

Chemical Speciation Network (CSN)

Annual Quality Report

Samples Collected January 1, 2019 through December 31, 2019

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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 data 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 standard 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: filters are analyzed at Research Triangle Institute International (RTI) using ion chromatography (IC) for a suite of six ions.
- Quartz filters: filters are analyzed at UC Davis for organic and elemental carbon — including carbon fractions — using thermal optical analysis (TOA).

Unless otherwise noted, data and discussions included in this report cover samples collected during the time period January 1, 2019 through December 31, 2019 (batches 51-62, where each month corresponds with a single calendar month).

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 (RTI Ion Chromatography Laboratory), Section 4.2 (UC Davis X-Ray Fluorescence Laboratory), and Section 4.3 (UC Davis Thermal Optical Analysis Laboratory).

Across the network, completeness — determined by the total number of valid samples relative to the total number of scheduled samples — was 95.6% for PTFE filters, 95.7% for nylon filters, and 93.6% for quartz filters. Data from sites with non-standard sampler configurations are not included in the completeness calculations.

The EPA conducted a Technical Systems Audit (TSA) of UC Davis laboratory and data handling operations on August 18 & 19, 2019; see Section 3.2.5.

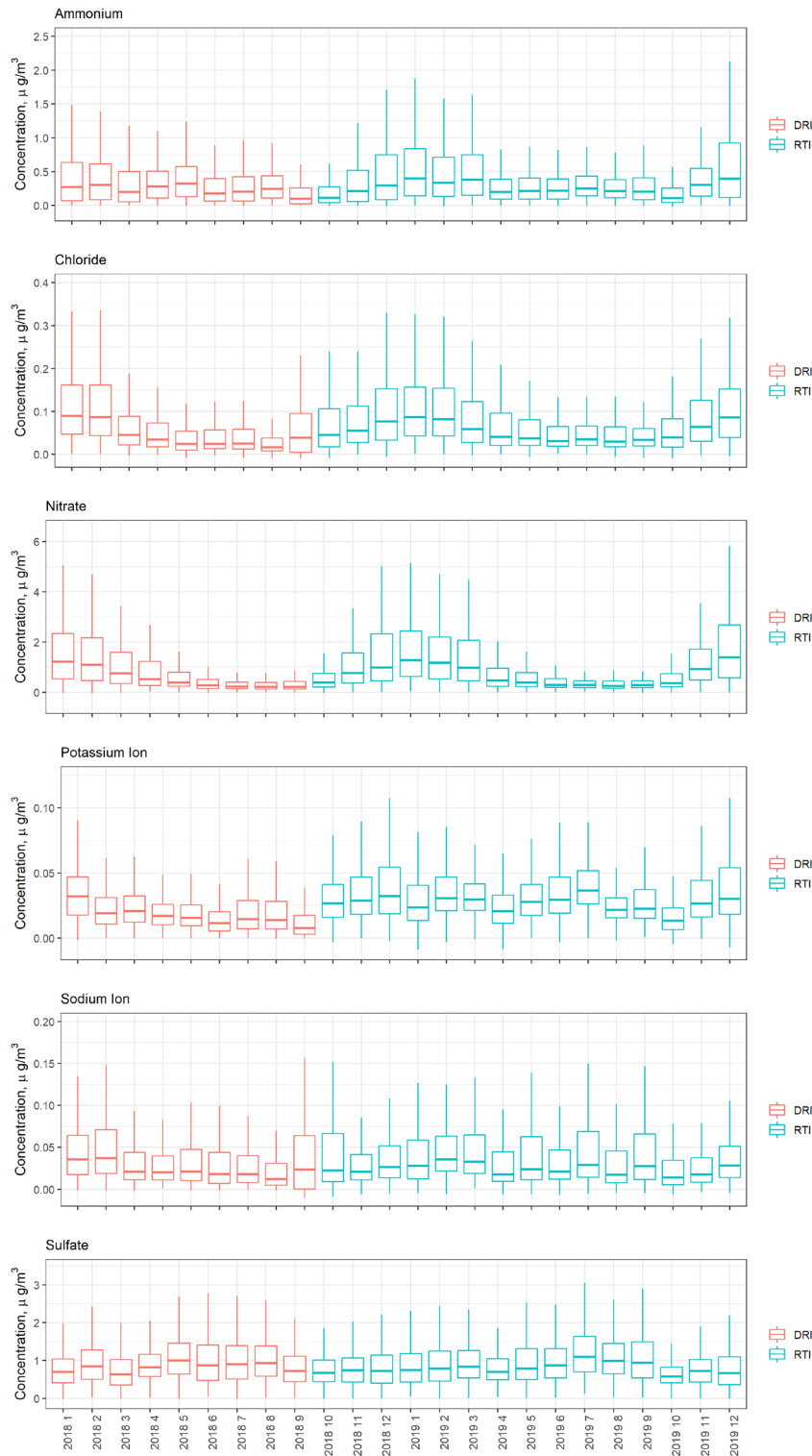
2. Summary of Laboratory Operation Issues

2.1 RTI Ion Analysis Laboratory

2.1.1 Continued Evaluation of Laboratory Transition

Beginning with samples collected October 1, 2018, nylon filters are analyzed for ions by IC at RTI; prior to October 1, 2018, nylon filters were analyzed for ions by IC at Desert Research Institute (DRI; Reno, NV). At the network level, there continues to be no evidence of a step change associated with the laboratory transition.

Figure 2.1-1: Monthly network wide results for ions; data from samples collected January 1, 2018 through December 31, 2019. Samples collected January 1, 2018 through September 30, 2018 were analyzed by DRI (red boxes) and samples collected October 1, 2018 through December 31, 2019 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 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).



2.2 UC Davis X-Ray Fluorescence Laboratory

2.2.1 Zinc

For analyses performed during this reporting period, intermittent zinc contamination was observed on the daily PTFE blanks analyzed on all of the EDXRF instruments. 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 2019 with unusual zinc mass loadings were investigated. Reanalysis results for two of these cases indicated contamination during the original analysis; the reanalysis results for these two samples were reported.

For further detail, see Section 3.2.1.1, Section 4.2.2.1, and Section 4.2.2.4.

2.2.2 Calcium

During this reporting period, some daily PTFE blanks showed a gradual increase in calcium mass loadings. The calcium buildup was likely caused by atmospheric deposition or instrument wear on these filters; these samples 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 were nine cases of reanalysis requests because of suspected calcium contamination. All reanalyses confirmed that contamination was not present and the original results were reported.

For further detail, see Section 3.2.1.2, Section 4.2.2.1, and Section 4.2.2.4.

2.2.3 Silicon

Beginning 12/12/2019 the XRF-2 instrument began failing the criteria for daily PTFE blanks and monthly reanalysis samples (see Table 4.2-2) for silicon. These failures were attributed to elevated silicon background within the instrument. The investigation is ongoing, however, silicon contamination in the X-ray path is suspected. Results for network samples are blank subtracted so the impact to the final data is expected to be minimal. However, because of the PTFE blank criteria failures beginning 12/12/2019 and calibration failure on 12/21/2019, analysis of CSN samples on XRF-2 was halted beginning 1/9/2020; analysis using this instrument will resume when the issue is resolved. Between 12/12/2019 and 1/9/2020, there were 349 samples were analyzed on XRF-2. These samples all had sampling dates in October 2019 (contractor batch ID A0000060). Discussion is ongoing about possible further actions, such as reanalysis of the samples.

For further detail, see Section 3.2.1.3, Section 4.2.2.1, and Section 4.2.2.4.

2.2.4 NIST SRM

The NIST SRM 2783 standard serial number 1720 has been used for monthly QC checks since 2013. Beginning with the December 2019 monthly check it displayed signs of contamination for sulfur. The standard was replaced with a new NIST SRM 2783 serial number 1617 which was measured starting 1/29/2020. The SRM change corrected the sulfur exceedances but caused a shift in the measured loadings for some elements, but these were within the acceptance criteria which are detailed in *UCD CSN SOP #302*. Additionally, XRF-1, XRF-2, and XRF-5 displayed

failures in aluminum. The variability of the aluminum measurement and the difficulty of this measurement using EDXRF suggest that the acceptance limits for this element, which were calculated as the root-mean-squared-relative-error plus 3 standard deviations from 44 measurements performed between January 2013 and July 2016, should be reevaluated.

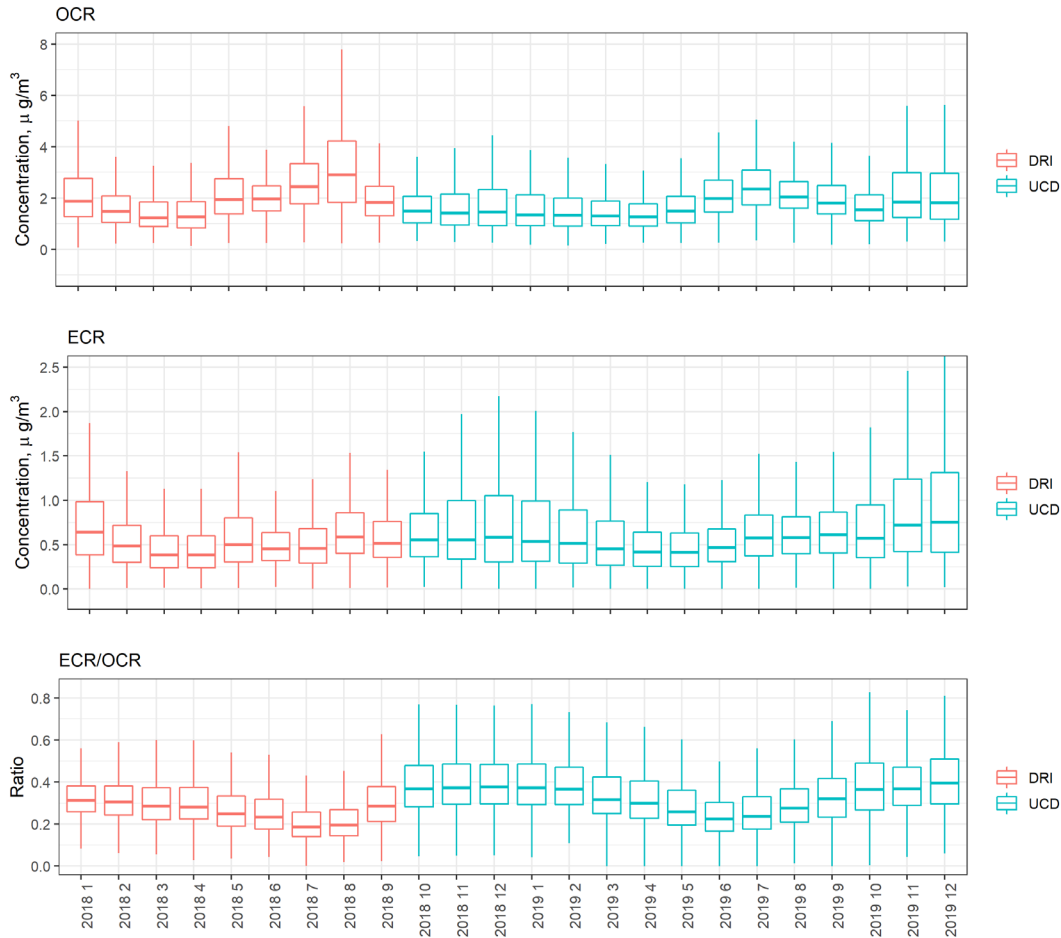
For further detail, see Section 4.2.2.5.

2.3 UC Davis Thermal Optical Analysis Laboratory

2.3.1 Continued Evaluation of Laboratory Transition

Beginning with samples collected October 1, 2018, quartz filters are analyzed for carbon by Thermal Optical Analysis (TOA) at UC Davis; prior to October 1, 2018, quartz filters were analyzed for carbon by TOA at Desert Research Institute (DRI; Reno, NV). At the network level, there continues to be 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 appear slightly elevated after the transition (Figure 2.3-1).

Figure 2.3-1: 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, 2019. Samples collected January 1, 2018 through September 30, 2018 were analyzed by DRI (red boxes) and samples collected October 1, 2018 through December 31, 2019 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 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).



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). Data from sites with non-standard sampler configurations are not included in the completeness calculations. Additionally, for completeness relative to the total number of collected samples, calculation results shown in Table 3.1-1 and Table 3.1-2 do not include placeholder records generated for samples that were scheduled but not collected. The completeness is comparable for PTFE and nylon filters which are both collected by the Met One SASS / Super SASS sampler;

however, the number of invalid samples is higher for quartz filters, which are collected by the URG sampler.

Table 3.1-1: Network sample completeness by filter type, January 1, 2019 through December 31, 2019. 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 # of collected samples)	% Valid (relative to # of scheduled samples)
PTFE	13,520	13,384	12,921	463	96.5	95.6
Nylon	13,520	13,384	12,939	445	96.7	95.7
Quartz	13,520	13,366	12,651	715	94.7	93.6

Across the network there were six sites with completeness (relative to the number of collected samples, and determined for null codes applied at the filter level) less than 75% for at least one filter type (Table 3.1-2), considering samples collected January 1, 2019 through December 31, 2019.

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, 2019 through December 31, 2019. 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
12-073-0012-5	Tallahassee Community College	31.1%	67.2%	98.4%	AH (95%) AF (2.5%) AN (2.5%)	AH (90%) AF (5%) AN (5%)	AO (100%)
28-049-0020-5	Jackson NCore	99.2%	99.2%	71.1%	BJ (100%)	BJ (100%)	AH (100%)
32-003-0540-5	Jerome Mack Middle School	98.3%	98.3%	57.9%	AV (100%)	AV (100%)	AH (92%) AV (4%) Other (4%)
46-099-0008-5	Sioux Falls School of Deaf	100%	100%	74.4%	---	---	AH (45%) AN (42%) Other (13%)
47-093-1020-5	Knoxville - Spring Hill Elementary School	67.2%	67.2%	68.9%	AN (80%) AH (15%) BJ (5%)	AN (80%) AH (15%) BJ (5%)	AH (100%)
72-021-0010-5	Jail at Bayamon, PR	64.9%	78.4%	16.2%	AH (46%) AN (31%) Other (23%)	AN (50%) AF (25%) Other (25%)	AN (58%) AH (26%) Other (16%)

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, 2019 through December 31, 2019. Codes are ordered by frequency of occurrence.

Null Code	SASS PTFE	SASS Nylon	URG Quartz	Null Code Description
AR	1	0	0	Lab Error
BE	0	0	2	Building/Site Repair
AI	2	0	0	Insufficient Data, Cannot Calculate
SA	1	1	1	Storm Approaching
TS	2	1	0	Holding Time Or Transport Temperature Is Out Of Specs.
AC	2	2	1	Construction/Repairs in Area
AK	0	0	5	Filter Leak
BB	2	2	2	Unable to Reach Site
AL	3	3	3	Voided by Operator
AQ	3	4	7	Collection Error
AS	0	0	14	Poor Quality Assurance Results
BI	6	6	9	Lost or damaged in transit
AO	7	7	12	Bad Weather
SV	6	8	17	Sample Volume Out of Limits
AB	12	12	8	Technician Unavailable
BA	12	12	9	Maintenance/Routine Repairs
AJ	23	16	3	Filter Damage
AG	14	14	20	Sample Time out of Limits
BJ	52	52	30	Operator Error
AV	62	62	76	Power Failure
AN	116	119	183	Machine Malfunction
AH	95	82	278	Sample Flow Rate or CV out of Limits
AF*	163	163	174	Scheduled but not Collected

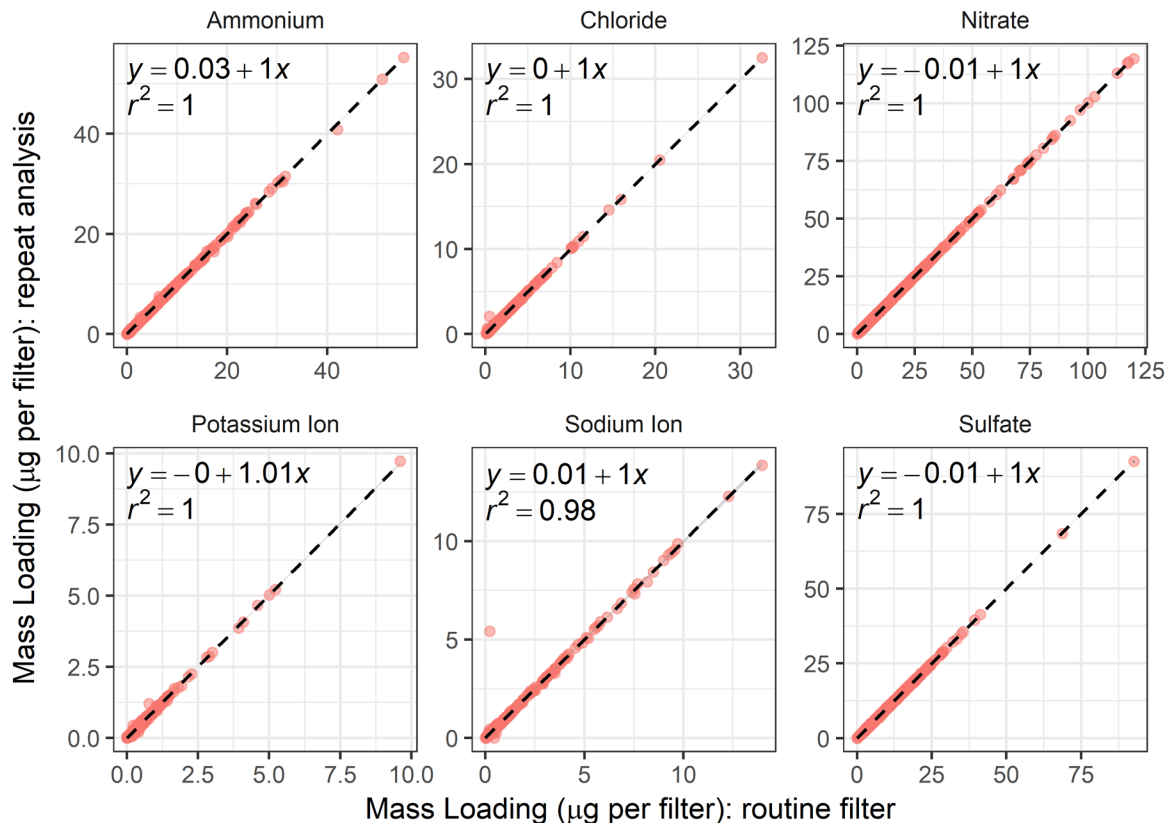
* The majority of records that receive this flag are for samples where physical filters and associated electronic records were not generated at the Sample Handling Laboratory because shipment of filters to the site was paused.

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 extract 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.

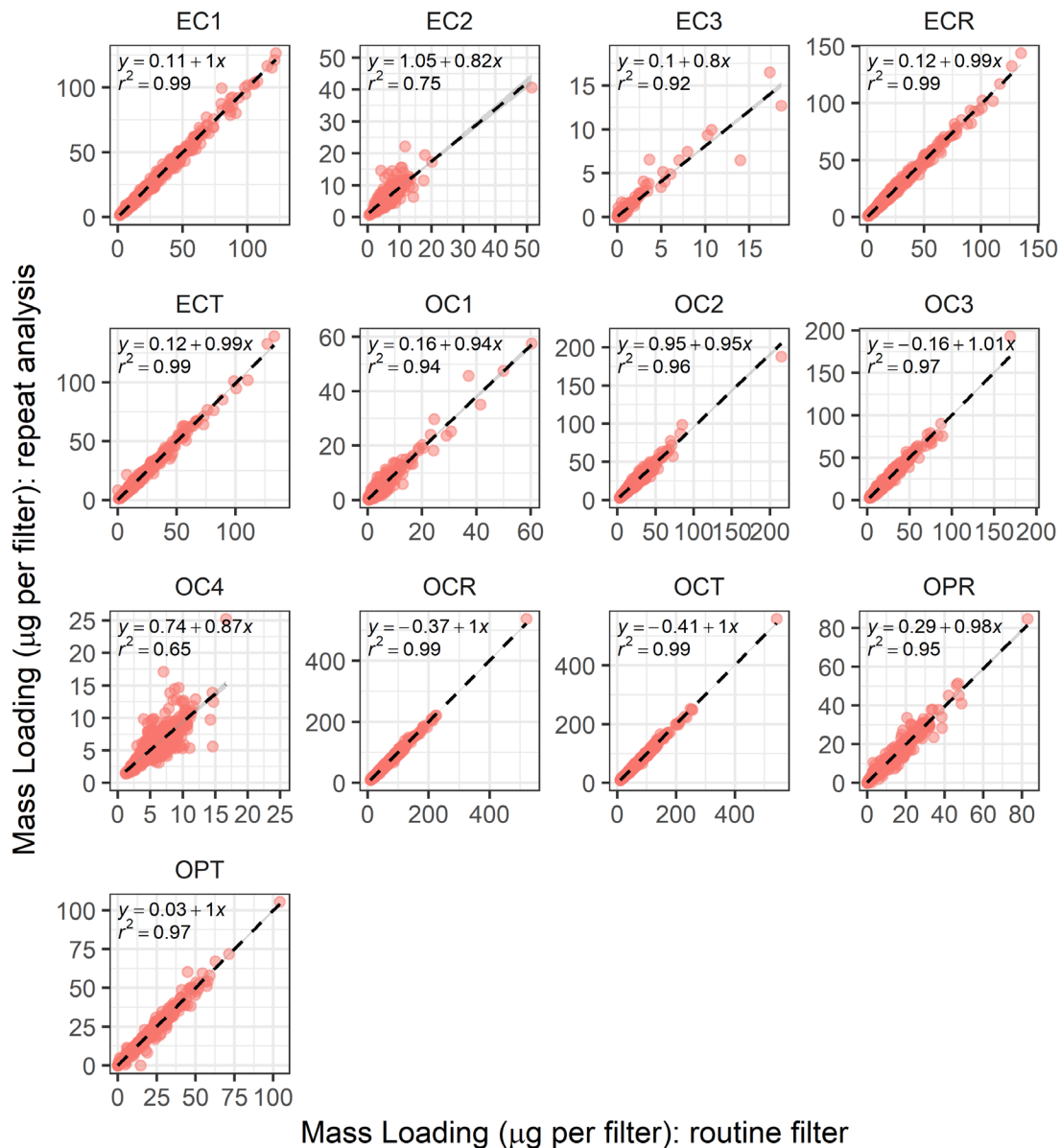
Comparisons of ion mass loadings from repeat analyses (replicates and/or duplicates) on nylon filters analyzed by IC show agreement (Figure 3.1-1). Ten different IC instruments were used for routine and repeat analyses where both replicate and duplicate analyses are performed using the same extract.

Figure 3.1-1: Ion repeat analysis (replicates and/or duplicates) results; data from valid samples collected January 1, 2019 through December 31, 2019.



Comparison of carbon mass loadings from repeat analyses (replicates and/or duplicates) on valid quartz filters analyzed by TOA generally show agreement (Figure 3.1-2), with agreement deteriorating for carbon fractions with lower mass loadings (e.g. EC2, EC3, OC4). Repeat analyses are performed on the same filter as the routine analyses; different punches are used for each analysis.

Figure 3.1-2: Carbon repeat analysis (replicates and/or duplicates) results; data from samples collected during January 1, 2019 through December 31, 2019. 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 due to time limitations, as analyses take approximately 65 minutes per sample, and to preserve volatile elements like chlorine and bromine, and to a lesser extent sulfur, which are lost when the sample is analyzed under vacuum on the EDXRF. Work is being done to address time limitations to allow for repeat analysis. Currently, reanalysis is performed on the same set of monthly reanalysis samples, which are UCD-made multi-element reference materials, (see Table 4.2.2) 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 QA 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).

Beginning in May 2017, field blanks are collected once per month for each filter type per site; prior to May 2017 field blanks were collected less frequently.

There is some variability in field blank mass loadings by species. The 10th percentile of network sample mass loadings, before artifact correction, is indicated in Figure 3.1-3 through Figure 3.1-15 to facilitate understanding of field blank mass loadings in context of network sample mass loadings; 90% of network sample mass loadings 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 against influence from occasional outliers.

Field blank mass loadings for the ion species (Figure 3.1-3 through 3.1-8) are examined in an effort to identify changes that may be associated with the October 1, 2018 laboratory transition from DRI to RTI (see Section 2.1.1) or changes that may be occurring independently from the laboratory transition. The monthly 10th percentile ammonium mass loading of network samples increased in November 2017 and has become increasingly elevated relative to earlier years. Additionally, the monthly median ammonium mass loading of field blanks increased corresponding with the laboratory transition. For potassium ion, the monthly 10th percentile mass loading of network samples – as well as the monthly field blank median mass loading and variability – increased corresponding with the laboratory transition. Conversely, monthly median mass loadings of field blanks were generally lower for nitrate (specifically April through August 2019) and sulfate following the laboratory transition.

Figure 3.1-3: Time series of ammonium measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

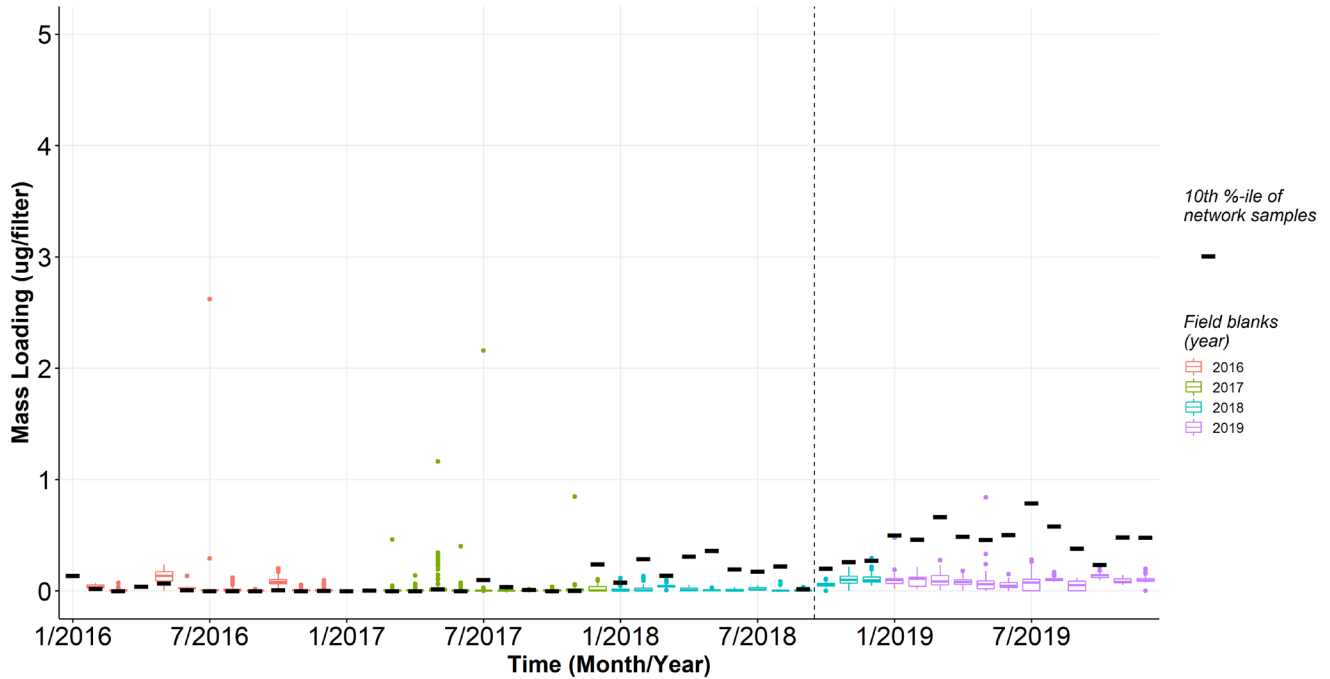


Figure 3.1-4: Time series of chloride measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

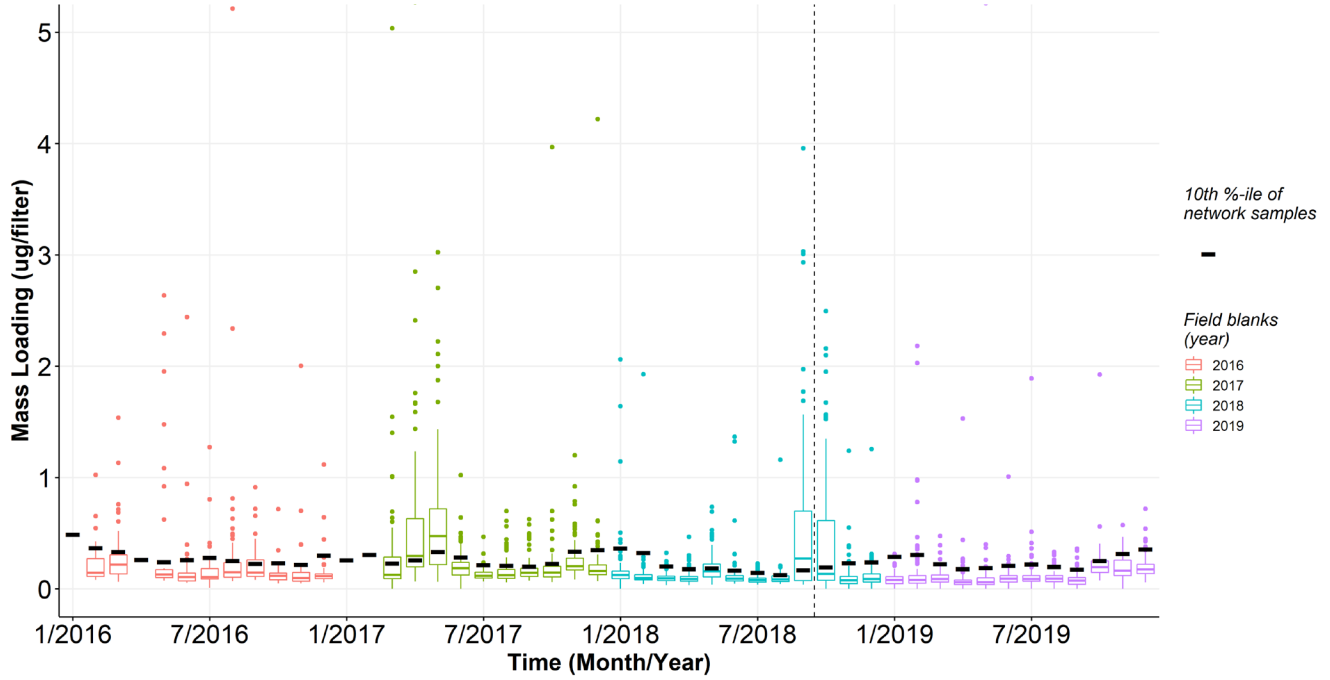


Figure 3.1-5: Time series of nitrate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

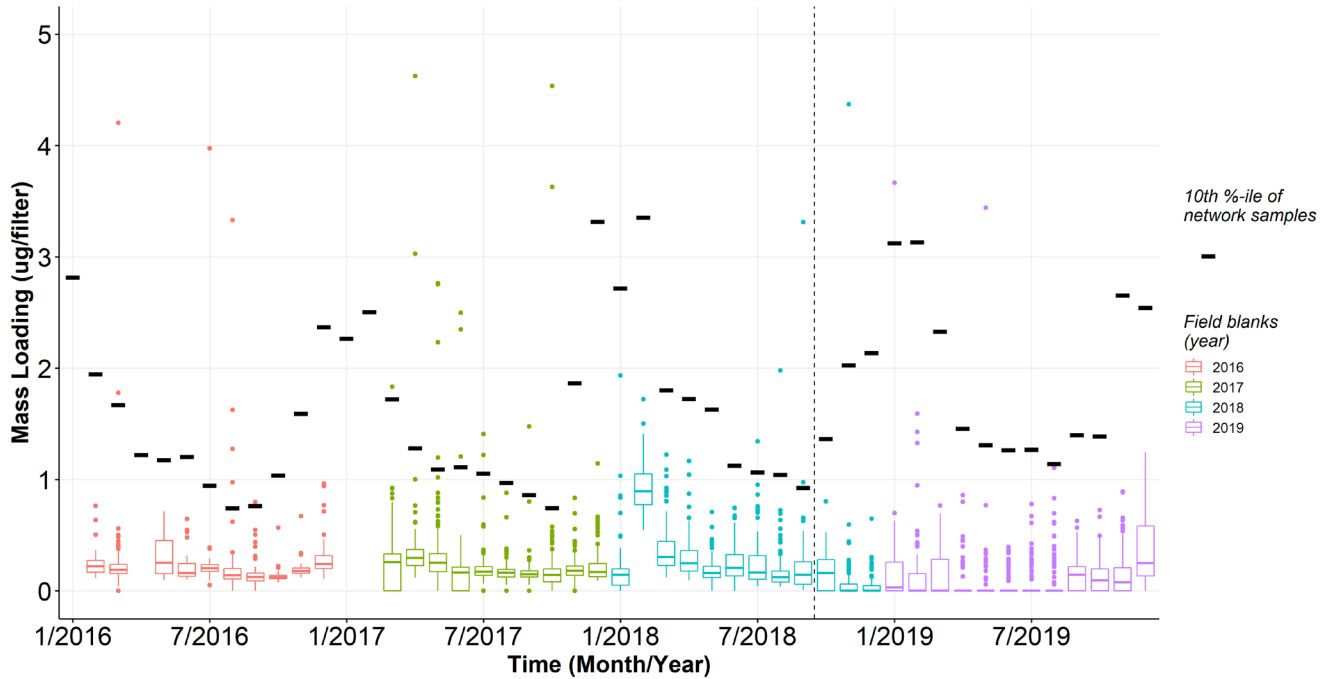


Figure 3.1-6: Time series of potassium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

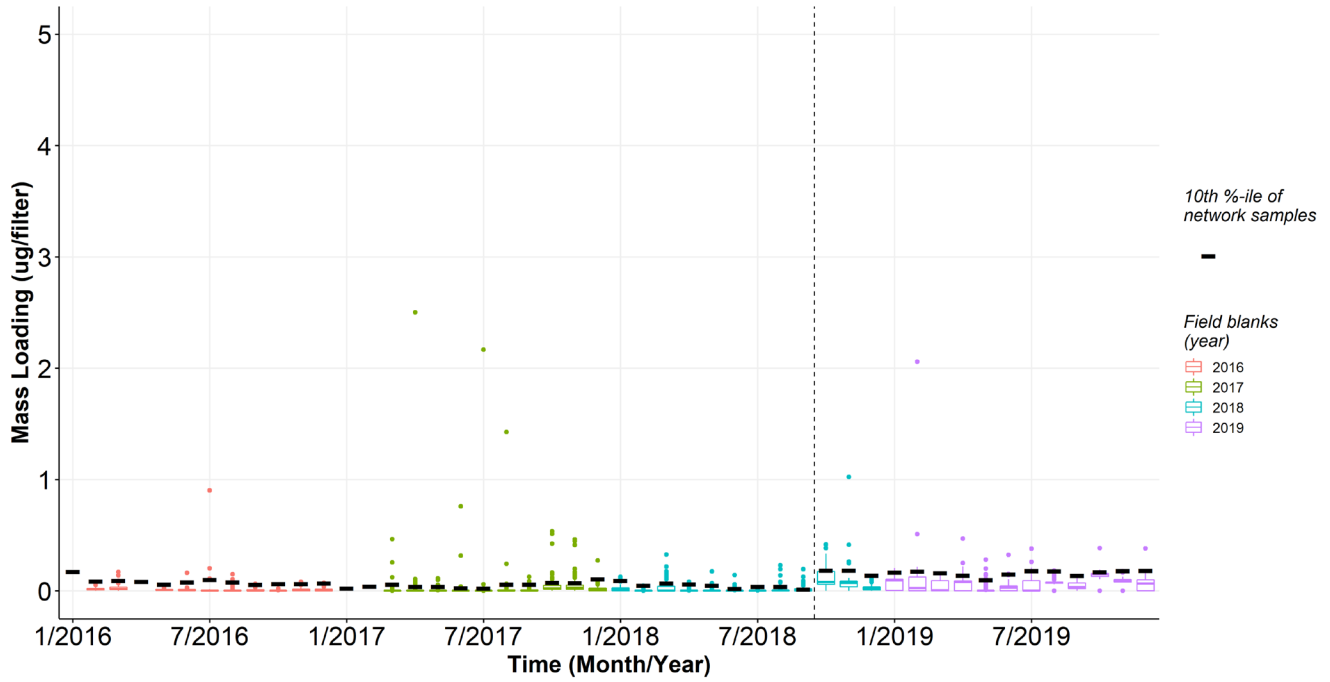


Figure 3.1-7: Time series of sodium ion measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.

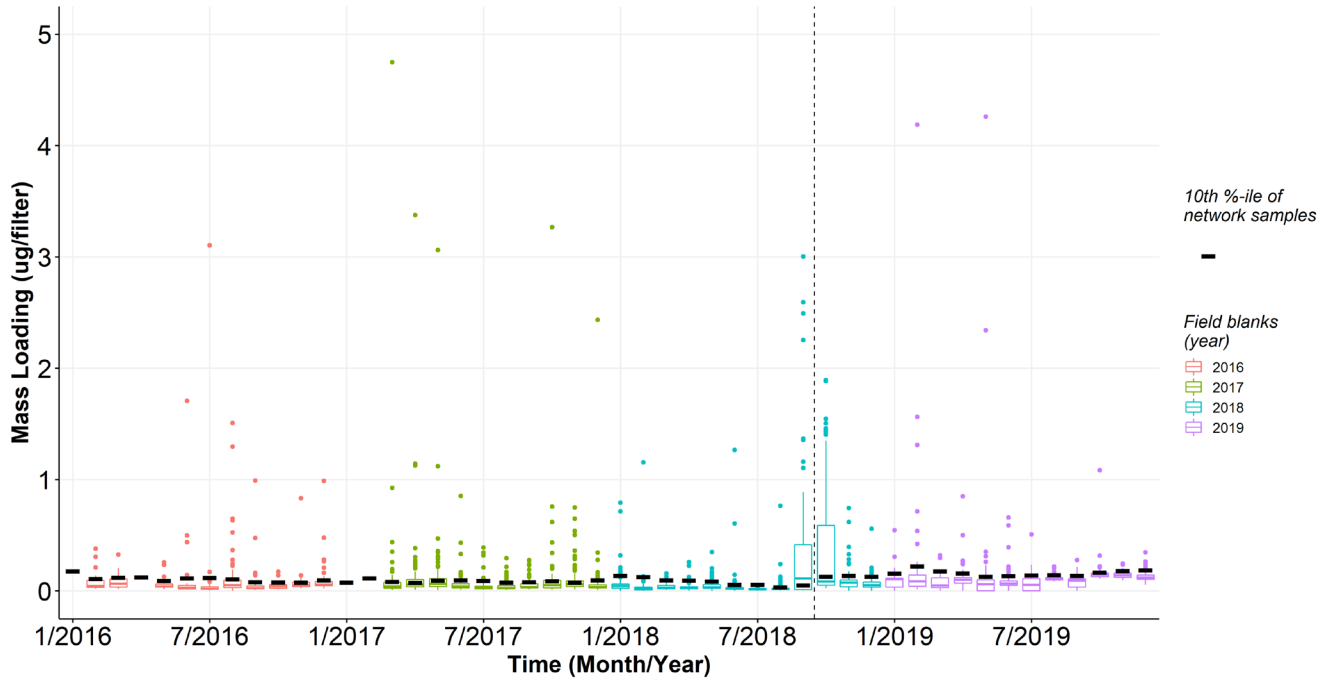
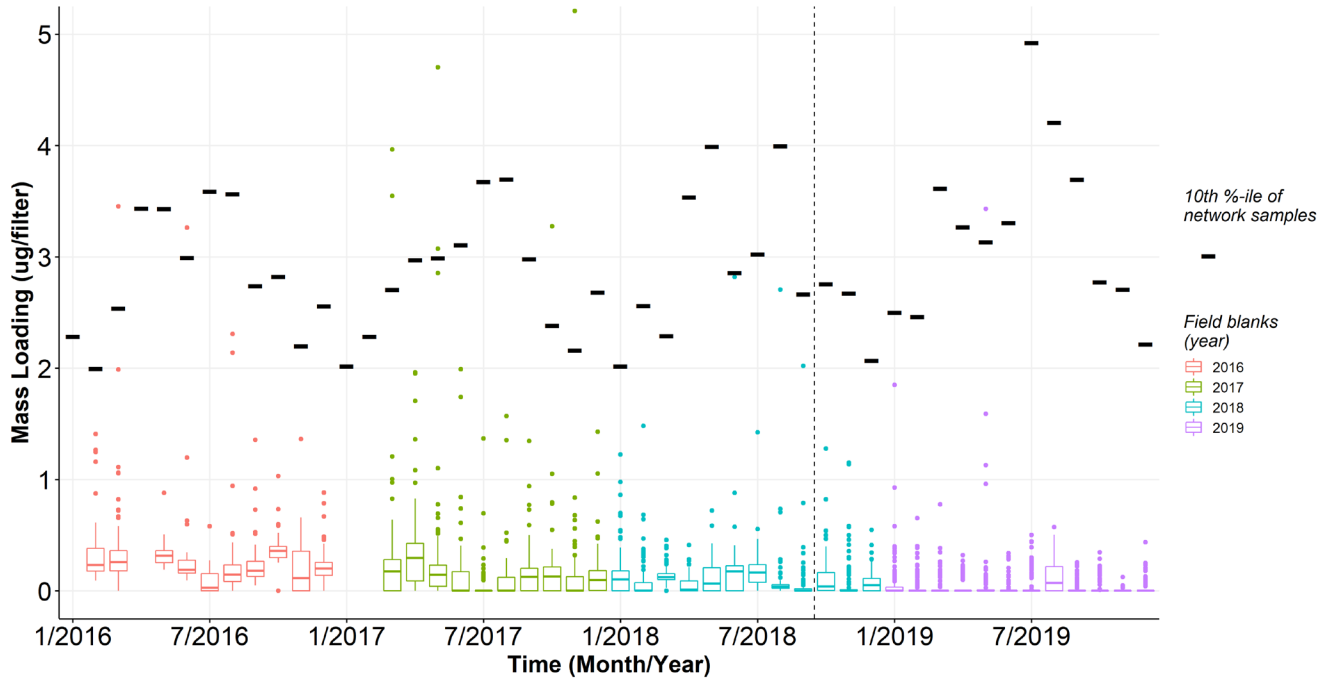


Figure 3.1-8: Time series of sulfate measured on nylon filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no nylon filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to RTI. The black horizontal dashes indicate the 10th percentile of network samples.



Field blank mass loadings for organic carbon (3.1-9) and elemental carbon (Figure 3.1-10) are examined in an effort to identify changes that may be associated with the October 1, 2018 laboratory transition from DRI to UC Davis (see Section 2.3.1) or changes that may be occurring independently from the laboratory transition.

Both the monthly 10th percentile organic carbon mass loading of network samples and the monthly median organic carbon mass loading of field blanks show some variability and increases during the time series, January 1, 2016 through December 31, 2019. Corresponding with the October 1, 2018 laboratory transition, there is an increase in the monthly median organic carbon mass loading of field blanks, which is likely caused by change in the signal integration threshold and other small differences between instrumentation and laboratory methods associated with the transition. Additionally, following the transition, and particularly for field blanks collected during November and December 2019, there are numerous cases of field blanks with elevated mass loadings; these cases are being investigated. No evidence of an analytical issue has been found. Lab blanks show low concentrations suggesting the contamination is arising from sample handling in the lab or field. Investigations are on-going.

Conversely, the monthly median elemental carbon field blank mass loadings decreased with the laboratory transition. Changes in the monthly median elemental carbon mass loading of field blanks is likely caused by differences in the organic and elemental carbon split point associated with the transition.

Figure 3.1-9: Time series of organic carbon by reflectance (OCR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no quartz filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5xIQR. Black vertical dotted line indicates laboratory transition from DRI to UC Davis. The black horizontal dashes indicate the 10th percentile of network samples.

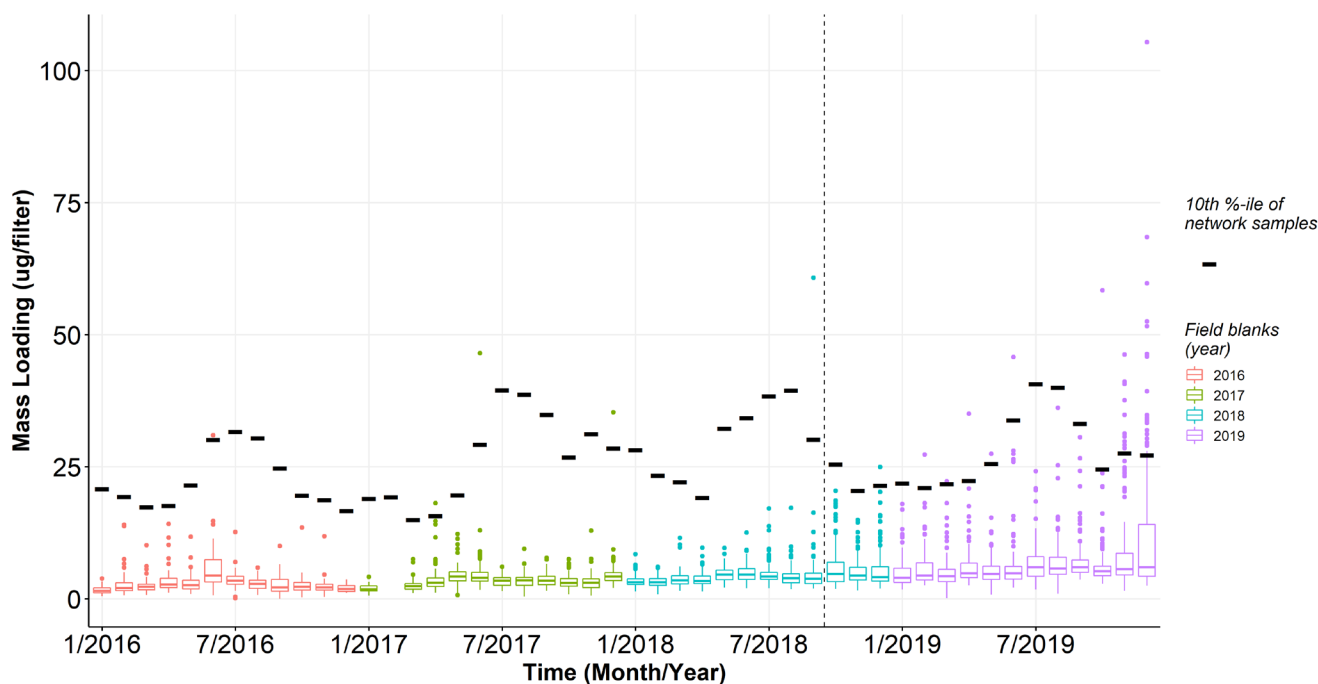
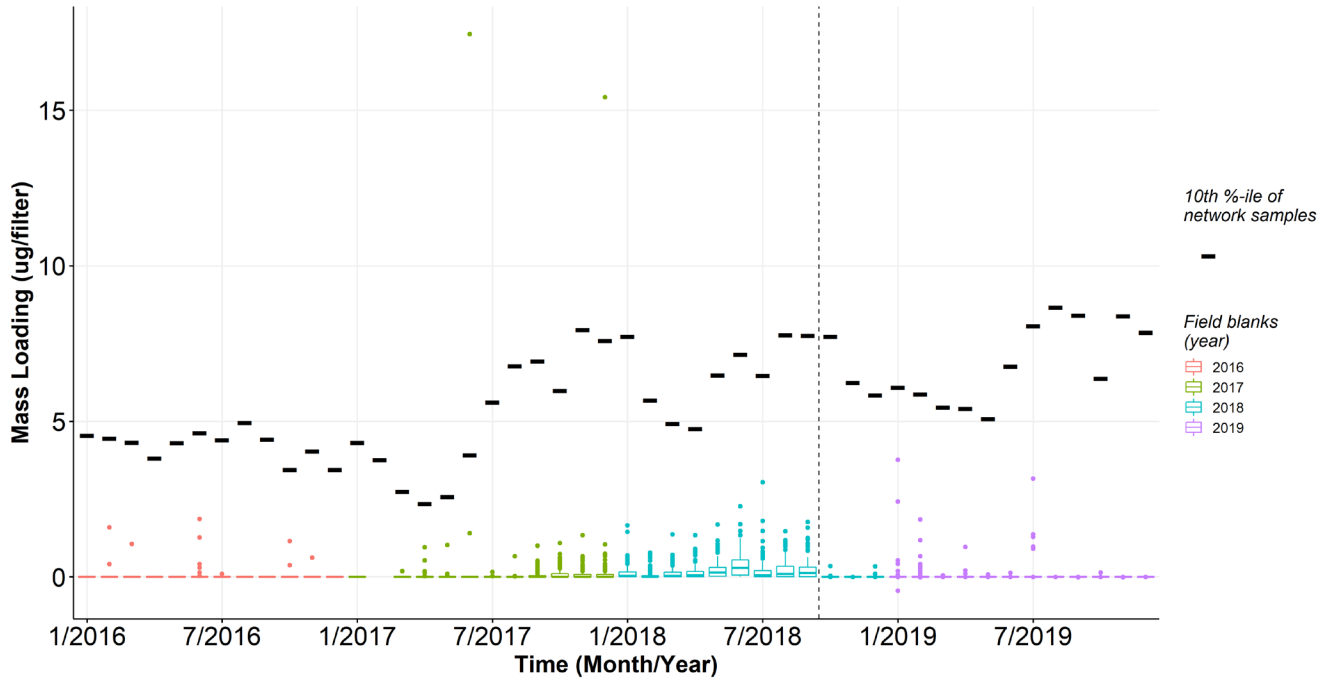


Figure 3.1-10: Time series of elemental carbon by reflectance (ECR) measured on quartz filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no quartz filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates laboratory transition from DRI to UC Davis. The black horizontal dashes indicate the 10th percentile of network samples.



Time series of monthly median mass loading of field blanks and monthly 10th percentile mass loading of network samples are shown Figure 3.1-11 through 3.1-16 for select well-measured element species (species where at least 50% of the network sample concentrations are above the reported method detection limit, see Table 3.1-4). As discussed in the CSN 2018 Annual Quality Report, the EDXRF analysis conditions (including the secondary targets and integrations times, collectively referred to as the *application*) were changed in December 2018, which impacted data beginning with samples and field blanks collected October 2018. There does not appear to be evidence of unexpected shifts or changes to the monthly median mass loading of field blanks or monthly 10th percentile mass loading of network samples for calcium (Ca; Figure 3.1-11), iron (Fe; Figure 3.1-12), potassium (K; Figure 3.1-13), sulfur (S; Figure 3.1-14), or zinc (Zn; Figure 3.1-16). However, silicon (Si; Figure 3.1-15) monthly median field blank mass loadings show increased variability following the EDXRF application change, including an unexpectedly elevated median mass loading for the May 2019 field blanks. Elevated monthly median field blank mass loadings for silicon are being investigated and may be related to elevated silicon background within the EDXRF instrument; however, the analysis dates for the May 2019 field blanks (see Table 4.2.1) do not correspond with the XRF-2 silicon criteria failures for PTFE blanks and monthly reanalysis samples (see Section 2.2.3, Section 3.2.1.3, Section 4.2.2.1, and Section 4.2.2.4).

Figure 3.1-11: Time series of calcium (Ca) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no PTFE filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

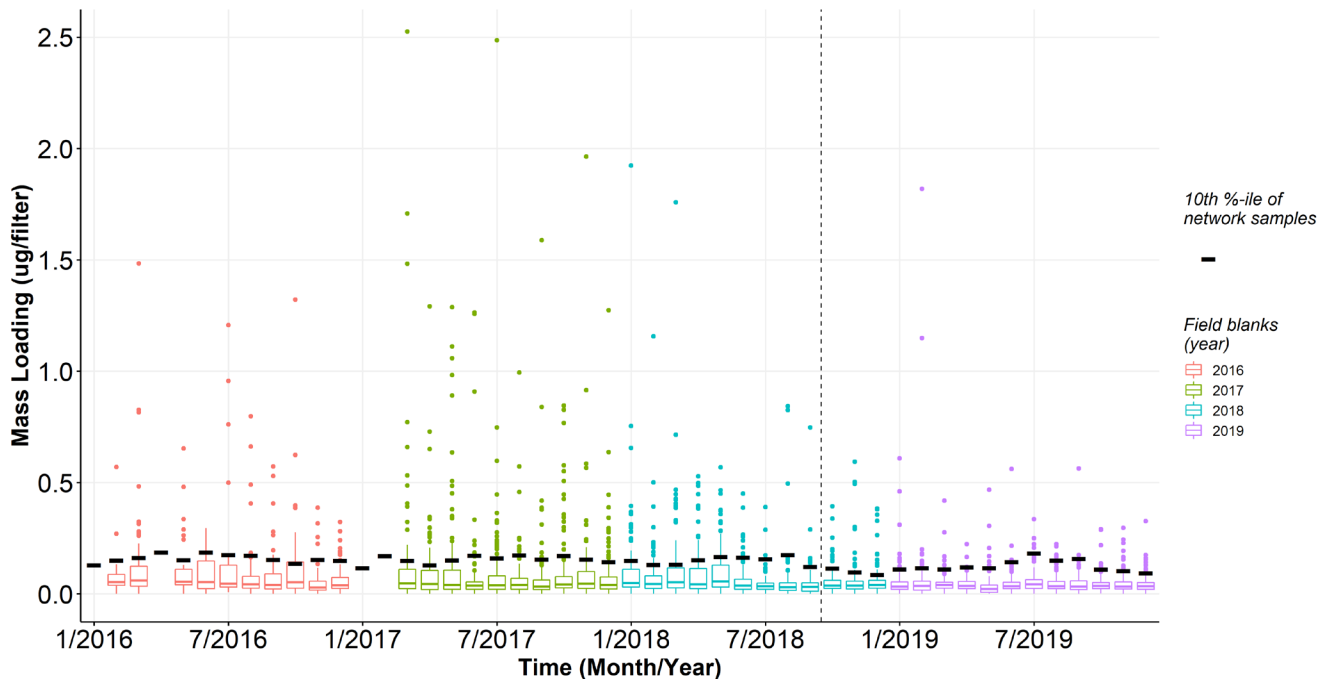


Figure 3.1-12: Time series of iron (Fe) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no PTFE filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

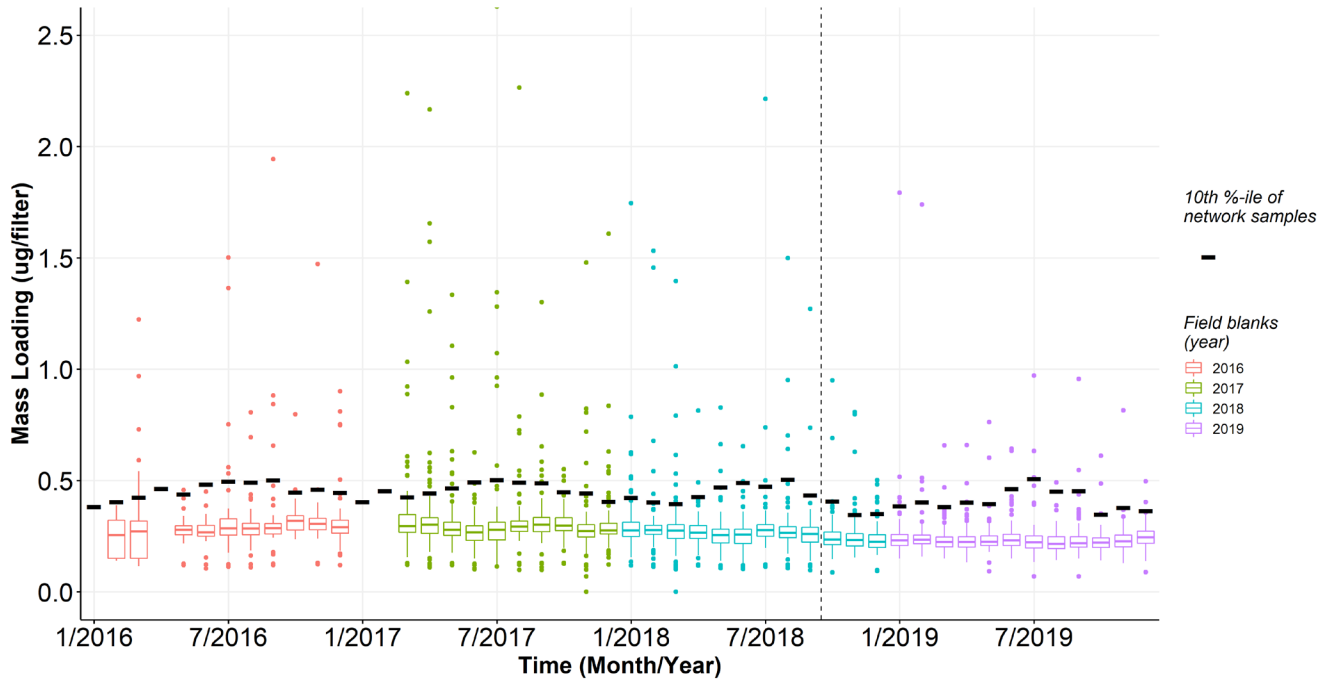


Figure 3.1-13: Time series of potassium (K) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no PTFE filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

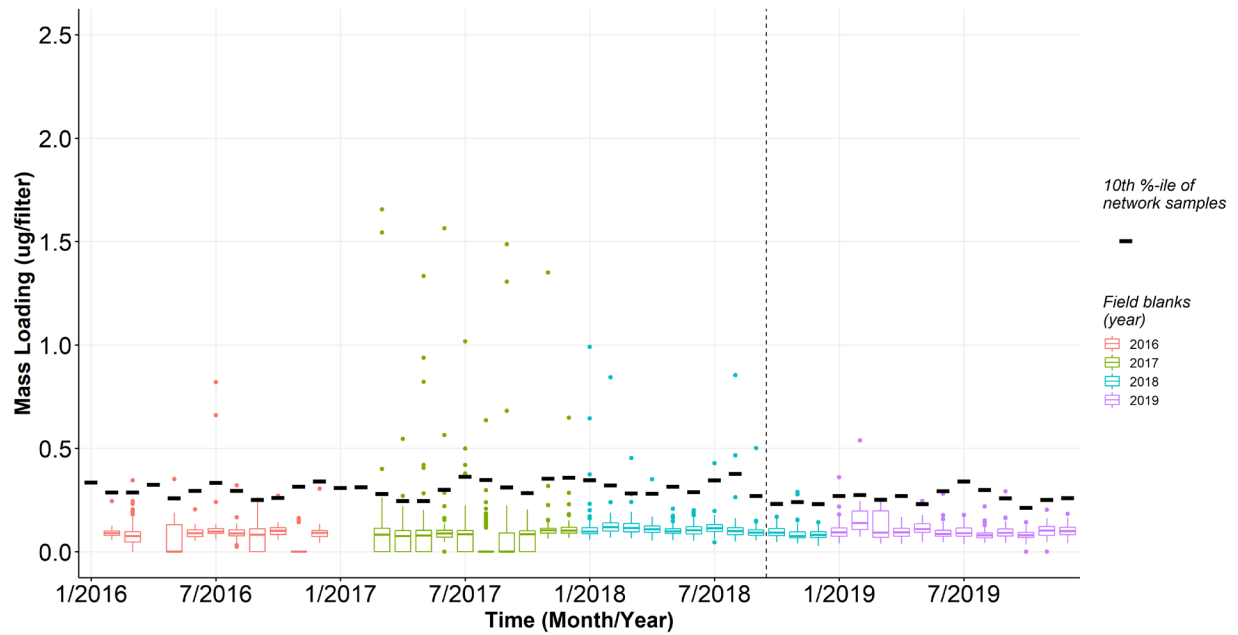


Figure 3.1-14: Time series of sulfur (S) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no PTFE filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

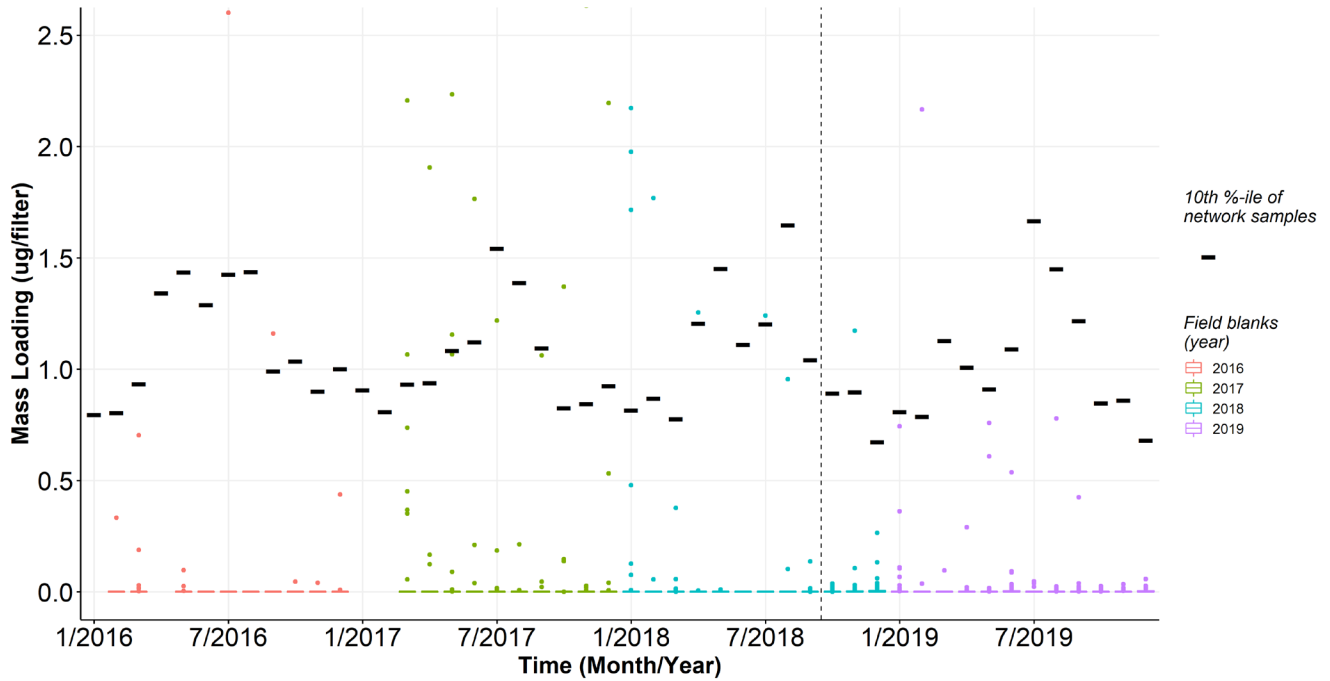


Figure 3.1-15: Time series of silicon (Si) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no PTFE filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. The black horizontal dashes indicate the 10th percentile of network samples.

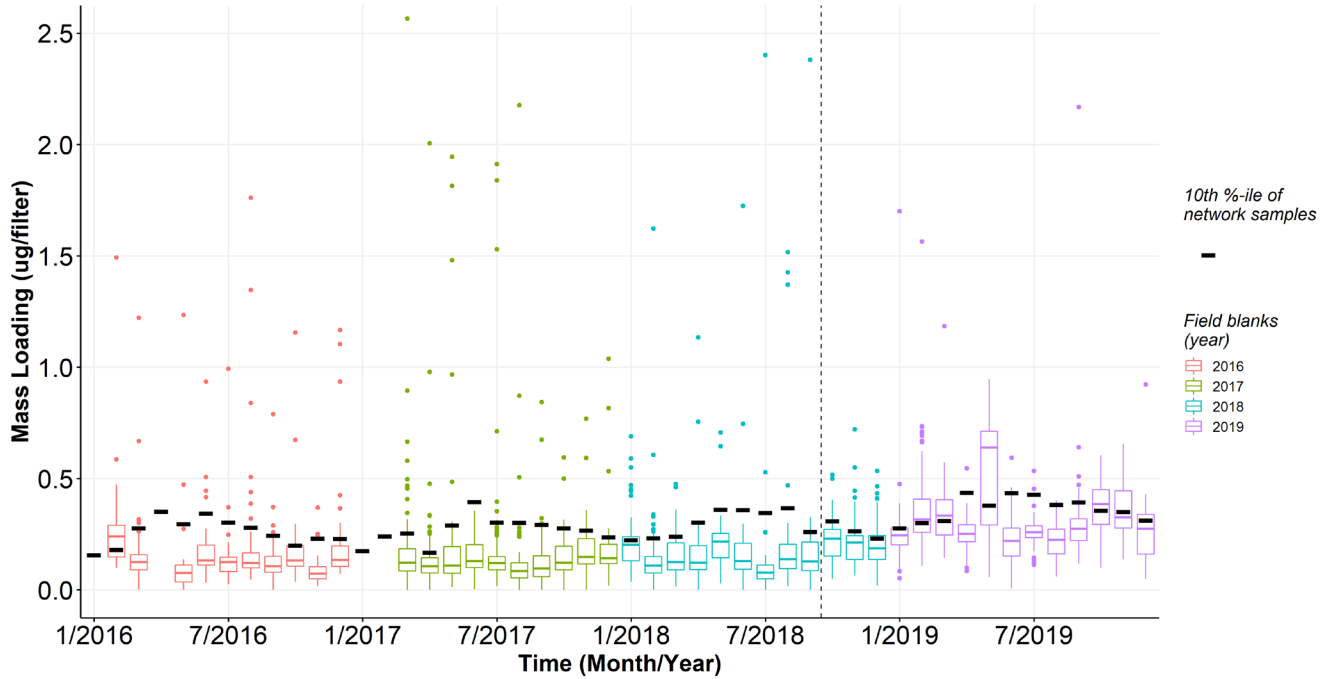
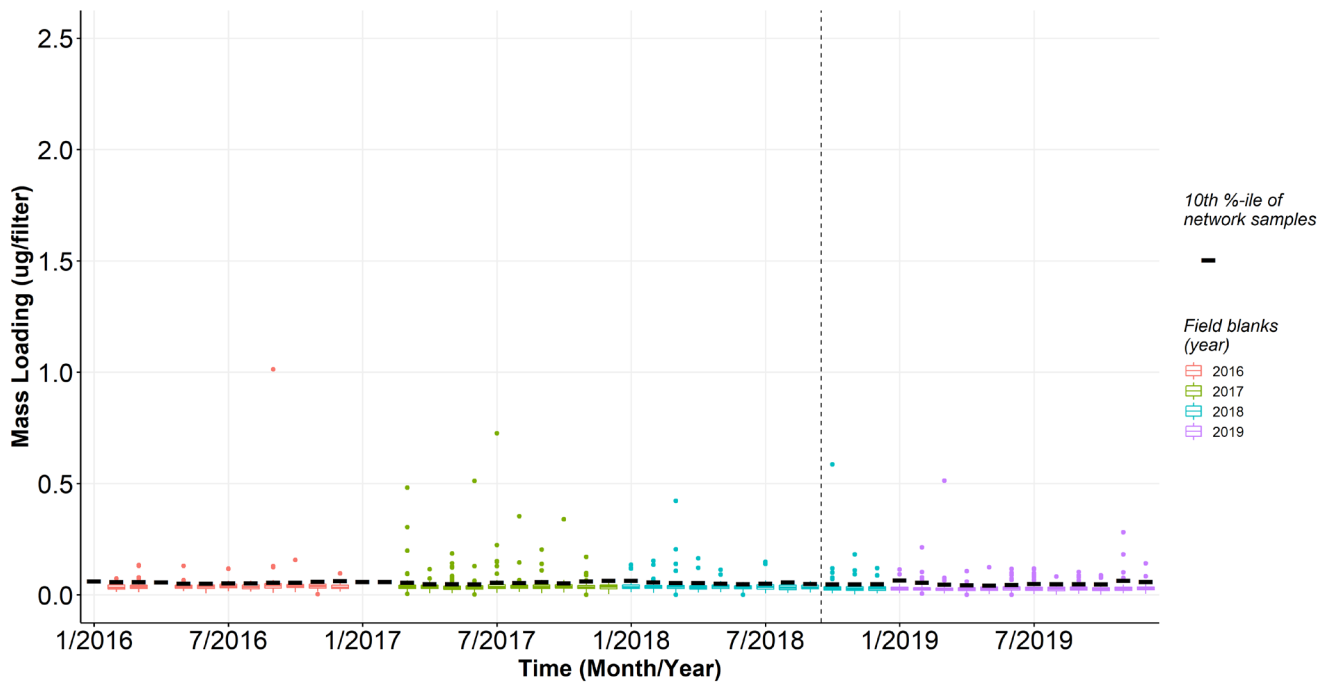


Figure 3.1-16: Time series of zinc (Zn) measured on PTFE filter field blanks (FB), for valid field blanks collected January 1, 2016 through December 31, 2019. Gaps in time series are present when no PTFE filter field blanks were collected. The colored (red, 2016; green, 2017; blue, 2018; purple, 2019) 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). Dots indicate individual data points beyond 1.5×IQR. Black vertical dotted line indicates XRF application change. 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. Field blanks are collected once per month for each filter type per site since May 2017; the median value is typically calculated using field blanks from the sample month only.

3.1.3.2 Method Detection Limits

Network wide method detection limits (MDLs) are updated monthly and are delivered to AQS for each species. The MDL calculation is harmonized for all analysis pathways, calculated as 95th percentile minus median of field blanks, using 50 field blanks collected in or closest to the sampling month for each respective filter type. Field blanks are collected once per month for each filter type per site since May 2017, 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, 2019 through December 31, 2019) are compared to those calculated using the same method from the

previous reporting period (samples collected January 1, 2018 through December 31, 2018) (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 2019 MDLs are lower (improved) or higher (degraded): (1) elemental species calcium (Ca) and phosphorous (P) 2019 MDLs are lower and higher, respectively, relative to their 2018 MDLs; (2) ion species chloride and sodium ion 2019 MDLs are both lower relative to their 2018 MDLs; (3) several carbon species and fractions have higher 2019 MDLs relative to their 2018 MDLs. MDL differences may be related to changes in filter media cleanliness, EDXRF application changes (see CSN 2018 Annual Quality Report, Section 2.3.1 and Section 4.2.2.5), and laboratory transitions (see CSN 2018 Annual Quality Report, 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 January 1, 2018 through December 31, 2018 (previous reporting period) and January 1, 2019 through December 31, 2019 (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 $\geq 50\%$ between those reported for the previous reporting period (2018) and the current reporting period (2019).

Species	EPA Attachment D	2018 (previous reporting period)		2019 (current reporting period)	
	Typical MDL, $\mu\text{g}/\text{m}^3$	Average MDL, $\mu\text{g}/\text{m}^3$	% Above MDL	Average MDL, $\mu\text{g}/\text{m}^3$	% Above MDL
Ag	0.037	0.016	2.6	0.016	4.1
Al	0.025	0.032	37.0	0.032	31.2
As	0.003	0.002	4.3	0.002	0.1
Ba	0.059	0.080	1.3	0.080	0.2
Br	0.002	0.005	12.0	0.005	2.7
Ca	0.008	0.018	74.1	0.009	89.7
Cd	0.023	0.016	3.2	0.016	5.4
Ce	0.087	0.095	1.3	0.095	0.1
Cl	0.011	0.005	38.2	0.004	41.9
Co	0.002	0.003	0.9	0.003	0.6
Cr	0.003	0.003	25.4	0.003	24.8
Cs	0.045	0.054	2.2	0.054	0.3
Cu	0.002	0.011	9.8	0.011	6.3
Fe	0.003	0.018	88.7	0.018	90.5
In	0.033	0.038	0.0	0.038	0.1
K	0.011	0.005	99.2	0.006	98.1
Mg	0.019	0.043	14.4	0.046	16.0
Mn	0.003	0.006	8.2	0.006	10.1
Na	0.055	0.089	23.5	0.092	26.5
Ni	0.002	0.002	16.2	0.002	15.0
P	0.015	0.002	7.3	0.003	5.4
Pb	0.006	0.012	6.9	0.012	5.3
Rb	0.003	0.009	0.2	0.009	0.1
S	0.010	0.004	99.5	0.004	99.6

Species	EPA Attachment D	2018 (previous reporting period)		2019 (current reporting period)	
	Typical MDL, $\mu\text{g}/\text{m}^3$	Average MDL, $\mu\text{g}/\text{m}^3$	% Above MDL	Average MDL, $\mu\text{g}/\text{m}^3$	% Above MDL
Sb	0.052	0.039	1.8	0.039	0.1
Se	0.003	0.005	1.4	0.005	0.4
Si	0.019	0.016	82.3	0.018	73.8
Sn	0.036	0.049	0.4	0.049	0.0
Sr	0.004	0.007	1.7	0.007	0.9
Ti	0.005	0.003	44.1	0.004	39.1
V	0.004	0.001	6.7	0.001	3.5
Zn	0.004	0.003	79.6	0.003	86.1
Zr	0.023	0.036	0.7	0.036	0.1
Ammonium	0.025	0.005	95.2	0.007	98.4
Chloride	0.027	0.036	71.1	0.015	89.0
Nitrate	0.022	0.035	99.0	0.039	99.5
Potassium Ion	0.024	0.061	10.4	0.061	13.9
Sodium Ion	0.030	0.026	73.5	0.009	85.0
Sulfate	0.035	0.025	99.6	0.022	99.8
Elemental Carbon (EC1)	0.095	0.015	99.9	0.029	99.9
Elemental Carbon (EC2)	0.063	0.017	97.7	0.023	99.5
Elemental Carbon (EC3)	0.063	0.003	22.2	0.004	80.3
Elemental Carbon (ECR)	0.063	0.018	99.8	0.012	99.9
Elemental Carbon (ECT)	0.063	0.016	99.7	0.012	99.8
Organic Carbon (OC1)	0.063	0.015	84.9	0.016	77.4
Organic Carbon (OC2)	0.063	0.035	99.8	0.046	99.5
Organic Carbon (OC3)	0.095	0.077	96.1	0.225	85.8
Organic Carbon (OC4)	0.095	0.034	96.1	0.074	89.5
Organic Carbon (OCR)	0.063	0.134	99.5	0.350	95.6
Organic Carbon (OCT)	0.063	0.138	99.6	0.354	96.4
Organic Pyrolyzed (OPR)	0.095	0.022	78.8	0.052	91.1
Organic Pyrolyzed (OPT)	0.063	0.028	94.2	0.052	94.4

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 2019.

3.2.1 Elemental Analysis

3.2.1.1 Zinc

As discussed in Section 2.2.1, Section 4.2.2.1, and Section 4.2.2.4, the design of the sample changer arm on the EDXRF instruments results in occasional intermittent cases of zinc contamination. During this reporting period, nine samples identified as having potential

contamination were reanalyzed. Reanalysis results for two of these cases indicated contamination during the original analysis; the reanalysis results for these two samples were reported.

3.2.1.2 Calcium

As discussed in Section 2.2.2, Section 4.2.2.1, and Section 4.2.2.4, 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 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 QC checks for calcium contamination. During this reporting period, nine cases identified as having potential contamination was reanalyzed. All reanalyses confirmed that contamination was not present and the original results were reported.

3.2.1.3 Silicon

As discussed in Section 2.2.3, Section 4.2.2.1, and Section 4.2.2.4, beginning 12/12/2019 the XRF-2 instrument began failing the criteria for daily PTFE blanks and monthly reanalysis samples (see Table 4.2-2) for silicon. On 1/9/2020 all CSN sample analysis was stopped on this instrument. Between those dates the instrument underwent calibration which did not correct the issue. However, no issues were observed for the other QC measures including analysis of daily and weekly UC Davis multi-element samples and monthly SRM. Investigation is ongoing.

3.2.2 Ion Analysis

No corrective actions during this reporting period.

3.2.3 Carbon Analysis

No corrective actions during this reporting period.

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.

3.2.4.2 Chromium and Nickel Contamination

As discussed in the CSN 2018 Annual Quality Report (Section 3.2.1.3), UC Davis identified a potential chromium and nickel contamination issue that impacts data from prior to the contract transition (November 20, 2015). Per direction for the EPA, UC Davis coordinated with the Sample Handling Laboratory (Wood PLC) to investigate this issue. The source of the contamination has not been identified, but is likely related to the Met One SASS / Super SASS samplers. As discussed in the data advisory posted to the UC Davis AQRC website (<https://airquality.ucdavis.edu/csn-documentation>), species associated with the contamination (chromium, nickel, iron, cobalt, and copper) will be assigned the SC null data qualifier (SC –

sampler contamination) prior to delivery to DART, beginning with samples collected January 2020.

3.2.4.3 Delivery of Composite Variables

Beginning with data from samples collected June 1, 2019, UC Davis began calculating and delivering composite variables for reconstructed mass (RCM) and soil to DART and AQS (see *UCD CSN TI #801B* for further information and equations for calculation of RCM and soil). Subsequently, UCD retroactively delivered RCM and soil results for samples collected January 1, 2018 through May 31, 2019. For composite variable results, if any of the contributing species are invalid, the composite variable is delivered as invalid with the AI null code (AI – Insufficient Data, Cannot Calculate).

3.2.5 Technical System Audit

The EPA conducted a Technical Systems Audit (TSA) of UC Davis laboratory and data handling operations on August 18 & 19, 2019; on-site audit activities were performed by Battelle (Columbus, OH) as an EPA contractor. Audit findings were detailed in a report from the EPA delivered to UC Davis on January 16, 2020. Discussion and resolution of the corrective action findings is ongoing, and are documented in a corrective action report (CAR) prepared by UC Davis and delivered to the EPA (initially on February 13, 2020, and with revisions on March 31, 2020).

4. Laboratory Quality Control Summaries

4.1 RTI Ion Chromatography Laboratory

The RTI Ion Chromatography Laboratory, as a subcontractor to UC Davis, received and analyzed extracts from nylon filters for batches 51 through 62, covering the sampling period January 1, 2019 through December 31, 2019. Analysis of these samples was performed March 26, 2019 through March 5, 2020. Using ion chromatography, RTI analyzed for both anions (chloride [Cl⁻], nitrate [NO₃⁻], and sulfate [SO₄²⁻]) and cations (sodium [Na⁺], ammonium [NH₄⁺], and potassium [K⁺]) using five Thermo Dionex ICS systems and four Thermo Dionex Aquion systems (five anion systems: A11, A12, A9, A10, and A8; four cation systems: C9, C10, C3, and C6) and reported the results of those analyses to UC Davis.

Table 4.1-1: Sampling dates and corresponding IC 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 Month (2019)	Analysis Batch #	IC Analysis Dates
January	51	3/19/2019- 5/17/2019
February	52	4/15/2019- 6/7/2019
March	53	5/10/2019 – 7/2/2019
April	54	6/10/2019 – 8/1/2019
May	55	7/12/2019 – 9/10/2019
June	56	8/12/2019 – 10/9/2019
July	57	9/16/2019 – 11/16/2019
August	58	10/14/2019 – 12/09/2019
September	59	11/11/2019 – 2/26/2019
October	60	12/16/2020 – 2/26/2020
November	61	1/16/2020 – 3/26/2020
December	62	2/10/2020 – 4/30/2020

4.1.1 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, ICS-3000, and Aquion systems following *RTI SOP #Ions1*. The laboratory acquired four new Thermo Dionex Aquion systems in 2019. Thermo Dionex AS-AP autosamplers were purchased with the four systems and an additional AS-AP autosampler was purchased to replace AS-40 autosamplers on a dual anion/cation ICS-3000 system. A comparability study was performed on all new systems prior to beginning routine analysis (see Section 4.1.2.8). Extraction procedures are documented on worksheets which are maintained with the associated analysis files. The QC measures for the RTI ion analysis are summarized in Table 4.1-2. The table details the frequency and standards required for the specified checks, along with the acceptance criteria and corrective actions. Stated acceptance criteria are verified and documented on review worksheets, and reviewers document acceptance criteria not met, corrective actions, samples flagged for reanalysis, and subsequent reanalysis dates.

Table 4.1-2: RTI quality control measures for ion (anion and cation) analysis by ion chromatography.

Activity	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 set of 50 samples	Relative % Difference = 10% at 10x MDL Relative % Difference = 200% at MDL	Investigate; reanalyze
Spiked sample extract	2 per set of 50 samples	Recoveries within 90 to 110% of target values	Investigate; reanalyze
Reagent blanks	One reagent blank per reagent used (DI H ₂ O 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 per month	Not applicable; data reported and compared annually	Investigate
Reanalysis	5% per of all samples, reanalyzed on different day and as requested	MDL to 10 times MDL: RPD up to 200%, 10 to 100 times MDL: RPD < 20%, >100 times MDL: differences within 10%	Investigate and reanalyze samples if needed

4.1.2 Summary of QC Results

RTI followed the acceptance criteria stated in Table 4.1-2. 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 all samples) 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 set of 50 samples were reanalyzed.

4.1.2.1 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 to 2,000 parts per billion (ppb) for chloride and from 50 to 10,000 ppb for nitrate and sulfate. A high calibration standard at 5,000 ppb for chloride and 25,000 ppb for sulfate and nitrate are used in the calibration curve only for samples exceeding 2,000 and 10,000 ppb, respectively. Cation instruments are calibrated from 10 to 1,000 ppb for sodium, ammonium, and potassium. A high calibration standard at 3,000 ppb is used only for samples whose concentrations exceed 1,000 ppb. The correlation coefficients for the daily calibration must be at least 0.999. If the 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 acceptance 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 samples, extraction QC checks, three sets of replicate samples, two matrix spikes, and continuing calibration verification (CCV) standards analyzed at a frequency of every 10 samples.

4.1.2.2 *Continuing calibration verification (CCV) check standard*

Instrument QC samples are used to verify the initial and continuing calibration of the ion chromatography system. These solutions are prepared at the low, medium, medium-high and high end of the calibration curve. Table 4.1-3 and 4.1-4 lists the concentrations.

Table 4.1-3: Target concentrations of anion CCV check standards for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019).

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 4.1-4: Target concentrations of cation CCV check standards for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019).

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

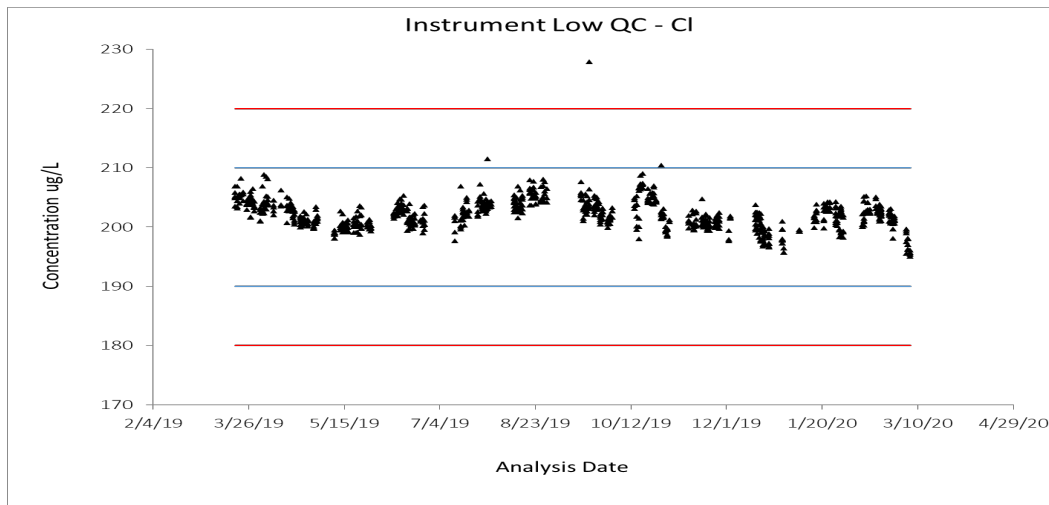
At least two CCV check standards are analyzed immediately after the calibration standards and a single CCV check standard is analyzed after every ten samples. When an instrument CCV check standard fails the acceptance criteria by falling outside of the control limits, impacted samples are reanalyzed. If a CCV check standard fails, and there is a second CCV check standard measured immediately following the failure which passes, 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 analysis records for each set of 50 samples analyzed.

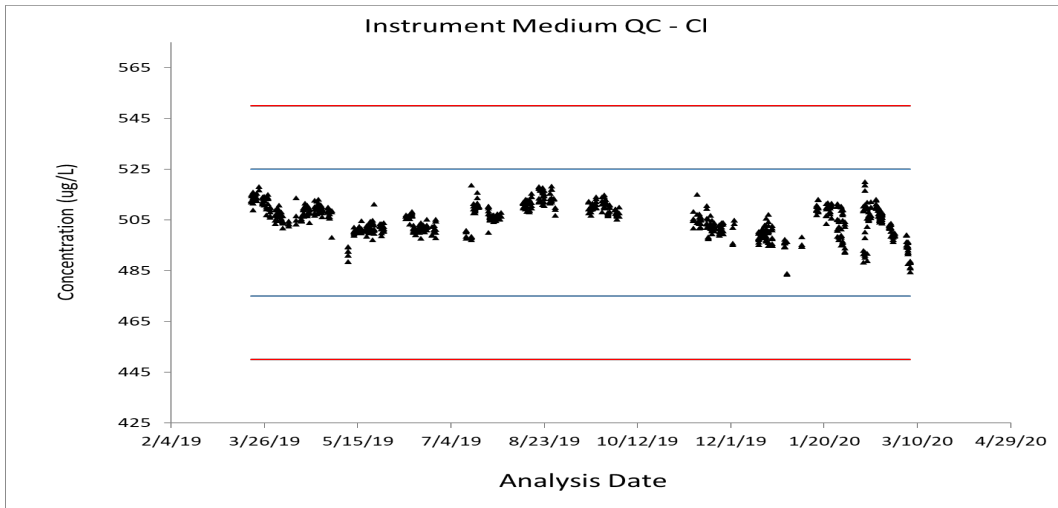
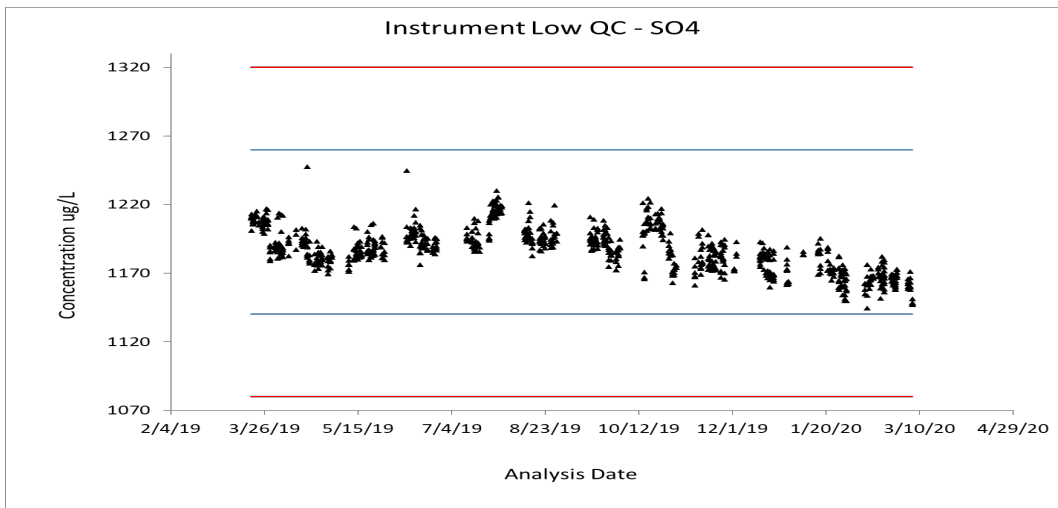
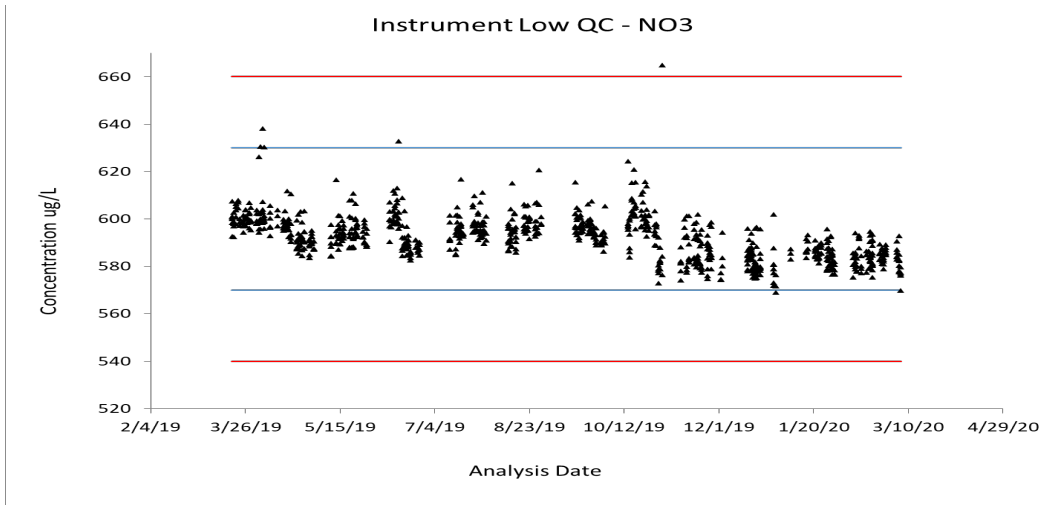
Control charts were prepared for anion (Figure 4.1-1) and cation (Figure 4.1-2) CCV check standards. Most CCV check standards were within the stated control limits. There were three cases where CCV check standards failed the acceptance criteria for anions: (1) two of these were a low CCV check standard for chloride and nitrate, and the impacted samples were reanalyzed; (2) one of these was a high CCV check standard for chloride, and the impacted samples were reanalyzed. There were nine cases where CCV check standards failed the acceptance criteria for cations: (1) one of these was a low CCV check standard for ammonium, and the impacted samples were reanalyzed; (2) one of these was a medium CCV check standard for potassium ion, and the impacted samples were reanalyzed; (3) seven of these were low CCV check standards for potassium ion, the impacted samples were not reanalyzed because there was a second CCV

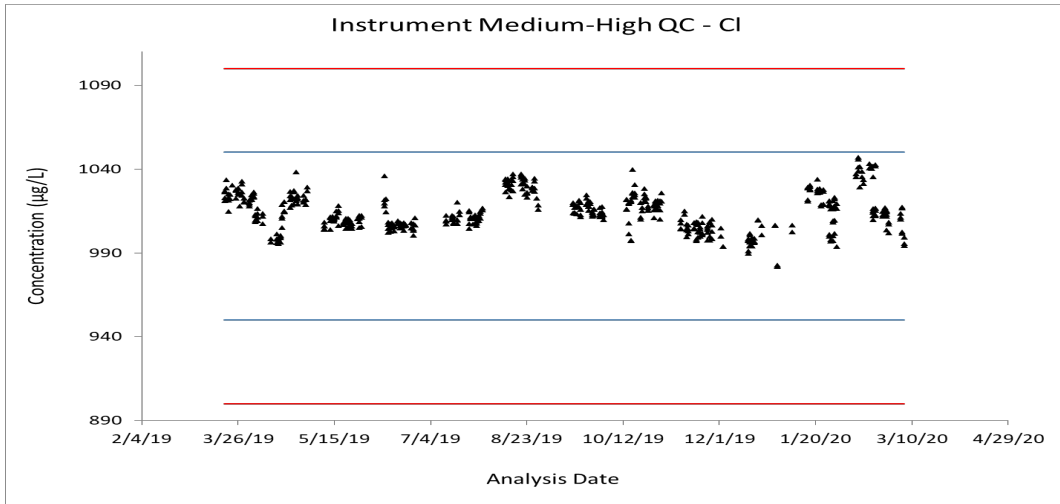
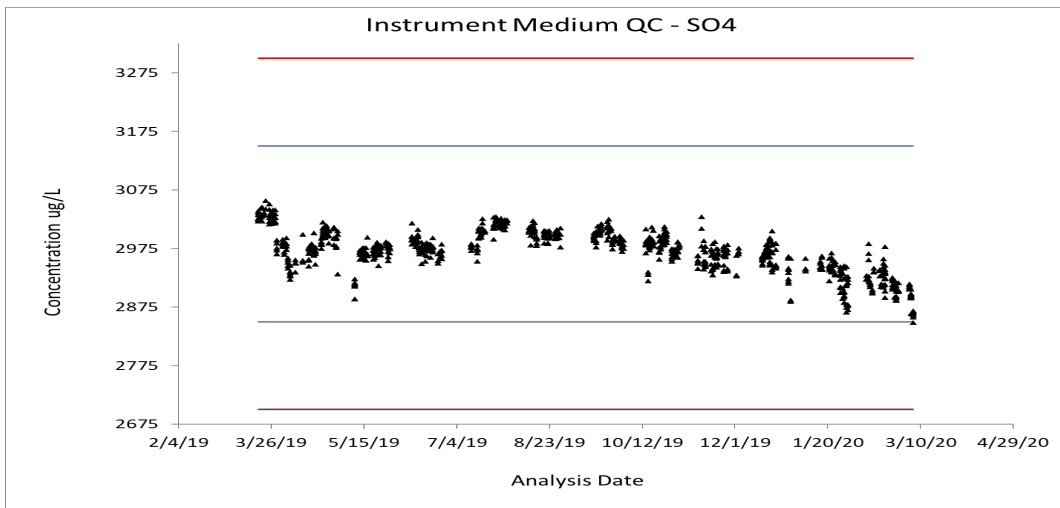
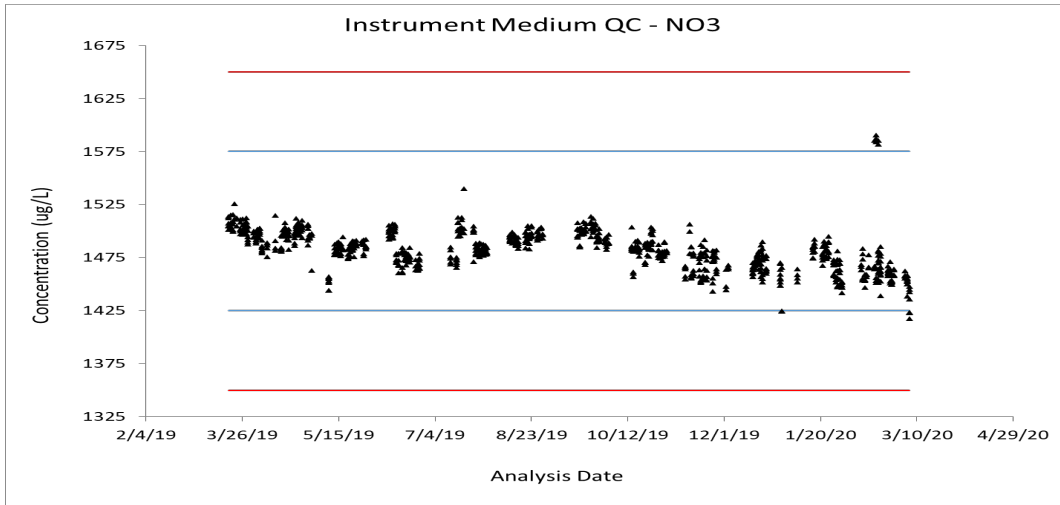
check standard that was acceptable. The potassium acceptance criteria failures occurred on one instrument (C3); these cases were queued immediately following calibration curve analysis and may have been impacted by carryover.

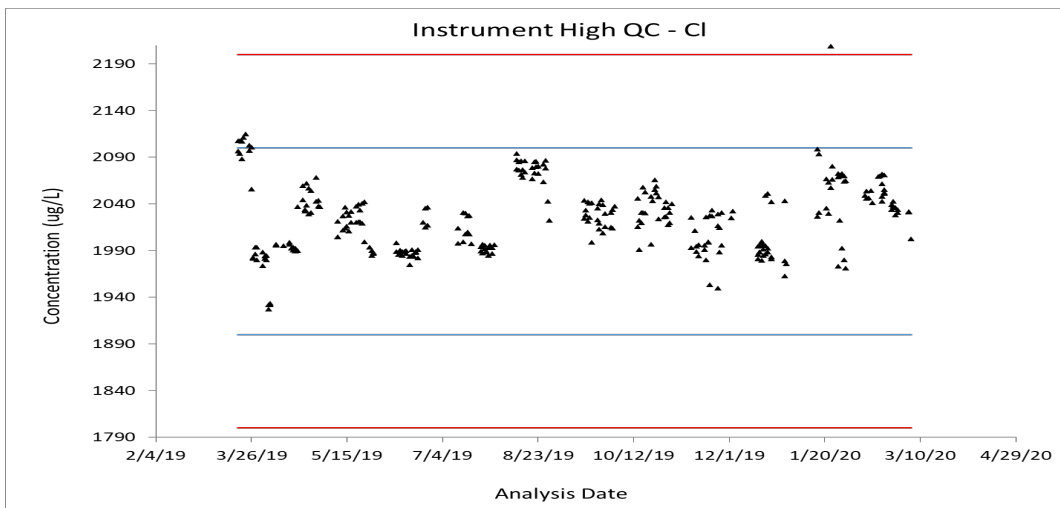
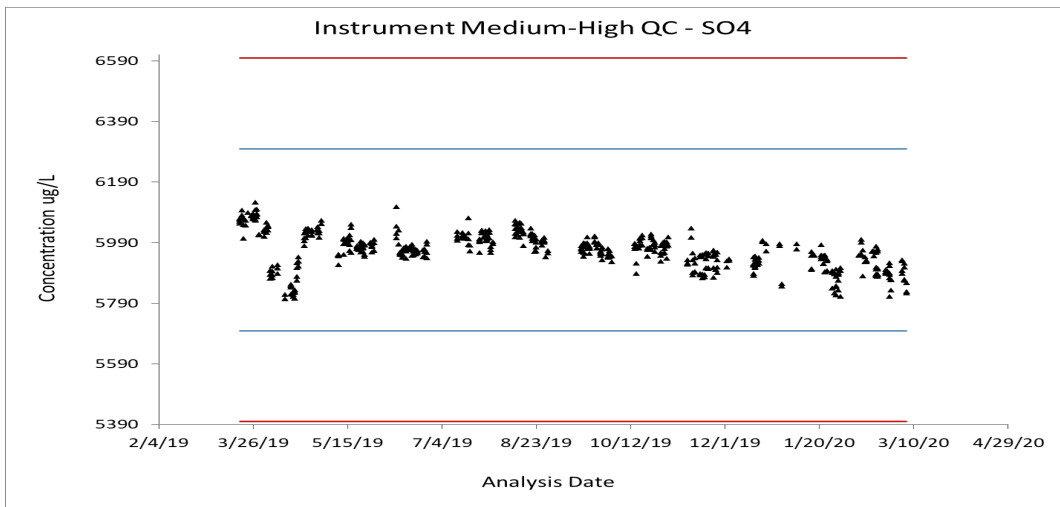
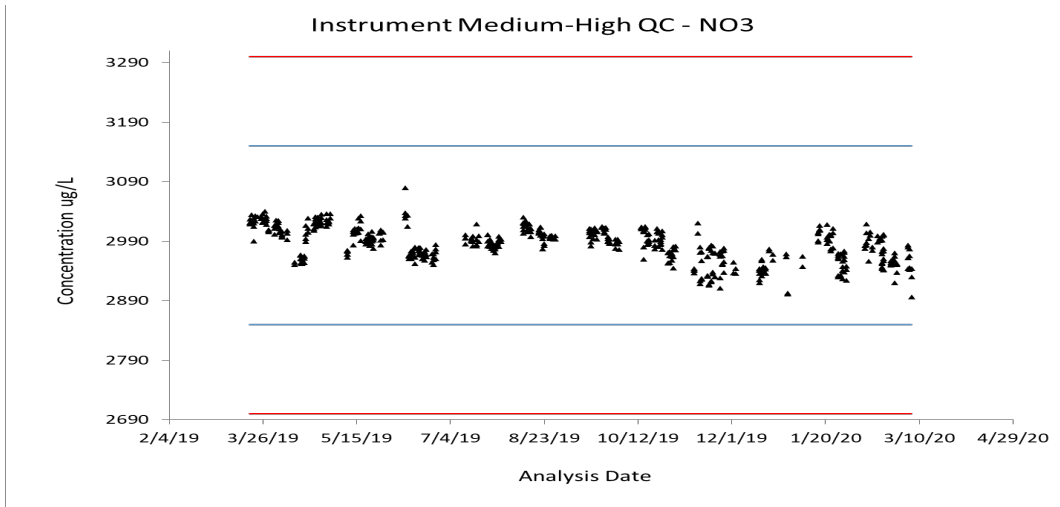
The IC delivery system introduces samples via a sample loop, which is rinsed using excess sample. Carryover is evaluated by analyzing DI water blanks immediately after analysis of calibration standards containing ions at various concentrations. Residual ions measured in the DI water blank should be at concentrations at or below the instrument detection limit, and carryover is assumed to be present if residual ion concentrations exceed the instrument detection limits. Results from DI water blanks analyzed immediately after the analysis of standards prepared at 2,000 ppb, 1,000 ppb, and 500 ppb did not produce carryover above the 5 ppb instrument detection limit. To prevent carryover from impacting sample analysis, a DI water blank is analyzed immediately after the calibration standards. As an additional precaution, samples analyzed immediately after a sample with concentration above 1,000 ppb are repeated to check for carryover.

Figure 4.1-1: Control charts for anion CCV check standards at low, medium, medium-high, and high concentrations measured in units of $\mu\text{g}/\text{mL}$ (see Table 4.1-3) for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019). Red lines show upper and lower control limits set at $\pm 10\%$ of the nominal concentrations for the low, medium, medium-high, and high standards. Blue lines show upper and lower warning limits.









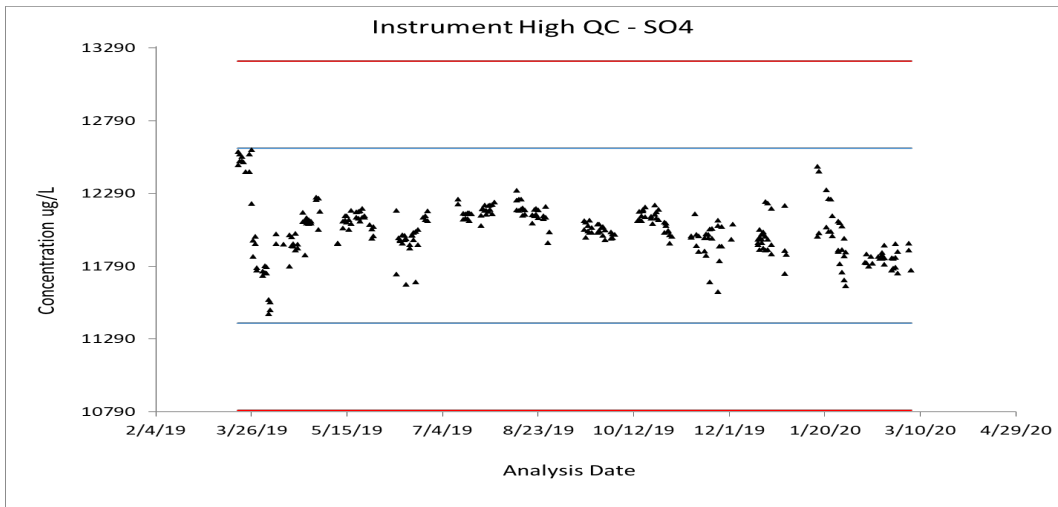
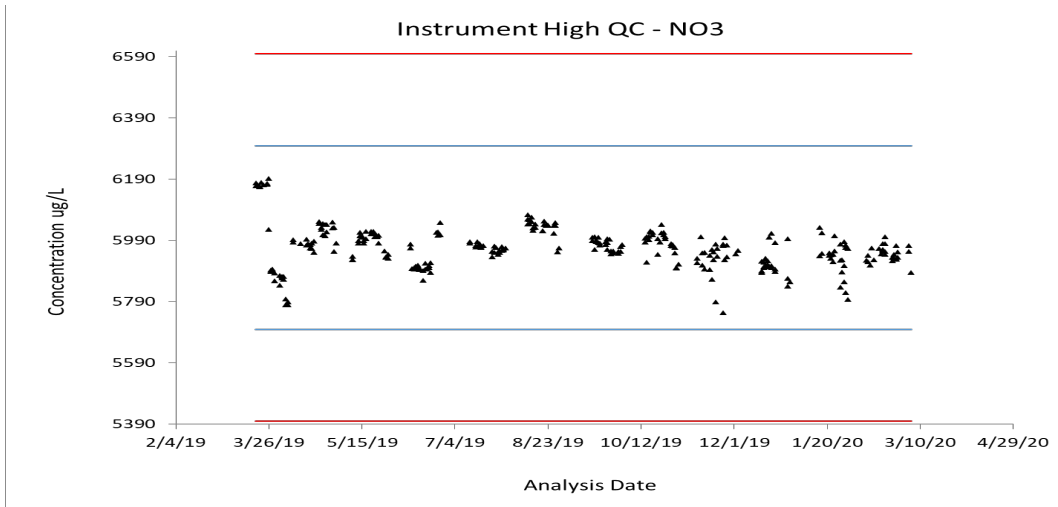
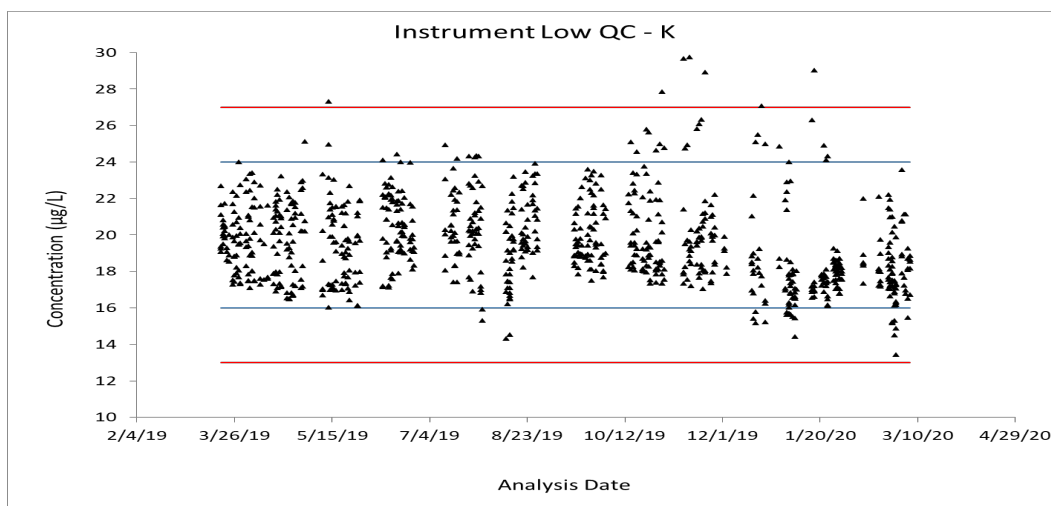
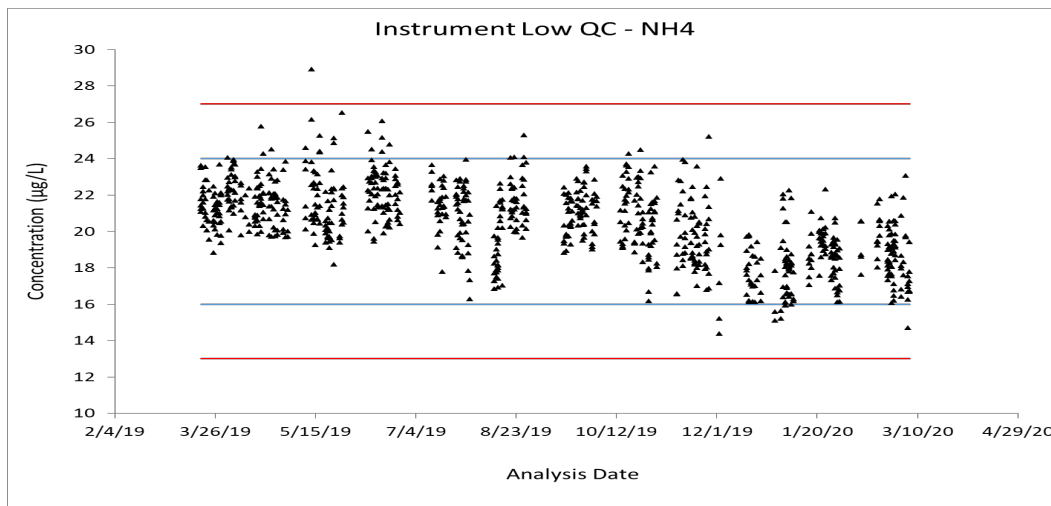
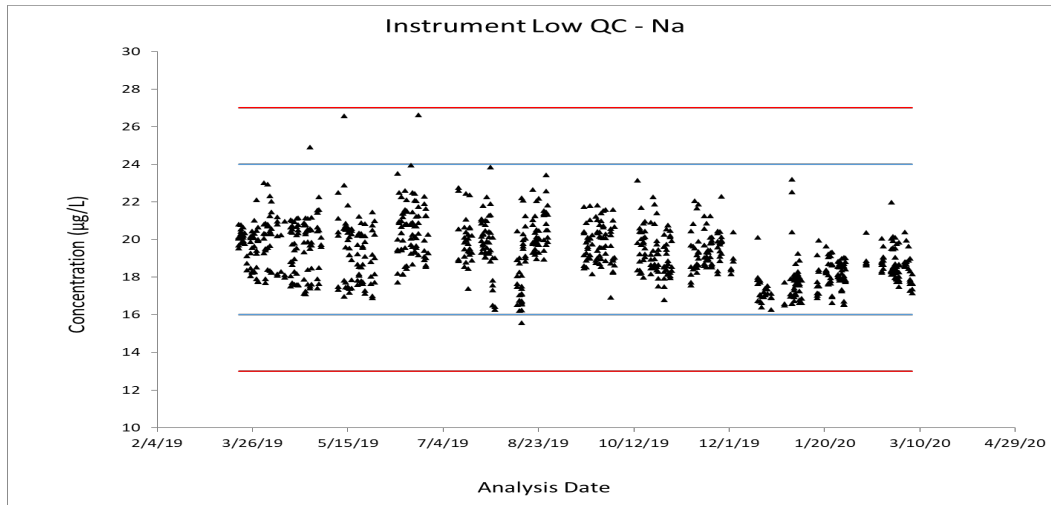
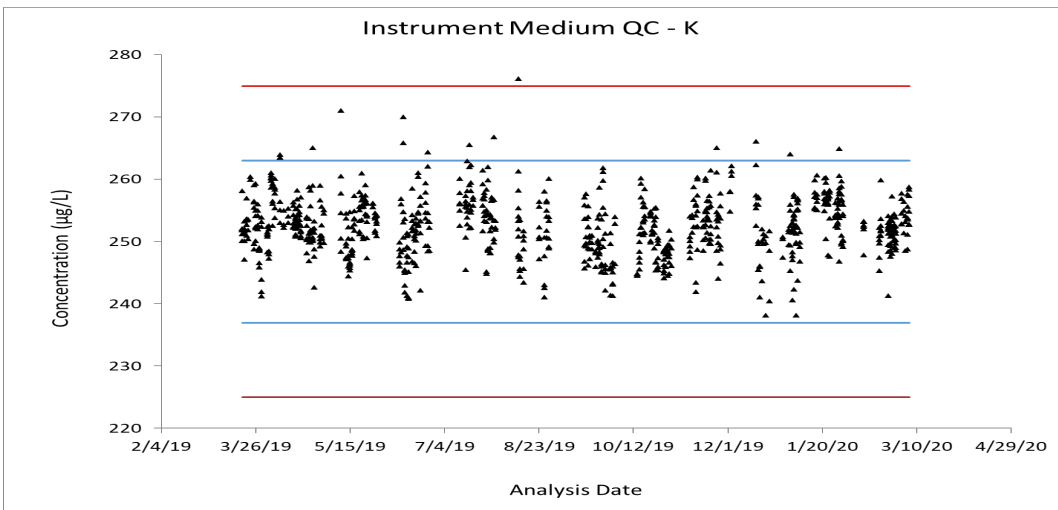
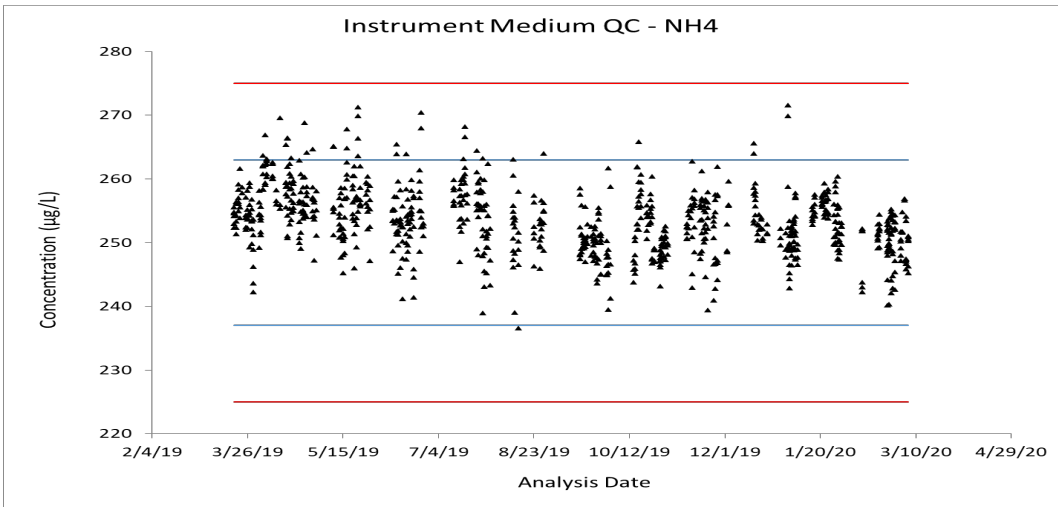
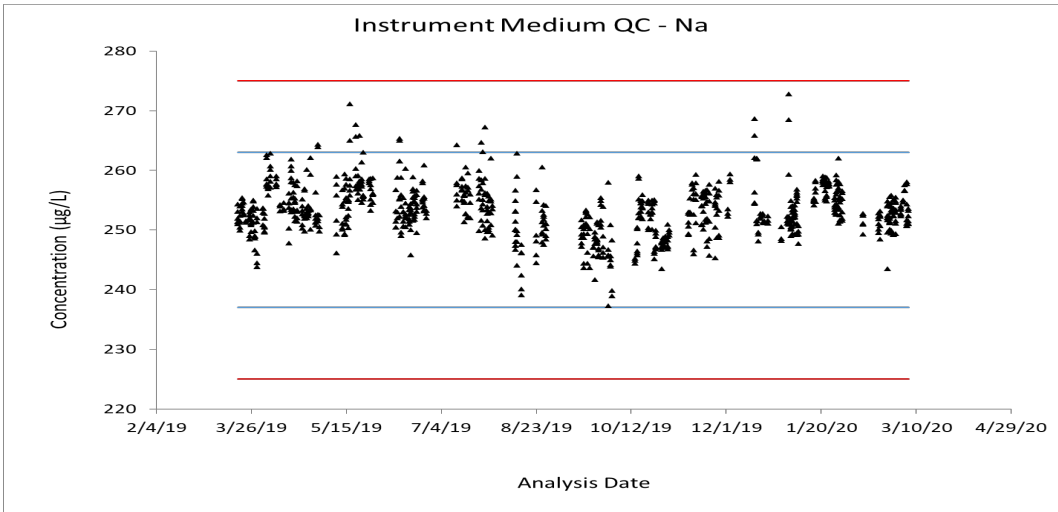
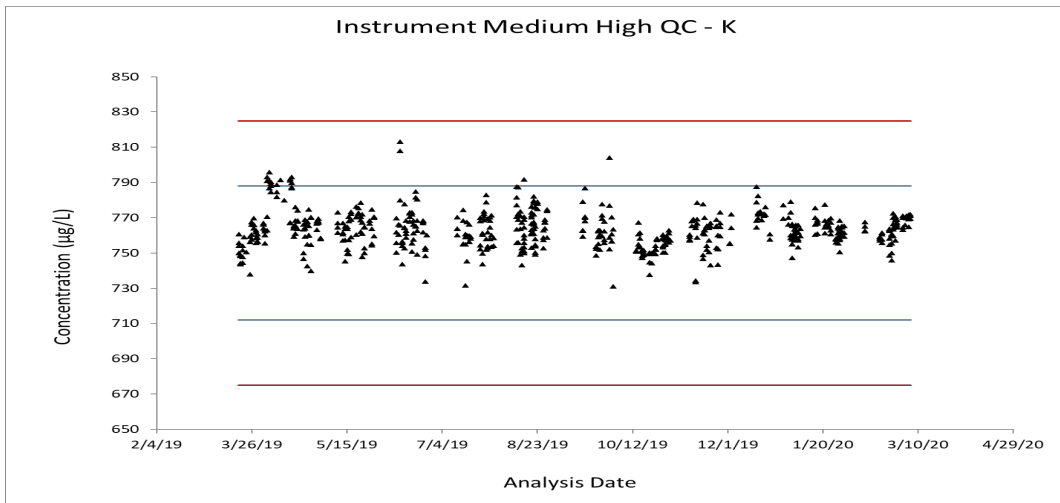
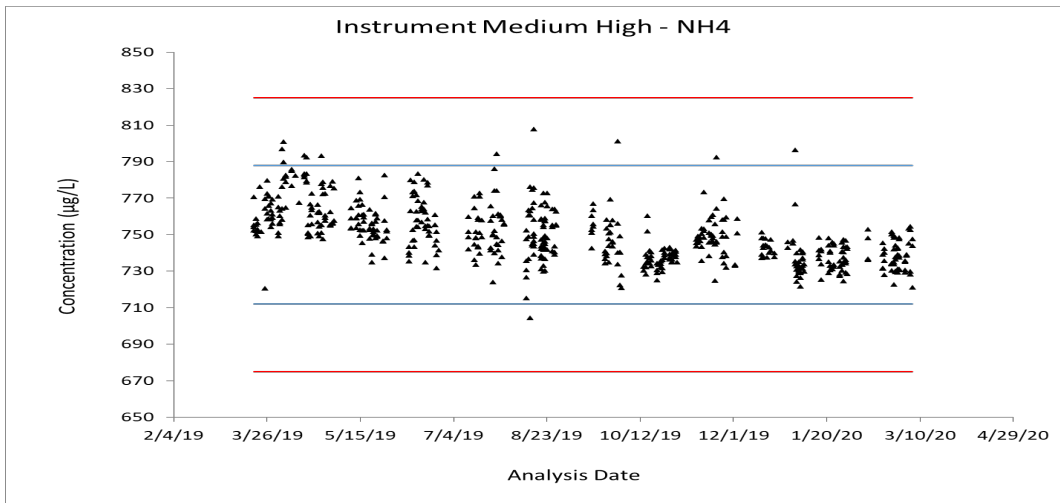
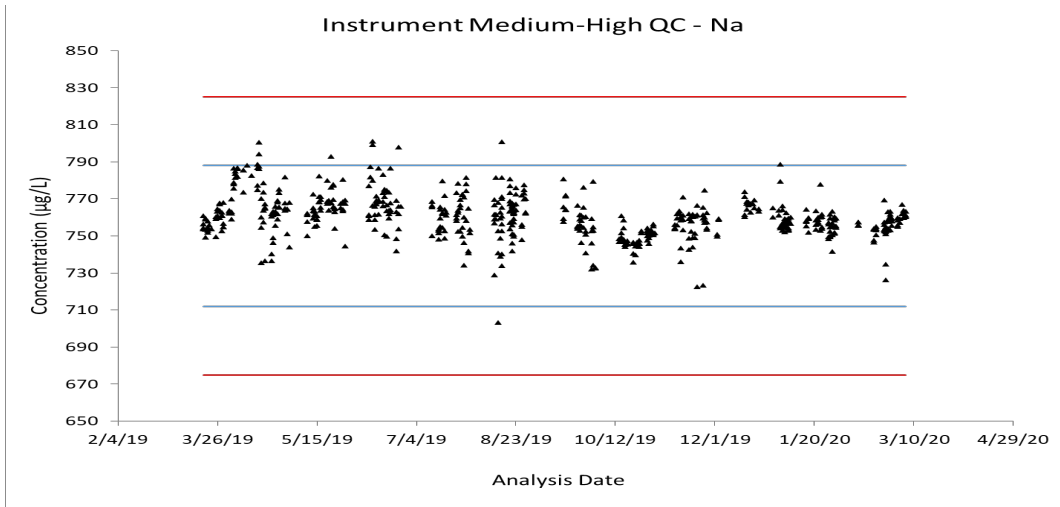
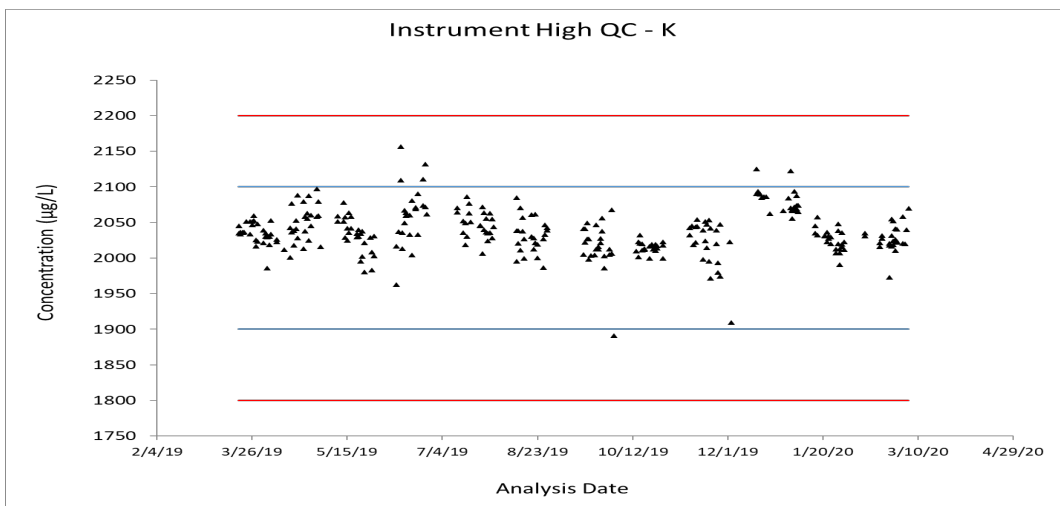
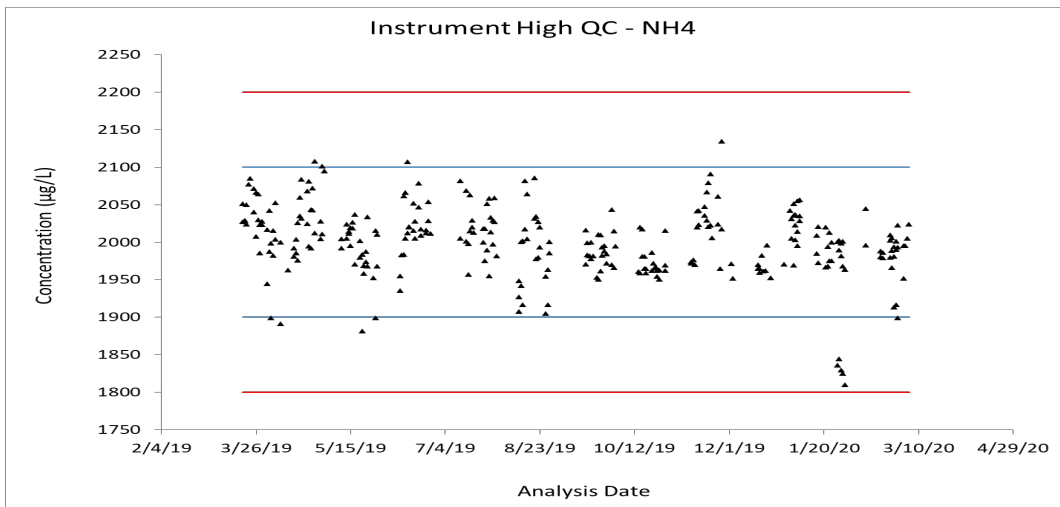
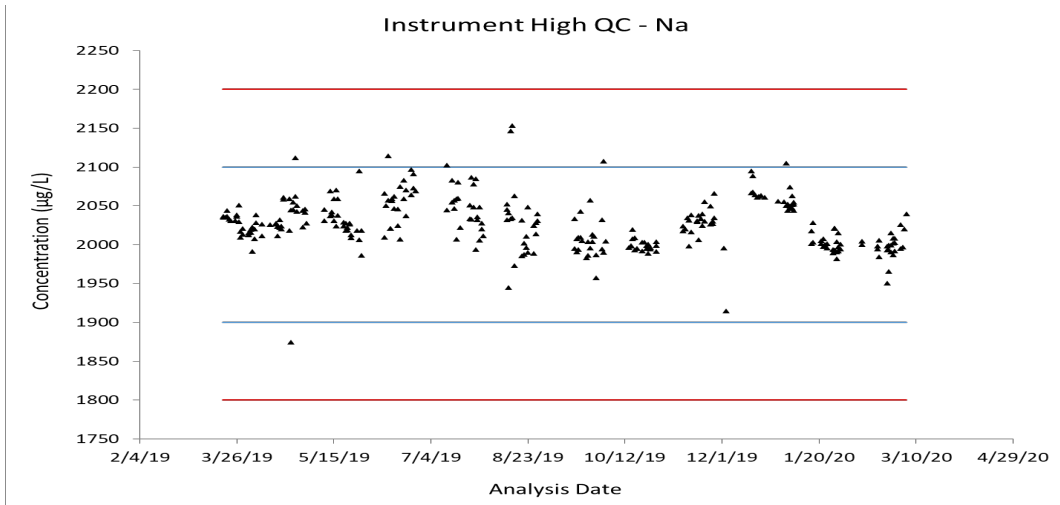


Figure 4.1-2: Control charts for cation CCV check standards at low, medium, medium-high, and high concentrations measured in units of $\mu\text{g}/\text{mL}$ (see Table 4.1-4) for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019). Red lines show upper and lower control limits set at $\pm 35\%$ of the nominal concentrations for the low standards and $\pm 10\%$ of the nominal concentrations for the medium, medium-high, and high standards. Blue lines show upper and lower warning limits.



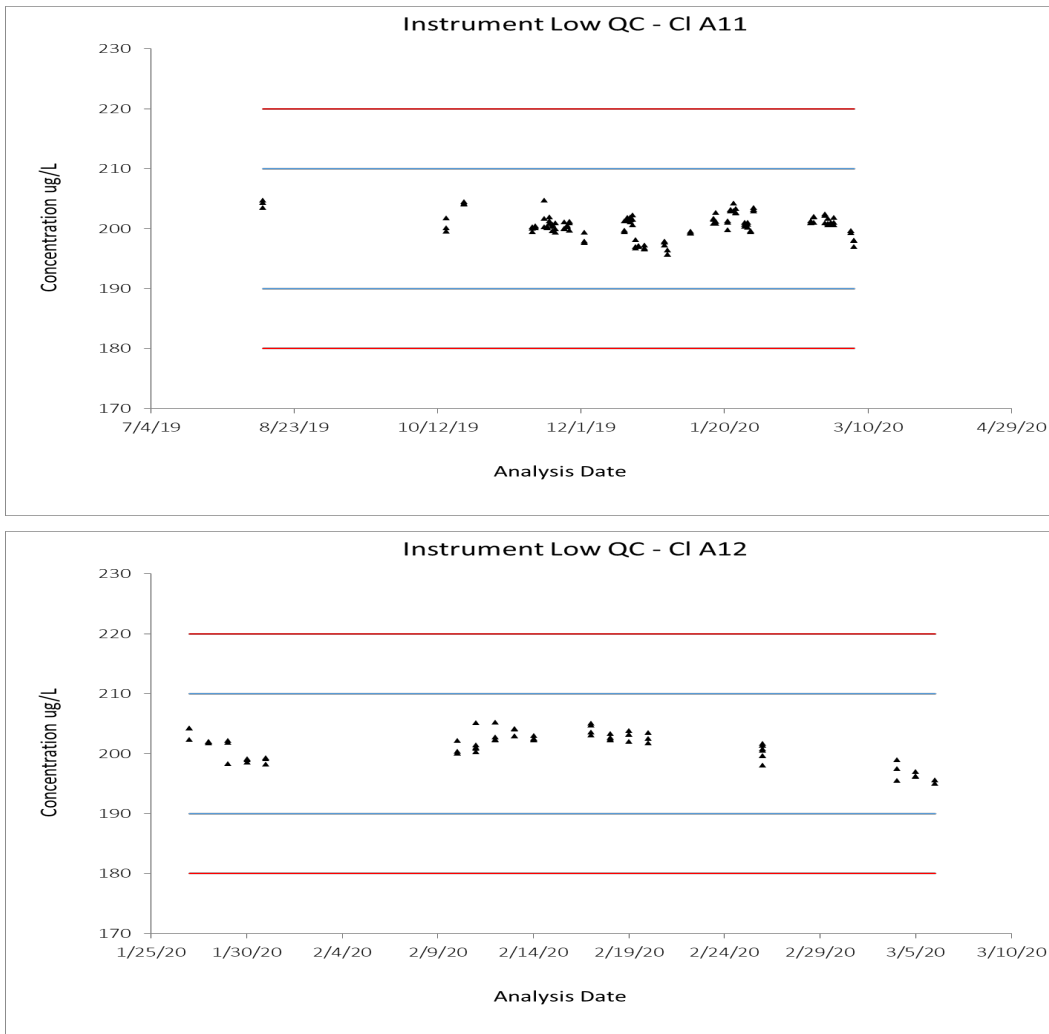


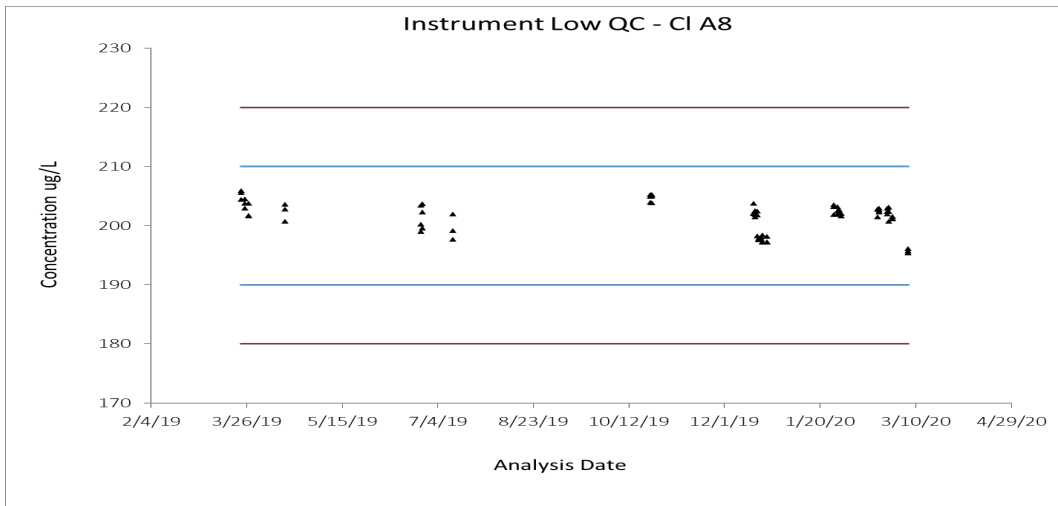
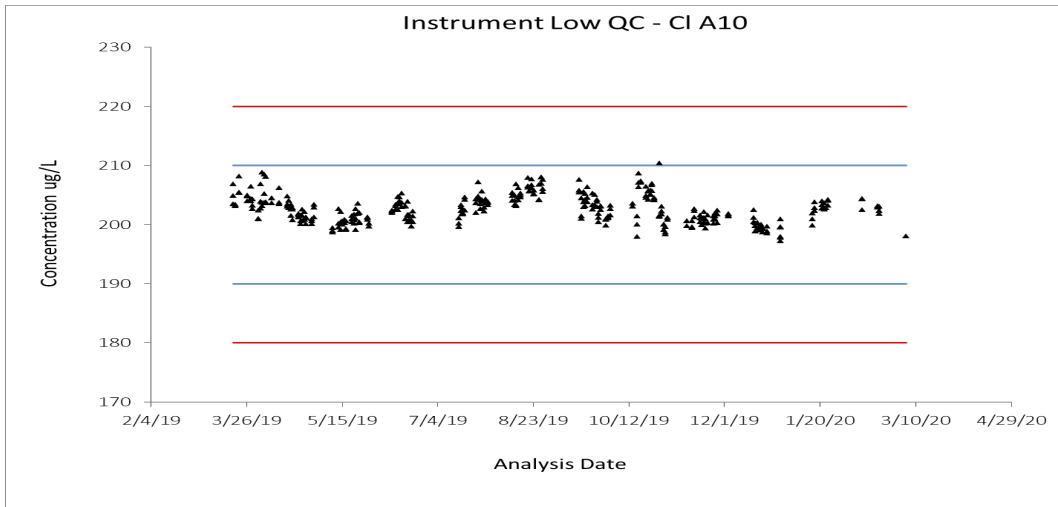
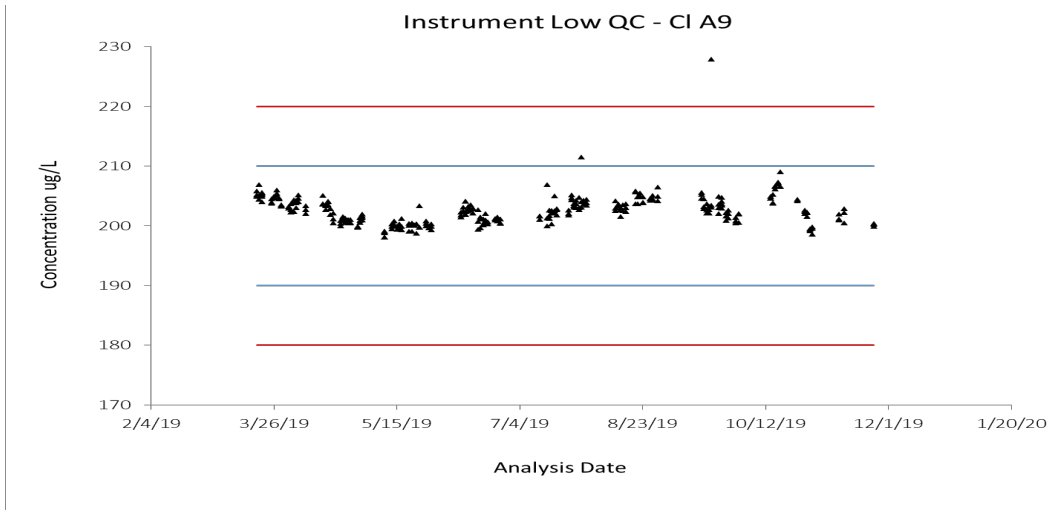


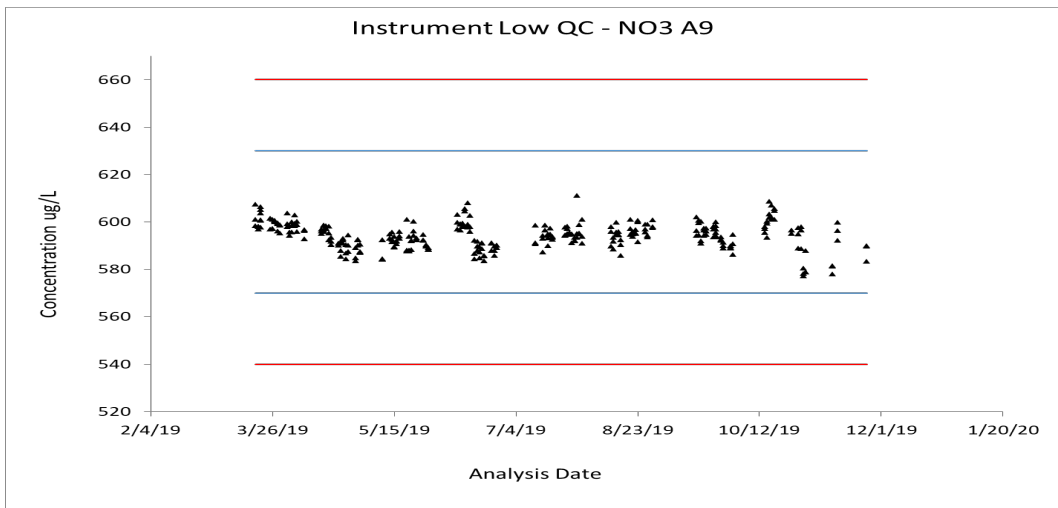
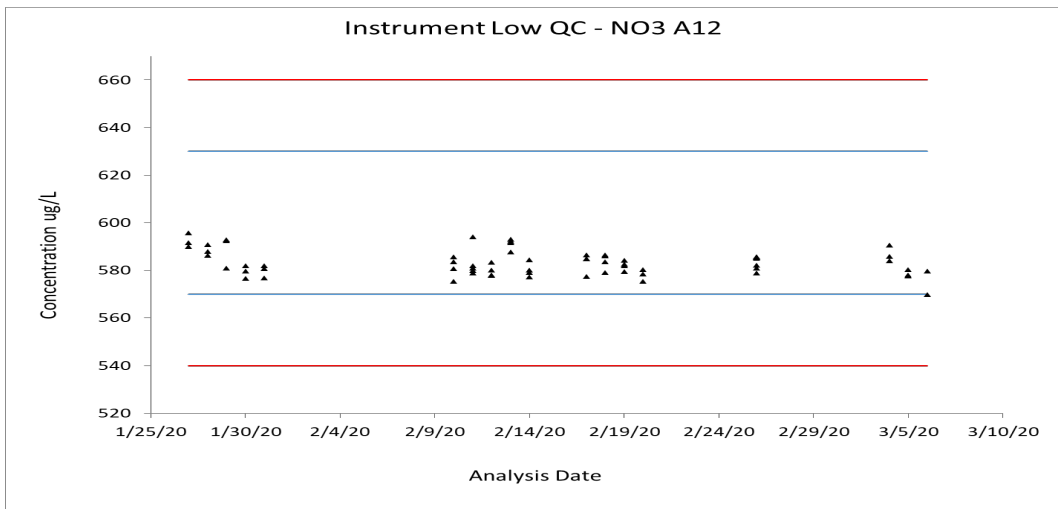
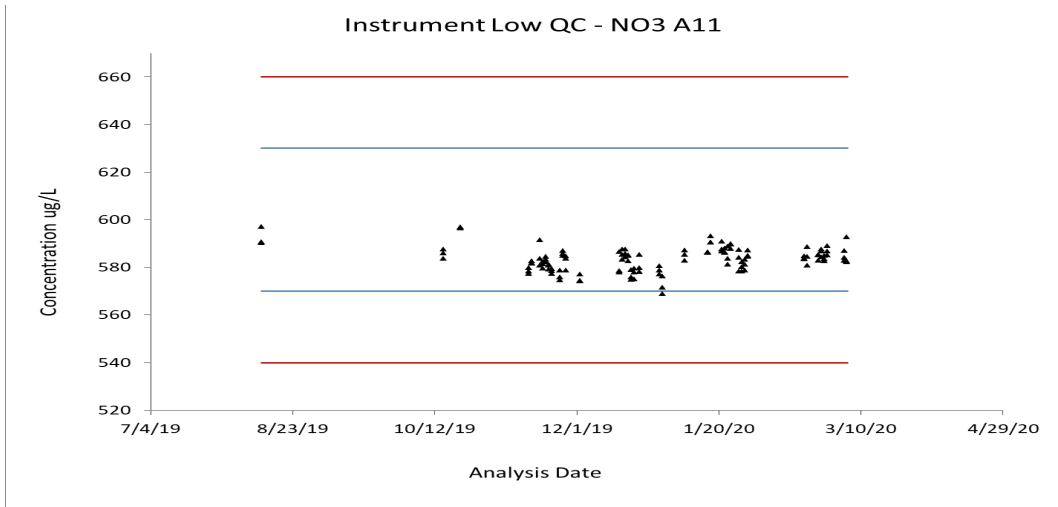


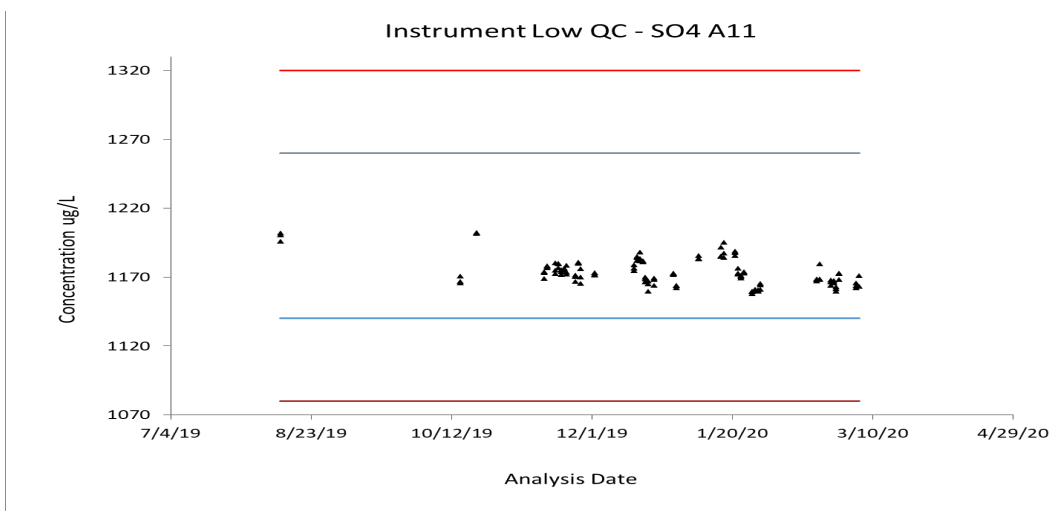
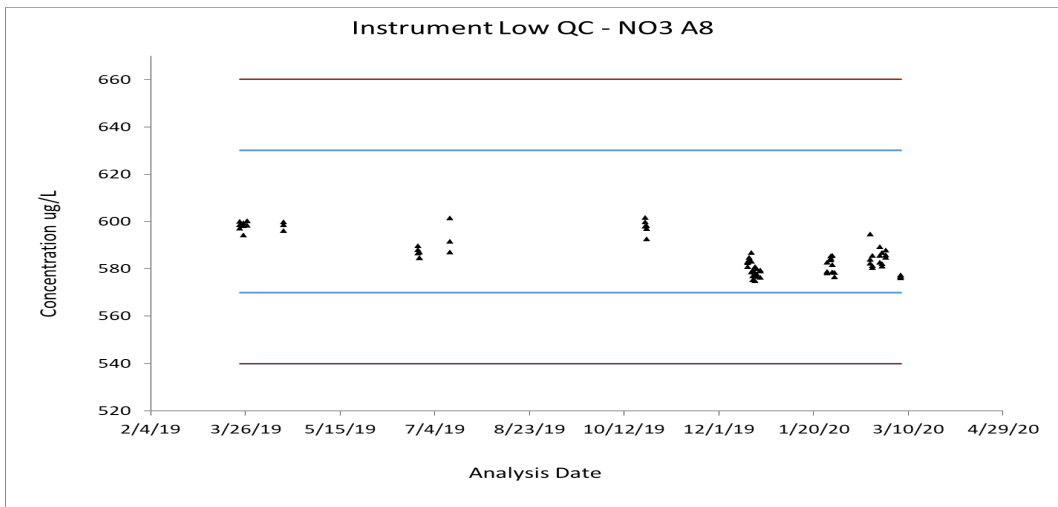
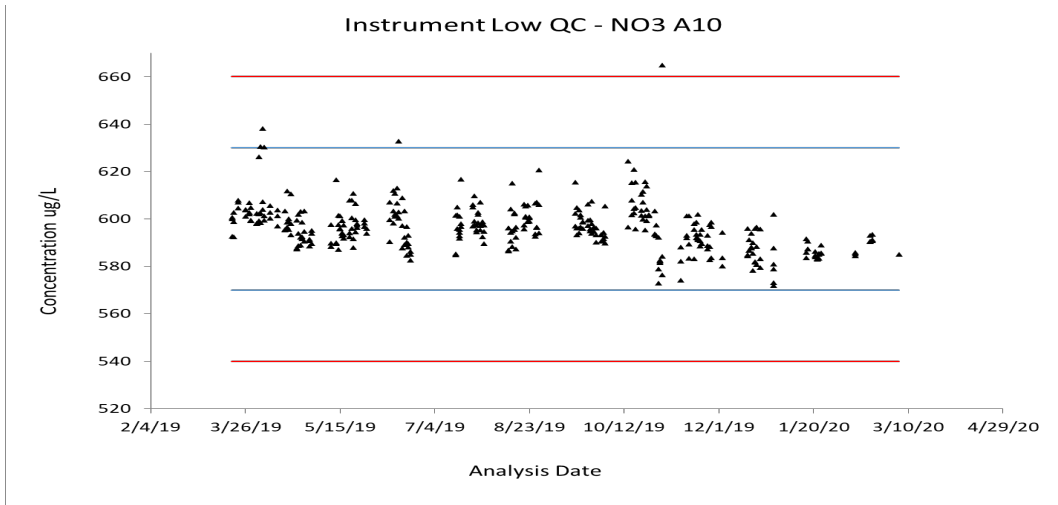
For the purpose of demonstrating instrument-to-instrument performance, control charts for the lowest CCV check standards were generated, where instruments A11, A12, A9, A10, and A8 are compared for anions (Figure 4.1-3) and instruments C9, C10, C3, and C6 are compared for cations (Figure 4.1-4). The control charts illustrate consistent performance between instruments.

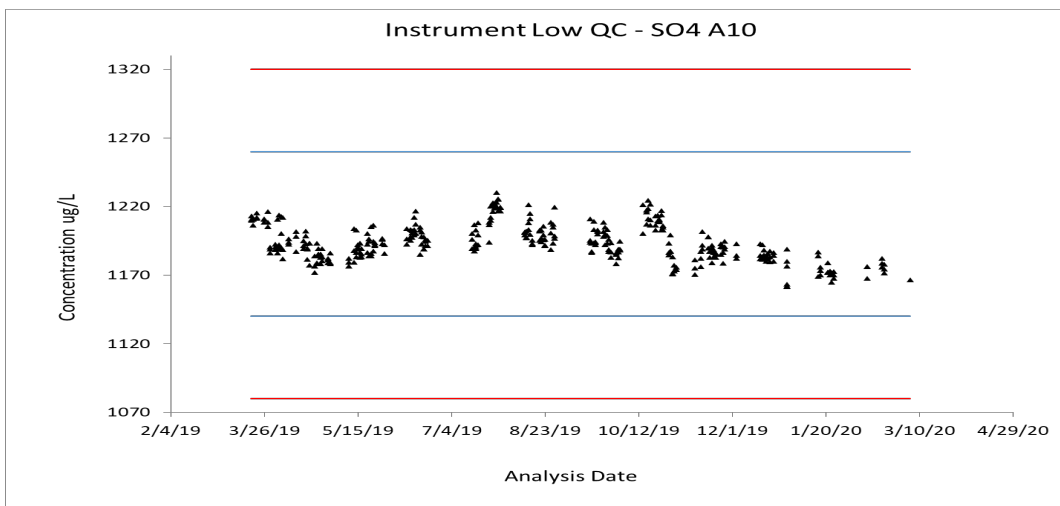
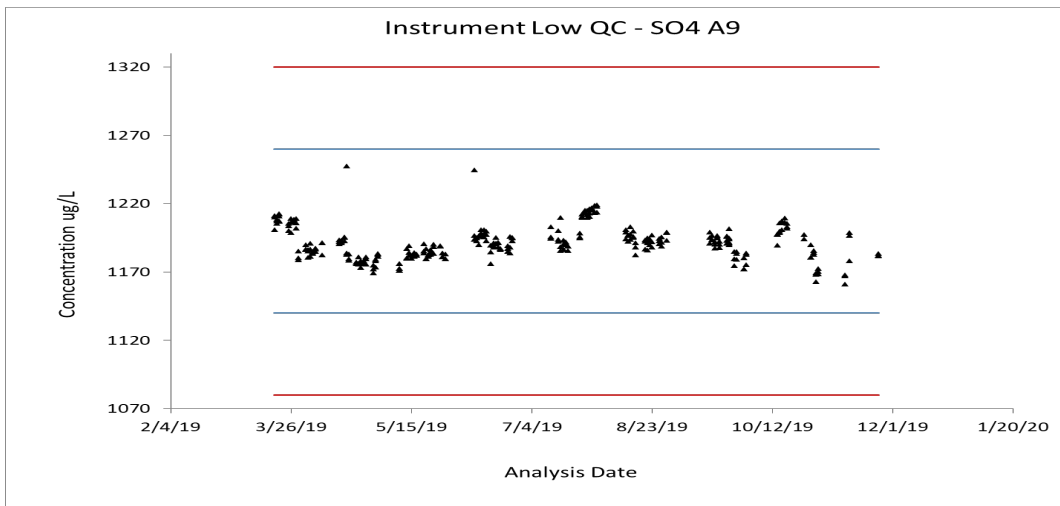
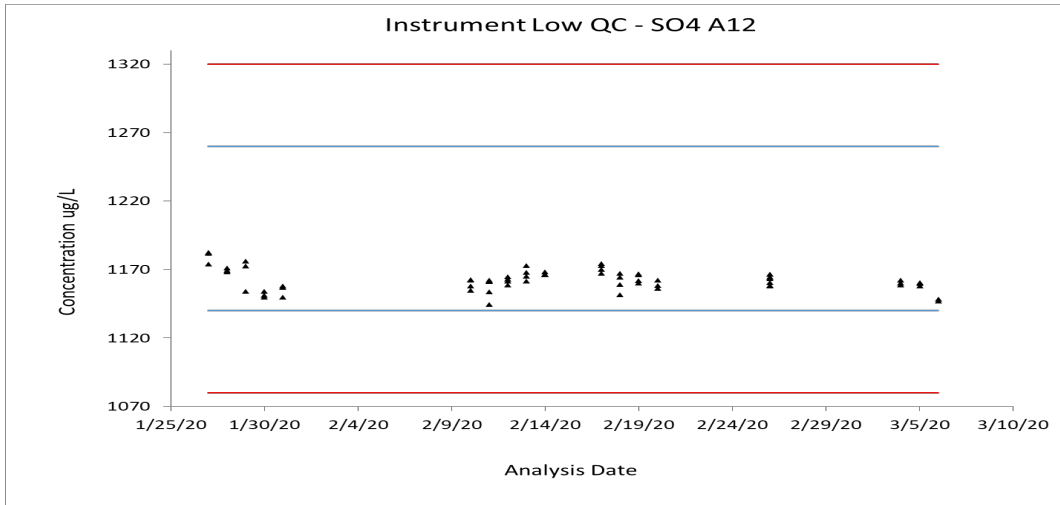
Figure 4.1-3: Control charts for anion CCV check standards showing comparability between instruments (A11 and A12, Thermo Dionex Aquion systems; A9, A10, and A8 Thermo Dionex ICS-3000 systems) at low concentrations (see Table 4.1-3) for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019). Red lines show upper and lower control limits set at $\pm 10\%$ of the nominal concentrations. Blue lines show upper and lower warning limits.











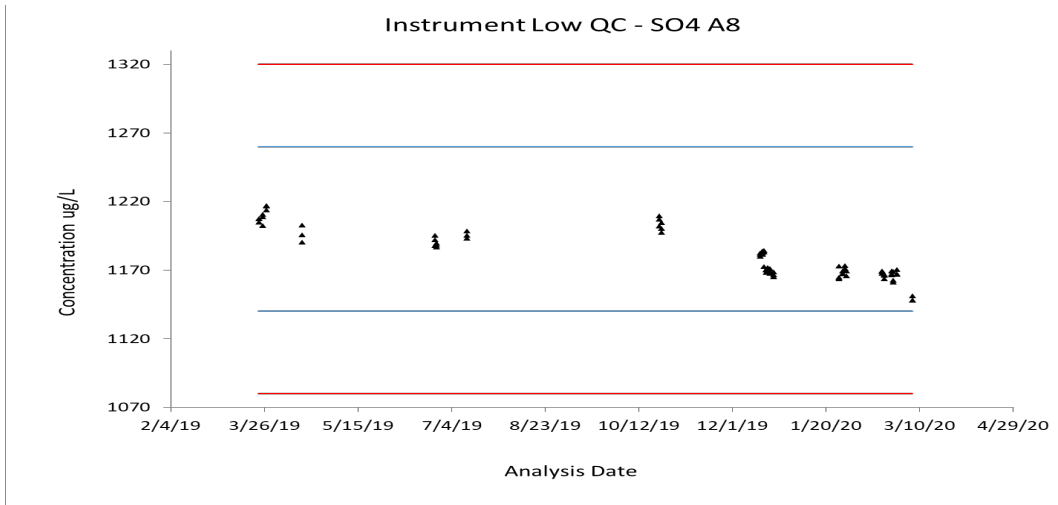
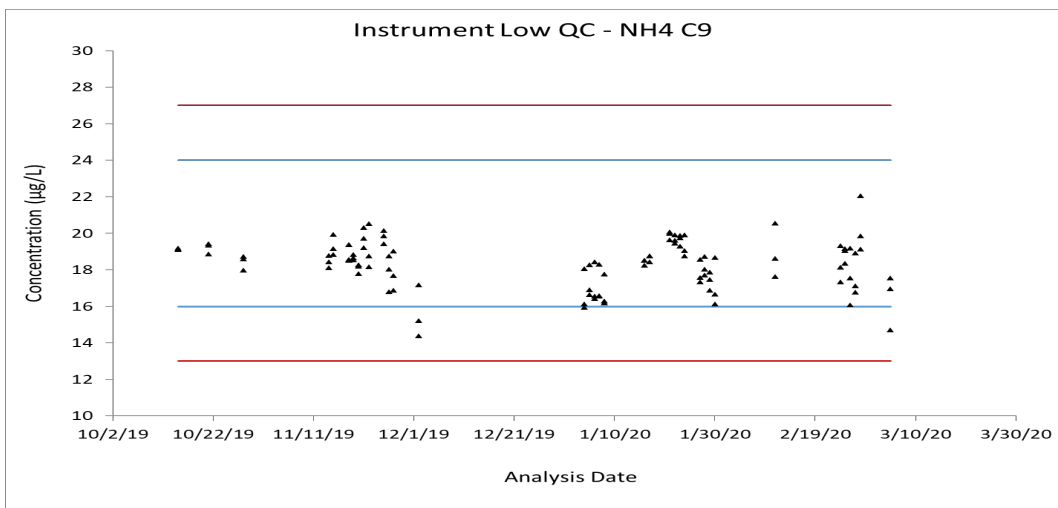
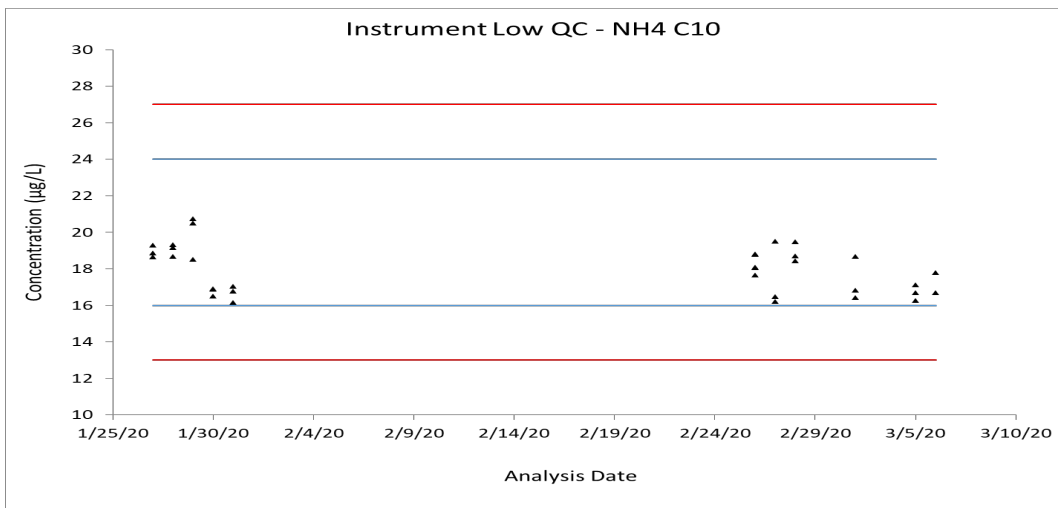
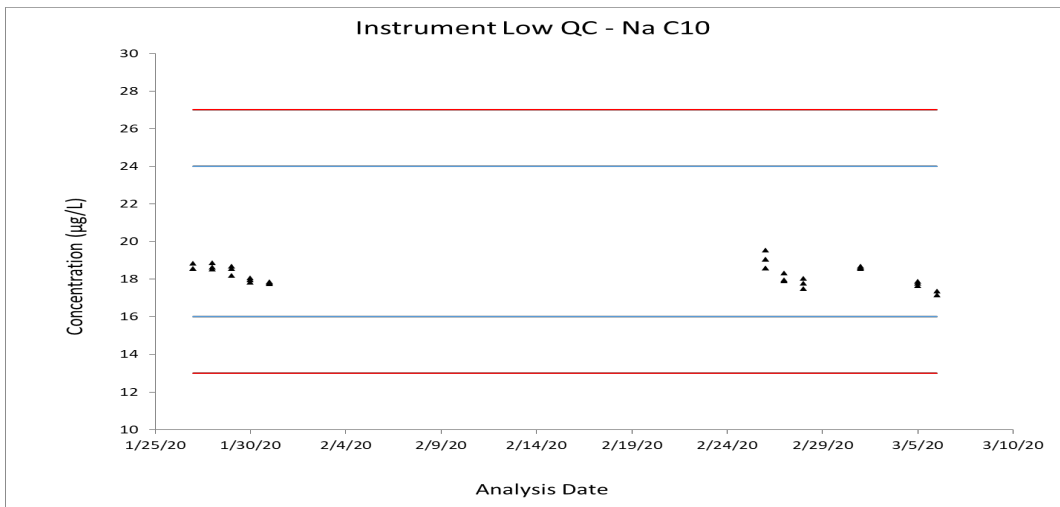
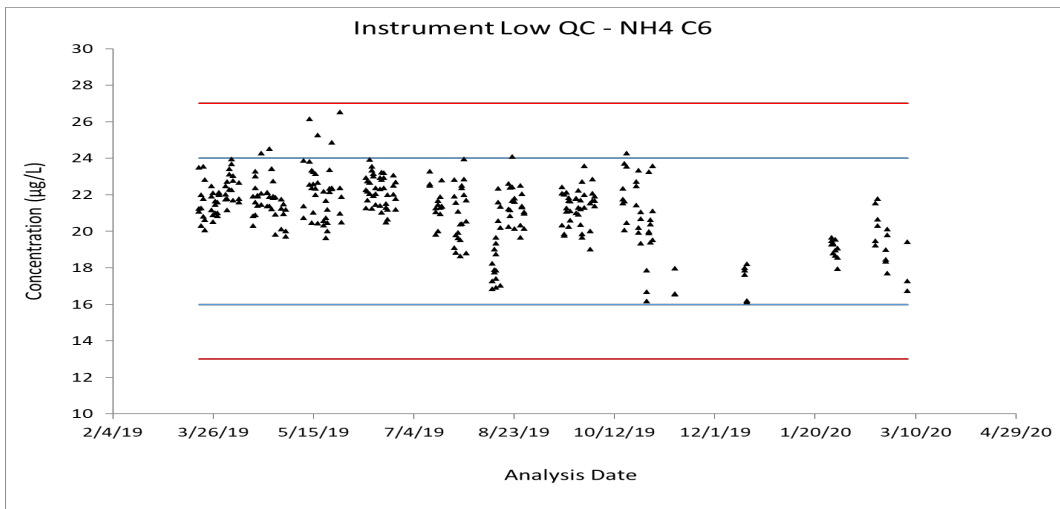
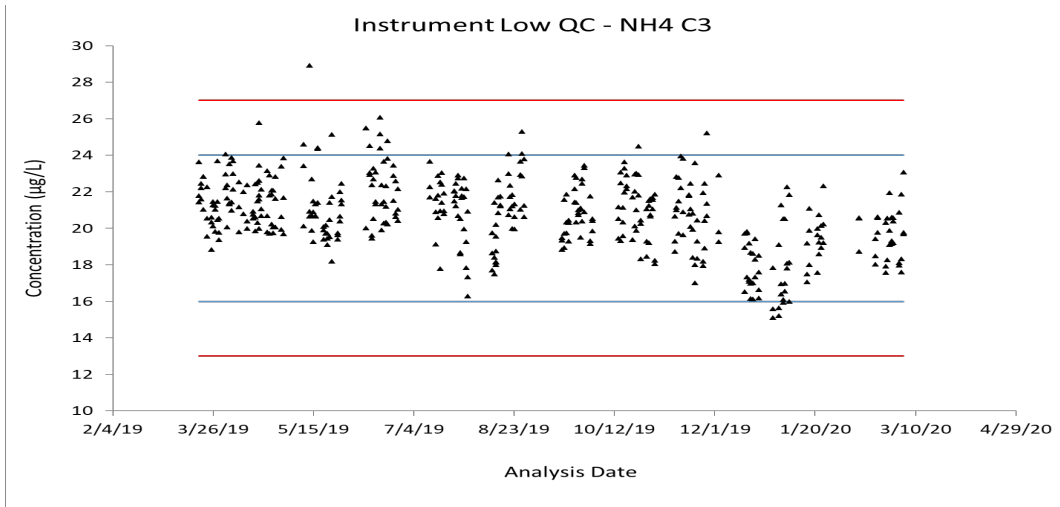
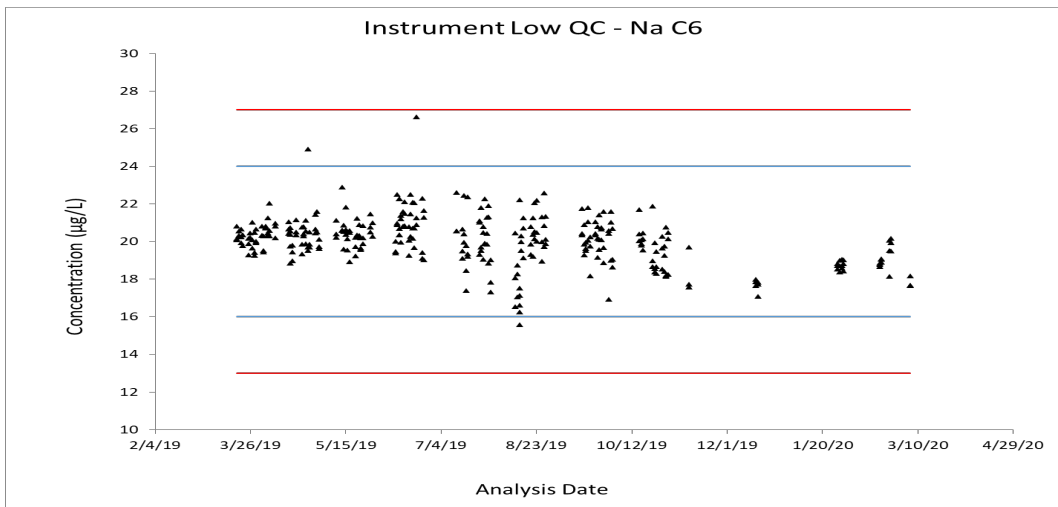
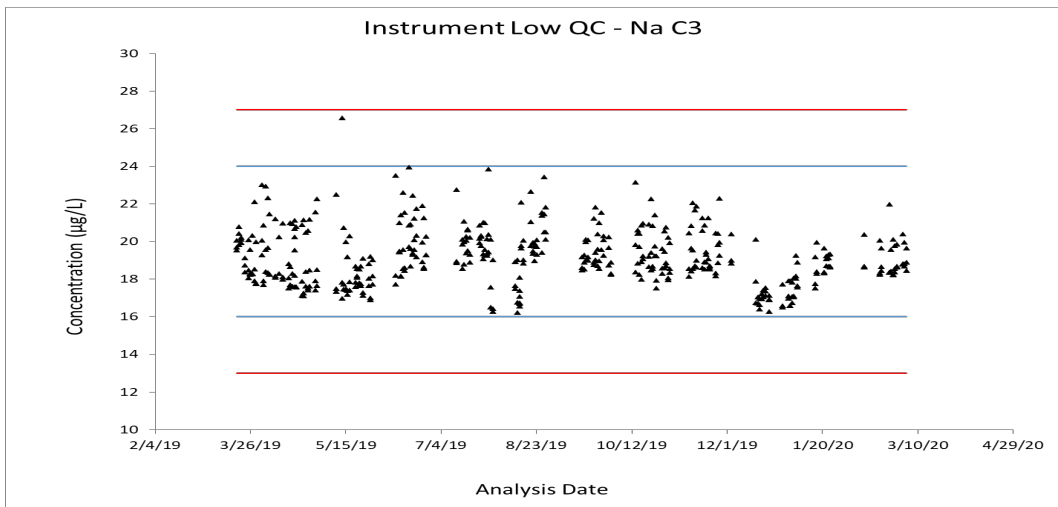
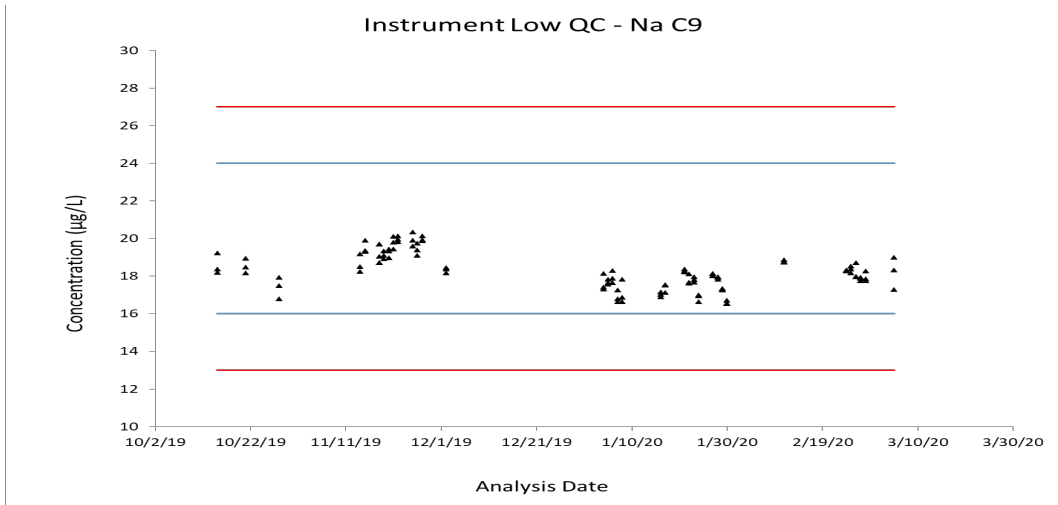
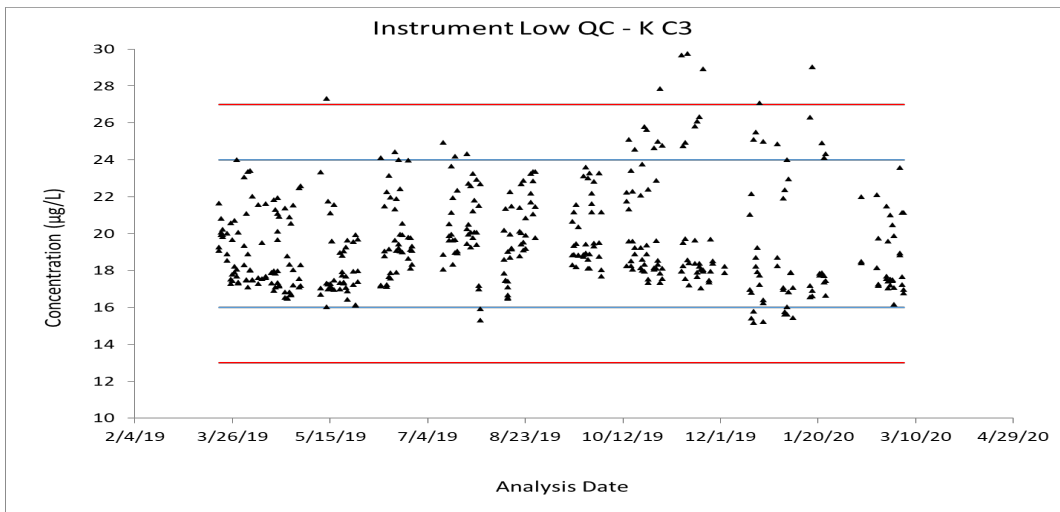
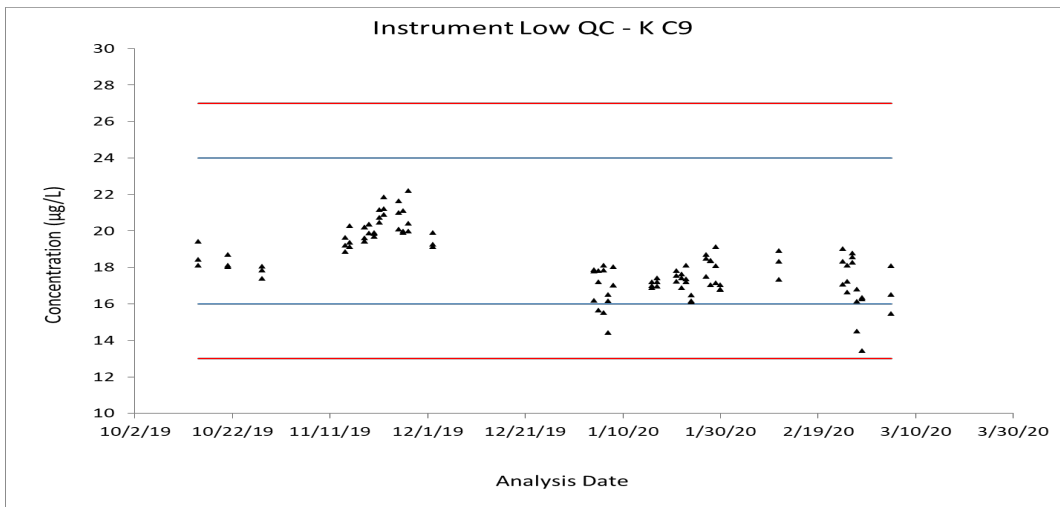
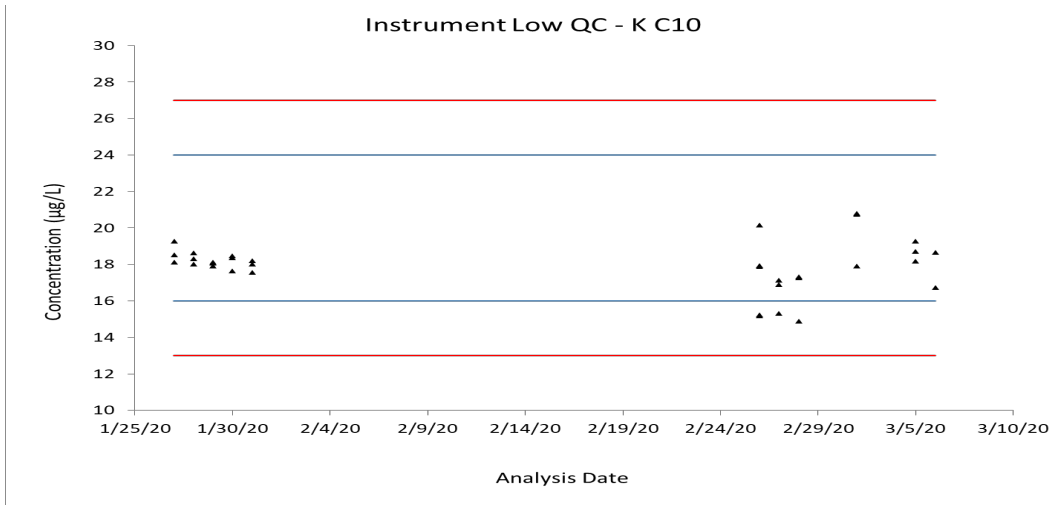


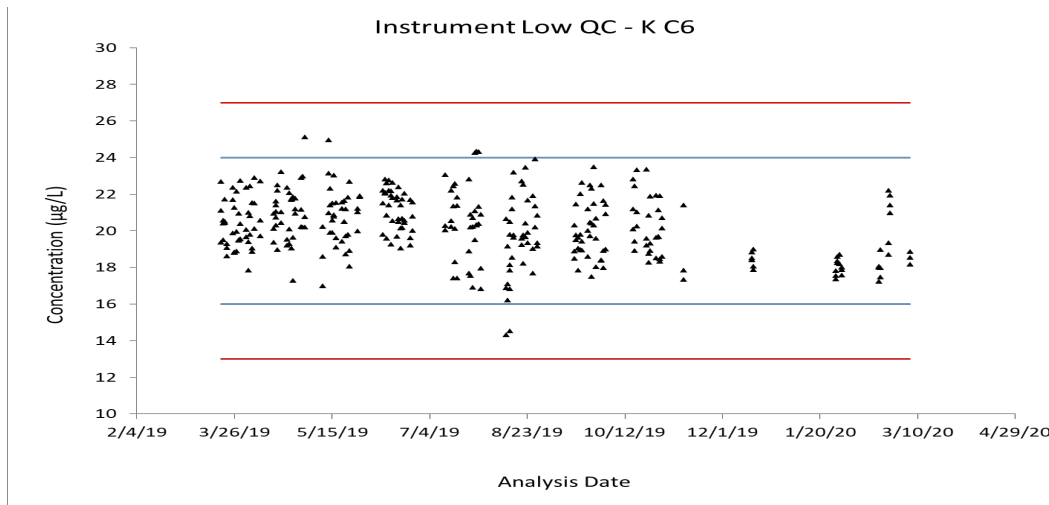
Figure 4.1-4: Control charts for cation CCV check standards showing comparability between instruments (C9 and C10, Thermo Dionex Aquion systems; C3 and C6, Thermo Dionex ICS-3000 systems) at low concentrations (see Table 4.1-4) for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019). Red lines show upper and lower control limits set at $\pm 35\%$ of the nominal concentrations. Blue lines show upper and lower warning limits.







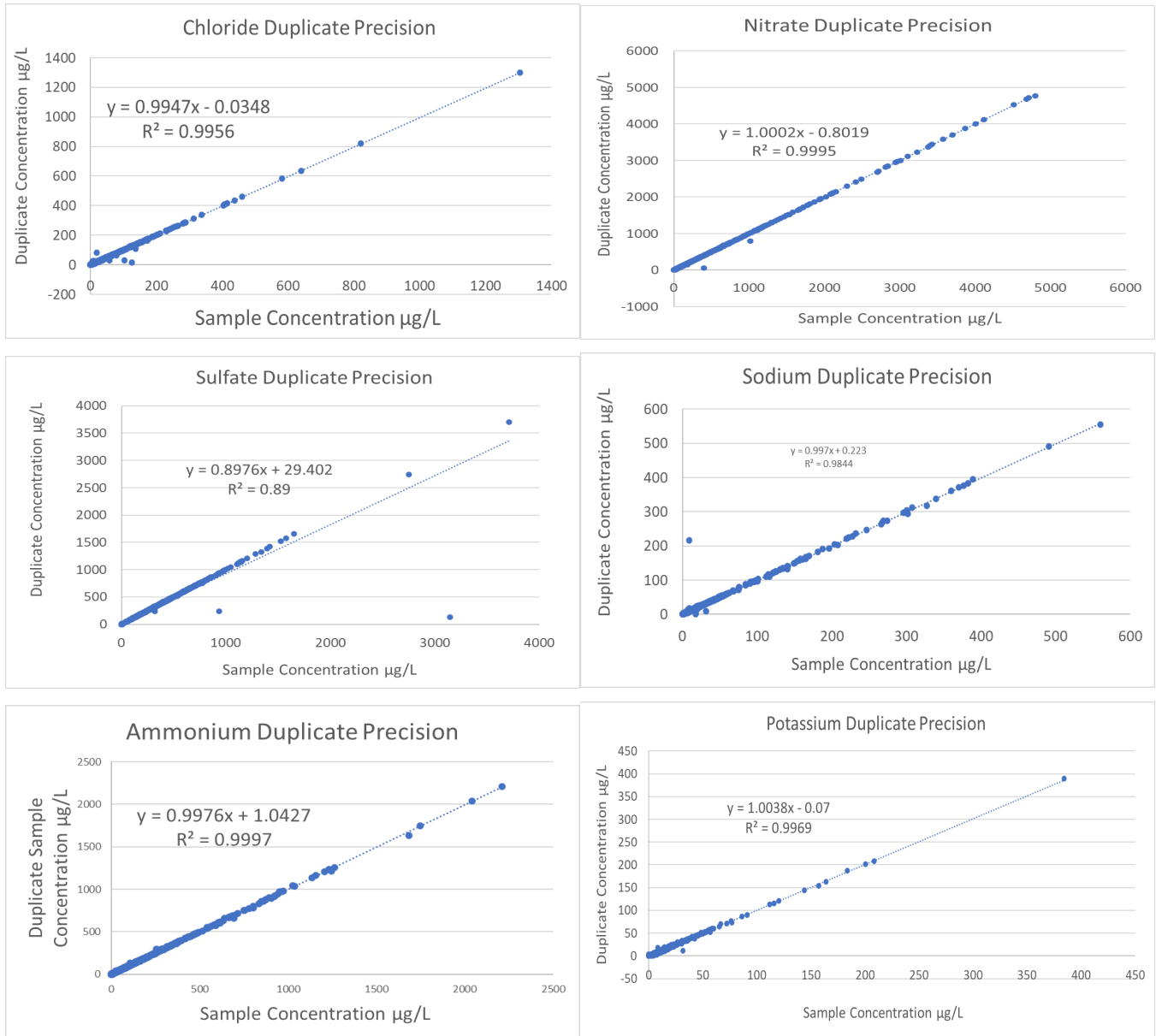




4.1.2.3 Duplicate Samples

Duplicate analysis results are obtained from two different aliquots of the same filter sample extract run on the same instrument sequentially; there are three sets of duplicate samples for every 50 samples analyzed. The relative percent difference (RPD) for duplicate samples must be within $\pm 10\%$ when sample concentrations are greater than ten times the analytical MDL and within $\pm 100\%$ when sample concentrations are at or up to ten times the analytical MDL. During the analysis period when samples collected during 2019 were analyzed (March 26, 2019 through March 5, 2020), there were a total of 916 duplicate samples analyzed for anions (Figure 4.1.5), with six cases where the RPD did not meet the acceptance criteria for chloride and three cases for nitrate and sulfate. Also during this analysis period, there were a total of 909 duplicate samples analyzed for cations (Figure 4.1.5), with three cases where the RPD did not meet the acceptance criteria for ammonium and one case for sodium; all RPD results met the acceptance criteria for potassium. In all cases when duplicate precision failed to meet the acceptance criteria, five reanalyses (one duplicate aliquot plus four randomly selected network samples) were performed from the analysis set. If any of the reanalyses failed to meet the acceptance criteria, the entire set of 50 samples was reanalyzed.

Figure 4.1.5: Ion duplicate analysis results for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019).



4.1.2.4 *Spiked Sample Extracts*

Matrix spikes are performed on 4% (two per set of 50 samples) of the samples analyzed. The matrix is deionized (DI) water, and spike samples typically meet the acceptance criteria with failures most likely resulting from introduced contamination. A total of 667 matrix spikes were analyzed for anions. There were ten cases where chloride, nitrate, and sulfate all failed spike recovery criteria (Figure 4.1-6); samples were reanalyzed for all ten cases. A total of 612 matrix spikes were analyzed for cations. There were twelve, ten, and five cases where spiked samples failed to meet recovery criteria for sodium, ammonium, and potassium spiked samples, respectively (Figure 4.1-6); samples were reanalyzed for all cases.

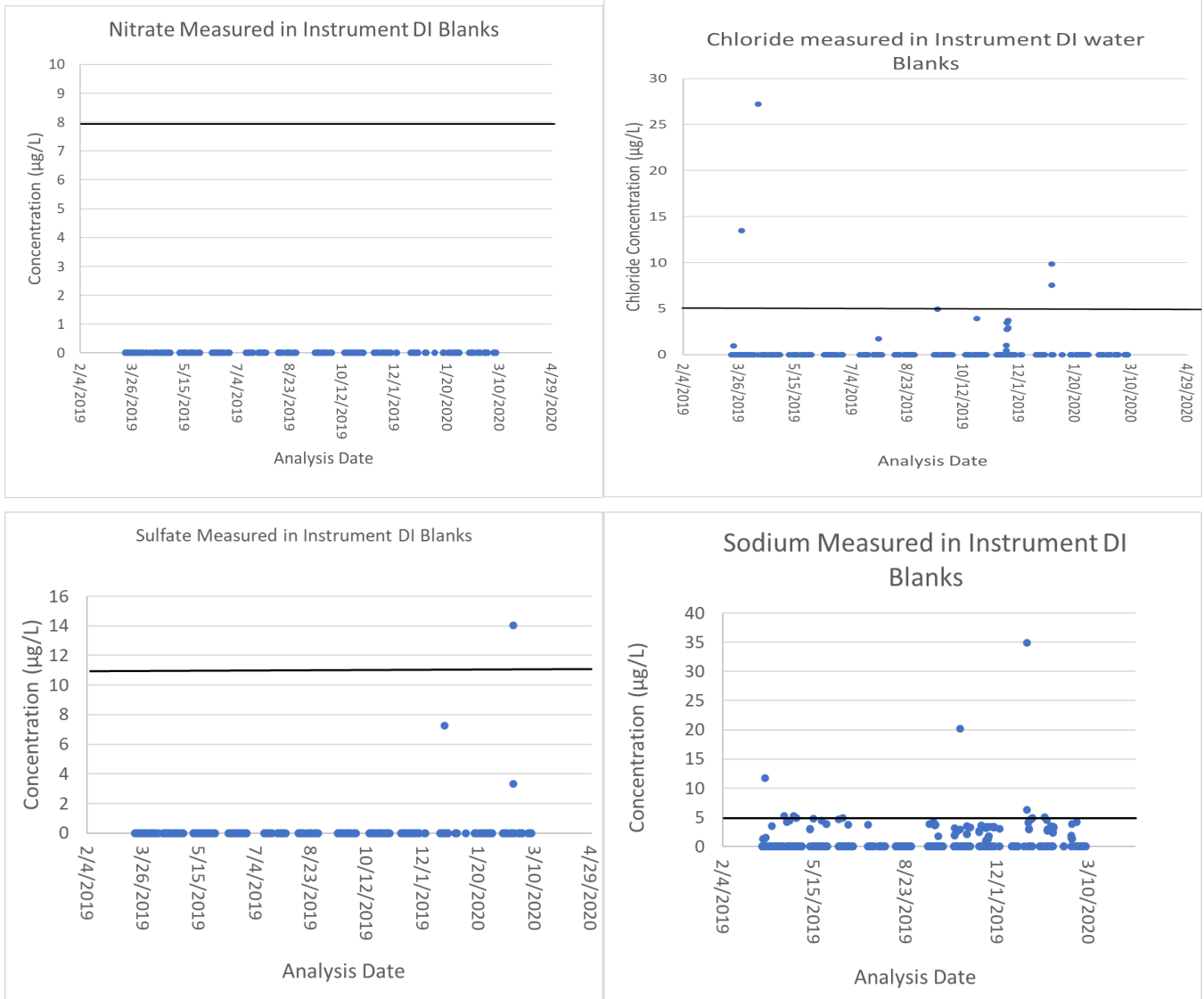
Figure 4.1-6: Time series of recovery (%) for anion and cation of matrix spikes for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019).



4.1.2.5 *Reagent Blanks and Spikes*

All analyses begin with the injection 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 (25.0 mL) is added to the method blank and LCS vials as is added to the vials with the filter samples to be extracted.

Figure 4.1-7: Concentrations of anions and cations in DI water blanks for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019). Black line indicates the analytical method detection limit.



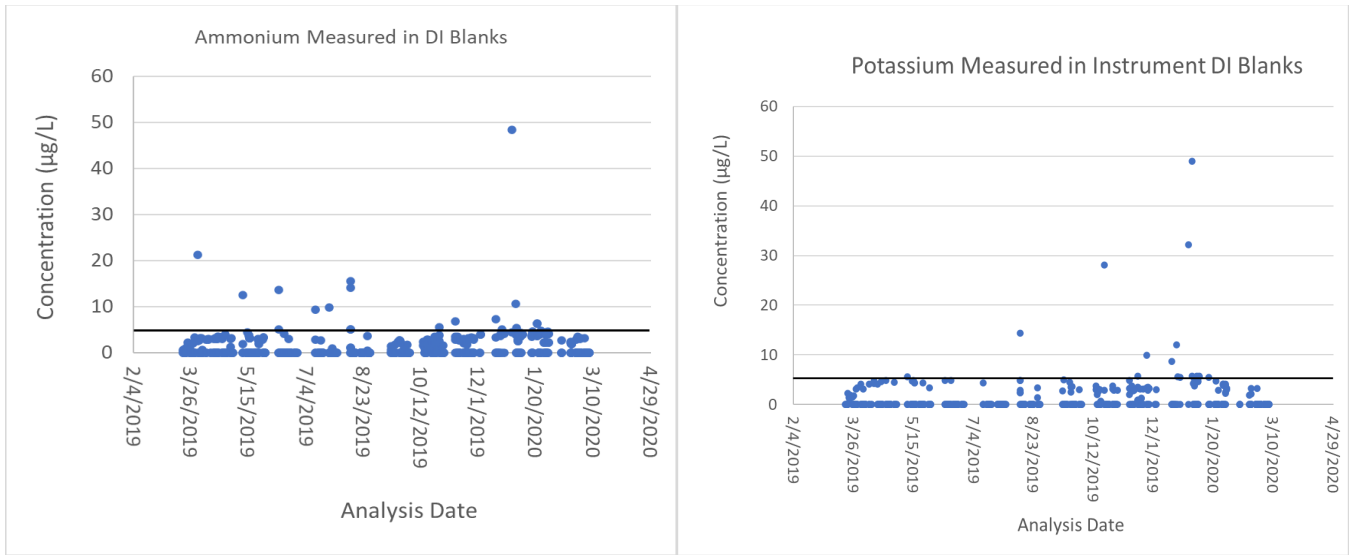
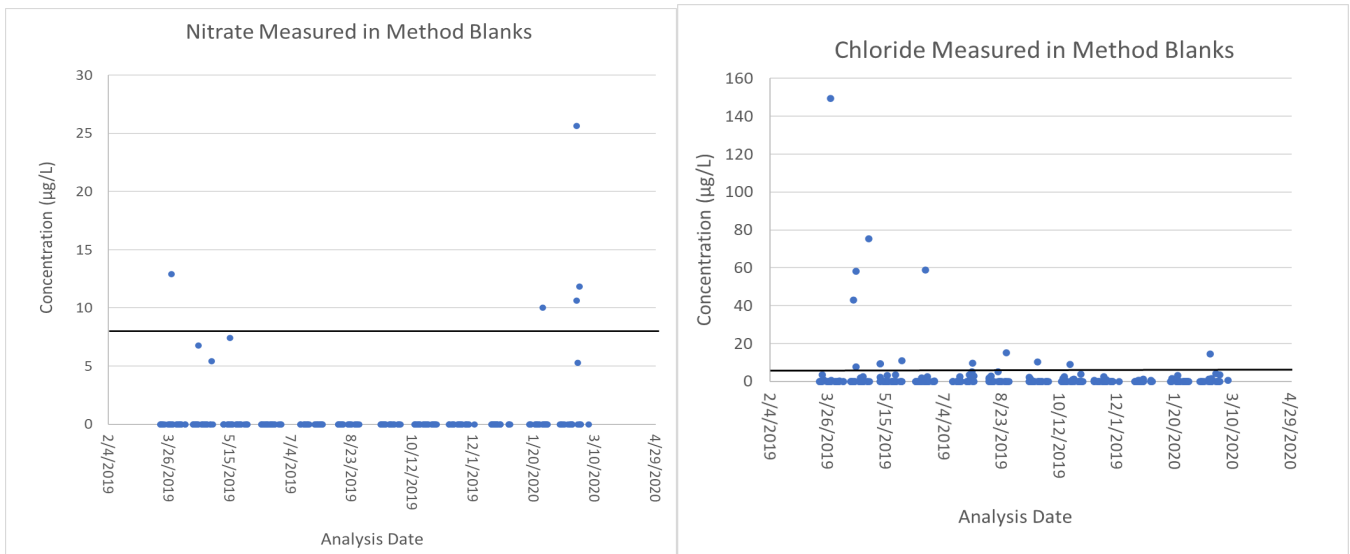
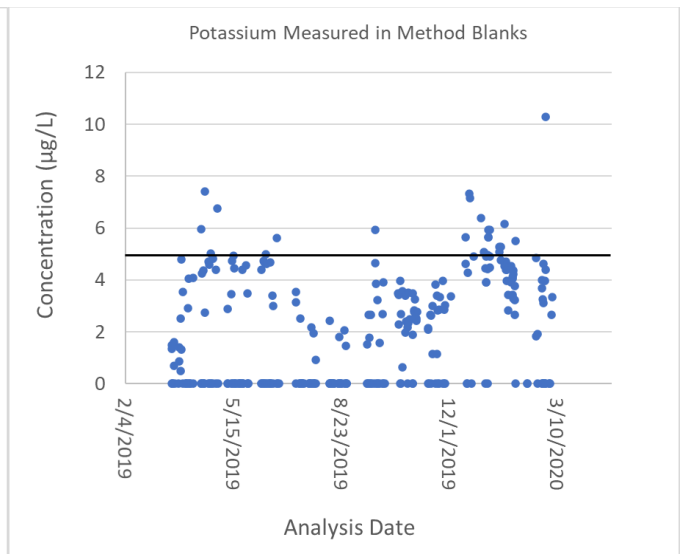
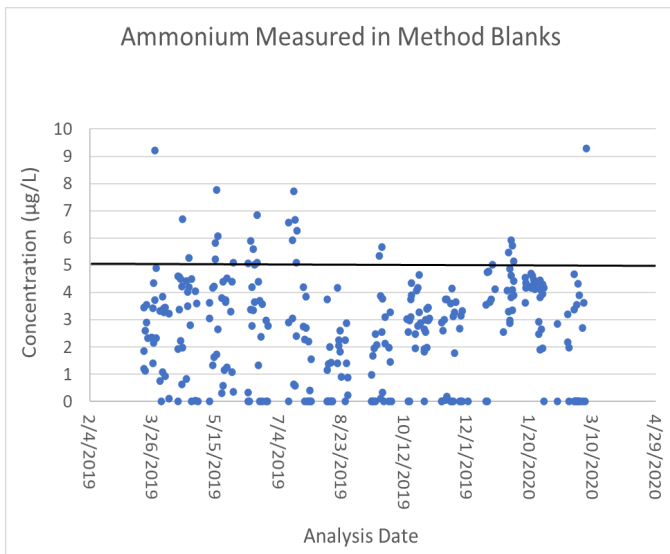
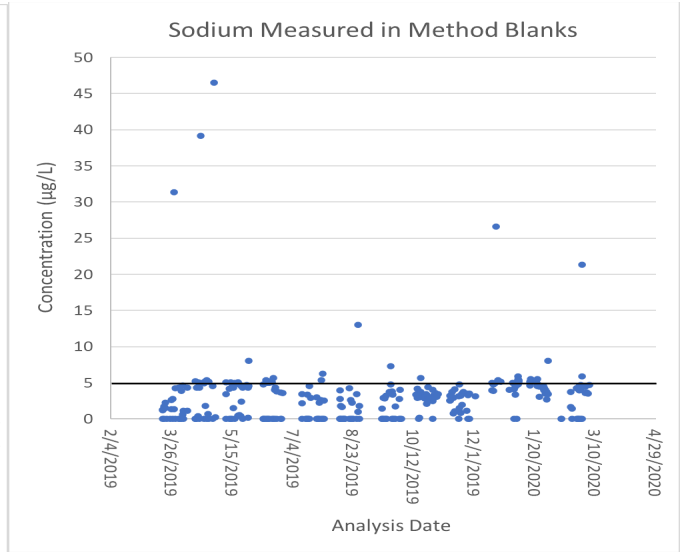
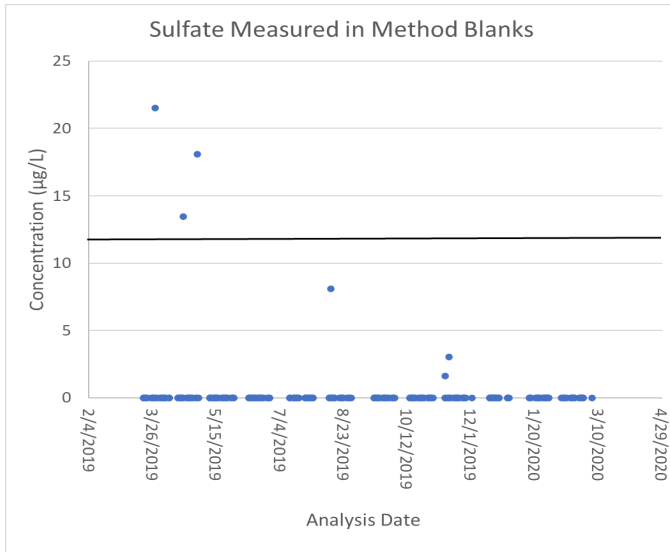


Figure 4.1-8: Concentrations of anions and cations in method blanks for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019). Black line indicates the analytical method detection limit.





The laboratory does not use the reagent blanks (instrument DI blanks and method blanks) or the LCS analyses for QC purposes, and (as noted in Table 4.1-2) there are no acceptance criteria associated with these measures. Because the concentrations in the LCS (Table 4.1-5 and Table 4.1-6) 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 4.1-9 and Figure 4.1-10) have more frequent outliers relative to the CCV check standards (Figure 4.1-1 and Figure 4.1-2), suggesting that background contamination may be introduced during the sample handling and processing of samples and is less likely to occur from instrumental issues. The method blanks and LCS analysis results are useful as early indicators of potential background issues during the analysis process. Review of the LCS and method blank results relative to the CCV check standards is performed routinely.

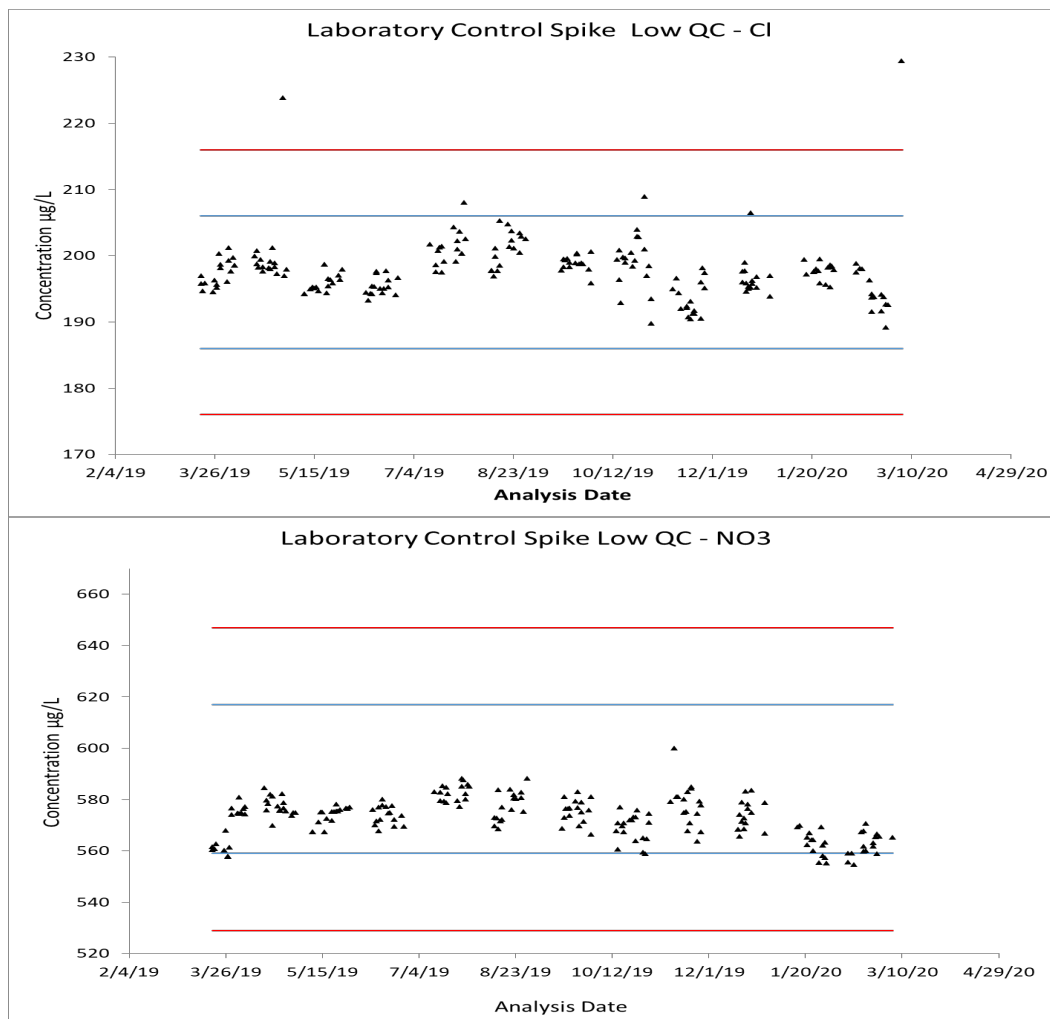
Table 4.1-5: Target concentrations for anion LCS for the analysis period 03/26/2019 through 03/05/2020 (samples collected 1/1/2019 through 12/31/2019).

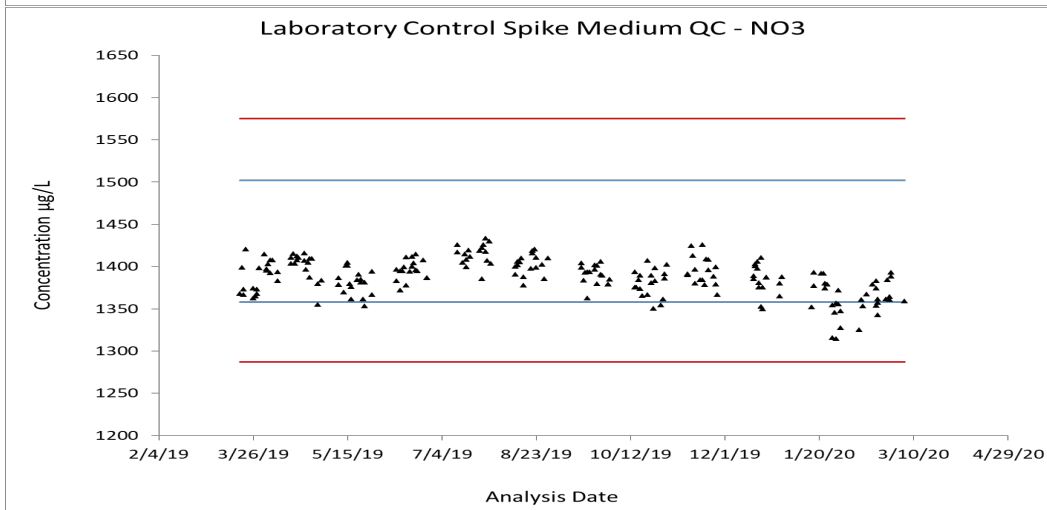
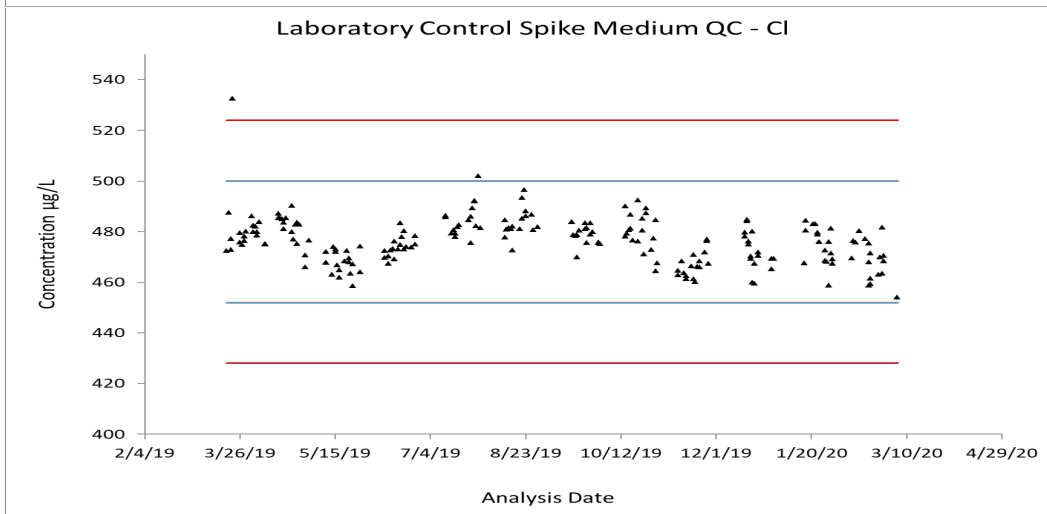
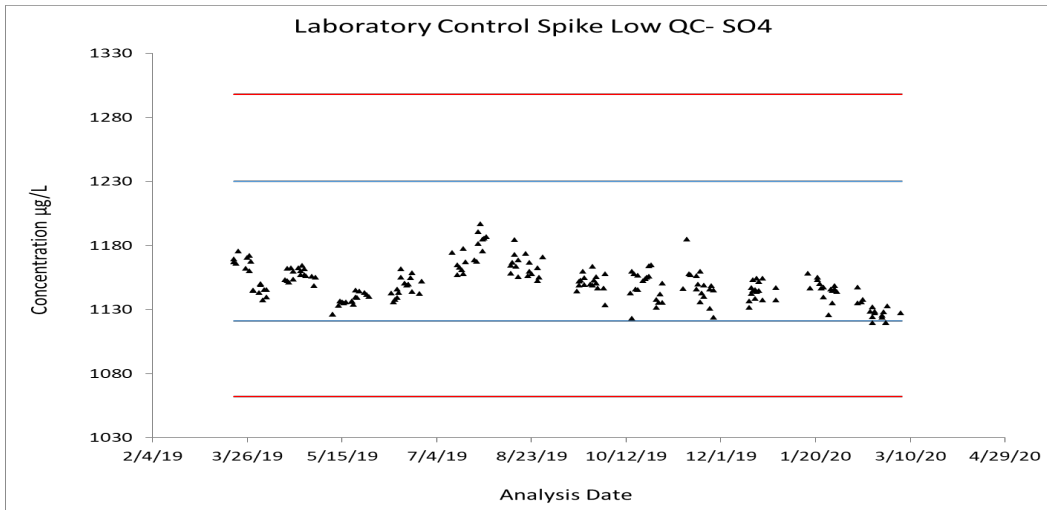
QC Sample	Cl ⁻ (ppb)	NO ₃ ⁻ (ppb)	SO ₄ ²⁻ (ppb)
LCS Low	196	588	1180
LCS Medium	476	1430	2860
LCS High	2000	6000	12000

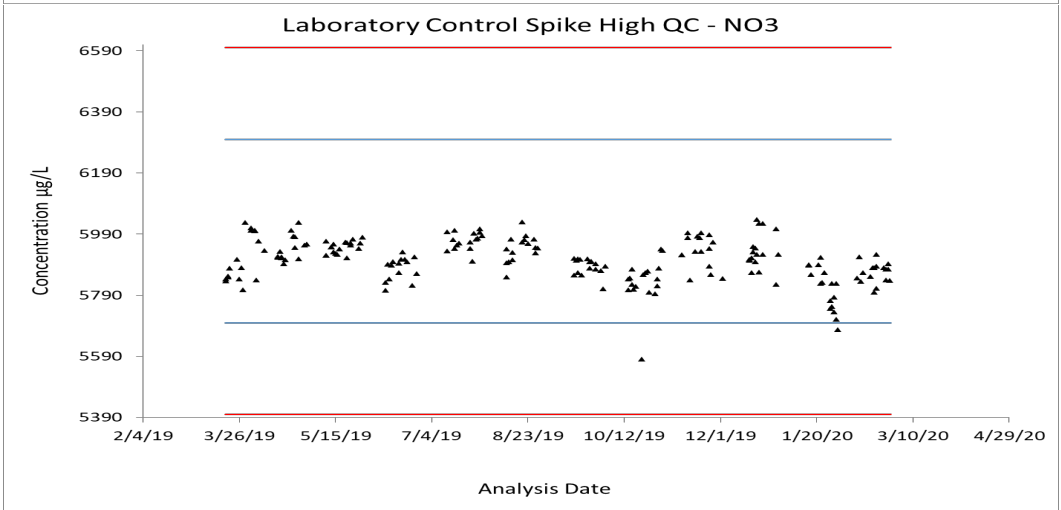
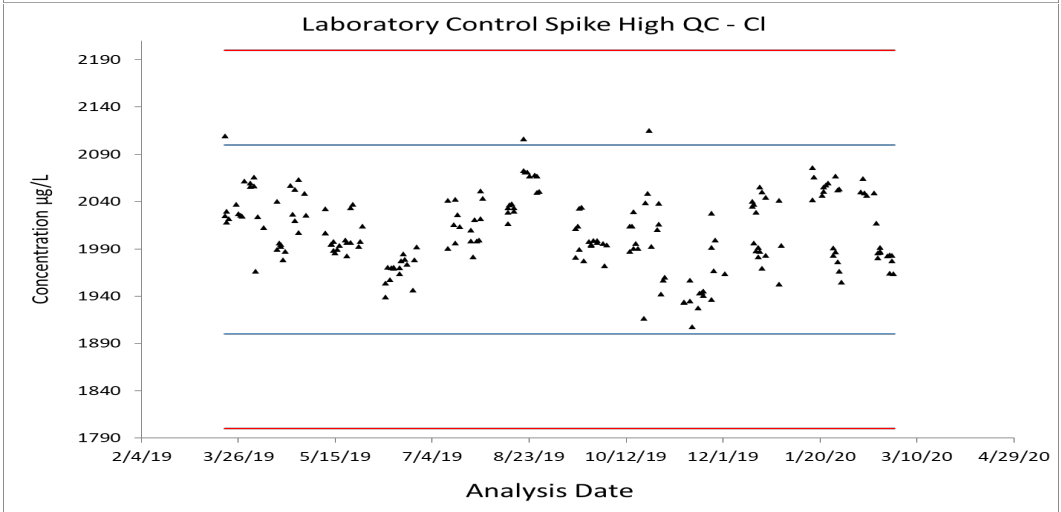
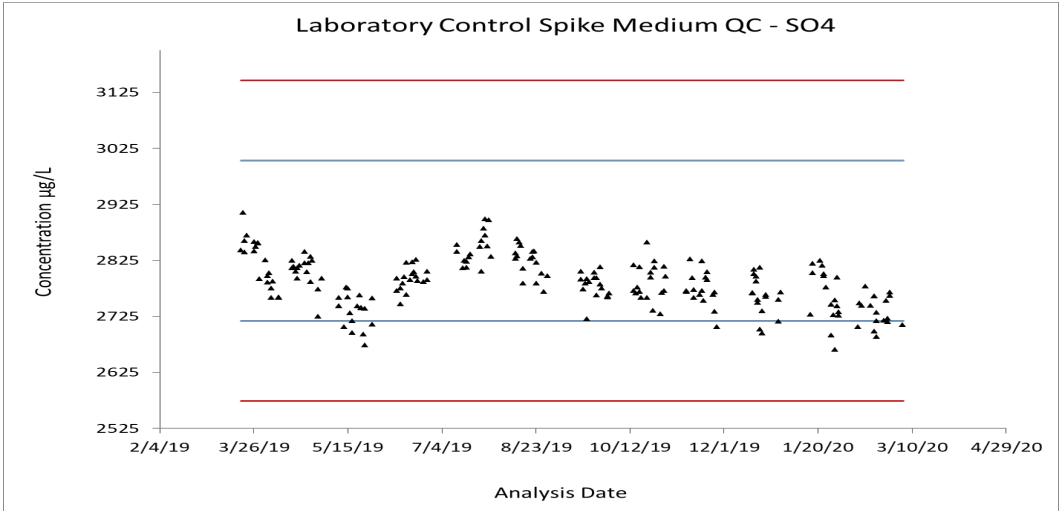
Table 4.1-6: Target concentrations for cation LCS for the analysis period 3/26/2019 through 03/05/2020 (samples collected 1/1/2019 through 12/31/2019).

QC Sample	Na ⁺ (ppb)	NH ₄ ⁺ (ppb)	K ⁺ (ppb)
LCS Low	20	20	20
LCS Medium	276	276	276
LCS High	769	769	769

Figure 4.1-9: Control charts for anion LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/26/2019 through 3/05/2020 (samples collected 1/1/2019 through 12/31/2019). Red lines show upper and lower control limits per the CCV check standard acceptance criteria. Blue lines show upper and lower warning limits.







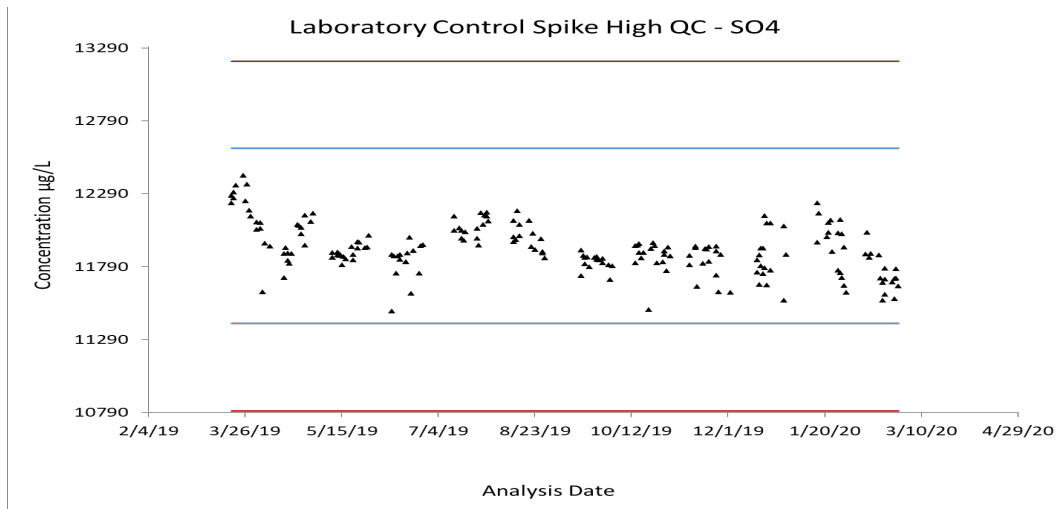
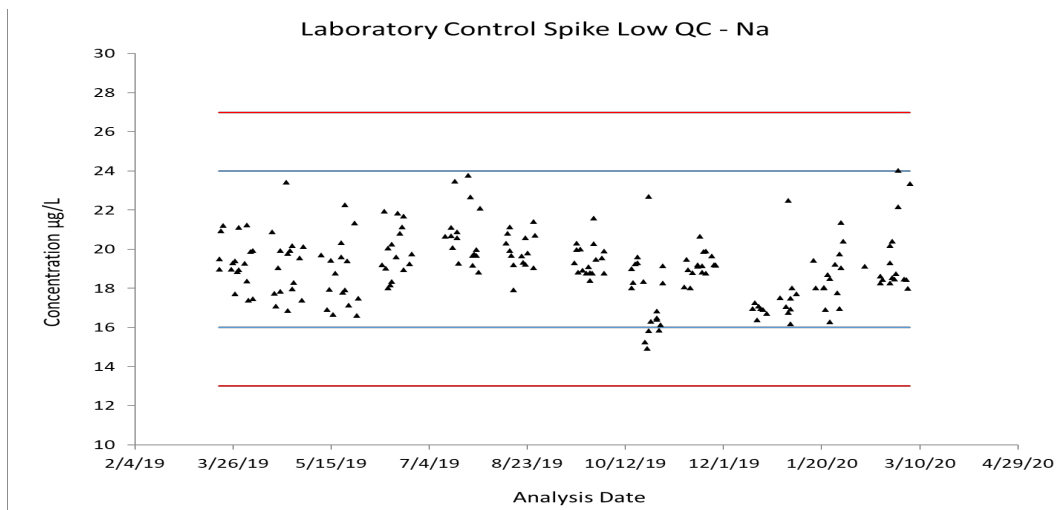
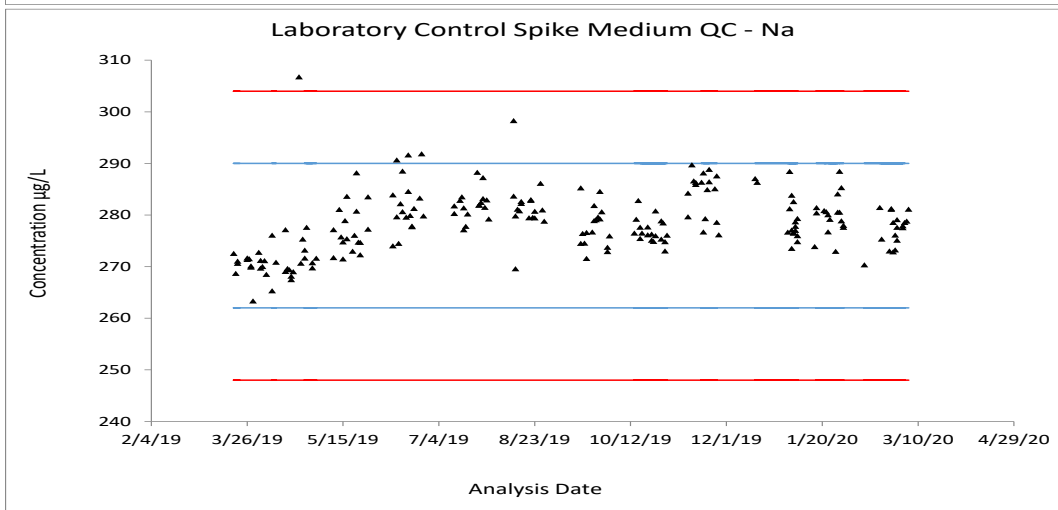
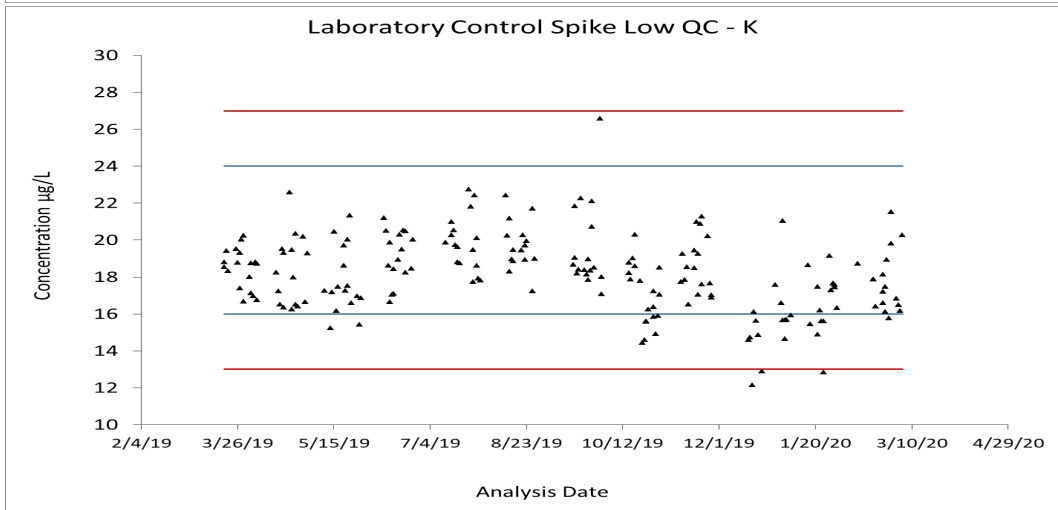
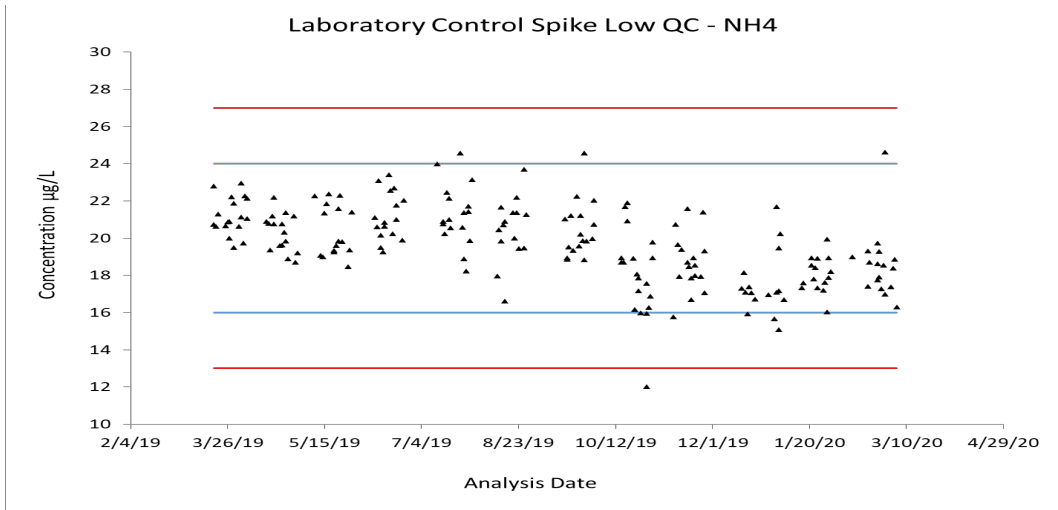
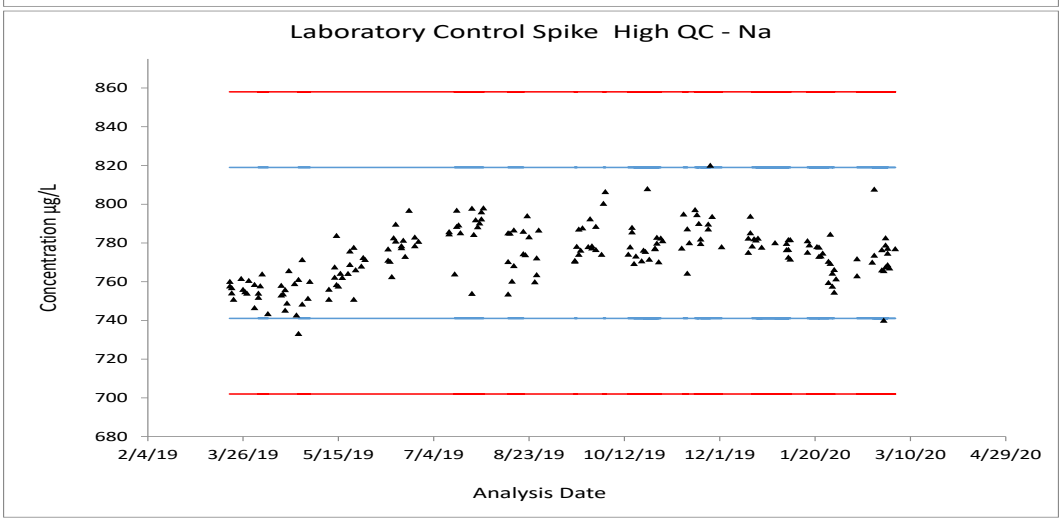
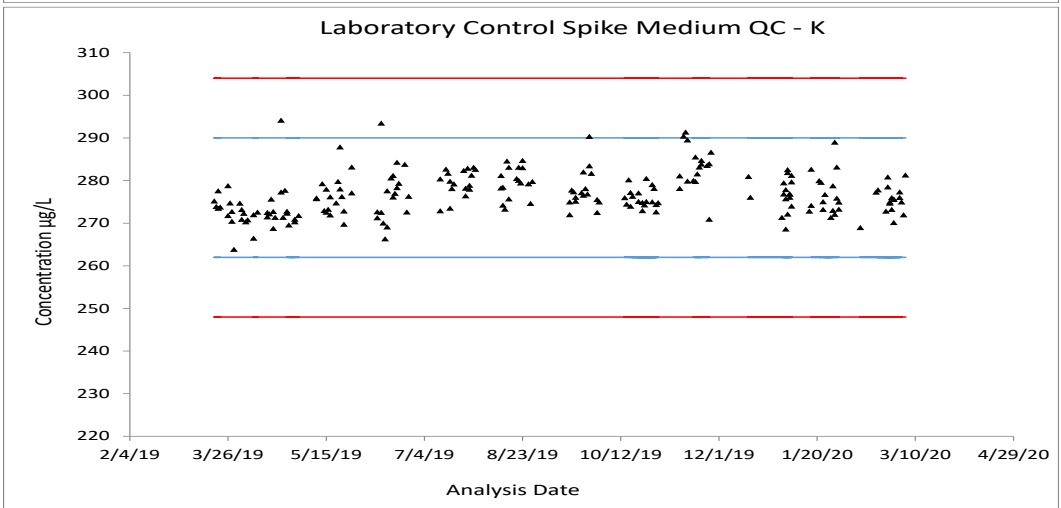
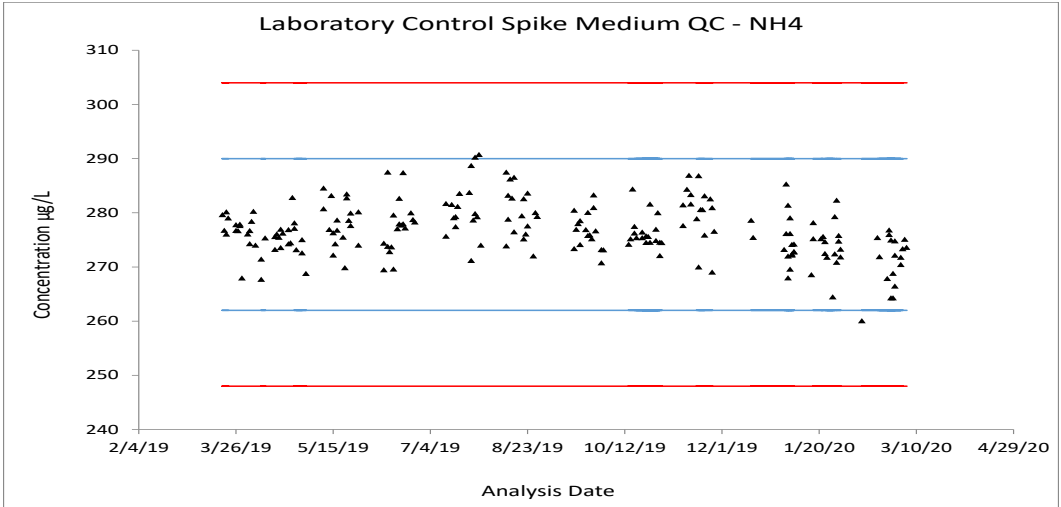
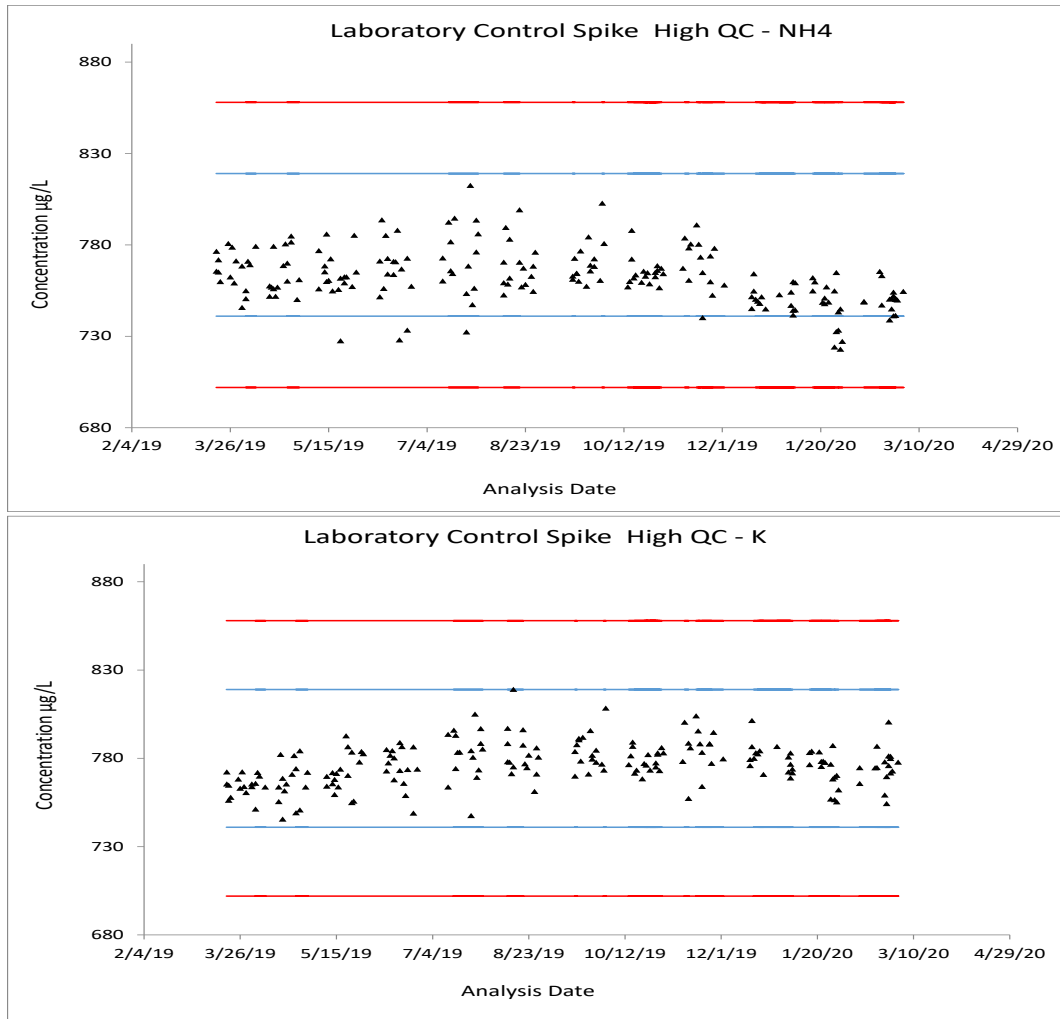


Figure 4.1-10: Control charts for cation LCS analyses relative to the CCV check standard acceptance criteria for the analysis period 3/26/2019 through 3/05/2020 (samples collected 1/1/2019 through 12/31/2019). Red lines show upper and lower control limits per the CCV check standard acceptance criteria. Blue lines show upper and lower warning limits.









4.1.2.6 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 2019 results is available upon request. Reports from prior years are available online and conclude that RTI had comparable, low overall variability among the participating laboratories for chloride, nitrate, sulfate, sodium, potassium, and ammonium (Wetherbee and Martin, 2020).

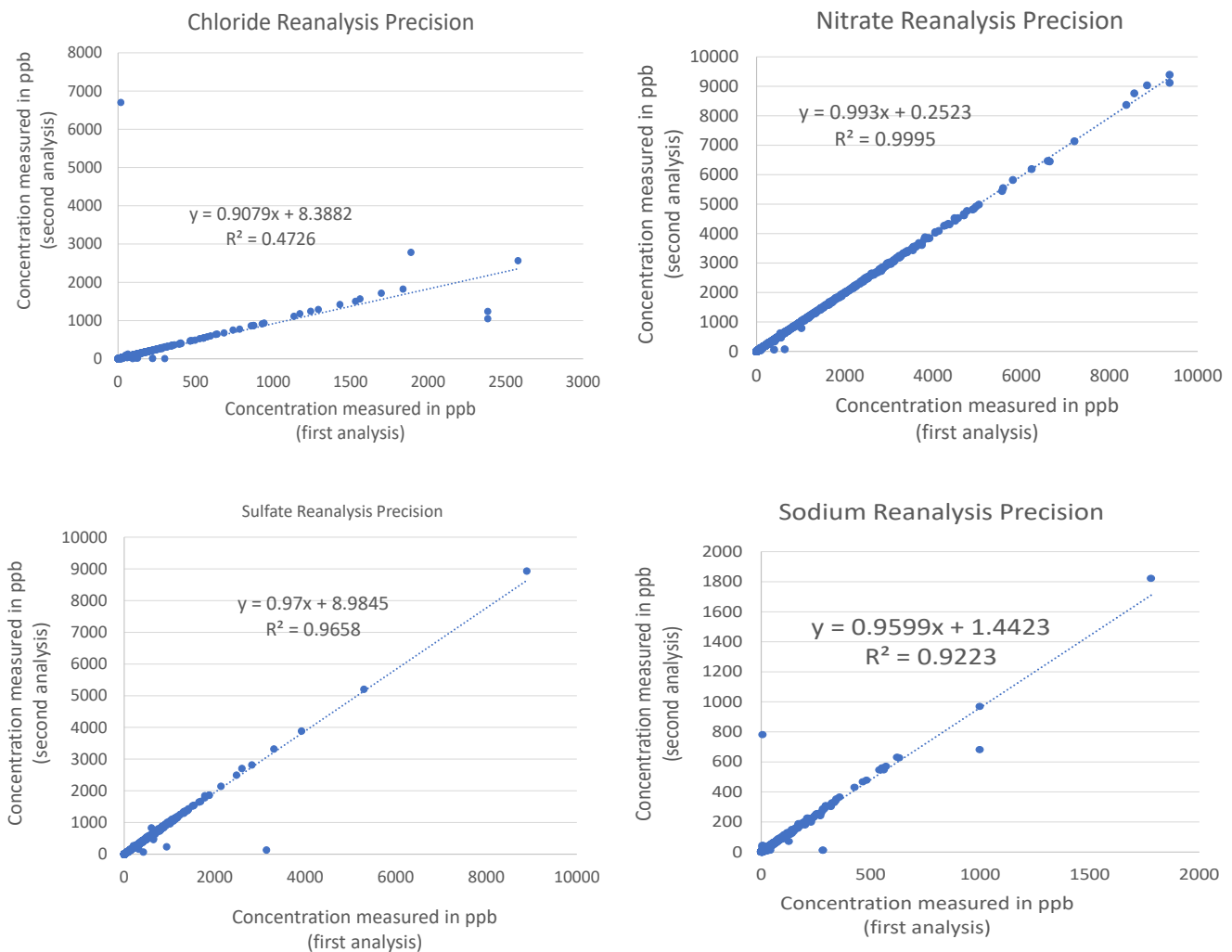
4.1.2.7 Reanalysis

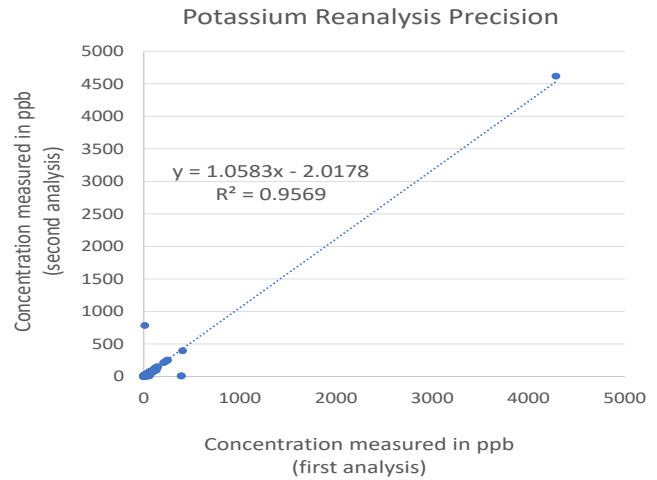
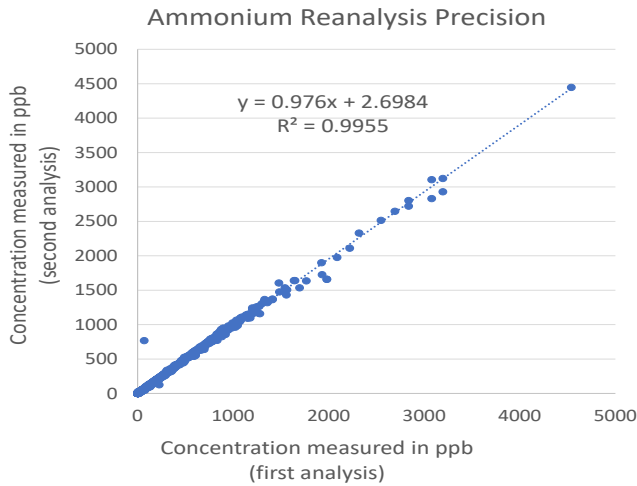
Five percent of all samples are reanalyzed using different instruments and different calibration curves (these reanalyses are specific to the analytical acceptance criteria described in Table 4.1-2, distinct from additional reanalyses that may be requested later during the UC Davis Level 0 or Level 1 validation process described in Section 6). 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 acceptance criteria for reanalysis samples are not met. When more than one analysis within an analysis set fails to meet the acceptance criteria as outlined in Table 4.1-2, the whole set of samples is reanalyzed. The majority of reanalyzed samples are from acceptance 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 1,741 samples reanalyzed for anions and 1,596 samples reanalyzed for cations (Figure 4.1-11). Less than 1.0% and 0.4% of samples reanalyzed for anions and cations, respectively, failed to meet the acceptance criteria for precision between the original and reanalysis result. For cases that failed, a third analysis was performed. The reanalysis result was reported only for the impacted ion species. Typically, a sample only fails the acceptance criteria for one of ion species and these failures are usually caused by contamination introduced during the analysis.

Figure 4.1-11: Ion reanalysis results for the analysis period 3/26/2019 through 3/05/2020 (samples collected 1/1/2019 through 12/31/2019).

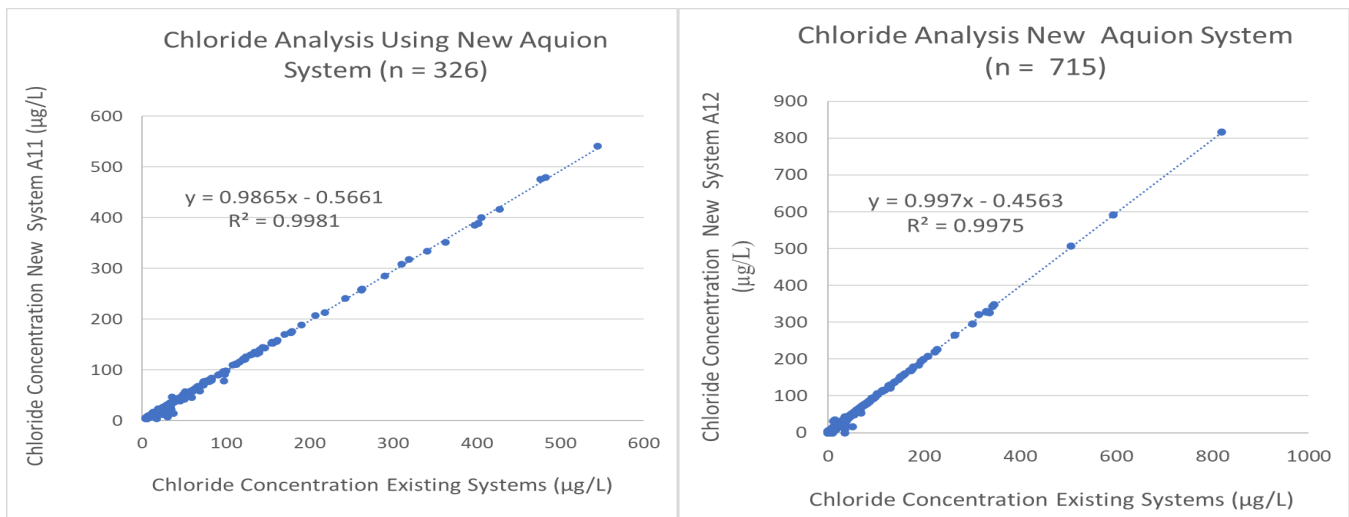




4.1.2.8 New Instrument Performance

Performance of the new ion chromatograph systems was evaluated using archived samples, duplication of processed samples, and QC standards. The data were evaluated using t-tests at 99% confidence intervals, control charts, scatter plots, and box plots. The t-test results indicated no significant differences between analyses on the new and existing systems. The first Thermo Dionex Aquion anion (A11; Figure 4.1-12) and cation (C9; Figure 4.1-13) systems were placed into service on 10/15/2019, followed by additional Thermo Dionex Aquion anion (A12; Figure 4.1-12) and cation (C10; Figure 4.1-13) systems on 1/27/2020. The AS-40 autosampler was replaced by an AS-AP autosampler, which was first evaluated using an existing ICS-3000 system (A8/C6) before being placed into service on 12/14/2019 (Figure 4.1-14). Comparisons between new and existing systems for most ions show R^2 close to one; the potassium ion comparisons result in a lower R^2 , particularly for the comparison with the new system C9, driven by greater variability at low concentrations (Figure 4.1-13).

Figure 4.1-12: Scatter plot of anion concentrations from samples analyzed on the new systems (A11 and A12) and the existing systems.



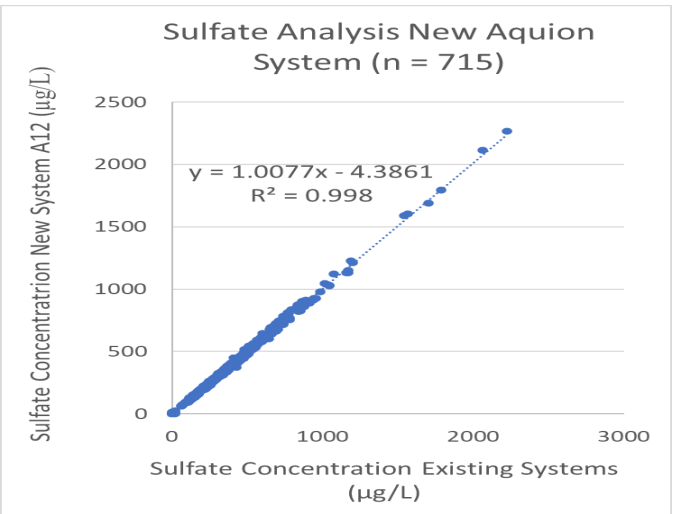
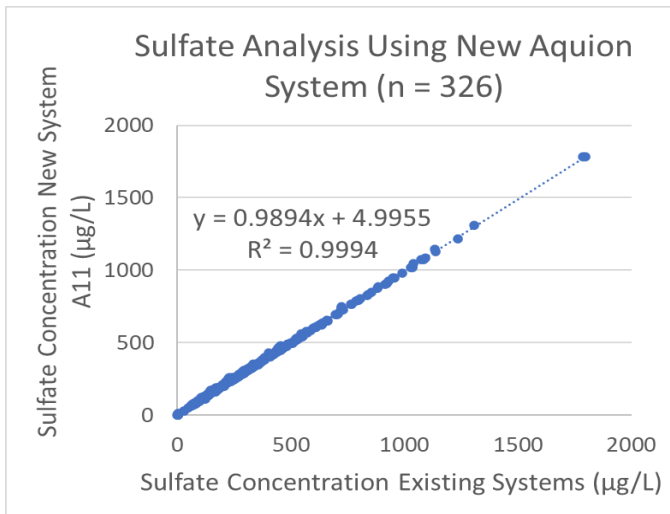
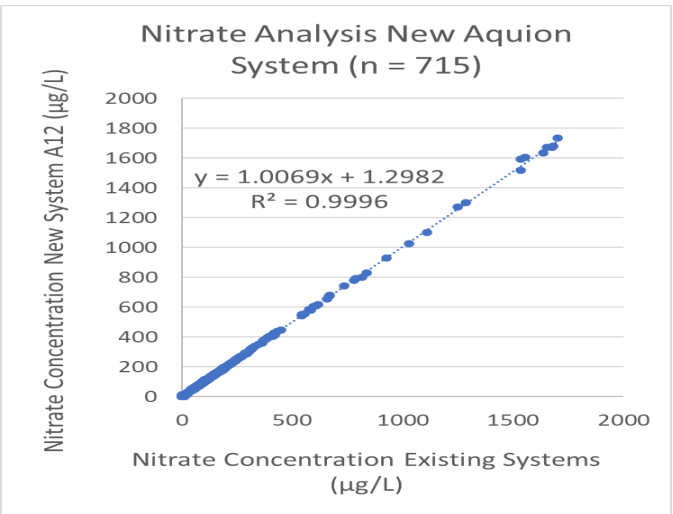
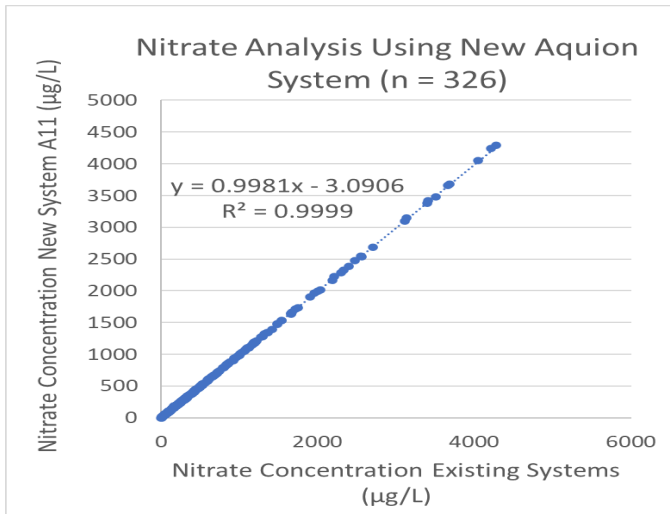
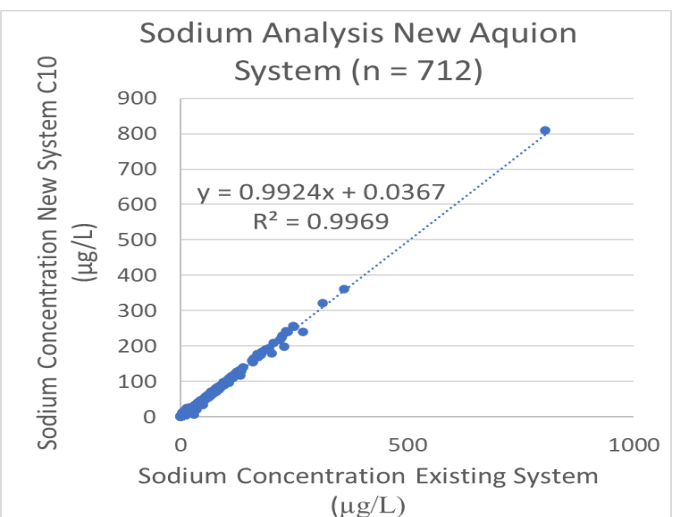
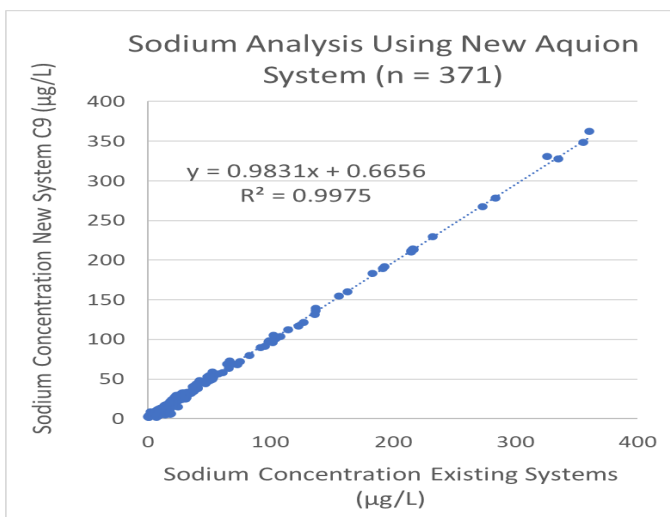


Figure 4.1-13: Scatter plot of cation concentrations from samples analyzed on the new systems (C9 and C10) and the existing systems.



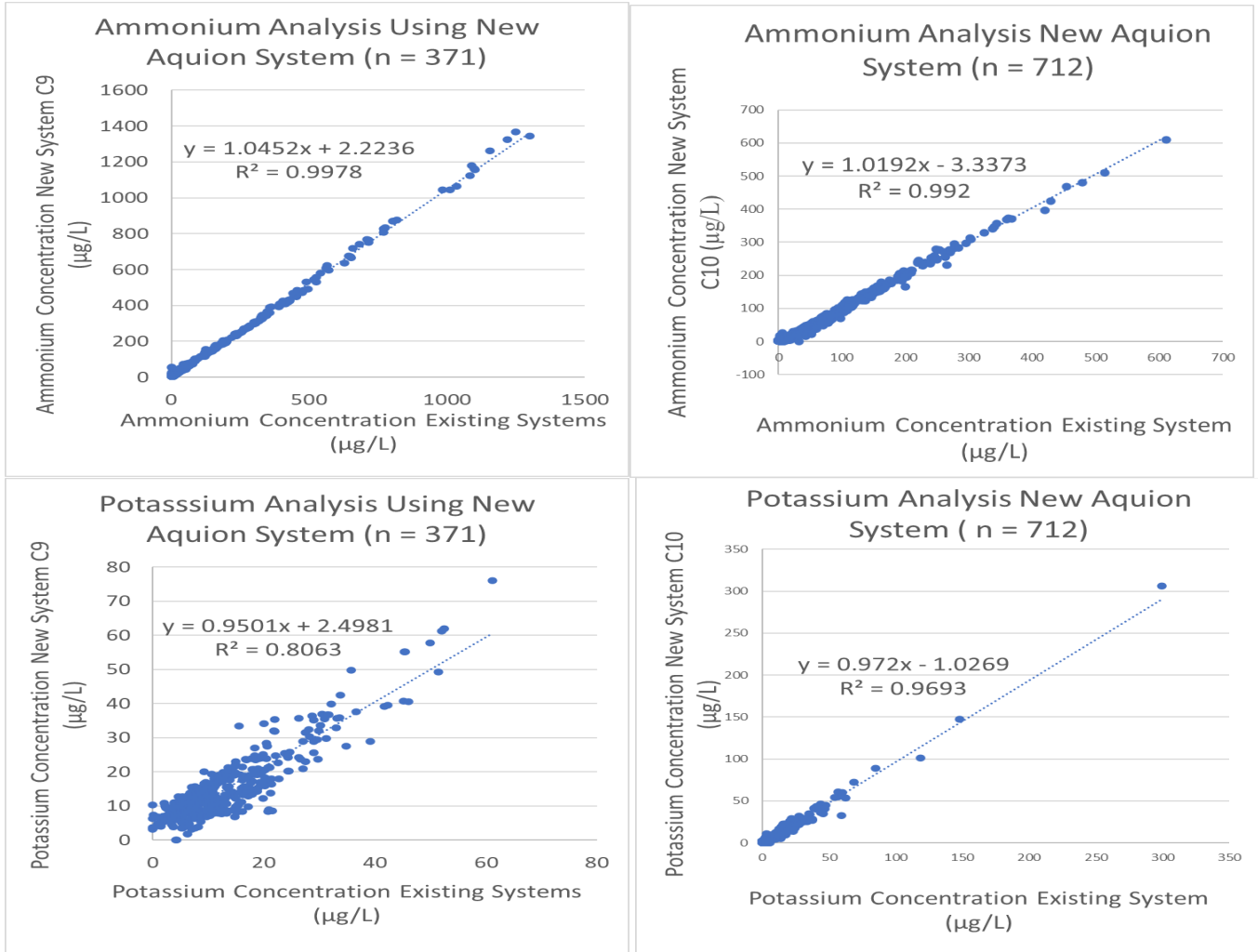
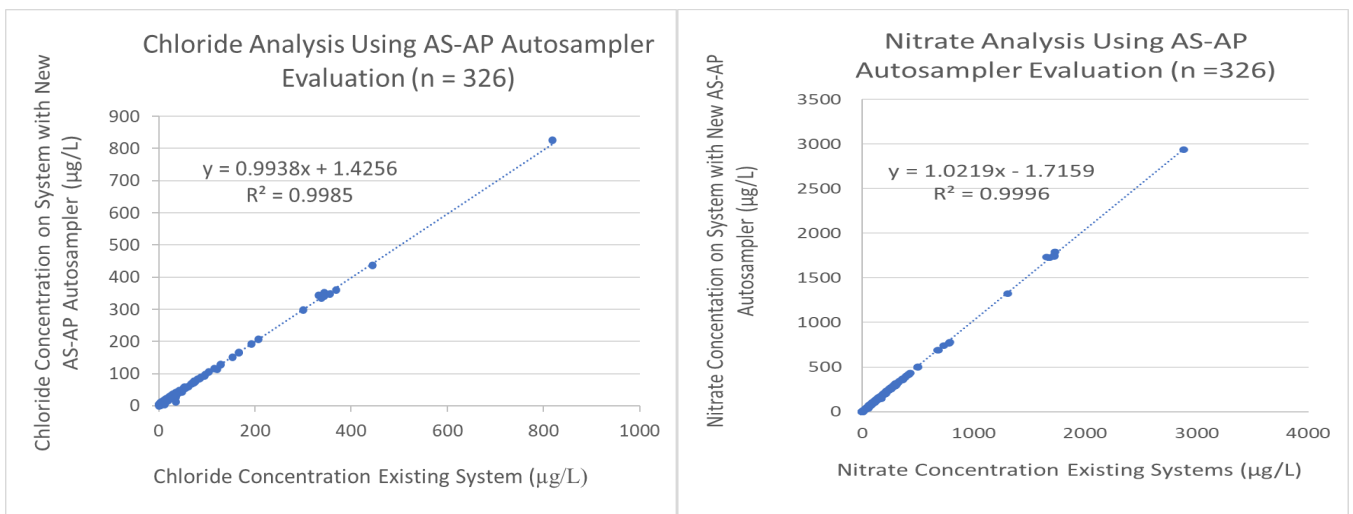
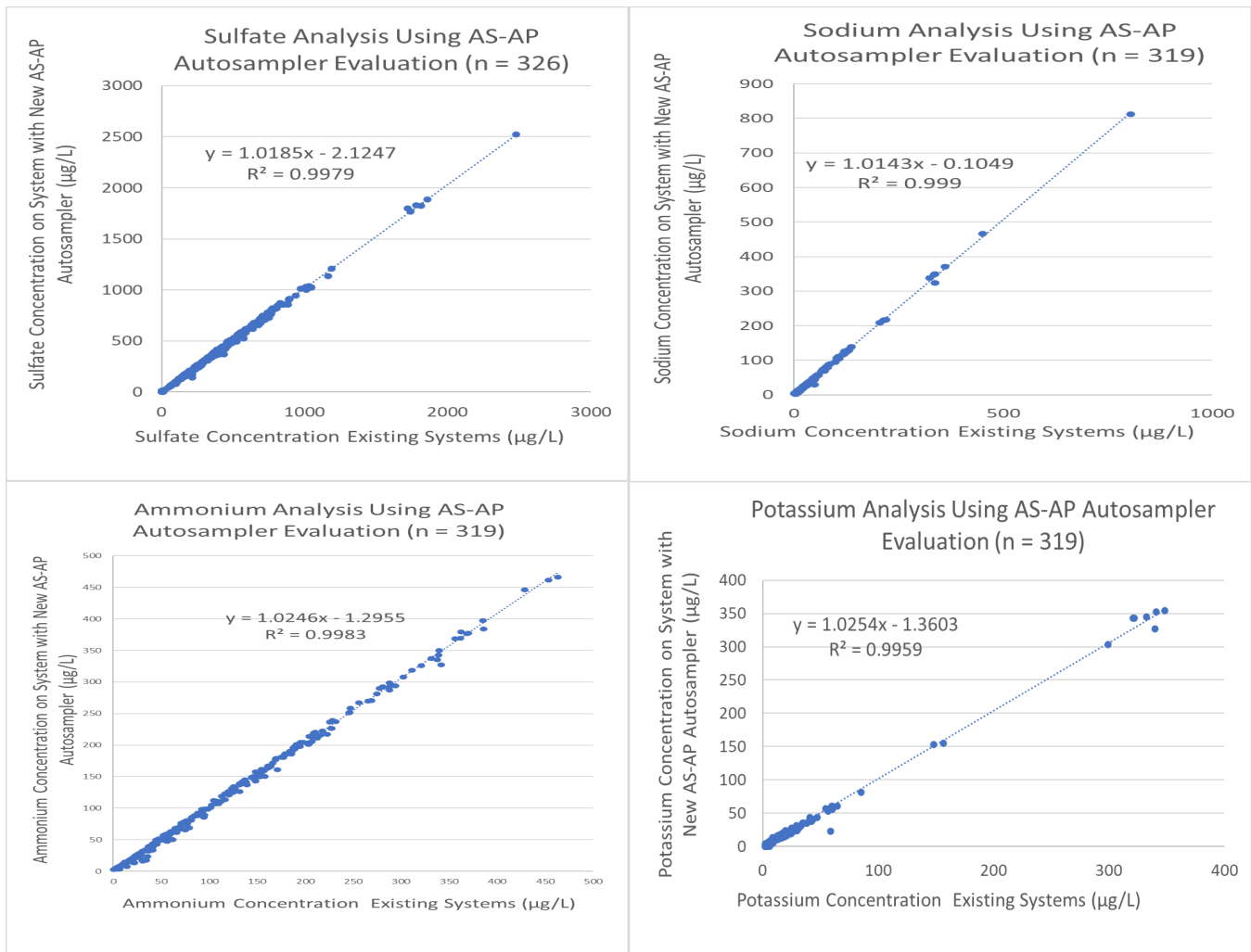


Figure 4.1-14: Scatter plot of anion and cation concentrations from samples analyzed using the new AS-AP autosampler and the existing system.





4.1.3 Determination of Uncertainties and Method Detection Limits

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

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

4.1.4 Audits, Performance Evaluations, Training, and Accreditations

4.1.4.1 System Audits

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

4.1.4.2 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.

4.1.5 Summary of Filter Field Blanks

Over the sampling period (January 1, 2019 through December 31, 2019) there were 1,694 valid nylon filter field blanks. Table 4.1-7a and Table 4.1-7b summarize the field blank statistics.

Table 4.1-7a: Nylon filter field blank statistics in $\mu\text{g/mL}$ for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019).

Ions	Count	Median ($\mu\text{g/mL}$)	Average ($\mu\text{g/mL}$)	Min ($\mu\text{g/mL}$)	Max ($\mu\text{g/mL}$)	St. Dev. ($\mu\text{g/mL}$)
Cl^-	1,694	0.004	0.005	0.000	0.282	0.011
NO_3^-	1,694	0.000	0.005	0.000	0.246	0.011
SO_4^{2-}	1,694	0.000	0.002	0.000	0.620	0.016
Na^+	1,694	0.004	0.004	0.000	0.170	0.007
NH_4^+	1,694	0.004	0.003	0.000	0.034	0.002
K^+	1,694	0.003	0.002	0.000	0.082	0.003

Table 4.1-7b: Nylon filter field blank statistics in $\mu\text{g/filter}$ (extraction volume 15 mL) for the analysis period 3/26/2019 through 3/5/2020 (samples collected 1/1/2019 through 12/31/2019).

Ions	Count	Median ($\mu\text{g/filter}$)	Average ($\mu\text{g/filter}$)	Min ($\mu\text{g/filter}$)	Max ($\mu\text{g/filter}$)	St. Dev. ($\mu\text{g/filter}$)
Cl^-	1,694	0.098	0.133	0.000	7.060	0.285
NO_3^-	1,694	0.000	0.124	0.000	6.147	0.271
SO_4^{2-}	1,694	0.000	0.050	0.000	15.502	0.401
Na^+	1,694	0.105	0.107	0.000	4.260	0.174
NH_4^+	1,694	0.089	0.084	0.000	0.840	0.052
K^+	1,694	0.070	0.062	0.000	2.058	0.075

4.2 UC Davis X-Ray Fluorescence Laboratory

The UC Davis X-Ray Fluorescence Laboratory received and analyzed PTFE filters from batches 51 through 62, which includes samples collected January 1, 2019 through December 31, 2019. 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 31, 2019 through March, 12, 2020. Five EDXRF instruments, XRF-1, XRF-2, XRF-3, 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 months during 2019 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 Month (2019)	Analysis Batch #	XRF-1 Analysis Dates	XRF-2 Analysis Dates	XRF-3 Analysis Dates	XRF-4 Analysis Dates	XRF-5 Analysis Dates
January	51	4/2/2019 – 4/27/2019	N/A	N/A	3/31/2019 – 4/26/2019	4/3/2019 – 5/15/2019
February	52	4/27/2019 – 5/15/2019	5/10/2019 – 5/15/2019	5/10/2019 – 5/15/2019	4/27/2019 – 6/13/2019	4/26/2019 – 5/15/2019
March	53	5/15/2019 – 6/2/2019	5/15/2019 – 6/2/2019	5/15/2019 – 6/1/2019	5/15/2019 – 6/2/2019	5/15/2019 – 6/2/2019
April	54	6/13/2019 – 6/28/2019	6/14/2019 – 6/28/2019	6/14/2019 – 6/28/2019	6/13/2019 – 6/29/2019	6/13/2019 – 6/29/2019
May	55	7/19/2019 – 8/4/2019	7/19/2019 – 8/3/2019	N/A	7/20/2019 – 8/6/2019	7/20/2019 – 8/6/2019
June	56	8/16/2019 – 9/8/2019	N/A	N/A	8/16/2019 – 9/8/2019	8/15/2019 – 10/11/2019
July	57	9/19/2019 – 10/11/2019	N/A	N/A	9/20/2019 – 10/13/2019	9/20/2019 – 11/17/2019
August	58	10/17/2019 – 11/12/2019	N/A	N/A	10/17/2019 – 11/14/2019	10/17/2019 – 11/14/2019
September	59	11/15/2019 – 1/13/2020	N/A	N/A	11/14/2019 – 12/8/2019	11/14/2019 – 12/9/2019
October	60	N/A	12/21/2019 – 1/9/2020	12/28/2019 – 1/9/2020	12/20/2019 – 2/11/2020	12/21/2019 – 1/9/2020
November	61	1/30/2020 – 2/13/2020	N/A	1/24/2020 – 2/11/2020	1/24/2020 – 2/12/2020	1/24/2020 – 2/12/2020
December	62	2/13/2020 – 3/9/2020	N/A	N/A	2/13/2020 – 3/12/2020	1/15/2020 – 3/10/2020
All Months	51-62	4/2/2019 – 3/9/2020	5/10/2019 – 1/9/2020	5/10/2019 – 2/11/2020	3/31/2019 – 3/12/2020	4/3/2019 – 3/10/2020

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.

Activity	Frequency	Acceptance Criteria	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	<ul style="list-style-type: none"> • XRF software automatically adjusts the energy channels
PTFE Blank	Daily	≤ acceptance limits with exceedance of a single element not to occur in more than two consecutive days	<ul style="list-style-type: none"> • Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UC Davis Multi-element reference material (ME-RM)	Daily	±10% of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb with exceedance of a single element not to occur in more than two consecutive days	<ul style="list-style-type: none"> • Check sample for damage/contamination • Further cross-instrumental testing • Replace sample if necessary
UC Davis Multi-element reference material (ME-RM)	Weekly	±10% of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb with exceedance of a single element not to occur in more than two consecutive days	
Reanalysis samples	Monthly	z-score between ±1 for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb	
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 UC Davis-made ME-RM is 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.

The elements monitored for the daily ME-RM and monthly Reanalysis Samples have changed relative to those listed in the *CSN 2018 Annual Quality Report*, and have been updated accordingly in *UCD CSN SOP #302* (Version 1.2; updated July 31, 2019). The QC ME-RMs used during this analysis period differ from those used during the 2018 report and the elements under test were changed to reflect the elements present on the daily ME-RM and monthly Reanalysis Samples used during this period, and for consistency with the other QC measures. The change was effective for the entirety of the analysis period for samples collected during 2019 (March 31, 2019 through March, 12, 2020). While every attempt is made to generate ME-RM filters that mimic ambient aerosol filters, the number of elements and relative concentrations are limited by the chemistry of mixing these elements together in certified solutions.

Additionally, the weekly QC measure using Micromatter Al & Si reference material that was included in the *CSN 2018 Annual Quality Report* has been discontinued; thus, is not included in this report and has been removed from Version 1.2 of *UCD CSN SOP #302*. These Micromatter

reference materials were aging, only included two elements, and had aluminum and silicon mass loadings many times higher than the 90th percentile concentrations of network samples; they did not accurately represent measurements of ambient network samples. Therefore, it was determined that inclusion of the Micromatter Al & Si reference material could be discontinued without impact to the overall EDXRF QC.

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 occasional acceptance criteria failures, 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 daily PTFE blank filters for all XRF analyzers. This intermittent 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 were not impacted. See Section 2.2.1, Section 3.2.1.1, Section 4.2.2.1, and Section 4.2.2.4 for further detail.

XRF-1 and XRF-4 each had an incident of high iron on the daily PTFE blank filter. The cause was attributed to a foreign contaminant likely resulting from the long duration that PTFE blank filters are exposed to the environment. Cleaning the PTFE blank filters by gently blowing air on the backside removed the contaminant; the iron concentration returned to acceptable levels.

XRF-2 had issues with elevated silicon background levels. This resulted in acceptance criteria failures for the daily PTFE blank and the monthly reanalysis sample. Analysis of CSN samples was stopped on this instrument beginning 1/9/2020 after the failures were initially identified beginning 12/12/2019. See Section 2.2.3, Section 3.2.1.3, Section 4.2.2.1, and Section 4.2.2.4 for further details.

Results from monthly reanalysis samples overall indicated stability across the analyzers. However, XRF-2 had increasing silicon z-scores which eventually exceeded the acceptance criteria, consistent with the silicon issue on the daily PTFE blank described above. Additionally, the individual z-score for potassium from reanalysis samples analyzed on XRF-3 dropped below acceptance criteria following the annual calibration performed on 12/27/2019. While the z-score calculated from the individual instrument reference value for the reanalysis samples became unacceptable, the z-score calculated from the inter-instrument mean reference improved; the new calibration improved the agreement between XRF-3 and the other instruments. Therefore, this acceptance criteria failure is attributed to the initial reference value determined for XRF-3 and is not considered impactful to instrument or calibration performance. See Section 4.2.2.4 for further details.

Results from the analysis of the NIST SRM2783 standard indicate that the accuracy of the EDXRF instruments are within the defined criteria. As described in Section 2.3.4, there was a contamination event that impacted the NIST SRM2783 standard serial number 1720, and it was subsequently replaced by the NIST SRM2783 standard serial number 1617. The SRM change resolved the contamination issues with sulfur, but it also revealed some differences in the results between SRM samples. Additionally, following the SRM change, the aluminum values for XRF-1, XRF-2, and XRF-5 had some failures. Aluminum is a difficult element to quantify by EDXRF

and the variability seen in these results suggest that the acceptance criteria for this element should be reevaluated. An investigation into reevaluating these acceptance limits has begun. See 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 daily PTFE blank. The EDXRF results are compared to acceptance criteria, which are calculated as three times the standard deviation plus the mean of a set of the PTFE blanks. Figure 4.2-1a and Figure 4.2-1b show the results of daily analyses of PTFE blanks for each instrument. If the mass loading exceeds the acceptance criteria for more than two consecutive days, the blank is replaced to distinguish between blank contamination and instrument contamination. Some occasional exceedance of the acceptance criteria 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 the PTFE blank. Sample analysis results are reviewed and elements associated with occasional contamination (e.g. zinc and calcium; see Section 2.2.1, Section 2.2.2, 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 2019 were reanalyzed for suspected zinc contamination. Of those, two were found to have zinc contamination and the reanalysis result was reported. For the rest the original valid result was reported. Nine samples were reanalyzed for suspected calcium contamination. The samples were found to have no calcium contamination and the original valid result was reported.

All XRF instruments had intermittent elevated measurements of zinc on the daily PTFE blank throughout the analysis period (as discussed in Section 2.2.1 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. Zinc contamination likely comes from wear on the sample changer; zinc is a common contaminant in elemental analysis systems.

XRF-1 and XRF-4 both had single elevated iron measurements above the acceptance criteria on 5/18/2019 and 6/29/2019, respectively. These incidents were corrected by cleaning the daily PTFE blank filters for each instrument, and did not impact instrument responses or network sample results.

XRF-3 had regular exceedances of the daily PTFE blank acceptance criteria for aluminum after the annual calibration on 12/27/2019. There was no acceptance criteria failure as the exceedances did not occur on more than two consecutive days. The exceedances appear to be caused by a shift of the background level of aluminum associated with the calibration. Network sample results are background corrected so the delivered data was not impacted by this shift. Analysis of PTFE blanks for XRF-3 also showed a gradual increase of potassium values with increasing exceedances for analyses performed during the later months of 2019. Again, there were no acceptance criteria failures as the exceedances did not occur on more than two consecutive days. This issue was resolved with the annual calibration on 12/27/2019.

XRF-2 exceeded and failed the daily PTFE blank acceptance criteria for silicon. The acceptance criteria exceedances began in late 2019 and continued to get worse; the first acceptance criteria failure occurred on 12/12/2019 just before the annual calibration. The UC Davis multi-element reference material results did not show any changes during this period and remained within the acceptance criteria. The cause of the daily PTFE blank acceptance criteria failure is still being

investigated, but as discussed in Section 2.2.3, silicon contamination of the X-ray path is suspected. Analysis of CSN samples on XRF-2 was halted beginning 1/9/2020.

As discussed in Section 2.2.2 and Section 3.2.1.2, all of the EDXRF instruments showed gradual increases in calcium which was reduced immediately after the PTFE blank filter was changed, indicating likely contamination of the PTFE blank filter likely from atmospheric deposition and/or instrument wear over long, multi-day residences.

Lastly, there were a few chlorine exceedances of the daily PTFE blank acceptance criteria on XRF-1, XRF-4, and XRF-5 instruments. For the larger exceedances, the PTFE blanks were replaced which corrected the exceedance; for others the signal decreased without correction. The cause of the chlorine exceedances is unknown; as a volatile element, chlorine has a highly variable signal from QC filters. These exceedances are caused by variability in the chlorine measurement, not contamination in the EDXRF instruments.

Figure 4.2-1a: Analysis results from daily PTFE blanks for the analysis period 3/31/2019 through 3/12/2020 (see Table 4.2-1 for corresponding sampling dates). Elements Na through Zn shown.

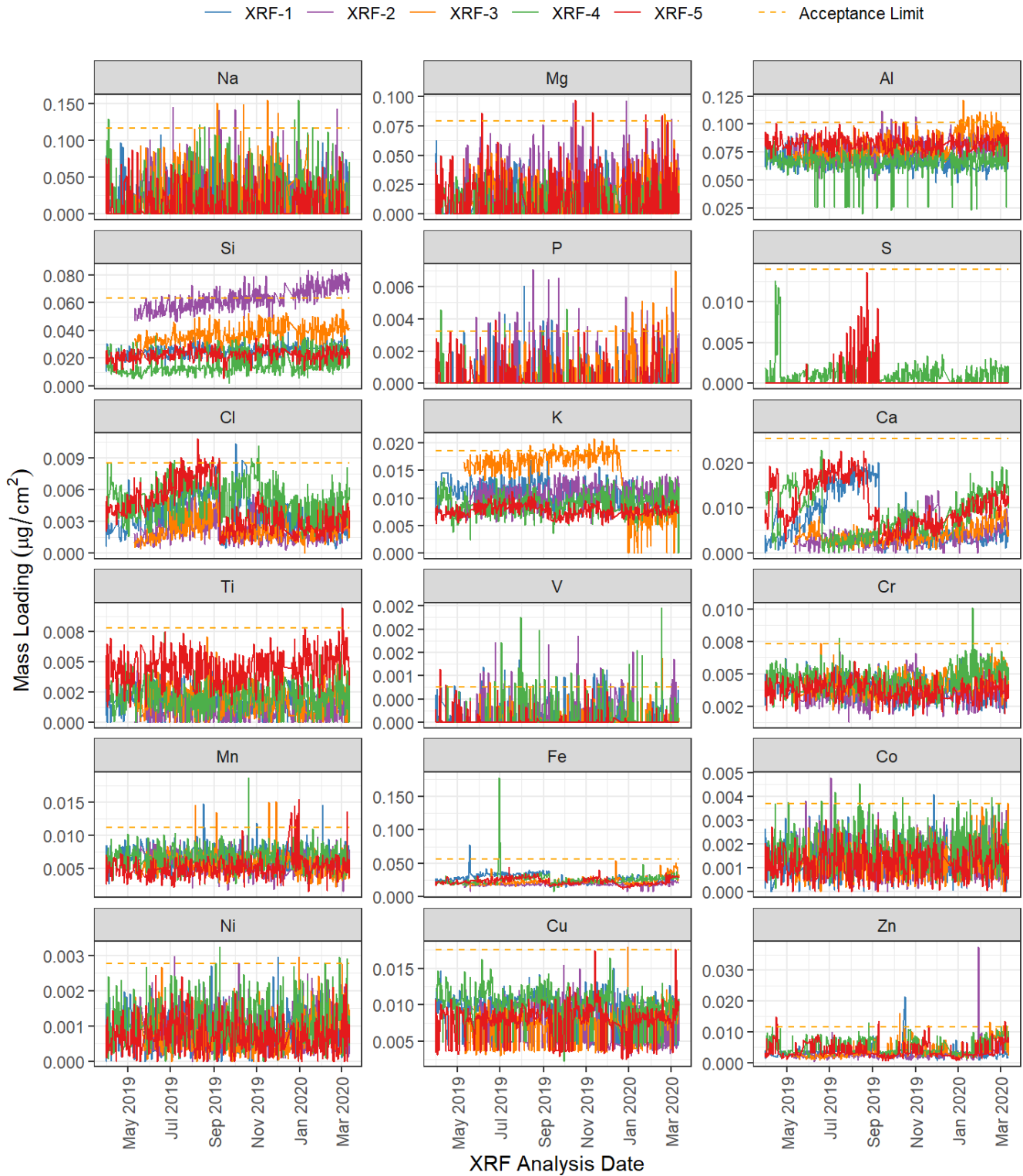
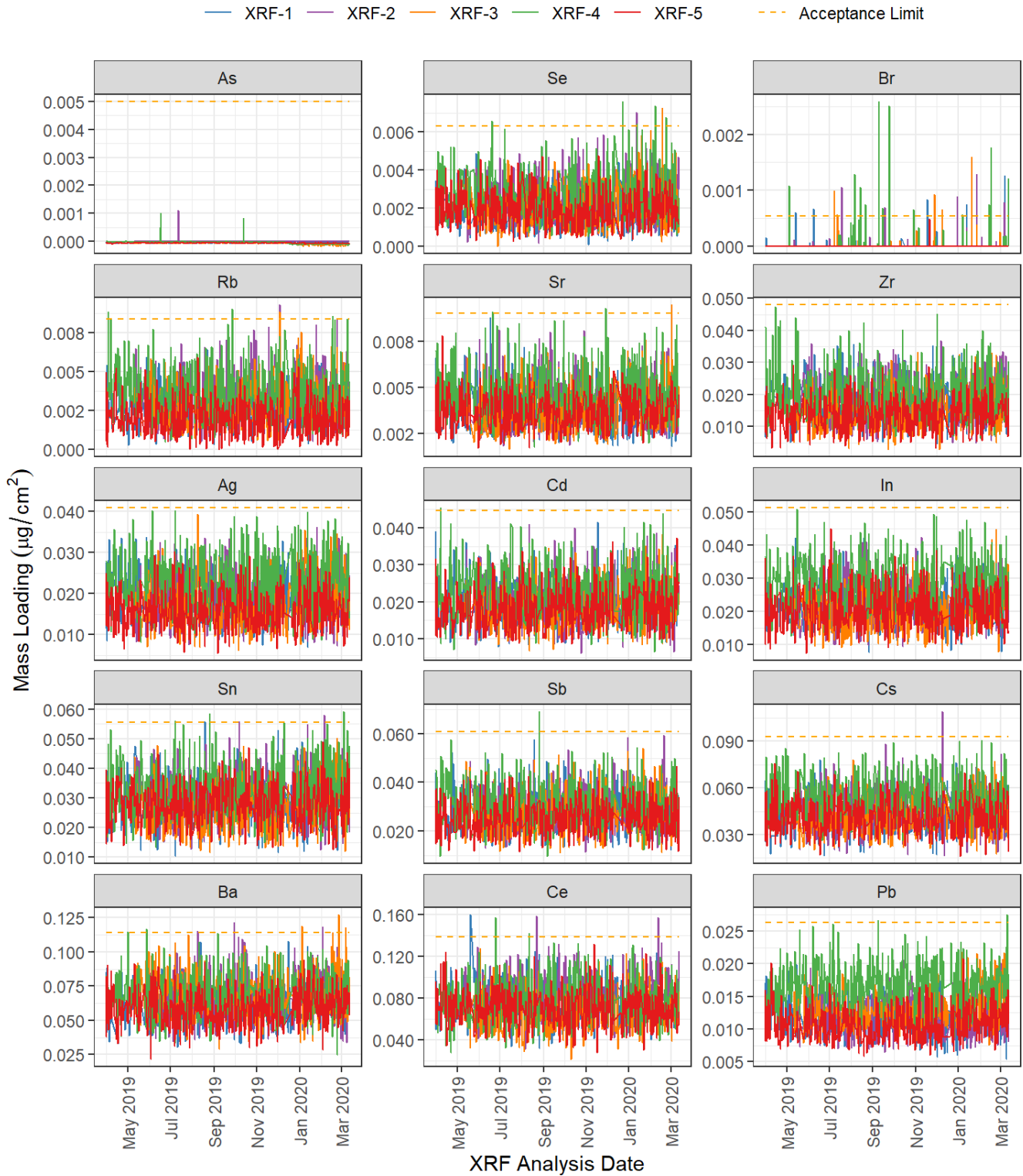


Figure 4.2-1b: Analysis results from daily PTFE blanks for the analysis period 3/31/2019 through 3/12/2020 (see Table 4.2-1 for corresponding sampling dates). Elements As through Pb shown.



Daily operational performance of the instruments is monitored using UC Davis produced ME-RM (different than the weekly ME-RM); each instrument had its own daily ME-RM. The acceptance criteria are +/- 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 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 through 4.2-7 show the results of the UC Davis ME-RMs. 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 lead are expected due to the low concentration of lead on the ME-RMs.

Table 4.2-3: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 3/31/2019 through 3/11/2020 (see Table 4.2-1 for corresponding sampling dates), N = 491.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	2.142	1.972	2.410	0	0	1.5
Si	0.771	0.692	0.846	0	0	2.0
S	16.404	14.989	18.320	0	0	0.7
K	2.325	2.111	2.580	0	0	0.9
Ca	2.286	2.028	2.479	0	0	0.8
Cr	0.933	0.840	1.027	0	0	0.7
Fe	2.635	2.315	2.829	0	0	1.5
Zn	0.319	0.282	0.345	0	0	1.5
As	0.637	0.571	0.698	0	0	1.1
Se	0.458	0.415	0.507	0	0	1.2
Rb	0.224	0.198	0.243	0	0	1.8
Sr	0.211	0.190	0.232	0	0	1.6
Cd	0.286	0.258	0.315	1.0	0	4.0
Sn	0.333	0.296	0.362	1.6	0	4.0
Pb	0.086	0.077	0.094	19.1	0	7.2

Table 4.2-4: Descriptive statistics of XRF-2 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 5/10/2019 through 3/11/2020 (see Table 4.2-1 for corresponding sampling dates), N = 568.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	2.073	1.863	2.278	0	0	3.4
Si	0.729	0.652	0.797	0	0	2.6
S	16.225	14.659	17.917	0	0	1.2
K	2.275	2.061	2.519	0	0	0.6
Ca	2.245	2.019	2.467	0	0	1.0
Cr	0.897	0.809	0.989	0	0	1.0
Fe	2.534	2.285	2.793	0	0	1.4
Zn	0.279	0.249	0.304	0	0	1.8
As	0.617	0.559	0.683	0	0	1.2
Se	0.427	0.385	0.471	0	0	1.5
Rb	0.219	0.198	0.241	0	0	1.8
Sr	0.208	0.187	0.229	0	0	1.9
Cd	0.281	0.248	0.303	4.8	0	4.4
Sn	0.334	0.300	0.367	1.4	0	4.1
Pb	0.100	0.090	0.110	18.0	0	7.3

Table 4.2-5: Descriptive statistics of XRF-3 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 4/17/2019 through 3/11/2020 (see Table 4.2-1 for corresponding sampling dates), N = 558.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.892	1.694	2.071	0.2	0	2.4
Si	0.800	0.708	0.865	2.3	0.538	3.0
S	15.337	13.737	16.790	0.2	0	1.2
K	2.119	1.896	2.317	0.2	0	1.
Ca	2.222	1.994	2.437	0	0	1.2
Cr	0.911	0.815	0.997	0	0	0.9
Fe	2.552	2.277	2.782	0	0	1.2
Zn	0.405	0.360	0.440	0	0	2.1
As	0.669	0.601	0.735	0	0	3.4
Se	0.447	0.402	0.492	0	0	1.6
Rb	0.222	0.199	0.244	0	0	1.7
Sr	0.211	0.188	0.230	0	0	1.8
Cd	0.283	0.253	0.309	1.1	0	4.0
Sn	0.326	0.294	0.359	1.6	0	3.9
Pb	0.085	0.076	0.093	15.8	0	8.1

Table 4.2-6: Descriptive statistics of XRF-4 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 3/31/2019 through 3/12/2020 (see Table 4.2-1 for corresponding sampling dates), N = 515.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.892	1.687	2.062	0.4	0	2.3
Si	0.988	0.869	1.062	1.0	0	3.1
S	16.525	14.879	18.186	0	0	0.8
K	2.331	2.099	2.566	0	0	0.6
Ca	2.308	2.069	2.528	0	0	0.8
Cr	0.948	0.860	1.051	0	0	0.9
Fe	2.629	2.363	2.888	0	0	1.3
Zn	0.339	0.294	0.359	0.6	0	2.5
As	0.649	0.584	0.714	0	0	1.1
Se	0.472	0.426	0.520	0	0	1.3
Rb	0.227	0.205	0.251	0	0	1.7
Sr	0.213	0.192	0.235	0	0	1.7
Cd	0.291	0.262	0.320	2.5	0	4.4
Sn	0.340	0.307	0.375	2.9	0	4.3
Pb	0.088	0.081	0.098	25.6	1.165	9.0

Table 4.2-7: Descriptive statistics of XRF-5 results ($\mu\text{g}/\text{cm}^2$) of the daily UC Davis ME-RM for the analysis period 3/31/2019 through 3/11/2020 (see Table 4.2-1 for corresponding sampling dates), N = 457.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	2.201	1.995	2.438	0	0	2.5
Si	0.764	0.667	0.815	0.2	0	2.3
S	16.606	15.068	18.416	0	0	1.2
K	2.359	2.141	2.616	0	0	1.1
Ca	2.288	2.033	2.485	0.2	0	1.1
Cr	0.953	0.856	1.047	0	0	0.6
Fe	2.625	2.349	2.871	0	0	1.0
Zn	0.365	0.325	0.397	0	0	2.2
As	0.647	0.580	0.709	0	0	0.8
Se	0.471	0.420	0.513	0	0	1.0
Rb	0.226	0.203	0.248	0	0	1.6
Sr	0.212	0.190	0.232	0	0	1.6
Cd	0.289	0.260	0.318	0.4	0	3.6
Sn	0.337	0.300	0.366	1.5	0	3.5
Pb	0.076	0.069	0.084	21.7	0.7	8.2

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). The UC Davis weekly ME-RM was replaced in December 2018. Weekly results are

compared to acceptance criteria 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 302* and *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.

XRF-5 was the only instrument that had unacceptable results; three results for cadmium on 4/24/2019, 5/2/2019, and 5/9/2019. The 4/24/2019 result was higher than the acceptance criteria while the 5/2/2019 and 5/9/2019 were lower than the acceptance criteria, indicating a higher than acceptable degree of variance in the results rather than a systematic issue with the instrument. Cadmium results for the daily ME-RM did not show any exceedances during this period. It was concluded that this was a statistical anomaly that had no impact on the reported network sample results.

Tables 4.2-8 through 4.2-12 show the EDXRF statistics of the weekly UC Davis ME-RM through 3/11/2020.

Table 4.2-8: Descriptive statistics of XRF-1 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 4/4/2019 through 3/11/2020 (see Table 4.2-1 for corresponding sampling dates), N = 47.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.170	1.062	1.298	0	0	2.1
Si	1.164	1.045	1.277	0	0	1.4
S	9.331	8.541	10.440	0	0	1.4
K	1.283	1.153	1.409	0	0	0.9
Ca	1.169	1.047	1.279	0	0	1.2
Cr	0.460	0.413	0.505	0	0	1.0
Fe	1.298	1.161	1.419	0	0	1.1
Zn	0.353	0.316	0.386	0	0	1.3
As	0.320	0.289	0.353	0	0	1.9
Se	0.228	0.206	0.252	0	0	1.4
Rb	0.114	0.102	0.125	0	0	2.9
Sr	0.114	0.103	0.126	0	0	2.4
Cd	0.157	0.139	0.170	12.766	0	6.4
Pb	0.233	0.205	0.251	0	0	2.7

Table 4.2-9: Descriptive statistics of XRF-2 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 5/15/2019 through 3/11/2020 (see Table 4.2-1 for corresponding sampling dates), N = 42.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.175	1.063	1.299	0	0	3.5
Si	1.115	1.002	1.225	0	0	1.8
S	9.312	8.470	10.352	0	0	1.0
K	1.260	1.135	1.387	0	0	0.7
Ca	1.149	1.030	1.259	0	0	1.3
Cr	0.450	0.403	0.493	0	0	1.0
Fe	1.279	1.147	1.402	0	0	1.6
Zn	0.348	0.310	0.379	0	0	1.5
As	0.312	0.282	0.344	0	0	1.8
Se	0.225	0.202	0.247	0	0	2.1
Rb	0.112	0.103	0.126	0	0	3.6
Sr	0.113	0.102	0.124	0	0	2.8
Cd	0.157	0.139	0.170	16.7	0	6.3
Pb	0.226	0.207	0.253	2.4	0	3.7

Table 4.2-10: Descriptive statistics of XRF-3 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 4/17/2019 through 3/10/2020 (see Table 4.2-1 for corresponding sampling dates), N = 44.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.141	1.022	1.249	0	0	2.1
Si	1.160	1.040	1.271	0	0	1.8
S	9.480	8.640	10.560	0	0	1.1
K	1.271	1.138	1.391	0	0	0.9
Ca	1.158	1.033	1.263	0	0	1.7
Cr	0.460	0.413	0.505	0	0	0.9
Fe	1.290	1.154	1.410	0	0	1.1
Zn	0.354	0.315	0.385	0	0	1.4
As	0.333	0.300	0.366	0	0	3.9
Se	0.224	0.201	0.246	0	0	2.2
Rb	0.113	0.100	0.123	0	0	2.7
Sr	0.114	0.102	0.125	0	0	2.6
Cd	0.155	0.135	0.166	18.2	0	6.3
Pb	0.238	0.210	0.256	0	0	3.3

Table 4.2-11: Descriptive statistics of XRF-4 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 4/2/2019 through 3/5/2020 (see Table 4.2-1 for corresponding sampling dates), N = 48.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.020	0.928	1.135	0	0	2.5
Si	1.227	1.091	1.333	0	0	2.7
S	9.442	8.635	10.554	0	0	1.4
K	1.309	1.176	1.438	0	0	0.7
Ca	1.193	1.069	1.306	0	0	1.1
Cr	0.467	0.419	0.512	0	0	1.2
Fe	1.300	1.162	1.421	0	0	1.2
Zn	0.353	0.314	0.384	0	0	2.2
As	0.328	0.297	0.363	0	0	1.9
Se	0.230	0.207	0.253	0	0	1.6
Rb	0.116	0.105	0.129	2.1	0	3.1
Sr	0.115	0.105	0.128	2.1	0	3.2
Cd	0.162	0.145	0.177	14.6	0	7.1
Pb	0.243	0.220	0.269	0	0	4.3

Table 4.2-12: Descriptive statistics of XRF-5 results ($\mu\text{g}/\text{cm}^2$) of the weekly UC Davis ME-RM for the analysis period 4/1/2019 through 3/5/2020 (see Table 4.2-1 for corresponding sampling dates), N = 47.

Element	Average	Lower Limit	Upper Limit	% Exceedance	% Unacceptable	RSD %
Al	1.197	1.072	1.310	0	0	2.8
Si	1.146	1.019	1.246	0	0	1.6
S	9.316	8.487	10.373	0	0	1.7
K	1.268	1.137	1.390	0	0	1.2
Ca	1.147	1.016	1.242	0	0	1.3
Cr	0.459	0.413	0.505	0	0	0.9
Fe	1.289	1.152	1.407	0	0	1.3
Zn	0.352	0.313	0.382	0	0	1.9
As	0.317	0.286	0.350	0	0	1.4
Se	0.226	0.203	0.249	0	0	1.7
Rb	0.114	0.103	0.126	0	0	2.8
Sr	0.113	0.102	0.125	0	0	2.1
Cd	0.154	0.139	0.170	12.8	6.4	6.8
Pb	0.228	0.203	0.249	0	0	2.6

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. Figure 4.2-2 plots the elemental concentrations for the weekly UC Davis ME-RM sample used during this analysis. 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 the instrument results:

$$Ref_i = \frac{1}{N} (\sum XRF1_i + \sum XRF2_i + \sum XRF3_i + \sum XRF4_i + \sum XRF5_i),$$

where $XRF1_i$, $XRF2_i$, $XRF3_i$, $XRF4_i$, 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,

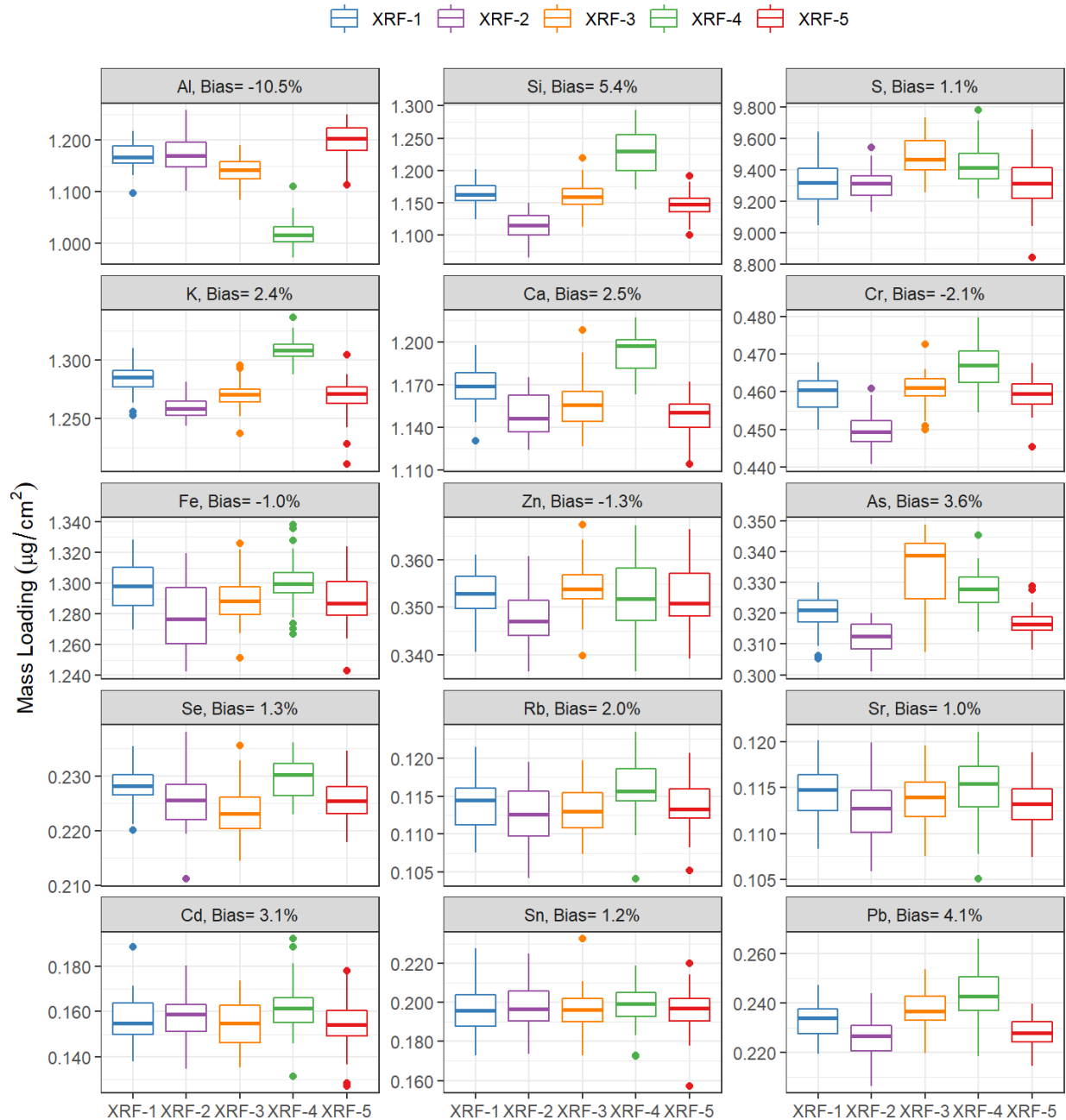
$$Precision_i = \sqrt{\frac{n \sum_{j=1}^n d_{i,j}^2 - (\sum_{j=1}^n d_{i,j})^2}{n(n-1)}}$$

The results from this analysis, for the elements listed for the weekly ME-RM in Table 4.2-2, averaged over the UC Davis ME-RM sample used during the analysis period, are presented in Table 4.2-13. Boxplots of the mass loading results from the instruments are presented in figure 4.2-2 for each weekly ME-RM sample.

Table 4.2-13: Precision and bias of all EDXRF instruments from the weekly UC Davis ME-RM calculated for the analysis period 3/31/2019 through 3/12/2020 (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-2 Bias %	XRF-3 Bias %	XRF-4 Bias %	XRF-5 Bias %	XRF-1 Prec. %	XRF-2 Prec. %	XRF-3 Prec. %	XRF-4 Prec. %	XRF-5 Prec. %
Al	2.7	3.1	0.1	-10.5	5.1	2.1	3.6	2.1	2.2	2.9
Si	0.0	-4.2	-0.3	5.4	-1.5	1.4	1.7	1.8	2.9	1.6
S	-0.5	-0.7	1.1	0.7	-0.6	1.4	1.0	1.2	1.4	1.7
K	0.3	-1.5	-0.6	2.4	-0.8	0.9	0.7	0.9	0.8	1.2
Ca	0.5	-1.3	-0.5	2.5	-1.4	1.2	1.2	1.7	1.1	1.2
Cr	0.0	-2.1	0.2	1.6	0.0	1.0	1.0	0.9	1.2	0.9
Fe	0.5	-1.0	-0.1	0.7	-0.2	1.1	1.6	1.1	1.2	1.3
Zn	0.2	-1.3	0.7	0.3	-0.1	1.3	1.5	1.4	2.2	1.9
As	-0.6	-3.2	3.6	1.8	-1.7	1.9	1.7	4.0	1.9	1.4
Se	0.7	-0.5	-1.3	1.3	-0.4	1.4	2.0	2.2	1.6	1.7
Rb	0.1	-1.3	-0.8	2.0	-0.2	2.9	3.6	2.7	3.1	2.8
Sr	0.5	-1.0	0.0	1.0	-0.6	2.4	2.8	2.6	3.2	2.1
Cd	-0.1	0.2	-1.5	3.1	-1.8	6.4	6.3	6.2	7.4	6.7
Sn	-0.5	0.6	-0.7	1.2	-0.6	6.3	6.1	5.6	5.2	5.7
Pb	-0.3	-3.4	1.7	4.1	-2.4	2.7	3.6	3.4	4.4	2.6

Figure 4.2-2: Instrumental comparison using the weekly UC Davis ME-RM. Bias shown in plot labels is the maximum bias between any two instruments. 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 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). Dots indicate individual data points beyond 1.5×IQR.



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 consists of 16 UC Davis produced ME-RMs and covers a range of mass loadings simulating the range of real CSN samples. In order to compare multiple filters with different mass loadings, the

results of reanalysis are first converted to z-scores. For a given month, the z-score for the i^{th} element and j^{th} filter is

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

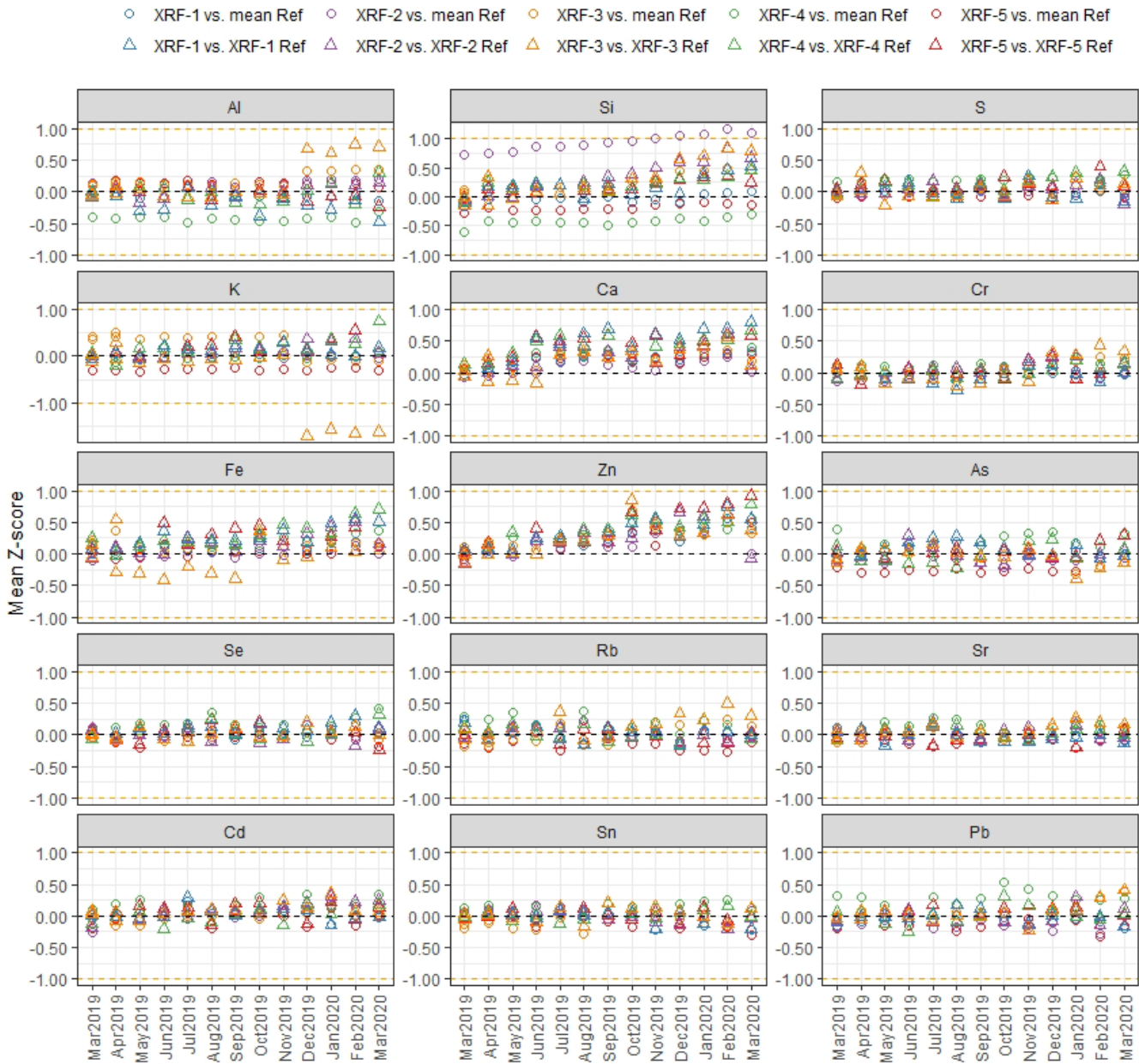
where x_{ij} is that month's result, \widehat{x}_{ij} is the reference value for element i in filter j , and $U(x_{ij})$ and $U(\widehat{x}_{ij})$ are the uncertainty of that month's result and the reference uncertainty respectively. The instrument-specific reference values for the samples of the reanalysis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

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

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 4.2-3 shows the mean z-score plots during the analysis period. Issues observed include increasing mean z-scores for silicon, calcium, and zinc which are most likely indicative of environmental contamination build up on the monthly reanalysis samples. Additionally, the silicon z-score for XRF-2 exceeded the acceptance criteria beginning December 2019. This increase is coincident with an increase in silicon on the daily PTFE blank, as discussed in Section 2.2.3, Section 3.2.1.3, and Section 4.2.2.1. This issue is still being investigated; silicon contamination of the X-ray path is suspected. Analysis of CSN samples on XRF-2 was halted beginning 1/9/2020. Finally, the potassium z-score based on the individual instrument reference for XRF-3 fell below the acceptance criteria beginning December 2019, caused by a slight shift in the potassium annual calibration. The new calibration improved the agreement between XRF-3 and the inter-instrument reference values for the reanalysis samples. However, the new calibration caused the agreement between the new measurement values and the original individual reference calculated for just XRF-3 to deteriorate. All other QC measures suggest improved potassium results when compared to the other instruments and the NIST SRM. Therefore, no action was taken to correct this exceedance since it was caused by the initial individual reference value determined for XRF-3 and is not considered impactful to instrument or calibration performance.

Figure 4.2-3: Inter-instrument comparison by z-score of monthly reanalysis sample set. The orange dashed lines indicate the mean z-score acceptance criteria of ± 1 .



4.2.2.5 Calibration Verification with NIST SRM 2783

The EDXRF measurement of NIST SRM 2783 certified/reference mass loadings is monitored monthly for selected elements with loadings at least three times higher than the EDXRF analytical method 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 criteria calculated as \pm 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 results from this analysis period (3/31/2019 through 3/12/2020) are shown in Figure 4.2-4, and Table 4.2-14 summarizes the calibrations performed during this analysis period. All EDXRF instruments underwent routine annual calibrations in December 2018/January 2019, and again in December 2019/January 2020. XRF-3 also underwent calibration in April 2019 because of replacement of the X-ray tube and high voltage system; no samples from this reporting period were analyzed on this instrument prior to the replacement. Additionally, XRF-3 received a new detector prior to the annual calibration in December 2019.

The results from the monthly NIST SRM 2783 analyses indicate that calibrations for all instruments were stable over the calibration periods. However, there is evidence that NIST SRM 2783 serial number 1720 had sulfur contamination beginning December 2019, likely caused by vacuum pump oil from one of the instruments. The NIST SRM 2783 serial number 1720, used for this QC check since 2013, was therefore replaced beginning 1/29/2020 with NIST SRM 2783 serial number 1617. There are clear differences between the two SRM samples.

For XRF-2 there were NIST SRM 2783 acceptance criteria failures for aluminum throughout 2019, as well as on XRF-1 in December 2019 and XRF-5 in March 2020. The wide range of values suggest that the acceptance criteria for aluminum need to be reevaluated; aluminum is a difficult element to quantify for EDXRF and has high inter-instrument bias. Results from other QC measures for aluminum did not show any exceedances or other issues. Additionally, for XRF-5 there was a NIST SRM 2783 acceptance criteria failure for silicon in December 2019. Unfortunately, this failure occurred immediately following the annual calibration for XRF-5, before the calibration was finalized. The final result for this SRM measurement was not calculated until after December 2019 when the calibration was finalized, at which point it was too late to reanalyze the SRM. However, no other acceptance criteria failures for silicon were identified during December 2019, including for the monthly reanalysis samples which have silicon concentrations matching those found in network samples. Furthermore, the January 2020 SRM result from XRF-5 was well within the acceptance criteria. As such, it was determined that the anomalous NIST SRM 2783 acceptance criteria failure for XRF-5 did not warrant reanalysis of the network samples analyzed in December 2019. Future calibrations will not be scheduled near holidays to help ensure timely computation of the calibrations and results.

Figure 4.2-4: Error of each EDXRF instrument from the NIST SRM 2783 standard run monthly for the analysis period 3/31/2019 through 3/12/2020. The vertical red line indicates when the SRM sample was changed from NIST SRM 2783 serial number 1720 to NIST SRM 2783 serial number 1617.

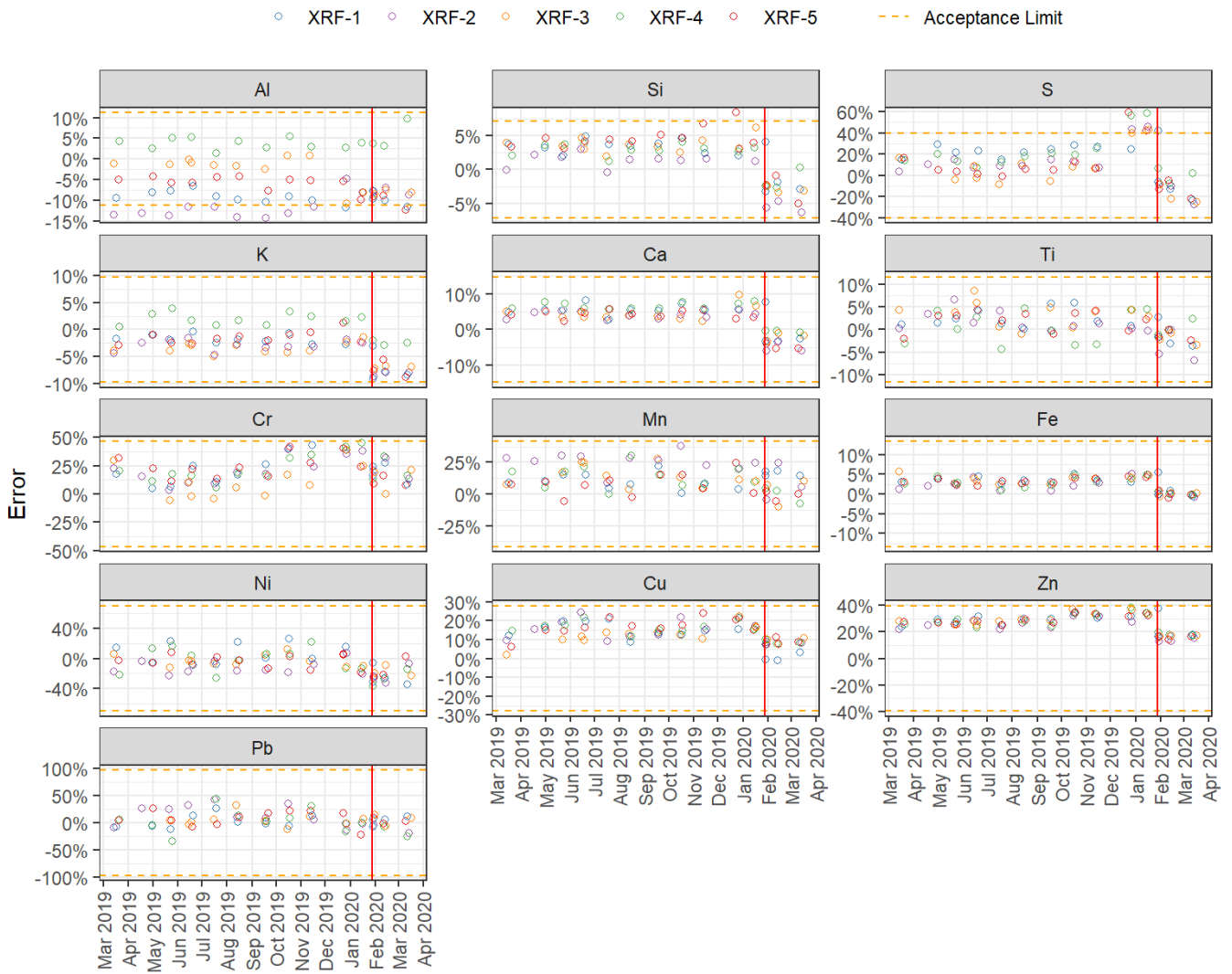


Table 4.2-14: Dates for calibrations performed on each EDXRF instrument during this analysis period (March 31, 2019 through March, 12, 2020).

EDXRF Instrument	Calibration Date	Reason for Calibration	Range of Sample Dates Analyzed
XRF-5	12/17/2019	Annual calibration	1/3/2019 – 9/30/2019
XRF-1	12/21/2018	Annual calibration	1/3/2019 – 9/30/2019
XRF-4	12/21/2019	Annual calibration	1/3/2019 – 9/30/2019
XRF-2	3/8/2018	Annual calibration	1/3/2019 – 9/15/2019
XRF-3	4/18/2019	Detector replaced	1/3/2019 – 9/30/2019
XRF-4	12/20/2019	Annual calibration	9/6/2019 – 12/29/2019
XRF-5	12/20/2019	Annual calibration	3/25/2019 – 12/29/2019
XRF-2	12/21/2019	Annual calibration	9/3/2019 – 12/29/2019
XRF-3	12/27/2019	Annual calibration	3/7/2019 – 12/29/2019
XRF-1	1/29/2019	Annual calibration	10/3/2019 – 12/29/2019

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 CSN 2018 Annual Quality Report, Section 2.3.1 and 4.2.2.5). 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.

The CSN 2018 Annual Quality Report (Section 4.2.2.5) discussed changes to the EDXRF measurement applications, which were made with the goal to reduce the variability and analytical method detection limits for some elements. The new application settings were implemented December 2018 (effective beginning with network samples collected October 1, 2018) and were used for the entirety of this analysis period. The results indicate that variability and analytical method detection limits were reduced for some elements. The analytical method detection limits were compared for one year of network samples analyzed prior to the application change and one year of network samples analyzed after the application change. The comparisons show that at least iron, zinc, manganese, nickel, copper, and lead have decreased analytical method detection limits resulting in an increase in detectable samples. These results are reported in a data advisory available on the UC Davis AQRC website (<https://airquality.ucdavis.edu/csn-documentation>).

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 conducted a Technical Systems Audit (TSA) of UC Davis laboratory and data handling operations on August 18 & 19, 2019; see Section 3.2.5.

4.2.4.2 *Performance Evaluations*

A UC Davis inter-laboratory comparison study utilizing UC Davis produced ME-RMs sent to five external XRF laboratories was started in late 2019. Results from this inter-comparison are pending and will be reported in the CSN 2020 Annual Quality Report.

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, 2019 through December 31, 2019) there were 1,687 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 March 31, 2019 through March, 12, 2020 (samples collected 1/1/2019 through 12/31/2019).

Species	Count	Median ($\mu\text{g}/\text{cm}^2$)	Average ($\mu\text{g}/\text{cm}^2$)	Min ($\mu\text{g}/\text{cm}^2$)	Max ($\mu\text{g}/\text{cm}^2$)	St. Dev. ($\mu\text{g}/\text{cm}^2$)
Ag	1687	0.018	0.018	0.006	0.041	0.006
Al	1687	0.079	0.079	0.021	0.147	0.013
As	1687	0.000	0.000	0.000	0.001	0.000
Ba	1687	0.062	0.063	0.025	0.120	0.015
Br	1687	0.000	0.000	0.000	0.002	0.000
Ca	1687	0.003	0.004	0.000	0.225	0.008
Cd	1687	0.019	0.019	0.006	0.042	0.006
Ce	1687	0.073	0.074	0.029	0.147	0.018
Cl	1687	0.002	0.003	0.000	0.299	0.008
Co	1687	0.001	0.001	0.000	0.005	0.001
Cr	1687	0.004	0.004	0.002	0.019	0.001
Cs	1687	0.042	0.044	0.014	0.085	0.012
Cu	1687	0.008	0.007	0.002	0.020	0.003
Fe	1687	0.019	0.020	0.006	0.273	0.009
In	1687	0.021	0.022	0.006	0.047	0.007
K	1687	0.008	0.009	0.000	0.045	0.004
Mg	1687	0.002	0.012	0.000	0.090	0.015
Mn	1687	0.006	0.006	0.001	0.017	0.002
Na	1687	0.000	0.018	-0.001	0.397	0.028
Ni	1687	0.001	0.001	0.000	0.006	0.001
P	1687	0.000	0.000	0.000	0.005	0.001
Pb	1687	0.012	0.012	0.005	0.026	0.003
Rb	1687	0.003	0.003	0.000	0.009	0.001
S	1687	0.000	0.001	0.000	0.489	0.013
Sb	1687	0.027	0.028	0.008	0.056	0.007
Se	1687	0.002	0.002	0.000	0.008	0.001
Si	1687	0.023	0.026	0.001	0.183	0.013
Sn	1687	0.028	0.029	0.008	0.062	0.008
Sr	1687	0.004	0.004	0.001	0.011	0.001
Ti	1687	0.002	0.002	0.000	0.017	0.002
V	1687	0.000	0.000	0.000	0.002	0.000
Zn	1687	0.002	0.002	0.000	0.043	0.002
Zr	1687	0.016	0.017	0.002	0.045	0.006

4.3 UC Davis Thermal Optical Analysis Laboratory

The UC Davis Thermal Optical Analysis (TOA) Laboratory received and analyzed quartz filters from batches 51 through 62, covering the sampling period January 1, 2019 through December 31, 2019. Analyses of these samples were performed April 1, 2019 through March 4, 2020. 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 4.3-1: Sampling months in 2019 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 Month (2019)	Analysis Batch #	TOA Analysis Dates
January	51	4/1/2019 – 4/19/2019
February	52	4/19/2019 – 5/8/2019
March	53	5/8/2019 – 5/29/2019
April	54	6/5/2019 – 6/26/2019
May	55	7/10/2019 – 7/31/2019
June	56	8/8/2019 – 8/30/2019
July	57	9/12/2019 – 10/9/2019
August	58	10/9/2019 – 11/5/2019
September	59	11/6/2019 – 12/6/2019
October	60	12/12/2019 – 1/9/2020
November	61	1/16/2020 – 2/7/2020
December	62	2/7/2020 – 3/4/2020
All month	51-62	4/1/2019 – 3/4/2020

4.3.1 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 QC checks are implemented to ensure data quality. Calibrations of the analyzers are performed semi-annually or as needed (e.g. when the CH₄/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 4.3-2.

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

Activity	Frequency	Acceptance Criteria	Corrective Action
Laboratory Blank Check	Beginning of analysis day	<1.0 $\mu\text{g C/cm}^2$	Repeat analysis. If same result, check filter lots for possible contamination and perform pre-firing.
Instrument Blank Check	Beginning of analysis day	Between -0.3 and 0.3 $\mu\text{g C/cm}^2$	Repeat analysis. If same result, check instrument and gas lines for possible contamination.
Single-point Sucrose Standard Check	Beginning of analysis day	Within $\pm 7\%$ 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 $\pm 10\%$ of the daily 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	First check laser-sample-detector alignment and/or examine top oven window for frosting or debris; replace laser source when necessary.
Network Sample Replicates	Every 20 th network sample analysis	$\pm 10\%$ when TC $\geq 10 \mu\text{g/cm}^2$ $\pm 20\%$ when ECR $\geq 2.5 \mu\text{g/cm}^2$ or $< \pm 1 \mu\text{g/cm}^2$ when TC $< 10 \mu\text{g/cm}^2$ $< \pm 0.5 \mu\text{g/cm}^2$ when ECR $< 2.5 \mu\text{g/cm}^2$.	Investigate instrument and sample anomalies. Analyze the third punch on a different analyzer.
Inter-instrument Comparison Check	Weekly	Measurement bias for a given analyzer should be $\leq 10\%$ for TC and OC and $\leq 20\%$ 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 IMPROVE_A protocol parameter file.
Temperature Calibrations	Every six months or after major instrument repair	NA	Change the temperature offset values in the IMPROVE_A protocol parameter file accordingly.

^a NA: Not Applicable.

4.3.2 Summary of QC Results

Detailed results from the TOA QC checks are presented in the subsections below. In addition to performing routine daily and weekly QC activities, readings of oven pressure, back oven temperature, methanator oven temperature, FID baseline, and initial laser transmittance/reflectance 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) FID baseline stability 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 acceptance criteria outlined in Table 4.3-2 are reanalyzed.

4.3.2.1 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 criteria. Table 4.3-3 lists the number of blanks analyzed during the report period and their areal density statistics.

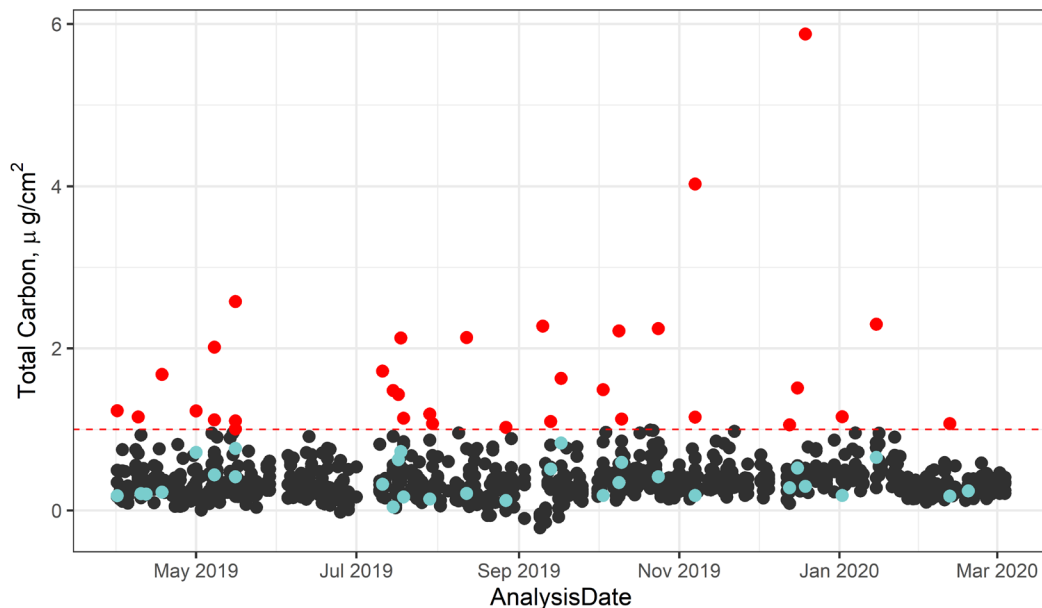
Table 4.3-3: Statistics of daily quartz filter laboratory blank and instrument blank analyses on all carbon analyzers for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019).

Blank Type	Count	Median ($\mu\text{g}/\text{cm}^2$)	Average ($\mu\text{g}/\text{cm}^2$)	Min ($\mu\text{g}/\text{cm}^2$)	Max ($\mu\text{g}/\text{cm}^2$)	St.Dev. ($\mu\text{g}/\text{cm}^2$)	# Exceedance
Laboratory Blank	1,005	0.322	0.389	-0.211	5.877	0.332	30
Laboratory Blank – R*	33	0.324	0.522	0.045	4.028	0.688	3
Instrument Blank	1,005	-0.036	-0.038	-0.289	0.271	0.098	0

*Laboratory Blank - R: repeated laboratory blank when original fails the acceptance criteria.

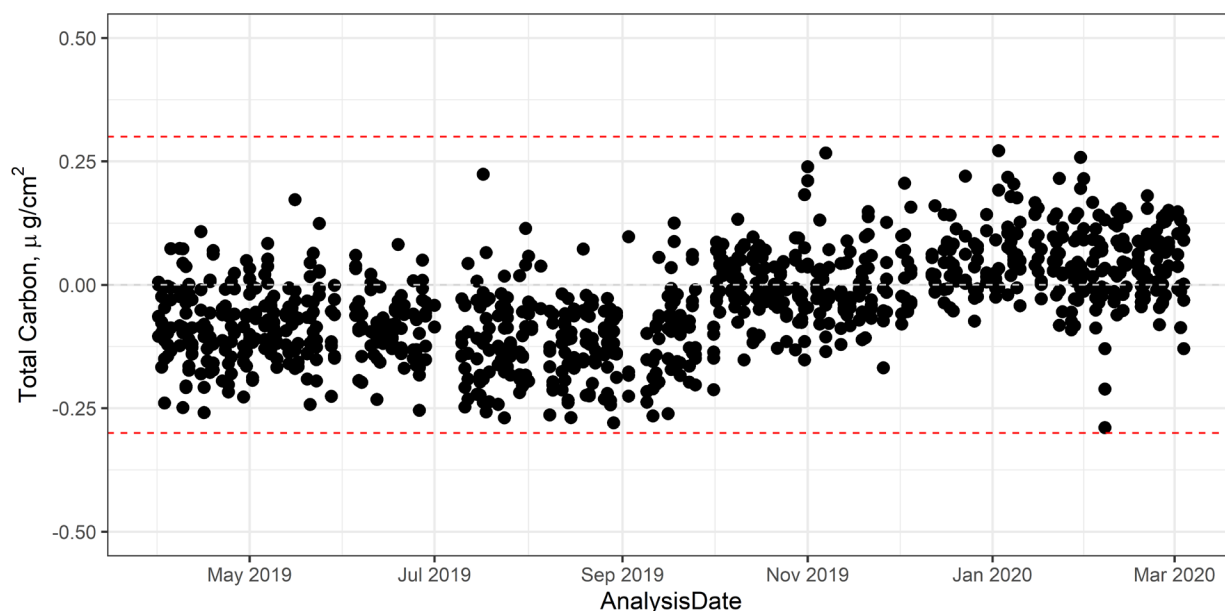
For laboratory blanks, if the TC areal density exceeds $1.0 \mu\text{g C}/\text{cm}^2$, a second punch taken from the same blank filter lot is analyzed (Laboratory Blank – R). If the original and repeated blank analyses on more than one instrument exceeds the acceptance criteria, or if the Laboratory Blank – R analysis still exceeds the limit (three cases during the report period), a new lot of quartz blank filters is used to distinguish filter lot contamination from system contamination. Figure 4.3-1 and Figure 4.3-2 show the results of daily laboratory and instrument blanks, respectively, analyzed on all five analyzers during this reporting period.

Figure 4.3-1: Results of daily quartz filter laboratory blanks for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). Red dashed line indicates the acceptance criteria of $1.0 \mu\text{g C}/\text{cm}^2$ for total carbon areal density. For cases when the acceptance criteria 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 criteria is TC within $\pm 0.3 \mu\text{g}/\text{cm}^2$. Figure 4.3-2 shows the results of daily analyses of instrument blanks on all five analyzers. The shift in instrument blank TC concentration observed beginning October 2019 coincides with changing the helium/oxygen compressed gas cylinder; small variations in the oxygen mixing ratio may have caused a slight baseline drift. Similar shifts were not observed for changes of the helium/oxygen compressed gas cylinder that occurred on June 20, 2019 and December 18, 2019. There were no instrument blank exceedances during this report period.

Figure 4.3-2: Results of daily instrument blanks for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). Red dash lines indicate the acceptance criteria of $\pm 0.3 \mu\text{g C}/\text{cm}^2$ for total carbon areal density.



4.3.2.2 *Single-Point Sucrose Standard Check*

Following the daily blank analyses, a single-point sucrose calibration check is performed to evaluate FID response by injecting $10 \mu\text{L}$ of sucrose standard solution onto a clean filter punch and analyzing for total carbon content. Table 4.3-4 summarizes the concentrations of all sucrose standard solutions generated for calibrating the carbon analyzers on a semi-annual basis. They cover a wide range of the TC levels typically seen from the CSN network samples. Among these standards, Sucrose #15 is chosen for daily single-point calibration check as its concentration is most comparable to the CSN median TC value.

Table 4.3-4: Sucrose solution standard concentrations in $\mu\text{gC}/\text{cm}^2$.

Sucrose ID	Concentration ($\mu\text{g C}/\text{cm}^2$)
Sucrose 11	210.50
Sucrose 12	105.25
Sucrose 13	42.10
Sucrose 14	21.05
Sucrose 15	10.53
Sucrose 16	2.11

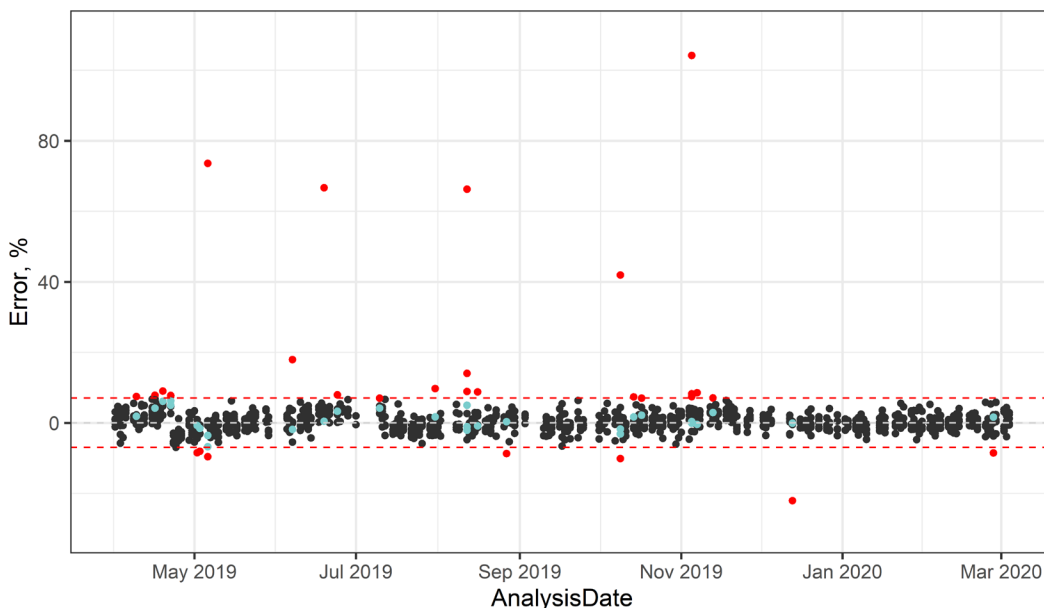
Upon completion of the sucrose analysis, the measured TC is compared against the true value (i.e. calculated TC). The % error between the measured and calculated TC is derived using Equation 4.3-1. If the error exceeds the $\pm 7\%$ acceptance criteria, a second analysis is performed before any network samples are analyzed on that instrument. If the second analysis still exceeds the acceptance criteria, or if a consistent one-sided bias (with error within $\pm 7\%$) 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 4.3-5 summarizes the statistics of the daily sucrose check. There were 30 exceedances out of the 1,013 sucrose runs during the report period. All second analyses of the sucrose solution showed acceptable results (Figure 4.3-3).

$$Error (\%) = \left(\frac{Measured\ TC - Calculated\ TC}{Calculated\ TC} \right) \times 100\% \quad (\text{Eq. 4.3-1})$$

Table 4.3-5: Statistics of daily single-point sucrose standard analyses on all carbon analyzers for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019).

Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
1,013	0.253	0.710	-22.054	104.209	5.807	30

Figure 4.3-3: Results of daily single-point sucrose calibration standard check for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). Red dashed lines indicate the acceptance criteria of $\pm 7\%$ error. For cases when original measured sucrose value (red points) exceeded the acceptance criteria, a repeated analysis was performed (blue points).



4.3.2.3 Calibration Peak Area Check

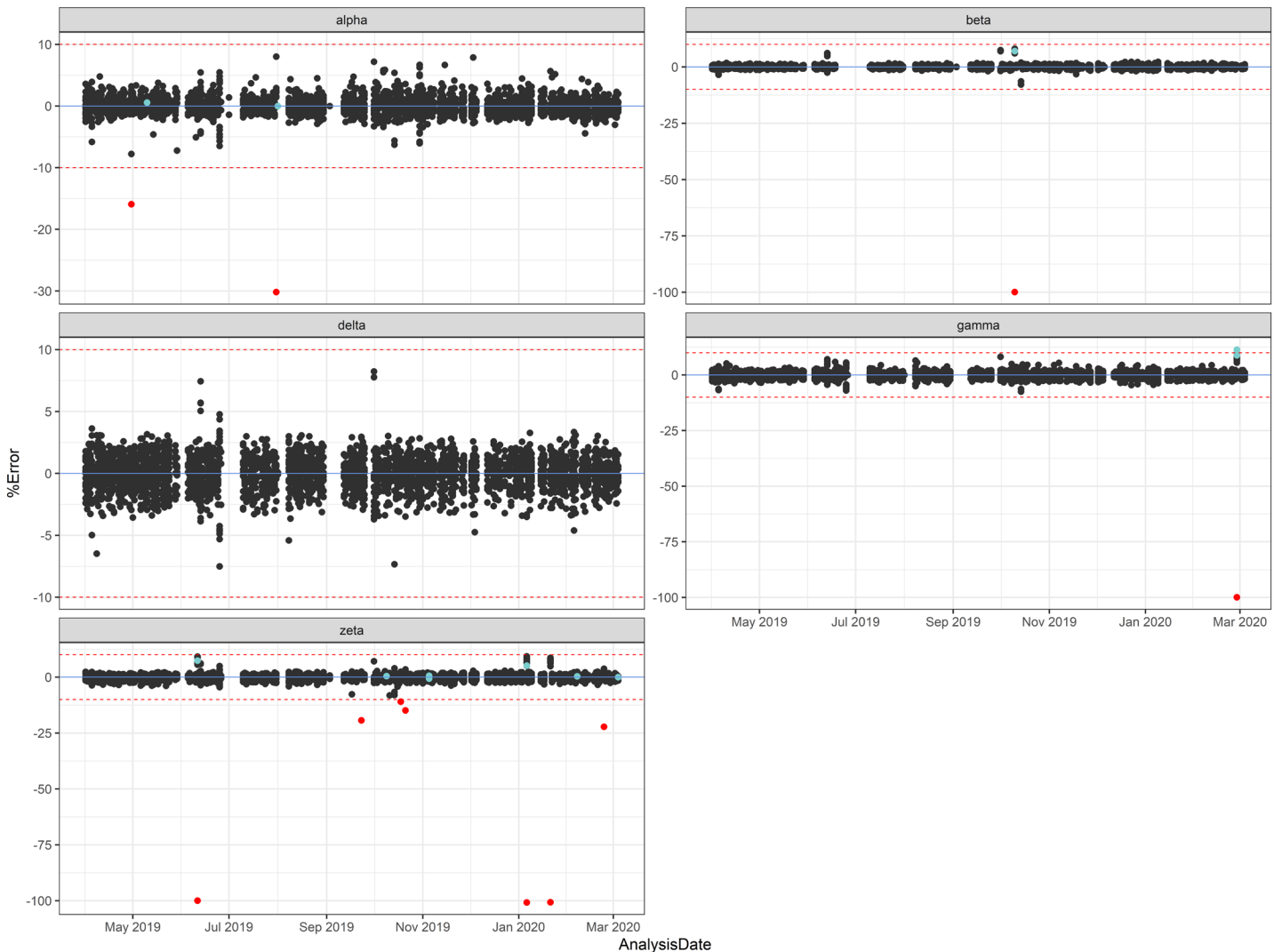
At the end of each analysis, a fixed amount of methane (CH_4) from a cylinder containing 5% CH_4 in helium is injected into the system as an internal gaseous standard. The CH_4 peak area is quantified and compared to the average peak area of all analyses performed on that instrument on that day. If the error (calculated using Equation 4.3-2) exceeds $\pm 10\%$ acceptance criteria, 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 the whole batch (not on the same day). Table 4.3-6 summarizes the statistics of the calibration peak area check. There were 11 exceedances during this reporting period. Six of the 11 exceedances occurred when the clamp that connects the oven ball joint was not sufficiently tightened, resulting in a leak in the system. The other exceedances occurred due to FID ignition being off during the analysis. All reanalyses of the affected samples had acceptable results.

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

Table 4.3-6: Statistics of internal calibration peak area check on all carbon analyzers for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019).

Analyzer	Count	Median Error (%)	Average Error (%)	Min Error (%)	Max Error (%)	St.Dev. Error (%)	# Exceedance
Alpha	3089	-0.094	0.000	-30.178	8.016	1.492	2
Beta	2862	-0.003	0.000	-99.933	8.098	2.057	1
Delta	3186	0.051	0.000	-7.506	8.235	1.343	0
Gamma	2936	0.099	0.000	-99.931	11.395	2.378	1
Zeta	3086	0.154	0.000	-100.779	9.308	3.489	7

Figure 4.3-4: Results of internal calibration area check for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). Red dashed lines indicate the acceptance criteria of $\pm 10\%$ error from the mean value. For cases when calibration area exceeded the acceptance criteria, a repeated analysis (blue points) was performed and the original analysis was voided (red points).



4.3.2.3 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, caused by either weak/non-functioning laser or laser-sample-detector misalignment, results in corrective actions (if applicable) and reanalysis of the sample. In addition, before starting the instrument blank analysis each day, the readings of clean filter reflectance and transmittance are checked to make sure they are above the initial laser acceptance criterion (i.e. 5000 a.u.). Figure 4.3-5 shows the filter reflectance and transmittance initial readings for all instrument blank analyses during the report period. There was one exceedance of both laser reflectance and transmittance (Gamma, 9/9/2019), which resulted in a laser source replacement on 9/12/2019. The initial clean filter reflectance of Beta and the initial clean filter transmittance of Alpha showed larger variability prior to 9/9/2019, which was much improved after laser fine-tuning and signal optimization performed on 9/9/2019 following the semi-annual maintenance.

Figure 4.3-5: Laser initial readings (top: Transmittance; bottom: Reflectance) of the instrumental blank analysis for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). Red dashed line indicates the acceptance criteria of 5000 a.u. of the laser signal. Black vertical lines indicate dates of related maintenance on the instrument optical components. Different analyzers are indicated by data point color.



4.3.2.4 Network Sample Replicates

Replicate analyses are performed on every 20th CSN filter (samples and field blanks), where replicate analysis results are obtained from a second punch from the same filter analyzed on a randomly selected analyzer. Table 4.3-7 lists the acceptance criteria for replicate analysis and the summary statistics from this reporting period. A total of 708 replicate analyses were performed out of the 15,099 samples and field blanks. For cases that exceeded the acceptance criteria, a third punch (if available) was analyzed on a different analyzer. All three sets of results (routine, replicate, and reanalysis) from the same filter are compared to determine analysis validity. Instrument anomaly and/or deposit inhomogeneity are also examined. Figure 4.3-6 shows the

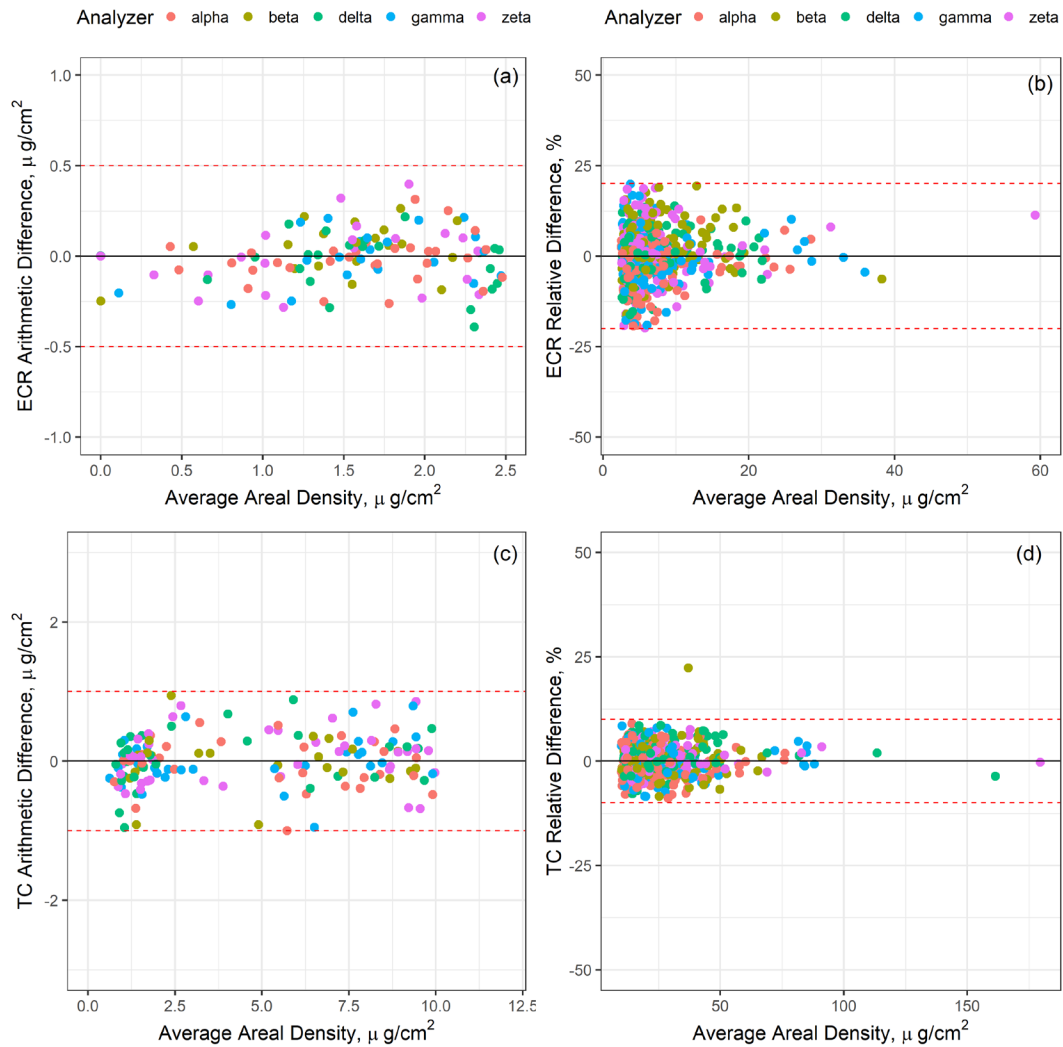
results of the replicate analysis. There were a total of 26 TC exceedances and seven ECR exceedances during this reporting period. Affected samples were reanalyzed on a third analyzer. One sample (sample event ID# Q0142019092102) failed the replicate analysis criteria for TC but was not reanalyzed because the sample deposit was determined to be inhomogeneous by visual inspection (see Figure 4.3-6, panel d). All other reanalyses had satisfactory results.

Table 4.3-7: Acceptance criteria and the summary statistics of the replicate analyses for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019).

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	708	26	25
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	708	7	7

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

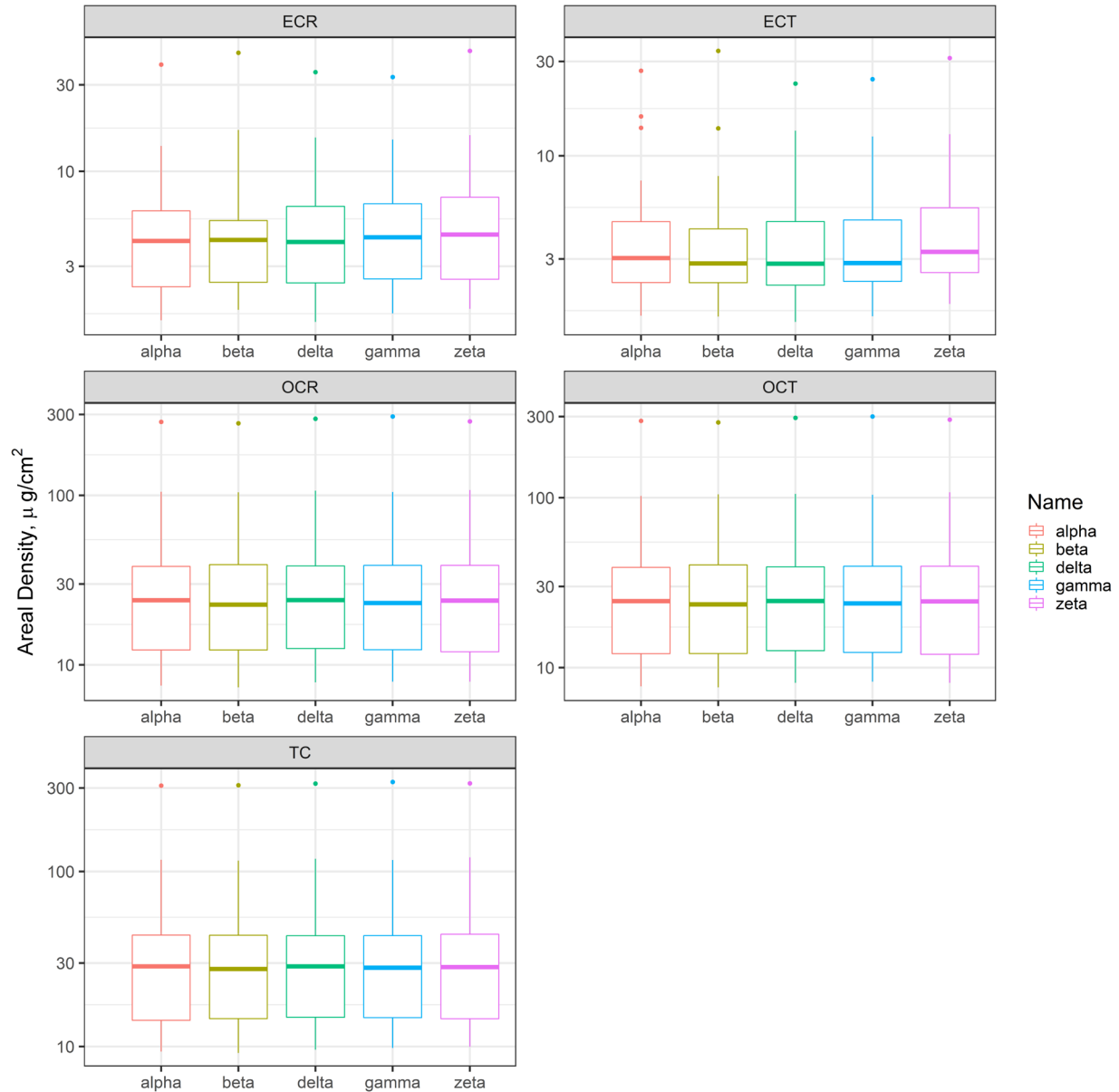
Figure 4.3-6: Results of CSN replicate analysis for ECR (Panel a and b) and TC (Panel c and d) for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). The red dashed lines in each panel represents the acceptance criteria.



4.3.2.5 Inter-instrument Comparison Check

Instrument inter-comparison is evaluated weekly by analyzing performance check samples collected at UC Davis. Pre-fired quartz filters with a diameter of 37 mm are used to allow enough deposit area for at least five 0.6 cm^2 punches. A total of 47 weekly performance check samples were analyzed during this reporting period. Figure 4.3-7 shows the statistical distribution of the EC, OC, and TC areal densities measured by each analyzer.

Figure 4.3-7: Distribution of ECR, OCR, and TC areal densities measured from the weekly performance check samples by each analyzer for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). 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 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). Dots indicate individual data points beyond 1.5×IQR.



The measured carbon areal density from each analyzer (A_x) is compared against the average value derived from measurements by all available analyzers on the same performance check sample. The bias for each carbon parameter ($Bias_i$) is calculated for each analyzer each week as:

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

The acceptance criteria for inter-instrumental bias is the same as that for the network sample replicates (Table 4.3-7). Exceeding the acceptance criteria 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 4.3-8 summarizes the statistics of the instrument bias for ECR and TC. There were no exceedances during this reporting period.

Table 4.3-8: Statistics (median, mean, minimum, maximum, and standard deviation) of the instrument bias (%) from the weekly performance check for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019).

Analyzer	Count	Elemental Carbon by Reflectance (ECR)					Total Carbon (TC)				
		Median	Mean	Min	Max	St.Dev.	Median	Mean	Min	Max	St.Dev.
Alpha	47	-2.787	-3.808	-13.019	3.518	3.977	-0.161	-0.527	-6.181	5.452	2.398
Beta	47	0.388	2.113	-9.564	13.684	6.432	-0.393	-0.297	-5.256	5.338	2.338
Delta	47	-2.795	-3.156	-14.581	4.778	4.542	1.085	0.656	-4.339	5.900	2.299
Gamma	47	-1.072	-0.664	-16.526	8.780	5.142	0.086	0.053	-8.253	8.921	2.506
Zeta	47	6.223	5.585	-7.422	18.469	6.310	-0.372	0.101	-4.009	4.068	2.010

4.3.2.6 Multi-point Sucrose Standard Check

A multi-point calibration is performed every six months, when the calibration gas cylinder or instrument main oven 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 six different concentration levels that cover a wide range of TC concentrations typically seen on the CSN samples (see Table 4.3-4 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 4.3-9 summarizes the multi-point sucrose calibrations performed during this reporting period.

Table 4.3-9: Summary of multi-point sucrose standard checks performed for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019).

Analyzer	Calibration Date	Slope	r^2	Calibration Constant
Beta	6/25/2019*	1.0039	0.9999	20.7840
Beta	9/5/2019	0.9906	0.9999	20.9813
Alpha	9/5/2019	0.9932	0.9993	20.8389
Gamma	9/5/2019	1.0218	0.9999	19.9059
Delta	9/5/2019	0.9866	0.9999	20.9735
Zeta	9/5/2019	1.004	0.9999	20.6595

* Beta sample oven replaced on 6/24/2019

4.3.2.7 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 difference (i.e. offset) between the oven temperature and sample temperature at each IMPROVE_A protocol temperature set point is determined by using a manufacturer-provided

temperature calibration device, inserted into the sample oven so that the external temperature probe sits where a sample 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 oven temperature probe (i.e. temperature offsets) are calculated and updated in the IMPROVE_A protocol parameter file. The system then goes through the IMPROVE_A protocol temperature cycle again to verify that the temperature readings from the two probes are within 10°C at all temperature steps. Table 4.3-10 summarizes the temperature calibrations performed on each analyzer during this reporting period.

Table 4.3-10: Summary of the temperature calibrations performed on each analyzer for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). Oven re-wrap refers to adjustment or replacement of heating coils that are wrapped around the sample oven.

Analyzer	Calibration Date	Oven Re-Wrapped?	Temperature Offsets (°C)					
			140°C	280°C	480°C	580°C	740°C	840°C
Beta	6/24/2019*	Yes	-7	-10	3	0	1	-2
	9/6/2019	No	-23	-44	-48	-49	-15	-22
Alpha	9/5/2019	No	15	28	30	27	-1	-15
Gamma	9/5/2019	No	-19	-42	-51	-55	-38	-46
Delta	9/5/2019	No	4	-1	-13	-22	-1	-7
Zeta	9/5/2019	No	-29	-52	-51	-50	-4	-14

* Beta sample oven replaced on 6/24/2019

4.3.3 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.

4.3.4 Audits, Performance Evaluations, Training, and Accreditations

4.3.4.1 System Audits

The EPA conducted a Technical Systems Audit (TSA) of UC Davis laboratory and data handling operations on August 18 & 19, 2019; see Section 3.2.5.

4.3.4.2 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 2020. Eight quartz filter samples and one solution sample were received and analyzed for OC, EC and TC. The results were submitted on 3/31/2020 and are pending evaluation by ECAC.

4.3.4.3 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.

4.3.4.4 Accreditations

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

4.3.5 Summary of Filter Blanks

Over the sampling period (January 1, 2019 through December 31, 2019) there were 1,686 valid quartz filter field blanks. Table 4.3-11 summarizes the field blank statistics.

Table 4.3-11: Quartz filter field blank statistics for the analysis period 4/1/2019 through 3/4/2020 (samples collected 1/1/2019 through 12/31/2019). 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	1,686	0.046	0.075	-0.109	1.917	0.147
EC2	1,686	0.088	0.119	-0.024	1.240	0.113
EC3	1,686	0.020	0.023	-0.041	0.456	0.027
ECR	1,686	0.000	0.003	-0.129	1.066	0.045
ECT	1,686	0.000	0.000	-0.004	0.456	0.011
OC1	1,686	0.239	0.240	-0.020	2.001	0.108
OC2	1,686	0.353	0.395	0.034	4.475	0.242
OC3	1,686	0.465	0.817	0.039	24.522	1.377
OC4	1,686	0.175	0.280	-0.018	2.037	0.287
OCR	1,686	1.462	1.946	0.032	29.855	1.883
OCT	1,686	1.464	1.949	0.032	29.855	1.885
OPR	1,686	0.155	0.214	-0.161	3.277	0.261
OPT	1,686	0.159	0.218	-0.161	3.277	0.262

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, 2019 through December 31, 2019. Data are expected to be delivered to AQS within 120 days of receipt of filters by the analytical laboratories.

Table 5.1-1: Summary of data deliveries to AQS for samples collected January 1, 2019 through December 31, 2019.

Sampling Month (2019)	Analysis Batch #	Filter Receipt Date	AQS Delivery Date	Days
January	51	March 6, 2019	July 11, 2019	127
February	52	April 3, 2019	August 1, 2019	120
March	53	May 8, 2019	September 5, 2019	120
April	54	June 5, 2019	October 1, 2019	118
May	55	July 9, 2019	November 6, 2019	120
June	56	August 7, 2019	December 5, 2019	120
July	57	September 10, 2019	January 8, 2020	120
August	58	October 9, 2019	February 6, 2020	120
September	59	November 6, 2019	March 9, 2020	124
October	60	December 11, 2019	April 15, 2020	126
November	61	January 14, 2020	May 13, 2020	120
December	62	February 5, 2020	June 5, 2020	121

6. Quality Assurance and Data Validation

6.1 QAPP Revisions

The UC Davis 2019 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 May 6, 2020. The document is reviewed and updated annually; the UC Davis 2020 QAPP was delivered to the EPA for review on August 21, 2020.

6.2 SOP Revisions

The UC Davis 2019 Standard Operating Procedures (SOPs) and Technical Information (TI) material for Laboratory Analysis and Data Processing/Validation for Chemical Speciation of PM_{2.5} Filter Samples were delivered to the EPA on July 31, 2019. The documents are reviewed and updated annually; the UC Davis 2020 SOPs and TIs were delivered to the EPA for review on August 21, 2020.

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 value 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, qualifier and null code flags, and comments) are received from the Sample Handling Laboratory (Wood PLC) via email and uploaded to the UC Davis CSN database. UC Davis EDXRF and TOA analysis results are transferred into the UC Davis CSN database through an automated service. RTI IC analysis result files are received via email from RTI and are ingested to the UC Davis CSN database. Additionally, for a select subset of field blanks and special studies, Wood PLC gravimetric mass result files are received via email from Wood PLC and 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 Laboratory.
- 3) *UCD CSN TI 801B, Data Processing*: Sample volume and analysis results are combined to calculate concentrations. Field 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. Laboratory 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) agency 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 performed at DRI using DRI Model 2001 analyzers; samples collected from January 2016 through September 2018 were analyzed at DRI using DRI Model 2015 analyzers; and, beginning with samples collected from October 2018 analysis was performed at UC Davis using the Sunset Laboratory Model 5L analyzer.

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).

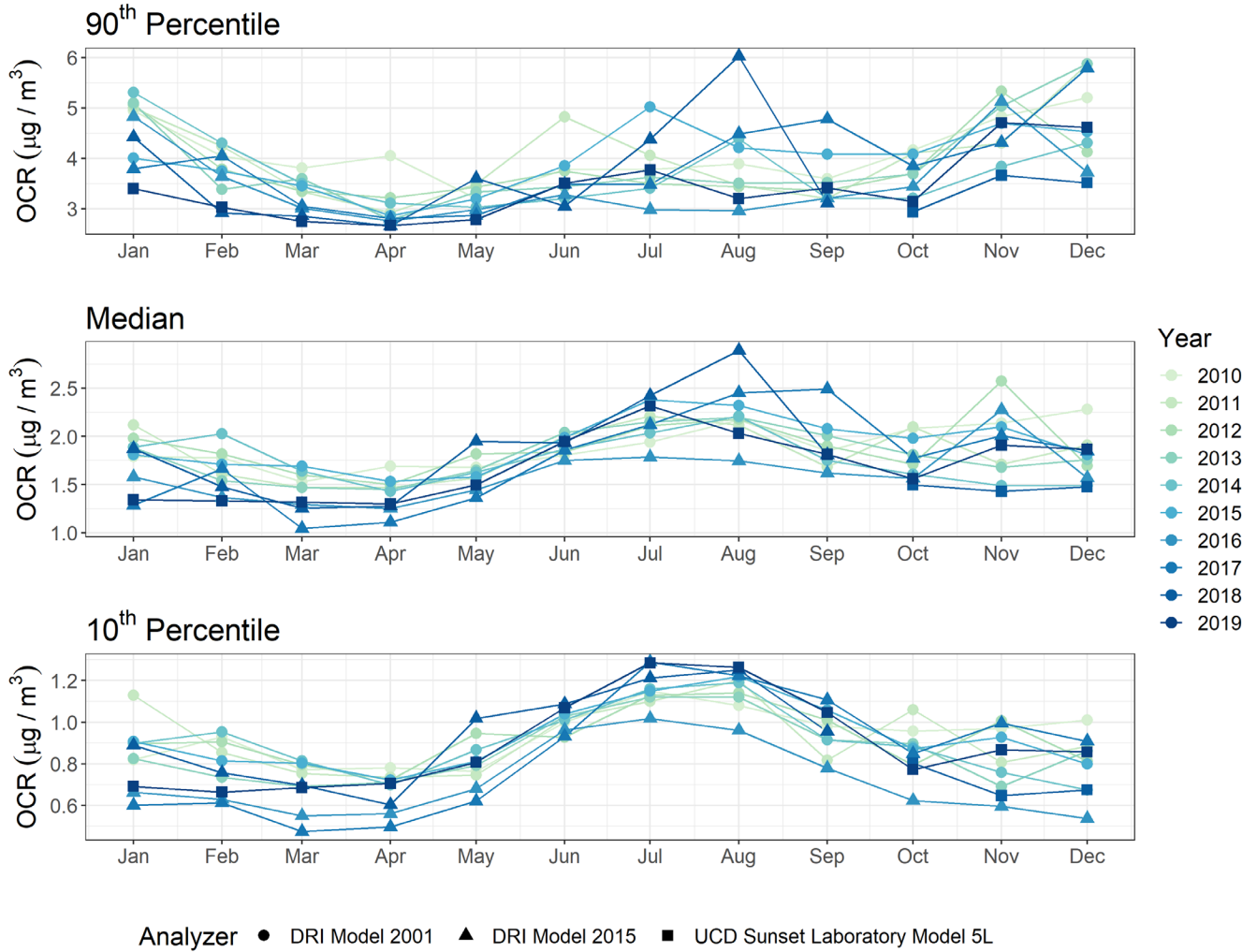
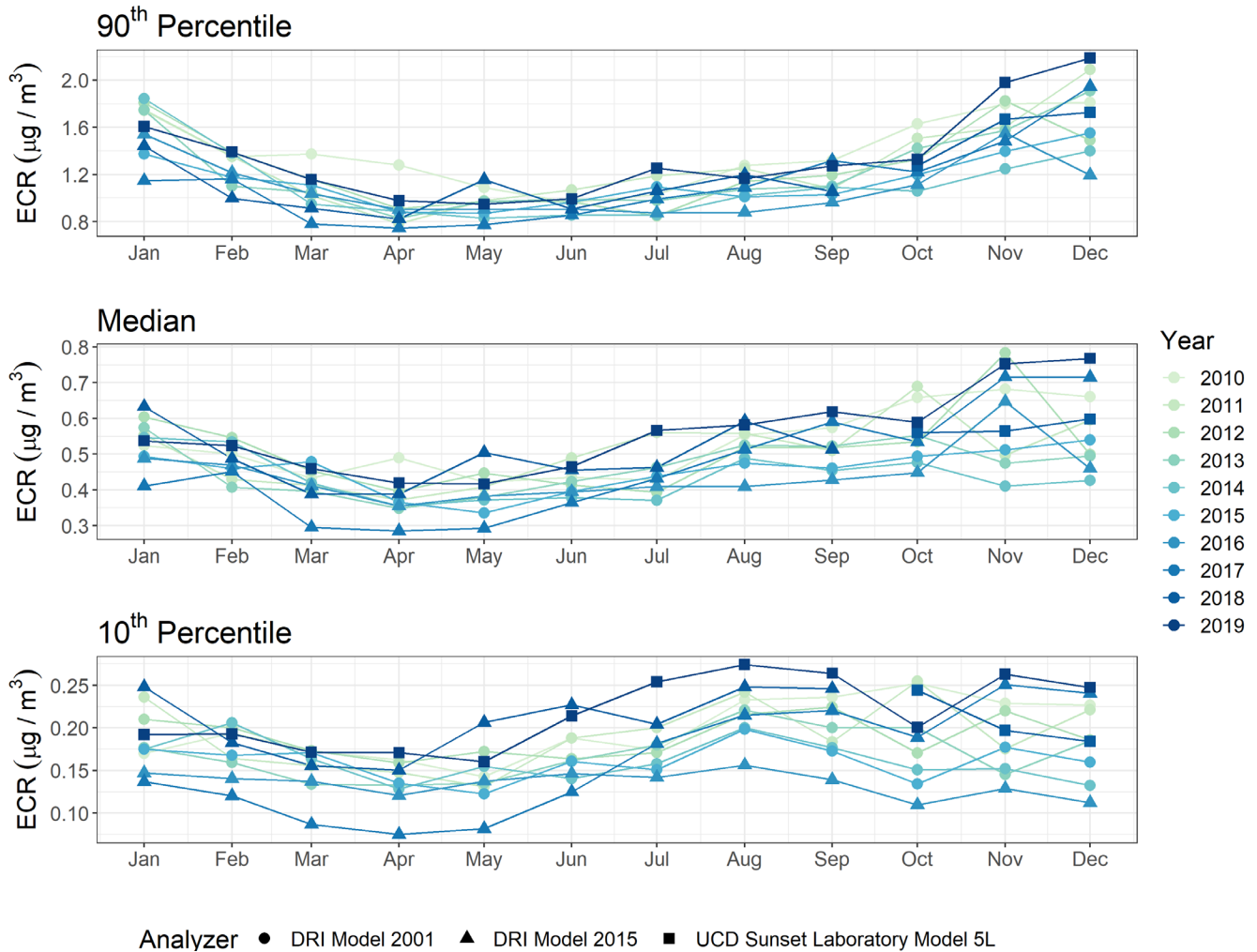
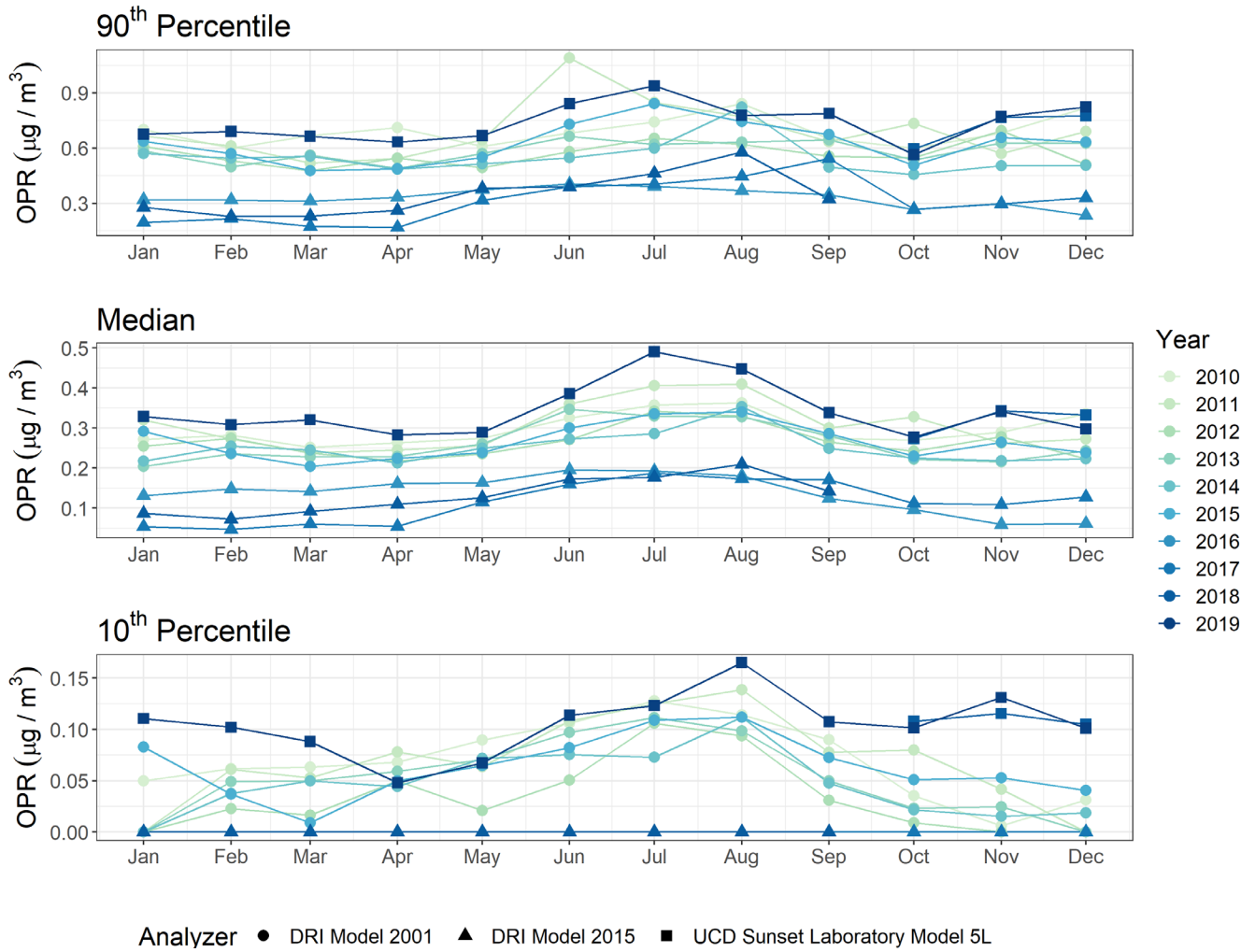


Figure 6.4-2: Multi-year time series of network-wide elemental carbon by reflectance concentrations (ECR; raw data without blank correction). Symbols denote laboratory and type of analyzer: DRI Model 2001 (circle), DRI Model 2015 (triangle), and UCD Sunset Laboratory Model 5L (square).



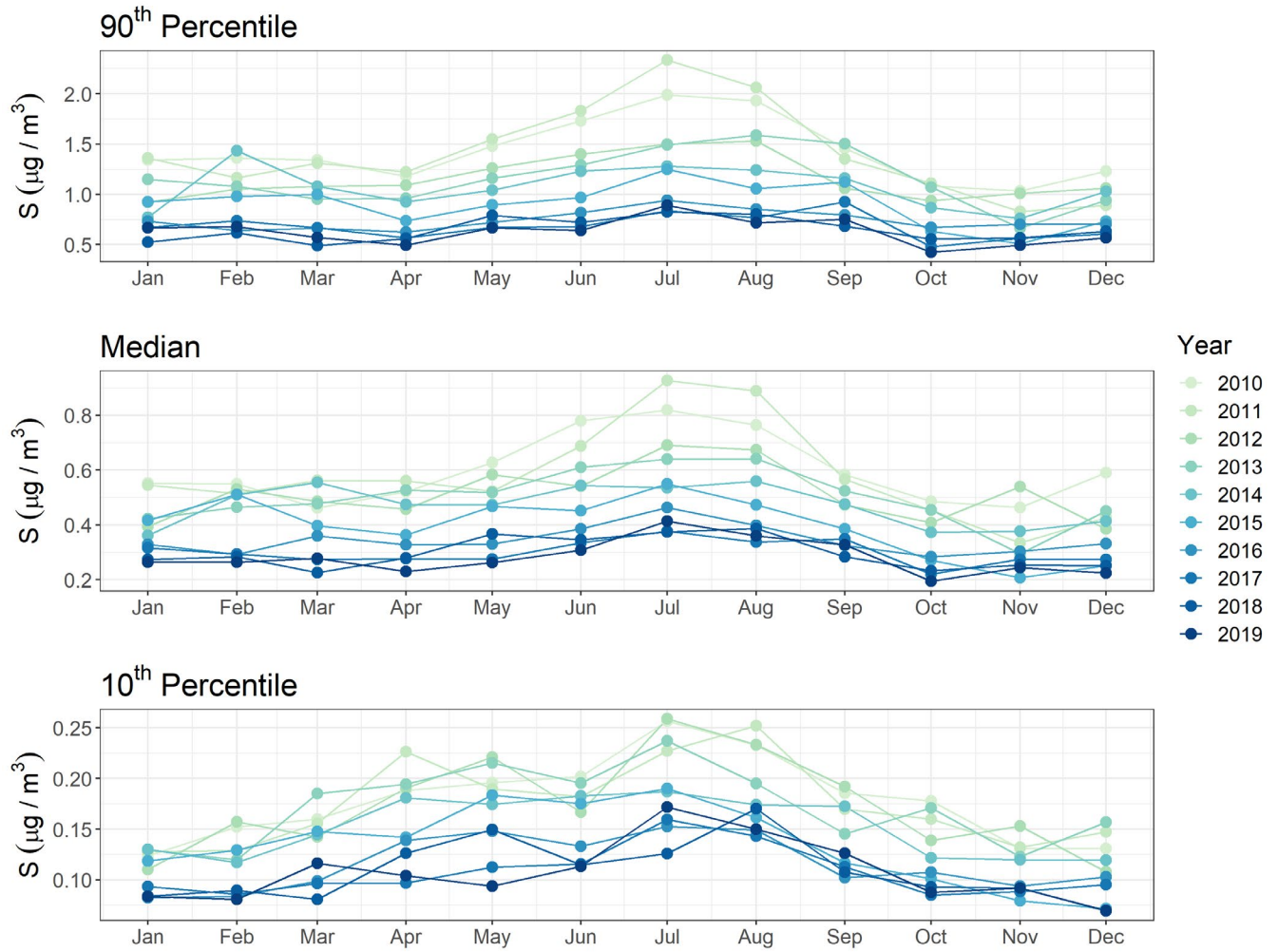
During TOA analysis some of the OC pyrolyzes upon heating in the inert environment. The organic pyrolyzed carbon (OPR) is combusted with the EC collected on the filter, and is accounted for by monitoring the laser signal and identifying an OC/EC split point based on return of the signal to its initial value. To some extent, the split point – and thus the amount of OPR – is operationally defined based on instrument parameter settings. However, seasonal variation and moderate multiyear variation in OPR are expected to be atmospherically real because OC from certain sources (such as biomass burning) pyrolyze more easily than from other sources. As seen in Figure 6.4-3, since the October 1, 2018 transition to UCD Sunset Laboratory Model 5L instruments the OPR concentrations are in closer alignment with results reported from the DRI Model 2001 instruments (used for samples collected through December 31, 2015), whereas the results from the DRI Model 2015 instruments (used for samples collected January 1, 2016 through September 30, 2018) are generally lower. The OPR shift corresponding with the laboratory transition suggests that the observed changes may be operational rather than atmospherically real.

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).



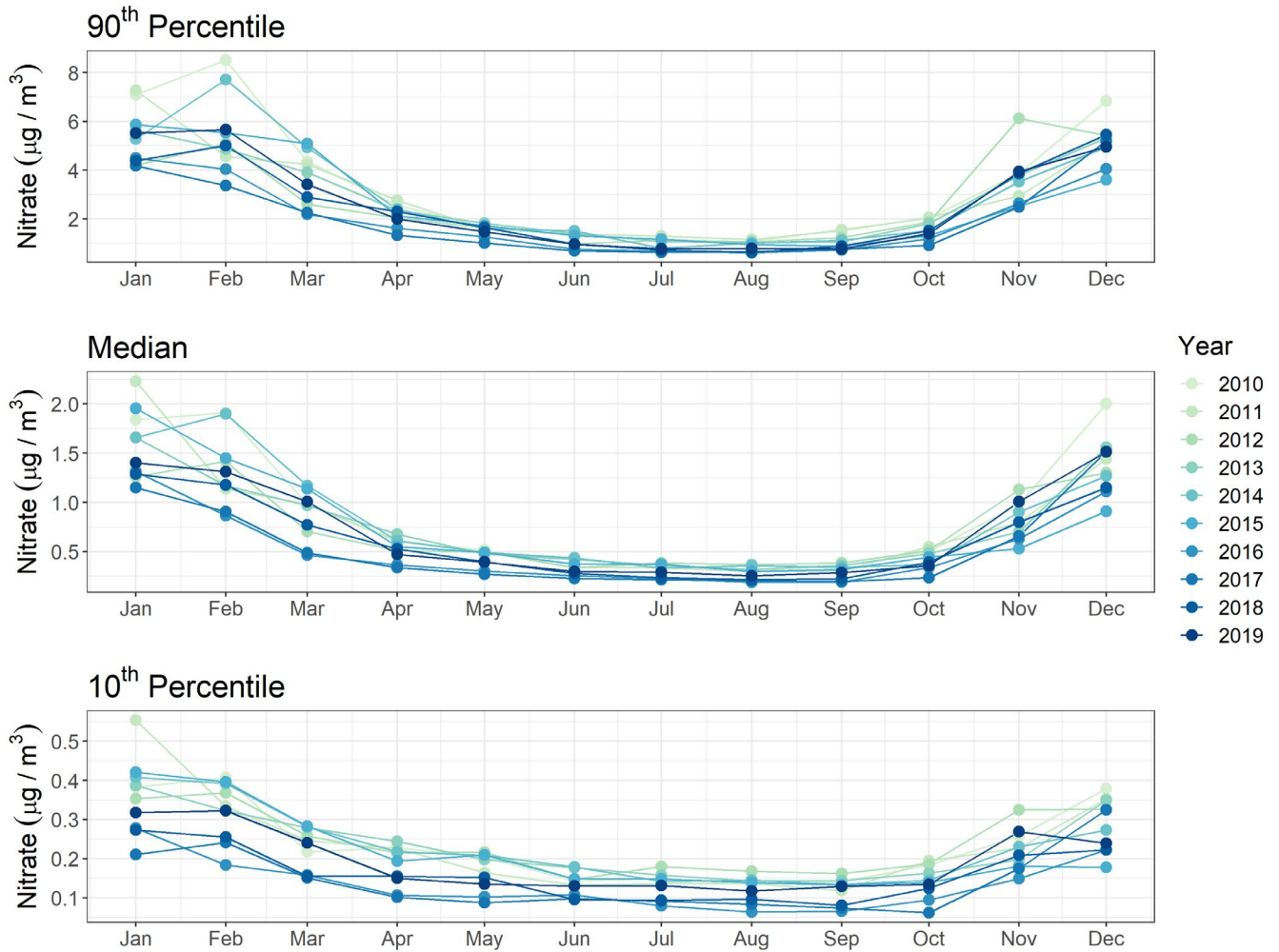
Similar to recent years, the 2019 sulfur concentrations generally continue to be low (Figure 6.4-4), with reduced seasonal variability.

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



The 2019 nitrate concentrations continue to show strong seasonality with elevated winter concentrations (Figure 6.4-5).

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



As discussed in Section 3.2.4.2, UC Davis calculated and delivered composite variables for reconstructed mass (RCM) and soil back to January 1, 2018; beginning with data for samples collected June 1, 2019, data for these parameters are included with routine data deliveries to DART and AQS. The 2018 and 2019 RCM and soil results are shown in Figure 6.4-6 and 6.4-7, respectively.

Figure 6.4-6: Multi-year time series of network-wide composite variable reconstructed mass (RCM) concentrations.

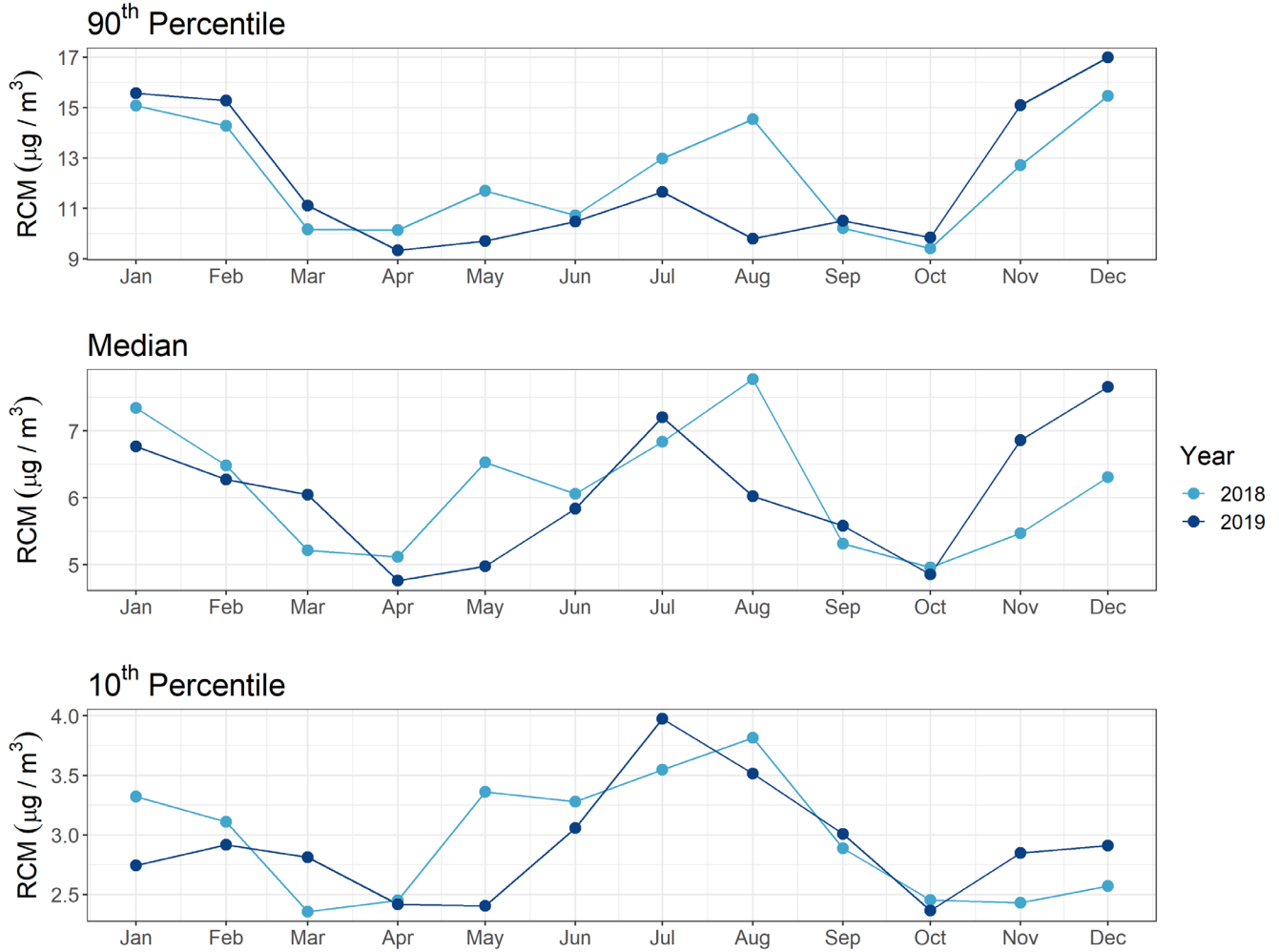
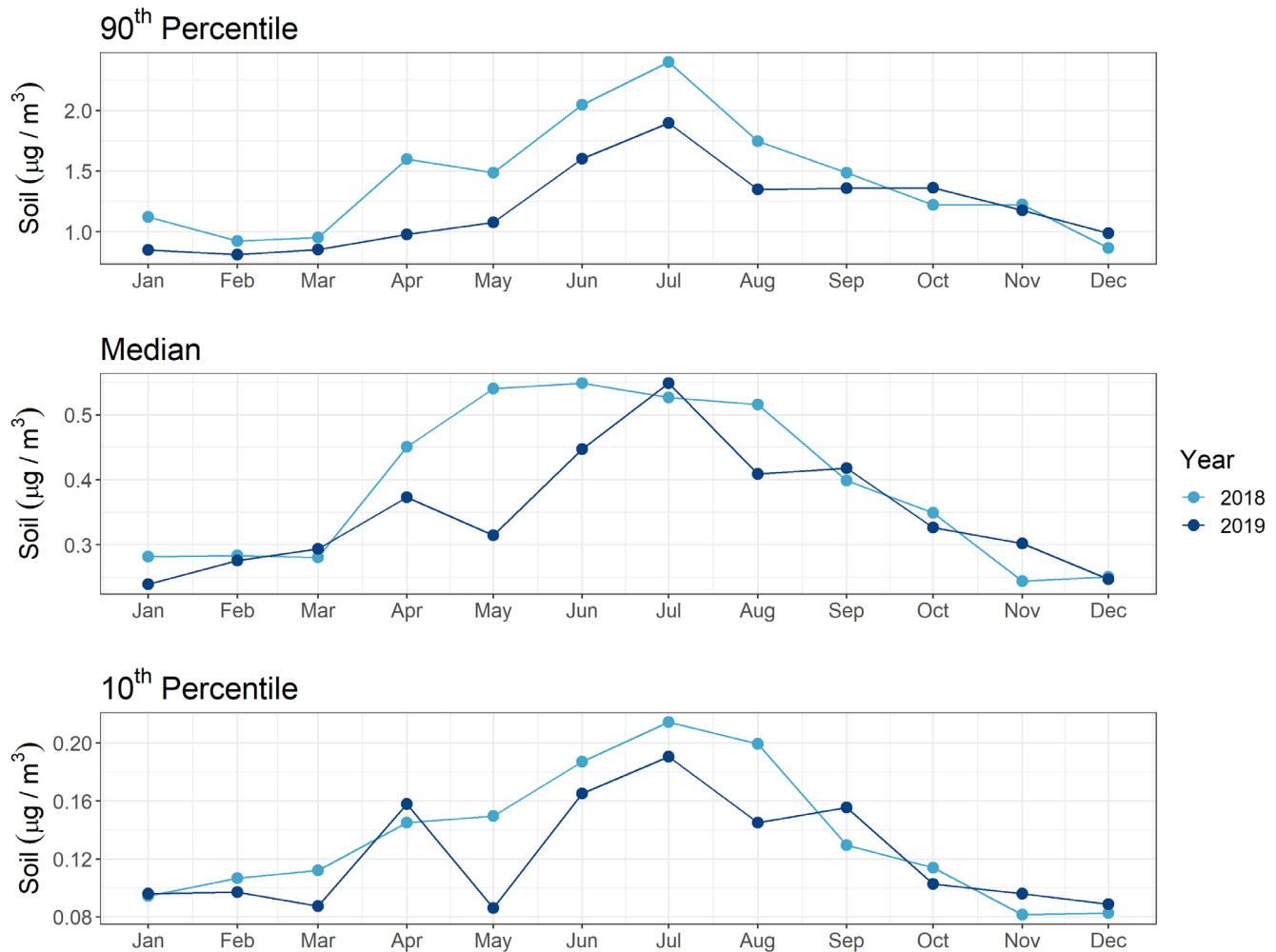


Figure 6.4-7 Multi-year time series of network-wide composite variable soil concentrations.



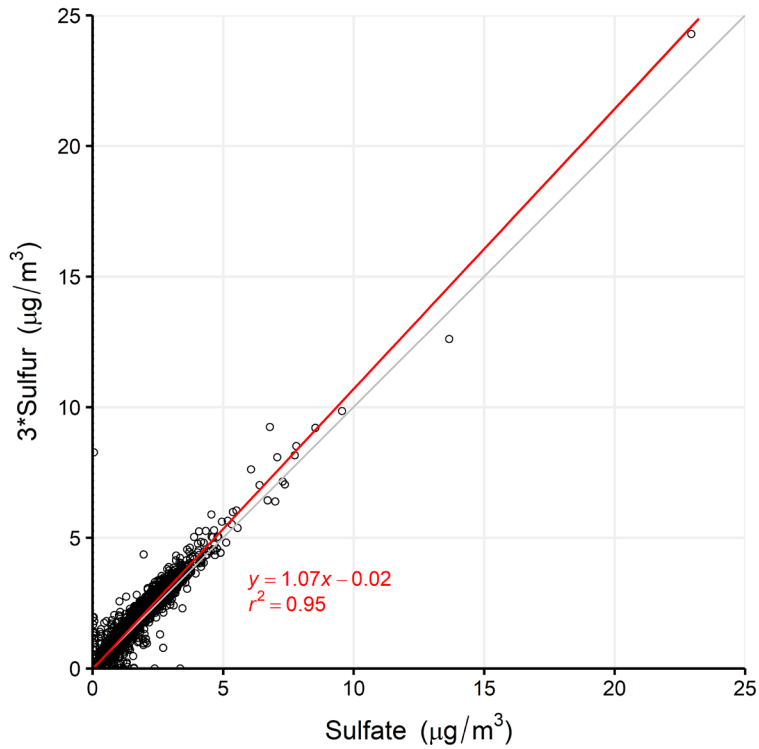
6.4.1.2 Comparisons Between Modules

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 (SO₄) using IC. The molecular weight of SO₄ (96 g/mol) is three times the atomic weight of S (32 g/mol), so the concentration ratio (3×S)/SO₄ 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 6.4-8), suggesting the presence of some sulfur in a non-water soluble form of sulfate or in a chemical compound other than sulfate.

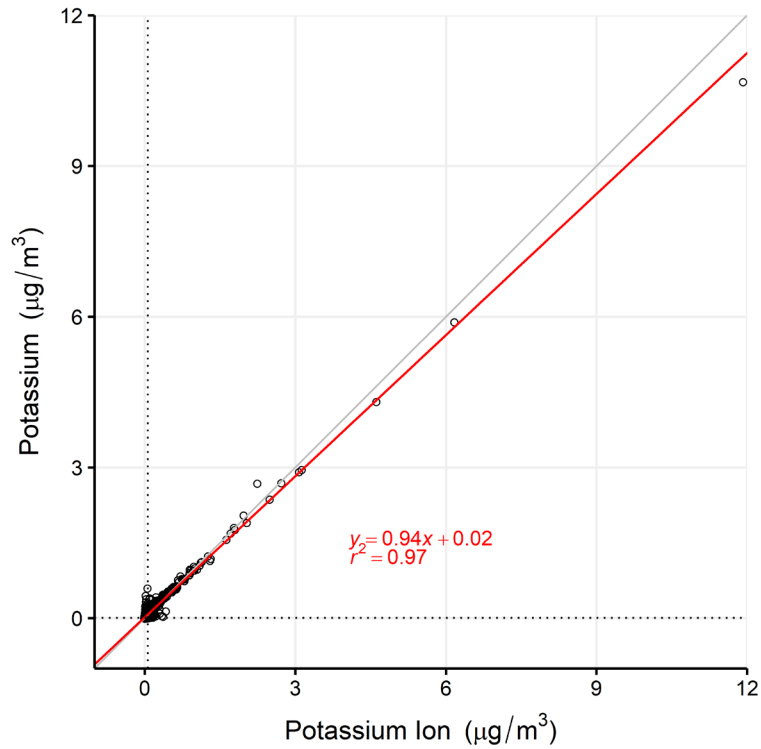
Figure 6.4-8 Scatter plot of (3×S) versus SO₄, samples collected January 1, 2019 through December 31, 2019. Number of observations (complete pairs) is 12,843. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression.



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/SO₄ 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 (Figure 6.4-9).

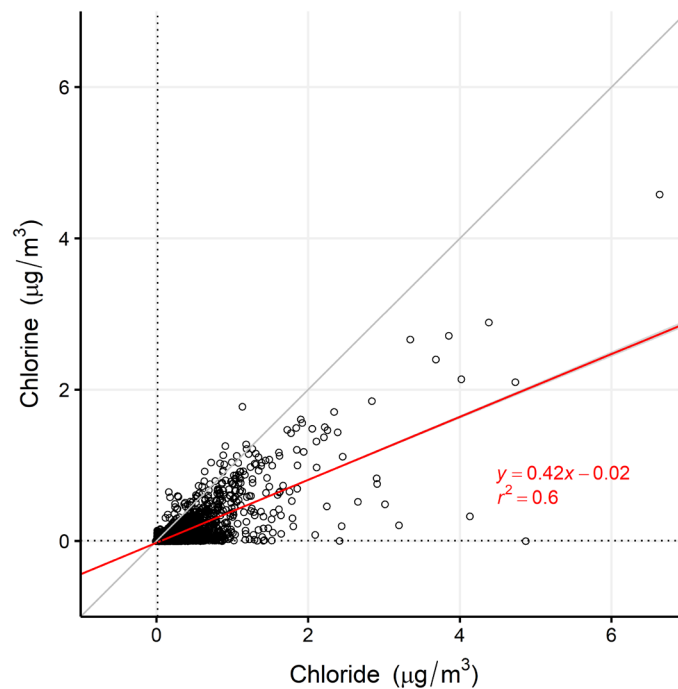
Figure 6.4-9: Scatter plot of potassium versus potassium ion, samples collected January 1, 2019 through December 31, 2019. Number of observations (complete pairs) is 12,846. Dotted black horizontal and vertical lines indicate MDLs. Solid gray line indicates 1:1. Solid red line indicates regression.



Chlorine versus Chloride

PTFE filters are analyzed for elemental chlorine using EDXRF, and nylon filters are analyzed for chloride using IC. Chloride ion is the reduced form of chlorine and chlorine in particulate matter is typically in the form of chloride. Similarly to the potassium/potassium ion relationship, in a scenario where all the particulate chlorine is present as water-soluble chloride ion, the chlorine/chloride ion ratio is expected to be near one (Figure 6.4-10).

Figure 6.4-10: Scatter plot of chlorine versus chloride ion, samples collected January 1, 2019 through December 31, 2019. Number of observations (complete pairs) is 12,848. 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 composite variable reconstructed mass (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:

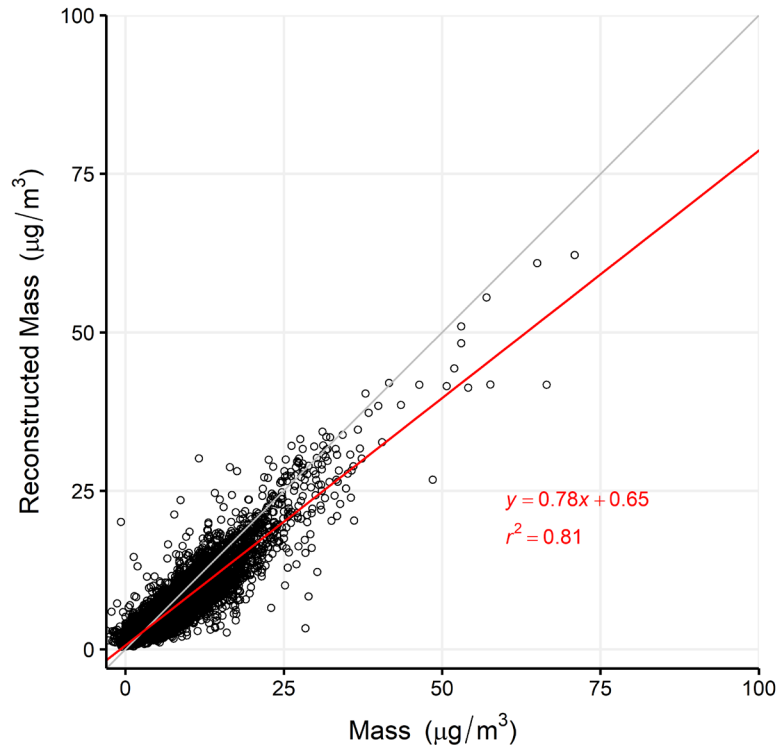
$$\text{RCM} = (4.125 \times \text{S}) + (1.29 \times \text{NO}_3^-) + (1.4 \times \text{OC}) + (\text{EC}) + \\ (2.2 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 2.42 \times \text{Fe} + 1.94 \times \text{Ti}) + (1.8 \times \text{chloride})$$

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

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 6.4-11), but RCM tends to underestimate AirNow Tech mass.

Figure 6.4-11: Scatter plot of reconstructed mass (RCM) versus AirNow Tech PM_{2.5} mass data (Mass), samples collected January 1, 2019 through December 31, 2019. Number of observations (complete pairs) is 9,541. Solid gray line indicates 1:1. Solid red line indicates regression.



6.5 Uncertainty Estimates and Collocated Precision Summary Statistics

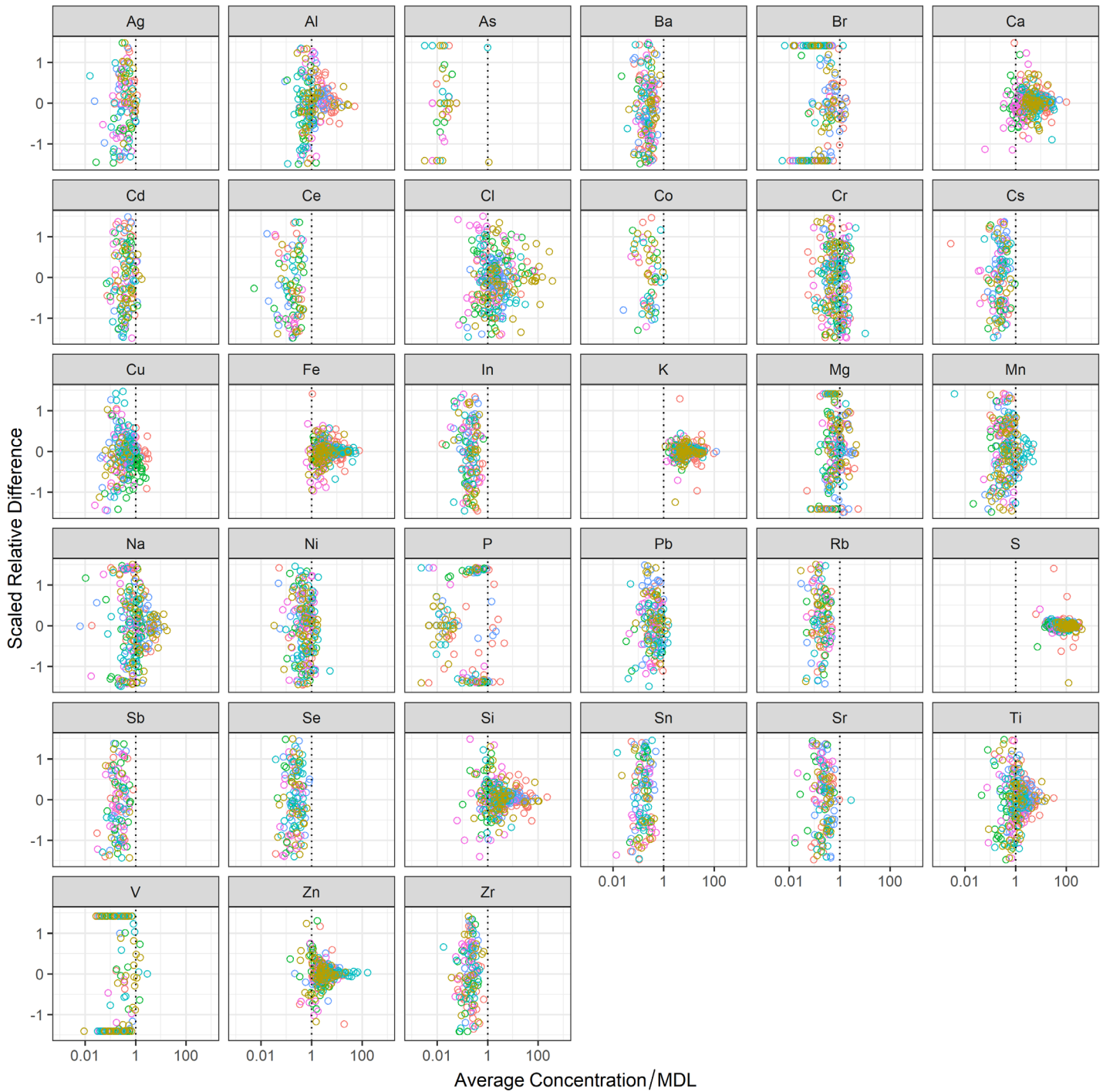
Several network sites are equipped with collocated samplers, where simultaneous samples are collected on independent samplers and analyzed using the same analytical protocols. Differences between the resulting data provide a measure of the total uncertainty associated with filter substrates, sampling 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).

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

The scaled relative differences are $\pm\sqrt{2}$ when one of the two measurements is zero, and vary between these limits at concentrations close to the detection limit. The scaled relative differences 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 differences for element measurements at sites with collocated samplers across the network (January 1, 2019 through December 31, 2019). Dotted vertical lines indicate MDL.



- | | |
|--|---|
| <ul style="list-style-type: none"> ○ Bakersfield - California Ave. (06-029-0014) ○ Deer Park (48-201-1039) ○ Dudley Square - Roxbury (Boston) (25-025-0042) | <ul style="list-style-type: none"> ○ G.T. Craig (39-035-0060) ○ Riverside - Rubidoux (06-065-8001) ○ Rutgers (34-023-0011) |
|--|---|

Figure 6.5-2: Scaled relative differences for ion measurements at sites with collocated samplers across the network (January 1, 2019 through December 31, 2019). Dotted vertical lines indicate MDL.

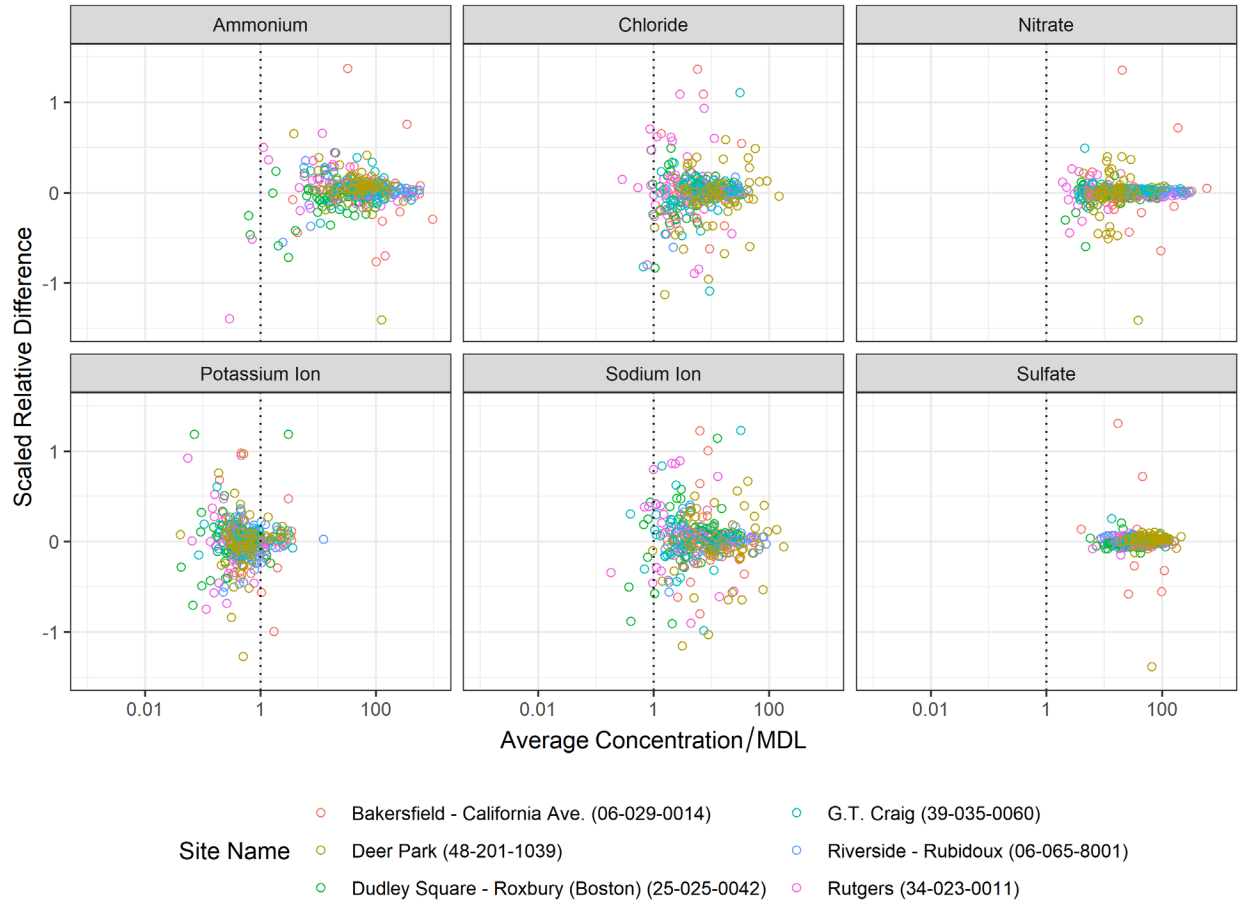
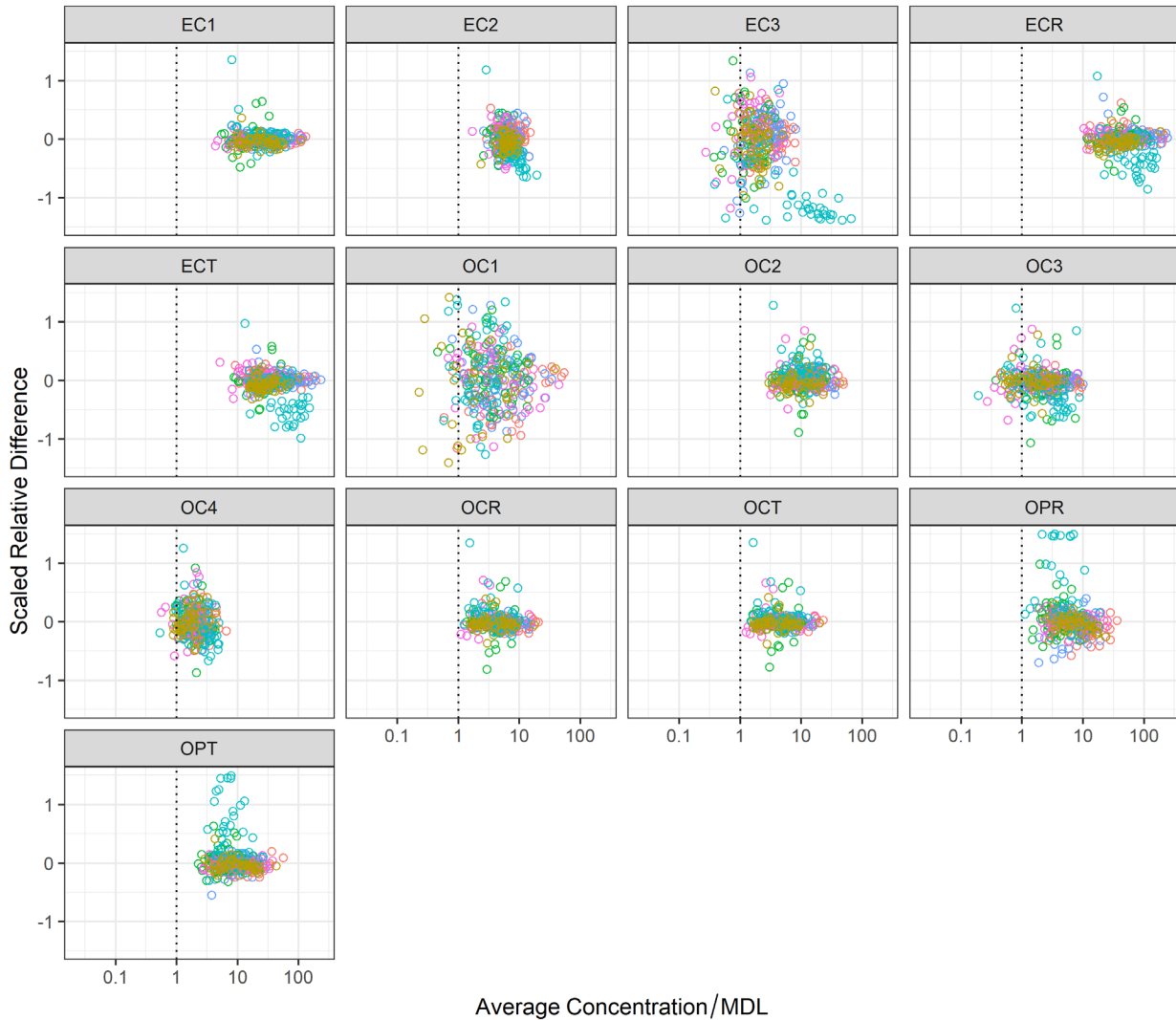
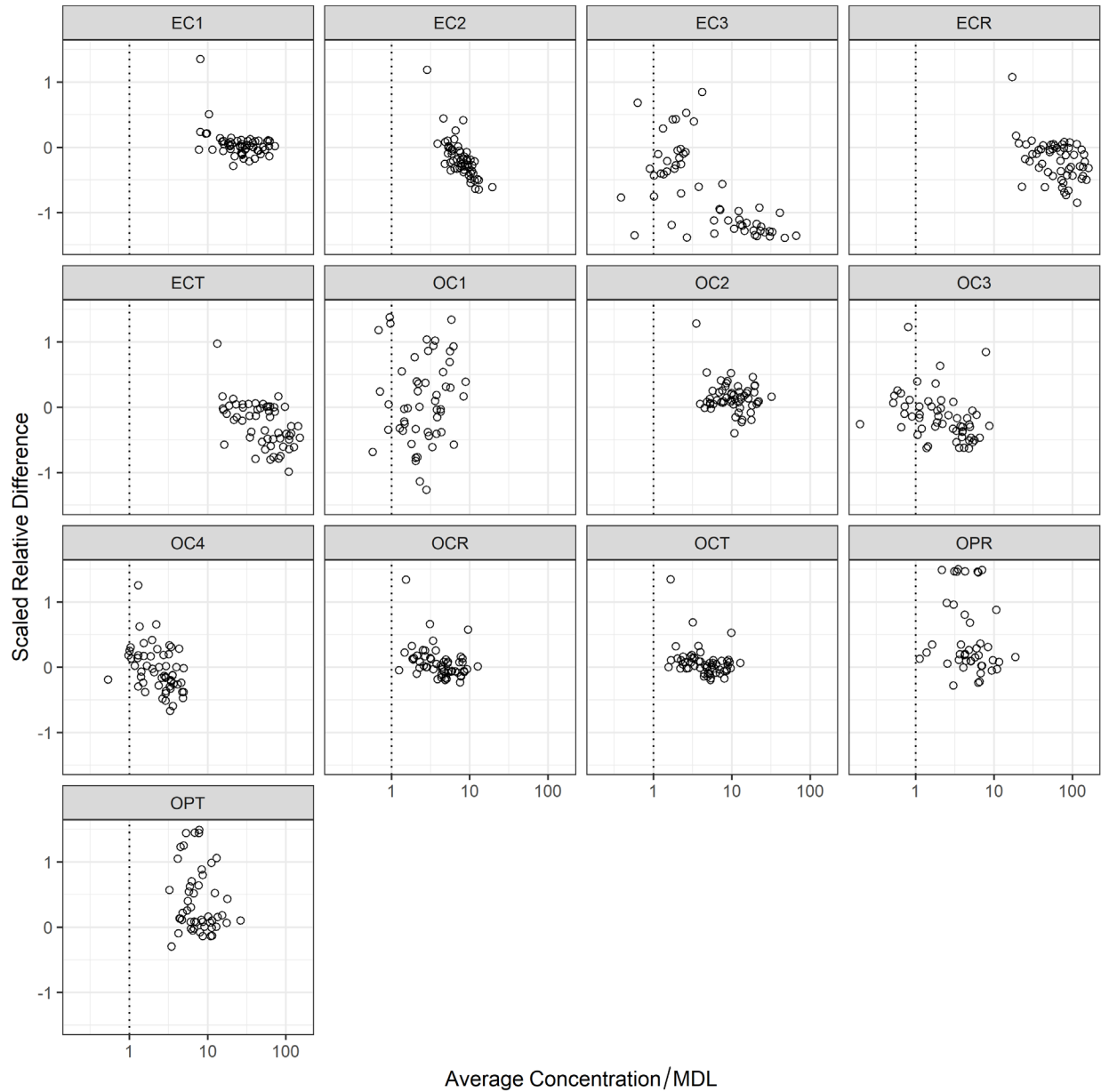


Figure 6.5-3: Scaled relative differences for carbon measurements at sites with collocated samplers across the network (January 1, 2019 through December 31, 2019). Dotted vertical lines indicate MDL. Elemental carbon (EC) fractions are indicated as (1) through (3), organic carbon (OC) fractions are indicated as (1) through (4). Organic pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).



The scaled relative differences for several of the carbon fractions measured at the G.T. Craig, OH site (AQS ID# 39-035-0060) stand out relative to the other sites, suggesting poor agreement at G.T. Craig between the collocated samplers. Examination of the scaled relative differences at G.T. Craig separately from the other sites further shows the poor agreement (Figure 6.5-4), particularly for ECR, ECT, OPR, and OPT.

Figure 6.5-4: Scaled relative differences for carbon measurements from collocated samplers at the G.T. Craig, OH (AQS ID# 39-035-0060) site, January 1, 2019 through December 31, 2019. 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 pyrolyzed (OP), elemental carbon (EC), and organic carbon (OC) are shown by reflectance (R) and transmittance (T).



Collocated precision is reported for CSN data 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. Beginning with samples collected January 1, 2019 through December 31, 2019, fractional uncertainty is updated annually and calculated using collocated data from the previous two years. For this reporting period (samples collected January 1, 2019 through December 31, 2019) the fractional uncertainty is calculated from sample pairs collected at CSN collocated sites June 1, 2016 through May 31, 2018, with a minimum of 60 collocated pairs. For cases where the total number of valid collocated pairs over the two-year period is less than 60, a value of 0.25 is adopted as the fractional uncertainty. The calculation for fractional uncertainty is documented in *UCD CSN TI 801B*, and summarized in Equation 6.5-1 and Equation 6.5-2.

Note: Prior to this reporting period fractional uncertainty was calculated from sample pairs collected at CSN collocated sites January 1, 2009 through December 31, 2014.

$$\text{Fractional Uncertainty (f)} = \frac{(\text{84th percentile of SRD}) - (\text{16th percentile of SRD})}{2} \quad (\text{Eq. 6.5-2})$$

Table 6.5-1 (elements), Table 6.5-2 (ions), and Table 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 a fractional uncertainty of 0.25 is assigned.

Each species concentration result delivered to AQS is accompanied by calculated method detection limit (MDL; see Section 3.1.3.2) and additive uncertainty (Equation 6.5-3). Additive uncertainty includes both fractional uncertainty (Equation 6.5-2) and analytical uncertainty as reported by the laboratories. Similar to the fractional uncertainty, beginning with samples collected January 1, 2019 through December 31, 2019 analytical uncertainties are reviewed annually and updated per direction from the laboratories.

$$\text{Additive Uncertainty} = \sqrt{(\text{Analytical Uncertainty})^2 - (f \times C)^2} \quad (\text{Eq. 6.5-3})$$

Where f is fractional uncertainty and C is ambient concentration.

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 (Rice and Landis, 2016), using the subset of observations with concentrations at least three times the MDL.

$$\text{Relative Percent Difference (RPD)} = \frac{X_i - Y_i}{(X_i + Y_i) / 2} \times 100 \quad (\text{Eq. 6.5-4})$$

$$CV_i = \frac{|RPD_i|}{\sqrt{2}} \quad (\text{Eq. 6.5-5})$$

where X_i and Y_i are the measurements from routine and collocated sites, respectively, for the i^{th} pair of measurements. Table 6.5-1 (elements), Table 6.5-2 (ions), and Table 6.5-3 (carbon) list median CV calculated from collocated samples collected during 2019.

Table 6.5-1: Fractional uncertainty (f) and median coefficient of variation (CV) for element species. For the previous reporting period, f is calculated from samples collected 2009 through 2014 and applied to samples between January 1, 2018 through December 31, 2018 and CV is calculated from samples collected January 1, 2018 through December 31, 2018. For the current reporting period, f is calculated from samples collected June 1, 2016 through May 31, 2018 and applied to samples between January 1, 2019 through December 31, 2019 and CV is calculated from samples collected January 1, 2019 through December 31, 2019. For both reporting periods, f and CV values are not calculated for species with less than 60 collocated pairs with concentrations at least three times the MDL.

Species	2018 (previous reporting period)				2019 (current reporting period)			
	Fractional Uncertainty (%)	Pairs	Coefficient of Variation (%)	Pairs	Fractional Uncertainty (%)	Pairs	Coefficient of Variation (%)	Pairs
Na	16.4	1,270	---	38	18.5	67	---	33
Mg	24.5	365	---	5	---	6	---	4
Al	25.2	1,209	---	55	13.2	79	---	36
Si	15.2	3,897	8.3	186	14.1	326	9.1	156
P	17.3	93	---	4	---	10	---	0
S	6.2	5,530	3.8	338	5.6	633	3.6	346
Cl	34.2	1,740	23.8	98	36.4	166	19.4	76
K	10.6	4,825	5.2	321	8.1	476	5.0	301
Ca	16.8	4,067	8.6	141	11.5	128	8.3	195
Ti	17.4	697	---	55	18.0	97	---	40
V	12.8	499	---	0	---	0	---	0
Cr	38.9	83	---	1	---	3	---	0
Mn	15.4	623	---	11	---	9	---	5
Fe	17	5,520	8.8	184	14.4	305	5.8	183
Co	---	10	---	0	---	0	---	0
Ni	17.8	400	---	0	---	1	---	0
Cu	26.9	2,313	---	4	---	12	---	0
Zn	12.3	3,144	7.0	123	11.0	244	5.9	127
As	18.8	155	---	0	---	0	---	0
Se	---	43	---	0	---	0	---	0
Br	15	1,610	---	0	---	1	---	0
Rb	---	0	---	0	---	0	---	0
Sr	---	58	---	0	---	1	---	0
Zr	---	3	---	0	---	0	---	0
Ag	---	1	---	0	---	0	---	0
Cd	---	0	---	0	---	0	---	0
In	---	0	---	0	---	0	---	0
Sn	---	0	---	0	---	0	---	0
Sb	---	0	---	0	---	0	---	0
Cs	---	7	---	0	---	0	---	0
Ba	16.5	123	---	0	---	1	---	0
Ce	---	21	---	0	---	0	---	0
Pb	18.5	381	---	0	---	0	---	0

Table 6.5-2: Fractional uncertainty (f) and median coefficient of variation (CV) for ion species. For the previous reporting period, f is calculated from samples collected 2009 through 2014 and applied to samples between January 1, 2018 through December 31, 2018 and CV is calculated from samples collected January 1, 2018 through December 31, 2018. For the current reporting period, f is calculated from samples collected June 1, 2016 through May 31, 2018 and applied to samples between January 1, 2019 through December 31, 2019 and CV is calculated from samples collected January 1, 2019 through December 31, 2019. For both reporting periods, f and CV values are not calculated for species with less than 60 collocated pairs with concentrations at least three times the MDL.

Species	2018 (previous reporting period)				2019 (current reporting period)			
	Fractional Uncertainty (%)	Pairs	Coefficient of Variation (%)	Pairs	Fractional Uncertainty (%)	Pairs	Coefficient of Variation (%)	Pairs
Ammonium	7.1	5,466	9.2	316	20.9	486	6.2	336
Chloride*	---	---	7.6	203	12.2	232	5.8	253
Nitrate	7.6	5,767	5.4	320	10.8	581	3.1	337
Potassium Ion	12.6	2,072	---	8	17.9	174	---	5
Sodium Ion	24.7	3,562	8.0	206	16.3	317	7.2	241
Sulfate	4.9	5,680	3.8	335	8.5	612	2.6	347

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

Table 6.5-3: Fractional uncertainty (f) and median coefficient of variation (CV) for carbon species. For the previous reporting period, f is calculated from samples collected 2009 through 2014 and applied to samples between January 1, 2018 through December 31, 2018 and CV is calculated from samples collected January 1, 2018 through December 31, 2018. For the current reporting period, f is calculated from samples collected June 1, 2016 through May 31, 2018 and applied to samples between January 1, 2019 through December 31, 2019 and CV is calculated from samples collected January 1, 2019 through December 31, 2019. For both reporting periods, f and CV values are not calculated for species with less than 60 collocated pairs with concentrations at least three times the MDL. 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	2018 (previous reporting period)				2019 (current reporting period)			
	Fractional Uncertainty (%)	Pairs	Coefficient of Variation (%)	Pairs	Fractional Uncertainty (%)	Pairs	Coefficient of Variation (%)	Pairs
Elemental Carbon (EC1)	12.9	1,948	8.6	337	15.2	595	5.4	335
Elemental Carbon (EC2)	36.8	992	18.1	235	32.0	380	14.5	304
Elemental Carbon (EC3)	---	4	---	12	---	0	15.5	63
Elemental Carbon (ECR)	15.5	1955	8.4	335	16.9	591	7.1	336

Elemental Carbon (ECT)	12.8	1,606	9.9	335	18.3	587	7.4	336
Organic Carbon (OC1)	32.9	1,039	20.7	219	33.5	357	21.7	131
Organic Carbon (OC2)	13.6	1,877	7.7	328	12.5	577	8.2	326
Organic Carbon (OC3)	17.8	1,860	8.8	286	15.1	530	7.3	162
Organic Carbon (OC4)	15.7	1,487	13.2	262	19.4	584	---	41
Organic Carbon (OCR)	11.6	2,033	5.8	315	10.3	580	5.5	265
Organic Carbon (OCT)	7.3	1,774	4.9	316	9.4	580	4.5	272
Organic Pyrolyzed (OPR)	25.1	919	16.7	197	37.7	291	10.0	255
Organic Pyrolyzed (OPT)	17.3	1,557	13.6	298	25.4	529	7.6	301

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