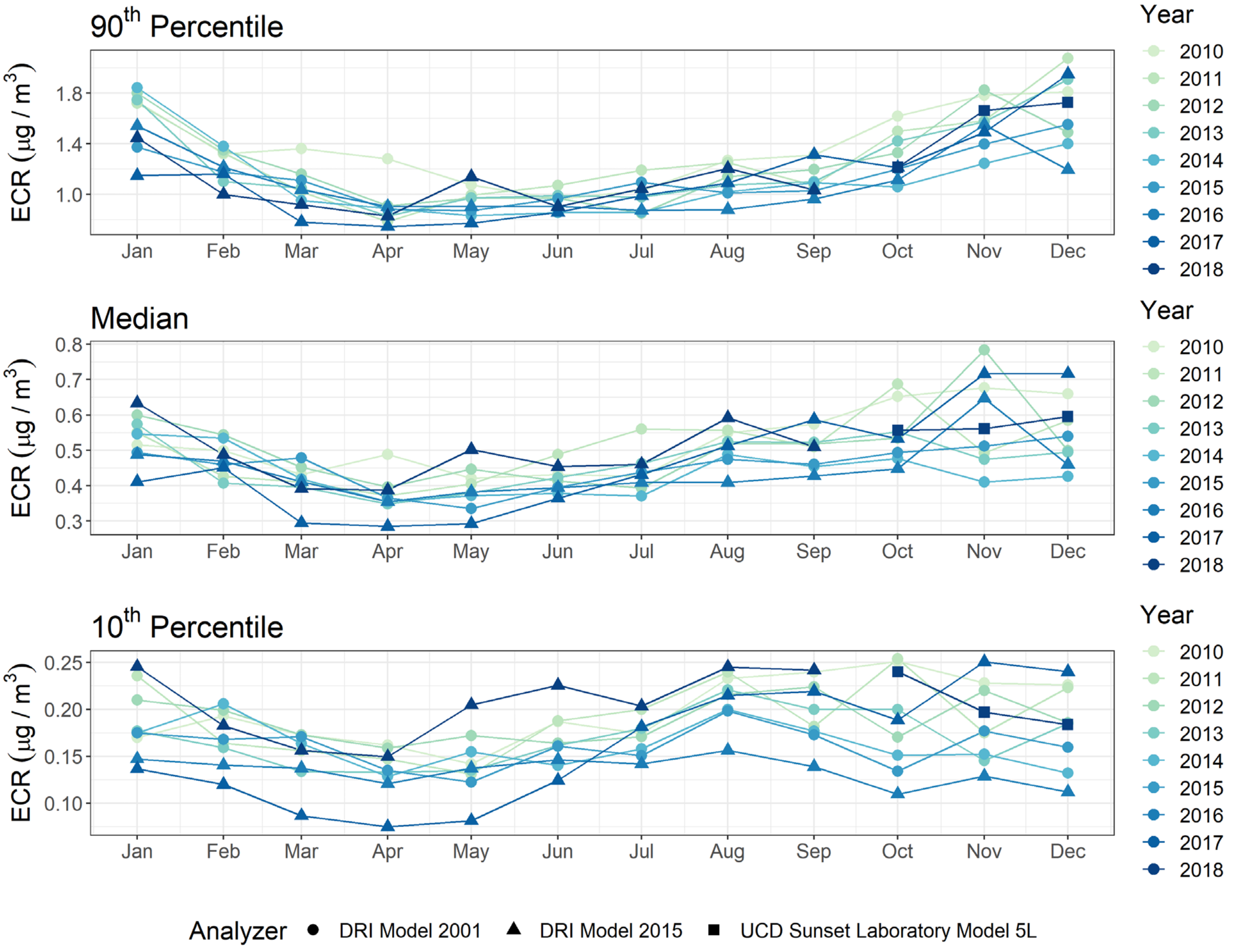
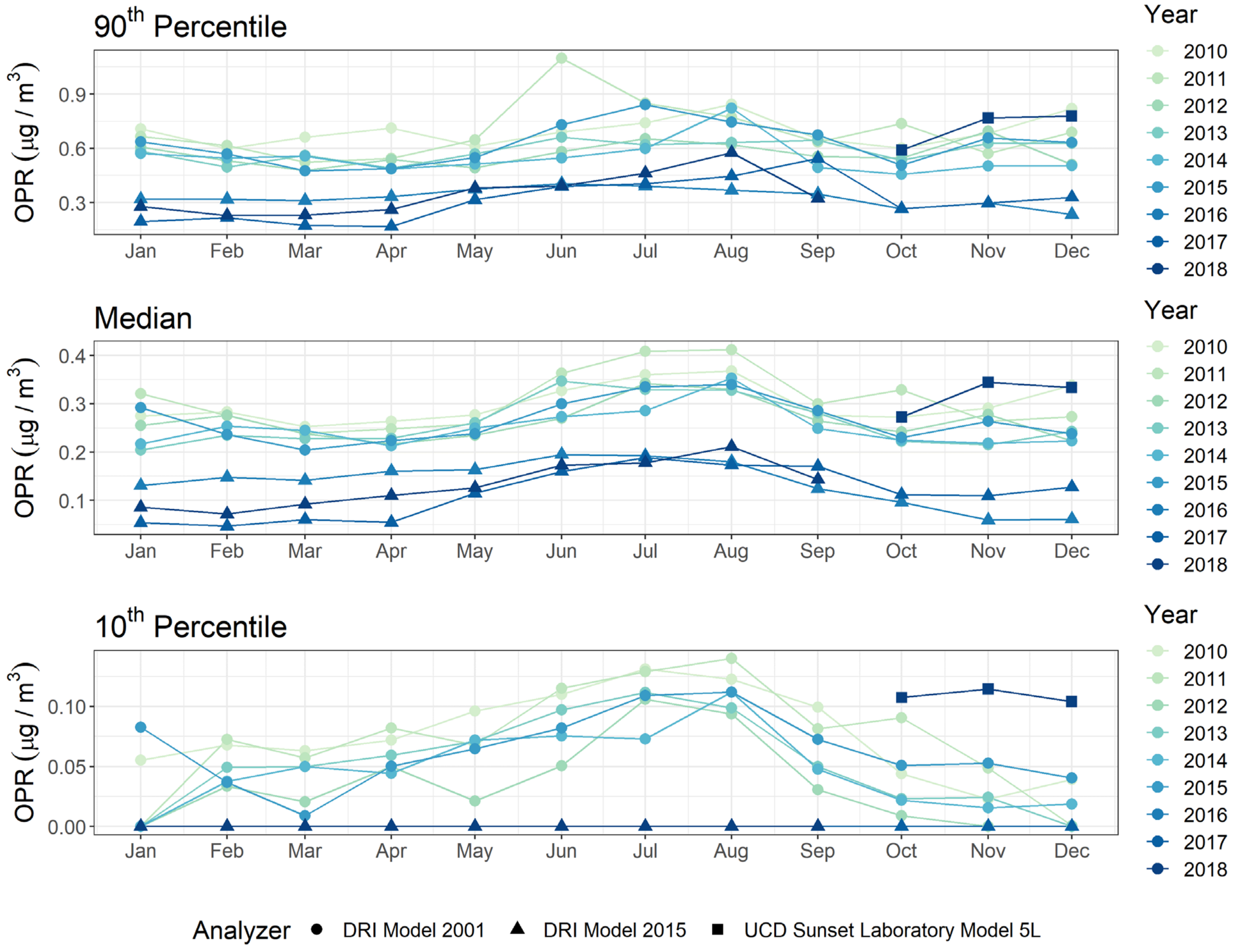


Figure 6.4-2: Multi-year time series of network-wide elemental carbon by reflectance concentrations (ECR; raw data without blank correction). Symbols denote laboratory and type of analyzer: DRI Model 2001 (circle), DRI Model 2015 (triangle), and UCD Sunset Laboratory Model 5L (square).



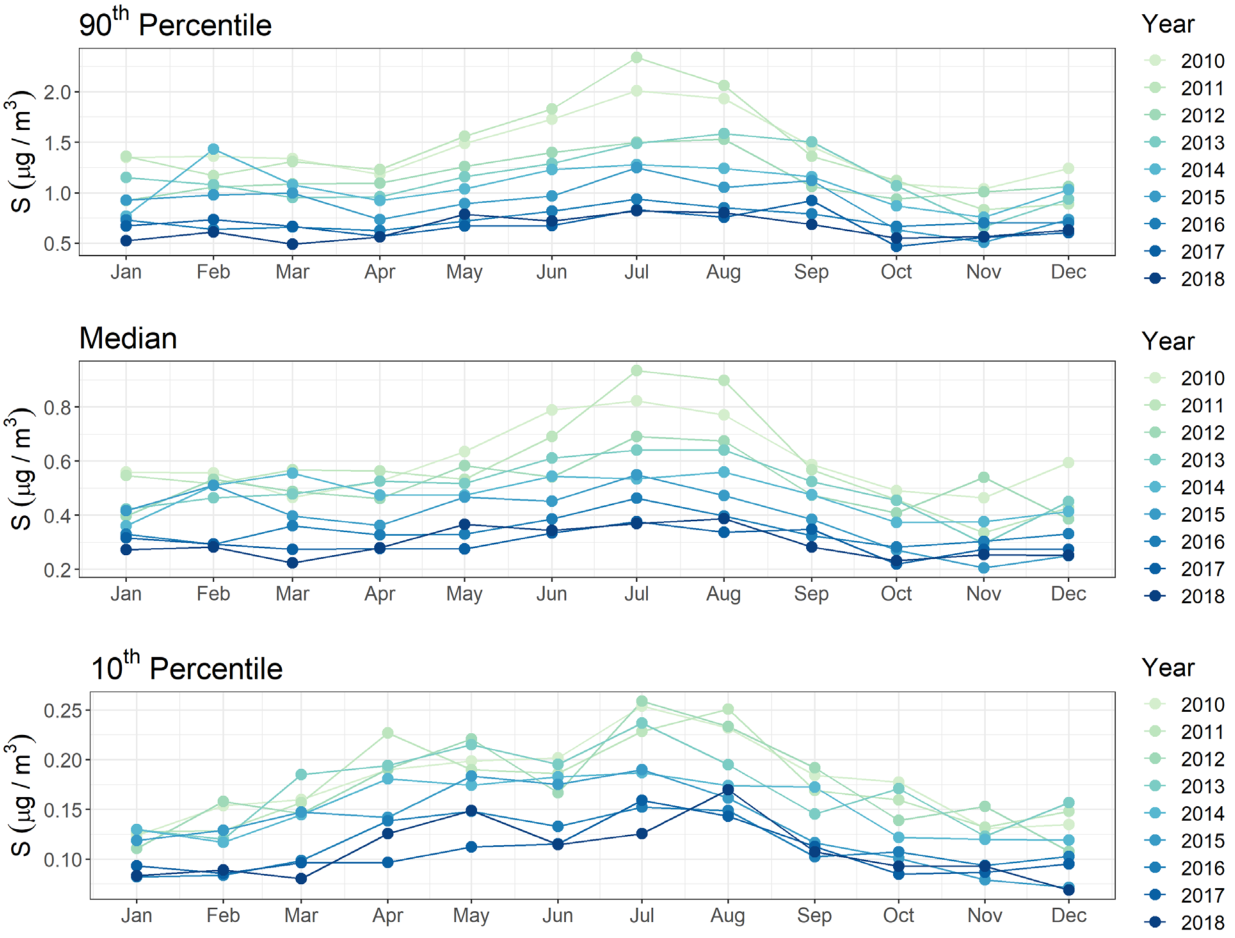
During TOA analysis some of the OC pyrolyzes upon heating under the inert environment. The organic pyrolyzed carbon (OPR) is combusted with the EC collected on the filter, and is accounted for by monitoring the laser signal and identifying an OC/EC split point based on return of the last signal to its initial value. To some extent, the split point – and thus the amount of OPR – is operationally defined based on instrument parameter settings. As seen in Figure 6.4-3, corresponding with the change in analyzers from DRI Model 2001 to DRI Model 2015 that occurred on January 1, 2016, the OPR concentrations at the median and 90th percentile decreased; and, corresponding with the laboratory transition from DRI (DRI Model 2015) to UC Davis (UCD Sunset Laboratory Model 5L) the OPR concentrations at the 10th percentile, median, and 90th percentile increased. The October, November, and December 2018 OPR concentrations at the median and 90th percentile are in closer alignment with those from DRI made prior to the instrument transition (DRI Model 2001 to DRI Model 2015).

Figure 6.4-3: Multi-year time series of network-wide organic pyrolyzed carbon by reflectance concentrations (OPR; raw data without blank correction). Symbols denote laboratory and type of analyzer: DRI Model 2001 (circle), DRI Model 2015 (triangle), and UCD Sunset Laboratory Model 5L (square).



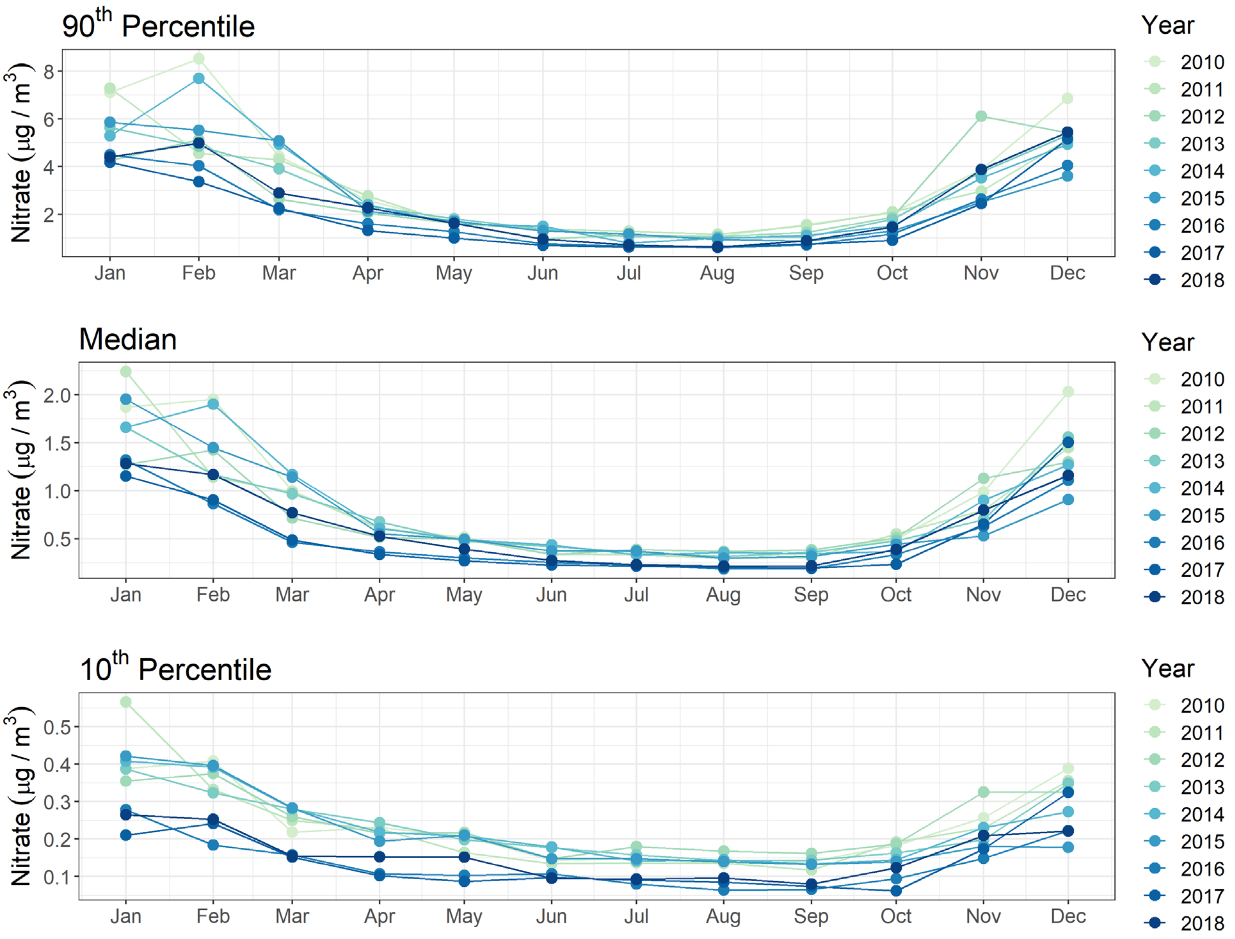
Similar to 2016 and 2017, the 2018 sulfur concentrations generally continue to be low (Figure 6.4-4), with reduced seasonal variability.

Figure 6.4-4: Multi-year time series of network-wide sulfur (S) concentrations.



The nitrate concentrations show strong seasonality with elevated winter concentrations; however, 2016, 2017, and 2018 concentrations are generally lower relative to previous years (Figure 6.4-5).

Figure 6.4-5: Multi-year time series of network-wide nitrate concentrations.



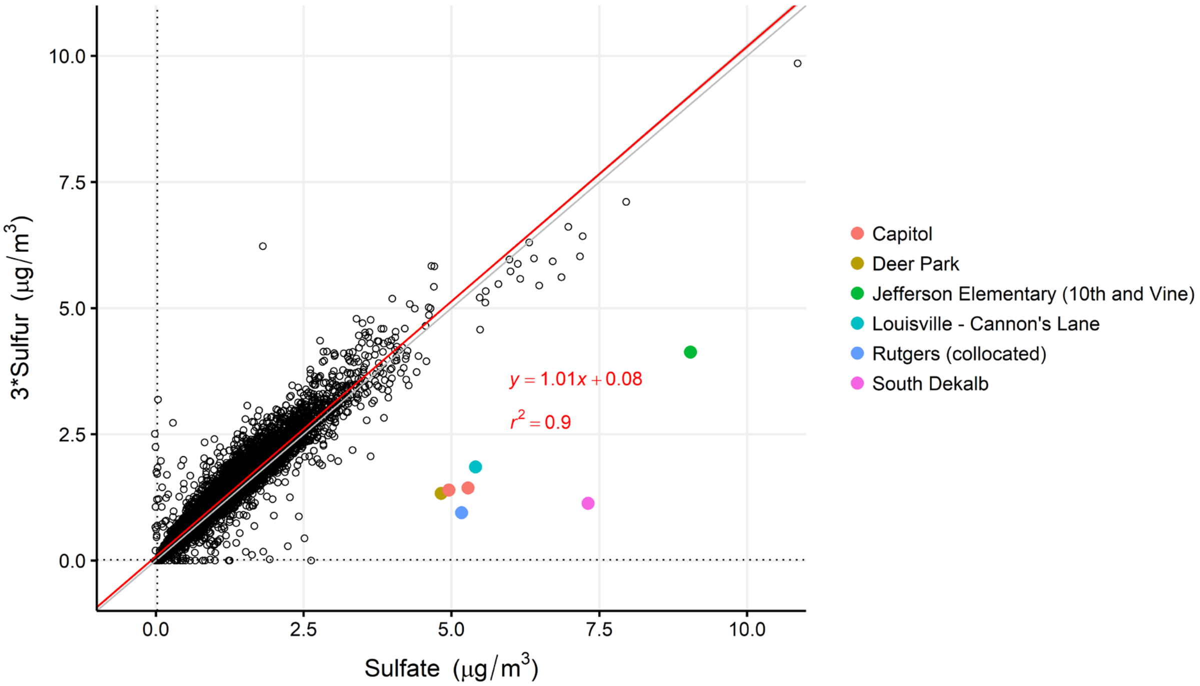
6.4.1.2 *Comparisons Between Modules*

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.

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 6.4-6), 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 6.4-6; colored points).

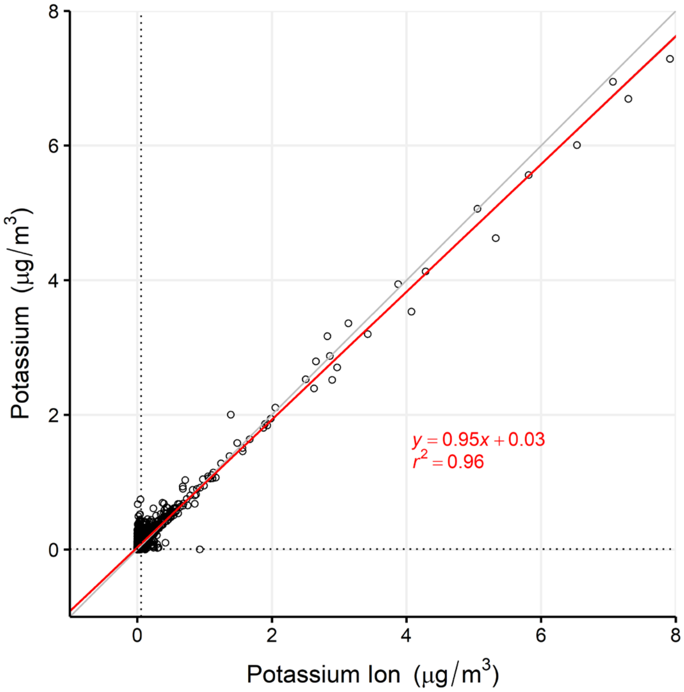
Figure 6.4-6: Scatter plot of (3×S) versus SO_4, samples collected January 1, 2018 through December 31, 2018. Number of observations (complete pairs) is 12,826. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression.



Potassium versus Potassium Ion

PTFE filters are analyzed for elemental potassium using EDXRF, and nylon filters are analyzed for potassium ion using IC. Similar to the S/SO_4 ratio 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 6.4-7). 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.

Figure 6.4-7: Scatter plot of potassium versus potassium ion, samples collected January 1, 2018 through December 31, 2018. Number of observations (complete pairs) is 12,826. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression.



$PM_{2.5}$ 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*. In the simple case where valid measurements are available for all needed variables, reconstructed mass is the following sum:

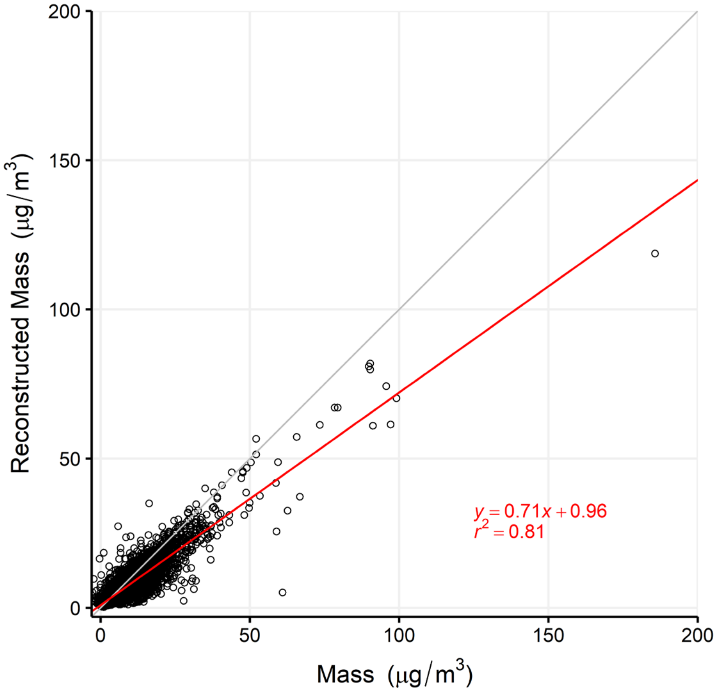
$$\begin{aligned}\text{RCM} = {} & (4.125 \times \text{S}) + (1.29 \times \text{NO}_3^-) + (1.4 \times \text{OC}) + (\text{EC}) + \\ & (2.2 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti}) + (1.8 \times \text{chloride})\end{aligned}$$

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

Gravimetric analysis is not routinely performed using CSN filters. Thus, for comparison purposes 24-hour average gravimetric $PM_{2.5}$ mass data from AirNow Tech is used as part of the validation process in DART. 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 to AirNow Tech mass ratio is expected to be near one. The RCM and AirNow Tech mass generally correlate (Figure 6.4-8), but RCM tends to underestimate AirNow Tech mass.

Figure 6.4-8: Scatter plot of RCM versus AirNow Tech PM2.5 mass data (Mass), samples collected January 1, 2018 through December 31, 2018. Number of observations (complete pairs) is 9,630. Solid gray line indicates 1:1. Solid red line indicates regression.



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 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.

Scaled relative difference between sample pairs collected at CSN collocated sites is calculated as shown in Equation 6.5-1 and used to evaluate collocated precision (Figure 6.5.1, elements; Figure 6.5-2, ions; Figure 6.5-3, carbon).

$$Scaled\ Relative\ Difference = \frac{(\text{collocated} \ - \ \text{routine}) \ / \ \sqrt{2}}{(\text{collocated} \ + \ \text{routine}) \ / \ 2} \qquad \text{(Eq. 6.5-1)}$$

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. This convergence is not observed for many elements and carbon fractions that are rarely measured above the MDL.

Figure 6.5-1: Scaled relative difference for element measurements at sites with collocated samplers across the network (January 1, 2018 through December 31, 2018). Dotted vertical lines indicate MDL.

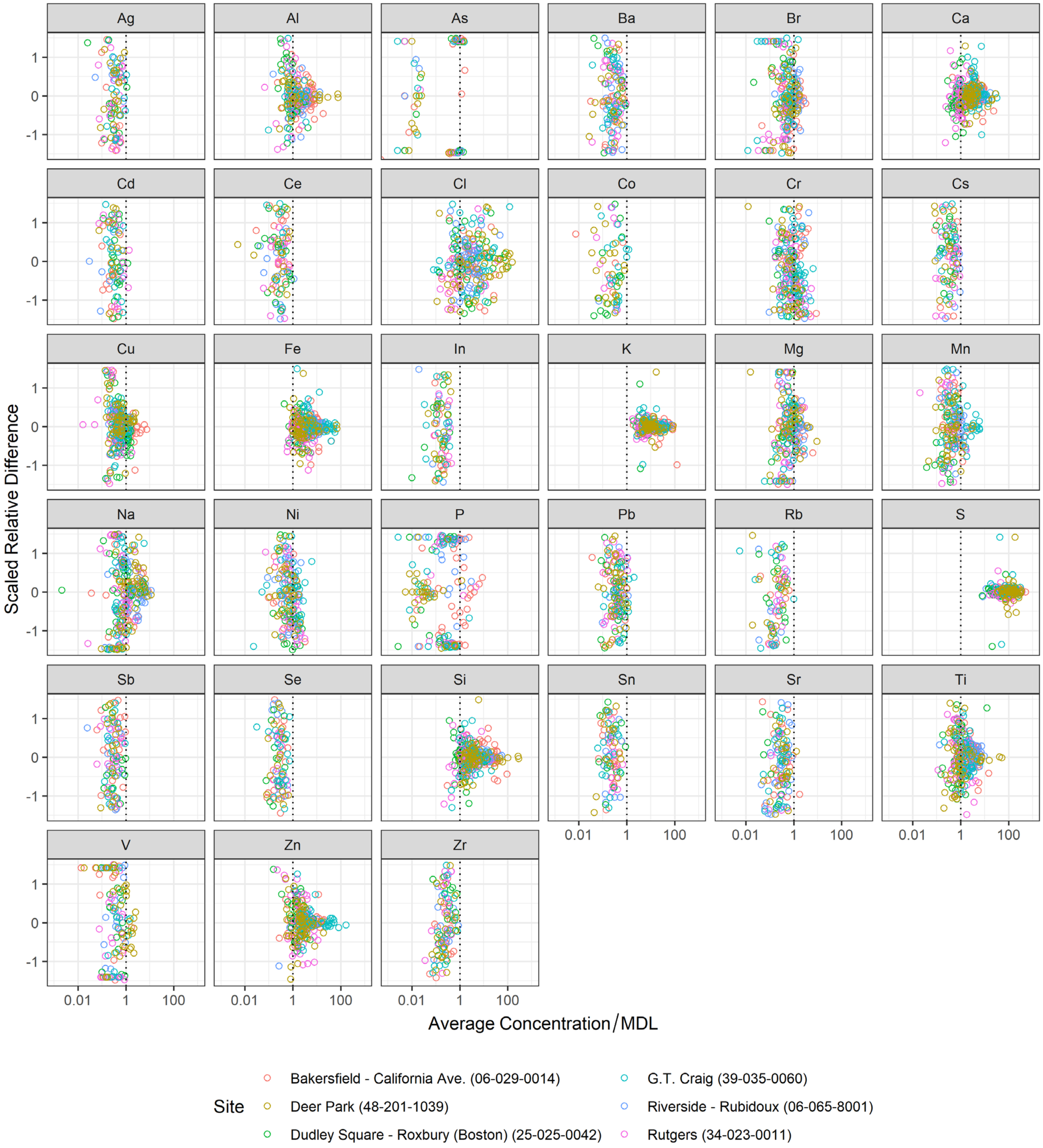


Figure 6.5-2: Scaled relative difference for ion measurements at sites with collocated samplers across the network (January 1, 2018 through December 31, 2018). Dotted vertical lines indicate MDL.

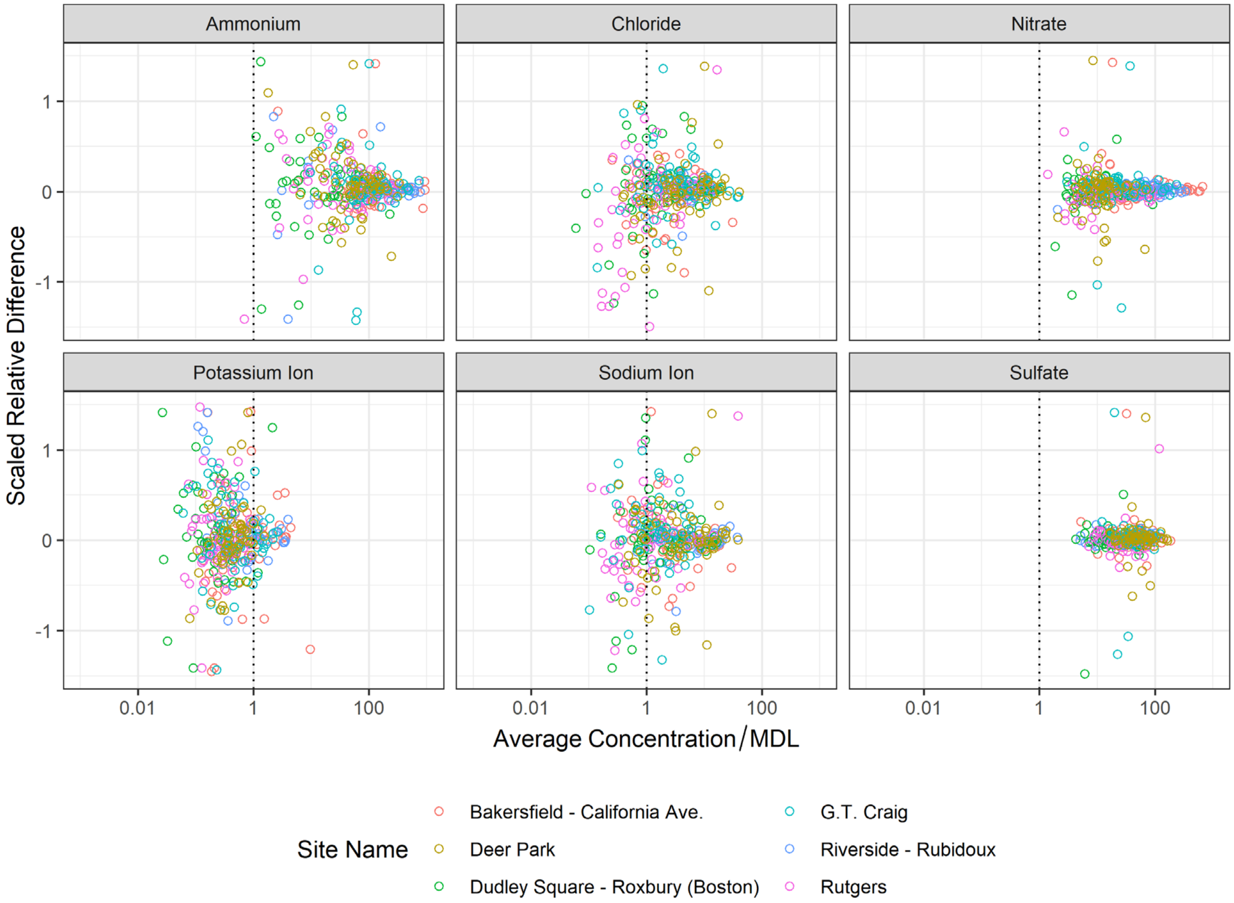
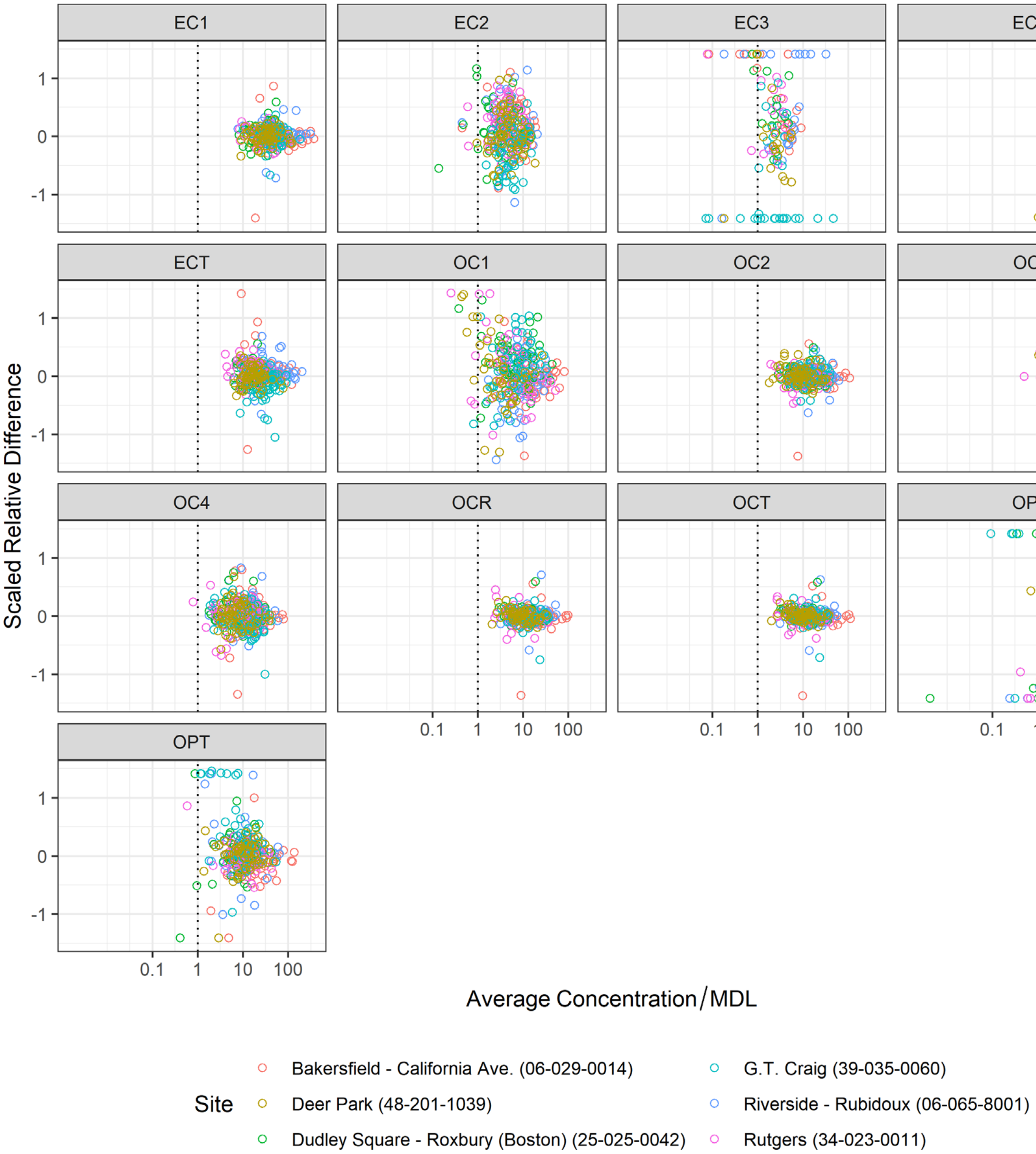


Figure 6.5-3: Scaled relative difference for carbon measurements at sites with collocated samplers across the network (January 1, 2018 through December 31, 2018). Dotted vertical lines indicate MDL. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolized (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).



Collocated precision is reported with CSN data delivered to AQS as fractional uncertainty. Fractional uncertainty is calculated from scaled relative differences (Equation 6.5-1) between sample pairs collected at CSN collocated sites, using the subset of observations with concentrations at least three times the MDL. To limit uncertainty in determination of the necessary percentiles, calculations are performed using multiple years of collocated data (January 1, 2009 through December 31, 2014 for this reporting period) with a minimum of 60 collocated pairs per year. The calculation for fractional uncertainty is documented in *UCD CSN TI 801B*, and summarized in Equation 6.5-1, Equation 6.5-2, and Equation 6.5-3.

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

(Eq. 6.5-2)

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

(Eq. 6.5-3)

Tables 6.5-1 (elements), 6.5-2 (ions), and 6.5-3 (carbon) list fractional uncertainties calculated for this reporting period. Since many species are routinely measured at or below the MDL, there are numerous instances where insufficient pairs were available, in which cases a fractional uncertainty of 0.25 is assigned. Historical data (2009-2014) are used to calculate fractional uncertainties for this reporting period. Beginning with the next reporting period (samples collected January 1, 2019 through December 31, 2019), fractional uncertainties will be updated annually and calculated using collocated data from the previous two years.

The network measurement quality objectives (MQOs) are based on the coefficient of variation (CV) between collocated measurements, and are defined as CV of 10% for ions, 20% for elements, and 15% for total carbon. As shown in Equation 6.5-4 and Equation 6.5-5, CV is calculated from sample pairs collected at CSN collocated sites, using the subset of observations with concentrations at least three times the MDL.

$$Relative\ Percent\ Difference\ (RPD) = \frac{X_i - Y_i}{(X_i + Y_i)\ /\ 2} \times 100$$

(Eq. 6.5-4)

$$CV_i = \frac{|\ \mathrm{RPD}\ |}{\sqrt{2}}$$

(Eq. 6.5-5)

where X_i and Y_i are the measurements from routine and collocated sites, respectively, for the i^{th} pair of measurements. Tables 6.5-1 (elements), 6.5-2 (ions), and 6.5-3 (carbon) list CV calculated from collocated samples collected during 2018.

Table 6.5-1: Fractional uncertainty (calculated from collocated samples collected 2009 through 2014) and median coefficient of variation (CV; calculated from samples collected during 2018) for elemental species. Fractional uncertainty and CV values not reported for species with less than 60 collocated pairs.

Species	Fractional Uncertainty (%) 2009 – 2014	Pairs	Coefficient of Variation (%) 2018	Pairs
Na	16.4	1,270	---	38
Mg	24.5	365	---	5
Al	25.2	1,209	---	55
Si	15.2	3,897	4.2	186
P	17.3	93	---	4
S	6.2	5,530	1.9	338
Cl	34.2	1,740	11.9	98
K	10.6	4,825	2.6	321
Ca	16.8	4,067	4.3	141
Ti	17.4	697	---	55
V	12.8	499	---	0
Cr	38.9	83	---	1
Mn	15.4	623	---	11
Fe	17	5,520	4.4	184
Co	---	10	---	0
Ni	17.8	400	---	0
Cu	26.9	2,313	---	4
Zn	12.3	3,144	3.5	123
As	18.8	155	---	0
Se	---	43	---	0
Br	15	1,610	---	0
Rb	---	0	---	0
Sr	---	58	---	0
Zr	---	3	---	0
Ag	---	1	---	0
Cd	---	0	---	0
In	---	0	---	0
Sn	---	0	---	0
Sb	---	0	---	0
Cs	---	7	---	0
Ba	16.5	123	---	0
Ce	---	21	---	0
Pb	18.5	381	---	0

Table 6.5-2: Fractional uncertainty (calculated from collocated samples collected 2009 through 2014) and median coefficient of variation (CV; calculated from samples collected during 2018) for ions. Fractional uncertainty and CV values not reported for species with less than 60 collocated pairs.

Species	Fractional Uncertainty (%) 2009 – 2014	Pairs	Coefficient of Variation (%) 2018	Pairs
Ammonium	7.1	5,466	4.6	316
Chloride*	---	---	3.8	203
Nitrate	7.6	5,767	2.7	320
Potassium Ion	12.6	2,072	---	8
Sodium Ion	24.7	3,562	4.0	206
Sulfate	4.9	5,680	1.9	335

*Collocated chloride results were not available/reported until February 2017.

Table 6.5-3: Fractional uncertainty (calculated from collocated samples collected 2009 through 2014) and median coefficient of variation (CV; calculated from samples collected during 2018) for carbon fractions. Fractional uncertainty and CV values not reported for species with less than 60 collocated pairs. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).

Species	Fractional Uncertainty (%) 2009 – 2014	Pairs	Coefficient of Variation (%) 2018	Pairs
Elemental Carbon (EC1)	12.9	1,948	4.3	337
Elemental Carbon (EC2)	36.8	992	9.0	235
Elemental Carbon (EC3)	---	4	---	12
Elemental Carbon (ECR)	15.5	1955	4.2	335
Elemental Carbon (ECT)	12.8	1,606	4.9	335
Organic Carbon (OC1)	32.9	1,039	10.4	219
Organic Carbon (OC2)	13.6	1,877	3.8	328
Organic Carbon (OC3)	17.8	1,860	4.4	286
Organic Carbon (OC4)	15.7	1,487	6.6	262
Organic Carbon (OCR)	11.6	2,033	2.9	315
Organic Carbon (OCT)	7.3	1,774	2.5	316
Organic Pyrolyzed (OPR)	25.1	919	8.4	197
Organic Pyrolyzed (OPT)	17.3	1,557	6.8	298

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